

PEROXY-SALTS OF THE ALKALI METALS AND  
RELATED SPECIES.

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## ABSTRACT

### Peroxisalts of the Alkali Metals and Related Species.

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The work described in this thesis is concerned mainly with the preparation, characterisation and physicochemical properties of a series of different inorganic peroxysalts, in particular the alkali metal percarbonates. Extensive use has been made of vibrational spectroscopy as a tool for obtaining structural information, with both  $^2\text{H}$  and  $^{13}\text{C}$  isotopic substitutions helping in the assignments of vibrational modes.

All of the peroxysalts studied fall into either of two categories. The first are perhydrates, which contain hydrogen peroxide of crystallisation, such as sodium oxalate monoperhydrate,  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  and "sodium percarbonate",  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ . The second group contain peroxy moieties bound to atoms other than hydrogen, e.g., boron in "sodium perborate",  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$  or carbon in potassium peroxydicarbonate,  $\text{K}_2\text{C}_2\text{O}_6$ , these types of compounds being referred to as "true" peroxysalts.

The structures of both of the commonly used bleaching agents "sodium percarbonate" and "sodium perborate" are described, full X-ray structural determinations having been carried out in the Chemical Crystallography Laboratories during the course of this work.

Due to particular interest in percarbonates, one of the very few known transition metal peroxy-carbonato complexes, bistriphenylphosphine peroxy-carbonato platinum(II) has been prepared and its structure also determined by X-ray crystallography.

Towards the latter part of this work, the potential use of the "true" percarbonates of the alkali metals and "sodium perborate" as oxidising agents has been studied as they resemble the relatively hazardous organic peroxides, ROOR, hydroperoxides, ROOH, and peracids  $RC(O)OOH$  in their structures and thus would be expected to possess similar oxidising properties.

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## NOMENCLATURE, ABBREVIATIONS AND SYMBOLS.

### Nomenclature.

The nomenclature of various peroxysalts is still not definitive in the literature. In the case of inorganic percarbonates, four different types have been reported and each is often referred to as simply the metal percarbonate. For convenience to the reader, rather than using the rather long-winded nomenclature based on IUPAC recommendations, the following names have been used throughout this thesis:-

(a) Compounds containing hydrogen peroxide of crystallisation are referred to as "perhydrates" with compounds containing both hydrogen peroxide and water of crystallisation being termed "perhydrate hydrates", e.g.,  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ , sodium oxalate monoperoxhydrate [IUPAC, sodium oxalate - hydrogen peroxide (1/1)];  $\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , sodium sulphate hemiperhydrate monohydrate [IUPAC, sodium sulphate - hydrogen peroxide - water (2/1/2)].

(b) Compounds containing the anion  $\text{C}_2\text{O}_6^{2-}$  are termed "peroxydicarbonates", e.g.,  $\text{K}_2\text{C}_2\text{O}_6$ , potassium peroxydicarbonate [IUPAC, dipotassium peroxodicarbonate].

(c) Compounds containing the anion  $\text{HCO}_4^-$  are termed "peroxybicarbonates", e.g.,  $\text{KHCO}_4$ , potassium peroxybicarbonate [IUPAC, potassium hydrogenperoxomonocarbonate].

(d) Compounds containing the anion  $\text{CO}_4^{2-}$  are termed simply "peroxycarbonates", e.g.,  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ , lithium peroxycarbonate monohydrate [IUPAC, dilithium peroxomonocarbonate - water (1/1)].

### Vibrational Spectra.

Frequencies for infrared and Raman spectra are quoted in wavenumbers,  $\text{cm}^{-1}$ . Bands obtained are described as s, strong ; m, medium ; w, weak ; b, broad or sh, shoulder and v, very. Raman bands are also described as p, polarised or dp, depolarised for solution spectra.

### Nuclear Magnetic Resonance Spectra, (n.m.r.).

Chemical shift values ( $\delta$ ) are quoted in ppm downfield relative to tetramethylsilane (T.M.S.,  $\delta = 0.00$ ).

### X-Ray Powder Diffraction (XRD).

d-Spacings ( $\text{\AA}$ ) are listed only for relatively stable peroxysalts, the intensities being estimated visually and described as s, strong ; m, medium ; w, weak and v, very.

TO MAXINE  
AND MUM AND DAD

## CHAPTER ONE

### ALKALI METAL AND AMMONIUM SALT PERHYDRATES

#### Abstract.

The preparation, characterisation and some physicochemical properties of several perhydrates of simple alkali metal and ammonium salts are described. Crystals were obtained for the X-ray crystal structure of the industrial bleaching agent "sodium percarbonate",  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ . Detailed vibrational spectroscopic data are presented for the series of alkali metal and ammonium oxalate and carbonate perhydrates, together with results for some species enriched in  $^2\text{H}$  and  $^{13}\text{C}$ . The vibrational spectra of both normal and  $^{13}\text{C}$ -enriched oxalate ion in aqueous solution are reported.

#### Section 1-A. Summary of the Chemistry of Perhydrates.

Just as numerous compounds crystallise from aqueous solutions as hydrates, containing varying amounts of water of crystallisation, many of the same compounds will crystallise from aqueous hydrogen peroxide solutions either solely with hydrogen peroxide of crystallisation or with both hydrogen peroxide and water of crystallisation. These species are referred to as perhydrates and perhydrate hydrates respectively.

In a few, rare cases, some compounds that do not form hydrates, nonetheless form perhydrates, e.g., lithium oxalate, which forms a monoperhydrate,  $\text{Li}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ .

The majority of perhydrates are formed from alkali metal and ammonium oxyacid salts such as carbonates, sulphates, acetates, formates, oxalates, nitrates and phosphates. However, perhydrates have also been reported for the series of alkali metal and ammonium fluorides<sup>1-3</sup> and also for such compounds as urea<sup>4,5</sup>, biuret,<sup>6</sup> dioxane,<sup>7</sup> triphenylphosphine oxide,<sup>8</sup> triphenylarsine oxide,<sup>9</sup> and various amino acids and acid amides.<sup>10</sup> It should be noted that there does not seem to be any means of predicting the formation or stoichiometry of a perhydrate of any compound.

All perhydrates are made simply by the crystallisation of the parent compound from an aqueous hydrogen peroxide solution, the stoichiometry of the product depending upon the hydrogen peroxide concentration and the temperature. Dissolution in water releases the hydrogen peroxide and it can be titrated against permanganate ion, this being the simplest method of analysing perhydrates for their peroxide content ( $\text{O}_2^{2-}$ ). Thus, perhydrates can be regarded as just a solid, portable form of hydrogen peroxide, and this is why they are suitable for use as bleaching agents in such commodities as packet detergents. A potential candidate for this purpose would be required to have a fairly high peroxide content combined with a reasonable solubility and possessing thermal and moisture stability. The moisture problem is always the most difficult to overcome, especially in the presence of

other washing powder constituents and is usually achieved by coating the peroxide-containing particles with various products.

Probably the first perhydrate reported was that of sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ , by Tanatar in 1899,<sup>11</sup> and although he formulated it incorrectly as  $\text{Na}_2\text{CO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , he nonetheless recognised the ability of hydrogen peroxide to hydrogen-bond to electronegative atoms such as oxygen in the same way as water does in hydrates. Since then numerous perhydrates have appeared in the literature, but it seems highly unlikely that all of the claimed hydrogen peroxide adducts are individual compounds. Many of the formulae quoted are most probably for products arising from insufficient drying, decomposition during drying or handling, or containing impurities.

Many vibrational spectroscopic and X-ray studies have been carried out on the hydrates of a wide range of substances but relatively little is known about perhydrates, even though many of these compounds are extremely good candidates for such studies, being reasonably stable and forming well-shaped crystals suitable for single crystal X-ray structural determinations.

To date, only twenty such studies have been reported and these are listed, together with references in Table 1-1.

#### Section 1-B. The Alkali Metal and Ammonium Oxalate Perhydrates, $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot n\text{H}_2\text{O}_2$ .

The remarkably stable oxalate monoperhydrates of the alkali metals,  $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  are of interest because X-ray crystal structure determinations show that, whereas the potassium,<sup>14</sup> rubidium<sup>14</sup> and ammonium<sup>15</sup> salts contain hydrogen peroxide hydrogen-bonded to the oxalate groups in its



Table 1-1

List of Perhydrates that have been Structurally Characterised by  
Single Crystal X-ray Methods.

Compound	Reference
$\text{Li}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	12
$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	13
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	14
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	14
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	15
$\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$	16,17
$\text{KF} \cdot 2\text{H}_2\text{O}_2$	18
$\text{RbF} \cdot \text{H}_2\text{O}_2$	3
$4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$	19,20
$[\text{C}(\text{NH}_2)_3]_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$	21,22
$[\text{C}(\text{NH}_2)_3]_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	23
$[\text{C}(\text{NH}_2)_3]_4(\text{O}_2\text{C})_2\text{C}_6\text{H}_2(\text{CO}_2)_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$	24
$[\text{C}(\text{NH}_2)_3]_4(\text{O}_2\text{C})_2\text{C}_6\text{H}_2(\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}_2$	25
$(\text{CH}_2)_6\text{N}_4\text{O} \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	26
$(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{O}_2$	4
$\text{BaO}_2 \cdot \text{H}_2\text{O}_2$	27
$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	27
$\text{SrO}_2 \cdot 2\text{H}_2\text{O}_2$	27
$\text{BaO}_2 \cdot 2\text{H}_2\text{O}_2$	27
$\text{KNb}(\text{O}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2) \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$	28,29

relatively normal skewed conformation, the lithium<sup>12</sup> and sodium<sup>13</sup> salts contain trans-planar H<sub>2</sub>O<sub>2</sub>. This work sought to investigate the validity of using vibrational spectra to distinguish between skewed and planar forms of hydrogen-bonded H<sub>2</sub>O<sub>2</sub> in these peroxy salts as they constitute relatively simple "model" systems for perhydrates. Infrared and Raman studies on Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> and its incompletely deuteriated form have already been reported,<sup>30</sup> as have infrared spectra of normal and deuteriated M<sub>2</sub><sup>I</sup>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> (M = Na, K, Rb) and M<sub>2</sub><sup>I</sup>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> (M = Li, Cs).<sup>31</sup> Detailed Raman and infrared data on normal and deuteriated Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub>, normal, deuteriated and <sup>13</sup>C-enriched M<sub>2</sub><sup>I</sup>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> (M = Na, K) and M<sub>2</sub><sup>I</sup>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> (M = Rb, Cs) are presented here.

The authors of the two previous vibrational spectroscopic studies on this series of compounds<sup>30,31</sup> have interpreted their results on the basis of the X-ray structures. However, by using <sup>2</sup>H- and <sup>13</sup>C-enriched reagents, more complete results have led to the changing of certain assignments for the vibrational modes.

Analytical data for the compounds are given in Table 1-2. The higher perhydrates of sodium, potassium and caesium have not been reported previously. Their hygroscopic nature and thermal instability prevented measurement of their infrared spectra but their Raman spectra, together with the complete vibrational spectra of the monoperhydrates and assignments are listed in Tables 1-3 to 1-5.

The bands due to H<sub>2</sub>O<sub>2</sub> in the compounds are identified by their shifts on deuteration and immobility on <sup>13</sup>C substitution. Previous practice in spectroscopic studies of perhydrates<sup>5,30,31</sup> has been followed

Table 1-3

## Vibrational Spectra of Lithium and Sodium Oxalate Monohydrates.

$\text{Li}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$		$\text{Li}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$		$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$		$\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$		$\text{Na}_2^{13}\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$		Assignments	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	$\text{C}_2\text{O}_4^{2-}$ modes	$\text{H}_2\text{O}$ modes
3120vw		3120vw		obscd.		3050vw		2970vw		$\nu_9 + \nu_{11}$	
3020vw	3040mb	2180wb	2100mb	3040m	3180mb	2240m	2140mb	3040m	3180mb		$\nu_1$
2940w		2960w		2890wsh		2915w		obscd.		$\nu_5 + \nu_9$	
2620m	2660mb	2060m	2000mb	2640s	2680mb	2040s	2030m	2640s	2680mb		$\nu_5$
n.o.		1855w		1884w		1900w		n.o.		$\nu_6 + \nu_9$	
	1731vw		1732vw		1740vw		1742vw		1680vw	$2\nu_2$	
1630vsb		1630vsb		1660sh } 1610vsb }		1670sh } 1620vsb }		1610sh } 1560vsb }		$\nu_{11}$	
	1698m		1674m		1604w		1646m } 1605m }		1596w } 1551m }	$\nu_5$	
	obscd.		1129vw		1578w		1174vw		1574w		$\nu_2$
	1498vs		1499vs		1460vs } 1442vw }		1460vs } 1442vw }		1426vs } 1380vw }	$\nu_1$	
1410w		1395m } 1380sh }		obscd.		1410m } 1390sh }		1365m } 1350sh }		$\nu_2 + \nu_{10}$	
n.o.		1000s		1409s		1025s		1408s			$\nu_6$
1330vs		1335vs		1308vs		1310vs		1285vs		$\nu_9$	
	926m } 865m }		922m } obscd. }		899s } 871m }		894m } 872m }		894s } 842m }	$\nu_2$	
	873vs		868vs		884vs		886vs		887vs		$\nu_3$
	854vw		n.o.		856vw		n.o.		856w		$R_N$ $\nu_4$
820m		580s		828s		590s		825s			
765s		772s		761s		770s		755s		$\nu_{12}$	
	613w		613w		597vw } 585vw }		594vw } 582vw }		592vw } 580vw }	$\nu_6$	
	529w		529w		513vw } 501w }		508vw } 498vw }		510vw } 499w }	$\nu_3$	
518s		514s		518s		515s		505s		$\nu_{10}$	

Table 1-4

## Vibrational Spectra of Potassium, Rubidium and Caesium Oxalate Monohydrates.

$K_2C_2O_4 \cdot H_2O$		$K_2C_2O_4 \cdot 2H_2O$		$K_2^{13}C_2O_4 \cdot H_2O$		$Rb_2C_2O_4 \cdot H_2O$		$Cs_2C_2O_4 \cdot H_2O$		Assignments	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	$C_2O_4^{2-}$ modes	$H_2O$ modes
3020m	3040mb	2220m	2230mb	3020m	3040mb	3030m	3040mb	3040m	3080mb		$\nu_1$
2650s	2700mb	2060s	2070mb	2650s	2700mb	2700sb	2740mb	2750sb	2780mb		$\nu_3$
1870vw		1870vw		1840vw		1860w		1850w		$\nu_6 + \nu_9$	
	1755w		1756vw		1697vw		1753w		1748w	$2\nu_2$	
1580vsb		1580vsb		1540vsb		1580vsb		1560vsb		$\nu_{11}$	
	1586m		1606w } 1595m }		1560w } 1543m }		1584m		1586w } 1573w }	$\nu_5$	
	1518w		1103vw		1518w		1513w		1463vw		$\nu_2$
1470s		1090s		1470s		1460s		1440sh			$\nu_6$
	1447vs } 1434w }		1449vs } 1433w }		1413vs } 1410s }		1442vs } 1437sh }		1430vs } 1417w }	$\nu_1$	
							1423w }		1406w }		
1410m } 1375sh }		1420m } 1380sh }		1375m } 1345sh }		1410m } 1375sh }		n.o. } n.o. }		$\nu_2 + \nu_{10}$	
1305vs		1310vs		1285vs		1302vs		1300vs		$\nu_9$	
940m	980vw } 930vw }	750m	n.o.	940m	980vw	920m	959w } 913w }	890m	937w } 926w }		$\nu_4$
880sh	882vs } 878s } 862m }	880m	882vs } 892m } 878m }	880sh	883vs } 858s } 846m }	875sh	874vs } 858m }	875sh	868vs } 875m } 846w }	$\nu_2$	$\nu_3$
870m	839w	630m } 610s }	n.o.	870m } 830sh }	830w	845m	840w	850sh } 845m } 830sh }	813w		$R_x$
755sh } 740s }		780s } 765s }		750sh } 737s }		770sh } 752s } 739s }		770sh } 745sh } 730s }		$\nu_{12}$	
	573m		573w } 567w }		569m } 558m }		572w		560w	$\nu_6$	
538s		540s		525s		531s		520s		$\nu_{10}$	
	484s } 477m }		480m } 474w }		481s } 474m }		476s } 467w }		468s } 460w }	$\nu_3$	

Table 1-5

## Raman Spectra of Higher Oxalate Perhydrates.

<u>Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2½H<sub>2</sub>O<sub>2</sub></u>	<u>K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O<sub>2</sub></u>	<u>Cs<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O<sub>2</sub></u>	<u>Assignments*</u>
1743vw	1758vw } 1734vw }	1740vw	2ν <sub>2</sub>
1658w } 1609vw }	1636vw	1610wb	ν <sub>11</sub> ?
1584w	1590m	n.o.	ν <sub>5</sub>
1463vs } 1400vwb }	1453sh } 1449s } 1438vw }	1461s } 1444s }	ν <sub>1</sub>
906sh } 902m }	909m	914m	ν <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> ?
888vs	885vs	876vs	ν <sub>3</sub> , H <sub>2</sub> O <sub>2</sub>
879vs	881m	obscd.	ν <sub>2</sub>
874vs } 867w } 860w }	868vs } 865s }	obscd.	ν <sub>2</sub>
830vwb	840w	850w	R <sub>X</sub> , H <sub>2</sub> O <sub>2</sub>
	738vw } 723vw }	770vwb	ν <sub>12</sub> ?
587w	578w	n.o.	ν <sub>6</sub>
	501w		ν <sub>10</sub> ?
502m	488m	477s	ν <sub>3</sub>

\* Assignments are for oxalate ion unless otherwise indicated.

by using the six normal modes<sup>32</sup> [symmetric and asymmetric O-H stretches ( $\nu_1$  and  $\nu_5$ ), deformations ( $\nu_2$  and  $\nu_6$ ), the torsion ( $\nu_4$ ) and the O-O stretch ( $\nu_3$ )] of  $\text{H}_2\text{O}_2$  as approximate descriptions for corresponding modes of the hydrogen-bonded  $\text{H}_2\text{O}_2$ . These vibrations are shown diagrammatically in Figure 1-1.

The results agree with the expectations that the vibrational spectra of  $\text{Li}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  and  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  should be a little simpler than those arising from the other monoperhydrates due to the trans-planar conformations of the  $\text{H}_2\text{O}_2$  moieties. Infrared and Raman selection rules predict that for a four-atomic  $\text{C}_{2h}$  molecule (such as a trans-planar  $\text{H}_2\text{O}_2$  molecule) there will be six internal vibrations, three of which will be Raman active and three infrared active with no coincidences, the rule of mutual exclusion applying here since there is a centre of symmetry. In the case of a four-atomic  $\text{C}_2$  molecule (such as a skewed  $\text{H}_2\text{O}_2$  molecule) all six internal vibrations will be active both in the Raman and infrared.

The X-ray investigations that have been carried out on the alkali metal monoperhydrates have shown that the oxalate ions are planar and centrosymmetric, the C-O distances being equal within experimental uncertainty and the O-C-C angles also being approximately equal; hence the oxalate ions possess  $\text{D}_{2h}$  symmetry and the frequency numbering scheme adopted by Arnau and Giguère<sup>30</sup> in their study of  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  has been used in order to make assignments here. Figure 1-2 depicts the twelve internal vibrations of a  $\text{D}_{2h}$  oxalate ion.

Typical infrared and Raman spectra, those of  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ , are shown in Figures 1-3 to 1-5, while Figure 1-6 depicts the great advantage of deuteration in this type of work, the infrared spectrum

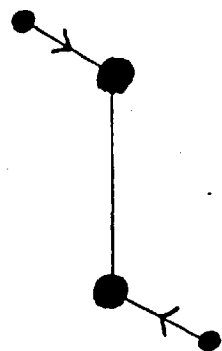
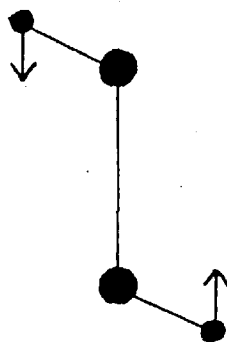
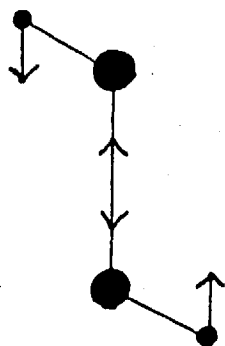
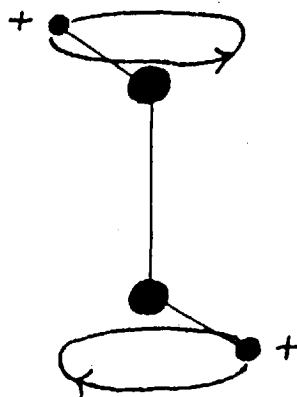
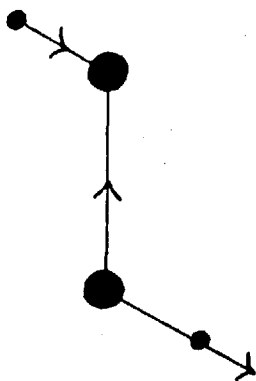
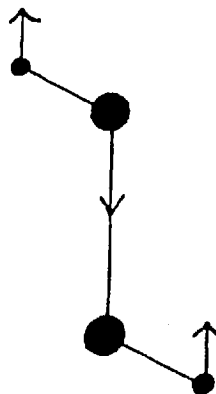
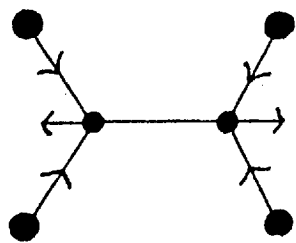
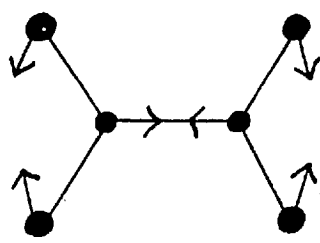
 $\nu_1$ , symm. O-H stretch $\nu_2$ , symm. def. $\nu_3$ , O-O stretch $\nu_4$ , O-O torsion $\nu_5$ , asymm. O-H stretch $\nu_6$ , asymm. def.

Figure 1-1. Normal Modes of Vibrational Motion for the Hydrogen Peroxide Molecule.



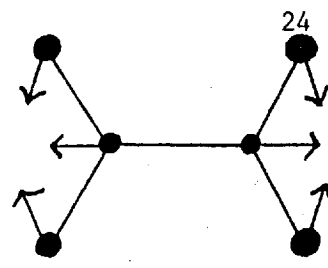
$\nu_1$ , symm. C-O stretch

$A_g$



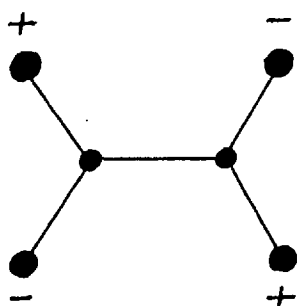
$\nu_2$ , C-C stretch

$A_g$



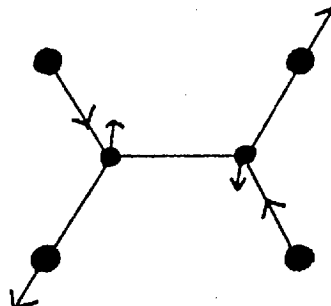
$\nu_3$ , symm. COO def.

$A_g$



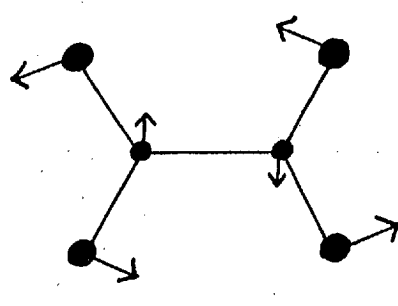
$\nu_4$ , C-C torsion

$A_u$



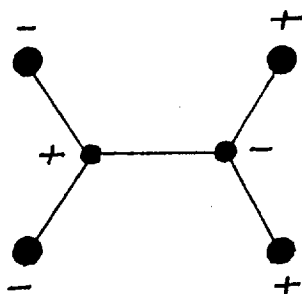
$\nu_5$ , symm. C-O stretch

$B_{1g}$



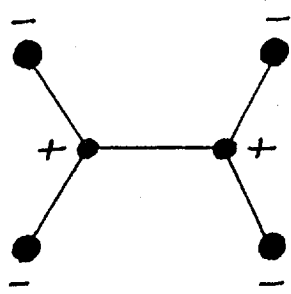
$\nu_6$ , COO rock ip

$B_{1g}$



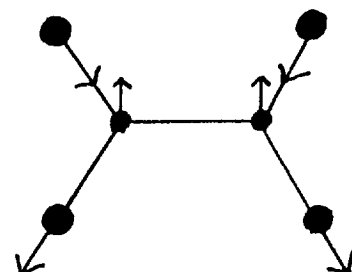
$\nu_7$ , COO rock oop

$B_{3g}$



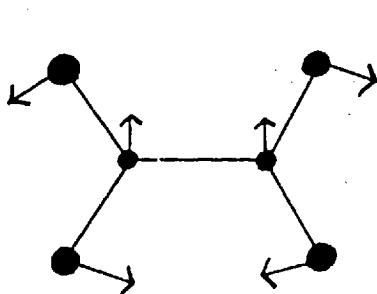
$\nu_8$ , COO rock oop

$B_{1u}$



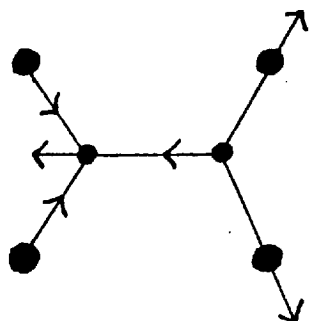
$\nu_9$ , asymm. C-O stretch

$B_{2u}$



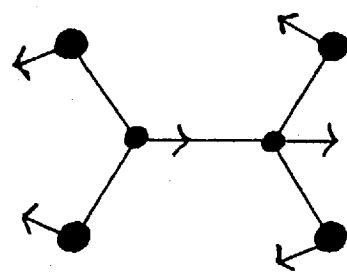
$\nu_{10}$ , COO rock ip

$B_{2u}$



$\nu_{11}$ , asymm. C-O stretch

$B_{3u}$



$\nu_{12}$ , asymm. COO def

$B_{3u}$

Figure 1-2. Normal Modes of Vibrational Motion for the Oxalate Ion with  $D_{2h}$  Symmetry.



of  $K_2C_2O_4 \cdot 2H_2O_2$  clearly revealing the O-O stretch at  $880\text{ cm}^{-1}$ , previously obscured by other  $H_2O_2$  modes which are shifted to lower frequency.

All the monoperhydrates show very strong Raman bands near  $880\text{ cm}^{-1}$  essentially unaffected by deuteration or  $^{13}C$  substitution, and these are assigned to  $\nu_3$ , the O-O stretch. In  $H_2O_2$  itself,  $\nu_3$  is found at  $863.5\text{ cm}^{-1}$  (gas)<sup>33</sup>,  $880\text{ cm}^{-1}$  (liquid)<sup>34</sup> and  $881\text{ cm}^{-1}$  (crystal)<sup>35</sup> in the Raman and is little affected by deuteration.<sup>35</sup> In the potassium, rubidium and caesium salts,  $\nu_3$  appears as a sharp band of moderate intensity in the infrared but, as expected from the above argument, is not observed in the infrared spectra of the lithium and sodium salts. The presence or absence of  $\nu_3$  in the infrared is probably the best guide as to whether the hydrogen-bonded  $H_2O_2$  is skewed or not.<sup>16,30,31</sup> Of the other two bands which might be expected to show similar differences,  $\nu_1$  and  $\nu_2$ , the former is assigned to the strong Raman band near  $3040\text{ cm}^{-1}$  in all the salts; this band, weaker in the infrared for the lithium and sodium compounds, as expected from the selection rules, shifts to ca.  $2200\text{ cm}^{-1}$  on deuteration as expected. The symmetric deformation,  $\nu_2$  is located only as a weak band in the Raman spectra at ca.  $1500\text{ cm}^{-1}$ , shifting by the appropriate amount on deuteration. In crystalline  $H_2O_2$  it also appears only weakly in the Raman at  $1421$  and  $1385\text{ cm}^{-1}$ <sup>35</sup> and in the gas at  $1393\text{ cm}^{-1}$ .<sup>33</sup> This band is not observed, as expected in the infrared spectra of the potassium, rubidium and caesium salts. A possible explanation for this is that there is degeneracy with the asymmetric deformation,  $\nu_6$ ; the latter is clearly observed at  $1470\text{ cm}^{-1}$  in the infrared spectrum of the potassium compound and shifts to  $1090\text{ cm}^{-1}$  on deuteration. In

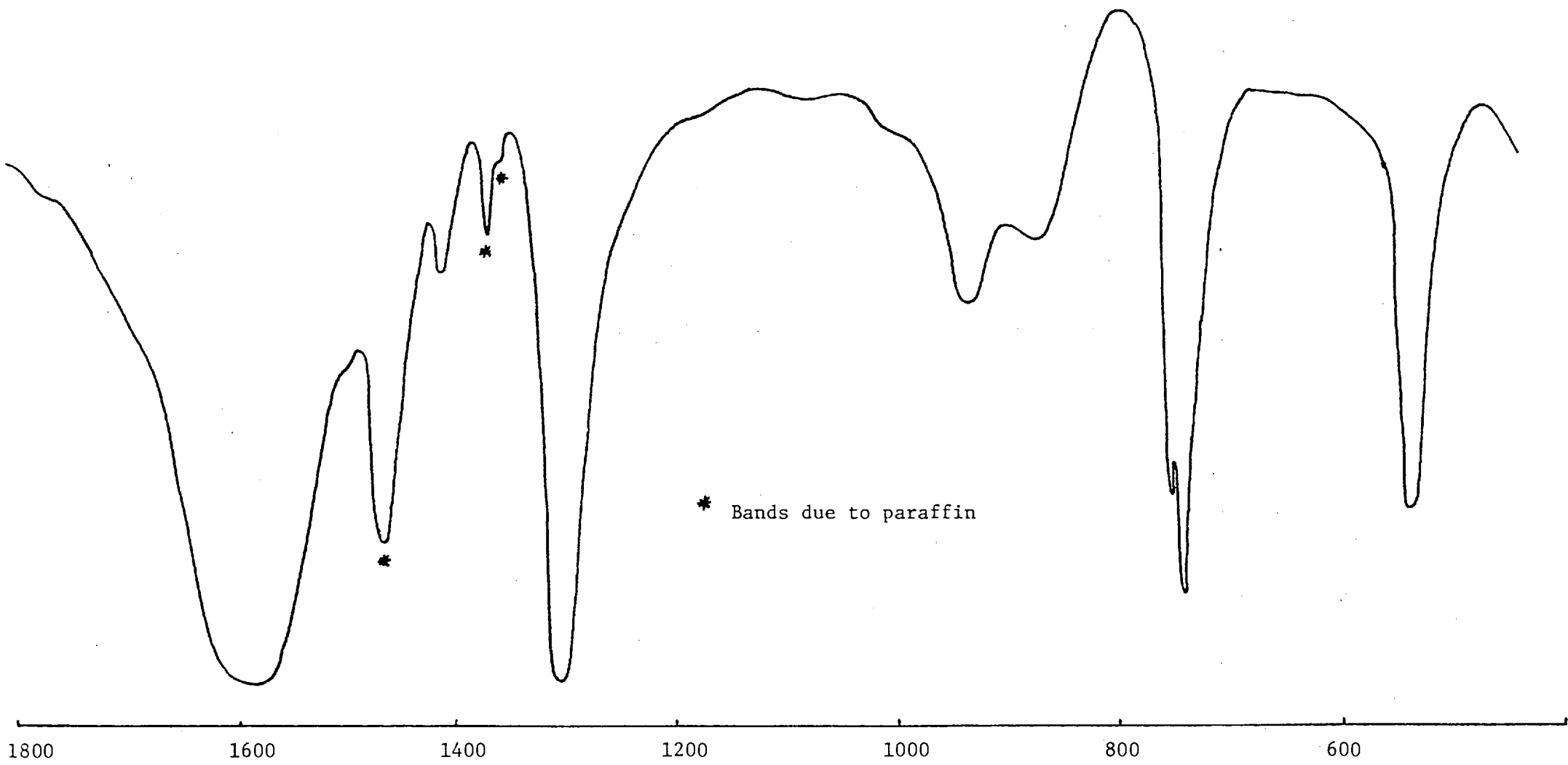
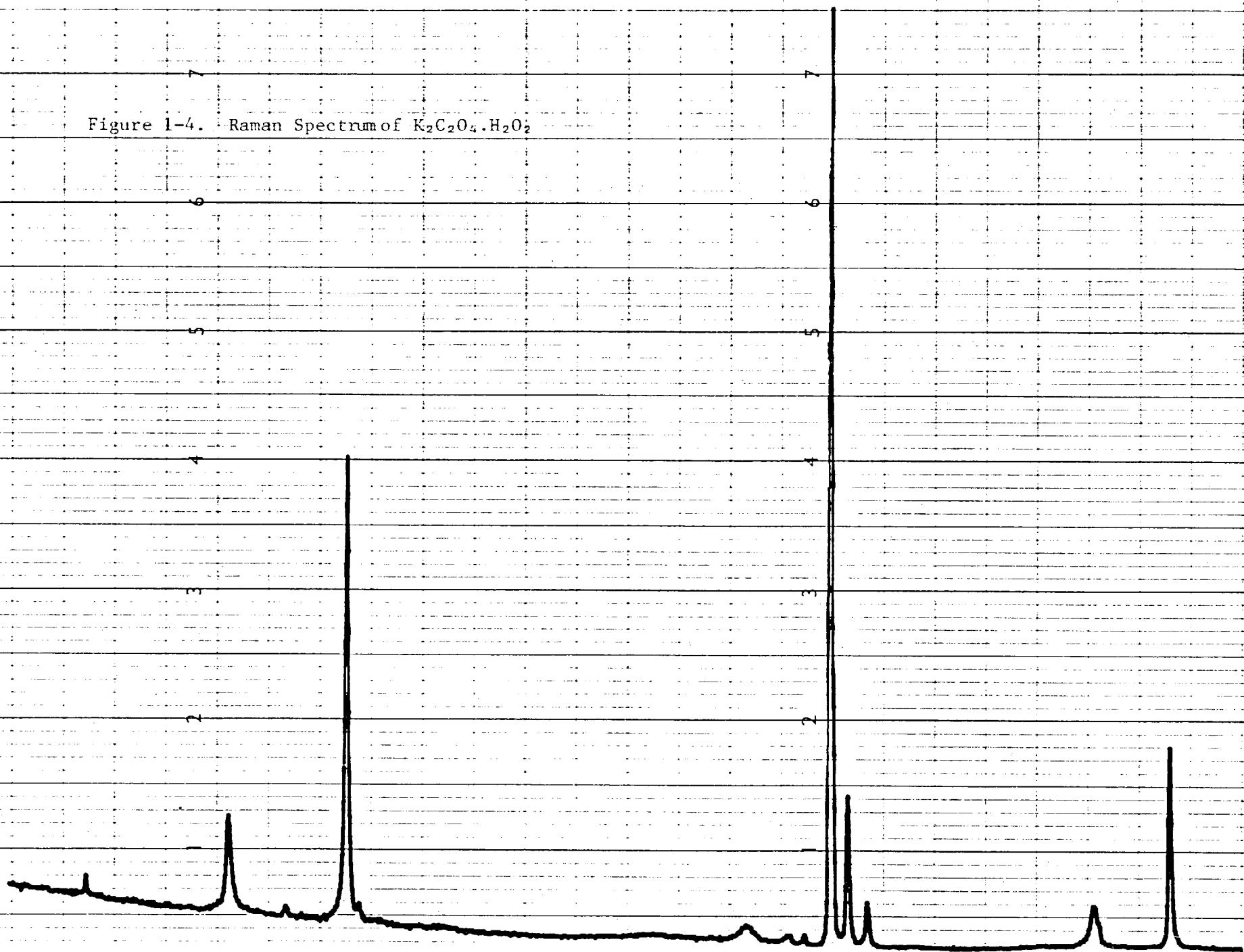


Figure 1-3. Infrared Spectrum of  $K_2C_2O_4 \cdot H_2O_2$

Figure 1-4. Raman Spectrum of  $K_2C_2O_4 \cdot H_2O_2$



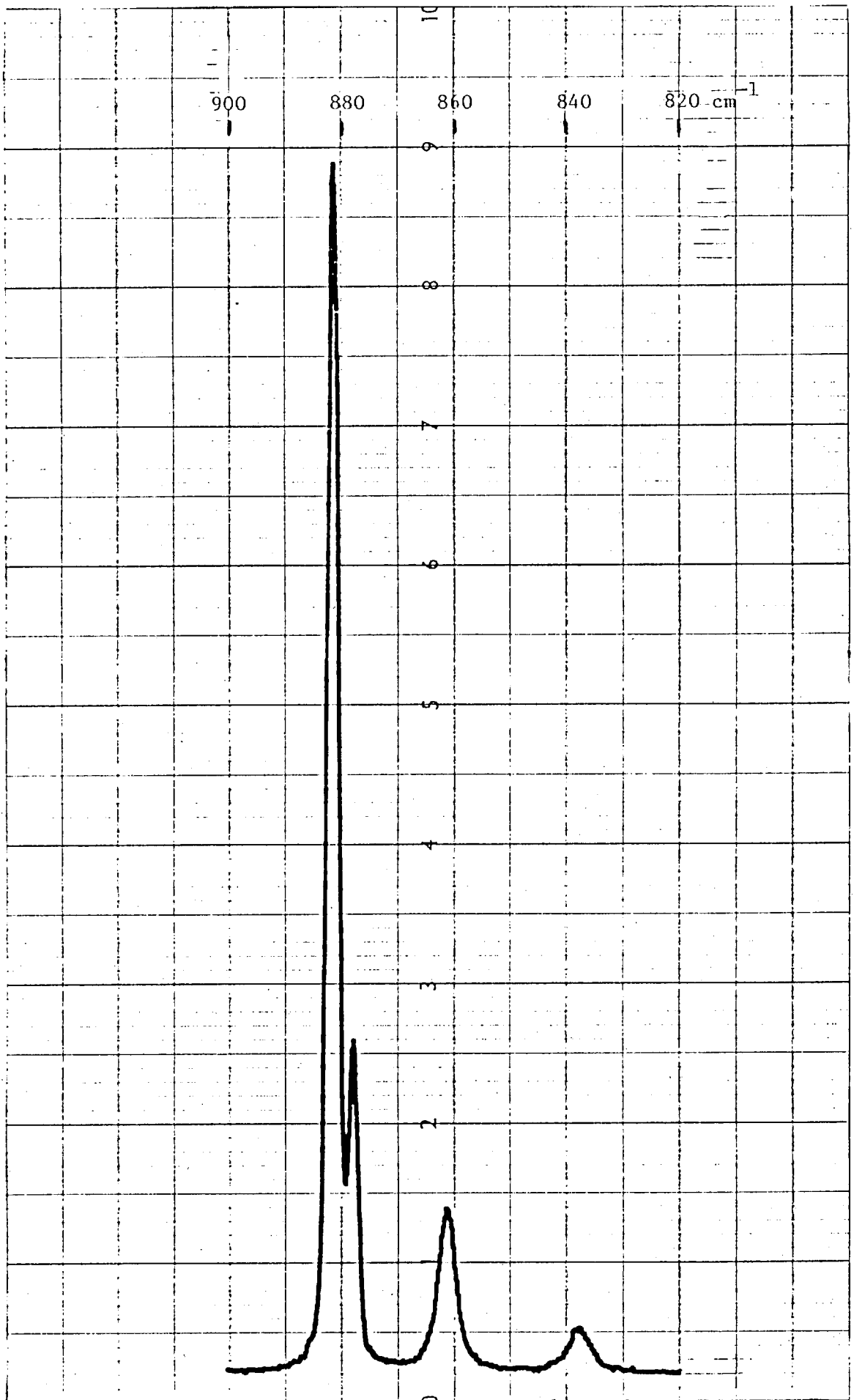


Figure 1-5. Raman Spectrum of  $K_2C_2O_4 \cdot H_2O_2$ , 800-900  $cm^{-1}$ .

