24

FREE ROTATION IN THE OXALATE GROUP AND THE RESONANCE BOND OF CARBOXYL.

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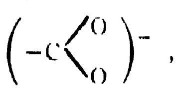
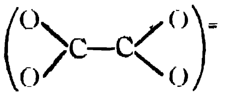
Plate IX.

ABSTRACT. The existence of axial rotation of the oxalate group about the C–C axis, postulated from an analysis of the modes of vibration of the group by the author in a previous paper, is confirmed by showing that the sharp Raman line at 1300 wavenumbers observed in the spectra of the oxalates in solution, which is "forbidden" in Raman effect if the ion remains rigidly planar, is totally absent in the spectra of the solids where the ion is known to remain planar in several oxalates from results of X-ray analysis The hypothesis of free rotation is preferred to a limited axial oscillation about the V_h configuration. The band at 1620 wavenumbers is identified with the anti-symmetric vibration ω_1 of the ionised carboxyl group  $\left(-C\begin{smallmatrix}O\\O\end{smallmatrix}\right)^-$, and connecting this with the crystal structure data for the O–C–O angle, the value of the resonance bond (C–O) is calculated. The value is intermediate between single and double bond values, but approaches more towards the single bond.

The classical method of structural formulation of organic compounds does not specify any particular configuration in cases where axial rotation of groups is apparently possible about a single bond, *e.g.*, in molecules like H_3C-CH_3, $Cl_2HC-CH\,Cl_2$, HO_2C-CO_2H, $Cl_3\,Si-Si\,Cl_3$, etc, but presupposes completely free rotation about these axes. Such a presupposition is, however, true only in a very limited number of cases ; for, in most of these molecules, the free rotation is hindered by the mutual interaction of the groups.[1] The potential energy values at different positions which such a molecule may assume during the axial rotation can be calculated by the quantum mechanical method developed by Slater,[2] and the maximum difference between the two extreme values is often found to exceed kT at room temperatures (ca. 600 calories per mole) which indicates considerable restriction of rotation. Even in a molecule like ethane, where free rotation about the C–C axis was accepted definitely,[3] the experimental determination of entropies from calorimetric measurements[4] and its comparison with the values obtained from statistical mechanical[5] and perturbation[6] calculations indicate the existence of a potential barrier of well over 2000 calories per mole, thus restricting to a high degree any internal rotation of the methyl groups.

It is thus apparent that such an axial rotation of groups about a single bond is more often restricted than allowed. When, therefore, in attempting to analyse the modes of vibrations of the oxalate group from the observed Raman frequencies, it was pointed out[7] that in the aqueous solutions, the oxalate ion  does not always maintain the V_h symmetry observed in the crystals of several oxalates,[8] the suggestion was unusual and waited confirmation. The reason for this extraordinary statement was that the sharp and intense line 1304 observed in the spectra of the oxalate solutions, and whose origin could be ascribed to no other mode of vibration of the oxalate group than the symmetrical one (fig. 1), is, from polarisability considerations, a forbidden line in Raman effect,

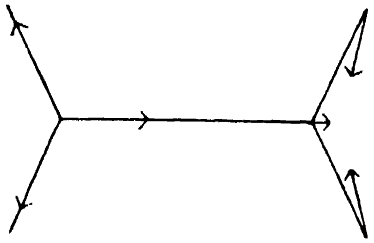


FIGURE 1.

if the ion is assumed to maintain the symmetry V_h. In order to explain the observed high intensity of the line, the hypothesis was advanced that in solution the V_h symmetry is non-existent, owing to axial rotation of the (COO) groups about the axis C – C, with the result that the nett change of polarisability is considerable.

This hypothesis of free rotation, it was argued, could be tested by examining the Raman spectra of oxalates under conditions where such a rotation is impossible, *viz.*, in the crystalline state at room temperature which is far below the melting point, and comparing the intensities of the Raman lines recorded in the two different states,—the line 1304 in particular, whose very origin in Raman effect is associated[7] with free rotation of the COO groups.

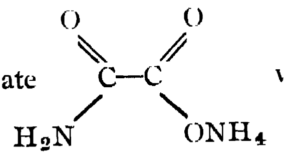
In the present investigation, therefore, the spectra of two typical oxalates, potassium and ammonium, have been examined both in the solid state and in solution. The configurations of the oxalate group are known in these two cases from results of X-ray analysis, being planar in one,[8] and the (COO) planes being inclined to each other at 28° in the other.[13] The alkali oxalate solution is examined at two different temperatures to observe any effect due to rise of temperature on the scattered spectrum.

