Some Pyrolytic Reactions of Salts of Organic Acids

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Summary

As a result of a number of isotopic and non-isotopic pyrolyses of salts of carboxylic acids, a new theory for the mechanism of these thermal decompositions has been proposed.

Pyrolyses were carried out of the acetates, and of equimolar mixtures of the acetates and formates, of the following metals :- lithium, potassium, calcium, strontium, barium, sodium, manganese(ous), magnesium, zinc and lead. A number of equimolar mixtures were also prepared in which one of the salts was enriched in the carboxyl position with ^{13}C, namely, acetate-formate, acetate-phenylacetate and formate-benzoate.

These investigations into the effect of the metal in the pyrolyses showed that, in general, an increase in the electronegativity of the cation is favourable to ketone formation, except in those cases where the pyrolysis residue consists of the metal oxide and not of the metal carbonate, and also that, when the carboxyl carbon of one of the salts is isotopically labelled, the enrichment of the carbonyl carbon of the resulting ketone is unaffected by changes in the cation.

Some pyrolyses were also carried out in an atmosphere containing nitric oxide and the results of these indicate that a free radical mechanism is not operative.

Calcium trimethylacetate was pyrolysed and the products of the decomposition were found to be isobutylene and trimethylacetaldehyde. An attempt was also made to reproduce the work of Kenner and Morton who obtained dibenzyl ketone on pyrolysis of the calcium salts of o-, m- and p-chlorophenylacetic acids. No dehalogenation was found however and the only product obtained was dichlorobenzyl ketone.

From these and other experiments, it is suggested that the first stage in these reactions is heterolytic cleavage of the R-C bond in the salt R-COOM to give the carbonium ion R^+ which then reacts with a further molecule of salt to give the ketone. It is unnecessary to propose complete separation of the ions and the existence of a transition state complex is suggested.

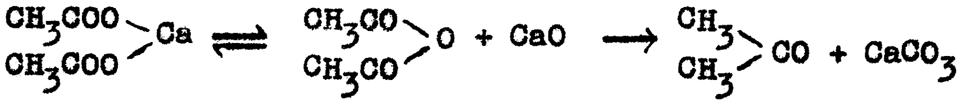
This mechanism satisfactorily explains the results of the experimental work and also allows an explanation to be given to certain observations of other workers, e.g. the rearrangements found by Cook, Miller and Whitmore in the catalytic decomposition of isobutyric acid and the work of Lee and Spinks who found in a series of carboxylic acids the order of ease with which the carboxyl group is lost in forming the ketone.

Part I -Historical Introduction.

For over a century it has been known that the thermal decomposition of salts of carboxylic acids gives rise to ketones. In 1852, Williamson (1) prepared n-butyl methyl ketone by the pyrolysis of a mixture of sodium acetate and potassium valerate and he predicted that an aldehyde would be formed when one of the salts used was a formate. This was in fact confirmed in 1856 by Limpricht and Ritter (2) who obtained acetaldehyde from a mixture of calcium acetate and calcium formate, and by Piria (3) who prepared benzaldehyde and cinnamaldehyde in a similar manner.

During the next fifty years very many carboxylates were pyrolysed and much work carried out to improve yields, for example in the preparation of acetone, but the mechanism of these reactions has not yet been soundly established.

In 1910, Bamberger (4) suggested that organic salts, e.g. calcium acetate, dissociated on heating first into the basic anhydride and the acid anhydride, i.e. into calcium oxide and acetic anhydride, but the latter, possibly due to the presence of the lime accelerating the reaction, decomposed at the high temperature necessary for the reaction with formation of carbon dioxide, giving calcium carbonate, and acetone.



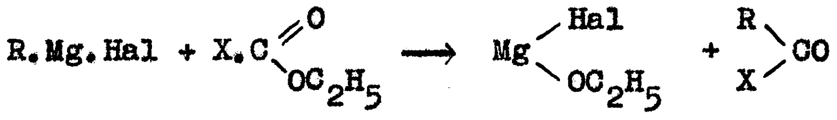
$$\begin{matrix}\mathrm{CH_3COO}\\\mathrm{CH_3COO}\end{matrix}\!>\!\mathrm{Ca} \rightleftharpoons \begin{matrix}\mathrm{CH_3CO}\\\mathrm{CH_3CO}\end{matrix}\!>\!\mathrm{O} + \mathrm{CaO} \longrightarrow \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\!\mathrm{CO} + \mathrm{CaCO_3}$$

This theory was developed by Dosios and Leucaditis (5) who postulated the intermediate formation of the mixed acid anhydride in the generation of unsymmetrical ketone from the pyrolysis of mixtures of acid salts. Kronig (6) also explained by this theory the formation of magnesium oxide when magnesium acetate was pyrolysed at a temperature beneath that required for the decomposition of magnesium carbonate.

The main evidence against this mechanism is the fact that the presence of steam during the pyrolysis actually increases the yield of ketone (7). It should be noted however, that as recently as 1948, Bamdas and Shemyakin (8) brought forward evidence to support this mechanism.

In 1939, Kenner and Morton (9) found that the lead salts of many acids decompose at lower temperatures than the corresponding calcium salts, frequently giving a better yield of ketone. They found evidence of a complex accumulating in the reaction mixture. On vigorous heating this formed a tar, but on treatment with formic acid liberated a further quantity of ketone. A theory analogous to that of the Grignard reaction was suggested to account for this behaviour.

Grignard:-



$$R.Mg.Hal + X.C\begin{matrix}{}^{\nearrow}O\\{}_{\searrow}OC_2H_5\end{matrix} \longrightarrow Mg\begin{matrix}{}^{\nearrow}Hal\\{}_{\searrow}OC_2H_5\end{matrix} + \begin{matrix}R\\X\end{matrix}\!>\!CO$$

Pyrolysis:-

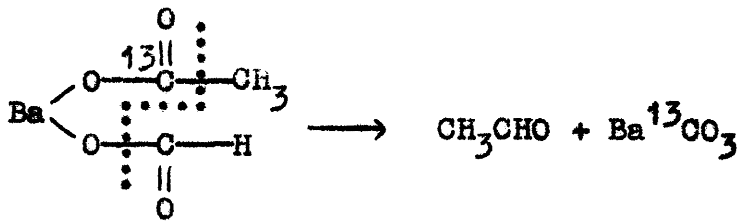
$$R.COO^- + R.C\begin{matrix}{}^{\nearrow}O\\{}_{\searrow}OPb^+\end{matrix} \longrightarrow CO_2 + PbO + \begin{matrix}R\\R\end{matrix}\!>\!CO$$

Also in 1939, Neunhoffer and Paschke (10) reported that no hexamethyl acetone was obtained on pyrolysing calcium trimethylacetate and from this and the observation of Farmer and Kracovski (11) that no cyclic ketone was obtained on pyrolysis of $\alpha,\alpha,\alpha',\alpha'$- tetramethyladipic acid, they deduced that an α-H atom was necessary for ketone formation. They suggested that the reaction took place in two steps.

$$(CH_3COO)_2Ca \longrightarrow CH_3COCH_2 \vdots COO \vdots CaO \vdots H \longrightarrow CH_3COCH_3 + \underset{(CaO\ +\ CO_2)}{CaCO_3}$$

In the first step, the corresponding β- keto acid, or its salt, is formed from two molecules of acid and in the second stage this decarboxylates to give the ketone. An α- hydrogen atom must therefore be available for preliminary enolisation. Similarly, Cook, Miller and Whitmore (12) postulated an aldol type of condensation as one of the steps leading to the ketone. This mechanism, however, does not appear to be acceptable since, apart from the fact that salts of carboxylic acids generally do not undergo such condensations, no mechanism involving such a condensation can be a general one because it certainly cannot account for the formation of diaryl ketones by the pyrolysis of salts of aromatic acids.

Phenylacetic anhydride was pyrolysed in 1933 by Hurd, Christ and Thomas (13) and they suggested that Rice's free radical mechanism of pyrolysis (14) might be extended to cover the thermal decomposition of acid anhydrides and salts. This view was suggested by Brown (15) when he reviewed the detailed study by Cook, Miller and Whitmore (12) of the products of catalytic decomposition of isobutyric acid. In 1950 Bell and Reed (16,17) observed an exclusive cleavage of the carbon - carbon bond in acetate when a mixture of barium acetate, enriched with ^{13}C in the carboxyl group, and barium formate was pyrolysed to give acetaldehyde.



It was suggested (17) that this reaction proceeded by a free radical chain mechanism which was initiated by the free methyl radical, rather than by the free formyl radical.

$$CH_3CO_2ba \longrightarrow CH_3^{\bullet} + {}^{\bullet}CO_2ba$$
$$(ba = \tfrac{1}{2}Ba)$$

Aldehyde and acetone formation could then be represented by the following equations:

$$CH_3^{\bullet} + HCO_2ba \longrightarrow CH_3CHO + {}^{\bullet}Oba$$
$$\text{and} \quad CH_3^{\bullet} + CH_3CO_2ba \longrightarrow CH_3COCH_3 + {}^{\bullet}Oba$$

Chain termination could be by various methods, e.g.

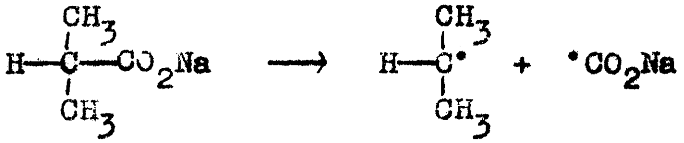
$$2\ CH_3^{\bullet} \longrightarrow C_2H_6 \quad \text{or} \quad CH_4 + CH_2\!: \quad \text{etc}$$

$$2\ {}^{\bullet}Oba \longrightarrow (Oba)_2$$

$${}^{\bullet}CO_2ba + {}^{\bullet}Oba \longrightarrow ba_2CO_3$$

but the relative importance of these could not be determined by the experimental methods used.

Also, O'Neill and Reed (18) found that pyrolysis of sodium isobutyrate yielded a substantial quantity of both di-n-propyl ketone and n-propyl iso-propyl ketone as well as the expected di-iso-propyl ketone. A free radical mechanism was again suggested to interpret these results, this being consistent with the fact that in general high temperatures are required for these reactions (19). It was assumed that rearrangement occurred in an intermediate radical



$$H\text{—}C(CH_3)_2\text{—}CO_2Na \longrightarrow H\text{—}C^{\bullet}(CH_3)_2 + {}^{\bullet}CO_2Na$$

followed by rearrangement of the alkyl radical.

The above is an outline of the theories regarding the mechanism of pyrolysis of salts of organic acids which had been proposed up to the time when the present research was commenced.

In 1953 however, Lee and Spinks (20) brought forward a new theory for the mechanism of these decompositions.

They pyrolysed a number of mixtures of labelled and unlabelled carboxylates and found the following order of ease with which the carboxyl group is lost in forming the ketone:- acetate > phenylacetate > valerate > formate > benzoate. From these results they critised the free radical mechanism on a number of grounds and these may be outlined as follows.

In the pyrolysis of a mixture of calcium acetate and calcium phenylacetate, two-thirds of the methyl benzyl ketone formed results from the loss of the carboxyl group in the acetate, whereas if the mechanism was of free radical type, one would expect the benzyl radical to be formed more readily than the methyl radical (21). Also, formates lose their carboxyl group more readily than benzoates, yet the energy of the carbon - hydrogen bond is known to be greater than that of the carbon-carbon bond (22) so that one would not expect a preference for the formation of the hydrogen radical over the phenyl radical. Furthermore, in the pyrolysis of isobutyrate (18) a rearrangement from a secondary to a primary carbon radical is required, whereas other established rearrangements involving free radicals (23, 24) indicate an opposite trend in that primary radicals tend to rearrange to the tertiary state.

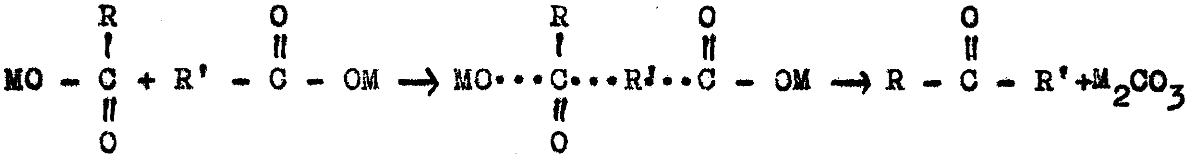
Lee and Spinks accordingly proposed a two-step ionic mechanism in which a carbonium ion $R - \overset{+}{C} = O$ is first formed and this then reacts with a further molecule of salt to give the ketone:

$$R - COOM \rightarrow R - \overset{+}{C} = O + MO^{-}$$

$$R - \overset{+}{C} = O + R'COOM \xrightarrow{slow} R.COR' + M^{+} + CO_2$$

where R and R' may be the same or different, aliphatic or aromatic and M a metal such as Ca, Ba, etc.

They suggested however that a transition state might be involved and that the decomposition might be by an intramolecular concerted process:



$$MO - \overset{\overset{R}{|}}{\underset{\underset{O}{\|}}{C}} + R' - \overset{\overset{O}{\|}}{C} - OM \rightarrow MO\cdots\overset{\overset{R}{|}}{\underset{\underset{O}{\|}}{C}}\cdots R'\cdots\overset{\overset{O}{\|}}{C} - OM \rightarrow R - \overset{\overset{O}{\|}}{C} - R' + M_2CO_3$$

The reaction could then involve either heterolytic or homolytic cleavage of the bonds concerned.

As will be seen from the above, the mechanism of thermal decomposition of salts of carboxylic acids has still to be soundly established and investigations have been carried out to see whether some more light may be thrown on certain aspects of these pyrolyses. Particular attention has been paid to an attempt to elucidate the function of the metal which has remained obscure in previous work.

Part II - Experimental Results

1. Pyrolysis of Calcium p-Chlorophenylacetate

According to Kenner and Morton (9), the distillation of calcium salts of *o*-, *m*- and *p*-chlorophenylacetic acids resulted in dehalogenation and formation of dibenzyl ketone, whereas the lead salts yielded smoothly the desired 1,3-bis(*p*-chlorophenyl)-2-propanone. Since this dehalogenation appeared to be of an unusual nature, and might help to indicate the mechanism these pyrolyses follow, it was decided to attempt to repeat part of this work.