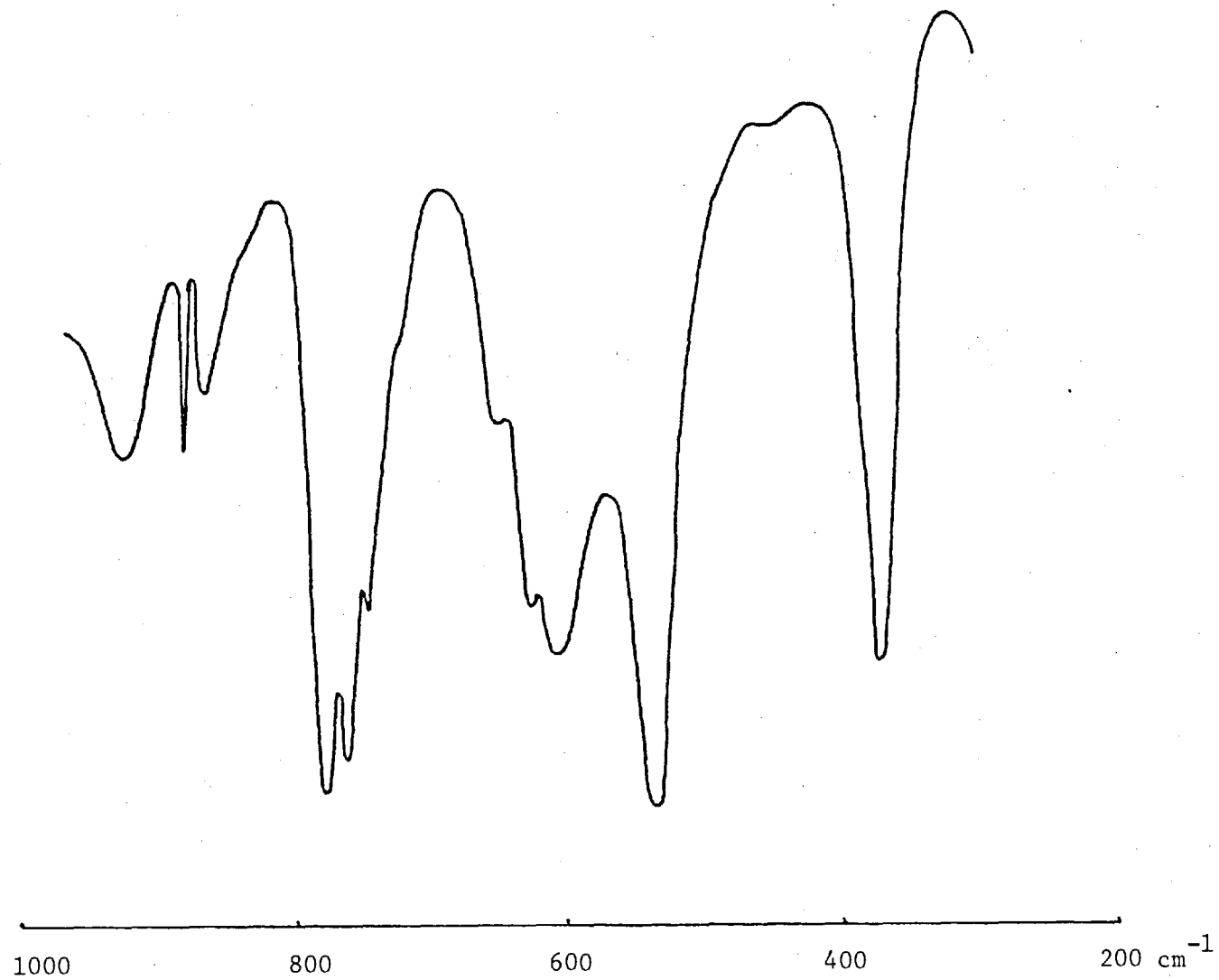


Figure 1-6. Infrared Spectrum of  $K_2C_2O_4 \cdot 2H_2O_2$

gaseous  $\text{H}_2\text{O}_2$ ,  $\nu_6$  appears at  $1266 \text{ cm}^{-1}$  in the infrared and at  $1385 \text{ cm}^{-1}$  in the crystal.<sup>34</sup>

The weaker Raman bands near  $2700 \text{ cm}^{-1}$  are strong in the infrared and shift to ca.  $2060 \text{ cm}^{-1}$  on deuteration, and these are assigned to  $\nu_5$ , the asymmetric O-H stretch. In gaseous  $\text{H}_2\text{O}_2$ ,  $\nu_1$  and  $\nu_5$  appear at  $3614$  and  $3610 \text{ cm}^{-1}$  respectively in the infrared, but in the hydrogen-bonded crystal they are found at  $3285$  and  $3192 \text{ cm}^{-1}$ .<sup>34</sup> However, in crystalline  $\text{H}_2\text{O}_2$  the hydrogen bonds are relatively long ( $2.799 \text{ \AA}$ )<sup>36</sup> in comparison with the much stronger hydrogen bonds (ca.  $2.59$ - $2.69 \text{ \AA}$ ) found in the perhydrates,<sup>12-15</sup> so lower O-H frequencies in the latter are to be expected. The torsion,  $\nu_4$ , may be one of the infrared bands near  $800$ - $900 \text{ cm}^{-1}$ , shifting to ca.  $600 \text{ cm}^{-1}$  on deuteration (in crystalline  $\text{H}_2\text{O}_2$ ,  $\nu_4$  appears at  $690 \text{ cm}^{-1}$  in the infrared<sup>34</sup>). This band is too weak to be observed in the Raman spectra of the potassium, rubidium and caesium salts. Finally, the weak Raman band at  $830$ - $850 \text{ cm}^{-1}$  has been assigned following Arnau and Giguère<sup>30</sup> to the rotational mode,  $R_x$ , this band also appearing in the infrared for the potassium, rubidium and caesium salts.

In all the  $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  salts the oxalate ion, as mentioned earlier, has planar,  $D_{2h}$  symmetry,<sup>12-15</sup> whereas in solution the free ion has  $D_{2d}$  symmetry.<sup>37,38</sup> There are no significant differences in the frequencies of oxalate modes between the perhydrates containing planar  $\text{H}_2\text{O}_2$  (lithium, sodium) and those with skewed  $\text{H}_2\text{O}_2$ . Assignments for the oxalate modes are generally in agreement with those of Arnau and Giguère<sup>30</sup> apart from the very strong band at  $882 \text{ cm}^{-1}$  in the Raman spectrum of  $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  which the above authors assign to the  $\nu_2$  oxalate mode

but which is now assigned, on the basis of its relative intensity and the various shifts observed in the other bands in this region, to the  $\nu_3$  peroxide mode.

The vibrational spectra of  $^{13}\text{C}_2\text{O}_4^{2-}$  have not previously been reported. In Table 1-6 the observed bands for  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{Na}_2^{13}\text{C}_2\text{O}_4$ , together with those for  $\text{C}_2\text{O}_4^{2-}$  and  $^{13}\text{C}_2\text{O}_4^{2-}$  in aqueous solution are listed, with assignments respectively for  $D_{2h}$  and  $D_{2d}$  symmetry using the frequency numbering scheme of Begun and Fletcher<sup>37</sup> for the  $D_{2d}$  form. The spectra and assignments of the anion modes in the solid oxalates are similar to those reported for  $\text{Na}_2\text{C}_2\text{O}_4$  by Arnau and Giguère<sup>30</sup> except for their assignment of the weak band at  $1418\text{ cm}^{-1}$  in the infrared which must be a combination rather than a fundamental, and similar also to those recently reported for  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .<sup>39</sup>

Assignments to bands observed in the Raman spectra of the higher perhydrates,  $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_2$  ( $\text{M} = \text{K}, \text{Cs}$ ) and  $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}_2$  are made tentatively as, in the absence of any infrared data and results for  $^{13}\text{C}$ - and  $^2\text{H}$ -substituted products, there are insufficient data available to confirm the assignments and those made are based solely on comparisons with spectra of the corresponding monoperhydrates.

Interpretation of vibrational spectra obtained for the ammonium salt,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$  is complicated firstly by the obscuring of some of the  $\text{H}_2\text{O}_2$  vibrations by  $\text{NH}_4^+$  modes and secondly by the fact that in this compound the oxalate ion is found to be non-planar, with the planes of the two  $\text{C}-\text{CO}_2$  groups of the ion inclined at an angle of  $28^\circ$ .<sup>15</sup>

Table 1-6

Vibrational Spectra of Normal and  $^{13}\text{C}$ -Enriched Oxalate Ion.

$\text{Na}_2\text{C}_2\text{O}_4$		$\text{Na}_2^{13}\text{C}_2\text{O}_4$		Aqueous $\text{C}_2\text{O}_4^{2-}$		Aqueous $^{13}\text{C}_2\text{O}_4^{2-}$		Assignments	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	$\text{D}_{2h}$	$\text{D}_{2d}$
3040vw		2975vw						$\nu_9 + \nu_{11}$	
2930w		2860w						$\nu_5 + \nu_9$	
	2910vw		n.o.					$2\nu_1$	
2760vw		2710vw						$\nu_1 + \nu_9$	
	2340vw		n.o.					$\nu_1 + \nu_2$	
1886w		1859w						$\nu_6 + \nu_9$	
	1750vw		1691vw					$2\nu_2$	
	1650s		1596m					$\nu_5$	
	1620m		1568m						
1665sh } 1630vsb }		1620sh } 1580vsb }		1580vsb	1580m(dp)	1535vsb	1532m(dp)	$\nu_{11}$	$\nu_5$
	1460vs } 1446w }		1421vs	1490wsh	1488vs(p)	1450wsh	1448vs(p)	$\nu_1$	$\nu_1$
					1460s(dp)		1420s(dp)		$2\nu_8$
1416m } 1400sh } 1340s } 1321s }		1371m } 1350sh } 1315s } 1297s }		1310vs	1310s(dp)	1290vs	1288s(dp)	$\nu_2 + \nu_{10}$	
	887s } 880s }		852s } 826m }		904vs(p)		892vs(p)	$\nu_9$	$\nu_7$
783s } 778s }		773s } 765s }		767s		758s		$\nu_2$	$\nu_2$
	575m } 571m }		560m } 548m }					$\nu_{12}$	$\nu_6$
520s		504s						$\nu_6$	
	486m		476m		448s(p)		448s(p)	$\nu_{10}$	
								$\nu_3$	$\nu_3$



Thus, the local symmetry of the oxalate ion is lowered from  $D_{2h}$  to  $D_2$  and therefore the mutual exclusion rule no longer applies to internal vibrations. However, the  $H_2O_2$  O-O stretching vibration is clearly visible both in the infrared and Raman spectra at 895 and 898  $cm^{-1}$  respectively and the medium intensity of the infrared band is in accordance with that expected for a  $H_2O_2$  molecule having a dihedral angle of  $121^\circ$ . (See Experimental section for a list of vibrational frequencies).

Section 1-C. The Alkali Metal and Ammonium Carbonate Perhydrates,  $M_2^I CO_3 \cdot nH_2O_2$

In general, reaction of alkali metal carbonates with aqueous hydrogen peroxide solutions yields the corresponding carbonate perhydrate [e.g.,  $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ ,<sup>16</sup>  $K_2CO_3 \cdot 3H_2O_2$ ,<sup>40</sup>  $Rb_2CO_3 \cdot 3H_2O_2$ <sup>41</sup> and  $Cs_2CO_3 \cdot 3H_2O_2$ <sup>42</sup>]; no lithium carbonate perhydrate has been reported and attempts to isolate such a compound have been unsuccessful. The preparations of these peroxysalts have been repeated in order to formulate them correctly on the basis of their analytical data and, by means of their vibrational spectroscopic data, to demonstrate that they are individual compounds.

The results show that  $M_2^I CO_3 \cdot nH_2O_2$  ( $M = Na, n = 1\frac{1}{2}$ ;  $M = K, Rb, Cs, n = 3$ ;  $M = NH_4, n = 1$ ) are single compounds and the large number of other alkali metal carbonate perhydrates, both anhydrous and hydrated, appearing in the literature are not individual salts but mixtures. In the case of sodium carbonate alone, twelve different compounds have been reported with varying amounts of hydrogen peroxide and water of crystallisation (e.g., 43-45), but the only perhydrate

of sodium carbonate isolated in this work is  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ . With the other alkali metal carbonates only the triperhydrates seem to be individual compounds, although in the case of the rubidium salt a hexaperhydrate has been reported and demonstrated to be a single compound by means of a low temperature X-ray powder diffraction study.<sup>46</sup>

The ammonium carbonate perhydrate hydrate  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  has been reported briefly<sup>47</sup> but preparations in this work have always yielded a compound of stoichiometry  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$ . Analytical data for the series of carbonate perhydrates are given in Table 1-7.

Considering the relatively large number of papers and patents devoted to carbonate perhydrates, it is remarkable that only two report any vibrational spectra. The first of these<sup>48</sup> lists the infrared frequencies observed for  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot \frac{2}{3}\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot \frac{1}{3}\text{H}_2\text{O}$  and  $\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , none of which appear to be individual compounds. The second describes the infrared and Raman spectra of  $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .<sup>49</sup>

Table 1-8 lists the infrared and Raman stretching frequencies of the alkali metal and ammonium carbonate perhydrates together with their proposed assignments. The spectra are very similar, having features typical of normal  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}_2$  groups and clearly show that all the peroxide oxygen present in these compounds is in the form of hydrogen peroxide of crystallisation, hydrogen-bonded to the carbonate anions. The absence of any bands in the  $3200\text{--}3600\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  regions confirms that there is no water of crystallisation in these compounds.

Table 1-8

## Vibrational Spectra of the Alkali Metal and Ammonium Carbonate Perhydrates.

$\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$		$\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}^2\text{H}_2\text{O}_2$		$\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$	$\text{K}_2\text{CO}_3 \cdot 3^2\text{H}_2\text{O}_2$	$\text{Rb}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$	$\text{Cs}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$	$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}_2^*$		Assignments		
Infrared	Raman	Infrared	Raman	Raman	Raman	Infrared	Raman	Raman	Infrared	Raman	$\text{CO}_3^{2-}$ Modes	$\text{H}_2\text{O}_2$ Modes
3030w } 2900m } 2720sh } 2490s } 2350m } 1870vw 1660vw 1570w } 1550m } 1435vsb	2900wb  2600wb    1552w 1472w } 1400vwb } 1080s  n.o. n.o. 988w  873s } 869vs	2470w } 2210m } 1940sh } 1890s } 1820m }  1140w } 1135m } 1435vsb  1040s } 1035m }  660 635s } 873vw } 869vs	2200wb  1970wb    1136w 1472w } 1400vwb } 1080s  1074s n.o.  670w } 655s } 872s } 869w }  858m  710w } 698w }	n.o.  n.o.   n.o. n.o. 1068s 1070m 1071vs n.o. 900w  882vs } 869s }  858m  710vw } 702vw }	2300wb  2000wb   n.o. n.o. 1068s 1070m n.o. n.o. 674w  869s  830s  710vw } 702vw }	3100m  2650s } 2340m } 1740vw 1650vw  1520m 1400vsb  1070m  n.o. n.o. 884w 950sh } 920s } 860s 830s 700m 699vw }	n.o.  n.o.   n.o. n.o. 1070vs n.o. 884w 884w  876vs } 875vs } 870s } 869s } 865vs } 856s } 706vw } 698vw }	obscd. 2700vs } 2420sh } 2350sh }  n.o. 1440vsb  + 950w  + 870vs  810m 862s 700w } 690sh } 685m }	n.o.  n.o.   n.o. n.o. 1072vs n.o. 912w  870vs  830m 702vw } 689w }	$\nu_1$  $\nu_3$  $\nu_2$  $\nu_3$  $\nu_4$  $\nu_3$  $\nu_2$  $\nu_4$	$\nu_1$  $\nu_3$  $\nu_4$  $\nu_3$  $R_x$  $\nu_2$  $\nu_4$	

\* Bands due to  $\text{NH}_4^+$  are omitted for clarity.

+ Obscured by carbonate ion vibrations.

" Sodium Percarbonate" ,  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ .

Of the series of carbonate perhydrates, the sodium salt is particularly important. Not only is it the most stable both thermally and to moisture, but it is also used extensively in the detergents industry as a bleaching agent, and accounts for something of the order of 25% w/w of the well-known packet detergents " Drive" and " Persil Automatic" .

Since this compound has been formulated as  $\text{Na}_2\text{CO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,<sup>11,50</sup> and so many different anhydrous and hydrated sodium carbonate perhydrates have been reported to exist, crystals were prepared for a full X-ray structural determination and detailed vibrational spectroscopic studies have been carried out.

(a) X-ray Studies.<sup>†</sup>

Crystals were prepared by slow evaporation in air of a solution of anhydrous sodium carbonate in aqueous 10% w/v  $\text{H}_2\text{O}_2$  and proved to be orthorhombic, with  $\underline{a} = 9.183$ ,  $\underline{b} = 15.745$ ,  $\underline{c} = 6.730$  Å, space group Aba2 and  $\underline{z} = 8$ . Intensity data were collected on a Siemens four-circle off-line automatic diffractometer. A total of 490 independent reflections were observed to  $\theta = 70^\circ$ . The least-squares refinement reached a final R value of 0.029.

Figure 1-7 shows the structure of the compound, it basically being made up of sodium and carbonate ions and hydrogen-bonded hydrogen peroxide molecules. The interesting features of the structure are that two crystallographically distinct sites are occupied by the  $\text{H}_2\text{O}_2$  molecules and that the molecules are also disordered. The first type of hydrogen

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<sup>†</sup> The actual structure determination was carried out by

Drs. M.A.A.F. de C.T. Carrondo and A.C. Skapski.

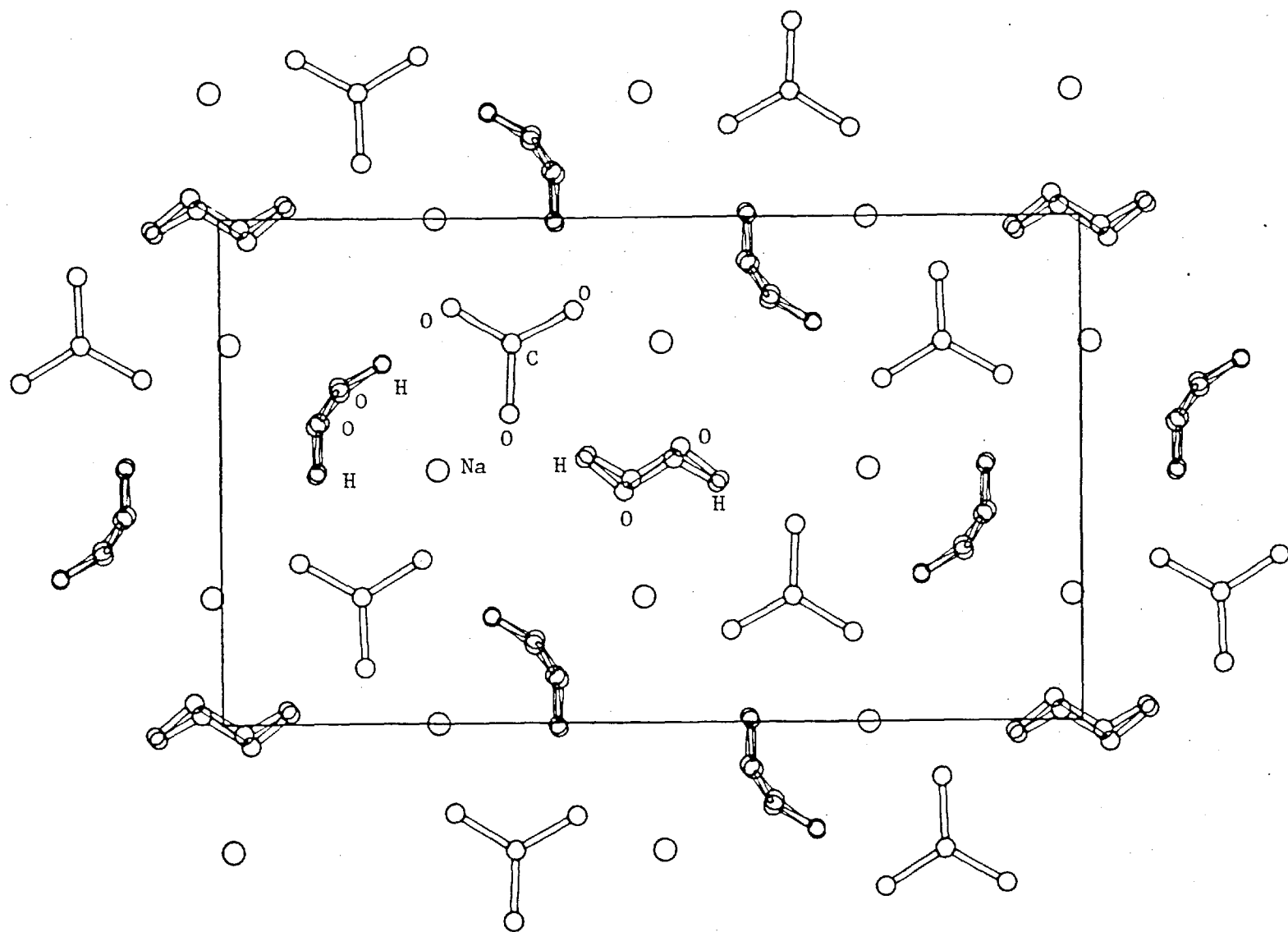


Figure 1-7. A [001] Projection of the Structure of "Sodium Percarbonate",  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ .

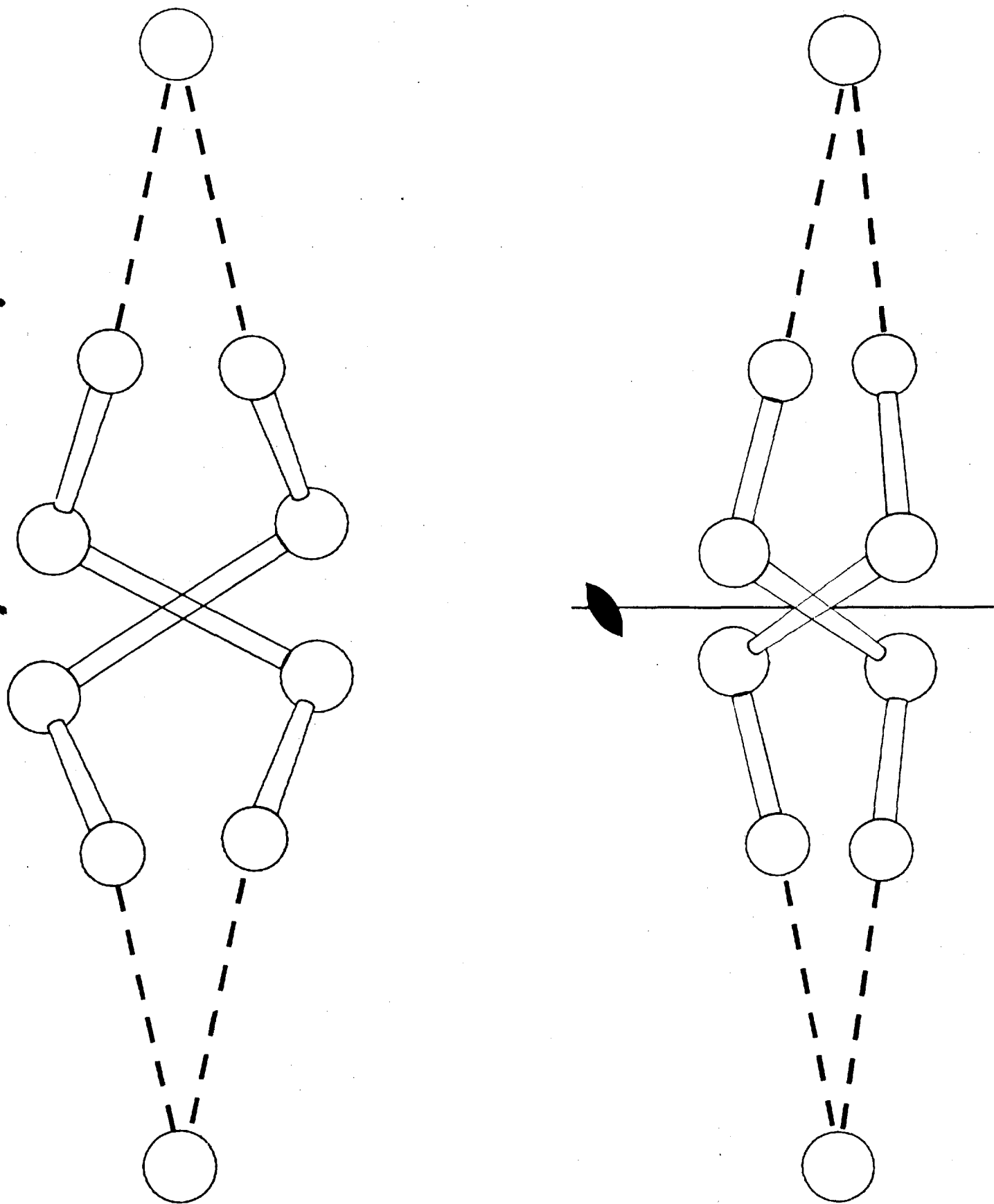


Figure 1-8. Disorder of the Hydrogen Peroxide Molecules in  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ .

peroxide is skewed with a dihedral angle of about  $125^\circ$  while the second type is nearly planar with a dihedral angle of about  $170^\circ$ .

Figure 1-8 shows the picture a bit more clearly, depicting the two different types of hydrogen peroxide molecules anchored to the carbonate ions. It is not surprising that the molecules are disordered, as in both sites the molecule can adopt either of two positions with equal probability, being hydrogen-bonded to the same two carbonate anions.

The presence of both skewed and planar hydrogen peroxide within the same unit cell has not been demonstrated before. However, since the barrier to rotation of hydrogen peroxide from its preferred, skewed conformation of  $111.5^\circ$  in the free molecule<sup>51</sup> to the trans-planar form is only about  $5 \text{ kJ mol}^{-1}$ ,<sup>52</sup> the adoption by the molecule of intermediate conformations due to hydrogen bonding is not surprising.

N.B. While this work was being carried out, another X-ray structure determination on  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  appeared in the literature.<sup>17</sup> This essentially agrees with the above structure, a less accurate determination having been made, reaching a final R factor of 0.114.

#### (b) Vibrational Spectra.

Since the disorder in the hydrogen peroxide molecules prevented as accurate a determination of their conformation as was wished, the vibrational spectra of  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  and its  $^2\text{H}$ - and  $^{13}\text{C}$ -enriched forms were studied at high resolution in order to supplement the X-ray data.

Identification and assignments of bands due to  $H_2O_2$  are made as for the alkali metal oxalate monoperhydrates and assignments of carbonate ion vibrations are made following those of Brooker and Bates.<sup>53</sup>

The  $H_2O_2$  Raman modes are intrinsically weak and broad, with the exception of  $\nu_3$ , but the infrared modes show a systematic splitting of each band into a doublet (with the exception of  $\nu_6$  which is obscured by the  $\nu_3$  carbonate vibration). The bands due to  $\nu_1$ - $\nu_3$  each have a weak and a strong component, whereas those of  $\nu_4$  and  $\nu_5$  have components of comparable intensities.

These splittings could arise from site symmetry or intra-unit cell coupling, but although neither possibility can be excluded, such splitting is not observed in other perhydrates (such as  $M_2^I C_2O_4 \cdot H_2O_2$ ) where only one type of peroxide is present; nor would the observed alternation of intensities be expected. Instead, the effect is attributed to the presence of the two types of peroxide. In the first, which gives rise to the strong infrared components of  $\nu_1$ - $\nu_6$ , the  $H_2O_2$  is considerably skewed and the intensity of  $\nu_3$  relative to the other modes in the infrared is comparable with that in  $(NH_4)_2 \cdot C_2O_4 \cdot H_2O_2$  where the dihedral angle,  $\phi$ , is  $121^\circ$ .<sup>15</sup> The second type of peroxide gives rise to the weaker components of  $\nu_1$ - $\nu_3$  in the infrared and to the second of each of the split bands in  $\nu_4$  and  $\nu_5$ . This fact is suggestive of a group in which the dihedral angle approaches  $180^\circ$  but does not reach it, i.e., a quasi-planar molecule. Thus the spectroscopic data support the X-ray evidence for the second  $H_2O_2$  molecule being almost, but not quite, planar.



The positions of the bands are similar to those found in the alkali metal oxalate perhydrates. The low values of  $\nu_1$  and  $\nu_5$  suggest an O-H $\cdots$ O distance much shorter than that found (2.799 Å) in crystalline H<sub>2</sub>O<sub>2</sub>,<sup>36</sup> comparable with the ca. 2.59-2.69 Å observed in the oxalate perhydrates<sup>12-15</sup> and in close agreement with the values obtained from the X-ray data (ca. 2.54-2.65 Å).

The vibrational spectra of the other members of the series of carbonate perhydrates reported here all exhibit bands characteristic of hydrogen-bonded H<sub>2</sub>O<sub>2</sub> and carbonate anions. The hygroscopic nature and thermal instability of the triperhydrates result in the obtaining of very poor quality infrared spectra and only the frequencies for the rubidium salt are listed in Table 1-8. In the case of the ammonium compound, certain features are masked by bands arising from vibrations of the NH<sub>4</sub><sup>+</sup> ion.

(c) Electron Spin Resonance Spectroscopy.

"Sodium percarbonate" is the only carbonate perhydrate for which e.s.r. spectra have been recorded. No resonance is obtained from this compound at room temperature, but on heating a sample in situ, a very broad signal is observed,  $\Delta H \sim 2500$  Gauss,  $g \sim 2.0$ . This signal is at a maximum at ca. 100°C and disappears on heating the sample to ca. 140°C.

These results are attributed to the formation of hydroperoxide radicals, HO<sub>2</sub> during the thermal decomposition of this compound.

(d) Thermal Decomposition.

It has been noticed that heating "sodium percarbonate" to ca. 80°C for about 1 hour has the effect of causing effervescence when the resulting solid is dissolved in water, giving rise to the term "fizzy percarbonate".<sup>†</sup> XRD data on a sample of  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  that had been stood in an oven in an open vessel at 80°C for 1 hour shows that the solid comprises a mixture of anhydrous  $\text{Na}_2\text{CO}_3$  and undecomposed starting material and presumably the effervescence observed on dissolution in water is due to the presence of some oxygen gas that has been formed during the decomposition and which has become trapped in the crystal lattice. A Raman study on the heated solid has failed to show a band in the region expected for the O=O stretch (ca.  $1550 \text{ cm}^{-1}$ )<sup>54</sup> and so the amount of oxygen concerned must be small. Thermogravimetric analysis (T.G.A) and differential scanning calorimetry (D.S.C) studies on samples of  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  give traces shown in Figures 1-9 and 1-10 respectively. The compound decomposes exothermically at 140-170°C with T.G.A. results giving the expected weight loss for decomposition to anhydrous  $\text{Na}_2\text{CO}_3$  (32.5%).

Section 1-D Other Perhydrates.

It has already been stated (Section 1-A) that perhydrates have been reported for the alkali metal salts of the majority of simple oxyacids but that there does not seem to be any means of predicting their formation or their stoichiometries.

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<sup>†</sup> The author is grateful to Dr. A. Smith of Laporte Industries Ltd., for drawing his attention to this fact.

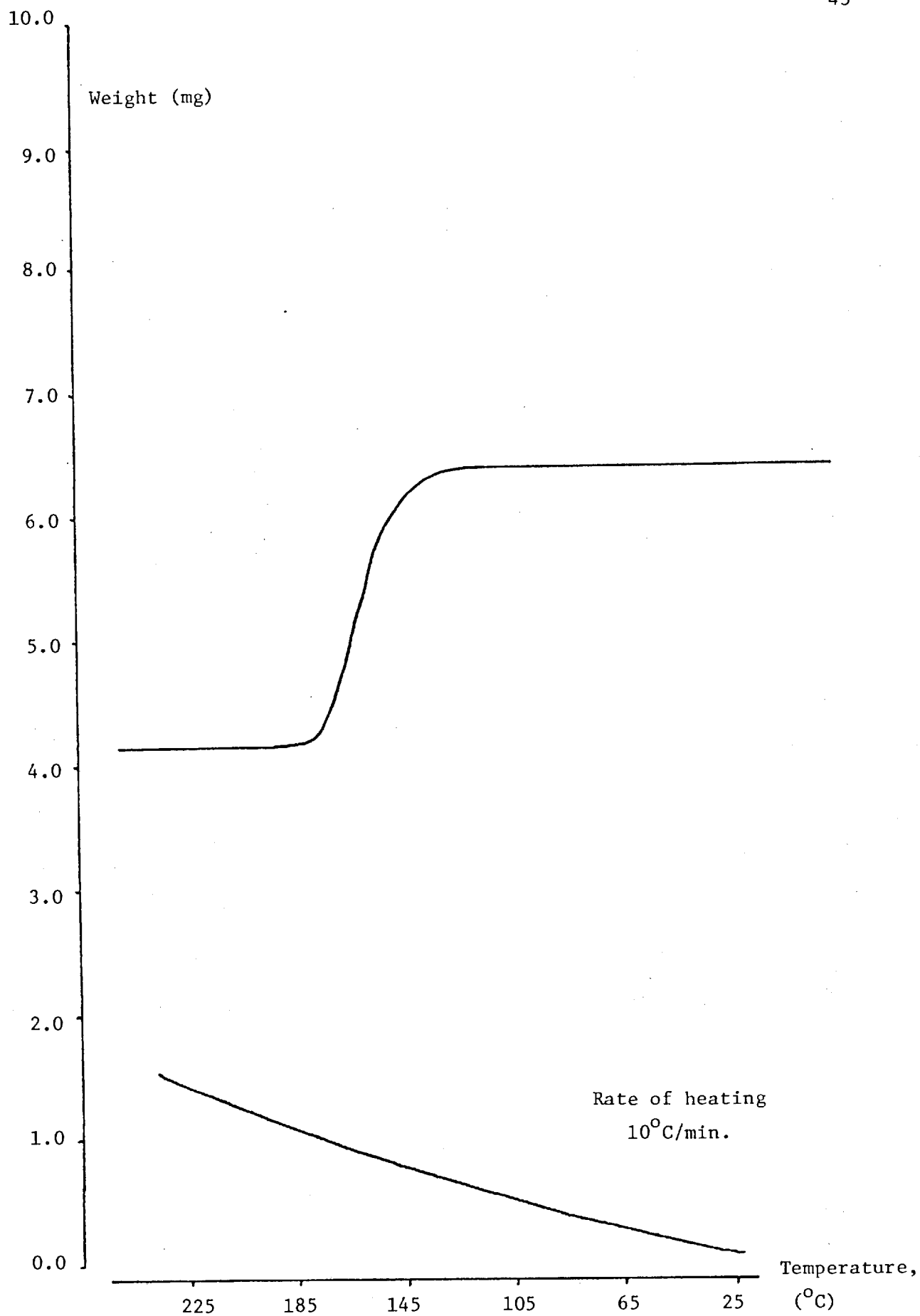


Figure 1-9. T.G.A. Trace for  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ .

