

253. *Isotopic Tracer Studies of Pyrolytic Reactions. Part I.
The Formation of Acetaldehyde.*

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The formation of acetaldehyde by the pyrolysis of a mixture of barium acetate and barium formate has been investigated by using an isotopic-tracer technique. It has been found that the ^{13}C content of the carbonyl-carbon atom of the acetaldehyde is approximately normal when the experiments are conducted with barium acetate having an enhanced concentration of ^{13}C in the carboxyl group. This requires the fission of the carbon-carbon bond in the acetate, and a free-radical mechanism has been suggested which is consistent with these observations.

IN describing the preparation of *n*-butyl methyl ketone by the distillation of a mixture of sodium acetate and potassium valerate, Williamson (*J.*, 1852, **4**, 228) predicted the formation of an aldehyde in the case where one of the salts used was a formate. This prediction was confirmed by Limpricht and Ritter (*Annalen*, 1856, **97**, 368), who obtained acetaldehyde from a mixture of calcium acetate and calcium formate. By similar methods Piria (*ibid.*, 1856, **100**, 104) prepared benzaldehyde and cinnamaldehyde.

The appearance of reduction products in such reactions has been reported. Thus the pyrolysis of calcium formate has been shown to yield methyl alcohol by Friedel and Silva (*Bull. Soc. chim.*, 1873, **19**, 481; *Compt. rend.*, 1873, **76**, 1545), and independently by Lieben and Paterno (*Gazzetta*, 1873, **3**, 290). Pagliani (*Ber.*, 1887, **10**, 2055; *Gazzetta*, 1878, **8**, 1) has reported the formation of ethyl alcohol as well as acetaldehyde in the products of salt pyrolysis, and in the reaction between calcium butyrate and calcium formate he obtained dipropylcarbinol and butyl alcohol as well as dipropyl ketone and propaldehyde. He also observed that the pyrolysis of calcium butyrate produced none of the carbinol but only the ketone. Further examination of the pyrolytic decomposition of calcium butyrate showed that the product consisted of a mixture of aldehydes and ketones [Soc. Lefranc et Cie., Can. P. 257 435 (1926); B.P. 216 120 (1923); U.S.P. 1 656 488 (1929); *Chem. Abs.*, 1925, **19**, 77; 1926, **20**, 2332; 1928, **22**, 965; Dépasse, *Bull. Assoc. chim. Sucr. Inst.*, 1926, **43**, 409; *Chem. Abs.*, 1927, **21**, 296; Barbiaglia and Gucci, *Ber.*, 1880, **13**, 1572; Glücksmann, *Monatsh.*, 1895, **16**, 897; Dilthey, *Ber.*, 1901, **34**, 2115].

Kenner and Morton (*Ber.*, 1939, **72**, 452) showed that lead salts of many acids decomposed at lower temperatures than the corresponding calcium salts, frequently giving a better yield of the ketone. In these studies, evidence was obtained of the accumulation in the reaction mixture of a complex which on vigorous heating gave rise to a tar. Treatment of the residue containing the complex with formic acid, however, liberated a further quantity of ketone. A theory analogous to that of the Grignard reaction was suggested to account for the behaviour of lead salts on pyrolysis.

Neunhoffer and Paschke (*Ber.*, 1939, **72**, 919) proposed a mechanism similar to the aceto-acetic ester condensation for the pyrolysis of the salts of dicarboxylic acids in which it was claimed that the reaction proceeded only when an α -hydrogen atom was available for the enolisation which was regarded as the first step in the reaction sequence. This theory was not applied to the pyrolysis of the salts of monocarboxylic acids. A detailed study of the products of the catalytic decomposition of *isobutyric* acid vapour on thoria by Cook, Miller, and Whitmore (*J. Amer. Chem. Soc.*, 1950, **72**, 2732) has been suggested by Brown (*Quart. Reviews*, 1951, **5**, 146) to support the view that reactions of this type proceed by means of free radicals.