A second point of interest that has been raised and discussed in the present paper is the nature of the binding forces between the carbon and oxygen atoms in the ionised carboxyl group $(-COO)^-$. It is well-known that the salts of carboxylic acids completely fail to exhibit the normal characteristics of the carbonyl group, assumed to be present in the molecule from classical concepts of valency, viz., $\left(-C\begin{smallmatrix}\diagup O \\ \diagdown\!\!\diagdown O\end{smallmatrix}\right)^-$, both from the standpoints of reactivity and unsaturation. Examinations of their Raman spectra have revealed the remarkable fact that the line 1720 wavenumbers, which is normally strong, and is attributed to the inner vibration of the C =O group, is *totally* absent, although present with its usual intensity in the esters. Results of X-ray analysis have often indicated equivalence of both the oxygen atoms with respect to carbon [8],[22] while differences in the distances recorded in some cases[13] are only slight, and apparently within the limits of experimental error. The group therefore appears to exhibit a true resonance between (C–O) and (C=O) groups, In the present paper, an attempt has been made to identify some of the observed Raman lines of the salts with the modes of vibration of the $\left(-C\begin{smallmatrix}\diagup O \\ \diagdown O\end{smallmatrix}\right)^-$ group, where the thick line represents the resonance bond in place of either the single or the double bond, and hence a value of the force of resonance, assuming equivalence of the two bonds, has been calculated with the help of the valence force system.

EXPERIMENTAL.

Recrystallised lumps of transparent polycrystals of potassium and ammonium oxalates were obtained by sieving and hand-picking from large amounts of recrystallised samples. The spectrograms were recorded by the method of complementary filters. [9]

The aqueous solutions (nearly saturated) were prepared with usual precautions from the purest samples, freshly recrystallised. The spectrogram of the solution of potassium oxalate was recorded at two different temperatures: one at room temperature (31°C) and the other at 96°C with the help of a cylindrical electric heater which surrounds the Wood's tube on all sides but one to receive incident radiation from a quartz mercury arc. The relative intensities of the lines in the two spectrograms were compared and found to remain unchanged.

Ammonium oxamate  $H_2N(O)C{-}C(O)ONH_4$ was prepared by the hydrolysis of oxamethane [10] with strong ammonia. The free acid was precipitated by acidification with hydrochloric acid, and its purity confirmed by the melting point (210°C, with decomposition). The free acid was suspended in pure redistilled water and ammonia gas was bubbled through the suspension, when the acid dissolved with the formation of the ammonium salt. The solution was filtered and filled into the Wood's tube with usual precautions.

The results are tabulated below, and some of the spectrograms are reproduced in Plate IX.

Raman Lines in wavenumbers per cm. Figures in parantheses indicate relative intensities of lines (visual).

Potassium oxalate.		Ammonium oxalate.		Ammon oxamate. Solution.
Crystals †	Solution.	Crystals. †	Solution. ‡	
	295(1)			
				133(1)
	452(2)			
				815(1)
885(1)	898(2)			
			1300(1)	1085(1b)
	1305(3)			
				1305(½)
1442(1)	1460*(4)	1451*(3)	1465*(2)	
				1415*(4)
				1620(2b)
		2885(3b)		
				1690(2)
		2990(3b)		
			3175	3175
			3395	3395

DISCUSSION OF RESULTS.

(A) *Free Rotation.*

It can be seen from the preceding table, as well as from the spectrograms reproduced in Plate IX, that the line 1304 of the oxalate ion, which is extremely sharp and intense in the spectrum of the solution, is totally absent in that of the solid state. This cannot be due to an insufficiency of exposure in the case of the solid because, in the case of the solutions where the line 1304 is visible, the 1460 doublet is recorded with less intensity than in the solid: nor due to any fall of