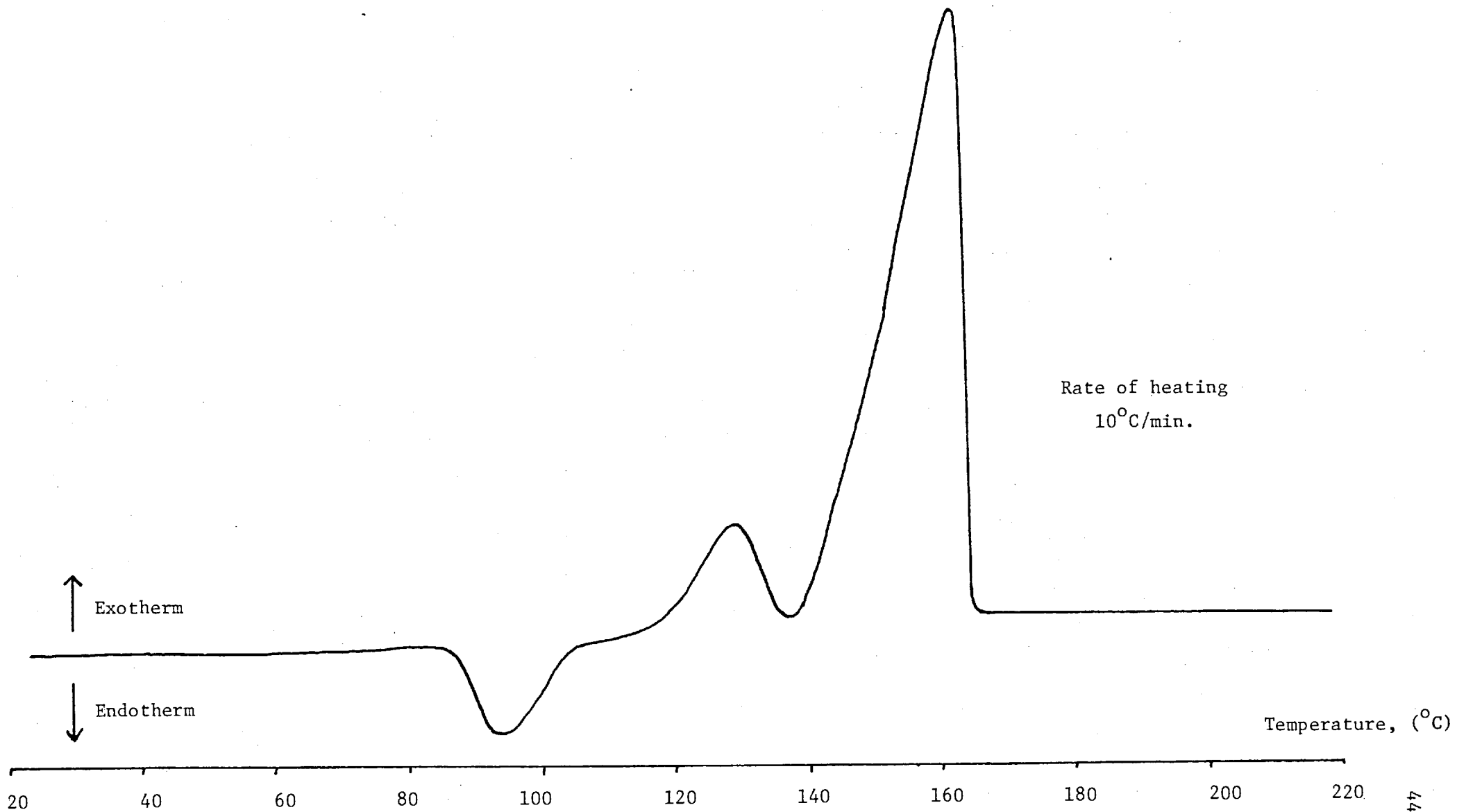


Figure 1-10. D.S.C. Trace for  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$

The work presented in this section is the result of an attempt to characterise a number of perhydrates, some of which either have not been reported previously or have been reported only briefly. The oxyacid salts used in this study were sulphates, orthophosphates, pyrophosphates, formates, acetates and nitrates. Only compounds which gave repeatedly consistent analytical results are reported here, although it is quite probable that other compounds of various stoichiometries do exist.

#### 1-D-1 Sulphate Perhydrates.

The literature reports the following sulphate perhydrates:-

$\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,<sup>55,56</sup>  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ ,<sup>55</sup>  $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$ ,<sup>57</sup>  $\text{Na}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}_2$ ,<sup>56</sup>  
 $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot 9\text{H}_2\text{O}$ ,<sup>58</sup>  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ ,<sup>55</sup>  $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$ <sup>56</sup> and the extremely thermally stable double salt perhydrate  $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$ , which was first reported in a Japanese patent<sup>59</sup> and has recently been the subject of a full X-ray structural determination.<sup>19,20</sup>

This work has characterised the compounds  $\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$ ,  $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$  and a new compound  $\text{KHSO}_4 \cdot \frac{1}{3}\text{H}_2\text{O}_2$  by means of analytical, vibrational spectroscopic, and, in some cases, thermogravimetric and XRD data. The vibrational spectra of these compounds (with the exception of  $\text{KHSO}_4 \cdot \frac{1}{3}\text{H}_2\text{O}_2$ ), together with assignments, are given in Table 1-9. Sparse infrared spectroscopic data have already been reported for  $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$ ,<sup>20</sup> but it should be noted that the two O-H stretching frequencies quoted (at 3200 and 3450  $\text{cm}^{-1}$ ) are grossly in error and in fact three bands are clearly seen at 2800, 2920 and 3140  $\text{cm}^{-1}$  in the infrared.

Table 1-9

## Vibrational Spectra of Sulphate Perhydrates\*

$\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}^\dagger$		$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$		$\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$		$4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$		$(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$		Assignments	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	$\text{SO}_4^{2-}$ Modes	$\text{H}_2\text{O}_2$ Modes
3520vs (2600)	3524s (2620)										$\nu_{\text{O-H}}, \text{H}_2\text{O}$
3405vs (2505)	3408s (2520)										$\nu_{\text{O-H}}, \text{H}_2\text{O}$
3280s (2410)		3310sh									?
3120s (n.o.)	3120w (n.o.)	3100vsb	3150w	3120vsb	n.o.	3140vsb	n.o.				$\nu_1$
3030s (n.o.)	3040w (n.o.)					2920s					?
2800vs (2250)	2820m (2275)	2790vs	2800w	2800vs	2860w	2800vs	2840w				$\nu_3$
1645vs (1210)	n.o. (1212vw)										$\delta_{\text{H}_2\text{O}}$
1440vs (obsd.)	1460vw (n.o.)	1465s } 1440s } 1410vs }	1424vw	1465s } 1437s } 1420s }	1445vw	1480w	1480vw				$\nu_2$
1325w (obsd.)		1370s } 1340sh }		1385sh } 1378s } 1340sh }	1384vw	1440vs } 1370w }					$\nu_6$
	1199w } (1192) } 1184w }		1178w } 1160vw }								
1150vsb } (1150) }	(1181) } 1138w }	1100vsb }	1150w } 1141w }	1150vsb }	1188w } 1090w }	1150vsb }	1163w } 1141w }	1150vsb }	1140m } 1095w }		
1070vsb } (1070) }	(1131) } 1085w } (1084) }	1070vsb }	1122w } 1104w } 1096w }	1070vsb }	1072w }	1070vsb }	1095sh } 1091w }	1050vsb }	1083vw } 1067w }	$\nu_3$	

Table 1-9 (cont.)

$\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}^\dagger$		$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$		$\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$		$4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$		$(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$		Assignments	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	$\text{SO}_4^{2-}$ Modes	$\text{H}_2\text{O}_2$ Modes
	1072w (1054)										$\nu_3$
984vs (984)	986vs (986)	995m } 985m }	997vs } 986m }	985vs	996vs	988vs	991vs	980s	983vs } 974w }		$\nu_1$
874s (874)	874s (878)	880m	882s } 872m }	889s } 870sh }	881vs } 870s }	888s	890s	865w	872s		$\nu_3$
840m (n.o.)		810mb	810vwb	840sh	850sh	770s	765w				$\nu_4$
638sh } (638)	634w } (640sh)	730m	720vwb } 644w }	765m	760vwb } 637w }	690w			635m } 623w }		$\nu_4$
620vs } (620)	617w } (624m)	625sh } 615vs }	630w } 620w }	625sh } 610vs }	624w } 612w }	620vs	634m } 621w }		604w }		
475s (475)	456m (457)	n.o.	469m } 458m } 450w }	n.o.	470sh } 463m }	470m } 451m }	468m } 455m }		471sh } 467m } 453m }		$\nu_2$

\* In the case of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$  only bands attributable to  $\text{SO}_4^{2-}$  or  $\text{H}_2\text{O}_2$  modes are listed.

† Values in parentheses are for  $^2\text{H}$ -substituted compound.

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Assignments for sulphate ion are made following those of Ross, the infrared spectra of the alkali metal sulphates having also, more recently, been reported by Takahashi, et al.<sup>61</sup> There are no unusual features arising from the spectra, the H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> modes occurring at the expected frequencies and the  $\nu_1$  sulphate mode becoming infrared active, while the degenerate frequencies  $\nu_3$  and  $\nu_4$  split as observed in hydrated sulphates. The reasons for the lowering of symmetry probably arise from a combination of three factors - distortion of the SO<sub>4</sub><sup>2-</sup> tetrahedra in the crystal lattices, covalent bonding of the sulphate to the metal through one or more oxygen atoms and a non-uniform field due to H<sub>2</sub>O<sub>2</sub> molecules around the cation. The most noteworthy feature of the spectra is the fact that a medium to strong intensity band appears at ca. 880 cm<sup>-1</sup> in all of the infrared spectra, indicating the presence of skewed H<sub>2</sub>O<sub>2</sub> molecules with various dihedral angles. This band is split in the Raman spectra of the mono- and diperhydrates, suggesting two crystallographically distinct H<sub>2</sub>O<sub>2</sub> sites, each probably possessing different dihedral angles as found in Na<sub>2</sub>CO<sub>3</sub>.1 $\frac{1}{2}$ H<sub>2</sub>O<sub>2</sub>.<sup>16</sup>

The infrared spectrum of KHSO<sub>4</sub>. $\frac{1}{3}$ H<sub>2</sub>O<sub>2</sub> is rather broad and featureless, presumably due to strong hydrogen-bonding and resembles that of KHSO<sub>4</sub> itself. However, the Raman spectrum consists of well-resolved bands attributable to HSO<sub>4</sub><sup>-</sup> and hydrogen-bonded H<sub>2</sub>O<sub>2</sub>. Frequencies for this compound are listed in Section 1-E-3.

#### 1-D-2 Phosphate Perhydrates.

Addition compounds between hydrogen peroxide and both alkali metal orthophosphates (mono-, di- and tribasic) and pyrophosphates are numerous



and, as in the case of the alkali metal carbonate perhydrates, many of the reported species are probably mixtures rather than individual compounds.

An early review on "perphosphates" by Husain and Partington<sup>62</sup> describes several phosphate perhydrates, giving the probable formulae and an indication of their stability. They conclude that there seems to be some relation between the alkalinity of the phosphate and the formation of perhydrates. Thus acidic phosphates do not form perhydrates or else give very unstable compounds, alkaline phosphates, such as dibasic orthophosphates and pyrophosphates, give stable adducts, while strongly alkaline phosphates, like  $K_3PO_4$ , decompose hydrogen peroxide.

More recently, a review by Creaser and Edwards<sup>63</sup> highlights the disagreement by different research groups on the compositions of products obtained from the same systems. For example, the relatively stable solid obtained from mixtures of  $Na_4P_2O_7$  and  $H_2O_2$  has been reported as  $Na_4P_2O_7 \cdot 2H_2O_2$ ,  $Na_4P_2O_7 \cdot 2\frac{1}{2}H_2O_2$ ,  $Na_4P_2O_7 \cdot 3H_2O_2$  and  $Na_4P_2O_7 \cdot 6H_2O_2$ .

A detailed study has been made on some of the physicochemical properties of the compounds  $K_3PO_4 \cdot nH_2O_2$  ( $n = 1, 2, 4$ ) and  $K_4P_2O_7 \cdot 6H_2O_2$ .<sup>64</sup> This includes thermal decomposition, electron spin resonance, infrared and density measurements.

In this work, products arising from the reaction between a large number of alkali metal and ammonium phosphates and hydrogen peroxide under different conditions have been obtained and analysed for peroxide content. As stated at the beginning of this section, only compounds which gave repeatedly consistent analytical results are reported, although perhydrates seem to be formed for all of the

following phosphates:-  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Na}_4\text{P}_2\text{O}_7$  and  $\text{K}_4\text{P}_2\text{O}_7$ . The compounds  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)\text{H}_2\text{PO}_4$  and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  do not form perhydrates under the conditions employed here. Consistent analytical results were obtained for salts of stoichiometries:-  $\text{Na}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{K}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}_2$ ,  $\text{K}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}_2$ ,  $\text{KH}_2\text{PO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}_2$ ,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}_2$ ,  $\text{K}_4\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}_2$  and  $\text{K}_4\text{P}_2\text{O}_7 \cdot 8\text{H}_2\text{O}_2$ . However, several of these are extremely hygroscopic and rather thermally unstable which prevented measurement of vibrational spectra, and therefore little structural information is available on this series of perhydrates. Analytical data and vibrational spectral frequencies are given in the Experimental Section.

### 1-D-3 Formate and Acetate Perhydrates.

The formation of a compound of stoichiometry  $\text{NaCOOCH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$  has been reported very recently following a study of the sodium acetate-water-hydrogen peroxide system.<sup>65</sup>

In this work, both the lithium and sodium acetate hemiperhydrates have been prepared and characterised by their analytical and vibrational spectroscopic data. No formate perhydrates appear to have been reported previously; a compound having the formula  $\text{NaCOOH} \cdot \text{H}_2\text{O}_2$  has been prepared together with its  $^{13}\text{C}$  and  $^2\text{H}_2\text{O}_2$ -enriched analogues, the latter in order to make correct vibrational band assignments.

N.B. In an attempt to prepare a perhydrate of potassium formate, an explosion resulted and so further experiments were not carried out. Vibrational spectra for these compounds are listed in Table 1-10 with assignments for acetate and formate ions based on those given by Ito and Bernstein.<sup>66</sup>

Table 1-10

Vibrational Spectra of Acetate and Formate Perhydrates

$\text{LiCOOCH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$	$\text{NaCOOCH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$		$\text{NaCOOH} \cdot \text{H}_2\text{O}_2^*$		Assignments		
Raman	Infrared	Raman	Infrared	Raman	Acetate Modes	Formate Modes	$\text{H}_2\text{O}_2$ Modes
4000-2000 $\text{cm}^{-1}$	3040w	n.o.	3100 (2240)m 3000 (2180)m 2930 (2110)m	4000-2000 $\text{cm}^{-1}$			$\nu_1$
Region not measured	3010w 2980w 2930w 2580sb 1570vs 1500sh	3020m 2985m 2930vs n.o.	2740 (2080)s 1560vsb		Region not measured	$\nu_7$ $\nu_{12}$ $\nu_1$	
			1490 (1110)m 1450 (1085)m	1490 (1114)vw 1465 (1085)w 1454 (obscd)w	$\nu_8$ $\nu_{13}$	$\nu_4$	$\nu_6$ $\nu_2$
	1432s 1422s 1414s	1443m 1431m	1475m		$\nu_9$ $\nu_2$ $\nu_3$	?	
1453m		1408s 1374w 1350m	1390s 1380s	1390m 1385m	?	$\nu_5$	
1360m	1330m	1333m	1355s	1364w 1351vs 1338w	?	$\nu_2$	
	1048s 1020s			1079vw 926 (790) vw	$\nu_{14}$ $\nu_{10}$	$\nu_6$	?
	945m	890 (630)m 923vs					$\nu_4$
957s					$\nu_4$		

Table 1-10 (cont).

LiCOOCH <sub>3</sub> · ½H <sub>2</sub> O <sub>2</sub>	NaCOOCH <sub>3</sub> · ½H <sub>2</sub> O <sub>2</sub>		NaCOOH · H <sub>2</sub> O <sub>2</sub> *		Assignments			
	Raman	Infrared	Raman	Infrared	Raman	Acetate Modes	Formate Modes	H <sub>2</sub> O <sub>2</sub> Modes
888vs	865sh	897s } 884s } 869vs }	875 (875)m		877 (879)vs			v <sub>3</sub>
	840m		840 (580)mb					R <sub>x</sub>
674s	657s } 650s }	662s } 650m }	773w } 755m } 743m }		742w } 736w }	v <sub>5</sub>	v <sub>3</sub>	
624m	624s	637w } 626m }				v <sub>15</sub>		

\* Values in parentheses for <sup>2</sup>H<sub>2</sub>O<sub>2</sub> - substituted compound

#### 1-D-4 Nitrate Perhydrates.

Perhydrates have been reported for both potassium and rubidium nitrates, the formulae quoted being  $\text{KNO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}_2$ ,  $\text{RbNO}_3 \cdot \frac{3}{7} \text{H}_2\text{O}_2$  and  $\text{RbNO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}_2$ .<sup>67</sup>

In this work, attempts to prepare perhydrates of  $\text{M}^{\text{I}}\text{NO}_3$  (M = Li, Na, K,  $\text{NH}_4$ ) have resulted in the isolation of only one such compound,  $\text{KNO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}_2$ .

Satisfactory elemental analyses and infrared data have not been obtained for this compound due to its instability but analyses for peroxide content of products from several preparations are consistent with this formula. Its Raman spectrum shows no contamination by anhydrous  $\text{KNO}_3$  or free  $\text{H}_2\text{O}_2$ , the nitrate and peroxide bands appear at frequencies different from those of the starting materials. These frequencies are given in the Experimental Section.

### Section 1-E EXPERIMENTAL

#### 1-E-1 Alkali Metal and Ammonium Oxalate Perhydrates, $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot n\text{H}_2\text{O}_2$ .

All monoperhydrates were prepared by the slow evaporation of a solution of the appropriate anhydrous or hydrated oxalate in aqueous 30% w/v  $\text{H}_2\text{O}_2$  in air or in a vacuum desiccator over  $\text{P}_2\text{O}_5$  at room temperature. This procedure invariably resulted in the formation of large, well-shaped crystals. The higher perhydrates,  $\text{Na}_2\text{C}_2\text{O}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}_2$  and  $\text{M}_2^{\text{I}}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_2$  (M = K, Cs) were made by evaporation of similar solutions in vacuo. The isotopically-enriched ( $^2\text{H}$ ,  $^{13}\text{C}$ ) forms were prepared from the appropriately substituted reactants. Sodium oxalate enriched to 91.3 atom % in  $^{13}\text{C}$  was purchased from the British Oxygen Company Ltd., and the corresponding potassium salt was generated from the sodium compound using a cation exchange resin ("Zerolit 225", B.D.H.

Table 1-2

Elemental Analyses for the Alkali Metal and Ammonium Oxalate Perhydrates\*

	% Found					% Required				
	O <sub>2</sub> <sup>-</sup>	C	H	N	<u>M</u>	O <sub>2</sub> <sup>-</sup>	C	H	N	<u>M</u>
Li <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	23.6	17.5	1.5			23.6	17.7	1.5		
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	18.6	14.1	1.2			19.0	14.3	1.2		
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	15.8	12.1	1.0		37.2	16.0	12.0	1.0		39.1
Rb <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	10.6	7.8	0.7		56.6	11.0	8.2	0.7		58.3
CS <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	7.6	6.2	0.6		65.2	8.2	6.2	0.5		68.5
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O <sub>2</sub>	20.4	15.8	5.1	17.5	22.3	20.2	15.2	6.4	17.7	22.8
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2½H <sub>2</sub> O <sub>2</sub>	36.2	10.6	1.0			36.6	11.0	2.3		
K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O <sub>2</sub>	25.8	10.7	0.9		31.7	27.4	10.3	1.7		33.4
CS <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O <sub>2</sub>	22.0	5.8	0.9		60.6	22.8	5.7	1.0		63.0

\* Further evidence as to the stoichiometry of the monoperhydrates was obtained thermogravimetrically, all salts losing close to the calculated weight of hydrogen peroxide at 75-100°C

Vibrational Spectral Data for  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ .

Infrared : 3200vsb, 2980vs, 2760vs, 2100w, 1860w, 1730w, 1700w,  
1650s, 1620vsb, 1450s, 1420s, 1320sh, 1310vs, 895m, 865w, 780s, 720m.

Raman : 1739w, 1725w, 1702w, 1620w, 1600w, 1586w, 1552w, 1466vs,  
1453m, 1444s, 1428w, 1307w, 898vs, 891s, 867w, 640w, 551w, 500w, 477m,  
460w.

Chemicals Ltd.). Aqueous 30% w/v  $\text{H}_2\text{O}_2$  enriched to ca. 95% in  $^2\text{H}$  was prepared by the repeated distillation in vacuo of  $\text{H}_2\text{O}_2$ - $^2\text{H}_2\text{O}$  solutions.

1-E-2. Alkali Metal and Ammonium Carbonate Perhydrates,  $\text{M}_2^{\text{I}}\text{CO}_3 \cdot n\text{H}_2\text{O}_2$ .  
Sodium Carbonate Sesquiperhydrate,  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ .

To a solution of anhydrous sodium carbonate (0.5 g, 4.7 mmol) in aqueous 15% w/v  $\text{H}_2\text{O}_2$  (10  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added dropwise, with stirring, ethanol (5  $\text{cm}^3$ ). The white precipitate formed was filtered off, washed copiously with ethanol and diethyl ether and dried in vacuo. XRD data are given in Table 1-11.

Potassium Carbonate Triperhydrate,  $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .

To a solution of anhydrous potassium carbonate (1.0 g, 7.2 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added dropwise, with stirring, ethanol (5  $\text{cm}^3$ ). An oil was formed together with some colourless microcrystals, and, after standing for several hours at  $-20^\circ\text{C}$  the oil slowly crystallised. The solid product was filtered off at  $-20^\circ\text{C}$  under nitrogen gas, washed copiously with ethanol and diethyl ether and dried in vacuo.

N.B. This compound is extremely hygroscopic and thermally unstable and is best stored under dry nitrogen gas at low temperature.

Rubidium Carbonate Triperhydrate,  $\text{Rb}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .

To a solution of anhydrous rubidium carbonate (0.2 g, 0.9 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (2.5  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added dropwise, with stirring, acetone (5  $\text{cm}^3$ ). A mass of colourless microcrystals formed almost immediately and the mixture was stood for several hours at  $-20^\circ\text{C}$  to ensure complete precipitation. The microcrystals were then



Table 1-7

Elemental Analyses for the Alkali Metal and Ammonium Carbonate Perhydrates.

	% Found					% Required				
	O <sub>2</sub> <sup>-</sup>	C	H	N	<u>M</u>	O <sub>2</sub> <sup>-</sup>	C	H	N	<u>M</u>
Na <sub>2</sub> CO <sub>3</sub> ·1½H <sub>2</sub> O <sub>2</sub>	30.6	7.8	2.1			30.6	7.7	1.9		
K <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>	40.0	6.9	1.6		34.8	40.0	5.0	2.5		32.6
Rb <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>	28.4	3.9	1.3		48.3	28.8	3.6	1.8		51.3
Cs <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>	22.4	3.2	1.5		61.3	22.4	2.8	1.4		62.1
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O <sub>2</sub>	24.8	8.9	6.9	19.5	25.1	24.6	9.2	7.8	21.5	27.7

filtered off under nitrogen at  $-20^{\circ}\text{C}$ , washed with acetone ( $10\text{ cm}^3$ ) and dried in vacuo. The properties of the product are similar to those of the potassium salt.

Caesium Carbonate Triperhydrate,  $\text{Cs}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .

To a solution of anhydrous caesium carbonate (1.0 g, 3.1 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  ( $3\text{ cm}^3$ ) at  $0^{\circ}\text{C}$  was added dropwise, with stirring, acetone ( $7\text{ cm}^3$ ). A mass of colourless microcrystals formed almost immediately and these were collected in the same manner as the rubidium analogue. Its properties are similar to the potassium salt.

Ammonium Carbonate Monoperhydrate,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$ .

A solution of ammonium hydrogen carbonate (1.0 g, 14.9 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  ( $5\text{ cm}^3$ ) was allowed to evaporate slowly in a watch-glass in a refrigerator at  $5^{\circ}\text{C}$  over a period of 3-4 days. This procedure resulted in the formation of well-shaped crystals which were washed copiously with ethanol and diethyl ether and dried briefly in air. (This compound decomposes in vacuo).

The isotopically-enriched forms ( $^2\text{H}$ ,  $^{13}\text{C}$ ) were prepared from the appropriately substituted reactants. Sodium carbonate enriched to 92.1 atom % in  $^{13}\text{C}$  and potassium carbonate enriched to 92.2 atom % in  $^{13}\text{C}$  were purchased from the British Oxygen Company Ltd.

1-E-3 Other Salt Perhydrates.

Sodium Sulphate Hemiperhydrate Monohydrate,  $\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ .

(a) To a solution of anhydrous sodium sulphate (2.0 g, 14.1 mmol) in aqueous 50% w/w  $\text{H}_2\text{O}_2$  ( $5\text{ cm}^3$ ) at  $0^{\circ}\text{C}$  was added dropwise, with stirring,

Table 1-11

XRD Data for  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ 

I	dÅ	I	dÅ	I	dÅ	I	dÅ
w	7.8	s	3.34	s	2.725	w	2.27
m	5.95	m	3.08	s	2.70	vw	2.22
m	4.58	m	3.07	vs	2.55	vw	2.19
m	3.94	vw	3.02	vw	2.45	vw	2.16
m	3.75	w	2.97	s	2.41	m	2.14
m	3.67	s	2.91	vw	2.36	vw	2.07
m	3.60	m	2.84	w	2.28	vw	2.00

Table 1-12

XRD Data for  $\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ 

I	dÅ	I	dÅ	I	dÅ	I	dÅ
m	8.7	s	3.38	vw	2.51	vw	2.22
vs	5.35	vs	3.14	w	2.475	vw	2.175
m	4.85	vs	3.01	w	2.44	s	2.15
m	4.35	s	2.73	s	2.42	m	2.13
m	4.25	s	2.68	vw	2.40	w	2.03
s	4.03	s	2.67	m	2.375	w	2.02
vs	3.65	s	2.65	s	2.28	m	2.00
s	3.45	s	2.57	w	2.25		

ethanol (5 cm<sup>3</sup>). The white, microcrystalline precipitate was filtered off, washed copiously with ethanol and diethyl ether and dried in vacuo. (Found : H, 1.5 ; S, 18.1 ; O<sub>2</sub><sup>2-</sup>, 9.0. H<sub>3</sub>Na<sub>2</sub>O<sub>6</sub>S requires H, 1.7 ; S, 18.1 ; O<sub>2</sub><sup>2-</sup>, 9.0%). This compound decomposes at 60-80°C, XRD data are given in Table 1-12.

(b) A dilute solution of anhydrous sodium sulphate in aqueous 15% w/v H<sub>2</sub>O<sub>2</sub> was allowed to evaporate slowly in air at room temperature. This procedure yielded large, well-shaped crystals which were washed with ethanol and diethyl ether and air-dried.

(c) To a solution of sodium hydrogen sulphate (2.0 g, 16.7 mmol) in aqueous 50% w/w H<sub>2</sub>O<sub>2</sub> (5 cm<sup>3</sup>) at 0°C was added dropwise, with stirring, ethanol (5 cm<sup>3</sup>). The precipitate formed was collected and dried in the same manner as for (a) above.

#### Sodium Sulphate Monoperhydrate, Na<sub>2</sub>SO<sub>4</sub>.H<sub>2</sub>O<sub>2</sub>.

A solution of anhydrous sodium sulphate (1.0 g, 7.0 mmol) in aqueous 30% w/v H<sub>2</sub>O<sub>2</sub> (5 cm<sup>3</sup>) was evaporated to dryness in vacuo at room temperature to yield colourless crystals of the product. (Found : H, 1.0 ; S, 15.6 ; O<sub>2</sub><sup>2-</sup>, 18.0. H<sub>2</sub>Na<sub>2</sub>O<sub>6</sub>S requires H, 1.2 ; S, 18.2 ; O<sub>2</sub><sup>2-</sup>, 18.2%).

#### Sodium Sulphate Diperhydrate, Na<sub>2</sub>SO<sub>4</sub>.2H<sub>2</sub>O<sub>2</sub>.

To a solution of anhydrous sodium sulphate (1.0 g, 7.0 mmol) in 86% w/w H<sub>2</sub>O<sub>2</sub> (2.5 cm<sup>3</sup>) at -10°C, was added dropwise, with stirring, ethanol (5 cm<sup>3</sup>). The precipitate formed was collected and dried in the usual manner. (Found : O<sub>2</sub><sup>2-</sup>, 28.4. H<sub>4</sub>Na<sub>2</sub>O<sub>8</sub>S requires O<sub>2</sub><sup>2-</sup>, 30.5%).

Sodium Sulphate-Sodium Chloride-Hydrogen Peroxide,  $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$ .

A solution of sodium chloride (0.1 g, 1.7 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (2  $\text{cm}^3$ ) was added dropwise, with stirring, to a solution of anhydrous sodium sulphate (0.97 g, 6.8 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) at room temperature. The resulting solution was allowed to evaporate slowly in air at room temperature to yield large, well-shaped crystals which were collected in the usual manner and air-dried. (Found : Cl, 5.0 ; H, 0.5 ; S, 17.9 ;  $\text{O}_2^{2-}$ , 9.2.  $\text{C}/\text{H}_4\text{Na}_9\text{O}_{20}\text{S}_4$  requires Cl, 5.1 ; H, 0.6 ; S, 18.5 ;  $\text{O}_2^{2-}$ , 9.2%). This compound is remarkably thermally stable, decomposing only at temperatures above ca.  $160^\circ\text{C}$ . XRD data are given in Table 1-13.

Ammonium Sulphate Monoperhydrate,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ .

(a) To a solution of ammonium sulphate (1.0 g, 7.6 mmol) in aqueous 30% w/v or 50% w/w  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added dropwise, with stirring, ethanol (5  $\text{cm}^3$ ). An oil was formed, which, on standing at  $-5^\circ\text{C}$  for 48 hours yielded large, well-shaped crystals which were collected in the usual manner and air-dried. (Found : H, 5.6 ; N, 18.5 ; S, 19.4,  $\text{O}_2^{2-}$ , 19.2.  $\text{H}_{10}\text{N}_2\text{O}_6\text{S}$  requires H, 6.1 ; N, 16.9 ; S, 19.3 ;  $\text{O}_2^{2-}$ , 19.2%).

(b) A solution of ammonium sulphate (1.0 g, 7.6 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) was evaporated to dryness in vacuo to yield the product as a colourless, microcrystalline solid.

Potassium Hydrogen Sulphate Perhydrate,  $\text{KHSO}_4 \cdot \frac{1}{3} \text{H}_2\text{O}_2$ .

To a solution of potassium hydrogen sulphate (1.0 g, 7.3 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) at  $0^\circ\text{C}$  was added dropwise, with stirring,

Table 1-13

XRD Data for  $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$ 

I	dÅ	I	dÅ	I	dÅ	I	dÅ
w	7.5	s	3.30	w	2.48	w	2.10
w	6.6	s	3.25	w	2.44	w	2.06
s	5.3	w	3.15	w	2.41	w	2.04
vw	4.75	w	3.10	w	2.35	w	2.02
w	4.20	s	2.79	vw	2.26	w	2.01
vw	4.10	s	2.76	vw	2.23		
w	3.75	m	2.63	vw	2.19		
w	3.68	s	2.61	vw	2.14		

Table 1-14

XRD Data for  $\text{KHSO}_4 \cdot \frac{1}{3}\text{H}_2\text{O}_2$ 

I	dÅ	I	dÅ	I	dÅ	I	dÅ
vw	8.0	w	3.91	s	3.04	w	2.57
vw	7.1	w	3.52	vs	3.00	vw	2.53
w	6.0	w	3.49	vw	2.975	s	2.50
w	5.3	vs	3.40	vw	2.86	vw	2.47
m	4.90	vw	3.32	vw	2.83	m	2.40
w	4.80	vs	3.29	vw	2.77	w	2.35
m	4.72	vw	3.22	vw	2.76	m	2.31
w	4.58	vs	3.14	w	2.67		
vw	4.01	vw	3.11	w	2.58		

ethanol (5 cm<sup>3</sup>). The colourless, microcrystalline precipitate was collected and dried in the usual manner. (Found: H, 0.8 ; S, 12.7 ; O<sub>2</sub><sup>2-</sup>, 7.0 ; K, 32.2. H<sub>5</sub>K<sub>3</sub>O<sub>14</sub>S<sub>3</sub> requires H, 1.1 ; S, 21.7 ; O<sub>2</sub><sup>2-</sup>, 7.2 ; K, 26.5%). This compound is relatively thermally stable, losing close to the calculated amount of hydrogen peroxide at 100-110°C.

Raman Spectrum: 3325m, 3050w, 1233w, 1227w, 1202w, 1145vw, 1096m, 1048m, 1015vw, 988s, 930w, 922w, 894m, 886w, 864s, 638m, 624w, 605m, 600m, 588m, 475m, 452w, 432m, 427m. XRD data are given in Table 1-14.

Trisodium Orthophosphate Pentaperhydrate Monohydrate, Na<sub>3</sub>PO<sub>4</sub>.5H<sub>2</sub>O<sub>2</sub>.H<sub>2</sub>O.

Anhydrous Na<sub>3</sub>PO<sub>4</sub> (1.0 g, 6.1 mmol) was dissolved, portionwise in aqueous 30% w/v H<sub>2</sub>O<sub>2</sub> (7 cm<sup>3</sup>) at 0°C. To this solution was added dropwise, with stirring, ethanol (7 cm<sup>3</sup>). Some crystals formed, together with an oil and the mixture was stood at -20°C overnight for complete crystallisation to occur. After 24 hours the crystals were collected and dried in the usual manner. (Found : H, 3.4 ; P, 8.1 ; O<sub>2</sub><sup>2-</sup>, 43.0. H<sub>12</sub>Na<sub>3</sub>O<sub>15</sub>P requires H, 3.4 ; P, 8.8 ; O<sub>2</sub><sup>2-</sup>, 45.2%).

Trisodium Orthophosphate Hexaperhydrate Monohydrate, Na<sub>3</sub>PO<sub>4</sub>.6H<sub>2</sub>O<sub>2</sub>.H<sub>2</sub>O.

This compound was prepared as above, using aqueous 50% w/w H<sub>2</sub>O<sub>2</sub>. (Found : H, 3.3 ; P, 9.4 ; O<sub>2</sub><sup>2-</sup>, 47.0. H<sub>14</sub>Na<sub>3</sub>O<sub>17</sub>P requires H, 4.0 ; P, 7.7 ; O<sub>2</sub><sup>2-</sup>, 47.6%).

Tripotassium Orthophosphate Tetrahydrate,  $K_3PO_4 \cdot 4H_2O_2$ .

This compound was prepared as above, using anhydrous  $K_3PO_4$  (1.0 g, 4.7 mmol), aqueous 50% w/w  $H_2O_2$  (3 cm<sup>3</sup>) and ethanol (5 cm<sup>3</sup>). The crystals were collected and dried after 6 days at -20°C. (Found : H, 3.0 ; P, 9.2 ;  $O_2^{2-}$ , 35.6.  $H_8K_3O_{12}P$  requires H, 2.3 ; P, 9.0 ;  $O_2^{2-}$ , 36.8%).