In a review of the conditions for the pyrolysis of isotopically labelled barium acetate, Calvin, Heidelberger, Reid, Tolbert, and Yankwich ("Isotopic Carbon," 1949, John Wiley and Sons Inc., New York, p. 249) recorded that the best procedure involved sweeping out the reaction vessel with nitrogen in preference to the vacuum-distillation method. It was observed that methyl-labelled acetate on pyrolysis at 525° left about 3.5% of the methyl-carbon in the carbonate residue whereas 15% remained if the pyrolysis was carried out at 450°. Using carboxyl-labelled acetate it was shown that no carboxyl-carbon appeared in the iodoform obtained by the hypiodite reaction on the acetone formed.

In a preliminary note (Bell and Reed, *Nature*, 1950, **165**, 402) on the use of the isotopic-tracer technique in the formation of acetaldehyde by pyrolysis, it was shown that the

TABLE I.

Expt. no.	Temp. (1)	Acetate Formate (mol. ratio) (2)	Carbonyl-carbon of Ba(OAc) ₂ (3)	Carbonyl-carbon of pyrolysis mixture (4)	Residual BaCO ₃ :		Carbonyl-carbon atom		
					found (5)	calc.* (6)	CH ₂ O (7)	CMe-CHO (8)	COMe ₂ (9)
1	650°	0.2	5.45	1.85	2.19	2.18	—	0.98 †	—
2	"	0.2	2.58	1.36	1.54	1.43	—	1.08	—
3	"	0.5	4.03	2.09	2.43	2.20	—	—	—
4	"	1.0	2.97	2.05	2.31	2.22	—	0.99 †	2.18
5	480	0.2	1.45	1.17	1.20	1.20	—	1.11	1.16
6	"	0.5	1.41	1.21	1.27	1.26	1.14	1.13	1.39

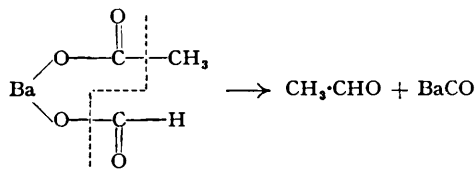
* These values were calculated from the quantity of acetaldehyde produced (determined by titration as acetic acid), on the assumption that the carbonyl groups of the acetaldehyde and formaldehyde had a normal ¹³C value, whereas that of the acetone had the same enrichment as the carboxyl-carbon atom of the barium acetate.

† Converted into *p*-nitrobenzyl acetate for combustion.

aldehyde obtained from barium acetate enriched with ^{13}C in the carboxyl group had an approximately normal isotopic enrichment value. A fuller examination of this reaction has now been carried out. In these experiments the pyrolysis of mixtures of barium acetate and barium formate yielded a mixture of volatile products, a residue of barium carbonate, and a small quantity of tar. A small volume of gas in which carbon dioxide has been detected was also produced. The volatile products consisted principally of a mixture of acetaldehyde and acetone, together with some formaldehyde and, possibly, alcohols formed by the reduction of these. No attempt was made to detect or separate any of the derived alcohols, and the method of isolation of the acetaldehyde present, that of selective oxidation, was not invalidated by their presence. The results, shown in Table I, have confirmed the fact that, where the concentration of ^{13}C in the carboxyl group of the acetate was enhanced, the isotopic ratio for the carbonyl-carbon atom of the acetaldehyde formed was approximately normal.

The enrichment of the barium carbonate residue is shown by a comparison of columns (4) and (5).

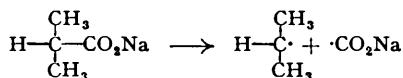
The formation of the acetaldehyde may be represented schematically as follows :



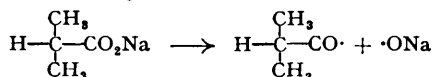
The observation that the acetaldehyde has an approximately normal ^{13}C content is clearly inconsistent with the theory that the acetaldehyde was formed by reduction of the acetate, the formate having acted as a reducing agent. Such a hypothesis would require that the carbonyl-carbon atom should have an enhanced concentration of ^{13}C , having been derived from the enriched carboxyl-carbon atom of the acetate. Moreover, as the above scheme shows, the formation of "normal" acetaldehyde must be accompanied by a separation of the methyl group from the carboxyl group.