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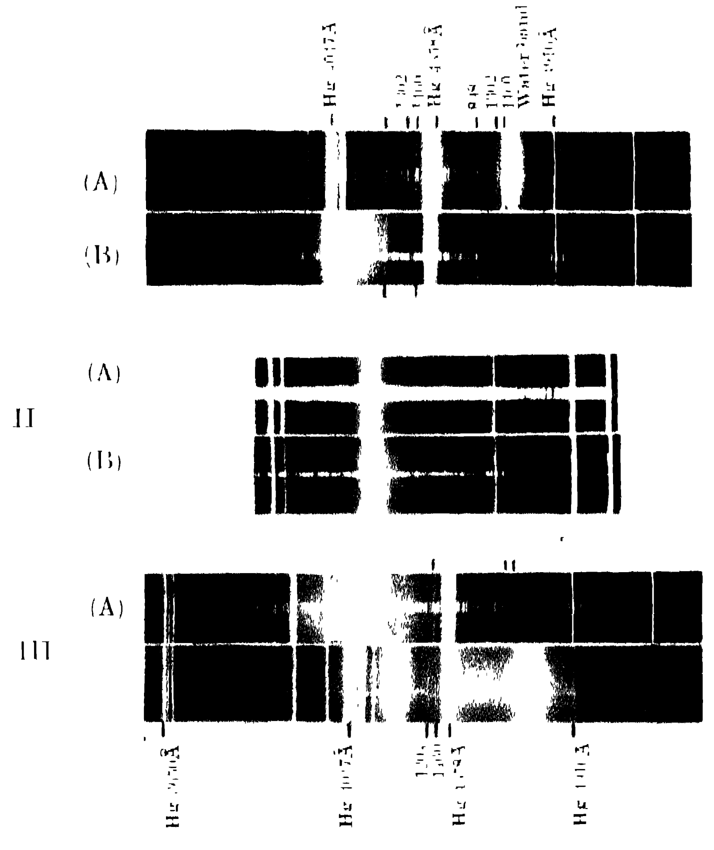
* Close doublets.

† (500-1500) and (1800-4000) wavenumbers.

‡ For a more complete data (lines in other regions), see Gupta, *Ind. J. Phys.*, **10**, 199 (1936).



Raman Spectra.

I (A) Potassium Oxalate solution in water
(B) " " crystals.

II (A) solution at room temperature (31° C)
solution at an elevated temperature (96° C)

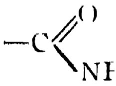
III (A) Ammonium Oxalate crystals.
(B) " " solution in water.

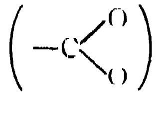
sensitivity of the plate used for photographing the spectrum of the solid, in the region of $\Delta\nu 1300\ \mathrm{cm}^{-1}$ (exciting radiation Hg 4047Å), because the same variety of plates (Ilford's Special Rapid, H and D 270) was used for recording the spectrograms of both solids and their solutions. This fact therefore clearly confirms the view [7] regarding the existence of axial rotation of the (COO) groups in the oxalate ion in solution.

Similar conclusions were arrived at by Martin and Partington [11] from measurements of the dipole moment of oxalyl chloride. From a comparison of the experimentally determined value with theoretically deducible values by Zahn's method, [12] they postulate the existence of free rototion or axial oscillation of the COCl groups about some stable form. In the present case of the oxalate ion in solution, the hypothesis of free rotation is preferred to that of a limited axial oscillation about the V_h configuration, for the following reasons :—

(1) In the spectrogram of crystalline oxalate, where the planes of the molecule are known [13] to be inclined to each other by 28°, the line 1304 is not recorded with any appreciable intensity, showing that a slight departure of the oxalate ion from the V_h configuration is not sufficient to explain the intensity of the said Raman line.

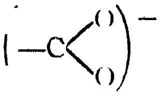
(2) The relative intensities of the Raman lines of the spectrum of potassium oxalate solution remain unchanged at two different temperatures. If axial rotation of the (COO) groups were restricted to any extent at room temperature, an elevation of temperature would have augmented this rotation, resulting in an increase in the intensity of the line 1304 as compared to other Raman lines of the spectrum.

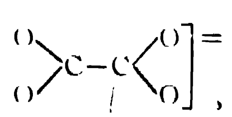
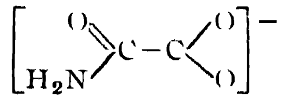
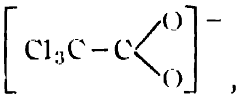
The substitution of one of the carboxyl group by  $-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NH_2}$ interferes greatly with the intra-molecular rotation as may be seen from the vanishing intensity of the 1304 line in the spectrum of the oxamate. The restriction of intramolecular rotation due to the presence of the amino group is noteworthy, and have been observed by Choudhuri [14] also.

(*B*) *The force of Resonance*  $\left(-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}\right)$

It can be observed, on comparing the spectrograms of potassium and ammonium oxalates in the solid state and in solution, that, apart from the variation of intensity of the line 1304 in the two states, other lines attributed to vibrations of the C_2O_4 group, *e.g.*, 898 and 1460, do not undergo any considerable change of position, so that the structure of the group may be assumed to be essentially the same in both the states. The X-ray data for ammonium oxalate crystals [13] and the spectral data for its solution can therefore be correlated.