Tripotassium Orthophosphate Hexahydrate,  $K_3PO_4 \cdot 6H_2O_2$ .

A solution of anhydrous  $K_3PO_4$  (0.5 g, 2.4 mmol) in aqueous 50% w/w  $H_2O_2$  (1.5 cm<sup>3</sup>) was evaporated to dryness in vacuo at room temperature to yield the product. (Found : H, 2.7 ; P, 7.9 ;  $O_2^{2-}$ , 46.2.  $H_{12}K_3O_{16}P$  requires H, 2.9 ; P, 7.5 ;  $O_2^{2-}$ , 46.2%).

Potassium Dihydrogen Orthophosphate Sesquihydrate,  $KH_2PO_4 \cdot 1\frac{1}{2}H_2O_2$ .

Prepared in the same manner as above using  $KH_2PO_4$  (1.0 g, 7.3 mmol) and aqueous 50% w/w  $H_2O_2$  (3 cm<sup>3</sup>). (Found : H, 1.7 ; P, 16.7 ;  $O_2^{2-}$ , 25.2.  $H_5KO_7P$  requires H, 2.7 ; P, 16.6 ;  $O_2^{2-}$ , 25.6%).

Diammonium Hydrogen Orthophosphate Monohydrate,  $(NH_4)_2HPO_4 \cdot H_2O_2$ .

Prepared in the same manner as  $Na_3PO_4 \cdot 5H_2O_2 \cdot H_2O$  using  $(NH_4)_2HPO_4$  (1.0 g, 7.6 mmol), aqueous 30% w/v or 50% w/w  $H_2O_2$  (3 cm<sup>3</sup>) and ethanol (5 cm<sup>3</sup>). This procedure results in large single crystals of the product. (Found : H, 6.4 ; N, 15.8 ;  $O_2^{2-}$ , 19.2.  $H_{11}N_2O_6P$  requires H, 6.7 ; N, 16.9 ;  $O_2^{2-}$ , 19.2%).

Tetrasodium Pyrophosphate Diperhydrate Octahydrate,  $Na_4P_2O_7 \cdot 2H_2O_2 \cdot 8H_2O$ .

Prepared in the same manner as above using  $Na_4P_2O_7 \cdot 10H_2O$  (1.0 g, 2.2 mmol), aqueous 30% w/v  $H_2O_2$  (5 cm<sup>3</sup>) and ethanol (5 cm<sup>3</sup>).



(Found : H, 4.1 ; P, 13.0 ;  $O_2^-$ , 13.8.  $H_{20}Na_4O_{19}P_2$  requires H, 4.2 ; P, 13.0 ;  $O_2^-$ , 13.4%).

Tetrasodium Pyrophosphate Triperhydrate,  $Na_4P_2O_7 \cdot 3H_2O_2$ .

Prepared in the same manner as  $K_3PO_4 \cdot 6H_2O_2$  using  $Na_4P_2O_7 \cdot 10H_2O$  (1.0 g, 2.2 mmol) and aqueous 30% w/v  $H_2O_2$  (5  $cm^3$ ). (Found : H, 1.6 ; P, 17.4 ;  $O_2^-$ , 25.8.  $H_6Na_4O_{13}P_2$  requires H, 1.6 ; P, 16.8 ;  $O_2^-$ , 26.2%).

Tetrapotassium Pyrophosphate Hexaperhydrate,  $K_4P_2O_7 \cdot 6H_2O_2$ .

Prepared in the same manner as  $K_3PO_4 \cdot 4H_2O_2$  using anhydrous  $K_4P_2O_7$  (0.2 g, 0.6 mmol), aqueous 50% w/v  $H_2O_2$  (2  $cm^3$ ) and ethanol (5  $cm^3$ ). (Found : H, 2.5 ; P, 11.9 ;  $O_2^-$ , 36.2.  $H_{12}K_4O_{19}P_2$  requires H, 2.3 ; P, 11.6 ;  $O_2^-$ , 36.0%).

Tetrapotassium Pyrophosphate Octaperhydrate,  $K_4P_2O_7 \cdot 8H_2O_2$ .

Prepared in the same manner as  $K_3PO_4 \cdot 6H_2O_2$  using anhydrous  $K_4P_2O_7$  (0.2 g, 0.6 mmol) and aqueous 30% w/v  $H_2O_2$  (2  $cm^3$ ). (Found : H, 2.9 ; P, 10.1 ;  $O_2^-$ , 42.4.  $H_{16}K_4O_{23}P_2$  requires H, 2.9 ; P, 10.3 ;  $O_2^-$ , 42.6%).

Sodium Formate Monoperhydrate,  $NaCOOH \cdot H_2O_2$ .

A solution of anhydrous sodium formate (0.5 g, 7.4 mmol) in aqueous 30% w/v  $H_2O_2$  (2  $cm^3$ ) was evaporated to dryness in vacuo at room temperature to yield a white solid. (Found : C, 12.0 ; H, 2.9 ;  $O_2^-$ , 30.9.  $CH_3NaO_4$  requires C, 11.8 ; H, 3.0 ;  $O_2^-$ , 31.4%). N.B.

An explosion occurred following a similar procedure with a  $KCOOH/H_2O_2$  solution.

Lithium Acetate Hemiperhydrate,  $\text{LiCOOCH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$ .

A solution of lithium acetate dihydrate (1.0 g, 9.8 mmol) in aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ) was evaporated to dryness in vacuo at room temperature to yield a white solid. (Found : C, 29.9 ; H, 4.8 ;  $\text{O}_2^-$ , 19.7.  $\text{C}_2\text{H}_4\text{LiO}_3$  requires C, 28.9 ; H, 4.9 ;  $\text{O}_2^-$ , 19.8%).

Sodium Acetate Hemiperhydrate,  $\text{NaCOOCH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$ .

This was prepared in the same fashion as the lithium analogue using sodium acetate trihydrate (1.0 g, 7.3 mmol) and aqueous 30% w/v  $\text{H}_2\text{O}_2$  (5  $\text{cm}^3$ ). (Found : C, 22.7 ; H, 3.5 ;  $\text{O}_2^-$ , 16.0.  $\text{C}_2\text{H}_4\text{NaO}_3$  requires C, 24.3 ; H, 4.1 ;  $\text{O}_2^-$ , 16.2%).

Potassium Nitrate Hemiperhydrate,  $\text{KNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$ .

A solution of anhydrous  $\text{KNO}_3$  (1.0 g, 9.9 mmol) in aqueous 50% w/w  $\text{H}_2\text{O}_2$  (3  $\text{cm}^3$ ) was evaporated to dryness in vacuo at room temperature. (Found :  $\text{O}_2^-$ , 14.0.  $\text{HKNO}_4$  requires  $\text{O}_2^-$ , 13.6%).

Vibrational Spectra.

$\text{K}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}_2$  : Raman, 873vs,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ).

$(\text{NH}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}_2$  : Raman, 986vs,  $\nu_{\text{P-O}}$  ( $\text{HPO}_4^{2-}$ ); 879vs,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ).

$\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$  : Infrared, 3250vsb,  $\nu_{\text{O-H}}$  ( $\text{H}_2\text{O}$ ); 3100sb,  $\nu_1$  ( $\text{H}_2\text{O}_2$ ); 2600sb,  $\nu_5$  ( $\text{H}_2\text{O}_2$ ); 1650m,  $\delta_{\text{O-H}}$  ( $\text{H}_2\text{O}$ ); 1490m, 1420m, 1370m,  $\nu_2$ ,  $\nu_6$  ( $\text{H}_2\text{O}_2$ ); 1100vsb, 910s, 890s,  $\nu_{\text{P-O}}$  ( $\text{P}_2\text{O}_7^{4-}$ ). Raman, 1030vs,  $\nu_{\text{P-O}}$  ( $\text{P}_2\text{O}_7^{4-}$ ); 896vs, 882m,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ).

$\text{Na}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}_2$  : Infrared, 3000m,  $\nu_1$  ( $\text{H}_2\text{O}_2$ ); 2600sb,  $\nu_5$  ( $\text{H}_2\text{O}_2$ ); 1400s,  $\nu_6$  ( $\text{H}_2\text{O}_2$ ); 1130vs, 1025m, 995m, 894m,  $\nu_{\text{P-O}}$  ( $\text{P}_2\text{O}_7^{4-}$ ); 860sh,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ). Raman, 1032s, 1026s,  $\nu_{\text{P-O}}$  ( $\text{P}_2\text{O}_7^{4-}$ ); 869vs, 864s,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ); 717s,  $\nu_{\text{P-O}}$  ( $\text{P}_2\text{O}_7^{4-}$ ).

$\text{KNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$  : Raman, 1412m,  $\nu_3$  ( $\text{NO}_3^-$ ); 1316w,  $\nu_2$  ( $\text{H}_2\text{O}_2$ );  
1055vs,  $\nu_1$  ( $\text{NO}_3^-$ ); 880s,  $\nu_3$  ( $\text{H}_2\text{O}_2$ ); 725m, 716m,  $\nu_4$  ( $\text{NO}_3^-$ ).

#### 1-E-4 Stability of Perhydrates.

In order to gain a rough idea of the stability of the perhydrates prepared in this work, the peroxide oxygen content of several of these compounds was checked periodically and any losses noted. The results are listed in Table 1-15. All compounds were stored in screw-capped sample tubes at  $-5^\circ\text{C}$ .

Table 1-15

Indication of Stability of Perhydrates

Compound	No. of Days	% Peroxide Loss
$\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$	45	5.4
$\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$	1	8.4
$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$	13	16.1
$\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	68	6.5
$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$	29	1.3
$\text{KHSO}_4 \cdot \frac{1}{3}\text{H}_2\text{O}_2$	51	13.5
$\text{Na}_3\text{PO}_4 \cdot 5\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	41	3.7
$\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	21	5.0
$\text{K}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}_2$	7	0
$\text{K}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}_2$	22	4.5
$\text{KH}_2\text{PO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$	29	9.2
$(\text{NH}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}_2$	30	1.9
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$	41	2.8
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}_2$	4	2.2
$\text{K}_4\text{P}_2\text{O}_7 \cdot 6\text{H}_2\text{O}_2$	6	6.8
$\text{K}_4\text{P}_2\text{O}_7 \cdot 8\text{H}_2\text{O}_2$	6	5.2
$\text{KNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2$	22	7.9

## CHAPTER TWO

### THE "TRUE" ALKALI METAL PERCARBONATES AND "SODIUM PERBORATE".

#### Abstract.

The preparations and physicochemical properties of the alkali metal percarbonates  $M_2^I C_2O_6$  ( $M = Na, K, Rb, Cs$ ),  $M^I HCO_4$  ( $M = Na, K, Rb$ ) and  $Li_2CO_4 \cdot H_2O$  are described and their likely structures discussed on the basis of their vibrational spectra. Electron spin resonance spectra show the presence of free radicals in several of these percarbonates and their nature is also discussed together with the bleaching action of the compounds. The X-ray crystal structure of the industrial bleaching agent "sodium perborate",  $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$  is described, together with the vibrational spectra of this salt.

#### Introduction.

This chapter is principally concerned with inorganic peroxysalts which are likely to contain C-O-O bonds. The species considered are firstly the peroxydicarbonates ( $M_2^I C_2O_6$ ,  $M = Na, K, Rb, Cs$ ) which probably contain  $C-O-O-C$  units (Section 2-A), then the peroxybicarbonates ( $M^I HCO_4$ ,  $M = Na, K, Rb$ ) which are probably hydrogen-bonded species containing  $C-O-O-H \cdots O-O-C$  units (Section 2-B), and then the compound lithium peroxycarbonate monohydrate,  $Li_2CO_4 \cdot H_2O$

which must also contain a  $C \begin{array}{l} \diagup O \\ \diagdown O \end{array}$  unit (Section 2-C). Consideration is then given (Section 2-D) to the nature of the species existing in aqueous solutions of  $H_2O_2$  and  $HCO_3^-$ ; this is likely to be  $HCO_4^-$ . Finally, the bleaching action of some of these compounds is described (Section 2-E) and the structure and vibrational spectra of a species known to contain a cyclic  $B \begin{array}{l} \diagup O-O \\ \diagdown O-O \end{array} B$  group briefly discussed (Section 2-F).

N.B. All attempts to grow single crystals of any of the "true" percarbonates have been unsuccessful and thus their structural characterisation is based solely on their physicochemical properties, particularly their vibrational spectra.

Section 2-A The Alkali Metal Peroxydicarbonates,  $M_2^I C_2O_6$  (M = Na, K, Rb, Cs).

2-A-1 Preparations.

This class of compounds can generally be prepared in two ways according to the literature, either by the electrolytic anodic oxidation of a saturated aqueous solution of the alkali metal carbonate at low temperature (a process first described by Constam and Hansen in 1896<sup>68</sup>), or by the action of carbon dioxide on the alkali metal peroxide in the presence of moisture, the most convenient method of carrying out the latter process being the admixture of the alkali metal hydroxide and concentrated aqueous hydrogen peroxide at below  $0^\circ C$  in a 2:1 ratio followed by treatment with  $CO_2$  gas. The Na, K and Rb salts are also said to be formed by the oxidation of the corresponding carbonate or bicarbonate by fluorine.<sup>69</sup> All four compounds have been

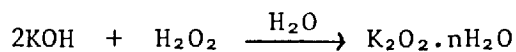
Prepared by the reaction of carbon dioxide with the alkali metal peroxide (e.g., 70-73) but only the K, Rb and Cs salts have been obtained electrolytically in a relatively pure state.<sup>74</sup> The sodium salt obtained "chemically" always contains some water even after several hours drying in vacuo<sup>70</sup> whereas the remaining compounds are anhydrous.

In this work only the potassium salt has been obtained electrolytically but the complete series has been prepared "chemically" in order to study some of their physicochemical and chemical properties, in particular their vibrational spectra, with a view to gaining information on their structures and reactivities. All products were subjected to elemental analysis in order to ascertain their purity before recording their vibrational spectra and the analytical results are given in Table 2-1.

Most of the work has been concentrated upon the potassium salt,  $K_2C_2O_6$  because of its greater stability, its ease of preparation in an analytically pure state, and the relative expense of rubidium and caesium compounds. Perhaps its most interesting feature is that, as prepared by the reaction of KOH and  $H_2O_2$  with  $CO_2$  at below  $-15^\circ C$ , it is orange in colour (form "A"), but the electrolytic anodic oxidation procedure at this temperature gives a pale sky-blue product (form "B"). These two forms give identical vibrational spectra and X-ray powder diffraction patterns (confirming the literature observation<sup>75</sup>) but different e.s.r. spectra (see Section 2-A-3).

One other interesting observation has been made during the course of several preparations of this salt under slightly different conditions. By varying the temperature, it has been found that two different compounds, each having the formulation  $K_2C_2O_6$  can be isolated from the reaction of

KOH and H<sub>2</sub>O<sub>2</sub> with CO<sub>2</sub>. The initial product in this reaction is obviously potassium peroxide, K<sub>2</sub>O<sub>2</sub>·nH<sub>2</sub>O:-



This compound then adds two moles of CO<sub>2</sub> to yield K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> and this reaction gives products with different vibrational spectra and XRD patterns when carried out at -20 and -5°C (forms "A" and "C" respectively). The most plausible explanation for this is that two isomeric forms of K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> exist, having anions with different conformations, resulting in different crystallographic packing (see Section 2-A-2). XRD data for all three forms of K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> are given in Tables 2-2 to 2-4.

Table 2-2

XRD Data for "Chemical" K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> (Form "A").

I	dÅ	I	dÅ	I	dÅ	I	dÅ
vw	6.9	s	3.30	s	2.63	w	2.20
w	6.3	vs	3.24	m	2.56	vw	2.19
m	5.41	m	3.16	vw	2.54	m	2.13
w	4.40	m	3.10	vw	2.52	vw	2.10
w	4.08	vw	3.00	w	2.47	w	2.07
w	3.90	vw	2.94	w	2.42	w	2.04
w	3.80	vw	2.90	w	2.30	w	2.03
w	3.67	w	2.81	vw	2.27		
w	3.55	vw	2.78	w	2.26		
vw	3.42	vw	2.73	vw	2.25		
w	3.38	m	2.69	vw	2.21		



Table 2-3  
XRD Data for Electrolytic K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> (Form " B" ).

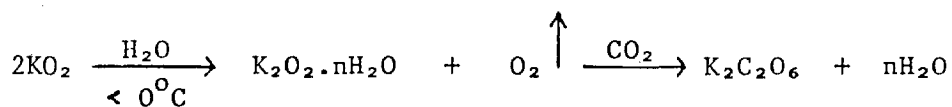
I	dÅ	I	dÅ	I	dÅ	I	dÅ
vw	6.9	s	3.30	vw	2.81	vw	2.27
w	6.3	vs	3.24	vw	2.76	w	2.26
m	5.41	m	3.16	vw	2.72	vw	2.25
w	4.40	m	3.10	w	2.68	vw	2.21
w	4.08	vw	3.08	m	2.63	w	2.20
w	3.90	vw	3.02	m	2.56	vw	2.19
w	3.80	vw	2.98	vw	2.54	m	2.13
w	3.67	vw	2.96	vw	2.52	vw	2.10
w	3.55	vw	2.91	w	2.47	w	2.07
vw	3.42	vw	2.89	w	2.42	w	2.04
w	3.38	vw	2.85	w	2.30	w	2.03

Table 2-4

XRD Data for "Chemical"  $K_2C_2O_6$  (Form "C").

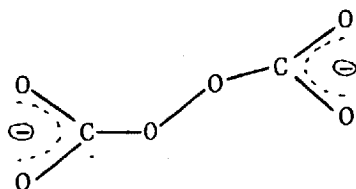
I	dÅ	I	dÅ	I	dÅ	I	dÅ
vw	5.05	vs	2.91	m	2.25	vw	1.888
w	3.71	vs	2.85	m	2.22	w	1.861
vw	3.56	w	2.65	w	2.18	w	1.859
m	3.42	vw	2.55	w	2.12	vw	1.839
vw	3.24	m	2.52	vw	2.08	vw	1.815
m	3.07	w	2.47	vw	2.06	vw	1.783
m	2.99	w	2.43	w	1.995	m	1.765
m	2.95	m	2.33	m	1.942		

Both the "A" and "C" forms of  $K_2C_2O_6$  have also been obtained by the reaction of  $CO_2$  with potassium superoxide,  $KO_2$  in the presence of moisture at different temperatures. Once again the reactive intermediate is hydrated potassium peroxide, as only the superoxide oxygen is evolved at below  $0^\circ C$  in the reaction between  $KO_2$  and water.<sup>76,77</sup> When using this method of preparation, the product is always unavoidably contaminated with bicarbonate, presumably due to the presence of  $KOH$  formed by the initial reaction.



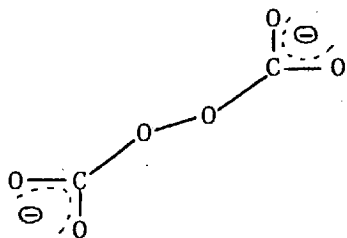
#### 2-A-2 Vibrational Spectra.

Only the vibrational spectra of the electrolytically-prepared potassium salt have been recorded previously<sup>49,78</sup> and the results are interpreted on the basis of a planar,  $C_{2h}$  structure for the anion:-



The vibrational spectral bands for all compounds prepared in this work are listed, together with assignments, in Table 2-5 and the results indicate that the structures of the  $C_2O_6^{2-}$  anions are indeed close to this in  $Na_2C_2O_6 \cdot nH_2O$ ,  $K_2C_2O_6$  and  $Rb_2C_2O_6$  as the rule of mutual exclusion applies to the infrared and Raman bands, confirming that the anions have a centre of symmetry, and assignments are made accordingly. Figures 2-1 and 2-2 depict the 18 fundamental vibrations of a planar,  $C_{2h}$   $C_2O_6^{2-}$  anion and Figures 2-3 and 2-4 show the infrared and Raman spectra of a sample of  $K_2C_2O_6$  (form "A").

The reasons for the different vibrational spectra for forms "A" and "C" of  $K_2C_2O_6$  are best explained by firstly assuming a planar structure for the anions in both forms. In theory, ignoring any rotations about the carbon-peroxide bonds, the two extreme structures

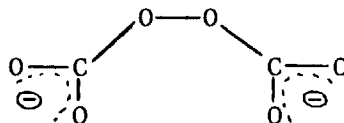


trans-planar

$$\phi = 180^\circ$$

$C_{2h}$  symmetry

and



cis-planar

$$\phi = 0^\circ$$

$C_{2v}$  symmetry

Table 2-5

Vibrational Spectra of the Alkali Metal Peroxydicarbonates,  $M_2C_2O_6$ .

$Na_2C_2O_6 \cdot nH_2O$		$K_2C_2O_6^a$		$K_2C_2O_6^b$		$K_2^{13}C_2O_6^a$		$Rb_2C_2O_6$		$Cs_2C_2O_6$	Assignments
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Raman	
	1753vw		1737w		1740vw } 1711w }		1688w		1744	1729w	$\nu_1, C-O$ st
1800sh } 1745vs } 1700sh } 1660sh }		1750vs } 1710vs }		1700vsb		1740s } 1700vs } 1660vs }		1740vs } 1715vs } 1650vs }			$\nu_{13}, C-O$ st
	1355s		1356vw } 1331s } 1268vw }		1341s		1324vw } 1310s } 1252vw }		1367vw } 1340m } 1332s } 1260vw }	1331s } 1323s }	$\nu_2, C-O$ st
1440s } 1370s } 1310vs } 1280vs }		1350sh } 1337vs } 1305s } 1280sh } 1269vs }		1280sh,b } 1260vs }		1322sh } 1310vs } 1280sh } 1250vs } 1230sh }		1400m } 1360sh } 1317vs } 1265vs }			$\nu_{14}, C-O$ st
	974w		907s		905sh		884s		920vs	915s	$\nu_3, C-O$ st $\nu_{15}, C-O$ st
917vs		950sh } 910vs }		975m		910sh } 895vs }		910s			
	885vs		896sh } 888vs }		912vs } 886w }		897vs		900w } 890vs }	894sh } 886vs }	$\nu_4, O-O$ st
	870vw		853w		872m } 804w }		837w		858w } 815vw }	878m } 855w }	$\nu_5, CO_2$ def
895vs		875sh } 868vs } 851vs }		880vsb		860sh } 845vs } 805vs }		880s } 860vs }			$\nu_{16}, CO_2$ def

Table 2-5 (cont.)

$\text{Na}_2\text{C}_2\text{O}_6 \cdot n\text{H}_2\text{O}$		$\text{K}_2\text{C}_2\text{O}_6^{\text{a}}$		$\text{K}_2\text{C}_2\text{O}_6^{\text{b}}$		$\text{K}_2^{13}\text{C}_2\text{O}_6^{\text{a}}$		$\text{Rb}_2\text{C}_2\text{O}_6$		$\text{Cs}_2\text{C}_2\text{O}_6$	Assignments
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Raman	
820w } 801w } 786s } 774w }		809vs		810sh		780vs		830m } 803s }			$\nu_{17}$ , $\text{OCO}_2$ def
		795vs		790vs } 775sh }		768vs		791s			$\nu_8$ , $\text{OCO}_2$ def
	737s		734vw } 725vw }		738vs		733vs } 723vw }		746vw } 734vw }	743vw	$\nu_8$ , $\text{OCO}_2$ def
		701s	704s			697s	701s	689m	696s	694s } 674m }	$\nu_{11}$ , $\text{CO}_2$ def
661m } 645s }		631m	633vw	660s } 642m } 636m }		625m	630vw	625m	656vw } 634vw }	639m } 631w }	$\nu_{10}$ , $\text{CO}_2$ def
	460w		449m		455m } 444w }		444m		452s	449s	$\nu_7$ , $\text{CO}_2$ def

<sup>a</sup> Prepared at  $-20^\circ\text{C}$ , spectra identical for both "A" and "B" forms.

<sup>b</sup> Prepared at  $-5^\circ\text{C}$  (Form "C").

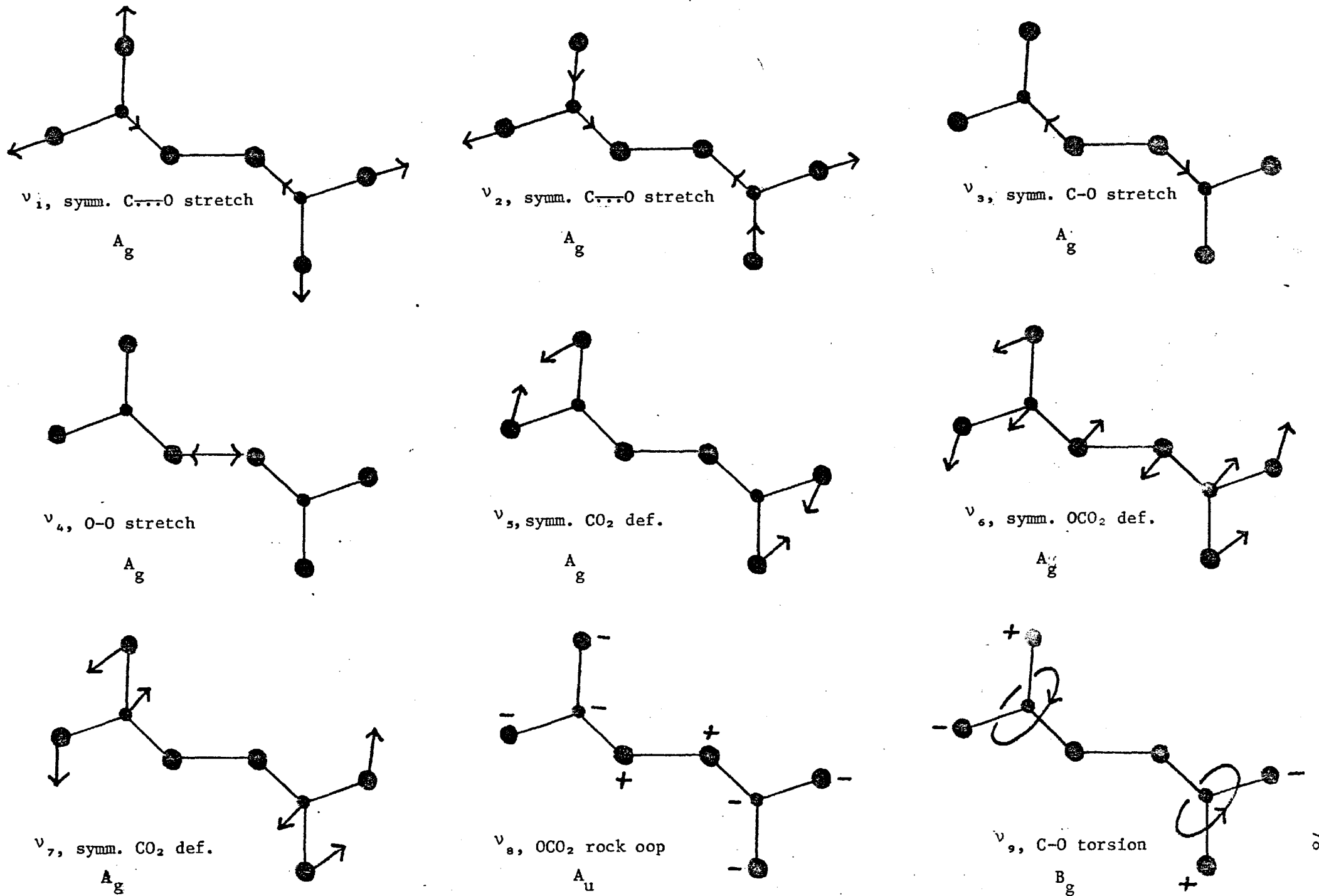


Figure 2-1. Normal Modes of Vibrational Motion for the  $C_2O_6^{2-}$  anion with  $C_{2h}$  Symmetry.

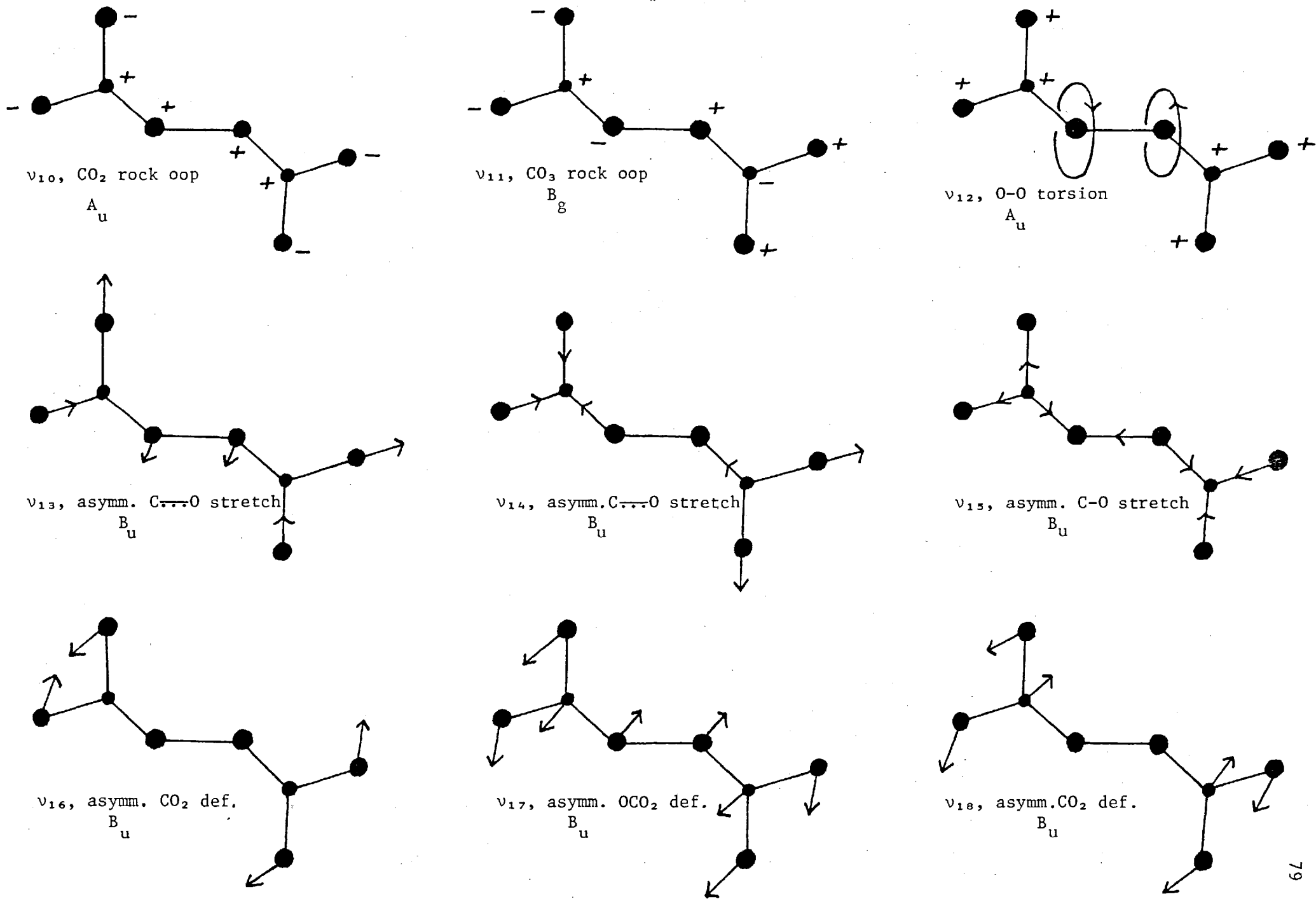


Figure 2-2. Normal Modes of Vibrational Motion for the C<sub>2</sub>O<sub>8</sub><sup>2-</sup> Anion with C<sub>2h</sub> Symmetry.

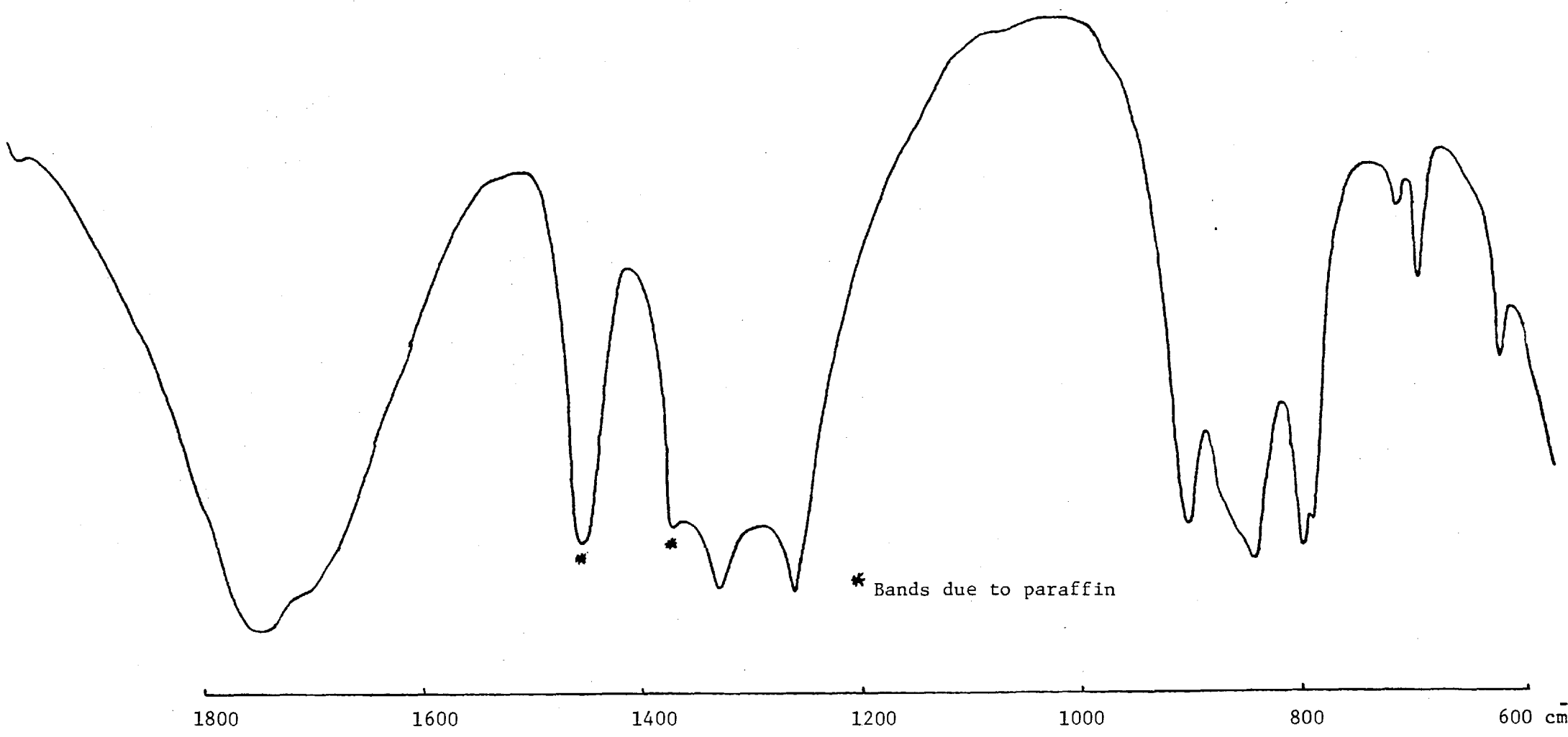
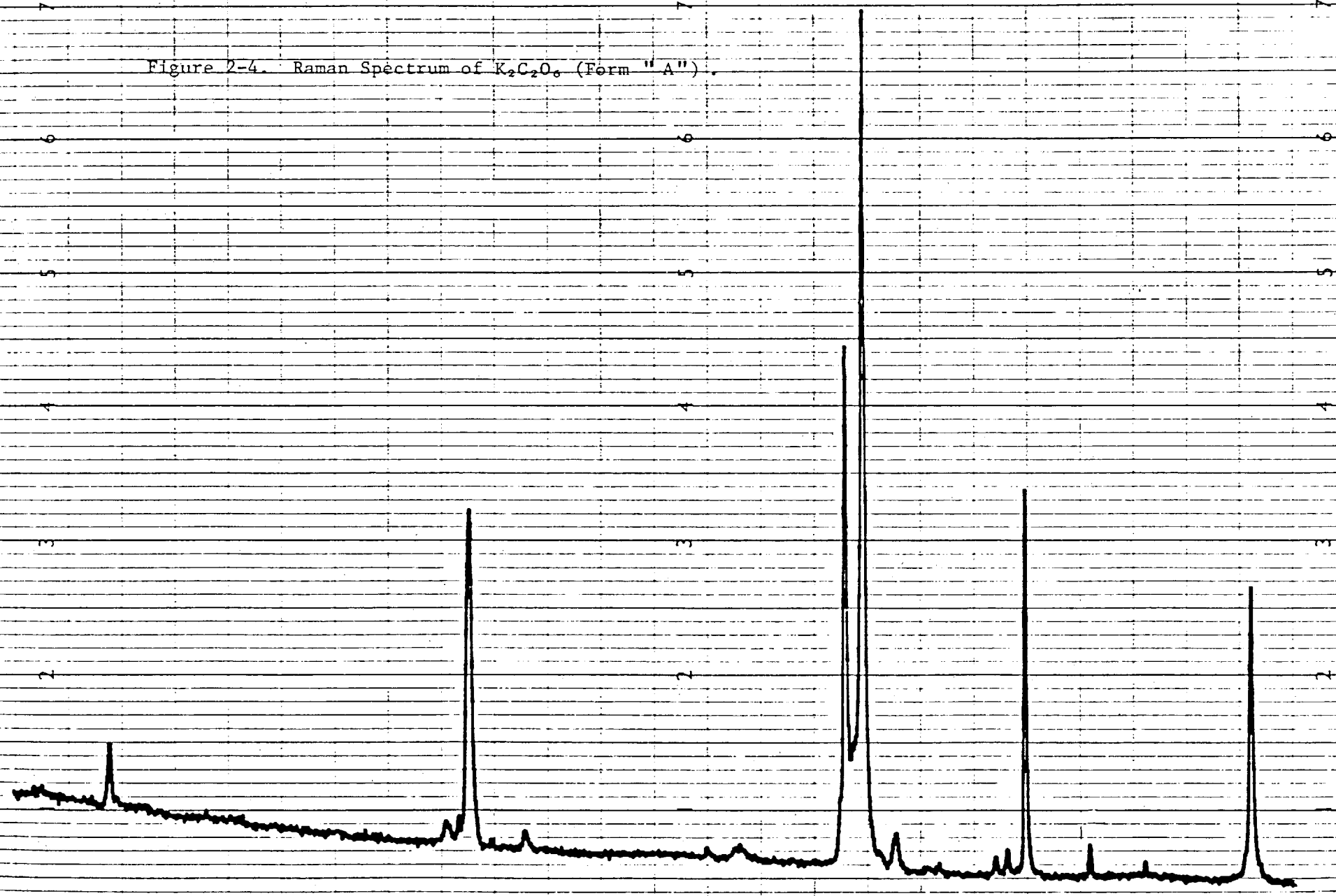


Figure 2-3. Infrared Spectrum of  $\text{K}_2\text{C}_2\text{O}_6$  (Form "A").