Calcium *p*-chlorophenylacetate was chosen as a salt for pyrolysis and it was synthesised according to the following reaction scheme:

$$C_6H_5CH_2CN \xrightarrow[H_2SO_4]{HNO_3} \underline{p}\text{-}NO_2C_6H_4CH_2CN \xrightarrow{H_2O} \underline{p}\text{-}NO_2C_6H_4CH_2COOH$$

$$\xrightarrow{(NH_4)_2S_x} \underline{p}\text{-}NH_2C_6H_4CH_2COOH \xrightarrow[+\ Cu_2Cl_2]{\text{diazotise}} \underline{p}\text{-}ClC_6H_4CH_2COOH$$

$$\xrightarrow{CaCO_3} (\underline{p}\text{-}ClC_6H_4CH_2COO)_2Ca$$

On pyrolysis of this salt, a red semi-crystalline distillate was obtained, which on recrystallisation was shown to be di*para*chlorobenzyl ketone - 1,3-bis(*p*-

chlorophenyl)-2-propanone. Attempts to isolate dibenzyl ketone both by recrystallisation and chromatography of the 2,4-dinitrophenylhydrazone failed, the product in all the pyrolyses, the conditions of which varied, being the halogenated ketone.

From this failure to repeat Kenner and Morton's work it would appear that this dehalogenation is not a general reaction and must have been due to the particular conditions operative in their pyrolyses.

2. Pyrolysis of Trimethylacetates (Pivalates).

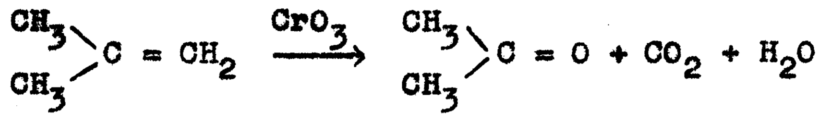
One of the major pieces of evidence put forward by Neunhoffer and Paschke (10) for their theory that an α - hydrogen atom was necessary for ketone formation in the pyrolysis of carboxylates, was the fact that no ketonic products are obtained by pyrolysing calcium trimethylacetate. *Iso*butylene was however reported as the main product. Cook, Miller and Whitmore (12) passed trimethylacetic acid vapour over thoria and detected amongst the products the following compounds: *t*-butyl isobutyl ketone (major product - 15%), *t*-butyl methyl ketone (9%) trimethylacetaldehyde (3%) crotonaldehyde (3%) and *t*-butyl ethyl ketone (0.7%). They suggested that the acid was adsorbed on the catalyst to form the thorium salt, which then decomposed, the role of the catalyst therefore being to orientate two or more acid molecules into reactive positions.

Since there was no satisfactory account in the literature of a straightforward distillation of a salt of trimethylacetic acid, it was decided to carry out such a pyrolysis and to make an attempt at characterising the products.

The lithium salt was first chosen since previous workers, e.g. Rojahn and Schulten (25), have shown that in many cases lithium salts give excellent yields and also since the cation would be of small size compared with thorium. It was found however, that lithium trimethylacetate sublimed at about 380°, which is beneath its decomposition point, and was thus unsatisfactory for pyrolysis. The calcium salt was therefore used in the distillations.

Calcium trimethylacetate was pyrolysed by strong heating in a simple distillation apparatus at atmospheric pressure. From 5 gm. of salt about 0.25 ml. of a clear distillate was obtained together with a large quantity of an inflammable gas. The residue consisted of a charred mass of carbon and calcium carbonate.

The hydrocarbon formed was shown to be unsaturated and had the smell of isobutylene which had, as mentioned above, been previously reported by Neunhoffer and Paschke. On oxidation with chromic acid, the products, namely acetone and absence of acids, confirmed the presence of isobutylene in the pyrolysis products.



$$(CH_3)_2C = CH_2 \xrightarrow{CrO_3} (CH_3)_2C = O + CO_2 + H_2O$$

On addition of 2,4-dinitrophenylhydrazine to the distillate immediately after the pyrolysis was complete, a precipitate was obtained, the melting point of which, after recrystallisation, corresponded to the 2,4-

dinitrophenylhydrozone of trimethylacetaldehyde. The semicarbazide from the distillate similarly corresponded to that of trimethylacetaldehyde.

A sample of trimethylacetaldehyde was synthesised by treatment of trimethylpyruvic acid, prepared by oxidation of pinacolone, with diphenylamine:

$$(CH_3)_3C.COCH_3 \xrightarrow{KMnO_4} (CH_3)_3\,CCO.COOH \xrightarrow{\text{diphenylamine}}$$

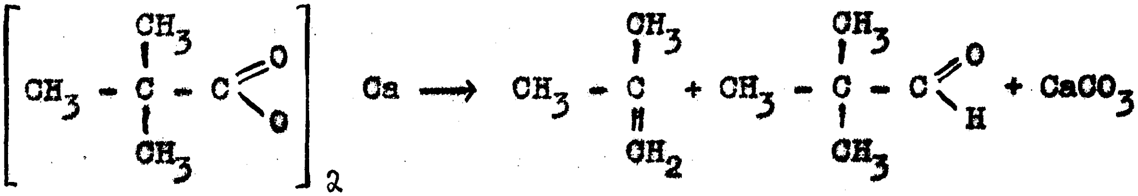
Pinacolone trimethylpyruvic acid.

$$(CH_3)_3CHO$$

trimethylacetaldehyde.

Mixed melting points with derivatives from this trimethylacetaldehyde confirmed the presence of trimethylacetaldehyde in the pyrolysis products. It is rather an unstable compound, being readily oxidised in air to trimethylacetic acid. The distillate must therefore be examined immediately after pyrolysis, a negative result being otherwise obtained when tests are made for the carboxyl group.

Attempts to separate the original 2,4-dinitrophenylhydrazone and semicarbazide failed and therefore the thermal decomposition of calcium trimethylacetate would appear to be substantially as shown:



$$\left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\overset{O}{\underset{O}{\lessgtr}}\right]_2 Ca \longrightarrow CH_3-\overset{CH_3}{\underset{CH_2}{\overset{|}{\underset{\|}{C}}}} + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\overset{O}{\underset{H}{\lessgtr}} + CaCO_3$$

3. Pyrolyses in the Presence of Nitric Oxide.

Bell and Reed (17) have, as mentioned in the introduction, proposed a free radical chain mechanism for the thermal decomposition of salts of carboxylic acids, but previous workers, e.g. Stavely and Hinshelwood (26); Forsyth (27), have shown that nitric oxide removes free radicals from a system and hence causes termination in any free radical chain reaction. Indeed, to quote Hinshelwood, nitric oxide provides a definite quantitative test for the presence of chains and absence of inhibition may be taken as evidence for their absence.

Consequently some pyrolyses of barium acetate and barium acetate - formate mixtures were carried out in an atmosphere containing nitric oxide since, although no quantitative significance could be attached to the results, it was considered that any appreciable drop in the yields of acetone and acetaldehyde obtained from these pyrolyses would indicate the presence of free radicals and thus help to confirm the mechanism proposed by Bell and Reed.

Barium was chosen as the cation in these pyrolyses since its salts give a good yield of acetone and acetaldehyde, making any reduction in yields more significant, have a high decomposition temperature, making it easier to carry out the pyrolyses slowly, and give results which are much more readily reproducible than with calcium salts, which also would satisfy the first two conditions.

The nitric oxide was prepared by Winkler's method (41).

$$HNO_2 + HI \longrightarrow H_2O + I_2 + NO$$

The barium acetate and barium acetate-formate mixtures were slowly decomposed in an electric furnace while a stream of nitrogen containing nitric oxide flowed through the pyrolysis tube. Since gaseous products are formed the actual composition of the pyrolysis atmosphere was unknown and mixtures of 1% of nitric oxide to 99% of nitrogen and 10% of nitric oxide to 90% of nitrogen were arbitrarily chosen as the gases to be passed over the decomposing salt.

Since acetone itself decomposes at the reaction temperature, known weights of acetone were passed through the furnace and the following results were obtained.

Acetone recovery under 1% NO = 97.88%
" " " 10% NO = 87.36%

All yields obtained when nitric oxide was present were therefore corrected by these values so that they could be compared with those obtained under pure nitrogen. The results obtained are given in Tables I and II and are summarised in Table III. In Table I, the yields of acetone are expressed as percentages of that theoretically possible. In Table II, the yields of acetone and acetaldehyde are both expressed as percentages of that possible if each were the only product formed. The sum of these two yields - Total Yield in Table III - indicates what percentage of the methyl groups of the acetate react to give acetone or acetaldehyde. For acetone yields with 100% N_2, the yields in the actual and corrected columns are the same since in this case no correction needs to be applied.

The analyses were carried out as described later in Section IV,3b.

Table I

Gas Composition %age N_2	Wt. of Acetate gm.	Wt. of Acetone gm.	Yield of Acetone	
			Actual %	Corrected %
100	0.5031	0.09956	87.07	87.07
100	0.4775	0.09517	87.68	87.68
100	0.5055	0.1004	87.40	87.40
99	0.5811	0.1060	80.37	82.11
99	0.4708	0.08543	79.91	81.63
90	0.2187	0.02920	58.80	67.31
90	0.4007	0.04882	53.64	61.41

Table II

Gas Composition %age N_2	Wt. of Mixture gm.	Wt. of CH_3CHO gm.	Wt. of Acetone gm.	Yield of CH_3CHO %	Yield of Acetone	
					Actual %	Corrected %
100	0.2628	0.01389	0.01474	28.97	46.50	46.50
100	0.3362	0.01777	0.01812	28.96	44.50	44.50
100	0.2380	0.01382	0.01292	30.31	45.11	45.11
99	0.5163	0.02587	0.02701	27.50	43.54	44.48
99	0.4743	0.02873	0.02451	27.73	43.00	43.94
90	0.5028	0.02063	0.02122	19.74	35.14	40.22
90	0.5036	0.02065	0.02084	19.63	34.45	39.42

Table III.

Gas Composition % age N_2	Acetate-Formate Mixtures			Acetate Alone
	Yield of Acetaldehyde %	Yield of Acetone. %	Total Yield %	Yield of Acetone. %
100	29.41	45.37	74.78	88.31
99	27.62	44.21	71.83	81.87
90	19.69	39.82	59.51	64.36

From these results it will be seen that there is in fact a reduction in yields when nitric oxide is present but that this reduction is much greater with the larger percentage of nitric oxide. This suggests that the reduction is due to simple chemical reaction rather than to the termination of free radical chains since in the latter case only a trace of nitric oxide should be sufficient to cause a significant drop in yields.

The results therefore, although not so decisive as might be hoped, would not appear to favour a free radical mechanism.

4. Investigations into the Function of the Cation.

In the pyrolysis of acetates it has been shown by many workers that the yield of acetone obtained varies markedly with variation of the metal cation, even when such changes are restricted to the alkaline and alkaline earth metals (6, 9). Similar variations have also been reported in the decomposition of formates (28) and perfluoro-carboxylates (29).

The function of the metal in the reaction mechanism has remained obscure however, and there is no evidence to decide whether the salt reacts in the covalent form, or whether reaction occurs between the carboxylate ions. In general, the former postulate has been preferred (17, 20) since it is then easier to explain variations in yields.

A considerable number of pyrolyses have accordingly been carried out on certain organic salts, and mixtures of salts, both isotopic and non-isotopic, with a view to determining to what extent and in what manner the yields of products vary with variations in the cation.

5. Pyrolysis of Acetates.

Previous workers (19) have remarked on the difficulty of obtaining reproducible results in pyrolyses of a similar type to those carried out in the present work. It was found in this research that variations in the yields of acetone occurred with variations in the pyrolysis temperature and in the rate of nitrogen passage. Small changes in molar composition of mixtures also caused large changes in yields. Preliminary experiments were therefore carried out to determine the necessary conditions for reproducibility.

(a) Effect of Variations in Pyrolysis Temperature.

Since there is rather a wide range of decomposition temperatures of acetates, and acetate-formate mixtures, it was necessary to find what effect small variations in pyrolysis temperature had on yields. Acetate-formate mixtures of lithium and magnesium salts were pyrolysed at various temperatures. The results obtained are given in Table IV and summarized in Table V. The yields of acetone and acetaldehyde are both expressed as percentages of that possible if each were the only product formed. Analysis of the pyrolysis products was carried out as described in Section IV, 6b.

Table IV.

Cation	Temperature °C	Wt. of Mixture gm.	Wt. of CH_3CHO m. gm.	Wt. of Acetone m. gm.	Yield of CH_3CHO %	Yield of Acetone. %
Mg	420	0.1639	15.92	7.423	28.81	20.02
	420	0.1817	19.54	8.203	31.34	19.97
	450	0.2076	21.68	9.391	30.42	20.01
	450	0.1725	19.03	7.791	32.15	20.45
	480	0.1984	22.24	9.154	32.65	20.39
	480	0.1986	22.31	9.596	32.73	21.36
Li	420	0.2136	37.34	12.56	46.80	23.90
	420	0.1968	35.81	12.07	48.72	24.92
	450	0.2091	43.69	12.66	55.97	24.61
	450	0.1776	38.00	11.28	57.29	25.81
	480	0.1317	29.08	8.194	59.13	25.28
	480	0.1893	41.71	11.88	58.99	25.48

Table V.

Temperature °C	Magnesium		Lithium	
	Yield of CH_3CHO %	Yield of Acetone. %	Yield of CH_3CHO %	Yield of Acetone %
420	29.83	20.00	47.76	24.41
450	31.29	20.23	56.63	25.21
480	32.69	20.88	59.06	25.38

(b) Effect of Variation in Rate of Nitrogen Flow.

Ardagh, Barbour, McClellan and McBride (19) showed that the rate of flow of nitrogen had an important effect on the yield of acetone obtained from calcium acetate. They found that a rate of flow corresponding to 2 litres per hour was most satisfactory. In the present work, calcium and sodium acetates were pyrolysed under identical conditions but with varying rates of gas flow. At the higher rates of flow, fluctuating results were obtained at first, but on using more efficient traps, reproducibility was obtained. Analysis of the products was carried out as described in Section IV, 5 c and the results obtained are given in Table VI.