Experiments with non-isotopic materials showed that the decomposition of barium acetate proceeded rapidly only at temperatures above 440° . In the pyrolysis of calcium acetate Ardagh, Barbour, McClellan, and McBride (*Ind. Eng. Chem.*, 1924, **16**, 1133) reported that this reaction only became rapid at temperatures around 430° although small traces of acetone were formed at temperatures as low as 160° . The high temperatures required for rapid reaction are consistent with the formation of free radicals and it is suggested that the high-temperature reaction proceeds by a chain mechanism. Such a mechanism in order to be consistent with the isotopic distribution amongst the products, must be initiated either by the formation of free methyl radicals, or by free formyl radicals. It is considered that the reaction is initiated by the free methyl radical, a view favoured by the following observations.

Cook, Miller, and Whitmore (*J. Amer. Chem. Soc.*, 1950, **72**, 2732) have reported the formation of a small quantity of *n*-propyl isopropyl ketone, in addition to the expected diisopropyl ketone, formed by passing isobutyric acid vapour over heated thoria. O'Neill and Reed (unpublished observations) have shown that pyrolysis of sodium isobutyrate, a compound which decomposes about 400° , yielded a substantial quantity of both di-*n*-propyl ketone and *n*-propyl isopropyl ketone as well as the expected diisopropyl ketone. These results can most readily be interpreted by assuming that the rearrangement occurred in an intermediate radical, and it is considered that this evidence favours the process :

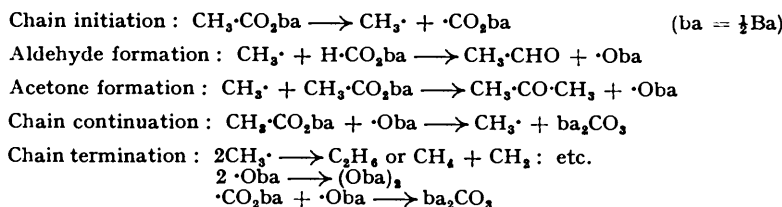


followed by rearrangement of the alkyl radical, rather than :



in which the alkyl group which undergoes rearrangement does not contain the electron-deficient centre.

A chain mechanism which is in general agreement with these results is as follows :



The relative importance of the methods of chain termination cannot be decided by the present experimental method and the above reactions have been listed as probable processes which are consonant with the remainder of the proposed mechanism.

The function of the metal is obscure, and there is no evidence to decide whether the salt reacts in the covalent form as indicated in the above reaction scheme, or whether the reaction occurs between the carboxylate ions. The former postulate is preferred as considerable evidence has been accumulated which shows that the yield of acetone varies markedly with variation of the metal even when such changes are restricted to the alkali and alkaline-earth metals (Rojan and Schulten, *Ber.*, 1926, 59, 499; Kronig, *Z. angew. Chem.*, 1924, 37, 667). Similarly no decision can be made as to the mode of formation of formaldehyde, its reduction, or decomposition products, except in so far as the high temperatures employed are again consistent with a mechanism involving homolytic fission.

Examination of the isotopic values for the carbonyl-carbon atom of the acetaldehyde shows that the value for the ^{13}C abundance is slightly lower than the usual value of 1.12%. This may be connected with the "isotope effect" (Roe and Hellmann, *J. Chem. Phys.*, 1951, 19, 660) in which at least at moderate temperatures the fission of a ^{12}C - ^{12}C bond is appreciably favoured with respect to that of a ^{12}C - ^{14}C bond. The value for the ratio of relative frequencies of fission of the two types of bond apparently depends to some extent on the reaction involved, and the usual value at room temperature is about 1.05, so that at the high temperatures used in the present experiments, where the ^{12}C - ^{13}C bond is concerned, the "isotope effect" is probably negligible. Recent work by Evans and Huston (*ibid.*, 1951, 19, 1214) suggests that the effect may, however, be operative in the combustions.