1600 1300 1000 700 400  $\text{cm}^{-1}$

Figure 2-4. Raman Spectrum of  $\text{K}_2\text{C}_2\text{O}_6$  (Form "A").



can exist by rotation about the O-O bond. It is difficult to establish which form of  $K_2C_2O_6$  is nearer to the trans-planar conformation as the number and frequencies of bands in the infrared and Raman spectra are very similar for both forms. This suggests that neither structure fits the two extremes with dihedral angles of  $180^\circ$  and  $0^\circ$  but must lie somewhere between the two, probably much nearer the structure with  $\phi = 180^\circ$ . Thus there may be an analogy between  $C_2O_6^{2-}$  and  $H_2O_2$  itself; the latter can also adopt different conformations with different dihedral angles by rotation about the O-O bond (see Chapter One).

Form "A" of  $K_2C_2O_6$  has been prepared using  $^{13}C$ -enriched  $CO_2$  gas in order to simplify band assignments and both forms "A" and "C" have been prepared from  $^2H$ -enriched  $^2H_2O_2$  in order to ascertain that there is no hydrogen present in these compounds (a fact that is confirmed by elemental analyses which indicate only traces of hydrogen, probably arising from moisture or bicarbonate impurities). One would expect certain bands in the vibrational spectra to shift on deuteration if there were any hydrogen present and the spectra obtained are unchanged.

Both the infrared and Raman spectra of all of the peroxydicarbonates studied here show bands in the same regions and by comparing the spectra with those of carbonates and also with those obtained for peroxodisulphate,  $S_2O_8^{2-}$  and peroxodiphosphate,  $P_2O_8^{4-}$  ions<sup>79,80</sup> which are known to contain trans-planar  $S-O-O-S$  and  $P-O-O-P$  linkages (e.g., 81), the various bands can be assigned reasonably well for a  $C_{2h}$  anion. Thus in the Raman,  $\nu_1$  and  $\nu_2$ , the symmetric  $C-O-O$  stretches are assigned to the bands at  $1711-1753\text{ cm}^{-1}$  and  $1260-1367\text{ cm}^{-1}$  respectively ( $1285\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$  in  $Na_2S_2O_8$ ;  $1116\text{ cm}^{-1}$  and  $1067\text{ cm}^{-1}$  in  $P_2O_8^{4-}$ );  $\nu_3$ , the symmetric C-O stretch is observed at  $905-974\text{ cm}^{-1}$

(1080 and 1008  $\text{cm}^{-1}$ );  $\nu_4$ , the O-O stretch at 885-912  $\text{cm}^{-1}$  (840 and 890  $\text{cm}^{-1}$ ) and bands below 900  $\text{cm}^{-1}$  are due to the various in plane and out of plane deformations. In the infrared spectra, the asymmetric C-O stretches,  $\nu_{13}$  and  $\nu_{14}$ , give rise to bands at 1650-1800  $\text{cm}^{-1}$  and 1265-1440  $\text{cm}^{-1}$  (ca. 1300  $\text{cm}^{-1}$  and ca. 1100  $\text{cm}^{-1}$  in  $\text{Na}_2\text{S}_2\text{O}_8$ ) and  $\nu_{15}$ , the asymmetric C-O stretch at 910-975  $\text{cm}^{-1}$  again with the various deformations appearing as bands below 900  $\text{cm}^{-1}$ .

Relatively higher frequencies are observed for some vibrations of the peroxydicarbonates compared with the analogous  $\text{S}_2\text{O}_8^{2-}$  and  $\text{P}_2\text{O}_8^{4-}$  vibrations. This is to be expected as carbon-oxygen bonds are generally shorter than S-O or P-O bonds of the same order and this is also seen when comparing the vibrational spectra of  $\text{CO}_3^{2-}$  ions with those of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  ions.

### 2-A-3 Electron Spin Resonance Spectroscopy (E.s.r.).

The orange colourations of the "chemically" -prepared peroxydicarbonates and the blue colour of electrolytically-prepared  $\text{K}_2\text{C}_2\text{O}_6$  are indicative of the presence of free radicals and the e.s.r. spectra of some of these compounds have been recorded in an attempt to identify the different radicals present.

#### (a) "Chemically" -Prepared $\text{K}_2\text{C}_2\text{O}_6$ .

Both forms ("A" and "C") give rise to a very strong signal at room temperature, the shape and g-values of which resemble very closely those obtained from ozonide ions,  $\text{O}_3^-$ .<sup>82</sup> The signal begins to lose its structure on heating, indicating possibly that the radicals are beginning to move around within the lattice to give an average g-value. At liquid nitrogen temperature the signal obtained is identical in shape to that obtained at room temperature. On cooling a sample which

has been heated to 110°C back to room temperature, the original spectrum is obtained but with a loss of intensity, substantiating the theory that heating the sample to this temperature causes a reversible physical change together with some ozonide decomposition; (the sample noticeably loses a lot of its orange colouration on heating). A typical room-temperature spectrum is shown in Figure 2-5.

The spectra are very different from those obtained by Franchuk<sup>58</sup> from the same compound irradiated with U.V. and the spectrum for  $K_2^{13}C_2O_6$  is identical to those of the normal isotopic forms, which indicates that the radical present is not a carbon-containing species.

Intensity measurements of the signal obtained from  $K_2C_2O_6$  (form "A") have been carried out. By comparing the intensity with those from standard compounds, under the same conditions, the amount of free radicals present in a sample of  $K_2C_2O_6$  is calculated to be of the order of 10 ppm.

N.B. Apart from e.s.r. spectroscopy, the nature of the radicals present in  $K_2C_2O_6$  prepared "chemically" has been studied using reflectance spectroscopy in the visible region. The orange-coloured samples all give rise to an absorption at 460 nm, which is the same region in which authentic sodium ozonide shows an absorption band,<sup>83</sup> providing more evidence for the presence of small amounts of  $KO_3$  impurities.

(b) Electrolytically-prepared  $K_2C_2O_6$ .

No explanation for the blue colouration of this compound has yet been offered and its e.s.r. spectra are the most interesting of the compounds studied. The room-temperature spectrum is very different from that of the "chemically"-prepared salt and this time heating the sample has the effect of changing the signal quite drastically.

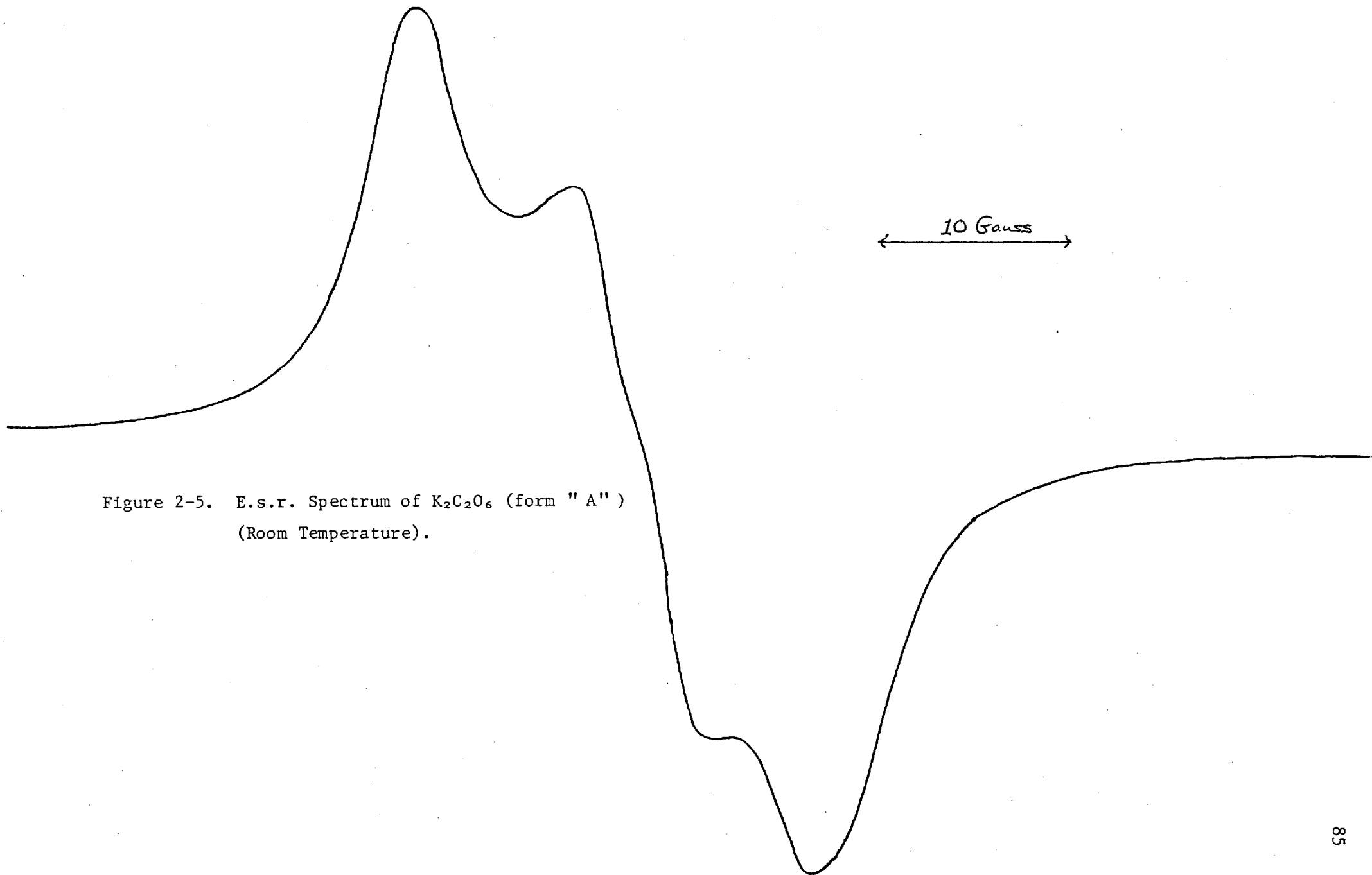


Figure 2-5. E.s.r. Spectrum of  $K_2C_2O_6$  (form "A")  
(Room Temperature).

The variation of the signal with temperature is depicted in Figures 2-6 and 2-7, these diagrams showing the spectra obtained from a sample at room temperature and then from the same sample cooled to room temperature after heating to 130°C. The latter spectrum is somewhat similar to the spectra obtained by Franchuk<sup>58</sup> from electrolytic K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> after irradiation with U.V. Thus it would seem that heating the sample has the same effect as U.V. irradiation but the exact nature of the radicals involved is unknown.

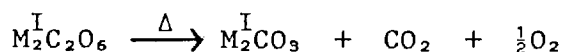
A reasonable explanation is the homolytic rupture of the O-O bond to form CO<sub>3</sub><sup>-</sup> radicals but if this is the case it cannot readily be proven as authentic samples of CO<sub>3</sub><sup>-</sup>, prepared by γ-irradiation of both KHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> give rise to quite different e.s.r. signals.

(c) Rb<sub>2</sub>C<sub>2</sub>O<sub>6</sub>.

The e.s.r. signals obtained both at liquid nitrogen and at room temperature are almost identical to those obtained by heating "chemically" -prepared K<sub>2</sub>C<sub>2</sub>O<sub>6</sub>. This again shows the presence of ozonide ions (also indicated by the orange colour of the sample) and in this case it would seem as if the radical has some freedom of movement within the lattice even at liquid nitrogen temperature as the signal has no structure and only an average g-value is obtained.

2-A-4 Thermal Decomposition.

The thermal decomposition of peroxydicarbonates proceeds according to the equation:-



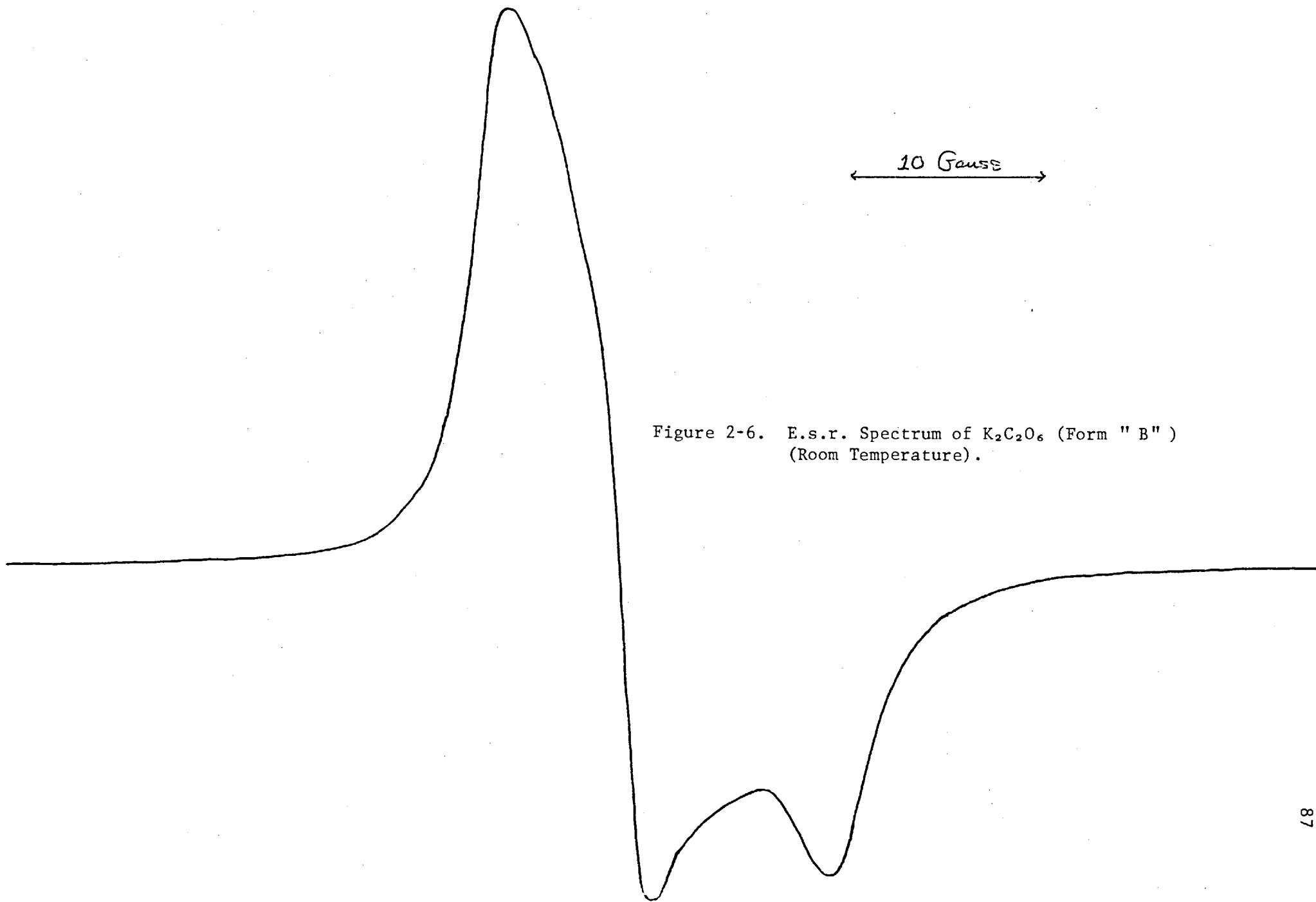


Figure 2-6. E.s.r. Spectrum of  $K_2C_2O_6$  (Form "B")  
(Room Temperature).

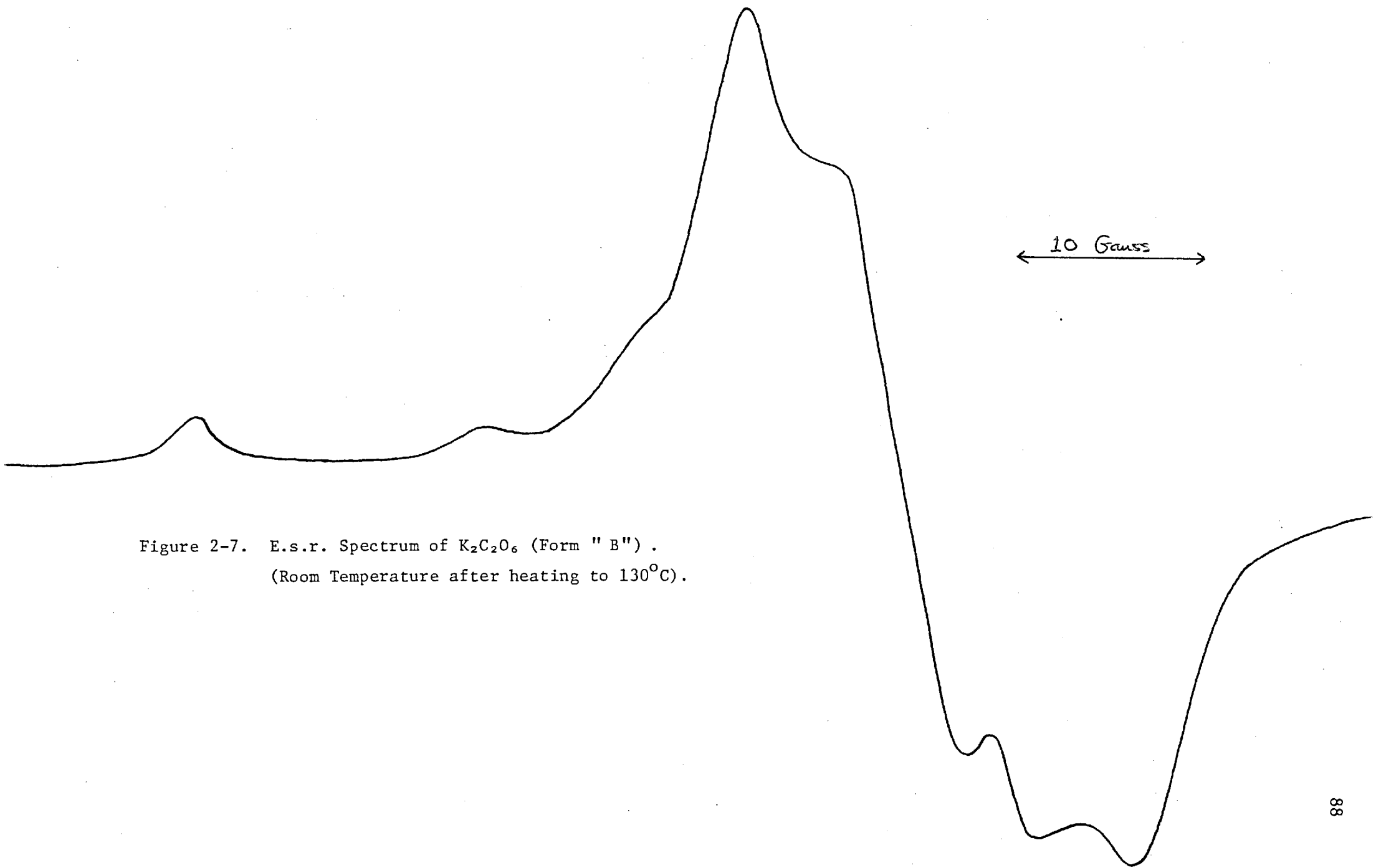


Figure 2-7. E.s.r. Spectrum of  $K_2C_2O_6$  (Form "B") .  
(Room Temperature after heating to  $130^{\circ}C$ ).



For  $K_2C_2O_6$  (form "A"), this decomposition has been studied using differential scanning calorimetry (D.S.C.) combined with evolved gas analysis and it is found that rapid decomposition occurs endothermically at  $140-160^\circ C$  with  $CO_2$  and  $O_2$  being evolved in the ratio 2:1. The solid decomposition product is shown to be anhydrous  $K_2CO_3$  by its infrared spectrum.

Thermogravimetric analysis (T.G.A.) confirms the D.S.C. results with close to the calculated weight being lost in the same temperature range.

## Section 2-B The Alkali Metal Peroxybicarbonates, $M^I HCO_4$ ( $M = Na, K, Rb$ ).

### 2-B-1 Preparations.

All three of these compounds have been reported previously (e.g., 70, 71, 84) but the vibrational spectra of only the potassium salt have been recorded.<sup>49</sup> In order to gain structural information on this series of compounds, their preparations have been repeated and the products obtained subjected to elemental analysis to ascertain their purity before recording their vibrational spectra.

The compounds are most easily synthesised by the reaction of the appropriate alkali metal hydroperoxide,  $M^I OOH \cdot nH_2O$  with  $CO_2$  gas. One of the most convenient methods of doing this is to mix the alkali metal hydroxide with concentrated aqueous hydrogen peroxide in a 1:1 ratio at low temperature ( $< 0^\circ C$ ) and to treat the resulting mixture with  $CO_2$ . The potassium salt has also been prepared enriched in  $^{13}C$  in order to make correct assignments of the vibrational bands. The sodium salt crystallises as the monohydrate whereas the potassium and rubidium compounds are anhydrous. Analytical data are given in Table 2-6 and

XRD data for the potassium salt are given in Table 2-7.

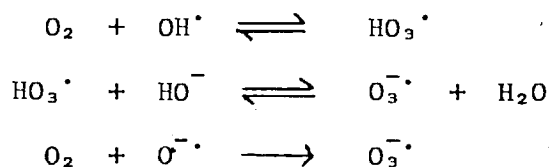
Table 2-7  
XRD Data for KHCO<sub>4</sub>

I	dÅ	I	dÅ	I	dÅ	I	dÅ
m	5.80	m	2.95	vw	2.56	vw	2.19
vw	5.00	s	2.90	w	2.51	m	2.15
vw	4.50	vw	2.86	vw	2.46	m	2.12
m	4.15	w	2.84	vw	2.44	w	2.075
w	3.90	vw	2.80	vw	2.42		
w	3.70	m	2.75	w	2.39		
w	3.34	vw	2.70	m	2.34		
w	3.28	vw	2.66	vw	2.275		
m	3.20	vw	2.62	vw	2.24		
vs	3.09	vw	2.58	w	2.21		

It is noticeable that when KHCO<sub>4</sub> is stored for prolonged periods at -20°C and protected from water vapour it slowly begins to turn orange. This change is fairly rapid (1-2 hours) at room temperature, especially when the sample is exposed to the atmosphere and under both sets of conditions a gradual loss of peroxide oxygen occurs. The XRD data and Raman spectrum of a partially decomposed sample show that it contains a large proportion of K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> (form "C"), together with some of form "A" of the same compound and some KHCO<sub>3</sub>, with none of the original KHCO<sub>4</sub> present. Rearrangement of KHCO<sub>4</sub> during gradual loss of half of its peroxide oxygen to form K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> has been noted previously<sup>71</sup> as has the tendency to turn orange on storage.<sup>50</sup> The mechanism of such a rearrangement is difficult

to postulate as the solid-state structure of  $\text{KHCO}_4$  is unknown, but the orange colour is almost certainly due to traces of ozonide ion formed during the decomposition. Formation of ozonide during the decomposition of alkaline hydrogen peroxide solutions has already been established although the mechanism involved is obscure.<sup>83</sup>

Small amounts of moisture in the presence of peroxides can give rise to such reactions as:-



These same reactions must also be responsible for the orange colour of the alkali metal peroxydicarbonates when formed from highly alkaline  $\text{H}_2\text{O}_2$  solutions of the metal hydroxides (see Section 2-A-1).

#### 2-B-2 Vibrational Spectra.

The vibrational spectra for these compounds are listed in Table 2-8, together with assignments. The Raman spectrum of  $\text{KHCO}_4$  is depicted in Figure 2-8. Assignments have been made following those of Giguère and Lemaire,<sup>49</sup> assuming that the  $\text{HCO}_4^-$  ion is planar, possessing  $\text{C}_s$  symmetry, in which case all twelve internal fundamental vibrations should be both infrared and Raman active. These twelve vibrations are shown diagrammatically in Figures 2-9 and 2-10. The assumption that the geometry around the carbon atom is planar is not unreasonable as the  $\text{HCO}_4^-$  ion must resemble very closely the  $\text{HCO}_3^-$  ion

Table 2-8

Vibrational Spectra of the Alkali Metal Peroxybicarbonates,  $M\text{HCO}_4$ 

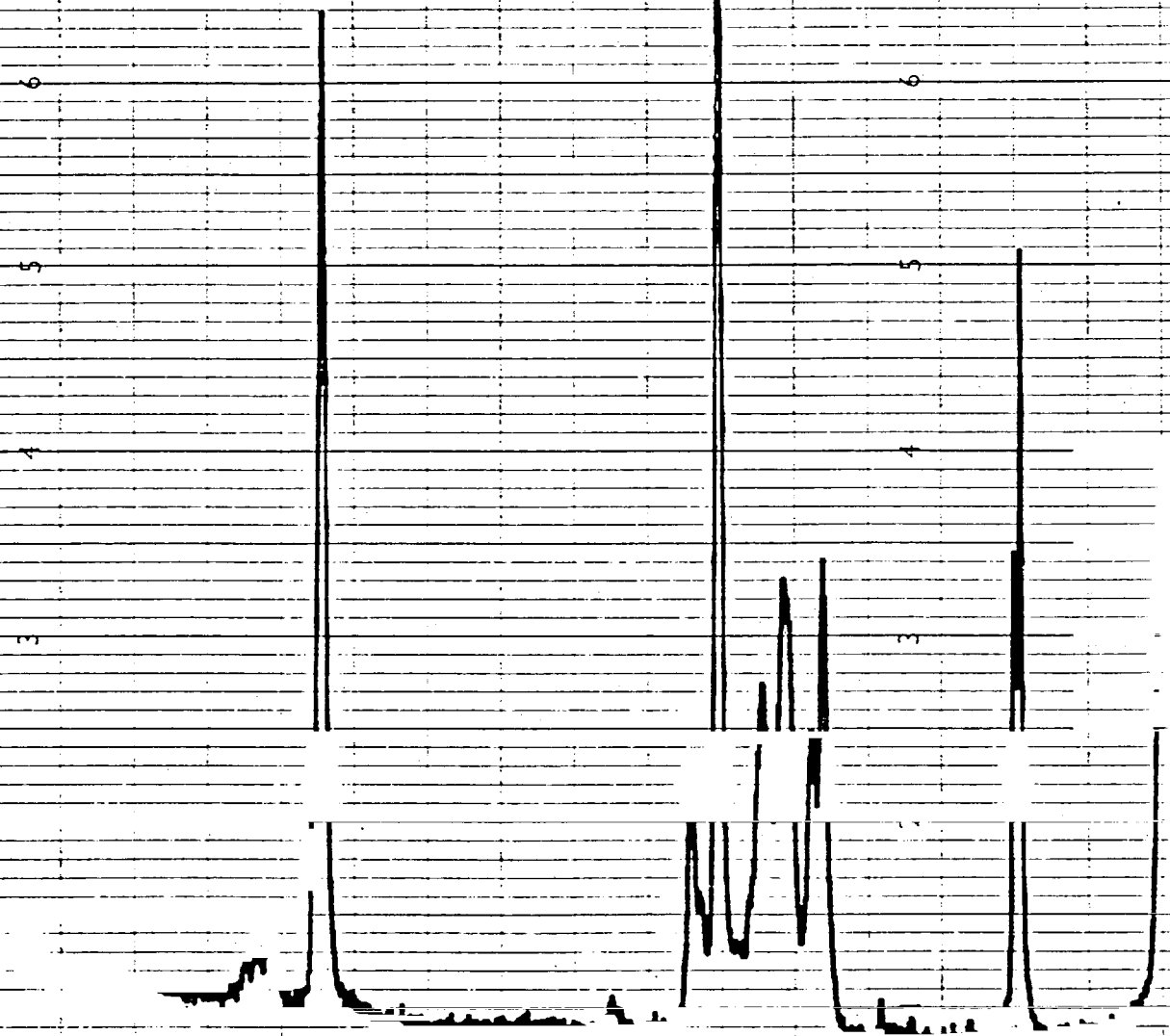
$\text{NaHCO}_4 \cdot \text{H}_2\text{O}$		$\text{KHCO}_4$		$\text{RbHCO}_4$		Assignments
Infrared	Raman	Infrared	Raman	Infrared	Raman	
3540vs } 3380vs }	3530w } 3365w }					$\nu_{\text{O-H}}, \text{H}_2\text{O}$
3080vsb } 3000sh } 2810vs }	3100vwb } 2835vw }	3040sb } 2740vsb }	n.o. n.o.	3120sb } 3020sh } 2800vs }	n.o. n.o. n.o.	$\nu_1, \text{O-H st}$
1770w } 1685vs }	1730vw	1700vsb	n.o.	1700vsb	n.o.	$\nu_2, \text{C-O st}$
1630s 1435vs	n.o. 1444vw	1470vs	n.o.	1430vs	n.o.	$\text{H}_2\text{O def}$ $\nu_3, \text{OOH def}$
1370sh } 1338vs } 1310vs }	1357w } 1308m }		1342w } 1320vw } 1310w } 1304vw } 1268s }	1320vs	1320s } 1264m }	$\nu_4, \text{C-O st}$
970s	986m } 975w }		967m } 960sh } 944vs }		944w } 930m }	$\nu_5, \text{C-O st}$
n.o.	930w		911m		917s	$\nu_{10}, \text{OH torsion}$
895s	902vs } 886w } 870w }		892m } 868m } 860m }		887vs } 872m } 866s } 830vw }	$\nu_6, \text{O-O st}$
798s } 762vw }	n.o.		812vw		756vw	$\nu_7, \text{CO}_2 \text{ def}$

Table 2-8 (cont).

NaHCO <sub>4</sub> ·H <sub>2</sub> O		KHCO <sub>4</sub>		RbHCO <sub>4</sub>		Assignments
Infrared	Raman	Infrared	Raman	Infrared	Raman	
715w	738w } 724m }		739w } 700m } 696s }		696w } 686m } 624vw }	v <sub>11</sub> , CO <sub>3</sub> def
n.o.	592w 562m		582sh } 578m } 573sh } 550vw }		570w	v <sub>8</sub> , OCO <sub>2</sub> def

1900 1600 1300 1000 700 400  $\text{cm}^{-1}$

Figure 2-8. Raman Spectrum of  $\text{KHCO}_3$ .