Table VI

Cation	Rate of Flow litres/hour	Wt. of Acetate gm.	Wt. of Acetone gm.	Yield of Acetone %
Ca^{++}	½	0.3079	0.09517	84.21
	½	0.3196	0.09922	84.57
	1	0.3566	0.1176	89.82
	1	0.2271	0.07498	89.95
	2	0.1812	0.06207	93.33
	2	0.2079	0.07238	94.84
	4	0.2890	0.1009	95.12
	4	0.3074	0.1075	95.30
Na^{+}	½	0.1094	0.02740	70.76
	½	0.1075	0.02695	70.81
	1	0.1020	0.02574	71.31
	1	0.1092	0.02765	71.55
	2	0.1021	0.02610	72.23
	2	0.1069	0.02765	73.06
	2	0.1425	0.03722	73.80
	4	0.0918	0.02407	74.10
	4	0.1349	0.03546	74.29

Table VII

Rate of Flow litres/hour	Yield of Acetone from Ca Acetate %	Yield of Acetone from Na Acetate %
½	84.39	70.79
1	89.89	71.43
2	94.09	73.03
4	95.21	74.20

It will be seen from the summary of results (Table VII) that provided efficient traps are used an increased rate of flow favours the reaction. It was previously found, in the nitric oxide work - Section II,3 - that appreciable decomposition, or polymerisation, of acetone occurs under the conditions of the pyrolysis. It was therefore concluded that a high flow rate of nitrogen is advantageous since the products are then more quickly removed from the furnace. Similarly, with a higher pyrolysis temperature, the products are generated more rapidly and again are removed from the furnace more quickly. This would explain the results set out in Table V.

In all of the pyrolyses the salt, or mixture, was introduced into the furnace while it was at a temperature beneath that required for decomposition. Its temperature was then raised fairly rapidly through the decomposition point and the heating continued until pyrolysis was complete (about 20 minutes). By carrying out the pyrolyses in this manner, rather than at a fixed temperature, the results obtained for various cations should be more readily comparable since the rate of generation of products will be approximately the same in each case. This would reduce any error introduced by variations in the time in which the products remain within the pyrolysis tube.

(c) Method of Pyrolysis and Results

The acetates of the following metals were prepared:- lithium, sodium, potassium, calcium, strontium, barium, manganese(ous), magnesium, and lead. These salts, about 0.1-0.3gm per pyrolysis, were heated in an electric furnace in the manner just described while the pyrolysis tube was swept out with purified nitrogen (2 litres per hour). The acetone which was formed was collected in spiral liquid air traps, washed out with water and estimated by adding an excess of iodine to a portion of this solution after it had been made alkaline. The solution was then shaken for ten minutes and the iodine, which was liberated on acidification, titrated against standard thiosulphate.

The following results were obtained (Table VIII) and they are summarised in Table XII.

Table VIII

Cation	Wt. of Acetate gm.	Wt. of Acetone gm.	Yield of Acetone %
Li	0.1075	0.03835	81.07
	0.0894	0.03233	82.21
	0.0785	0.02854	82.68
Na	0.1021	0.02610	72.23
	0.1069	0.02765	73.06
	0.1425	0.03722	73.80

Table VIII (Cont.)

Cation	Wt. of Acetate gm.	Wt. of Acetone gm.	Yield of Acetone %
K	0.1251	0.01390	37.56
	0.1593	0.01782	27.83
	0.1454	0.01656	38.48
Ca	0.1812	0.06207	93.33
	0.2079	0.07238	94.84
	0.2917	0.1007	94.11
Sr	0.2102	0.05315	91.37
	0.3092	0.07066	89.35
	0.1899	0.04805	91.41
Ba	0.5031	0.09956	87.07
	0.4775	0.09517	87.68
	0.5055	0.1004	87.40
Zn	0.2257	0.05859	82.03
	0.1452	0.03847	83.73
	0.1572	0.03774	81.30
Mn(ous)	0.2121	0.06561	92.17
	0.1244	0.03858	92.39
	0.1586	0.04946	92.90
Mg	0.1642	0.05240	78.27
	0.1645	0.05383	80.26
	0.1267	0.04130	79.95
Pb	0.3665	0.03278	50.10
	0.3400	0.03055	50.32
	0.4170	0.03855	51.78

6. Pyrolysis of Acetate - Formate Mixtures

(a) Non-equimolar

Since small changes in the molar composition of mixtures cause considerable variations in the yields of pyrolysis products, preliminary experiments were carried out to find the order of this variation. In the case of non-equimolar mixtures, the yield of acetaldehyde may be given as the percentage of that which would be formed either if all the acetate reacted to give acetaldehyde (column A) or if all the formate reacted to give acetaldehyde (column B).

Lithium and magnesium acetate-formate mixtures containing a 3:1 excess of acetate were prepared and pyrolysed. The products were analysed as described in Section IV,6b and the results so obtained are shown in Table IX. They are compared with those from equimolar mixtures in Table X.

In all other pyrolyses of mixtures, both isotopic and non-isotopic, equimolar quantities were used.

Table IX

Cation	Wt. of Mixture gm.	Wt. of Acetone gm.	Wt. of CH_3CHO gm.	Yield of Acetone %	Yield of CH_3CHO %	
					A	B
Li	0.1476	0.03038	0.01480	58.26	19.46	59.88
	0.1594	0.03150	0.01835	57.21	21.27	62.31
Mg	0.1966	0.03127	0.01871	49.44	19.19	57.47
	0.1618	0.02678	0.01368	51.29	17.62	54.96

Table X

Cation	Ratio of $\frac{\text{Formate}}{\text{Acetate}}$	Yield of CH_3CHO(A) %	Yield of Acetone %	Total Yield %
Li	1:1	56.63	25.21	81.84
	1:3	20.37	57.74	78.11
	Acetate alone	—	81.99	81.99
Mg	1:1	31.29	20.33	51.62
	1:3	18.41	50.37	68.78
	Acetate alone	—	79.49	79.49

(b) Equimolar

The formates of the metals listed in the previous section were prepared and equimolar acetate-formate mixtures made up. These were then pyrolysed (about

0.1-0.3 gm. per run) exactly as for acetates. The weighed quantity of mixture was introduced into the furnace, which was not sufficiently hot for decomposition to begin, and the temperature was raised fairly rapidly through the decomposition point. The pyrolysis products were swept from the pyrolysis tube by a stream of purified nitrogen and collected in spiral liquid air traps.

The acetone and acetaldehyde content was then determined by selective oxidation of this distillate. Full details of this procedure are given in Section IV,6b. In brief, it consisted of oxidising the distillate with a dilute solution of chromic acid and steam distilling. After neutralisation, the acetone was distilled out and estimated by Messinger's method, the remaining solution being again oxidised, this time by an alkaline permanganate solution. This served to convert any formic acid, obtained by oxidation of formaldehyde, to carbon dioxide. The mixture was again steam distilled and by titration with standard sodium hydroxide the amount of acetic acid present was determined, thus enabling the amount of acetaldehyde in the original pyrolysis distillate to be calculated.

The results obtained are tabulated below (Table XI) and are summarised in Table XII. They will be discussed in Part III.

Table XI

Cation	Wt. of Mixture gm.	Wt. of CH_3CHO gm.	Wt. of Acetone gm.	Yield of CH_3CHO %	Yield of Acetone %
Li	0.2029	0.04238	0.01238	55.93	24.78
	0.1373	0.03941	0.008666	57.33	25.64
	0.1717	0.03632	0.01064	56.64	25.18
Na	0.1626	0.003302	0.01642	7.26	52.19
	0.1667	0.003958	0.01764	7.66	54.74
	0.1586	0.003477	0.01607	8.13	52.38
K	0.2237	0.000701	0.006892	1.50	37.45
	0.2512	0.000610	0.007266	1.17	35.17
	0.2116	0.000592	0.006473	1.34	37.20
Ca	0.2089	0.02776	0.01266	43.48	30.09
	0.2531	0.03416	0.01498	44.17	29.39
	0.2786	0.03815	0.01606	44.81	28.64
Sr	0.3184	0.02344	0.01840	35.18	38.93
	0.3604	0.02474	0.02113	32.80	39.54
	0.3068	0.02210	0.01716	34.44	37.70
Ba	0.2628	0.01389	0.01474	28.97	46.50
	0.3362	0.01777	0.01812	28.96	44.50
	0.2380	0.01382	0.01292	30.31	45.11
Zn	0.1669	0.009877	0.01184	22.76	41.42
	0.1791	0.01033	0.01296	22.19	42.23
	0.2271	0.01376	0.01588	23.31	40.83

Table XI (Contd.)

Cation	Wt. of Mixture gm.	Wt. of CH_3CHO gm.	Wt. of Acetone gm.	Yield of CH_3CHO %	Yield of Acetone %
Mn(ous)	0.1380	0.01751	0.006386	45.78	25.34
	0.1899	0.02449	0.008061	46.52	23.24
	0.2048	0.02719	0.009307	47.90	24.88
Mg	0.1978	0.02125	0.009059	31.31	20.24
	0.2145	0.02369	0.009754	32.18	20.10
	0.1609	0.01679	0.007667	30.39	20.36
Pb	0.5032	0.005540	0.01394	7.78	29.69
	0.5327	0.006667	0.01471	8.84	29.60
	0.6751	0.006714	0.01764	7.03	28.02

Table XII

Cation	Acetate-Formate Mixtures			Acetate Alone
	Yield of CH_3CHO %	Yield of Acetone %	Total Yield %	Yield of Acetone %
Li	56.63	25.21	81.84	81.99
Na	7.68	53.10	60.78	73.03
K	1.34	36.61	37.95	38.29
Ca	44.15	29.37	73.52	92.91
Sr	34.14	38.72	72.86	90.71
Ba	29.41	45.37	74.78	87.38
Zn	22.75	41.39	64.14	82.35
Mn(ous)	46.73	26.49	71.22	92.41
Mg	31.29	20.33	51.52	79.49
Pb	7.78	29.10	36.88	50.73

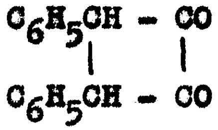
7. Pyrolysis of Phenylacetates.

Since it was intended to carry out pyrolyses of mixtures of isotopically labelled phenylacetates and non-enriched acetates to find whether the nature of the product, i.e. the enrichment of the carbonyl group of the non-symmetrical ketone, was affected by changes in the cation, it was decided to perform some non-isotopic pyrolyses and examine the yields of products obtained. As a preliminary, calcium, strontium and barium phenylacetates were pyrolysed separately, and the amount of dibenzyl ketone formed estimated by the oxime method (Section IV, 7c)

Due to the high boiling-point (331°) of this ketone at atmospheric pressure, and the consequent difficulty of removing it from the pyrolysis tube, these pyrolyses were carried out under vacuum. The products were collected in a liquid air trap, washed out with ether and to them was added an excess of a solution of hydroxylamine hydrochloride. The liberated hydrochloric acid was then titrated with standard alkali.

The residue from the pyrolysis was the carbonate of the metal caked together with some carbon. The distillate was semi-crystalline and red in colour. It is possible that this is the same red product reported by Kalmin (30) in the pyrolysis of phenylacetic anhydride.

He found it to be diphenyl-<u>cyclo</u>butane-α-dione



$$\begin{array}{ccc} C_6H_5CH & - & CO \\ | & & | \\ C_6H_5CH & - & CO \end{array}$$

and regarded it as a pyrolytic product of an unsymmetrical dimer of enolic phenylacetic anhydride.

In the present pyrolyses, however, which were on a semi-micro scale, no attempt was made to characterise this red constituent of the products. Since preliminary analyses showed that dibenzyl ketone was the only product giving oxime, estimations were carried out directly on the distillate. The results of these analyses are in Table XIII (summarized in Table XV).

Table XIII

Cation	Wt. of Phenylacetate gm.	Wt. of dibenzyl Ketone gm.	Yield of Dibenzyl Ketone %
Ca	1.0830	0.5658	77.20
	0.8213	0.4285	77.07
	0.9497	0.4995	77.69
Sr	1.0194	0.4566	76.43
	0.9287	0.4134	75.91
	1.1670	0.5188	75.78
Ba	1.4120	0.5509	75.73
	1.0084	0.3977	76.60
	1.2485	0.4943	76.81

8. Pyrolysis of Acetate-Phenylacetate Mixtures.

Equimolar acetate-phenylacetate mixtures of calcium, strontium and barium salts were prepared and pyrolysed under vacuum exactly as in the previous section. The products, which were collected in a liquid air trap, were washed out with ether and analysed for acetone, methyl benzyl and dibenzyl ketones. The acetone was removed with the ether and estimated by Messinger's method, the two remaining ketones being then separated by fractional distillation. The methyl benzyl ketone was also estimated by Messinger's method and the dibenzyl ketone by the oxime method.

As a preliminary, a series of estimations was carried out on known mixtures of acetone, methyl benzyl and dibenzyl ketones in order to check the accuracy of the method of analysis. It was found that this method gave reproducible results and the following are the percentages of the known content which were obtained for the various ketones in these trial mixtures.

Percentage found for acetone = 98.35%
" " " methyl benzyl ketone = 102.1%
" " " dibenzyl ketone. = 93.63%

These values were used in calculating the yields in these acetate-phenylacetate pyrolyses, and the results so obtained are reported in Table XIV with a summary in Table XV. The yields of the ketones are expressed as percentages of the theoretically possible if each were the only product formed and not as percentages of the total products formed. This means that the sum of the yields of acetone and methyl benzyl ketone will give the total percentage of methyl groups from the acetate which react to give a ketone and likewise the sum of the yields of methyl benzyl and dibenzyl ketones will give what fraction of the phenylacetate reacts to give ketones. The sum of all three values in the table has therefore no significance.

Table XV

Cation	Acetate-Phenylacetate Mixtures			Phenylacetate alone
	Yield of Acetone %	Yield of Methyl Benzyl Ketone %	Yield of Dibenzyl Ketone %	Yield of Dibenzyl Ketone %
Ca	44.18	25.21	54.98	77.32
Sr	43.77	27.63	55.65	76.04
Ba	41.32	28.70	54.20	76.38

Table XIV

Cation	Wt. of Mixture gm.	Wt. of Acetone gm.	Wt. of Methyl Benzyl Ketone gm.	Wt. of Dibenzyl Ketone gm.	Yield of Acetone %	Yield of Methyl Benzyl Ketone %	Yield of Dibenzyl Ketone %
Ca	1.0301	0.05597	0.1489	0.2542	43.84	25.24	54.99
	0.9432	0.05174	0.1327	0.2332	44.25	24.56	55.36
	0.9888	0.05449	0.1463	0.2423	44.45	25.84	54.59
Sr	1.1308	0.05105	0.1492	0.2388	43.78	27.64	56.65
	1.3616	0.06194	0.1778	0.2848	44.13	27.45	56.06
	1.1776	0.05270	0.1557	0.2381	43.40	27.80	54.24
Ba	1.3845	0.05016	0.1608	0.2373	41.33	28.72	54.10
	1.6360	0.05984	0.1923	0.2828	41.76	29.09	54.58
	1.3470	0.04825	0.1541	0.2300	40.88	28.30	53.91

9. Isotopic Pyrolysis of Acetate-Formate Mixtures.

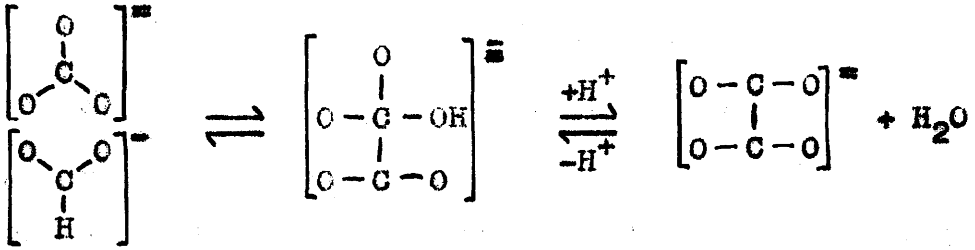
As has been mentioned in the introduction, Bell and Reed (17) observed an almost exclusive cleavage of the carbon-carbon bond in acetate when a mixture of barium acetate, enriched with ^{13}C in the carboxyl group, and barium formate were pyrolysed to give acetaldehyde. Since this pyrolysis, using a labelled salt, had only been carried out using barium as cation, it was decided to see whether the direction of cleavage was influenced by the nature of the cation. A series of carboxyl labelled metal acetates, namely those of calcium, strontium, barium, lithium and magnesium, were prepared and, after mixing with an equimolar quantity of the respective formate, pyrolysed exactly as for non-isotopic samples.