As a result of the simple theory proposed the carbonyl-carbon atom of the acetone should have the same ^{13}C content as the original acetate. The measured values for experiments (4) and (6) are of the order of magnitude expected, and the deviations are within the probable experimental error. In experiment (5), where the acetate/formate ratio is smaller, the probable error is larger since a disadvantage of the method of selective oxidation used to isolate the acetaldehyde is its failure to cause complete conversion into acetic acid. A consequence of this is that any aldehyde left unoxidised by the chromic acid appears finally along with the acetone as acetic acid.

EXPERIMENTAL

Synthesis of Carboxyl-labelled Barium Acetate.—Carboxyl-labelled barium acetate was prepared by a method substantially the same as that recorded by Calvin *et al.* (*op. cit.*, p. 178). ^{13}C -Enriched carbon dioxide, prepared by treating enriched barium carbonate with an excess of concentrated sulphuric acid, was distilled on to a calculated quantity of previously prepared methylmagnesium iodide frozen in liquid nitrogen in a high-vacuum system. The mixture was then warmed to about -15° and agitated to facilitate the absorption of the carbon dioxide. Nitrogen was passed into the system, and the reaction vessel removed. A small excess of dilute sulphuric acid was added to decompose the Grignard reagent, the solution neutralised with sodium hydroxide solution, and the ether removed by evaporation. After cooling, the solution was reacidified with dilute sulphuric acid, and an excess of silver sulphate solution added, the silver iodide formed being filtered off and the acid filtrate steam-distilled. The distillate was titrated with barium hydroxide solution, and

evaporated to dryness. The yield of barium acetate, determined by titration and weighing the residue on evaporation, varied from 68—90%.

Pyrolysis.—Weighed quantities of isotopically enriched barium acetate and normal barium formate were mixed, dissolved in a small quantity of water, and evaporated to dryness on a water-bath, and the mixed salt was heated at 120° for several hours. The dried mixture was finely powdered and a known weight, usually 200—400 mg., used in each pyrolysis.

The pyrolyses were carried out as follows. The salt mixture, in a silica boat, was placed in a silica tube 20 cm. long and 1 cm. in diameter. The outlet of the tube was connected by means of standard ground joints to two spiral traps in series immersed in liquid nitrogen, and then to a bubbler containing saturated aqueous dimedone solution. The tube was heated by means of a manually controlled electric furnace. The furnace, constructed in two sections, was brought to the required temperature and then placed in position around the silica tube. During the pyrolysis 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 the gas to cool, and finally through phosphoric oxide. The volatile products were swept into the spiral traps in which they condensed, the gases passing through the bubbler. The bubbler enabled the rate of flow of the nitrogen to be determined, this rate having been shown to have an important effect on the yield (Ardagh, Barbour, McClellan, and McBride, *loc. cit.*). The dimedone solution also made it possible to determine whether or not any aldehyde passed through the spiral traps. It was found that if the rate of flow was greatly in excess of 2 l. per hour a considerable quantity of the dimedone-aldehyde adduct was obtained. In cases where the rate of nitrogen flow was at or slightly below this figure, the precipitate was slight and as far as could be determined by m. p. and mixed m. p. determinations was the formaldehyde-dimedone derivative.

In several reactions a small quantity of tar condensed on the cooler parts of the reaction tube and did not reach the spiral traps. The bulk of this deposit was ether-soluble. In one case it was assayed for the ¹³C content and found to be slightly enriched.

The contents of the traps were allowed to warm to about 0°, there being then in most cases a slight evolution of gas. This gas was shown in two non-isotopic experiments to be carbon dioxide, giving a turbidity with lime water.

The liquid contents of the tube were washed out with a known volume of water and oxidised by a chromic acid mixture.