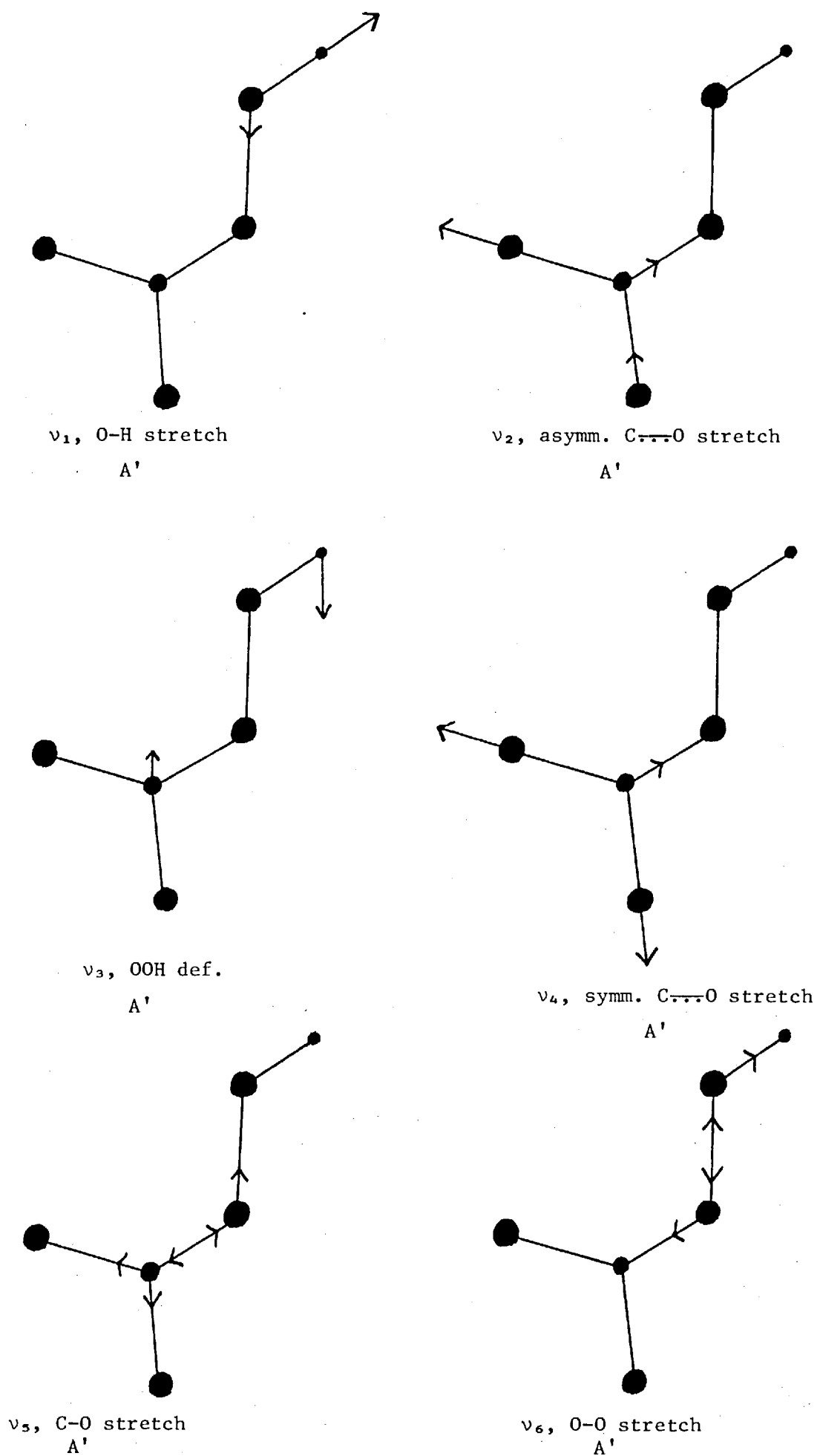
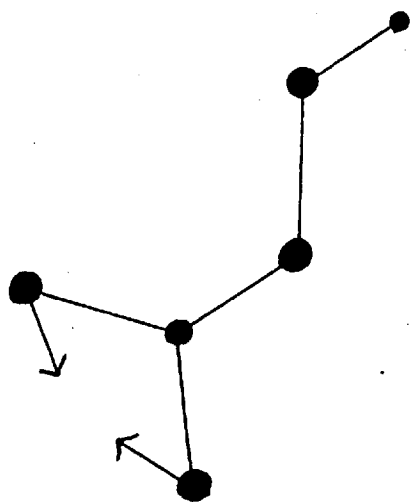
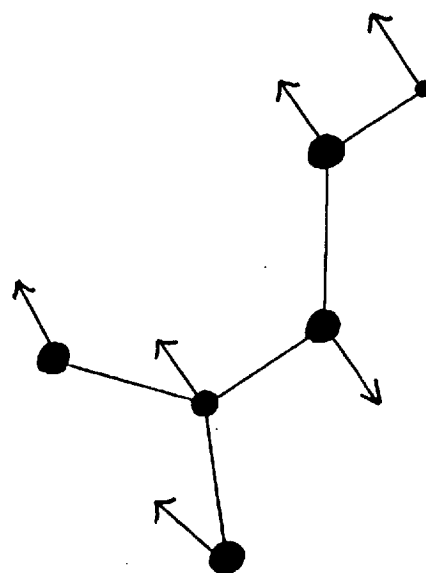
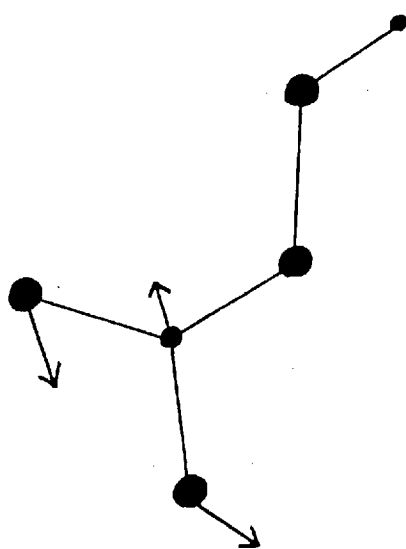
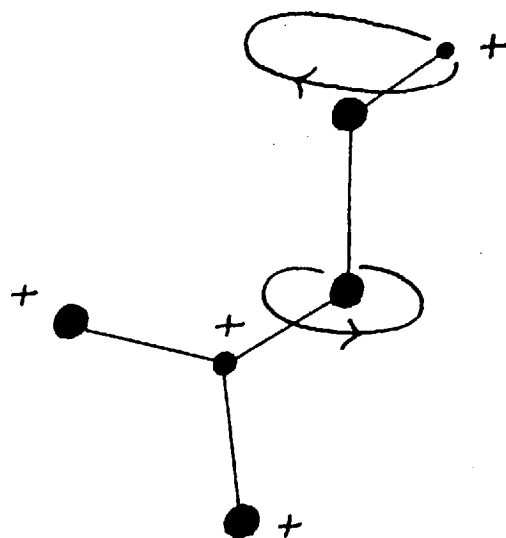
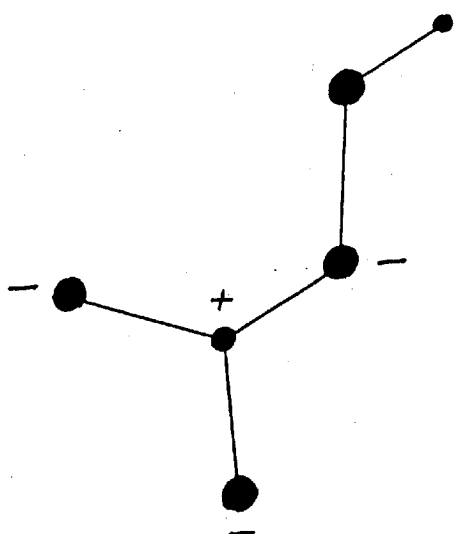
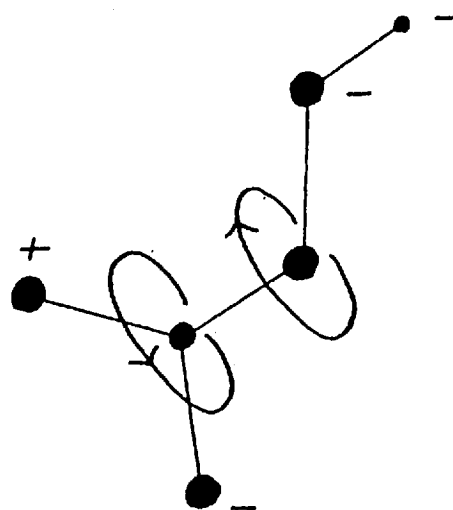
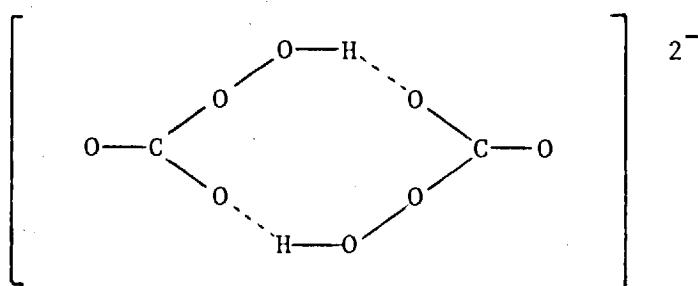


Figure 2-9. Normal Modes of Vibrational Motion for the  $\text{HCO}_4^-$  Anion with  $C_s$  Symmetry.

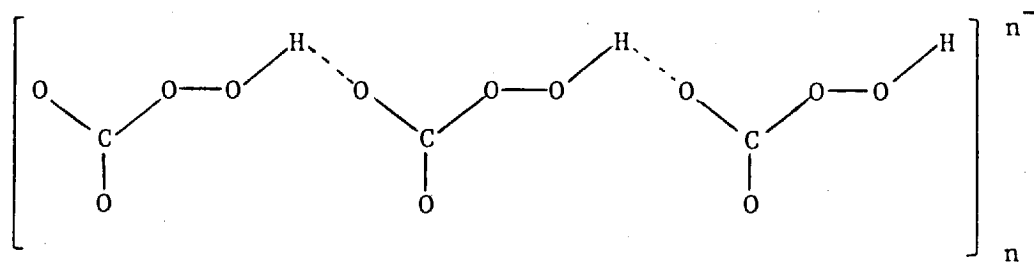
 $\nu_7$ , symm.  $\text{CO}_2$  def. $A'$  $\nu_8$ ,  $\text{OCO}_2$  def. $A'$  $\nu_9$ , asymm.  $\text{CO}_2$  def. $A'$  $\nu_{10}$ , O-O torsion $A''$  $\nu_{11}$ ,  $\text{CO}_3$  rock oop $A''$  $\nu_{12}$ , C-O torsion $A''$ Figure 2-10. Normal Modes of Vibrational Motion for the  $\text{HCO}_3^-$  Anion with  $C_s$  Symmetry.



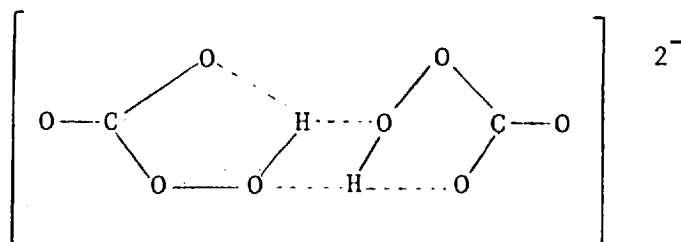
and this is also in keeping with observations on  $C_2O_6^{2-}$  (see Section 2-A-2). However, straightforward assignments of bands based on a monomeric anion should be treated with caution, as in the solid state the  $HCO_3^-$  ion almost certainly does not exist as a monomeric entity but is likely to dimerise or polymerise through hydrogen-bonding to give



similar to the anionic species found in  $KHCO_3$ <sup>85</sup> or forms endless strings as in  $NaHCO_3$ <sup>86</sup> to give:-

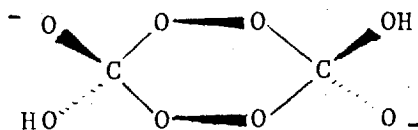


Other possibilities include a structure similar to that found in the solid state for some organic peroxyacids,  $RCO_3H$ .<sup>87</sup>



It should be noted here that an X-ray crystal structure determination on peroxyperlargonic acid,  $\text{CH}_3(\text{CH}_2)_7\text{CO}_3\text{H}$  has shown that intermolecular hydrogen-bonding occurs to form infinite spirals and that the  $-\text{COOO}$  group is planar.<sup>88†</sup>

One further possibility for this type of compound is a structure analogous to that reported for "sodium perborate",<sup>89,90</sup> which is isoelectronic with the following structure:-



but this can probably be ruled out since the vibrational spectra are very different from those of "sodium perborate" (see Section 2-F).

The formulation  $\text{M}_2^{\text{I}}\text{C}_2\text{O}_6 \cdot \text{H}_2\text{O}_2$  can also be excluded as a possibility both on the basis of the vibrational spectra and on the results of  $^1\text{H}$  n.m.r. studies on the solids,<sup>84,91</sup> the latter method showing that there is no  $\text{H}_2\text{O}_2$  of crystallisation in the peroxybicarbonates as the width of the n.m.r. absorption signals and the values of the second moments differ substantially from those obtained in similar studies on perhydrates.<sup>92,93</sup>

The assignments of the vibrational spectral bands for the peroxybicarbonates compare favourably with those reported for  $\text{NaHCO}_3$ <sup>94</sup> and  $\text{KHCO}_3$ ,<sup>95</sup> the evidence again pointing to dimeric or polymeric structures for the anions. The O-H stretch gives rise to bands at  $3120\text{--}2800\text{ cm}^{-1}$

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† For a review on the structure of organic peroxyacids see "Organic Peroxides", Vol. 1, Ed., D. Swern, 1970, p.313. Wiley-Interscience.

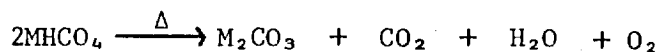
in the infrared (cf. 2620-1943  $\text{cm}^{-1}$  in  $\text{NaHCO}_3$  and  $\text{KHCO}_3$ ), the asymmetric C $\rightarrow$ O stretch appears as a very strong band in the infrared spectra at ca. 1700  $\text{cm}^{-1}$  (1698-1618  $\text{cm}^{-1}$ ), the symmetric C $\rightarrow$ O stretch at 1337-1268  $\text{cm}^{-1}$  (1300-1283  $\text{cm}^{-1}$ ), the OOH deformation at 1470-1430  $\text{cm}^{-1}$  (1458-1405  $\text{cm}^{-1}$ ), the C-O stretch at 986-930  $\text{cm}^{-1}$  (1052-1001  $\text{cm}^{-1}$ ) and the various carbonate deformations at 812-550  $\text{cm}^{-1}$  (837-630  $\text{cm}^{-1}$ ). The O-O stretch gives rise to bands in the 902-830  $\text{cm}^{-1}$  region of the spectra..

### 2-B-3 Electron Spin Resonance Spectroscopy.

The only compound of this series studied by e.s.r. spectroscopy is the potassium salt and the signal obtained is almost identical to that obtained from "chemically" -prepared  $\text{K}_2\text{C}_2\text{O}_6$ . This result again indicates the presence of ozonide ions. As stated in Section 2-B-1, small amounts of ozonide seem to accumulate during the slow decomposition of the alkali metal peroxybicarbonates, particularly so in the case of  $\text{KHCO}_4$ , the initially colourless compound gradually turning orange on storage.

### 2-B-4 Thermal Decomposition.

Thermal decomposition of the alkali metal peroxybicarbonates proceeds according to the equation:-



For  $\text{KHCO}_4$ , rapid decomposition occurs exothermically at 60-80°C, with release of all the peroxide oxygen and a considerable part of the  $\text{CO}_2$  and water. An endothermic effect is observed at 185-200°C due to

the decomposition of any  $\text{KHCO}_3$  formed during the initial decomposition reaction.<sup>71</sup> T.G.A. confirms the D.S.C. results, close to the calculated weight being lost.

#### 2-B-5 Organic Percarbonates.

Organic analogues of the alkali metal peroxybicarbonates have been reported - these are the lithium, sodium and potassium 0,0  $\alpha$ ,  $\alpha$ -dimethylbenzyl monoperoxybicarbonates,  $\text{ROOC(O)OM}$  ( $\text{R} = (\text{CH}_3)_2\text{C}_6\text{H}_5\text{C}$ ), formed by the reaction of  $\text{CO}_2$  with the alkali metal hydroperoxides in hydrocarbon solvents.<sup>96</sup> Like the alkali metal peroxybicarbonates, these compounds decompose at  $65\text{--}70^\circ\text{C}$  and are hydrolysed on dissolution in water to the hydroperoxide. On acidification  $\text{CO}_2$  is liberated.

### Section 2-C Lithium Peroxycarbonate Monohydrate, $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ .

#### 2-C-1 Preparation and Spectroscopic Data.

Lithium seems to be the only alkali metal to form a percarbonate of the form  $\text{M}_2^{\text{I}}\text{CO}_4$  although the ammonium analogue has been reported to exist<sup>73</sup> and recently the synthesis and some properties of calcium peroxycarbonate dihydrate,  $\text{CaCO}_4 \cdot 2\text{H}_2\text{O}$  have been published.<sup>97</sup>

$\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  was first prepared by Partington and Fathallah<sup>50</sup> but its existence was subsequently denied by Cohen.<sup>98</sup> For the present study the method of synthesis used was that of reference 99 (i.e., the reaction of  $\text{LiOH}$  and  $\text{H}_2\text{O}_2$  with  $\text{CO}_2$  gas). Its vibrational spectra have not been previously reported and the  $^{13}\text{C}$ -enriched analogue has been prepared in order to help make correct assignments of vibrational bands. The frequencies and assignments are given in Table 2-9 and the

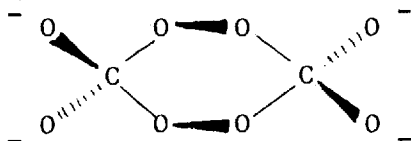
Table 2-9

Vibrational Spectra of Lithium Peroxycarbonate,  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ 

$\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$		$\text{Li}_2^{13}\text{CO}_4 \cdot \text{H}_2\text{O}$		Assignments
Infrared	Raman	Infrared	Raman	
3420vs  3340vs		3420vs  3340vs		$\nu_{\text{O-H}}$ , $\text{H}_2\text{O}$
1660vsb	n.o.	1660vsb	n.o.	$\text{H}_2\text{O}$ def
1605vsb	n.o.	1580vsb	n.o.	$\nu_1$ , C-O st
1480m	n.o.	1450m	n.o.	?
1350vsb	1344m	1330vsb	1313m	$\nu_2$ , C-O st
1035s	1042m	1030s	1039m	$\nu_3$ , C-O st
897s	902vs	897s	900vs	$\nu_4$ , O-O st
822m	n.o.	800m	n.o.	$\nu_5$ , $\text{CO}_2$ def.
735m	740m	730m	736m	$\nu_8$ , $\text{CO}_3$ def.
	606m		604m	$\nu_6$ , $\text{OCO}_2$ def

Raman spectrum is depicted in Figure 2-11.

One possible explanation for the non-formation of  $\text{Li}_2\text{C}_2\text{O}_6$  by further reaction of  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  with  $\text{CO}_2$  is that the  $\text{CO}_4^{2-}$  anion is dimeric, having a structure analogous to the cyclic perborate anion in "sodium perborate" (see Section 2-F).



However, the vibrational spectroscopic data indicate that a planar, monomeric structure is more likely as frequencies are characteristic of C-O bonds of order  $> 1$  and a planar geometry around the carbon atom is more in keeping with carbonate and percarbonate chemistry. Thus, the spectra are interpreted on the basis of a monomeric species with  $C_s$  symmetry; the fundamental internal vibrations of such a species are shown diagrammatically in Figure 2-12.

The water bands are clearly seen in the infrared spectra at 3420 and 3340  $\text{cm}^{-1}$  (O-H stretches) and 1660  $\text{cm}^{-1}$  ( $\text{H}_2\text{O}$  deformation). The asymmetric and symmetric C-O stretches give rise to bands at 1605 and 1350  $\text{cm}^{-1}$  in the infrared (shifting to 1580 and 1330  $\text{cm}^{-1}$  on  $^{13}\text{C}$ -substitution), the latter being observed in the Raman spectrum at 1344  $\text{cm}^{-1}$  (1313  $\text{cm}^{-1}$ ). The C-O stretch is observed at ca. 1040  $\text{cm}^{-1}$  and the O-O stretch at ca. 900  $\text{cm}^{-1}$  with the deformations appearing at 822-606  $\text{cm}^{-1}$ .

The XRD data for  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  confirm its singularity, with no evidence of contamination by carbonate, hydroxide, hydroperoxide or peroxide and the d-spacings are listed in Table 2-10.

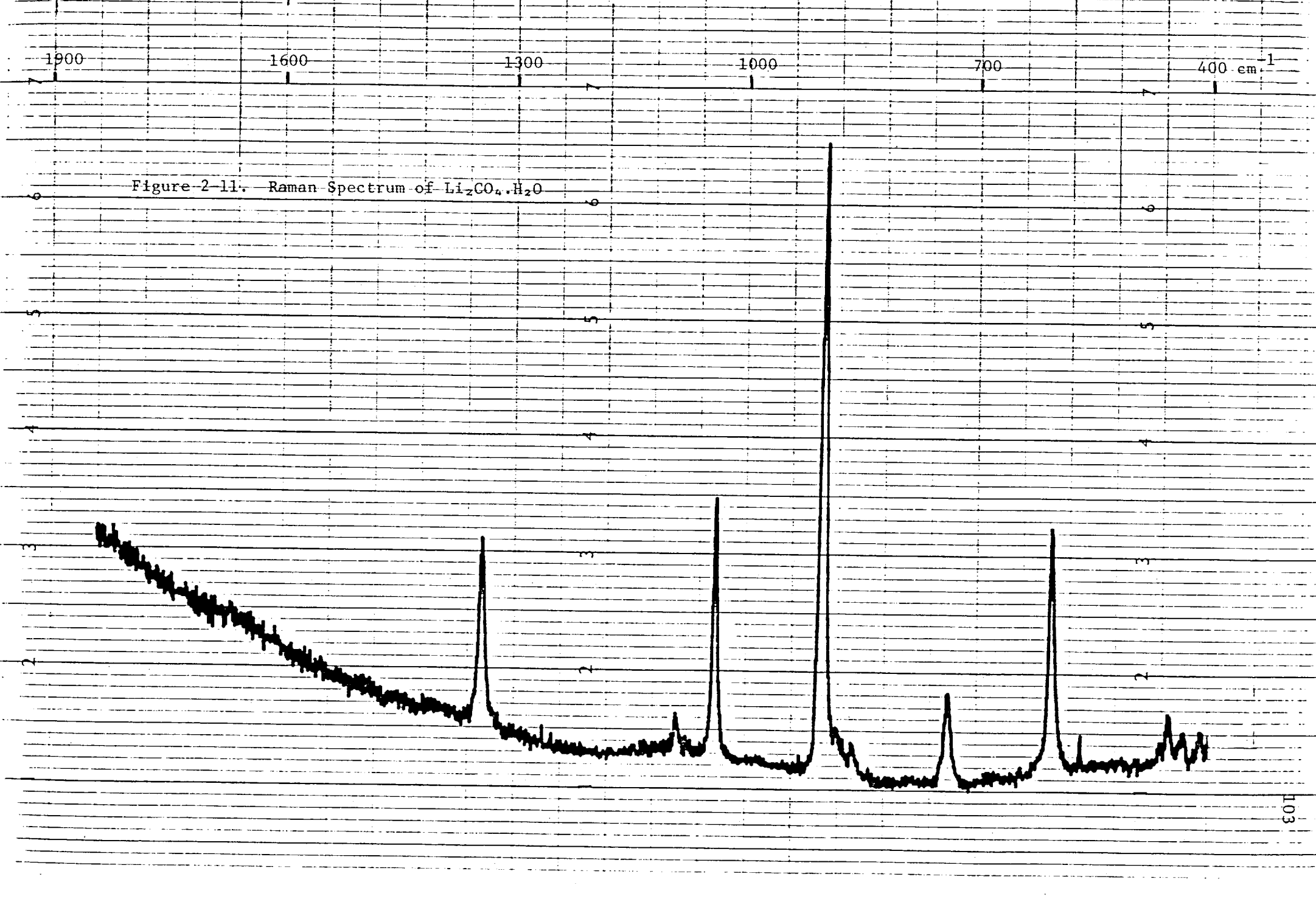


Figure 2-11. Raman Spectrum of  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$

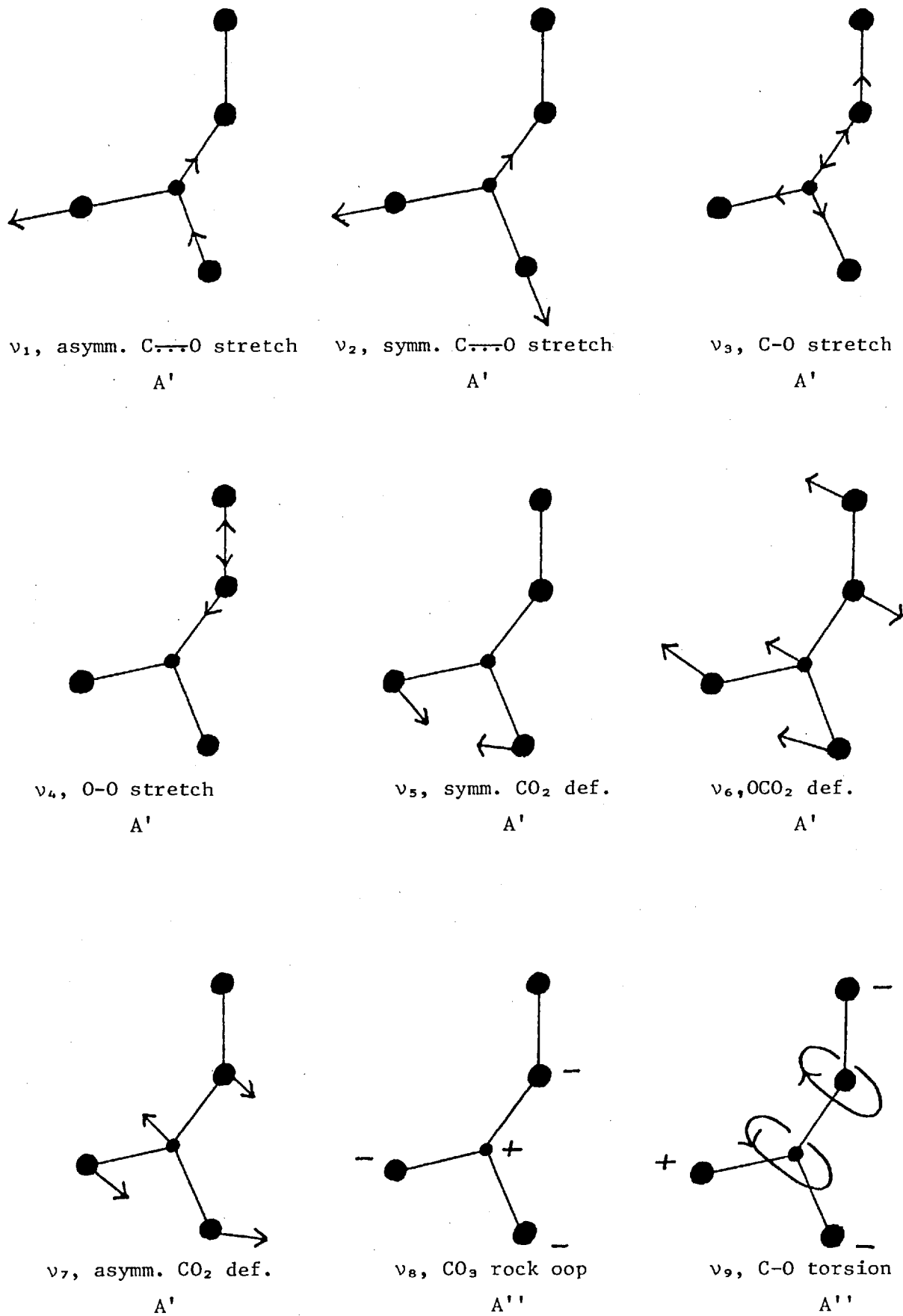


Figure 2-12. Normal Modes of Vibrational Motion for the  $\text{CO}_3^{2-}$  Anion with  $C_s$  Symmetry.



Table 2-10

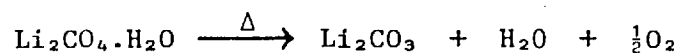
XRD Data for Li<sub>2</sub>CO<sub>4</sub>.H<sub>2</sub>O

I	° dÅ	I	° dÅ	I	° dÅ	I	° dÅ
s	6.3	vs	3.22	m	2.625	w	2.29
m	5.00	vs	3.16	m	2.59	vw	2.24
w	4.42	vs	3.09	vw	2.51	w	2.22
w	4.21	s	3.00	s	2.475	vw	2.16
w	4.19	vw	2.95	vw	2.45	m	2.14
s	3.90	vw	2.85	vw	2.40	w	2.11
s	3.77	vw	2.77	m	2.38	vw	2.07
m	3.51	s	2.66	m	2.31	vw	2.03

E.s.r. spectra of Li<sub>2</sub>CO<sub>4</sub>.H<sub>2</sub>O exhibit a very weak signal at room temperature which suddenly increases in intensity when the sample is heated to ca. 120°C (i.e., above its decomposition temperature). The new, moderately strong signal again resembles that of ozonide ion and is still present at 220°C.

2-C-2 Thermal Decomposition.

The thermal decomposition of Li<sub>2</sub>CO<sub>4</sub>.H<sub>2</sub>O proceeds according to the equation:-

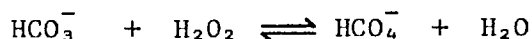


D.S.C. traces exhibit an exotherm at ca. 80°C accompanied by an endotherm at ca. 110°C with evolved gas analysis showing the liberation of oxygen and water vapour in the ratio 1 : 2. These data are supported by T.G.A. results.

## Section 2-D Percarbonate Species in Solution.

### Introduction.

It has been noted<sup>100</sup> and also shown in this work, that the solid produced as a result of the preparation of  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  from  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}_2$  at  $-10^\circ\text{C}$  contains a large proportion of  $\text{NaHCO}_4 \cdot \text{H}_2\text{O}$  and also that relatively pure  $\text{KHCO}_4$  can be prepared from the interaction of  $\text{KHCO}_3$  with  $\text{H}_2\text{O}_2$  at below  $0^\circ\text{C}$ .<sup>101</sup> Thus, it would seem that an equilibrium could exist in solution between  $\text{HCO}_3^-$  and  $\text{H}_2\text{O}_2$ , the position of the equilibrium being dependent on the concentrations of the two species, the temperature, and the pH of the solution.



In order to gain some insight into this reaction, solutions of  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$  in aqueous  $\text{H}_2\text{O}_2$  have been studied both by  $^{13}\text{C}$  n.m.r. and Raman spectroscopy. The potassium salts were used rather than the sodium so that higher concentrations could be obtained.

### 2-D-1 $^{13}\text{C}$ n.m.r. Spectroscopy.

An aqueous solution of potassium bicarbonate or carbonate or a mixture of both gives rise to only one resonance in the  $^{13}\text{C}$  n.m.r. spectrum, positioned at the average of the two resonances expected for the pure species due to rapid proton exchange between the two.<sup>102</sup> Thus, the exact position of the resonance is pH-dependent and results in this work have shown that this resonance varies in its position between 161.4 and 168.8 ppm depending upon the pH of the solutions.

However, aqueous hydrogen peroxide solutions of potassium bicarbonate give rise to two resonances, the first of which is attributed to  $\text{HCO}_3^-/\text{CO}_3^{2-}$  (161.4-167.3 ppm) and the second to  $\text{HCO}_4^-/\text{CO}_4^{2-}$  (159.5-160.5 ppm). It has been established that this second resonance cannot be due to dissolved  $\text{CO}_2$  as this species gives a resonance at 125.4 ppm.<sup>102</sup> Figure 2-13 shows a typical  $^{13}\text{C}$  n.m.r. spectrum of a solution of  $\text{KHCO}_3$  in aqueous  $\text{H}_2\text{O}_2$ .

Due to lack of time available and supplies of  $\text{KH}^{13}\text{CO}_3$  (see Experimental Section), quantitative measurements of absolute intensities of the two carbon-containing species have not been carried out as yet and the slow decomposition of solutions of this type (typically 1.0 M  $\text{KH}^{13}\text{CO}_3$  in aqueous 15-30% w/v  $\text{H}_2\text{O}_2$ ), more pronounced at high pH, which in turn causes a change in pH during the 15-30 minutes required to record the spectrum, makes accurate measurements impossible. However, the peak attributable to  $\text{HCO}_4^-/\text{CO}_4^{2-}$  certainly grows in intensity relative to the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  peak as the  $\text{H}_2\text{O}_2$  concentration increases and rough chemical shift vs. pH measurements can be plotted to give the sort of curves that might be expected for  $\text{H}_2\text{CO}_3(\text{H}_2\text{O} + \text{CO}_2)/\text{HCO}_3^-/\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_4/\text{HCO}_4^-/\text{CO}_4^{2-}$  equilibria. These curves are shown in Figures 2-14 and 2-15. The mid-points of the steeper parts of the curves correspond roughly to the  $\text{pK}_a$  values of the species concerned.<sup>†</sup>

---

<sup>†</sup> The  $\text{pK}_a$  value is the point at which, for  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$  (e.g.,  $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ ),  $[\text{HA}] = [\text{A}^-]$  and since  $\delta_{\text{obs.}} = (\delta_{\text{HA}} \times \text{mole fraction of HA}) + (\delta_{\text{A}^-} \times \text{mole fraction of A}^-)$ , when  $[\text{HA}] = [\text{A}^-]$ ,  $\delta_{\text{obs.}}$  will have a value mid-way between the values observed for pure HA and pure  $\text{A}^-$  respectively.

PPM

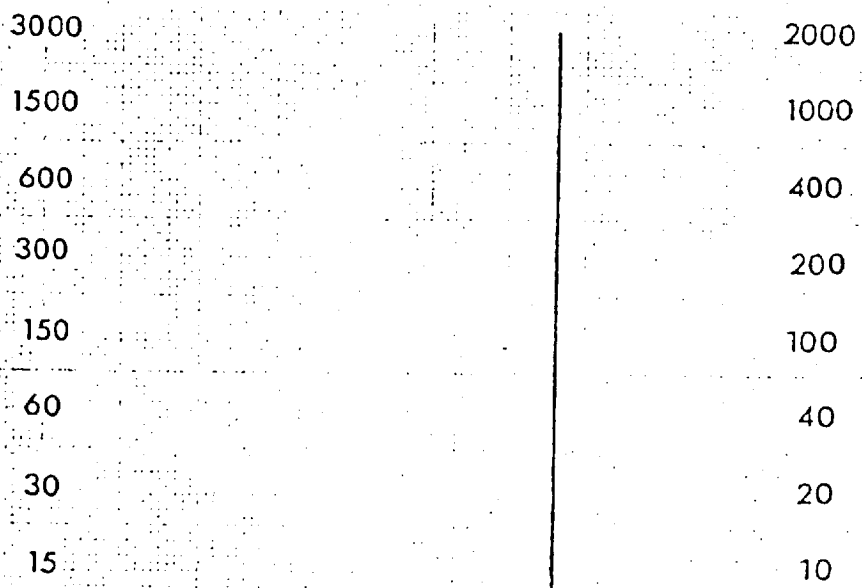


Figure 2-13.  $^{13}\text{C}$  n.m.r. Spectrum of a Hydrogen Peroxide Solution of  $\text{HCO}_3^-$  Anion.

PPM

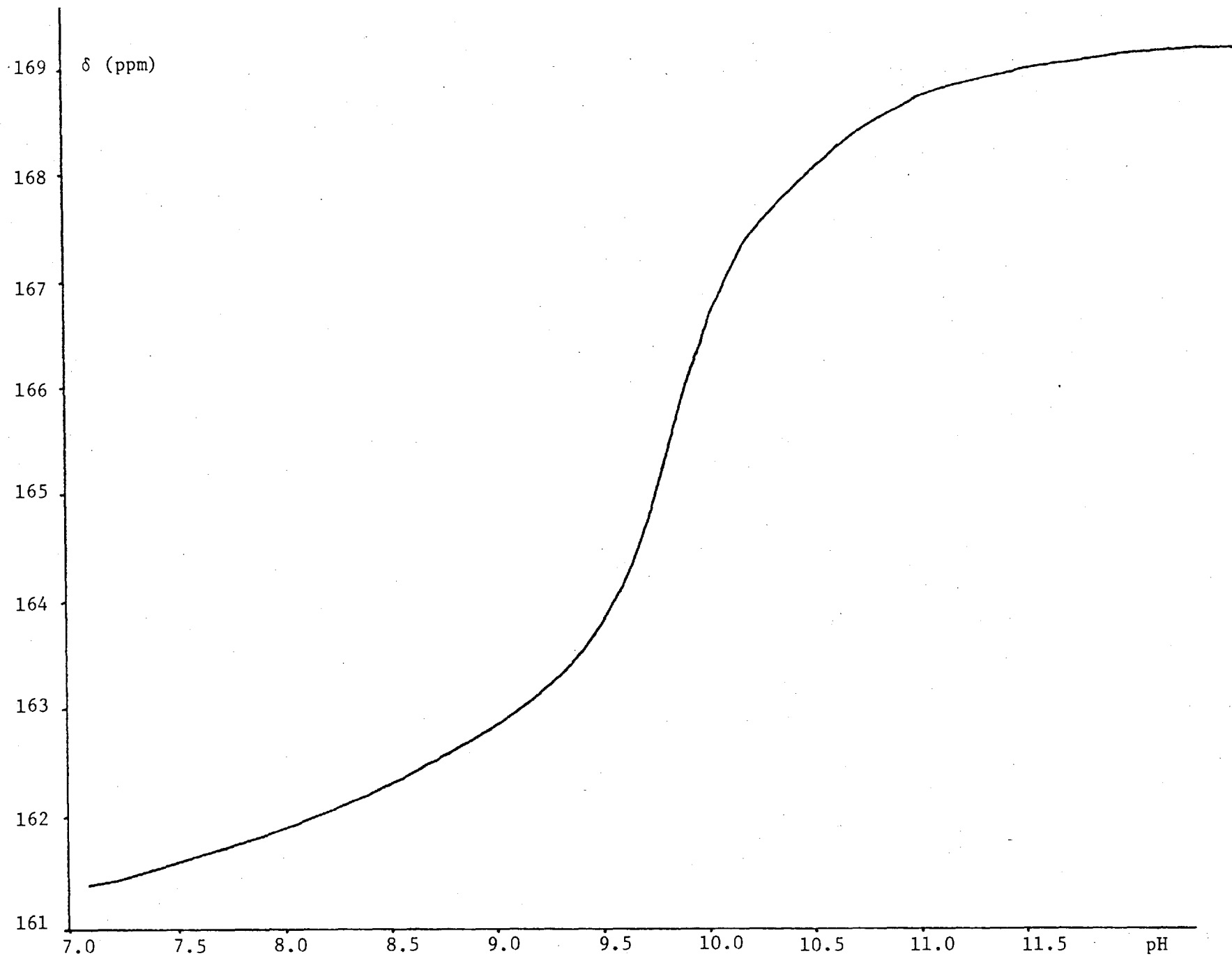


Figure 2-14. Curve Obtained for Plot of  $\delta$  vs. pH for  $\text{HCO}_3^-/\text{CO}_3^{2-}$  in  $\text{HCO}_3^-/\text{H}_2\text{O}_2$  Solutions.