The acetaldehyde formed was oxidised to acetic acid using a chromic acid solution of such concentration that the acetone, which was also formed, was unoxidised. After steam distillation, the acetic acid was recovered as barium acetate which could then be assayed for ^{13}C content. The carbonate residues were also assayed for ^{13}C. In the case of magnesium, the residue consists of magnesium oxide and a specimen of carbon dioxide was obtained from the liquid air traps by distillation from a solid CO_2-acetone bath.

All samples assayed were converted into carbon dioxide by the "wet combustion method" of van Slyke and Folch (31). The carbon dioxide samples so obtained were assayed on a Metropolitan-Vickers Ltd., Mass Spectrometer, Type M.S.2., the abundance ratio being determined from the intensities of the peaks of mass numbers 44 and 45.

(a) Attempted Synthesis of ^{13}C-carboxyl Labelled Formates

Grant and Turner (32) found, in an investigation into the formation of ^{14}C-labelled formates by hydrolysis of Na^{14}CN, that there is an exchange reaction between the carboxyl carbon of sodium formate and the carbon of sodium carbonate. They postulated a mechanism of the following type.



This seemed to show promise of being a simple and elegant method of labelling formates. Enriched sodium carbonate was therefore prepared by bubbling $^{13}CO_2$, obtained by warming enriched barium carbonate with an excess of concentrated sulphuric acid, through a solution of a calculated quantity of sodium hydroxide. A solution of the $Na_2{}^{13}CO_3$ thus prepared was sealed in a Carius tube with the quantity of sodium formate required by the above formulation and heated at 180° for 8 hours.

The carbonate in solution, containing 44.59% ^{13}C, was then recovered by precipitation as barium carbonate and the formate, after acidification with sulphuric acid, steam distillation and titration of the distillate with barium hydroxide, was obtained as barium formate on evaporation to dryness. Isotopic assay showed the ^{13}C content of this formate to be 1.210%. It may be seen therefore that some enrichment took place but it was felt that it was insufficient to merit further investigation of the method.

(b) Synthesis of ^{13}C-carboxyl Labelled Acetates

^{13}C-carboxyl labelled acetates were prepared by a method substantially the same as that recorded by Calvin et al. (33). ^{13}C-enriched carbon dioxide was distilled on to previously prepared methyl magnesium iodide. When the reaction was complete, at -15°C, the Grignard reagent was decomposed with dilute sulphuric acid and, after removal of iodine by addition of an excess of silver sulphate solution, the enriched acetic acid was steam distilled out of the solution. This distillate was then neutralised in successive experiments with, respectively, lithium hydroxide, calcium, strontium and barium carbonates and magnesium oxide to give the required acetates. The yields of acetic acid obtained by this method varied from 85 - 95%.

(c) Results of Pyrolyses

The results obtained from these isotopic pyrolyses, shown in Tables XVI and XVII, confirm Bell and Reed's observation that, where the concentration of ^{13}C in the carboxyl group of the acetate was enhanced, the carbonyl carbon of the acetaldehyde formed was derived principally from the carboxyl group of the formate, i.e., there is an almost exclusive cleavage of the carbon-carbon bond of the acetate in acetate-formate pyrolyses.

Because of the considerably greater enrichment used in these experiments compared with those of Bell and Reed, and the corresponding increase in accuracy, it will be seen that about 1.6 - 1.8% of the acetaldehyde formed has in fact carbonyl carbon derived from the acetate. Within experimental error however, this fraction from the acetate is independent of the cation used.

The values for residual barium carbonate in Table XVI were calculated from the average quantity of acetaldehyde produced in non-isotopic pyrolyses. It was assumed that the carbonyl group of the formaldehyde formed would have a normal ^{13}C value, whereas that of the acetate would have the same enrichment as the carboxyl-carbon of the barium acetate. The discrepancy in the case of magnesium is probably due to decarboxylation of the acetate during the pyrolysis. Some carbon dioxide is generally formed in these decompositions and this of course would reduce the accuracy of the magnesium value since in this case, as was mentioned before, the enrichment of the residue was determined from a sample of carbon dioxide obtained from the liquid air traps, and not from the material remaining in the furnace which consisted of magnesium oxide.

Table XVI

Cation	% age ^{13}C in acetate	% age ^{13}C in acetaldehyde.	% age ^{13}C in residual carbonate.	
			found	calculated
Ca	28.73	1.647	40.79	40.93
Sr	30.58	1.686	40.98	40.62
Ba	30.58	1.634	40.37	39.24
Li	5.732	1.218	8.312	8.322
Mg	5.732	1.214	7.673	7.167

Table XVII

Cation	% age ^{13}C in >CO of acetate	% age ^{13}C in >CO of acetaldehyde.	% age of acetaldehyde from acetate.
Ca	56.32	2.154	1.838
Sr	60.02	2.232	1.855
Ba	60.02	2.128	1.678
Li	10.32	1.296	1.699
Mg	10.32	1.288	1.613

10. Isotopic Pyrolysis of Acetate-Phenylacetate Mixtures.

The work of Lee and Spinks (20) showed that in the pyrolysis of a mixture of calcium acetate and calcium phenylacetate, two-thirds of the benzyl methyl ketone obtained resulted from the loss of the carboxyl group in the acetate. Also in the pyrolysis of a mixture of calcium benzoate and calcium formate, 10% of the benzaldehyde resulted from the loss of the carboxyl group in the formate. In neither of these cases is exclusive cleavage taking place and it seemed probable that if the cation influenced which bond was broken, it would most readily be detected in these two cases.

For acetate-phenylacetate mixtures, the series calcium-strontium-barium was chosen since non-isotopic studies had already been made using these cations.

^{13}C-carboxyl labelled phenylacetic acid was prepared by carbonation of benzyl magnesium chloride with enriched carbon dioxide, the Grignard reagent being decomposed by addition of excess sulphuric acid and the free acid extracted with sodium hydroxide. After recrystallisation from petroleum ether, the pure acid (75% yield based on barium carbonate) was divided into three and neutralised with calcium, strontium and barium carbonates. Equimolar mixtures of the respective acetates and labelled phenylacetates, the enrichment of which had been reduced by dilution with non-enriched material, were then prepared and pyrolysed as in non-isotopic experiments. After preliminary separation, the methyl benzyl and dibenzyl ketones were carefully fractionated, only the middle portions being taken in each case, to obtain samples for isotopic analysis. The ketones were oxidised directly since the formation of derivatives would have increased the number of carbon atoms per molecule and so reduced the accuracy of the experiments. The values obtained are given in Tables XVIII and XIX.

Table XVIII

Cation	% age concentration of ^{13}C in				
	Phenyl-acetate	Methyl Benzyl Ketone	Dibenzyl Ketone	Carbonate found	Carbonate Calc.
Ca	2.793	2.069	2.045	7.301	7.312
Sr	2.298	1.763	1.751	5.487	5.501
Ba	2.770	2.027	2.032	7.203	7.239

Table XIX

Cation	% age Concentration of ^{13}C in CO of			% age of ketone from phenylacetate.
	Phenyl-acetate	Dibenzyl Ketone	Methyl Benzyl Ketone.	
Ca	14.36	14.71	9.50	63.24
Sr	10.40	10.31	6.75	60.60
Ba	14.18	14.52	9.12	61.20

If it is assumed that the carbonyl carbon of dibenzyl ketone has the same enrichment as the carboxyl carbon of the phenylacetate from which it is formed, the discrepancies in the values above (columns 2 and 3, Table XIX) gives an idea of the experimental error involved in these experiments. From these results it would appear that here again the site of bond fission is unaffected by the nature of the cation.

11. Isotopic Pyrolysis of Benzoate-Formate Mixtures.

For these pyrolyses, lithium and calcium, i.e. an alkali and an alkali-earth metal, were chosen as cations.

Benzoic acid, ^{13}C-labelled in the carboxyl position, was prepared by carbonation of phenylmagnesium bromide with enriched carbon dioxide. The purified acid was neutralised with lithium hydroxide and calcium carbonate to give the desired salts which were then diluted with non-enriched material and mixed with an equimolar quantity of the correct formate. These mixtures were then pyrolysed under vacuum.

The products of the decomposition were oxidised by Fouchet's method (44). This method of selective oxidation converted formaldehyde to carbon dioxide, benzaldehyde to benzoic acid and left benzophenone unchanged. After oxidation, the solution was steam-distilled, and the benzoic acid recovered as barium benzoate which could then be analysed for ^{13}C content.

The results of these experiments are given in Tables XX and XXI.

Table XX

Cation	%age Concentration of ^{13}C in		
	benzoate	benzaldehyde	carbonate
Li	2.258	2.112	4.872
	2.258	2.127	4.859
Ca	2.296	2.161	4.783
	2.296	2.164	4.772

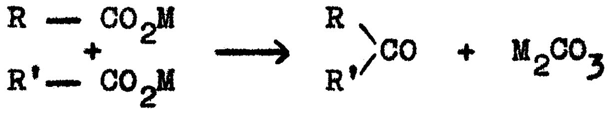
Table XXI

Cation	%age ^{13}C in >CO position in		% age of ketone from benzoate	Average
	benzoate	benzaldehyde		
Li	8.996	7.944	86.98	87.63
	8.966	8.049	88.28	
Ca	9.232	8.287	88.33	88.96
	9.232	8.308	89.59	

From these results (Table XXI) it will be seen that here again the enrichment of the unsymmetrical pyrolysis product (benzaldehyde in this case) is unaffected by the nature of the cation.

Part III - Theoretical Discussion

In the formulation of a general mechanism of thermal decomposition of salts of carboxylic acids,



$$\begin{matrix} R - CO_2M \\ + \\ R' - CO_2M \end{matrix} \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>CO + M_2CO_3$$

where R and R' may be the same or different, H, aliphatic or aromatic, and M a metal, the following possibilities may be considered:

1. Preliminary attack by the carboxyl carbon on R followed by fission of the R-C bond, this fission being either heterolytic or homolytic.
2. Preliminary cleavage of the R-C bond, either (a) homolytic or (b) heterolytic, followed by an attack on the carboxyl carbon by R.

Mechanism 1 has been suggested by Lee and Spinks (20). They propose a two-step mechanism in which an acyl cation is produced by a fairly rapid process, which is reversible, followed by a rate controlling S_E2 type of decarboxylation with the acyl cation acting as the electrophilic component.

$$R - COOM \rightleftharpoons R - \overset{+}{C} = O + MO^-$$

$$R - \overset{+}{C} = O + R'COOM \xrightarrow{\text{slow}} RCOR' + M^+ + CO_2$$

A serious objection to this mechanism is that it becomes necessary to explain the preferred fission in the pyrolysis of acetate-benzoate, acetate-formate and benzoate-formate mixtures by means of steric hindrance and it is unlikely that a steric factor would be of such great importance at the high temperatures required for decomposition. Moreover, in the attack of $R-\overset{+}{C}=O$ on, say, $CH_3-CO_2^-M^+$ the carboxyl carbon will be more negatively charged than the methyl carbon and should therefore prove a more suitable site for attack.

Mechanism 2(a) i.e. homolytic cleavage of the R-C bond, was suggested by Bell and Reed (16,17) who put forward a free radical chain mechanism. In the present research, however, the results of pyrolyses carried out in the presence of nitric oxide (Section II,3) suggest that decomposition does not take place by a chain mechanism although of course, free radicals might still be formed at some stage of the reaction. In addition, Lee and Spinks have pointed out that, if the reaction were of free radical type, the benzyl radical would be formed more readily than the methyl whereas their results showed that in the pyrolysis of a mixture of calcium acetate and phenylacetate two-thirds of the methyl benzyl ketone resulted from R-C bond fission in the acetate. They also note that to account for the appearance of n-propyl iso-propyl ketone from the pyrolysis of isobutyrate (18), a rearrangement from a secondary to a primary carbon radical, is required, whereas established rearrangements involving free radicals (23,24) indicate that primary radicals tend to rearrange to the tertiary state.

The possibility of homolytic cleavage occurring in a transition state complex will be discussed at a later stage.

If the possibility of heterolytic cleavage occurring, mechanism 2(b), is now considered it will be seen that this can occur in two ways.

1. $R\vdots - CO_2M \longrightarrow R^+ + {}^-CO_2M$ - carbonium ion formation

2. $R - \vdots CO_2M \longrightarrow R^- + {}^+CO_2M$ - carbanion formation.

For ketone formation, attack is required on a negative centre, namely the carboxyl carbon, and this makes improbable any mechanism involving carbanion formation. A mehcanism requiring preliminary formation of a carbonium ion will now be considered.

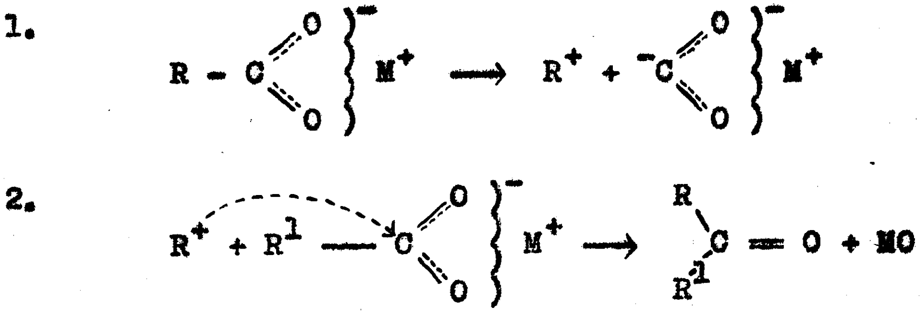
The yields obtained from acetate and acetate-formate mixture pyrolyses for a range of metals were given in Table XII and these are now retabulated (Table XXII) with the metals arranged in the order of their electronegativity (34).