The method of calculation here adopted, *viz.*, the acceptance of certain frequencies as inner frequencies of a portion of a molecule, is quite in accord with empirical observations, and is not in conflict with some of the methods recently developed.[15] A simple calculation is here made on this basis for determining the magnitude of the resonance force of the ionised carboxyl, from the value of α known accurately from X-ray analysis,[13] and the result may not be expected to be greatly in error.[16]

The anti-symmetric vibration ω_1 of the  group is identified with the Raman line $\triangle\nu$ 1620, for the following reasons—

(1) The line remains in the same region in all the three ions  ,  and  , the ions of oxalic, oxamic and trichloroacetic[17] acids respectively, with the same character (very broad) and relative intensity (weak).

(2) The line is observed to be totally depolarised, and is therefore not of the same origin as the 1720 line of the ketones and other carboxyl compounds. This latter frequency, which is attributed to the inner oscillation of the (C=O) group, gives rise to a Raman line usually polarised to a considerable extent.[18] The polarisation character of the line 1620 therefore indicates an anti-symmetric nature of the vibration in which it has its origin.

(3) The 1620 line of the oxalates is identified with ω_1 for a single ionised carboxyl group because, in the mode of vibration representing the origin of this line (fig. 2),

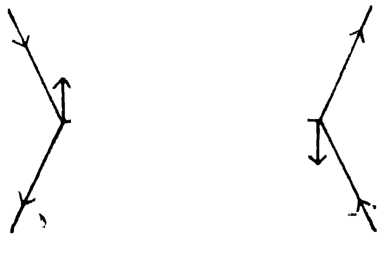
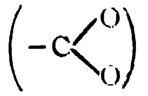


FIGURE 2.

(ω IV)[7]

it may be observed that the vibration of each of the (COO) groups is not greatly affected by the mass of the other, the resultant motion of the carbon atoms being perpendicular to the C—C axis of the molecule. Each half of the molecule is executing an antisymmetric vibration, without any apparent mutual interference.

The antisymmetric vibration frequency, ω_1, of the ionised carboxyl group  is deduced to be 1620 on the preceding arguments. The angle O–C–O=129°, from Hendricks and Jefferson's measurements.[13] The determinantal equation (valence force system) for linear, symmetric, triatomic oscillators correlating the above constants is[19]

$$n_1{}^2 = \frac{f}{m}\left\{\frac{m}{M}(1+\cos\alpha)+1\right\}$$

where $n_1{}^2 = \dfrac{4\pi^2c^2}{L}\,\omega_1{}^2$, c being the velocity of light and L the Loschmidt number

$= 5{\cdot}863\times10^{-2}\,\omega_1{}^2$,

f = elastic force between carbon and oxygen atoms,

m, M = atomic weights of oxygen and carbon respectively,

α = supplement of the angle O–C–O

$= 51°$,

which gives the value of

$$f = 7{\cdot}7\times10^5 \text{ dynes per cm.}$$

The force constant for the single bond (C–O) is 5×10^5, and for the double bond (C=O) $10{\cdot}9\times10^5$ dynes per cm., accepting Kohlrausch's values.[20] The force of linkage is thus undoubtedly a resonance force, resonating between (C–O) and (C=O) values, but approaches the character of a single bond, as was suggested by Peychès[21] on empirical evidences. The very broad nature of the 1620 band (nearly 50 wavenumbers) indicates that the force has not a very sharp value, but is varying within narrow limits (7·4—8·0), as may be the case during resonance.

The Badger relation[3] connecting the value of the force constant with interatomic distance, *viz.*,

$$r_e = (C_{ij}/k_e)^{\frac{1}{3}} + d_{ij},$$

where r_e = the equilibrium internuclear distance,

k_e = the bond force constant,

and C_{ij} and d_{ij} are constants, the values of which depend upon the positions of the constituent atoms in the periodic table, gives

$$r_e = \frac{{\cdot}571}{({\cdot}77)^{1/3}} + {\cdot}68 = {\cdot}62 + {\cdot}68 = 1{\cdot}30\text{Å}$$

for the distance C—O. Pauling's value[22] from X-ray analysis of basic beryllium acetate is 1·29 Å, and is therefore in agreement with the value calculated from the spectral data.

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