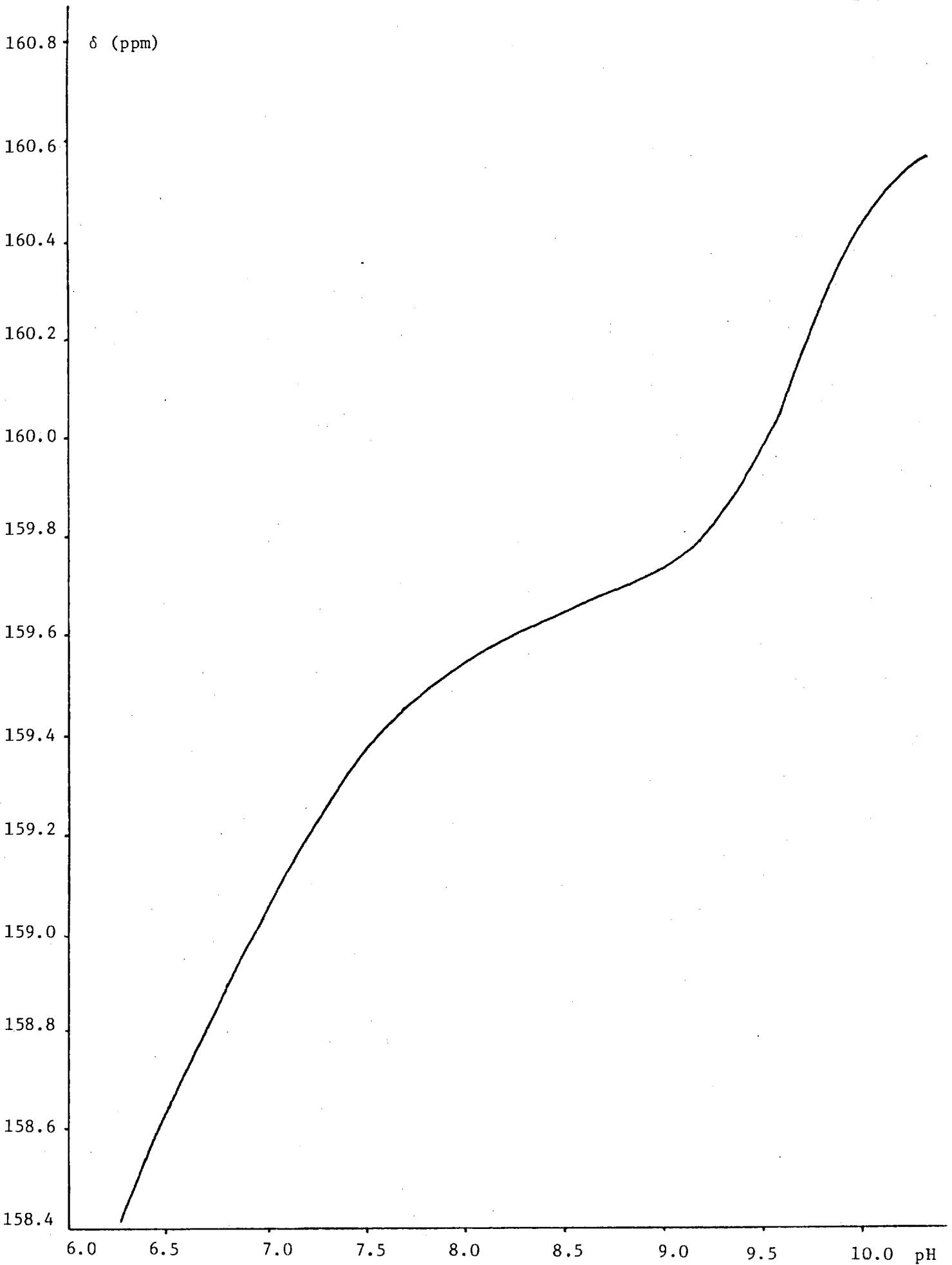
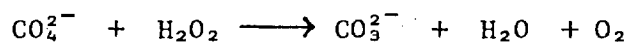


Figure 2-15. Curve Obtained for Plot of  $\delta$  vs. pH for  $\text{H}_2\text{CO}_4/\text{HCO}_4^-/\text{CO}_4^{2-}$  in  $\text{HCO}_3^-/\text{H}_2\text{O}_2$  Solutions.

It is noticeable that no peroxy carbonate is formed at  $\text{pH} > 10.5$ . A possible explanation is that such a species will react with  $\text{H}_2\text{O}_2$  at this and higher  $\text{pH}$ , oxidising it to give oxygen and water.



Also, at  $\text{pH} > 10.5$  there should be very little  $\text{HCO}_3^-$  present as the  $\text{pK}_a$  value for  $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$  is 10.25 (at  $25^\circ\text{C}$ ). It is likely that  $\text{CO}_3^{2-}$  is inert to such a species as  $\text{OOH}^-$  and therefore formation of peroxy carbonate will not occur at this  $\text{pH}$ . The active species is  $\text{HCO}_3^-$  which probably forms  $\text{HCO}_4^-$  by nucleophilic attack of  $\text{OOH}^-$  and subsequent loss of  $\text{OH}^-$ .

The variation of  $\delta$  with  $\text{pH}$  for  $\text{HCO}_4^-/\text{CO}_4^{2-}$  is much smaller than that for  $\text{HCO}_3^-/\text{CO}_3^{2-}$  and this is to be expected as protonation of an oxygen two atoms removed from a carbon atom will have far less effect on the carbon atom nucleus than would protonation of an adjacent oxygen atom.

#### 2-D-2. Raman Spectroscopy.

At room temperature, solutions of  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$  in aqueous  $\text{H}_2\text{O}_2$  of  $> 10\%$  w/v concentration in  $\text{H}_2\text{O}_2$  are rather unstable and exposure of these solutions to a focussed laser beam for the recording of their Raman spectra increases the rate of decomposition, sometimes quite drastically so that total decomposition occurs before a complete spectrum can be obtained, even when the solutions are rapidly spun. However, some spectra have been recorded together with spectra of frozen solutions. Both sets of spectra are very similar and exhibit bands attributable to  $\text{HCO}_4^-$  together with  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{H}_2\text{O}_2$  bands. Spectra of  $\text{H}_2\text{O}_2$  solutions

of  $\text{KH}^{13}\text{CO}_3$  have also been recorded and the frequencies of the bands obtained are lowered accordingly, indicating that the extra species is a carbon-containing entity and not a species such as  $\text{OOH}^-$  or  $\text{O}_2^{2-}$ . The frequencies and assignments are given in Table 2-11 and compared with similar data for solid  $\text{KHCO}_4$ .

Table 2-11

Raman Spectra of Hydrogen Peroxide Solutions of  $\text{HCO}_3^-$  and  $\text{H}^{13}\text{CO}_3^-$  Anions.\*

Frequency <sup>†</sup>	Assignments <sup>††</sup>	Solid $\text{KHCO}_4$
1320 (1288)	$\nu_4$	1268-1342
708 (700)	$\nu_{11}$	696-739
580 (560)	$\nu_8$	550-582

\* Bands attributable to  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{H}_2\text{O}_2$  are not included.

† Values in parentheses for  $\text{H}^{13}\text{CO}_3^-$  solutions.

†† See Section 2-B-2 for assignments of  $\text{HCO}_4^-$ .

Section 2-E. Bleaching Action of the Percarbonates,  $\text{K}_2\text{C}_2\text{O}_6$ ,  $\text{KHCO}_4$   
and  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ .

The peroxysalts "sodium percarbonate",  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  and "sodium perborate",  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$  are already well-established as industrial bleaching agents, comprising roughly 25% of the 350,000 tons of packet detergents sold each year in the United Kingdom.



Recently, tests have been carried out to evaluate the compounds  $K_2C_2O_6$ ,  $KHCO_4$ , and  $Li_2CO_4 \cdot H_2O$  as potential bleaching agents for domestic washing.<sup>†</sup> The bleaching performances of these percarbonates were studied at both 40 and 60°C under standard European washing conditions: i.e., 4 g/l marchon base, 250 ppm hard water 3:1 Ca:Mg, natural pH, 10 and 30 minute wash cycles, using red wine stained cloth.

The results indicate that at both 40 and 60°C the bleaching performances of the three percarbonates, at 100 ppm available oxygen level, were slightly inferior to those of "sodium percarbonate" and "sodium perborate" at 100 ppm available oxygen under the same conditions. Thus there appear to be no advantages in using  $K_2C_2O_6$ ,  $KHCO_4$  or  $Li_2CO_4 \cdot H_2O$  as bleaching agents for domestic washing especially as all three compounds are relatively unstable, the potassium compounds in particular being hygroscopic making storage for prolonged periods without loss of peroxide oxygen highly impractical. At room temperature in open containers, the loss of peroxide oxygen from the compounds was as follows:-

Number of Days	% Peroxide Loss		
	$K_2C_2O_6$	$KHCO_4$	$Li_2CO_4 \cdot H_2O$
2	4.2	0.7	1.4
7	52.0	59.7	10.9
14	65.8	88.1	27.1
21	95.7	94.0	31.3
28	-	-	41.7

---

<sup>†</sup> This work was kindly carried out by E. Smith and J. Monaghan of Laporte Industries Ltd.

Section 2-F "Sodium Perborate",  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ .

2-F-1 X-Ray Crystal Structure.

Disodium tetrahydroxo-di- $\mu$ -peroxo-diborate hexahydrate, more usually termed "sodium perborate" is by far the most common industrial bleaching agent and is incorporated in a wide range of packet detergents for this purpose. This compound had been variously described by the formulae  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$  or  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ , until its nature was determined crystallographically by Hansson<sup>89</sup> in 1961, who showed it to contain the cyclic  $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$  anion. His report, however, was based on unrefined data and no  $R$  was quoted. The unique structure of the anion and the industrial importance of this compound prompted an accurate determination based on diffractometer data in these laboratories.<sup>90</sup> † This work has essentially confirmed the original structure, but one water molecule has been found to be misplaced by 0.7 Å.

Crystals of  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$  were obtained as colourless, irregular prisms by the method of Hansson.<sup>89</sup> (Composition : found: H, 5.2 ;  $\text{O}_2^{2-}$ , 20.9% ;  $\text{B}_2\text{H}_{16}\text{Na}_2\text{O}_{14}$  requires : H, 5.2 ;  $\text{O}_2^{2-}$ , 20.8%.) Photographs confirmed that the crystals were triclinic with  $\underline{a} = 6.837$ ,  $\underline{b} = 7.084$ ,  $\underline{c} = 8.907$  Å,  $\alpha = 87.38$ ,  $\beta = 126.85$ ,  $\gamma = 116.10^\circ$ , space group  $\overline{\text{P1}}$  and  $\underline{Z} = 1$ . Intensity data were collected as for  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  (see Chapter One, Section 1-C) and a total of 1122 independent reflections were measured (to  $\theta = 70^\circ$ ). The least-squares refinement reached a final  $R$  value of 0.027.

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† The structural determination was carried out by Drs. M.A.A.F. de C.T. Carrondo and A.C. Skapski.

Figure 2-16 shows the structure of the perborate anion. The arrangement consists of two centrosymmetrically related boron atoms, each tetrahedrally coordinated to two OH groups and to two peroxide groups which act as bridges between the boron atoms. The resulting six-membered ring adopts a chair conformation and the water molecules, OH groups and peroxy groups form a network of hydrogen bonds. The accepted O-O single-bond distance is  $1.48 \text{ \AA}$ ,<sup>103</sup> and the O-O distance ( $1.480 \text{ \AA}$ ) in the peroxy bridge of this compound is identical to that value. The dihedral angle of the bridge is  $60.0^\circ$ , and is much more acute than those found in other compounds containing O-O linkages.<sup>104</sup> Its acuteness is a consequence of the chair conformation of the ring system and of the tetrahedral angles at the boron atoms.

#### 2-F-2 Vibrational Spectra.

The infrared and Raman spectra of "sodium perborate" have been recorded from  $4000\text{-}600 \text{ cm}^{-1}$  and the frequencies are listed in Table 2-12. The sharp band at  $3590 \text{ cm}^{-1}$  in both the Raman and the infrared is attributed to the O-H stretching vibration of the B-O-H groups and the two, broader bands at  $3420$  and  $3360 \text{ cm}^{-1}$  in the Raman ( $3400$  and  $3260 \text{ cm}^{-1}$  in the infrared) are due to O-H stretching vibrations of the water molecules. A band at  $1660 \text{ cm}^{-1}$  with a shoulder at  $1675 \text{ cm}^{-1}$  in the infrared arise from  $\text{H}_2\text{O}$  deformations and the remaining bands in both the Raman and the infrared are due to ring stretches and deformations with the O-O stretch giving rise to a very strong band in the Raman spectrum at  $900 \text{ cm}^{-1}$ . These results agree with those already reported.<sup>105</sup>

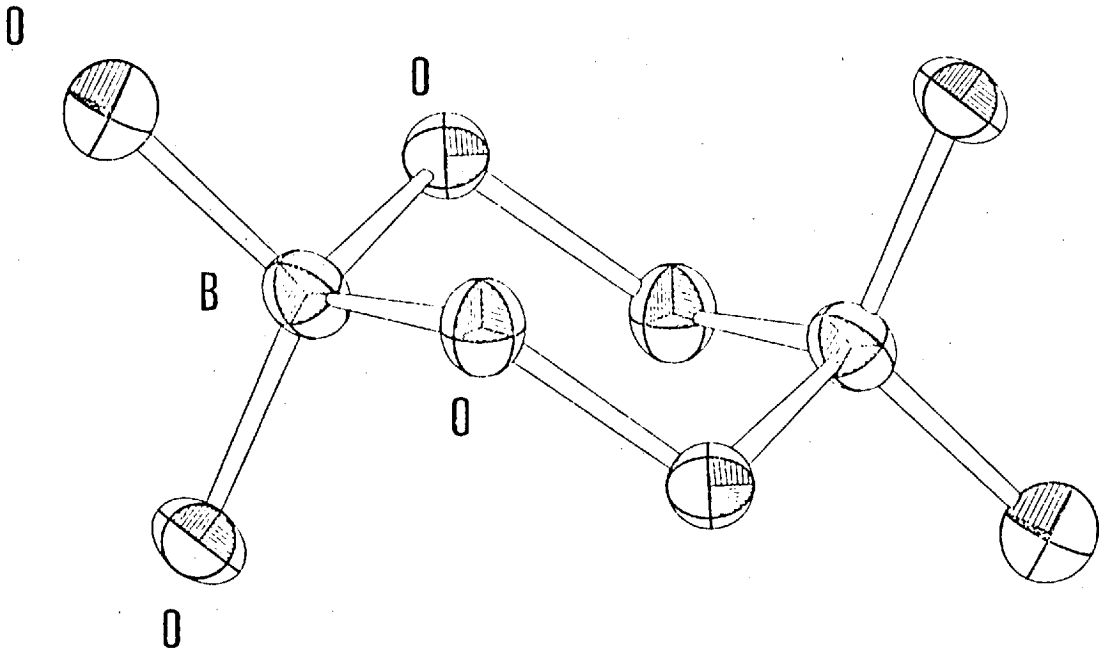


Figure 2-16. Structure of the Cyclic  $[B_2(O_2)_2(OH)_4]^{2-}$  Anion.

When dissolved in water, "sodium perborate" hydrolyses to release hydrogen peroxide which can be titrated against permanganate ion and thus it acts in the same way as a perhydrate, being a solid, portable form of hydrogen peroxide. However, the mechanism of the hydrolysis is uncertain and is probably complex, with covalent boron-oxygen bands having to be broken in order to form hydrogen peroxide.

It would seem that a detailed  $^{11}\text{B}$  n.m.r. study on borate/ $\text{H}_2\text{O}_2$  systems and perborate/ $\text{H}_2\text{O}$  systems would shed some light on both the mechanism of formation as well as that of hydrolysis of perborates.

Table 2-12

Vibrational Spectra of  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ .

Infrared	Raman
3590 vs	3590 m
3400 vsb	3420 mb
3260 vsb	3360 mb
2240 wb	
1675 sh	
1660 s	
1375 w	
1230 sb	
1165 sb	
1030 sb	
980 sb	
	970 sb
925 sb	
	900 vs
850 s	
780 m	
	710 sb

Section 2-G    E X P E R I M E N T A L2-G-1    The Alkali Metal Peroxydicarbonates,  $M_2^I C_2 O_6$ .Sodium Peroxydicarbonate,  $Na_2 C_2 O_6 \cdot n H_2 O$ .

An aqueous solution of 50% w/w  $H_2 O_2$  ( $3.0 \text{ cm}^3$ , 52.5 mmol  $H_2 O_2$ ) was stirred at  $-20^\circ C$  and a solution of sodium hydroxide (4.0 g, 100 mmol) in water ( $10 \text{ cm}^3$ ) was added dropwise, slowly. A thick, white precipitate was formed and the temperature was then allowed to rise to  $-5^\circ C$  before a stream of  $CO_2$  gas was passed over the surface of the stirred mixture for  $1-1\frac{1}{2}$  hours at this temperature. The white solid was then filtered off under suction, washed copiously with ethanol followed by diethyl ether and dried in vacuo.

Potassium Peroxydicarbonate,  $K_2 C_2 O_6$ .(a) Form "A"

An aqueous solution of 86% w/w  $H_2 O_2$  ( $1.8 \text{ cm}^3$ , 62.3 mmol  $H_2 O_2$ ) was stirred at  $-20^\circ C$  and a solution of potassium hydroxide (7.0 g, 125.0 mmol) in water ( $10 \text{ cm}^3$ ) was added dropwise, slowly. A clear solution resulted and this was continually stirred at  $-20^\circ C$  whilst a stream of  $CO_2$  gas was passed over the surface. A white film of solid began to form immediately and  $CO_2$  passage was stopped after 80 minutes by which time a thick, pale orange precipitate had formed. This was collected and dried as for the sodium salt.

(b) Form "C"

A compound having the same stoichiometry as the one above but different physical properties was prepared following procedure (a) but this time keeping the temperature at  $-5^\circ C$  during the passage of  $CO_2$ .

Table 2-1

Elemental Analyses for the Alkali Metal Peroxydicarbonates.

	% Found				% Required			
	O <sub>2</sub> <sup>-</sup>	C	H	<u>M</u>	O <sub>2</sub> <sup>-</sup>	C	H	<u>M</u>
Na <sub>2</sub> C <sub>2</sub> O <sub>6</sub> .nH <sub>2</sub> O	19.4				19.2	14.5	0	
" Chemical " K <sub>2</sub> C <sub>2</sub> O <sub>6</sub> <sup>a</sup>	16.0	11.9	0.1	39.5	16.2	12.1	0	39.5
" Chemical " K <sub>2</sub> C <sub>2</sub> O <sub>6</sub> <sup>b</sup>	15.6	11.9	0.5	39.5	16.2	12.1	0	39.5
Electrolytic K <sub>2</sub> C <sub>2</sub> O <sub>6</sub>	15.2	11.4	0.3	39.6	16.2	12.1	0	39.5
Rb <sub>2</sub> C <sub>2</sub> O <sub>6</sub>	11.0	8.0	0	57.8	11.0	8.3	0	58.8
Cs <sub>2</sub> C <sub>2</sub> O <sub>6</sub>	8.2	5.7	0.5	66.3	8.4	6.0	0	68.9

<sup>a</sup> Prepared at -20°C (Form " A " )

<sup>b</sup> Prepared at -5°C (Form " C " )

(c) Form " B "

A saturated solution of potassium carbonate in water at  $-20^{\circ}\text{C}$  was electrolysed at this temperature using apparatus similar to that described by Mel'nikov, et al.,<sup>106</sup> the solution being contained in an H-shaped vessel with a sintered glass diaphragm. The anode was a platinum wire and the cathode a platinum plate. The current passing through the electrolyte varied between 250 and 350 mA and the liquid in the anode compartment was continually stirred. Almost immediately, a pale-blue scum appeared on the surface of the anolyte, which gradually became turbid and after  $1\frac{1}{2}$ -2 hours a fine, pale-blue precipitate settled out. This was filtered off, washed with ethanol and diethyl ether and dried in vacuo.

Rubidium Peroxydicarbonate,  $\text{Rb}_2\text{C}_2\text{O}_6$ .

This was prepared as a pale orange powder in a similar fashion to the potassium analogue (using procedure (a)) with aqueous 86% w/w  $\text{H}_2\text{O}_2$  ( $0.4\text{ cm}^3$ ,  $13.9\text{ mmol H}_2\text{O}_2$ ) and a solution of rubidium hydroxide ( $2.75\text{ g}$ ,  $26.8\text{ mmol}$ ) in water ( $2\text{ cm}^3$ ), the reaction temperature being  $-20^{\circ}\text{C}$  and the time taken 15 minutes.

Caesium Peroxydicarbonate,  $\text{Cs}_2\text{C}_2\text{O}_6$ .

This was also prepared as a pale orange powder following procedure (a) for the potassium analogue with aqueous 86% w/w  $\text{H}_2\text{O}_2$  ( $0.16\text{ cm}^3$ ,  $5.5\text{ mmol H}_2\text{O}_2$ ) and a solution of caesium hydroxide ( $1.67\text{ g}$ ,  $11.1\text{ mmol}$ ) in water ( $0.5\text{ cm}^3$ ), the reaction temperature being  $-20^{\circ}\text{C}$  and the time taken 20 minutes.



2-G-2 The Alkali Metal Peroxybicarbonates,  $M^I\text{HCO}_4$ .

Sodium Peroxybicarbonate Monohydrate,  $\text{NaHCO}_4 \cdot \text{H}_2\text{O}$ .

An aqueous solution of 50% w/w  $\text{H}_2\text{O}_2$  ( $5.0 \text{ cm}^3$ ,  $87.8 \text{ mmol H}_2\text{O}_2$ ) was stirred at  $-20^\circ\text{C}$  and a solution of sodium hydroxide (2.8 g, 70 mmol) in water ( $10 \text{ cm}^3$ ) was added dropwise, slowly. A white precipitate was formed and the temperature was then allowed to rise to  $0^\circ\text{C}$  at which temperature most of the solid had dissolved. A stream of  $\text{CO}_2$  gas was then passed over the surface of the stirred mixture and after 35 minutes a thick, white precipitate formed which was collected and dried in the usual manner.

Table 2-6

Elemental Analyses for the Alkali Metal Peroxybicarbonates.

	% Found				% Required			
	$\text{O}_2^{2-}$	C	H	<u>M</u>	$\text{O}_2^{2-}$	C	H	<u>M</u>
$\text{NaHCO}_4 \cdot \text{H}_2\text{O}$	26.8	9.6	0.9		27.2	10.2	2.6	
$\text{KHCO}_4$	26.8	10.3	0.4	33.3	27.6	10.3	0.9	33.7
$\text{RbHCO}_4$	18.6	7.6	0.5	52.7	19.8	7.4	0.6	52.6

Potassium Peroxybicarbonate,  $\text{KHCO}_4$ .

An aqueous solution of 86% w/w  $\text{H}_2\text{O}_2$  ( $1.3 \text{ cm}^3$ ,  $45 \text{ mmol H}_2\text{O}_2$ ) was stirred at  $-10^\circ\text{C}$  and a solution of potassium hydroxide (2.5 g, 45 mmol) in water ( $5 \text{ cm}^3$ ) was added dropwise, slowly. A clear solution resulted and this was continually stirred for  $1\frac{3}{4}$  hours at  $-5^\circ\text{C}$  whilst a stream of  $\text{CO}_2$  gas was passed over the surface during which time a white precipitate formed. This was collected and dried as previously.

Rubidium Peroxybicarbonate,  $\text{RbHCO}_4$ .

This was prepared as a white powder in a similar fashion to  $\text{KHCO}_4$  using 86% w/w  $\text{H}_2\text{O}_2$  (1.0 cm<sup>3</sup>, 34.6 mmol  $\text{H}_2\text{O}_2$ ) and a solution of rubidium hydroxide (3.2 g, 30.9 mmol) in water (3 cm<sup>3</sup>).

2-G-3 Lithium Peroxycarbonate Monohydrate,  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ .

This compound was prepared following the method of Firsova, et al.<sup>99</sup> Solid, powdered lithium hydroxide monohydrate (3.5 g, 83 mmol) was added portionwise, over a period of 45 minutes, to an ice-cooled, stirred, aqueous solution of 50% w/w  $\text{H}_2\text{O}_2$  (5.0 cm<sup>3</sup>, 88.2 mmol  $\text{H}_2\text{O}_2$ ) whilst a continuous stream of  $\text{CO}_2$  gas was passed over the surface. A thick, white precipitate resulted and the mixture was stirred for a further 15 minutes under a  $\text{CO}_2$  atmosphere before collecting and drying the solid in the usual manner. (Found : C, 11.5 ; H, 1.7 ;  $\text{O}_2^-$ , 29.6.  $\text{CH}_2\text{Li}_2\text{O}_5$  requires C, 11.1 ; H, 1.9 ;  $\text{O}_2^-$ , 29.6%).

2-G-4  $^{13}\text{C}$ -Enriched Potassium Bicarbonate,  $\text{KH}^{13}\text{CO}_3$ .

A mixture of  $\text{K}_2^{13}\text{CO}_3/\text{KH}^{13}\text{CO}_3$  enriched to 87.0 atom % in  $^{13}\text{C}$  was purchased from the British Oxygen Company Ltd., and pure  $\text{KH}^{13}\text{CO}_3$  was obtained by repeated recrystallisation from water. Residues were recovered by acidification and passage of the  $^{13}\text{CO}_2$  gas evolved into aqueous KOH solution to re-form  $\text{K}_2^{13}\text{CO}_3$  and  $\text{KH}^{13}\text{CO}_3$ .

## CHAPTER THREE

### THE OXIDISING PROPERTIES OF PERCARBONATES, PERCARBONATO COMPLEXES AND PERBORATES.

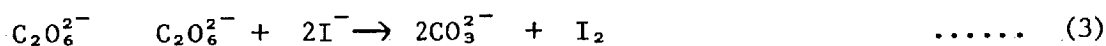
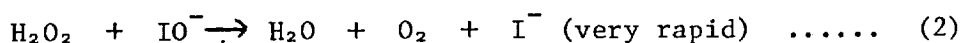
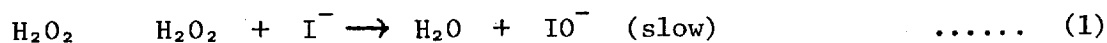
#### Abstract.

The potential use of the alkali metal percarbonates and "sodium perborate" as oxidising agents for both inorganic and organic species has been investigated. For comparison purposes, one of the very few known transition metal peroxy-carbonates, bistriphenylphosphine peroxy-carbonato platinum(II) has been prepared, its structure determined by X-ray crystallographic methods and its oxidising properties studied.

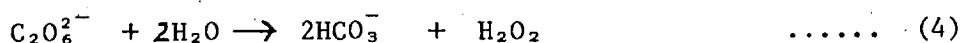
#### Section 3-A. Some Observations on the Oxidising Properties of the Alkali Metal Percarbonates and "Sodium Perborate".

The devising of a simple test to distinguish between "true" peroxy-compounds such as potassium peroxydicarbonate, and perhydrates, would be based on the differences in the ability of such compounds to act as oxidising agents. Such a test was proposed as early as 1909 by Riesenfeld and Reinhold,<sup>107</sup> based on the oxidation of neutral aqueous potassium iodide solutions, in which it was noticed that hydrogen peroxide and perhydrates liberate oxygen but hardly any iodine whereas "true" percarbonates, (i.e., those presumed to contain C-O-O bonds) such as  $K_2C_2O_6$ , liberate iodine immediately. These

observations were explained by the equations:-

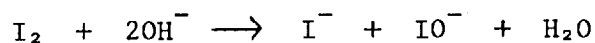


In competition with equation (3) is the hydrolysis reaction:-

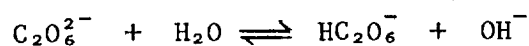


and so Tanatar's observation<sup>108</sup> that only solid samples or freshly-prepared solutions of  $\text{K}_2\text{C}_2\text{O}_6$  give the test seems reasonable.

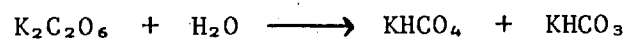
With alkaline solutions of KI, no iodine is liberated by  $\text{K}_2\text{C}_2\text{O}_6$  due to the reaction:-



The reason for the liberation of iodine by  $\text{K}_2\text{C}_2\text{O}_6$  can be explained on the basis of results obtained from a study of the hydrolysis of  $\text{K}_2\text{C}_2\text{O}_6$ .<sup>109</sup> The authors of this work suggest the occurrence of the acid-base hydrolysis

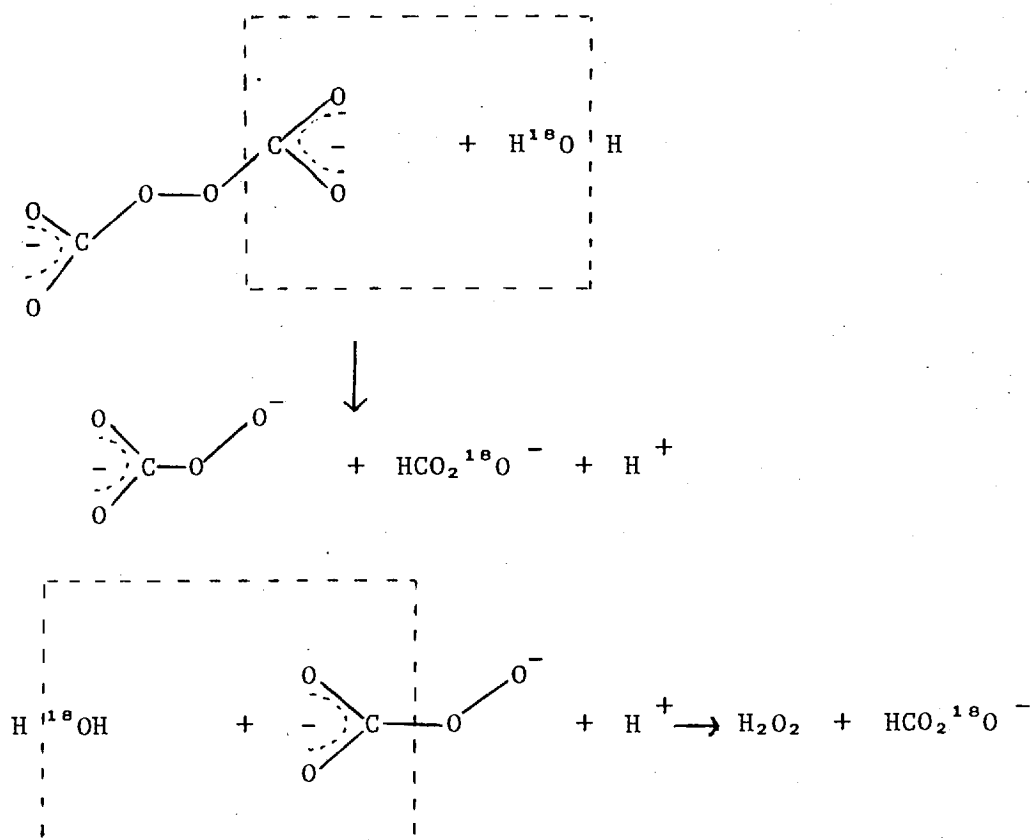


accompanied by other hydrolytic processes, such as



so that the hydrolysis involves several parallel reactions. The mechanism of  $\text{K}_2\text{C}_2\text{O}_6$  hydrolysis has also been studied using  $\text{H}_2^{18}\text{O}$ <sup>110</sup> which has

shown that the peroxide group passes without disruption into the  $H_2O_2$  formed, pointing to the following mechanism:-



Thus the oxidation of KI to  $I_2$  by  $K_2C_2O_6$  is probably due to the slow hydrolysis of this compound to  $H_2O_2$  via  $H_2C_2O_6$ ,  $HC_2O_6^-$  and  $HCO_4^-$  formation.

Samples of  $KHCO_4$ ,  $Li_2CO_4 \cdot H_2O$  and  $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$  liberate only oxygen from neutral KI solutions and this indicates that hydrolysis of these species to  $H_2O_2$  is rapid.

More recently, investigations have been carried out to make the Riesenfeld test more reproducible for peroxydicarbonate determinations in the presence of carbonate perhydrates and the latest of these<sup>111</sup> uses the difference in oxidation-reduction potential between  $H_2O_2$  and  $K_2C_2O_6$ , (measured to be 300-400 mV lower for  $H_2O_2$ <sup>112</sup>), whereby  $K_2C_2O_6$

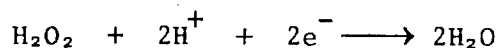
will oxidise  $\text{H}_2\text{O}_2$  in alkaline solutions according to the equation:-



Therefore a separate quantitative analysis of a mixture of  $\text{K}_2\text{C}_2\text{O}_6$  and  $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$  can be solved via two successive operations using different sample weights of the initial mixture: the total peroxide oxygen is determined in acid medium by permanganate titration, and the peroxide oxygen belonging to the excess component is determined in alkaline medium by adding excess 0.1 M hydrazine sulphate and titrating the excess hydrazine sulphate with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .

In this work the reactions between some simple inorganic species, including  $\text{I}^-$ , and the alkali metal percarbonates and "sodium perborate" have been studied and the results indicate that  $\text{C}_2\text{O}_6^{2-}$ ,  $\text{HCO}_4^-$ , and  $\text{CO}_4^{2-}$  react in a different way from hydrogen peroxide at a given pH. However, as these percarbonate species are relatively stable only at high pH, acidic  $\text{H}_2\text{O}_2$  solutions will certainly be more powerful oxidising agents than any of these anions.

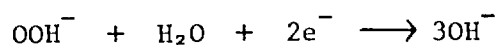
For  $\text{H}_2\text{O}_2$  acting as an oxidising agent under acidic conditions, the half-cell reaction may be written<sup>113</sup>:-



the potential being:

$$E = 1.76 + \frac{0.05916}{2} \log_{10} (a_{\text{H}_2\text{O}_2} \cdot a_{\text{H}^+}^2)$$

In basic solution, the half-cell reaction becomes:-



the potential then being:-

$$E = 0.87 + \frac{0.05916}{2} \log_{10} \left[ \frac{a_{\text{OOH}^-}}{a_{\text{OH}^-}^3} \right]$$

This variation in potential with pH is shown graphically in Figure 3-1, which is reproduced from reference 113.

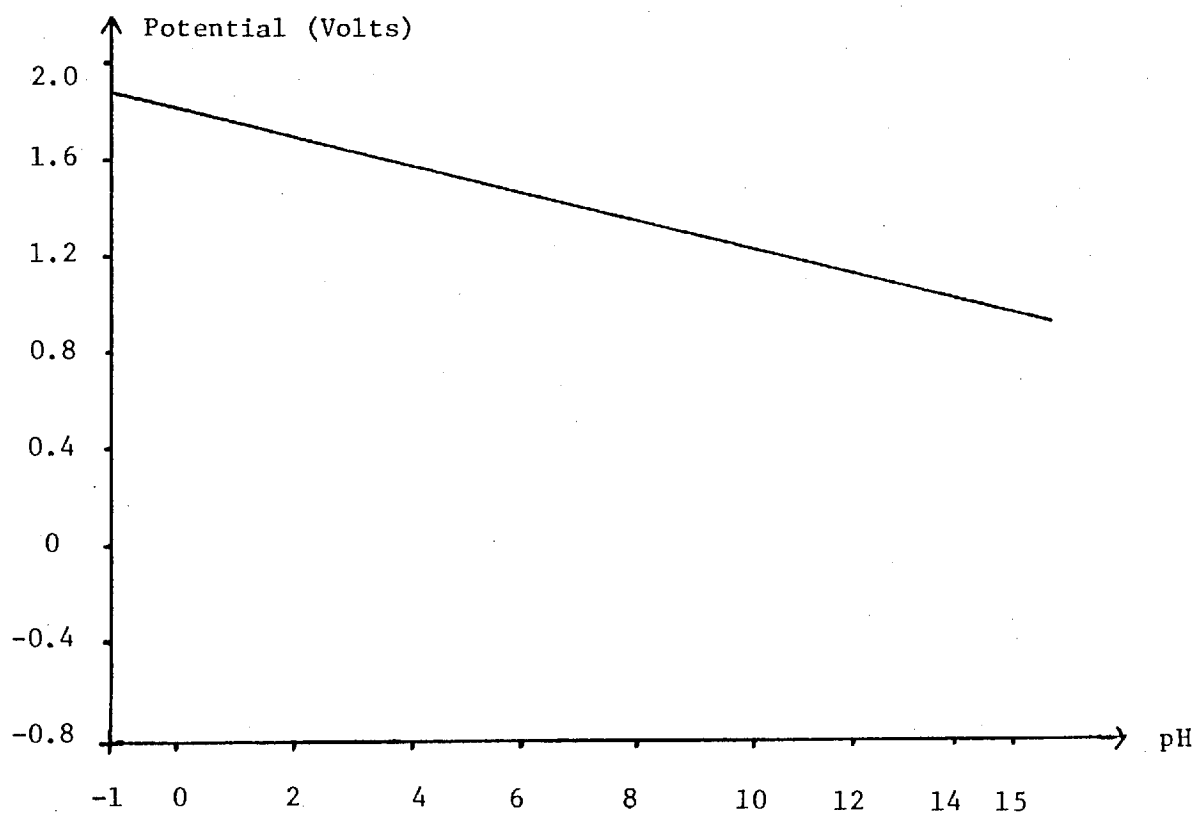


Figure 3-1. Potential-pH diagram for  $\text{H}_2\text{O}_2$ -water solutions at 1 mole/litre  $\text{H}_2\text{O}_2$  concentration.

It is to be stressed at this point that the hydroperoxomono-sulphate and peroxodisulphate anions,  $\text{HSO}_5^-$  and  $\text{S}_2\text{O}_8^{2-}$  are far more powerful oxidising agents than the percarbonate anions  $\text{C}_2\text{O}_6^{2-}$ ,  $\text{HCO}_4^-$  and  $\text{CO}_4^{2-}$  ( $E^\circ$  values are 1.81 V for  $\text{HSO}_5^-$ <sup>114</sup> and 2.01 V for  $\text{S}_2\text{O}_8^{2-}$ <sup>115</sup>).