Table XXII

Cation	Electro-negativity volts.	Acetate alone	Acetate-formate Mixtures	
		Yield of Acetone.	Yield of CH_3CHO %	CH_3CHO as % age of total yield.
K	-2.61	38.29	1.34	3.53
Na	2.45	73.03	7.68	12.64
Ba	2.15	87.38	29.41	39.31
Li	2.09	81.99	56.63	69.18
Sr	2.07	90.71	34.14	46.86
Ca	1.90	92.91	44.15	60.05
Mg	1.55	79.49	31.29	60.73
Mn(ous)	1.0	92.41	46.73	65.61
Zn	0.76	82.35	22.75	35.46
Pb	0.12	50.73	7.78	21.10

In column 5, the yields of acetaldehyde from the pyrolysis of acetate-formate mixtures are given as the percentage of the total acetaldehyde + acetone formed, thus allowing an indication to be given of the distribution of methyl groups from the acetate in the pyrolysis products. It will be seen from the table that, in general, there is an increase in yields as the electronegativity of the metal rises. There are a number of exceptions to this, viz. lithium and cations which give a residue of metal oxide rather than of the carbonate (magnesium, zinc and lead) but these will be discussed later.

In acetate pyrolyses, since the yield of acetone obtained is favoured by an increase in the electronegativity of the cation, it follows that a decrease in electron density on the carboxyl carbon is favourable to ketone formation. This decrease will in general tend to cause an electron displacement from the alkyl radical carbon to the carboxyl carbon and so facilitate heterolytic cleavage to give a carbonium ion. Also, the carboxyl carbon has a high electron density, since it is part of a negative centre, so that for bond formation attack by an electrophilic group is required. The following two-step mechanism may therefore be proposed for the reaction.

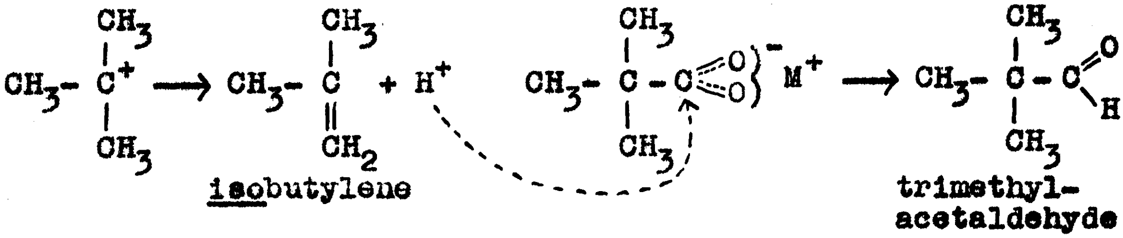


where R and R^1 may be the same or different, aliphatic, aromatic or H.

The first step, involving heterolytic fission, would be rate determining and, since a large amount of energy would have to be supplied to cause a cleavage of this kind to occur, the high temperature necessary for pyrolysis is explained. In the second stage, the carbonium ion formed reacts with a further carboxylate molecule and may give either a symmetrical or an unsymmetrical ketone.

It would also be expected that with a molecule larger than acetate there would be a diminution of the effect of the cation since any variations in charge would be partially distributed over a greater number of carbon atoms and, as will be seen from Table XV, this is actually found to be the case with phenylacetate pyrolyses.

The results of the trimethylacetate pyrolyses are also readily explicable by this mechanism. The tert-butyl ion is known to decompose to give isobutylene (35).



the hydrogen ion thus formed then reacting with a further molecule of trimethylacetate as shown. As will be seen therefore, this mechanism offers a simple explanation for the formation of isobutylene and trimethylacetaldehyde in the pyrolysis of calcium trimethylacetate.

Consideration of Lee and Spink's Results

The following table summarises the results of isotopic experiments carried out by Lee and Spinks, Bell and Reed, and in the present work. In column 1, the labelled component of the mixture is given first. Column 2 gives results using ^{14}C (i.e. Lee and Spink's results) and column 3 gives those with ^{13}C.

Table XXIII

Reactants	Average % age of original activity in ketone.	
Acetate + formate		1.7
Acetate + p-toluate	1.5	
Acetate + phenylacetate	33.3	38.4 ●
Acetate + valerate	18.9	
Acetate + benzoate	1.5	
Benzoate + formate	91.7	88.3
Benzoate + acetate	101.4	
Benzoate + propionate	101.3	

● In this case the phenylacetate was enriched.

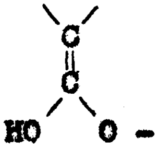
From these results, the following is the ease with which the carboxyl group is lost in forming the ketone:-

acetate > phenylacetate > valerate ≫ formate > benzoate.

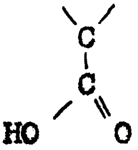
In interpreting these results, Lee and Spinks assumed that the C - C carboxyl bond in benzoate was of similar strength to the C - C carboxyl bonds in acetate, valerate etc. and was weaker than the H - C bond in formate. A recent X-ray study of benzoic acid by Sim, Robertson and

Goodwin (36) has however made this assumption doubtful.

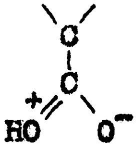
These workers found the length of the bond joining the carboxyl group to the benzene ring to be 1.48Å compared with the standard single-bond value of 1.54Å. This suggests that in benzoic acid the structure I makes considerable contribution in addition to the structures II and III which are usually present.



I



II



III

Knowing the bond length, it is possible to derive an approximate value for the heat of rupture of the bond (37). If it is assumed that the heat of atomisation of carbon is 150 k. cal/mole, then the following are the energies of standard bonds in k. cal/mole:- C-C (hydrocarbon) 71.8; Car-Car (benzene rings) 105.3; C=C (olefins) 125.1; C-H (hydrocarbons) 93.6. These values may be graphed against the respective internuclear distances and, from a graph of this kind, it was found that the approximate heat of rupture of the C-C bond in benzoic acid was 88.5 k. cal/mole. The same bond in p-toluic acid will probably be of similar strength. This it will be seen is of the same order as a C-H bond in a hydrocarbon (93.6 k. cal/mole). Exact comparison between these values is not possible since

E_{C-H} varies when derived from different hydrocarbons (38) and the C-H bond in formic acid is not strictly comparable with, say, the C-H bond in methane. Also the relative values of bond energies vary according to what value is chosen for the heat of vaporisation of carbon (L_2). The following shows how the energies of carbon-carbon bonds depend on L_2.

C - C (diamond)	$\frac{1}{2} L_2$
C = C (olefines)	$L_2 - 26$
C ≡ C (acetylene)	$3/2L_2 - 63$
C - H (hydrocarbons)	$\frac{1}{4} L_2 + 56$

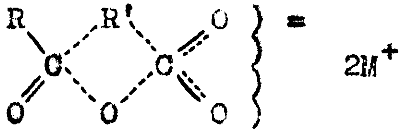
From this discussion it follows that for the purpose of heterolytic cleavage, the carboxylates which have been studied may be divided into two groups.

(i) Acetate, propionate, valerate, phenylacetate —— in which a normal carbon-carbon bond must be broken. The heats of rupture of these bonds are about 72 k.cal/mole

(ii) Formate, benzoate, p-toluate —— in which either a carbon-hydrogen or a carbon-carbon bond with partial double bond character must be broken. The heats of rupture of these bonds are about 90 k.cal/mole.

It would be expected therefore, that if a salt from group (i) were pyrolysed with a salt from group (ii) exclusive cleavage would occur in the salt with the weaker bond, whereas if salts from the same group were pyrolysed cleavage would not be so exclusive. As will be seen from Table XXIII this is in fact found experimentally.

Although a two-stage mechanism explains the above results, a serious theoretical objection is that a high energy barrier would have to be overcome for complete separation of ions to take place. This may be overcome by postulating the existance of a transition state complex, e.g.

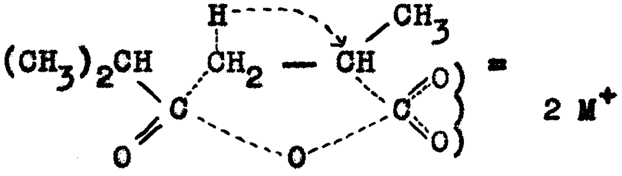


This complex intermediate anion would then decompose to give the ketone + $CO_3^{=}$. This is in agreement with the experimental results given in Tables XVII, XIX, and XXI, namely that the nature of the cation does not influence the site of bond fission. The cation affects the probability of bond fission occurring and so influences the yield of ketone, but once the intermediate complex is formed, the direction of cleavage can no longer be affected by changes of cation.

The preferred cleavage of the C-C bond in acetate in its pyrolyses with phenylacetate and <u>n</u>-valerate might then be explained partly on steric grounds, in that the smaller methyl group could take part in the transition complex with greater ease, and partly by the fact that the methyl group tends to release electrons more than either the n-butyl or the benzyl group and so favours heterolytic fission. The fission of the C-C bond in phenylacetate would be expected to require a lower energy of activation than C-C cleavage in n-valerate since this bond in phenylacetate is one C atom removed from an aromatic nucleus (20,35). This would explain the difference in extent of C-C cleavage in acetate when it is pyrolysed with phenylacetate and n-valerate.

A further advantage to postulating a transition state of the type shown is that it allows a more complete explanation to be given to the results in Table XXII. It will be seen that the obtained yields increase with increase in electronegativity but that magnesium, zinc and lead salts do not follow this general rule. In pyrolyses with salts of these elements, however, the residue is composed of the metal oxide and not of the carbonate, which suggests that a stable carbonate helps the reaction. This is consistent with the existance of an intermediate complex, since a tendency towards oxide formation would reduce the probability of formation of such a complex. It also explains the fact, noticed by Kronig (6), that magnesium oxide is formed in the pyrolysis of magnesium acetate at a temperature below the decomposition temperature of magnesium carbonate.

The formation of n-propyl ketones in the pyrolysis of sodium isobutyrate (18) would presumably take place by an attack by the β and not the α-carbon of the isobutyrate rather than by a rearrangement of the free ion. The complex intermediate ion would be of the following kind



Other rearrangements which have been found in carboxylate pyrolyses (12) may be similarly explained.

In the decomposition of the transition complex, either heterolytic or homolytic cleavage of the bonds concerned might be involved. If the latter, the above theory is in fundamental agreement with that proposed by Bell and Reed although a different initiation for the mechanism is suggested.

A drawback to the above mechanism, which is common to all theories which have been proposed up till the present, is that it offers no simple explanation of the formation of oxalates in the pyrolysis of formates. No satisfactory mechanism has been proposed for this reaction but it is hoped that work being carried out at present by Dr. R.I.Reed in this department will help to elucidate this point. If however, as appears probable, this decomposition takes place by a separate mechanism, presumably of a homolytic nature, it would offer an explanation of the figures in Column 5, Table XXII.

It is known that only the formates of the most electropositive metals form oxalates on pyrolysis (28), so that as the electronegativity of the metal increases, and the importance of this second mechanism decreases, there is a greater possibility of the formate reacting to give acetaldehyde. This agrees with the experimental results since in the pyrolysis of acetate-formate mixtures, the proportion of methyl groups reacting to give acetaldehyde increases with an increase in the electronegativity of the cation.

The mechanism proposed above would therefore appear to give a satisfactory explanation of most of the experimental data obtained by pyrolysing salts of organic acids.

Part IV - Details of Experimental Work.

1. (a) Synthesis of Calcium p - Chlorophenylacetate.

This salt was prepared from benzyl cyanide by the following reaction scheme.

$$C_6H_5CH_2CN \xrightarrow[H_2SO_4]{HNO_3} \underline{p} - NO_2C_6H_4CH_2CN \xrightarrow{H_2O} \underline{p} - NO_2C_6H_4CH_2COOH$$

$$\xrightarrow{(NH_4)_2S_x} \underline{p} - NH_2C_6H_4CH_2COOH \xrightarrow[+Cu_2Cl_2]{\text{diazotise}} \underline{p} - ClC_6H_4CH_2COOH$$

$$\xrightarrow{CaCO_3} (\underline{p} - ClC_6H_4CH_2COO)_2\ Ca$$

100 ml. (102 gm) of redistilled benzyl cyanide (b.p.110-115°, 17 mm.) was added with stirring over a period of about 90 minutes to a mixture of 275 ml. of conc. HNO_3 and 275 ml. of conc. H_2SO_4 which had been cooled to 10° in an ice bath, the temperature being maintained between 10° - 15°. After stirring for a further one hour at room temperature, the reaction mixture was poured on to 1200 gm. of crushed ice and the slightly yellow p-nitrobenzyl cyanide which separated on standing, was filtered off. On recrystallisation from 500 ml. of absolute alcohol, 90 gm. (63.5%) of material was obtained. m.p. 108-112° (115-116).

This was then refluxed for 15 minutes with 250 ml. of water and 270 ml. of conc. H_2SO_4, diluted with an equal volume of cold water and cooled to 0°. The resulting precipitate of p-nitrophenylacetic acid was filtered off and recrystallised from hot water giving 48.5 gm. (48.5%) of acid m.p. 151 - 152° (152).

The p-nitrophenylacetic was dissolved in 250 ml. of 6N ammonia, warmed to 45° and H_2S passed in for 2½ hours, the temperature not being allowed to rise above 50°. After boiling, and removal of the precipitate of sulphur so formed, 20 ml. of glacial acetic acid was added and the crude p-aminophenylacetic acid filtered off. Recrystallisation from hot water gave 30.5 gm. (75.5%) of pale yellow flakes m.p. 199° (200).

The diazo salt of this acid was then prepared by the slow addition of 15 gm. of $NaNO_2$ to an ice-cold suspension of the acid in 60 ml. of conc. HCl + 60 ml. of water. 75 gm. $CuSO_4$ and 20 gm. NaCl were dissolved in 240 ml. of boiling water and to the hot solution was slowly added with stirring a solution of 19 gm. of sodium metabisulphite and 11 gm. NaOH in 120 ml. water. The precipitate of Cu_2Cl_2 was washed by decantation and dissolved in 120 ml. conc. HCl. The cuprous chloride solution was heated to 50° and the cold diazo solution slowly added with stirring. The crude acid was filtered off and recrystallised from hot water giving pale yellow needles. This material was finally purified by dissolving it in benzene and passing the solution through an alumina column. This gave 23 gm. (68.0%) of white p-chlorophenylacetic acid, m.p. 105° (105°).