Oxidation.—The principal products of the pyrolyses were acetaldehyde and acetone, and possibly the reduction products ethyl and propyl alcohol respectively. The method of analysis was required to provide a pure sample of the acetaldehyde or the ethyl alcohol, or a product derived from one of these, not contaminated with acetone or with any products from the formaldehyde. The method of selective oxidation was chosen which had the advantage that the ethyl alcohol and the acetaldehyde were both oxidised to the same product, acetic acid, which could be determined by titration and the salt so formed easily recovered for isotopic analysis. The method adopted was that of Adams and Nicholls (*Analyst*, 1929, 54, 2; Nicholls, "The Determination of Alcohol," Tatlock Memorial Lecture, Royal Institute of Chemistry, 1948), whereby the formaldehyde or methyl alcohol would be oxidised to carbon dioxide and water, and the acetaldehyde or its reduction product to acetic acid. Any isopropyl alcohol formed would be oxidised to acetone whereas acetone would be unaffected. As the authors indicated, the method is not quantitative on a semi-micro-scale, and a short investigation was carried out to determine the discrepancies which would occur with such quantities as might be expected from the pyrolyses. The oxidations were carried out under the conditions recommended by the authors, as preliminary experiments showed that either increasing the strength of the oxidising mixture or lengthening the time of reaction caused a significant oxidation of the acetone.

Experiments were carried out with pure samples of methyl alcohol, ethyl alcohol, acetone, and acetic acid, each being treated separately in order to find the extent of oxidation and the loss on distillation. About 250 c.c. of the distillate were collected and titrated with carbonate-free sodium hydroxide.

The method, as shown by the results in Table 2, does not give a quantitative yield of acetic acid, and in the results listed in the discussion, the estimated yields of acetaldehyde have been corrected for this by means of an empirical multiplying factor obtained from the data described below. Another aspect to be considered was that the methyl alcohol was not oxidised quantitatively to carbon dioxide and water, and thus the acetic acid would be contaminated by formic acid. The latter acid was removed by the following procedure (Fouchet, *Bull. Soc. chim.*, 1912, 11, 325). After titration, the solution of the sodium salts was evaporated to dryness, the residue heated with alkaline permanganate on a water-bath for 30 minutes, allowed to cool, and

acidified with dilute sulphuric acid. Excess of ferrous sulphate solution was then added to destroy the permanganate, the solution refluxed to remove carbon dioxide, and steam-distilled as in the previous oxidation by chromic acid. About 250 c.c. of the distillate were collected, and again titrated with carbonate-free sodium hydroxide solution. The results of this treatment are tabulated in the last two columns of Table 2.

TABLE 2. *Efficiency of oxidations.*

Substance	Amount mmole	Oxidation by CrO_3			Subsequent oxidation by KMnO_4	
		Titre, ml.	Yield of acid,		Titre, ml.‡	Yield, %
mmol.†	%					
Titration blank	—	0.49	—	—	—	—
Acetic acid	0.119 0.457	5.17 18.90	0.114 0.447	95.8 97.8	*	—
Acetone	0.280 0.310 0.381	0.58 0.58 0.67	0.0002 0.0002 0.0004	0.07 0.07 0.14	—	—
Ethyl alcohol	0.104 0.448 0.783 0.794 0.832	4.34 16.40 30.59 28.88 30.61	0.0967 0.399 0.755 0.712 0.756	93.6 86.2 93.3 86.8 90.8	—	—
Methyl alcohol	0.144 0.156 0.175 0.203 0.297 0.586 0.818	1.71 1.84 1.81 2.23 4.44 11.54 23.05	0.0305 0.0339 0.0331 0.0436 0.0992 0.277 0.566	21.2 21.7 18.9 21.5 33.4 47.2 69.2	— — — — 0.45 1.65 1.68	— — — — nil 4.96 3.57

* Distillation loss, 3.3%.

† Yield of acid is corrected for titration blank, and loss of acetic acid in steam distillation.

‡ Titre for distillate after permanganate oxidation is corrected both for titration blank and for loss of acetic acid in steam-distillation.

A series of experiments was also carried out involving known mixtures of ethyl and methyl alcohols and acetone; the results are shown in Table 3. Each mixture was oxidised by the chromic acid method, steam-distilled, and titrated. The titrated solution was then distilled, the first 60 c.c. of distillate, which contained the acetone, being collected and reserved for further treatment. The residue was dried on a water-bath and heated with alkaline permanganate, treated as described above, and steam-distilled. This distillate contained the acetic acid which was then determined by titration. The neutralised solution was evaporated to dryness, and the resulting sodium acetate recrystallised from aqueous alcohol and retained for subsequent isotopic assay.