The problems arising in the study of oxidations by the alkali metal percarbonates are firstly that rapid hydrolysis occurs in acidic and neutral aqueous solutions leading to hydrogen peroxide formation and secondly, under alkaline conditions, peroxide solutions tend to be somewhat unstable, especially when the  $\text{H}_2\text{O}_2$  concentration is high. Solutions of the alkali metal carbonates and bicarbonates in aqueous hydrogen peroxide cause a gradual loss of peroxide oxygen, accompanied by a change in pH. Thus constant pH values are difficult to maintain.

The inorganic species studied and results obtained are as follows:-

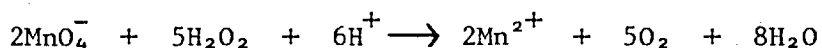
(a) Iodide Ion.

The Riesenfeld test was carried out on acidic, neutral and alkaline aqueous KI solutions and it was found that iodine was liberated from acidic solutions by aqueous 30% w/v  $\text{H}_2\text{O}_2$  and solids  $\text{K}_2\text{C}_2\text{O}_6$ ,  $\text{KHCO}_4$ ,  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{B}_2(\text{O}_2)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ . All five compounds liberated only oxygen from alkaline KI solutions and under neutral conditions (pH = 7), iodine was liberated only with  $\text{K}_2\text{C}_2\text{O}_6$ , in accordance with the arguments debated earlier in this section.



(b) Permanganate Ion.

Under acidic conditions, permanganate will oxidise  $\text{H}_2\text{O}_2$ , itself being reduced from Mn(VII) to Mn(II).



However, under alkaline conditions, the permanganate is reduced only to Mn(IV), in the form of  $\text{MnO}_2$ .



Species such as  $\text{C}_2\text{O}_6^{2-}$ ,  $\text{HCO}_4^-$  and  $\text{CO}_4^{2-}$  will be oxidised to  $\text{CO}_2$  and  $\text{O}_2$  by permanganate and in these cases the permanganate seems to be reduced only to the green-coloured manganate ion,  $\text{MnO}_4^{2-}$ , i.e., Mn(VI), if the reaction takes place under highly alkaline conditions at  $0^\circ\text{C}$ . Thus, solutions of  $\text{K}_2\text{C}_2\text{O}_6$ ,  $\text{KHCO}_4$  and  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  in concentrated aqueous KOH solution at  $0^\circ\text{C}$  give green solutions when aqueous  $\text{KMnO}_4$  solution is added, with further reduction to  $\text{MnO}_2$  occurring very slowly, presumably due to the slow hydrolysis of the excess percarbonate to  $\text{H}_2\text{O}_2$  under these conditions. The formation of  $\text{MnO}_2$  from  $\text{K}_2\text{C}_2\text{O}_6$  solutions is extremely slow at  $0^\circ\text{C}$ . Similar solutions of "sodium perborate" precipitate  $\text{MnO}_2$  immediately, indicating rapid hydrolysis to  $\text{H}_2\text{O}_2$ .

(c) Cerous Ion.

Aqueous solutions of cerous nitrate, (Ce(III)), are oxidised to the brown colouration of Ce(IV) by 30% w/v  $\text{H}_2\text{O}_2$  only above  $\text{pH} = \text{ca. } 7.0$ . Below  $\text{pH} = 7$  no colour change is observed. However, when

$\text{KHCO}_3$  is dissolved in the  $\text{H}_2\text{O}_2$  before its addition to the cerous solution, the brown colour of  $\text{Ce(IV)}$  is obtained even at  $\text{pH} = \text{ca. } 6.2$ . It is to be stressed that further work is required on this system before definite conclusions can be drawn but these initial observations provide more evidence for the presence of  $\text{HCO}_4^-$  in  $\text{HCO}_3^-/\text{H}_2\text{O}_2$  solutions (see Chapter Two, Section 2-D) and suggest that such a species is a more powerful oxidising agent than  $\text{H}_2\text{O}_2$  itself at the same pH.

No further examples have yet been found to demonstrate the differences in oxidising/reducing abilities between the "true" alkali metal percarbonates, "sodium percarbonate" and  $\text{H}_2\text{O}_2$  itself.

Before leaving this particular aspect of percarbonate chemistry, the use of polarography to study percarbonates in solution must be mentioned although time has not permitted studies by this technique in this work.

Van Rysselberghe and co-workers<sup>116</sup> reported the appearance of a new wave in polarograms of  $\text{CO}_2/\text{H}_2\text{O}_2$  solutions and  $\text{K}_2\text{C}_2\text{O}_6/\text{H}_2\text{O}$  solutions and they deduced that the new wave was due to either  $\text{H}_2\text{CO}_4$ ,  $\text{H}_2\text{CO}_5$ ,  $\text{H}_2\text{C}_2\text{O}_6$  or their ions. The only other reports of similar studies have been published in rather obscure Russian journals<sup>112,117,118</sup> and the abstracts of these indicate that the potentials of percarbonates in solution are higher than that of  $\text{H}_2\text{O}_2$  itself by 300-400 mV. Further studies in this field should prove useful in gaining information on the oxidising properties of percarbonates.

### Oxidation of Organic Species.

The use of organic peroxyacids as oxidising agents in organic chemistry has long been known<sup>119</sup> and many important oxidation reactions such as the epoxidation of olefins, the oxidation of sulphides to sulphoxides and the conversion of ketones to esters or lactones are effected. Organic peroxyacids have many advantages over inorganic oxidising agents due to their versatility, specificity, ease of preparation, and the frequent production of high yields of desired product under mild conditions. In general, the peroxyacid is prepared in situ by the action of hydrogen peroxide on the corresponding acid, the peroxide oxygen in  $H_2O_2$  itself not being readily available for most organic oxidation reactions.

From an inorganic viewpoint, the "activation" of the peroxide oxygen in  $H_2O_2$  by conversion to an organic peroxyacid, at least on the surface, seems to be replicated in the formation of percarbonates and perborates, the alkali metal peroxybicarbonates in particular resembling the organic peroxyacids and the peroxydicarbonates,  $M_2C_2O_6^I$  being the inorganic equivalents of the organic diacyl peroxides,  $RC(O)OOC(O)R'$ .

Results of some previous studies on the oxidation of organic species by "sodium perborate" are worth mentioning here as they seem to indicate that this compound is a better oxidising agent than  $H_2O_2$  itself. The use of "sodium perborate" in this context was first described by Allen and Clark<sup>120</sup> who successfully cleaved benzil (1,2-diphenyl-1,2-ethandione) to benzoic acid with this reagent. Later, Mehta and Vakilwala<sup>121</sup> reported the oxidation of aniline and a number of its para-substitution products to the corresponding azo-compounds with "sodium perborate" in glacial acetic acid as solvent, noting that

addition of water to the acetic acid markedly lowered the yield of oxidation product and that the "sodium perborate"-acetic acid reagent produced higher yields of azo-compounds than equivalent mixtures of hydrogen peroxide and acetic acid. Much more recently, the oxidation of 4-chloroaniline to 4,4'-dichloroazobenzene has been studied using sodium and ammonium perborates.<sup>122</sup> The authors of this latest report inexplicably interpret their results by concluding that perborates are not "true" peroxy salts but are borate perhydrates; this is obviously not so in the case of the sodium compound at least (see Chapter Two, Section 2-F).

These brief reports, together with the already well-established oxidising properties of organic peroxides and transition-metal peroxides prompted a study of the oxidising properties of the percarbonates  $K_2C_2O_6$  and  $KHCO_4$  (these being the best characterised and most stable of the peroxydicarbonates and peroxybicarbonates prepared in this work) with regard to organic substrates.

Initially, it was thought that the problem of solubilising these peroxy salts in organic solvents (glacial acetic acid being obviously unsuitable), would be easily overcome by use of the macrocyclic polyether, 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as a complexing agent. The use of such crown ethers to solubilise inorganic salts in organic solvents is well-known since their discovery in 1967,<sup>123</sup> and 18-Crown-6 has been reported to solubilise, amongst others,  $KMnO_4$ ,  $KIO_4$ ,  $KO_2$ ,  $KOH$ ,  $KF$  and  $KOCH_3$  in a wide range of solvents such as benzene, dimethyl sulphoxide and dichloromethane. (See reference 124 for a review on this topic). However, it was found that the solubilisation of  $K_2C_2O_6$  and  $KHCO_4$  by complexing with 18-Crown-6 is limited to methanol and ethanol of the more common organic solvents

and attempts to carry out oxidations that  $\text{H}_2\text{O}_2$  itself is incapable of achieving have been unsuccessful. Thus the epoxidation of cyclohexene (a facile reaction using peracetic acid as the oxidising agent) does not occur under these conditions, nor does the oxidation of pyridine to pyridine-N-oxide or cyclohexanone to  $\epsilon$ -Caprolactone (6-hexanolactone).

The success of such reactions as the cleavage of benzil to benzoic acid and the oxidation of p-anisidine (4-methoxy aniline) to p-azoxyanisole (4,4'-dimethoxy azoxybenzene) by both  $\text{K}_2\text{C}_2\text{O}_6$  and  $\text{KHCO}_4$  in aqueous methanol and water respectively is rather muted when one realises that  $\text{H}_2\text{O}_2$  itself will achieve these transformations and thus the oxidising agent may not be  $\text{C}_2\text{O}_6^{2-}$  or  $\text{HCO}_4^-$  but  $\text{H}_2\text{O}_2$ , resulting from the hydrolysis of the percarbonate.

Attempts to prepare organic-soluble percarbonates by the action of  $\text{CO}_2$  on hydrogen peroxide solutions of tetramethyl- and tetraethyl-ammonium hydroxides have also been unsuccessful, as have attempts to precipitate out tetraphenylarsonium and tetraphenylphosphonium percarbonates from  $\text{KHCO}_3/\text{H}_2\text{O}_2$  solutions by the addition of solid  $\text{Ph}_4\text{AsCl}$  and  $\text{Ph}_4\text{PCl}$ . However, the author feels that more work in this area could prove successful, providing the correct counter-cation is chosen in order to stabilise the product.

### Conclusions.

Although at first sight the percarbonates  $\text{K}_2\text{C}_2\text{O}_6$  and  $\text{KHCO}_4$  appear to be good candidates for effecting the oxidation of organic substrates, conditions for such reactions have not yet been discovered and the only successful oxidations have been those which  $\text{H}_2\text{O}_2$  itself can also achieve.

Section 3-B The X-Ray Crystal Structure and Oxidising Properties of Bistriphenylphosphine Peroxycarbonato Platinum(II).

The title compound was first prepared in 1969<sup>125</sup> and is the best characterised of the very few transition metal peroxycarbonato complexes yet reported. The others are the triphenylarsine and 1,2-bis(diphenylphosphino) ethane analogues and the palladium equivalent,  $(PPh_3)_2PdOCO_3$ .<sup>125,126</sup> More recently the compounds  $L_2PtOCO_3$  ( $L = PCy_3, P-iPr_3, P-nBu-tBu_2$  and  $PMe-tBu_2$ ;  $Cy =$  cyclohexyl)<sup>127</sup> and  $(PCy_3)_2NiOCO_3$ <sup>128</sup> have appeared in the literature.

It was felt that a knowledge of the structures and oxidising properties of the above compounds would be of use in helping to characterise better the alkali metal percarbonates, in particular the peroxybicarbonates and lithium peroxycarbonate monohydrate. As no single-crystal X-ray studies have been reported on any of these transition metal complexes, crystals of the triphenylphosphine platinum complex were grown in order to carry out a full structural determination.

(a) X-ray Crystal Structure.<sup>†</sup>

Bistriphenylphosphine peroxycarbonato platinum(II) was prepared by bubbling oxygen and carbon dioxide simultaneously through a benzene solution of tetrakis(triphenylphosphine) platinum(0).<sup>126</sup> Crystals were grown by the slow evaporation of a toluene-dichloromethane solution of the complex to give a compound of stoichiometry

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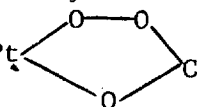
<sup>†</sup> The actual structure determination was carried out by Mr. N.D.S. Canning and Dr. A.C. Skapski.

$(\text{PPh}_3)_2\text{PtOCO}_3 \cdot \text{C}_7\text{H}_8$ . If benzene was used in place of toluene the crystals produced tended to crumble very rapidly due to the loss of the more volatile benzene of crystallisation.

The crystals proved to be triclinic, with  $a = 19.276$ ,  $b = 15.82$ ,  $c = 13.176 \text{ \AA}$ ,  $\alpha = 99.82$ ,  $\beta = 99.03$ ,  $\gamma = 104.44^\circ$ , space group  $\underline{\text{P1}}$  and  $Z = 4$ . Intensity data were collected as for  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  (see Chapter One, Section 1-C) and a total of 2274 independent reflections were measured (to  $\theta = 52^\circ$ ). The least squares refinement has reached an  $R$  value of 0.053.

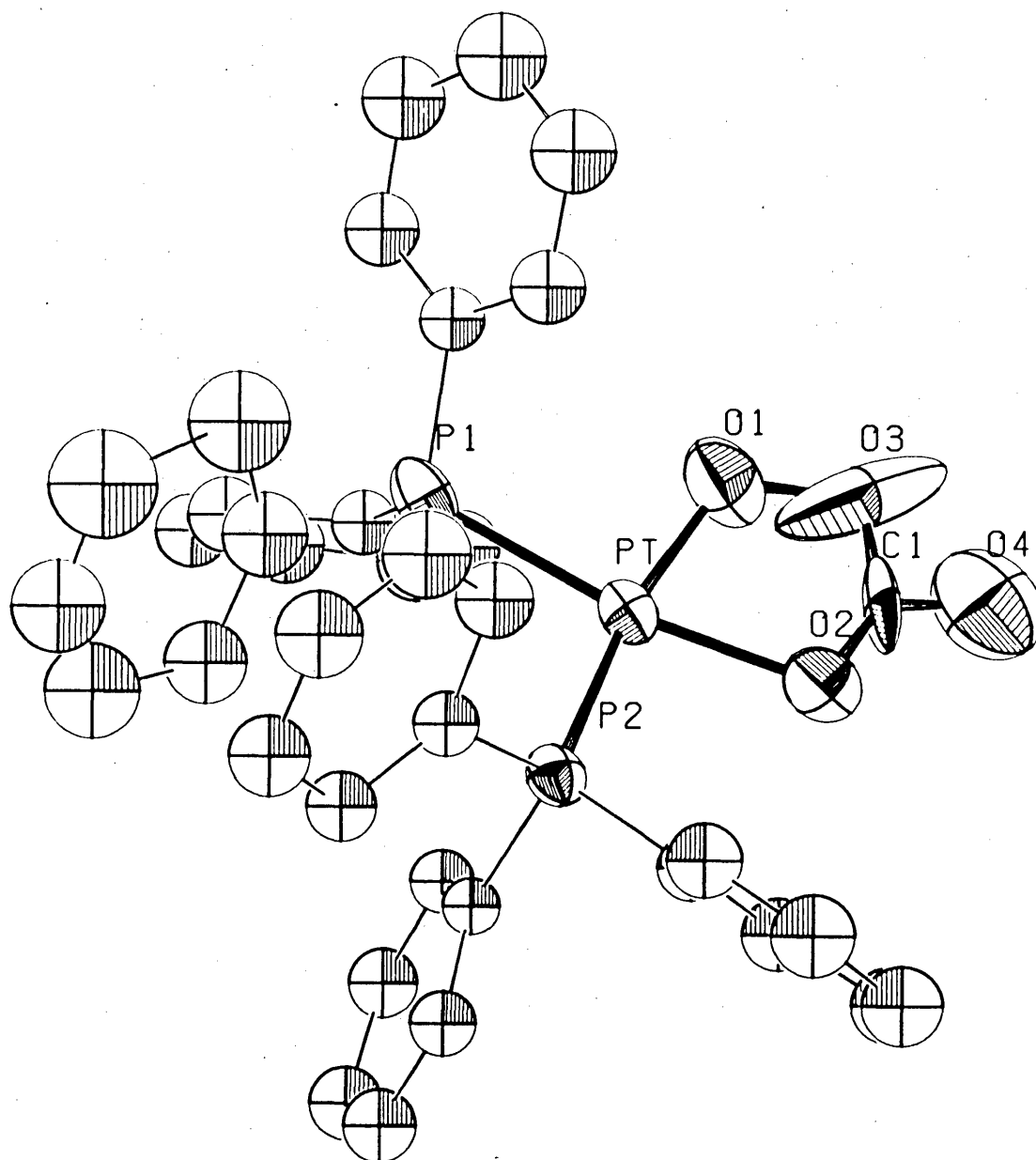
Figure 3-2 shows the molecular structure of the compound. The results so far are disappointing as the angles around C(1) are obviously incorrect, being greatly distorted from those of a regular carbonate group. The peculiar geometry can be explained either by disorder of the ring or by decomposition of the crystals during data collection, the disorder being an unlikely explanation as this would cause the Pt-P bond lengths to be equal, contrary to observation. Thus the most likely explanation is that one is looking at the average of a decomposed and undecomposed molecule and this is consistent with the decomposition noted during data collection.

The analogous carbonato complex  $(\text{PPh}_3)_2\text{PtCO}_3$  and the acetone complex,  $(\text{PPh}_3)_2\text{PtO}_3\text{C}(\text{Me})_2$ , prepared by the reaction of carbon monoxide and acetone with  $(\text{PPh}_3)_2\text{PtO}_2$  have had their structures determined previously<sup>129,130</sup> and the latter compound has a very similar structure to the peroxycarbonato complex in that it also contains a five-membered Pt



ring.

Figure 3-2. X-Ray Molecular Structure of Bistriphenylphosphine

Peroxycarbonato Platinum(II),  $(PPh_3)_2PtOCO_3$ .

Selected Interatomic Distances ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ ) with Estimated Standard Deviations in Parentheses.

Pt-P1	2.355(6)	O1-Pt-O2	79.0
Pt-P2	2.218(5)	Pt-O1-O3	119(2)
Pt-O1	2.02(2)	O1-O3-C1	97(3)
Pt-O2	1.99(2)	O3-C1-O2	139(3)
O1-O3	1.35(4)	Pt-O2-C1	103(1)
C1-O2	1.25(3)	O2-C1-O4	133(3)
C1-O3	1.38(4)	O3-C1-O4	87(3)
C1-O4	1.15(4)		



(b) Vibrational Spectra and Oxidising Properties.

The infrared spectrum of  $(\text{PPh}_3)_2\text{PtOCO}_3$  has already been reported.<sup>126</sup> In this work, more complete vibrational spectroscopic data have been obtained, with both the infrared and Raman spectra being recorded. Bands due to the  $\text{PtOCO}_3$  ring are identified by the various shifts observed for the  $^{13}\text{C}$ -enriched compound, which has been prepared by the reaction of  $(\text{PPh}_3)_2\text{PtO}_2$  with  $\text{CO}_2$  gas enriched in  $^{13}\text{C}$  to an extent of 92.1 atom %. The frequencies of bands attributable to peroxycarbonato modes are listed in Table 3-1 and the infrared results are generally in agreement with those already reported.

If one compares the spectra obtained for the coordinated  $\text{CO}_4^{2-}$  in this complex with those for  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ , the frequency changes produced should be similar to those observed in going from a free  $\text{CO}_3^{2-}$  ion to a coordinated, bidentate  $\text{CO}_3^{2-}$  ion. The infrared spectrum of  $(\text{PPh}_3)_2\text{PtCO}_3$  has been reported<sup>126</sup> and here the C=O stretch appears at  $1685 \text{ cm}^{-1}$  and the asymmetric and symmetric C-O stretches at  $1185$  and  $980 \text{ cm}^{-1}$ . In dilute aqueous solution, for the free  $\text{CO}_3^{2-}$  ion,  $\nu_1$ , the symmetric C-O stretch appears at  $1069 \text{ cm}^{-1}$  and  $\nu_3$ , the asymmetric C-O stretch, at  $1427 \text{ cm}^{-1}$ <sup>132</sup> with little change observed for solid  $\text{Li}_2\text{CO}_3$  ( $1079, 1083 \text{ cm}^{-1}$  ( $\nu_1$ ) and  $1413, 1425 \text{ cm}^{-1}$  ( $\nu_3$ )).<sup>53</sup> Here, for  $(\text{PPh}_3)_2\text{PtOCO}_3$ , the C=O stretch appears at ca.  $1680 \text{ cm}^{-1}$ , the asymmetric C-O stretch at ca.  $1250 \text{ cm}^{-1}$  and the symmetric C-O stretch at  $978 \text{ cm}^{-1}$  with the O-O stretch appearing at ca.  $780 \text{ cm}^{-1}$ . In  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  (see Chapter Two, Section 2-C), the asymmetric and symmetric C-O stretches are observed at  $1605$  and ca.  $1350 \text{ cm}^{-1}$ , the C-O stretch at ca.  $1040 \text{ cm}^{-1}$  and the O-O stretch at ca.  $900 \text{ cm}^{-1}$ . Thus, the frequency changes in going from  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  to  $\text{PtOCO}_3$  are in keeping with the transformation

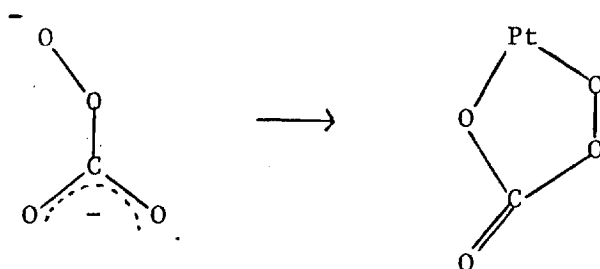
Table 3-1

Vibrational Frequencies of the PtOCO<sub>3</sub> Group in (PPh<sub>3</sub>)<sub>2</sub>PtOCO<sub>3</sub>.\*

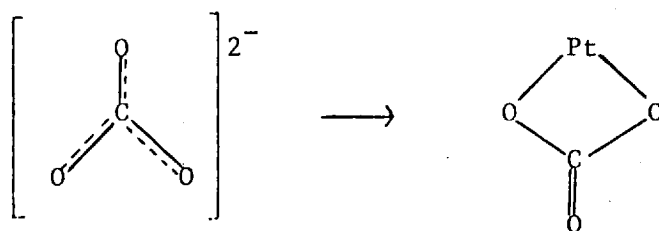
Infrared	Raman	Assignments <sup>†</sup>
1685 (1650)sh } 1678 (1640)s } 1630 (1605)sh }	1688 (1636)w	$\nu_1$ , C=O st
1245 (1220)s	1250 (1223)w	$\nu_5$ , asymm. C-O st
978 (978)s	obscd.	$\nu_2$ , symm. C-O st
780 (760)m	771 (758)w	O-O st
385 (385)m	not measured	$\nu_7$ , Pt-O st
305 (305)s	not measured	$\nu_4$ , Pt-O st

\* Bands for <sup>13</sup>C-substituted compounds are given in parentheses.

† Assignments are based on a bidentate carbonato ligand as a model.<sup>131</sup>



when compared with

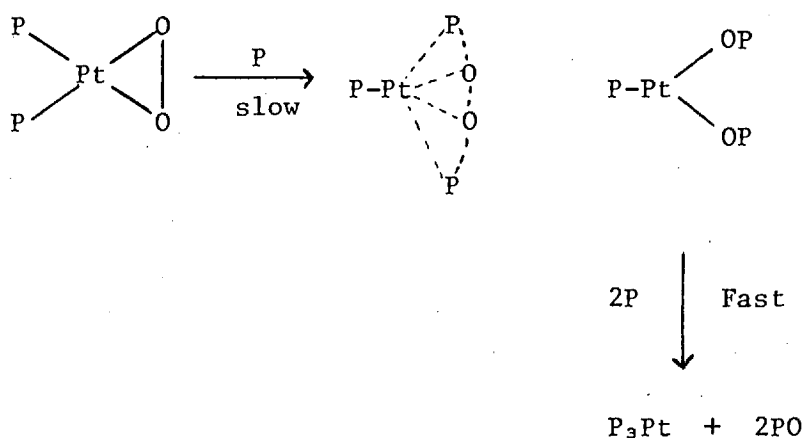


Attempts to prepare  $(\text{PPh}_3)_2\text{PtOCO}_3$  directly from  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{PPh}_3)_2\text{PtCl}_2$  have, unfortunately, been unsuccessful as this experiment would have provided clear evidence for the existence of a  $\text{CO}_4^{2-}$  monomeric anion in this lithium salt. The analogous carbonato complex can be prepared by the reaction of  $(\text{PPh}_3)_2\text{PtCl}_2$  with freshly-prepared  $\text{Ag}_2\text{CO}_3$ .<sup>126</sup>

Another line of approach adopted was the attempt to prepare a water-soluble peroxy-carbonato complex analogous to the platinum compound by the reaction of  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  or  $\text{LiOH}/\text{H}_2\text{O}_2/\text{CO}_2$  mixtures with the cobalt(III) complex  $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2](\text{ClO}_4)_3$ . It is already known that the cobalt pentammine complex  $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$  will react with either  $\text{Li}_2\text{CO}_3$  or  $\text{LiOH}/\text{H}_2\text{O}/\text{CO}_2$  mixtures at  $\text{pH} = 8-8.5$  to form the

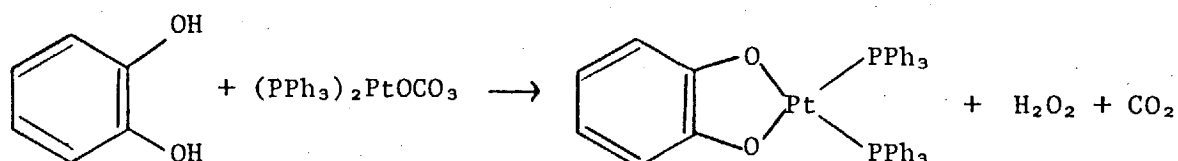
carbonato complex,  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)](\text{ClO}_4)$ ,<sup>133</sup> the carbonato ligand being monodentate, and a similar reaction with the tetrammine diaquo complex yields  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)](\text{ClO}_4)$ , the carbonato ligand being bidentate. However, several attempts to prepare the peroxycarbonato complex,  $[\text{Co}(\text{NH}_3)_4(\text{OCO}_3)](\text{ClO}_4)$  have failed, all reaction products corresponding to the bidentate carbonato complex.

When  $(\text{PPh}_3)_2\text{PtOCO}_3$  is refluxed under an inert gas atmosphere in the presence of excess triphenylphosphine, it is reduced to the carbonato complex  $(\text{PPh}_3)_2\text{PtCO}_3$ <sup>126</sup> and thus can be looked upon as an oxidising agent. However, unfortunately from the point of view of this work, under the same conditions the complex did not oxidise either diphenyl sulphide to diphenyl sulphoxide nor cyclohexene to cyclohexene epoxide. This may be due to the mechanism of oxidation which requires entry of the oxidisable species into the coordination sphere. It has been suggested, for instance, that the mechanism of the oxidation of triphenylphosphine by  $(\text{PPh}_3)_2\text{PtO}_2$  is<sup>134</sup>:-



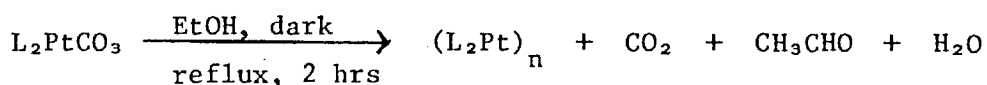
$(\text{PPh}_3)_2\text{PtOCO}_3$  is found to react with catechol (1,2-dihydroxy benzene) in the same manner as  $(\text{PPh}_3)_2\text{PtO}_2$ .<sup>135</sup> In this reaction effervescence is

observed, presumably due to the decomposition of "H<sub>2</sub>CO<sub>4</sub>" produced to give H<sub>2</sub>O<sub>2</sub> and CO<sub>2</sub>.

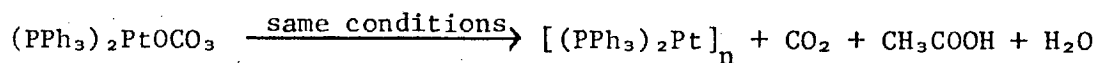


The catechol complex formed was identified by its infrared spectrum which was consistent with that reported.

By refluxing (PPh<sub>3</sub>)<sub>2</sub>PtOCO<sub>3</sub> in ethanol, the initial yellow solution rapidly becomes very dark and an orange solid can be isolated. This reaction is therefore analogous to that reported for (PPh<sub>3</sub>)<sub>2</sub>PtCO<sub>3</sub><sup>136</sup>; the orange solid is probably [(PPh<sub>3</sub>)<sub>2</sub>Pt]<sub>n</sub>.



Presumably,



NB. No attempt was made to detect acetaldehyde or acetic acid from this reaction.

### Section 3-C EXPERIMENTAL.

#### 3-C-1 Attempted Oxidations by K<sub>2</sub>C<sub>2</sub>O<sub>6</sub> and KHCO<sub>4</sub>.

(a) The attempted oxidations of diphenyl sulphide, cyclohexene and pyridine were carried out in methanol, dichloromethane, acetonitrile,

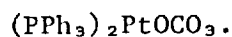
benzene, tetrahydrofuran and dimethyl sulphoxide as solvents using 18-Crown-6 (0.20 g, 0.76 mmol) and  $K_2C_2O_6$  (0.07 g, 0.35 mmol) or  $KHCO_4$  (0.08 g, 0.69 mmol) plus 0.35 or 0.69 mmol of the oxidisable substrate. The diphenyl sulphide reactions were followed by thin layer chromatography and the cyclohexene and pyridine reactions by gas-liquid chromatography.

(b) Cleavage of Benzil (1,2-diphenyl-1,2-ethandione).

Benzil (1.0 g, 4.8 mmol) was dissolved in hot methanol (10 cm<sup>3</sup>) and a solution of potassium peroxydicarbonate (0.95 g, 4.8 mmol) in aqueous 5% w/v sodium hydroxide (10 cm<sup>3</sup>) added. The solution was then evaporated to half its original volume, acidified to Congo Red with concentrated hydrochloric acid, and the partially separated benzoic acid was extracted into diethyl ether (2 x 25 cm<sup>3</sup>), dried over  $NaSO_4$  and the ether evaporated off in vacuo. The product was identified by its infrared spectrum.

(c) Oxidation of p-Anisidine (4-Methoxy Aniline).

Potassium peroxydicarbonate (0.59 g, 3.0 mmol) was dissolved in water (11.0 cm<sup>3</sup>) and the solution added to a suspension of p-anisidine (0.37 g, 3.0 mmol) in water (11.0 cm<sup>3</sup>) containing sodium acetate (1.21 g) and the mixture allowed to stand for 48 hours. The resulting brown precipitate was filtered off to yield a yellow product on crystallisation from ethanol. This was identified as p-azoxyanisole (4,4'-dimethoxy azoxybenzene) by its infrared spectrum.

3-C-2 Bistriphenylphosphine Peroxycarbonato Platinum(II),

A steady stream of oxygen and carbon dioxide gases was bubbled continually through a solution of tetrakis(triphenylphosphine) platinum(0) (2.0 g, 1.6 mmol) in dry benzene (50 cm<sup>3</sup>). The product began to precipitate out of solution after a few minutes and after one hour the mixture was reduced in volume to ca. 20 cm<sup>3</sup> and the solid product filtered off, washed with benzene and dried in vacuo to yield (PPh<sub>3</sub>)<sub>2</sub>PtOCO<sub>3</sub>.nC<sub>6</sub>H<sub>6</sub> (n = 0-1) (1.2 g, 87%). (Found : C, 57.4 ; H, 4.2 ; P, 7.2. C<sub>43</sub>H<sub>36</sub>O<sub>4</sub>P<sub>2</sub>Pt requires C, 59.1 ; H, 4.2 ; P, 7.1%).

(a) Reaction with Catechol (1,2-Dihydroxy Benzene).

(PPh<sub>3</sub>)<sub>2</sub>PtOCO<sub>3</sub> (0.1 g, 0.1 mmol) was dissolved in dichloromethane (2 cm<sup>3</sup>) and the solution cooled to 0°C. A solution of catechol (0.05 g, 0.5 mmol) in ethanol (5 cm<sup>3</sup>) was added dropwise to the stirred solution at this temperature. Some effervescence was observed and the solution became a deeper yellow colour. After one hour at 0°C the solution was evaporated to dryness in vacuo and the green solid obtained was washed copiously with ethanol to remove unreacted catechol and dried in vacuo. The catechol complex produced was identified by its infrared spectrum.

(b) Reaction with Ethanol.

(PPh<sub>3</sub>)<sub>2</sub>PtOCO<sub>3</sub> (0.15 g, 0.2 mmol) was stirred in degassed ethanol (20 cm<sup>3</sup>) and the mixture refluxed under nitrogen in the dark for two hours. A dark orange solution resulted, which, on evaporation to dryness in vacuo yielded an orange solid. This compound was not characterised.

3-C-3 Cobalt Complexes.Tetrammine Diaquo Cobalt(III) Perchlorate,  $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2](\text{ClO}_4)_3$ .

Tetrammine carbonato cobalt(III) nitrate (2.0 g, 8.0 mmol) (prepared by the method of reference 137) was dissolved in water (20 cm<sup>3</sup>) and aqueous 60% w/w perchloric acid (5 cm<sup>3</sup>) was added dropwise with stirring. The product was recrystallised from hot 0.1 M HClO<sub>4</sub>. (Found : H, 3.4 ; N, 11.8. C<sub>7</sub>CoH<sub>16</sub>N<sub>4</sub>O<sub>14</sub> requires H, 3.5 ; N, 12.1%).

Tetrammine Carbonato Cobalt(III) Perchlorate,  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)](\text{ClO}_4)$ .

(a) Tetrammine diaquo cobalt(III) perchlorate (0.2 g, 0.4 mmol) was dissolved in water (2 cm<sup>3</sup>) and a filtered, aqueous solution of lithium hydroxide (10% w/v) was added dropwise until pH 8-8.5 was attained. A stream of CO<sub>2</sub> gas was then bubbled through the solution for 15 minutes, dropwise addition of LiOH solution maintaining the alkaline pH. The carbonato complex formed was then filtered off, washed copiously with ethanol and diethyl ether and air-dried. (Found : C, 4.2 ; H, 4.1 ; N, 18.6. C<sub>7</sub>CoH<sub>12</sub>N<sub>4</sub>O<sub>7</sub> requires C, 4.2 ; H, 4.2 ; N, 19.6%).

(b) Alternatively, the above complex was prepared by the careful addition of solid lithium carbonate to a stirred solution of the diaquo complex (0.2 g, 0.4 mmol) in water (2 cm<sup>3</sup>) until pH 8-8.5 was reached. The solid product was collected and dried as above. (Found : C, 4.2 ; H, 4.1 ; N, 18.4. C<sub>7</sub>CoH<sub>12</sub>N<sub>4</sub>O<sub>7</sub> requires C, 4.2 ; H, 4.2 ; N, 19.6%).



Attempted Preparation of Tetrammine Peroxycarbonato Cobalt(III)

Perchlorate,  $[\text{Co}(\text{NH}_3)_4(\text{OCO}_3)](\text{ClO}_4)$ .

The preparations (a) and (b) above were repeated, substituting a 10% w/v solution of LiOH in aqueous 15% w/v  $\text{H}_2\text{O}_2$  for aqueous LiOH (10% w/v) in (a) and  $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$  for  $\text{Li}_2\text{CO}_3$  in (b). The product in both cases corresponded to the carbonato complex  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)](\text{ClO}_4)$  (identified by its infrared spectrum).

## PHYSICAL MEASUREMENTS

Microanalyses were performed by the Imperial College Organic Chemistry Department. Samples were analysed for peroxide content ( $O_2^{2-}$ ) by titration in aqueous sulphuric acid solution with 0.02 M potassium permanganate solution and potassium, rubidium, caesium and ammonium gravimetrically as tetraphenylborate. Infrared spectra were measured on Perkin-Elmer 257, 457, 597 and 325 instruments as Nujol and Voltalef-3S mulls at 25°C or as a thin film between  $CaF_2$  or  $AgCl$  plates for aqueous solutions. Raman spectra were obtained for powdered solids at -150°C in the case of peroxysalts and as a spinning disc in the case of  $(PPh_3)_2PtOCO_3$ , on a Spex Ramalog 5 instrument with a DPC-2 detector using krypton-ion laser excitation at 530.9 nm. Electron spin resonance spectra were recorded on an X-band Varian Associates E-9 spectrometer fitted with a Varian variable-temperature control unit.  $^{13}C$  n.m.r. spectra were measured on a Varian XL-100 Fourier-transform instrument operating at 25.2 MHz and equipped with an internal deuterium lock. D.S.C. traces were obtained on a Du Pont Thermal Analyser and thermogravimetric data on a Stanton Redcroft TG-750 thermo-balance, the weight losses being recorded on a Perkin-Elmer Model 56 Recorder. Gas-liquid chromatography was performed on a Perkin-Elmer F33 instrument using a Chromosorb 101, 80-100 mesh column, oven temperature 120°C.

X-Ray powder diffraction photographs were taken by Dr. R.S. Osborne of the University of London Intercollegiate X-ray service, using a Guinier Nonius Mark II camera employing  $Cu(K\alpha)$  radiation.

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