5.000 gm. of this acid were dissolved in hot water and neutralised by the addition of 1.462 gm. of 'Analar' calcium carbonate. Pure dry calcium p-chlorophenylacetate was then obtained by evaporation, m.p. (with decomposition) 128°.

(b) Pyrolysis of Calcium p-Chlorophenylacetate

(i) 5 gm. of calcium p-chlorophenylacetate were placed in a distilling flask, connected directly to a liquid air trap, and heated gently till melting and decomposition took place. The pyrolysis residue was tarry and contained much charred carbon in addition to calcium carbonate. The distillate (1.5 gm.) was red and semi-crystalline. On recrystallisation (3 times) from petroleum ether, 1.1 gm. (30.5%) of white crystalline diparachlorobenzyl ketone was obtained.

ketone	m.p. 93°	(93°)
oxime	m.p. 135°	(135°)
semicarbazone	m.p. 118°	(118°)

(ii) As in (i). In this case the distillate was chromatographed in an attempt to isolate a specimen of dibenzyl ketone but none was detected, the product again being the di-p-chloro ketone.

(iii) 5 gm. of the salt were pyrolysed under vacuum, when 1.4 gm. of a less tarry product was obtained. Here also, only the halogenated ketone was found.

2. (a) Attempted Pyrolysis of Lithium Trimethylacetate

5.000 gm. of trimethylacetic acid (B.D.H.) and 1.813 gm. of lithium carbonate were dissolved in water and the resulting lithium trimethylacetate recovered by evaporation to dryness.

This salt was found to sublime at about 480° and on heating it strongly in a distilling flask, a small amount of decomposition took place, judging by the smell, but the products were so contaminated with undecomposed salt which had sublimed over that the experiment was abandoned.

(b) Pyrolysis of Calcium Trimethylacetate

20.000 gm. of trimethylacetic acid (B.D.H.) was dissolved in water, neutralised with 9.804 gm. of calcium carbonate (Analar) and the calcium trimethylacetate recovered by evaporation to dryness.

A trial pyrolysis was carried out using 5 gm. of this salt. It was placed in a distilling flask connected directly to a small test-tube with a side arm and heated, gently at first, till decomposition took place. About 0.25 ml. of a clear liquid distillate was obtained, accompanied by the evolution of a large quantity of an inflammable hydrocarbon. The residue consisted of carbon and calcium carbonate. The distillate gave a precipitate with 2,4-dinitrophenylhydrazine.

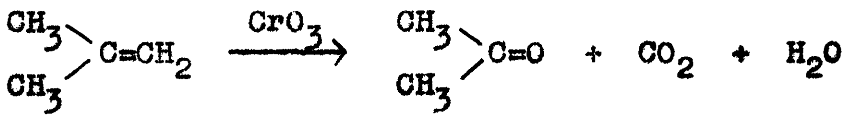
The pyrolysis was then repeated on a larger scale with a liquid air trap, to condense the hydrocarbon, connected to the exit tube of the apparatus.

(c) Examination of the Hydrocarbon

The hydrocarbon formed was shown to be unsaturated (decolourised $KMnO_4$ solution) and had the smell of isobutylene which had, as mentioned previously in Section II,2, been previously reported by Neunhoffer and Paschke (10). It was treated with a dilute chromic acid solution and, after standing for 30 minutes at room temperature, was neutralised with an excess of ferrous sulphate solution. The mixture was then steam distilled and titrated against 0.07693N NaOH solution, 0.81 ml. being required. This is of the order of the titration blank in oxidations of this type, as is seen in a later section, and it may therefore be concluded that the oxidation products do not contain an acid.

The first 100 ml. of the neutralised solution were distilled off and tested for acetone. On addition of sodium hydroxide and iodine solutions, a precipitate of iodoform was obtained. Excess iodine was removed, after acidification, by the addition of silver sulphate and the solution was then steam distilled, neutralised with NaOH and evaporated to dryness. From the salt thus obtained an S-benzyl-iso-thiuronium salt was prepared with m.p. 134° (cf. salt from acetate, m.p. 135°). A mixed melting point of these derivatives was also 134°, confirming the presence of acetic acid in the residual solution from the iodoform reaction, and hence acetone as an oxidation product. As a precaution, the unoxidised gases were tested for acetone but none was detected.

The above oxidation products, i.e. acetone and the absence of acids, confirm the formation of isobutylene in the pyrolysis of calcium trimethylacetate.



$$(CH_3)_2C{=}CH_2 \xrightarrow{CrO_3} (CH_3)_2C{=}O + CO_2 + H_2O$$

(d) Examination of the Distillate

The distillate was tested for carbonyl activity with 2,4-dinitrophenylhydrazine and a positive result was obtained. On recrystallisation, the 2,4-D.N.P. obtained had m.p. 204° and, on a second recrystallisation, 209°, which corresponds to that of trimethylacetaldehyde. An attempt was made to fractionate the original 2,4-D.N.P. by chromatography but the only band obtained was that of the 2,4-D.N.P. melting at 209°. There would appear therefore to be only the one carbonyl component in the products of the pyrolysis.

Some difficulty was experienced in obtaining a second derivative, but on pyrolysing directly into an aqueous solution of semicarbazide hydrochloride a semicarbazone was obtained which, after recrystallisation, melted at 188° (cf. trimethylacetaldehyde semicarbazone, m.p. 190°). For confirmation, a sample of trimethylacetaldehyde was synthesised, derivatives prepared and mixed melting points taken. The following were found:-

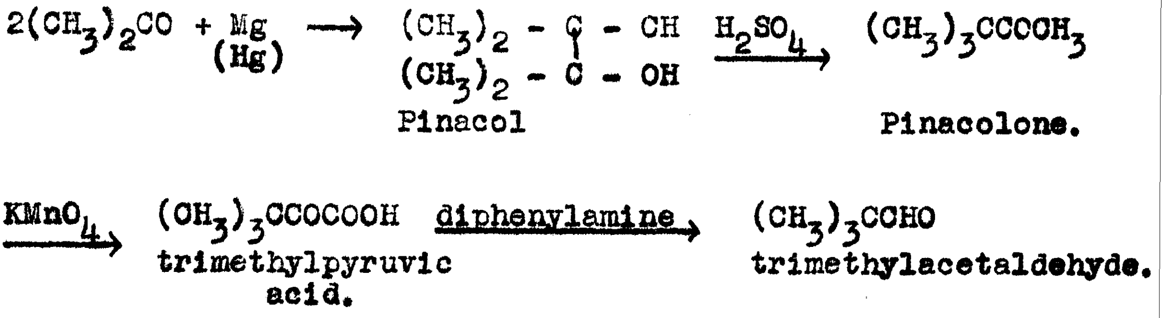
m.p. of 2,4-D.N.P. of trimethylacetaldehyde = 209°
" " " " pyrolysis product = 209°
mixed melting point = 209°

m.p. of semicarbazone of trimethylacetaldehyde = 189°
" " " " pyrolysis product = 188°
mixed melting point = 188.5°

Trimethylacetaldehyde would accordingly appear to be the principal component of the pyrolysis distillate.

(e) Synthesis of Trimethylacetaldehyde

An attempt was made to synthesise trimethylacetaldehyde by the condensation of ethyl orthoformate with the Grignard reagent prepared from *t*-butyl chloride but this proved unsuccessful and so the following method, due to Trister and Hibbert (39) was adopted.



$$2(CH_3)_2CO + \underset{(Hg)}{Mg} \longrightarrow \underset{\text{Pinacol}}{\begin{array}{l}(CH_3)_2 - C - CH \\ (CH_3)_2 - C - OH\end{array}} \xrightarrow{H_2SO_4} \underset{\text{Pinacolone.}}{(CH_3)_3CCOCH_3}$$

$$\xrightarrow{KMnO_4} \underset{\text{trimethylpyruvic acid.}}{(CH_3)_3CCOCOOH} \xrightarrow{\text{diphenylamine}} \underset{\text{trimethylacetaldehyde.}}{(CH_3)_3CCHO}$$

To 98 gm. of pinacol hydrate, prepared by condensation of acetone, was added 300 ml. of 6N sulphuric acid and the mixture distilled. The upper layer of the distillate was dried ($CaCl_2$) and distilled, the fraction 103-107° being collected. This gave 24.25 gm. (34%) of pinacolone which was then oxidised to trimethylpyruvic acid (40).

24.25 gm. of pinacolone, 75 gm. $KMnO_4$, 24 gm. NaOH and 1.5 litres of water were stirred for 4 hours at the end of which the MnO_2 was filtered off and the filtrate evaporated to 100 ml. After acidification with 150 ml. conc. HCl, the free acid was extracted with ether and vacuum distilled, giving 15 gm. (48.2%) of material b.p. 45° (5 mm.)

This, together with 7 gm. of diphenylamine was then heated with vigorous stirring to 200° so that the aldehyde was distilled out as rapidly as it was formed. The crude product was dried ($MgSO_4$), filtered and distilled, the fraction 74-78° being collected. This gave 4.6 gm. (46.5%) of trimethylacetaldehyde.

3. Pyrolyses in the Presence of Nitric Oxide.

a) Preparation of Nitric Oxide.

The nitric oxide was prepared by Winkler's method (41). A dilute solution of potassium iodide + potassium nitrite is placed in a flask fitted with a dropping tube containing 50% H_2SO_4 which is added dropwise.

$$HNO_2 + HI \longrightarrow H_2O + I + NO$$

The nitric acid thus liberated was collected by downward displacement of water. Measured quantities were then transferred, by means of a burette, to a 2 litre reservoir containing purified nitrogen, care being taken to exclude air at all times.

b) Pyrolysis Conditions and Analysis of Yields.

The apparatus used for these pyrolyses was the same as that described later in Section IV, 5b. In order that the generation of gaseous products during the pyrolyses would not take place too rapidly, and so prevent the decomposition taking place in an atmosphere containing nitric oxide, the furnace temperature was raised to just below the decomposition point and then slowly increased so that pyrolysis was complete in about 90 minutes.

Since the products formed were gaseous within the furnace, the actual composition of the pyrolysis atmosphere would be unknown. Accordingly, 1% of nitric oxide to 99% of nitrogen and 10% of nitric oxide to 90% of nitrogen were arbitrarily chosen as the compositions of the gas introduced into the pyrolysis tube. The gas mixture was passed through a P_2O_5 drying tube before entering the furnace.

The methods used to analyse the pyrolysis products were substantially the same as those described in Sections IV, 5c and IV 6b but the nitric oxide, which also was collected in the spiral liquid air traps of the apparatus, interfered with estimations of acetone by the Messinger method and accordingly had to be removed. Test estimations of acetone were carried out after refluxing with urea, but a fugitive end-point was obtained. It was found, however, that this could be avoided by making the solution alkaline, after refluxing with urea, and distilling out the acetone. No trouble with the end-point was experienced when this procedure was carried out.

Since acetone itself decomposes at the reaction temperature it was necessary to find how this decomposition was affected by the presence of nitric oxide. Known amounts of acetone were passed through the furnace under conditions identical with those of the actual pyrolyses and the amount trapped in the spirals estimated. The following results were obtained.

Acetone recovery under 1% NO = 87.24%
" " " 10% NO = 77.85%

These pyrolyses were being carried out much more slowly than those under pure nitrogen, and there is therefore more decomposition of the acetone within the furnace. On passing through acetone by itself, an average recovery of only 89.13% was obtained. In order that a comparison might be made between the yields obtained when nitric oxide is present and those when it is absent, the above values had to be corrected to give the following.

Acetone recovery under 1% NO = 98.88%
" " " 10% NO = 87.36%

All yields obtained were therefore corrected by these values.

5. Pyrolysis of Acetates.

a) Preparation of Salts for Pyrolysis.

The acetates and formates used in these pyrolyses were prepared by neutralisation of Analar glacial acetic acid and formic acid with the following salts, Analar grade being used where available:- Li_2CO_3, Na_2CO_3, K_2CO_3, $CaCO_3$, $SrCO_3$, $BaCO_3$, $ZnCO_3$, $MnCO_3$ MgO and PbO. In each case approximately 5% excess of acid was used and the required salt recovered by evaporation to dryness on a water bath. Any free acid remaining was then removed by heating in an oven at 125° for a period of 12 hours. In the case of the lead salts which tend to decompose at this temperature, heating was only to 100°.

For the pyrolysis of equimolar mixtures, weighed quantities of the respective acetates and formates were mixed, dissolved in water and evaporated to dryness on a water bath. The mixed salt was heated at 120° for several hours, then finely powdered and a known weight, usually 200-500 mg., used in each pyrolysis.

b) Method of pyrolysis and Apparatus Used.

The Pyrolyses were carried out as follows. The salt, which had been weighed into a small silica boat, was placed in a silica pyrolysis tube 20 cm. long and 1 cm. in diameter. The outlet of this tube was connected by means of standard ground joints to two spiral traps in series immersed in liquid air, and then to a bubbler which enabled the rate of flow of the nitrogen to be estimated. The tube was surrounded by a manually controlled electric furnace which was placed in position after the rest of the apparatus had been connected together. The temperature was then raised above that required for decomposition and maintained there for about 20 minutes in which time the pyrolysis was completed.

During this heating, the whole apparatus was swept out by a stream of nitrogen previously passed over copper turnings at red heat, then through a glass spiral to allow it to cool and finally through phosphorus pentoxide. This swept the volatile products into the spiral traps in which they condensed.

After the pyrolysis, the contents of the traps were allowed to warm to room temperature, there being in most cases a slight evolution of carbon dioxide. The liquid products were then washed out of the traps and their composition estimated.

c) Method of Analysis.

When acetates were pyrolysed alone, only acetone was estimated in the decomposition products and Messinger's method was used.

The acetone solution was shaken with 50 ml. of approximately normal KOH in a stoppered flask. About 40 ml. of a decinormal iodine solution was then added and the mixture shaken for ten minutes after which it was acidified with about 50 ml. of approximately normal H_2SO_4. The excess of iodine thereby liberated was titrated with decinormal sodium thiosulphate.

1 ml. Iodine solution = 0.00968 gm. acetone.

6. Pyrolysis of Acetate-Formate Mixtures.

a) Method of Pyrolysis.

These pyrolyses were carried out in the same manner and in the same apparatus as that described in the previous section (IV, 5b).

b) Analysis of Acetone-Acetaldehyde Mixtures.