20 C.c. of sodium hydroxide solution were added to the distillate containing the acetone followed by 20 c.c. of *N*-iodine. The mixture was set aside for about 15 minutes and the iodoform extracted with ether. The solution was evaporated to small bulk, allowed to cool, and acidified with dilute sulphuric acid. Excess of silver sulphate was then added and the silver iodide formed filtered off. The filtrate was steam-distilled and the distillate, about 250 c.c., titrated with carbonate-free sodium hydroxide solution. In the case of isotopically enriched samples, the neutralised solution was evaporated to dryness, and the sodium acetate recrystallised from aqueous alcohol.

TABLE 3.

Acetone, mmol.	Methyl alcohol, mmol.	Ethyl alcohol, mmol.	Titre after KMnO_4 oxidation, ml.	Yield (by titration), mmol.*	Yield of EtOH as AcOH, %
0.302	0.541	0.175	7.07	0.171	97.9
0.165	0.821	0.198	7.47	0.181	91.5
0.368	0.432	0.225	7.80	0.190	84.6
0.423	0.651	0.323	10.70	0.284	87.9
0.433	0.351	0.493	17.54	0.443	89.9

* The yield is corrected for two steam-distillations and the titration blank.

An average value for the extent of the oxidation of the ethyl alcohol in these mixtures is 90.4%, and accordingly the observed titration values in the isotopic experiments were multiplied by a factor of 1.11 to give the probable quantity of acetaldehyde formed, and provide a rough value for calculation of the theoretical enrichment of the barium carbonate on the basis of the suggested mechanism. It should be noted that when the acetone and ethyl alcohol were present in nearly equal amounts, a condition frequently fulfilled in the pyrolyses, the oxidation determined by titration was close to 90.4%, so that the errors involved in these experiments were not large.

Isotopic Assay.—The combustions were carried out directly on the sodium acetate, with two exceptions in which the salt was converted into *p*-nitrobenzyl acetate. This ester was prepared by heating *p*-nitrobenzyl bromide with the sodium acetate in ethyl alcohol under reflux for about 2 hours. The mixture was evaporated to dryness and dissolved in a small quantity of light petroleum. The ester was separated from the unchanged bromide by passing this solution down a small alumina column and eluting it with light petroleum-benzene, the unchanged bromide remaining strongly absorbed at the top of the column.

All samples assayed were converted into carbon dioxide by the "wet combustion method" of van Slyke and Folch (*J. Biol. Chem.*, 1940, **136**, 509) in the type of apparatus described by Weinhouse ("Preparation and Measurement of Isotopic Tracers," Edwards, Ann Arbor, Michigan, 1946, p. 43).

The carbon dioxide samples so obtained were assayed (in part) 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.

Materials.—*Diethyl ether.* A B.D.H. sample was dried (CaCl_2 , P_2O_5 , Na wire). Samples required for Grignard reactions were distilled immediately before use.

Acetone. B.D.H. acetone was refluxed for some hours with potassium permanganate, dried (Na_2SO_4), and distilled. A sample of this was then treated with sodium iodide, and the complex formed separated by filtration and decomposed by distillation, giving material of b. p. $56^\circ/760$ mm.

Ethyl alcohol. "Absolute" alcohol was dried by Smith's method (*J.*, 1927, 1288) as modified by Manske (*J. Amer. Chem. Soc.*, 1931, **53**, 1106). A sample of b. p. 78.4° was collected.

Methyl alcohol. This was dried by refluxing it with magnesium turnings, and then distilling it. The fraction of b. p. $65^\circ/765$ mm. was collected.

Methyl iodide. This was shaken with 10% sodium carbonate, water, sodium thiosulphate solution, and finally water, dried (P_2O_5), and distilled. A fraction of b. p. $41^\circ/734$ mm. was collected.

p-Nitrobenzyl bromide. A B.D.H. sample, recrystallised from aqueous alcohol and dried (CaCl_2), had m. p. 99° .

Barium formate. A sample of 70% formic acid was steam-distilled and neutralised with aqueous barium hydroxide. The crystals formed by evaporation of this solution were twice recrystallised from small quantities of water.

Inorganic materials. These were of "AnalaR" standard where possible.

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