The principle products of the pyrolysis of acetate-formate mixtures were acetaldehyde and acetone, with possibly the reduction products ethyl and propyl alcohol respectively (42). Since it was intended that some pyrolyses were to be carried out on isotopically labelled salts, it was necessary that a pure specimen of the acetaldehyde, or a product derived from it, could be obtained and therefore, for a method of analysis, that of selective oxidation was chosen. By this means the acetaldehyde was oxidised to acetic acid, which could be determined by titration and the salt so formed easily recovered for isotopic analysis if so required, whereas the acetone was unaffected. Any formaldehyde formed would be oxidised to carbon dioxide and water and so would not interfere with the estimations.

The method adopted was that of Adams and Nicholls (43) as modified by Bell and Reed (17) and all oxidations were carried out under the conditions recommended by the authors.

The pyrolysis distillate, made up to about 50 ml. with water, was oxidised with an equal volume of a stock oxidising mixture (10 gm. $K_2Cr_2O_7$ + 25 ml. conc. H_2SO_4 per 100 ml.) for 25 minutes. A solution containing 30 gm. of ferrous sulphate was then added and the mixture steam-distilled. The distillate was neutralised with NaOH and the acetone distilled out. It was all contained in the first 100 ml. and was estimated as previously described (Section IV, 5). Since the acetic acid, formed by oxidation of acetaldehyde, was contaminated at this stage with formic acid from the incomplete oxidation of formaldehyde, the remainder of the solution was then evaporated to small bulk and oxidised by Fouchet's method (44).

To the solution of the sodium salts was added 1.5 gm. of anhydrous sodium carbonate and 20 ml. of a 5 gm./l. $KMnO_4$ solution. This was maintained at 80° on a water bath for 30 minutes and, on cooling, 20 ml. of 50% H_2SO_4 and an excess of a ferrous sulphate solution were added. The solution was then refluxed for 15 minutes to remove carbon dioxide and steam distilled, about 250 ml. being collected. This was titrated immediately with carbonate free sodium hydroxide.

Since the above method is not quantitative on a semimicro scale, a preliminary investigation was carried out to find the efficiency of the oxidations and so obtain an empirical factor with which to multiply the results obtained.

Preparation of Materials.

Acetic Acid.

Analar acetic acid was refluxed twice for three hour periods with chromium trioxide, 1 gm. per 100 ml. of acid. The acid was then distilled, the fraction boiling between 116° and 118° being collected and cooled to 15°C. The supernatant liquid was discarded leaving glacial acetic acid.

Acetone.

The acetone was refluxed with successive small quantities of $KMnO_4$ until a violet colour persisted. It was then dried (K_2SO_4), filtered and distilled, the fraction boiling between 56-57° being collected. This was refluxed with sodium iodide (100 gm. to 440 gm. acetone) and cooled to -8°C. The crystals were filtered off and distilled giving pure acetone b.p. 56.2° (760 mm.)

Ethyl Alcohol.

Absolute alcohol was dried by Smith's method (45) as modified by Manske (46). A sample of b.p. 78.4° was collected.

Methyl Alcohol.

The methanol was refluxed with magnesium turnings and distilled, the fraction of b.p. 65° being collected.

Efficiency of Distillations.

A sample of distilled water was oxidised and distilled as described above, the following average titration blanks being obtained (0.03635N NaOH)

Blank for 1st oxidation = 1.17 ml.
" " 2nd " = 0.82 ml.

Weighed samples of acetic acid were then oxidised, distilled and estimated as described above. The average distillation loss was found to be 4.59% per distillation.

i.e. Recovery of acetic acid
after 2 distillations = 91.05%

Efficiency of Oxidations.

A series of estimations was carried out on known mixtures of acetone, ethyl and methyl alcohols, the results of which are shown in Table XXIV. Considerable difficulty was experienced in obtaining reproducible results and it was found that absolute standardisation of procedure in the $KMnO_4$ oxidation was essential, i.e. the volume of solution to be oxidised had to be exactly 50 ml. and the time of oxidation 30 minutes at 80°. Under these conditions the following average values were obtained after the two oxidations.

Recovery of ethanol (as acetic acid) = 90.67%
Recovery of acetone = 99.71%

Table XXIV

Wt. of Acetone gm.	Wt. of Ethanol gm.	Wt. of Methanol gm.	Wt. of Acetone found gm.	Wt. of Ethanol found gm.	Recovery of Acetone %	Recovery of Ethanol %
0.0282	0.0220	0.0250	0.02820	0.02009	100.0	91.32
0.0327	0.0253	0.0211	0.03250	0.02243	99.40	88.67
0.0306	0.0285	0.0294	0.03068	0.02576	100.3	90.41
0.0409	0.0292	0.0228	0.04089	0.02709	99.97	92.81
0.0262	0.0298	0.0188	0.02597	0.02726	99.12	91.49
0.0457	0.0369	0.0369	0.03670	0.03296	99.48	89.32

7. Pyrolysis of Phenylacetates

a) Preparation of Salts

Calcium, strontium and barium phenylacetates were prepared by the addition of an excess of Analar calcium, strontium and barium carbonates to a warm aqueous solution of recrystallised phenylacetic acid. Excess of the insoluble carbonate was removed by filtration of the hot solution and the desired salts were recovered by evaporation to dryness on a water bath. They were finally dried in an air oven at 120°.

For the pyrolysis of equimolar mixtures, weighed quantities of the respective acetate and phenylacetate were mixed, dissolved in water and evaporated to dryness on a water bath. After having been heated to 120° for several hours, the mixed salt was finely powdered and a known weight, usually 1.0-1.2 gm. used in each pyrolysis.

b) Method of Pyrolysis

Because of the high boiling point of the pyrolysis products, and the consequent difficulty in removing them from the pyrolysis tube, the method of decomposition under a stream of nitrogen proved unsatisfactory. It was accordingly decided to perform them under vacuum.

The salt mixture, weighed into a silica boat, was placed in a silica tube 25 cm. long and 2 cm. in diameter. This already contained a plug of glass wool to prevent the carrying over of undecomposed salt during evacuation of the apparatus. The outlet of the tube was connected by means of standard ground joints to two detachable liquid air traps in series and then to a 'Hyvac' pump. The glass joints of the apparatus were ungreased, since they had to be heated the conclusion of the pyrolysis, so that a pressure of about 1 mm. was obtainable.

The tube was heated with a manually controlled electric furnace which was heated quite quickly from room temperature to above that required for decomposition. It was maintained there for about 30 minutes, in which time pyrolysis was complete. That part of the apparatus not enclosed by the furnace was then flamed out to ensure that all the products were distilled into the liquid air traps.

c) Analysis of Products

Preliminary analysis showed that dibenzyl ketone was the only pyrolysis product containing a carbonyl group and it was therefore estimated directly in the distillate using an oxime method.

A mixture of hydroxylamine hydrochloride and the ketone was allowed to stand in a stoppered bottle at room temperature for 2 hours. The liberated HCl was then titrated with an alcoholic solution of KOH (0.3 N) using bromophenol blue as indicator. Since the ketone had been transferred directly from the liquid air trap with ether, there was an appreciable amount of yellow decomposition products (non-ketonic) also in solution. These prevented the developement of the full blue colour of the indicator being observed since the solution always appeared green. It was found however, that if water was added to the solution before titration all the yellow components remained in the ether layer allowing a good end-point to be obtained in the aqueous layer.

Trial estimations by this method are shown in Table XXVI and from these results an empirical correction factor was obtained

Indicator

This consisted of a 0.4% methanol solution of bromophenol blue (B.D.H.).

Alkali

KOH dissolved in 60% methanol to give a 0.3N solution and standardised against 0.3N HCl using bromophenol blue as indicator to full blue colour.

Hydroxylamine Hydrochloride

3.475 gm. of the pure hydrochloride, recrystallised from water, was dissolved in 95 ml. of 60% methanol, 10 drops of bromophenol blue added and the full blue colour adjusted by addition of alcoholic alkali. The solution was then made up to 100 ml. with 60% methanol.

It was desirable that the method of analysis adopted should be reasonably quick, while [illegible] the tedious methods of [illegible] [illegible] such as a fractional chromatographic [illegible] [illegible] [illegible] were not suitable and [illegible] method was therefore considered.

The [illegible] could readily be separated, [illegible] [illegible] by washing with water, and be [illegible] [illegible] method. The total [illegible] [illegible] determined by the [illegible] method, which [illegible] would give the [illegible] reaction. It also [illegible] [illegible] by Brockmann's method. [illegible] [illegible] present to be obtained by difference [illegible], trial determinations were carried out [illegible] [illegible] methods on both [illegible]

8. Pyrolysis of Acetate-phenylacetate Mixtures

a) Method of Pyrolysis

The pyrolyses were carried out in exactly the same manner as that described in the previous section (II,7b).

b) Method of Analysis of Pyrolysis Distillate

It was desirable that the method of analysis to be adopted should be reasonably quick, while remaining accurate. Thus the standard methods of estimating mixtures of ketones, such as a fractional chromatographic separation of 2,4-dinitrophenylhydrazones, were not suitable and the following method was therefore considered.

The acetone could readily be separated, either by distillation or by washing with water, and be estimated by Messinger's method. The total ketone remaining could then be determined by the oxime method and, since the methyl ketone would give the iodoform reaction, it also could be estimated by Messinger's method, allowing the amount of dibenzyl ketone present to be obtained by difference. With this in view, trial determinations were carried out by both the oxime and Messinger methods on both methyl benzyl and dibenzyl ketones. The results so obtained are given in Tables XXV - XXVIII.

Table XXV - Dibenzyl Ketone by the Oxime Method

Wt. of Ketone gm.	Wt. found gm.	% age found
0.4981	0.5090	102.2
0.5506	0.5632	102.3
0.4164	0.4247	102.0

Average found for dibenzyl ketone = 102.2 %

Table XXVI - Methyl Benzyl Ketone by the Oxime Method

Wt. of Ketone gm.	Wt. found gm.	% age found
3.1815	3.071	96.52
1.6729	1.614	96.45
2.1876	2.122	96,50

Average found for methyl benzyl ketone = 96.49 %

Table XXVII - Dibenzyl Ketone by Messinger's Method

Wt. of Ketone gm.	No. of atoms of I per molecule of ketone
0.2094	5.188
0.0707	5.157
0.0682	5.055

Average amount of iodine taken up = 5.133 I/molecule

Table XXVIII - Methyl Benzyl Ketone by Messinger's Method

Wt. of Ketone gm.	Wt. found gm.	% age found	No. of atoms of I per molecule of ketone
0.1238	0.1382	111.7	6.563
0.2931	0.3289	112.2	6.594
0.1154	0.1277	110.6	6.500
0.1299	0.1436	110.6	6.500
0.2539	0.2828	111.4	6.546

Average found for methyl benzyl ketone = 111.3 %

Average amount of iodine taken up = 6.541 I/molecule

As will be seen from Table XXVII, there was considerable iodination of dibenzyl ketone under the analysis conditions so that the method suggested above was not practicable.

The following method of analysis was therefore adopted.

The pyrolysis products were washed with ether from the liquid air traps of the pyrolysis apparatus into a distillation flask. By means of a water bath, the temperature was slowly raised to 100° and the distillate, which consisted of the ether together with all of the acetone, was collected directly in a liquid air trap. The acetone was then estimated, as before, by Messinger's method. The distillation flask was now allowed to cool and the apparatus evacuated. The water bath was again slowly raised to 50°, the distillation now taking place at a pressure of about 1 mm.

This was found to give a clean separation of the ketones. The residue, dibenzyl ketone, was estimated by the oxime method (Section IV,7c) and the distillate, methyl benzyl ketone, by Messinger's method.

A series of estimations were carried out on known mixtures of acetone, methyl benzyl and dibenzyl ketones, the results of which are shown in Tables XXIX - XXXI.

Table XXIX - Acetone

No. of Mixture	Wt. of Acetone gm.	Wt. found gm.	% age found
1	0.2635	0.2593	98.42
2	0.2820	0.2765	98.06
3	0.2654	0.2622	98.80
4	0.2129	0.2088	98.11

Table XXX - Methyl Benzyl Ketone

No. of Mixture	Wt. of Ketone gm.	Wt. found gm.	% age found
1	0.3941	0.3999	101.5
2	0.4259	0.4344	102.0
3	0.4943	0.5056	102.3
4	0.2780	0.2852	102.6

Table XXXI - Dibenzyl Ketone

No. of Mixture	Wt. of Ketone gm.	Wt. found gm.	% age found
1	0.4062	0.3800	93.56
2	0.5683	0.5389	94.84
3	0.4259	0.3947	92.66
4	0.2956	0.2764	93.48

Average found for acetone = 98.35 %
" " " methyl benzyl ketone = 102.1 %
" " " dibenzyl ketone = 93.63 %

These values were used in calculating all yields in acetate-phenylacetate pyrolyses.

c) Preparation of Materials

Acetone

The acetone was purified as described in Section IV,6b.

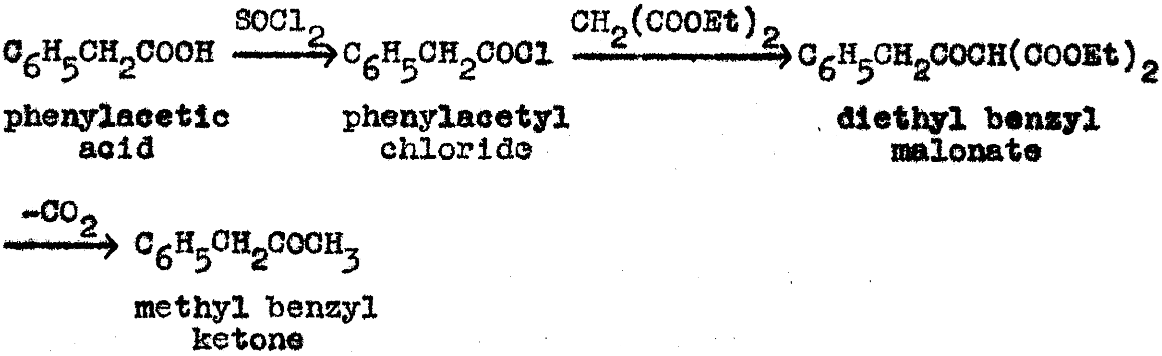
Dibenzyl Ketone

20 gm. of calcium phenylacetate were pyrolysed giving 12 gm. of crude product which was dissolved in ether, dried ($MgSO_4$) and, after removal of the solvent, fractionally distilled, that between 329° and 332° being collected. This

gave 4.65 gm. (68.5 %) of dibenzyl ketone, m.p. 34.5° (35°). Further fractionation was carried out to prepare a specimen for analysis.

Methyl Benzyl Ketone

Methyl benzyl ketone was synthesised according to the following reaction scheme (47)



$$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow{CH_2(COOEt)_2} C_6H_5CH_2COCH(COOEt)_2 \xrightarrow{-CO_2} C_6H_5CH_2COCH_3$$

phenylacetic acid
phenylacetyl chloride
diethyl benzyl malonate
methyl benzyl ketone

100 gm. of phenylacetic acid was refluxed on a water bath with 100 ml. of thionyl chloride for one hour. The mixture was then distilled, the fraction boiling between 205°- 212° being collected. The yield of phenylacetyl chloride was 51 gm. (45 %).

To 10.7 gm. of magnesium was added 10 ml. of absolute alcohol, 1 ml. of carbon tetrachloride and, after the reaction had proceeded a few minutes, 150 ml. of absolute ether. To the resulting mixture, on a steam bath, a solution of 64.4 gm. of malonic ester in 40 ml. of absolute alcohol and 50 ml. of absolute ether was added at such a rate that rapid refluxing was obtained. An ethereal solution of 51 gm. of phenylacetyl chloride was then added with vigorous stirring and the mixture refluxed for thirty minutes, it being then cooled and acidified with dilute H_2SO_4. The ether phase, with which an ether extract of the aqueous phase was combined, was washed with water and the solvent distilled off.

To the crude diethyl benzylmalonate was added a solution of 120 ml. of glacial acetic acid, 15 ml. conc. H_2SO_4 and 80 ml. of water and the mixture refluxed for 4 hours to complete the decarboxylation. The reaction mixture was chilled and extracted with ether. After drying (Na_2SO_4) and removal of the ether, the methyl benzyl ketone was distilled, the fraction 214°- 217° being collected. 31.10 gm. (70.5 %) of ketone was obtained. The melting point of this ketone is erroneously given in the literature as 27° but is in fact -15°.

This ketone was then fractionated a further three times to give a specimen for analysis.

9. (a) Attempted Synthesis of ^{13}C-carboxyl Labelled Formates

^{13}C enriched carbon dioxide, prepared by treating barium carbonate containing 66.8 % ^{13}C with an excess of conc. H_2SO_4, was bubbled gently in a stream of nitrogen through a solution containing 0.1349 gm. of NaOH. Non-enriched CO_2 was then bubbled through the solution to convert all of the hydroxide to carbonate. The $Na_2{}^{13}CO_3$ thus prepared was sealed in a Carius tube with 0.1905 gm. of sodium formate and heated at 180° for 8 hours.

An excess of baryta solution was added on cooling and the precipitate of barium carbonate filtered off. It weighed 0.2387 gm. (a 71.7% recovery) and contained 44.59% ^{13}C. The filtrate was acidified with sulphuric acid and steam distilled, the distillate being neutralised with baryta and the barium formate formed recovered by evaporation to dryness. Isotopic assay showed the ^{13}C content of this formate to be 1.210%.

b) Synthesis of ^{13}C-carboxyl Labelled Acetates

The method used was substantially the same as that recorded by Calvin et al. (33). ^{13}C enriched carbon dioxide, prepared by treating enriched barium carbonate with an excess of concentrated sulphuric acid, was distilled in a high vacuum system on to a threefold excess of previously prepared methyl magnesium iodide frozen in liquid air. After warming to -15°, the mixture was agitated to facilitate the absorption of the carbon dioxide. Nitrogen was allowed into the apparatus and a small excess of dilute sulphuric acid was added to decompose the Grignard reagent. The solution was then neutralised with NaOH and the ether removed by evaporation.

After cooling and reacidification with dilute sulphuric acid, an excess of silver sulphate solution was added, the silver iodide formed being filtered off and the filtrate steam distilled. The yields of acetic acid obtained by this method varied from 85 - 95%.

Lithium acetate was prepared by titration with lithium hydroxide solution, calcium, strontium and barium acetates by refluxing with the calculated quantity of the corresponding carbonate and magnesium acetate by refluxing with magnesium oxide. Analar materials were used where possible.

Equimolar pyrolysis mixtures were then prepared from weighed quantities of the isotopically enriched acetates and the corresponding normal formates

c) Pyrolyses in Isotopic Experiments

The pyrolyses were carried out exactly as described for non-isotopic experiments (Section IV,5a). The pyrolysis distillate was oxidised, steam distilled etc. as before and the final distillate neutralised with barium hydroxide solution. On evaporation to dryness the resulting barium acetate was recovered and retained for subsequent isotopic assay.

The carbonate residues were also assayed for ^{13}C. In the case of magnesium however, the pyrolysis residue consists of magnesium oxide and in this case the distillate from the pyrolysis was transferred from the liquid air to a Drikold - acetone bath, the carbon dioxide which evaporated being trapped and retained for isotopic analysis.

10. (a) Synthesis of ^{13}C-carboxyl Labelled Phenylacetates

A solution of benzylmagnesium chloride was prepared by standard technique (33) from 0.0818 gm. (0.00346 mole) of magnesium and 0.3958 gm. (0.00312 mole) of benzyl chloride in 3 ml. of dry ether.

Carbonation of this Grignard solution was effected at -20° with $^{13}CO_2$ generated from 0.4983 gm. (0.2528 m.mole) of ^{13}C-enriched barium carbonate. After addition of dilute H_2SO_4 to destroy the Grignard complex, the phenylacetic acid was isolated by extraction with alkali followed by acidification of the alkaline solution. The crude acid was purified by crystallisation from 5 ml. of petroleum ether (30°- 60°) giving 0.2572 gm. (75% based on $BaCO_3$) of pure acid. m.p. 75° (76°).

The enriched phenylacetic acid was then divided into three portions and excesses of calcium, strontium and barium carbonates were respectively added to these in boiling aqueous solution. The excess carbonate was filtered off and the phenylacetates recovered by evaporation to dryness.

After dilution with non-enriched material the resulting phenylacetates were intimately mixed with an equimolar amount of the corresponding acetate and about 0.5 gm. of this mixture was used in each pyrolysis, which were carried out exactly as for non-isotopic experiments.

b) Isolation of Samples for Isotopic Analysis

The mixture of ketones from the pyrolysis, which had collected in the liquid air trap of the apparatus, was preliminarily separated by the method previously described in Section IV,8b. In order to purify the fractions consisting of the methyl benzyl and the dibenzyl ketones, they were transferred with ether to 1 ml. flasks fitted with standard joints and the ether removed on a water bath.

Methyl Benzyl Ketone

The flask was connected as shown in Figure I and the apparatus evacuated.

Figure I

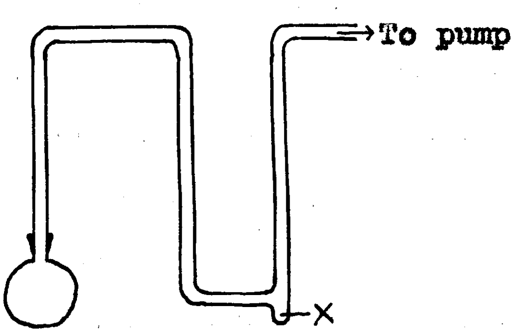
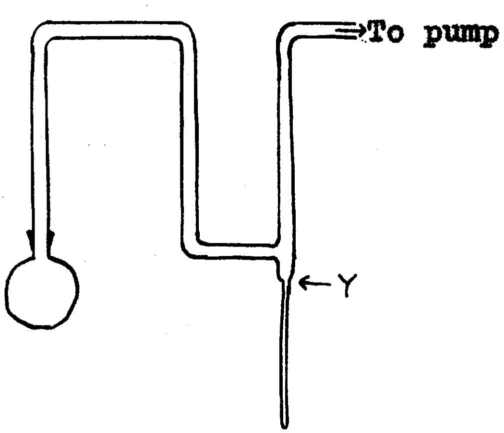


Figure II



The U-tube having been immersed in liquid air, the flask was placed in a water bath, the temperature of which was slowly raised to 50° and maintained there for ten minutes.

On removal from the liquid air trap, the methyl benzyl ketone collected at X. It was then transferred to a small glass ampule and retained for isotope assay.

Dibenzyl Ketone

The flask was connected as shown in Figure II, evacuated and heated, by means of a water bath, to 50° for ten minutes. The U-tube was immersed in liquid air and the temperature of the water bath raised to 100° for ten minutes, the dibenzyl ketone thereby being transferred to the U-tube. On removal from the liquid air and warming, the ketone collected in the capillary beneath Y, which was then sealed off at Y, and retained for subsequent analysis.

11. (a) Synthesis of ^{13}C-carboxyl Labelled Benzoates

An approximately 0.8 M solution of phenylmagnesium bromide in ether was prepared from 0.5026 gm. of bromobenzene and 0.0876 gm. of magnesium. This was carbonated at -20° with carbon dioxide generated from 0.4949 gm. of isotopically enriched barium carbonate. The reaction mixture was acidified and the organic material extracted with ether. Benzoic acid was then extracted from the ether with NaOH and reprecipitated with a slight excess of 6N HCl. This was again extracted with ether and the pure acid was recovered by evaporation to dryness. 0.1801 gm. (60% based on $Ba^{13}CO_3$) of acid was thus obtained. m.p. 122° (122°).

0.0900 gm. of this material, in aqueous solution, was neutralised with lithium hydroxide and the remainder with calcium carbonate. On evaporation to dryness on a water bath, lithium and calcium benzoates were obtained. These were then diluted with non-enriched material and intimately mixed with an equimolar quantity of the corresponding acetates.

The mixtures were pyrolysed as described for acetate-phenylacetate mixtures.

b) Isolation of Samples for Isotopic Analysis

Preliminary experiments with non-labelled material showed the yield of benzaldehyde on pyrolysis to be so small that isolation of it as such would prove very difficult. It was accordingly decided to selectively oxidise the pyrolysis products and so isolate the benzaldehyde as benzoic acid. The method due to Fouchet (44) was adopted since this converted formaldehyde to carbon dioxide and benzaldehyde to benzoic acid whereas benzophenone was untouched.

To the pyrolysis products, in about 50 ml. of water, was added 1.5 gm. of anhydrous sodium carbonate and 20 ml. of a solution containing 5 gm. of $KMnO_4$ per litre. This mixture was placed on a water bath and maintained at 80° for 30 minutes. On cooling, 20 ml. of 50% H_2SO_4 and an excess of ferrous sulphate solution were added to the solution which was then steam distilled. The distillate was neutralised with a barium hydroxide solution and evaporated to dryness in order to recover the barium benzoate.

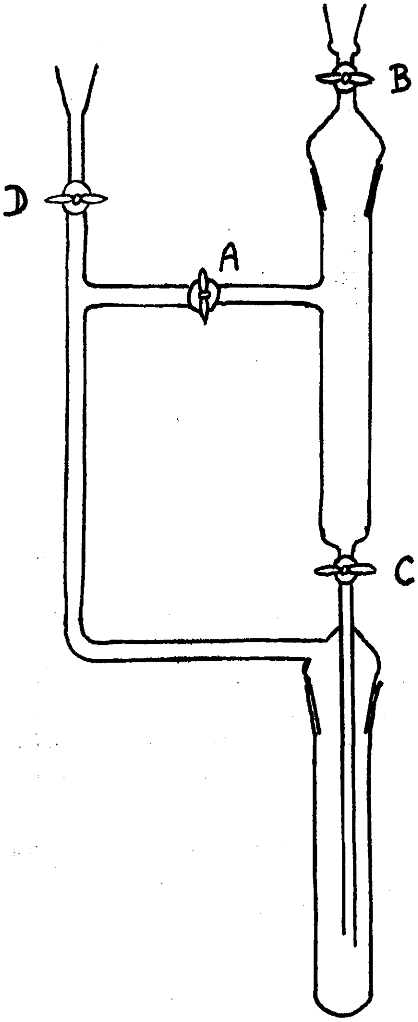
Preliminary experiments showed that 75 - 80% of the benzaldehyde could be converted to, and isolated as, barium benzoate in this manner. The barium benzoate was retained for subsequent isotopic assay.

12. Isotopic Assay

All combustions were carried out directly on the specimens obtained as previously described. The samples were converted into carbon dioxide by the wet combustion method of van Slyke and Folch (31).

A few milligrams of the sample were placed in the lower limb of the apparatus shown in Figure III.

Figure III



With tap B closed and A, C and D open, the apparatus was evacuated. Taps A and C were closed and B opened, allowing about 15 ml. of van Slyke and Folch reagent to be introduced into the upper half of the apparatus. The reagent was prepared by dissolving 25 gm. of CrO_3 and 5 gm. of KIO_3 in 167 ml. of phosphoric acid (density 1.7, made by boiling 85% phosphoric acid) and 333 ml. of fuming sulphuric acid containing 20% free SO_3.

Tap B was closed, tap A opened and the apparatus again evacuated, this time to remove any dissolved gas from the oxidising agent. After about five minutes taps A and D were closed and tap C opened, allowing most of the reagent to run on to the sample. The resulting solution was gently boiled for ten minutes, in which time all carbon present was converted to carbon dioxide. Tap A was then opened and the gas sample transferred, after drying in a Drikold-acetone trap, to a break-seal tube. This enabled the sample to be introduced directly into the mass spectrometer (Metropolitan-Vickers Ltd., Type M.S.2.).

The abundance was determined from the relative intensities of the peaks of mass numbers 44 and 45.

The following two sets of readings, chosen at random, illustrate how the abundance values, given in the tables in Section II, were obtained. They also indicate the degree of accuracy and reproducibility which may be expected. The numeral in brackets indicates the range on which the readings were taken.

Range 6 = 2 x range 7

Range 1 = 100 x range 7

Mass spectrometer scale readings with sample of CO_2 obtained by oxidation of methyl benzyl ketone

— I

Blanks:-	44	170(7)
	45	10(7)

Mass no. 44	560(1)	560	560	560	560	560	560	560
Mass no. 45	500(6)	505	505	500	500	505	505	505
	1.743	1.760	1.760	1.743	1.743	1.760	1.760	1.760

Percentage of ^{13}C present = 1.754%

— II

Blanks:-	44	170(7)
	45	0(7)

Mass no. 44	420(1)	422	420	415	422	421	420	420
Mass no. 45	380(6)	380	375	375	375	374	380	380
	1.784	1.776	1.762	1.782	1.754	1.753	1.784	1.784

Percentage of ^{13}C present = 1.772%

Mean value of ^{13}C content of methyl benzyl ketone = 1.763%

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