

*Isotopic Studies on the Formation of Ketones by the Catalytic
Decomposition of Certain Acids.*

By ROWLAND I. REED.

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Studies on ketones formed by passing the vapour of an isotopically enriched acid over suitable catalysts suggest that, in accordance with the general evidence, the reaction is essentially the breakdown of the salt initially formed.

EARLIER studies of the pyrogenetic formation of aldehydes and ketones by isotopic tracer techniques (Bell and Reed, *J.*, 1952, 1383; Lee and Spinks, *Canad. J. Chem.*, 1953, **31**, 103; *J. Org. Chem.*, 1953, **18**, 1079) have now been extended to the "catalytic" formation of ketones. This method, passage of acid vapours over a suitable catalyst, was introduced by Squibb (*J. Amer. Chem. Soc.*, 1895, **17**, 187) as an alternative method for preparing acetone. Subsequently, mixtures of acids were used to prepare unsymmetrical ketones, and catalysts other than barium and calcium carbonates (Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922, p. 839) were employed.

Experiments with [*carboxy*-¹³C]propionic acid, passed with other acids over various catalysts, have given the results shown in Table 1. Mixtures of barium phenylacetate and labelled propionate in various proportions have also been studied (see Table 2). The

TABLE 1.

Expt. no.	Temp.	$\frac{R \cdot CO_2H^a}{Et \cdot CO_2H}$ (mol. ratio)	R	Catalyst	Concn. (%) of ¹³ C in carbonyl-C			% of CO group from Et·CO ₂ H
					Et·CO ₂ H	R·COEt	R ₂ CO	
1	430.5°	1	CH ₂ Ph	ThO ₂	19.78	11.97	—	58.7
2	"	1	"	MnO	16.78	9.22	—	54.9
3	"	1	"	"	"	9.48	—	56.5
4	"	5	"	"	19.78	12.62	2.38	62.4
5	"	1	"	CaCO ₃	16.78	10.31	—	61.4
6	"	5	"	"	19.78	12.83	3.34	63.4
7	"	5	Ph ^b	"	"	1.98	1.14	3.8
8	"	10	H ^b	"	"	2.08	—	5.5
9	"	1	CH ₂ Ph	BaCO ₃	16.78	9.39	—	56.0
10	"	5	"	"	"	10.63	2.61	63.4
11	520°	"	"	"	19.78	4.66	—	19.6
12	"	"	"	"	"	4.82	—	20.6

^a This ratio is controlled by the partial vapour pressure of each component. ^b Comparable values for salt pyrolyses were obtained by Lee and Spinks (*loc. cit.*).

results show that the proportion of the carbonyl group in the benzyl ethyl ketone, derived from the propionate, is approximately constant at 60—65.8% whatever the relative proportions of the salts in the mixture. There is, moreover, no trend in the results with such a variation in the mixture.

TABLE 2. (Temperature 435–450°)

Expt. no.	Phenylacetate Propionate (mol. ratio)	Concn. (%) of ¹³ C in carbonyl-C					Yield (%) of CH ₂ Ph·COEt	% of CO group from propionate
		Pyrolysis mixture	BaCO ₃ residue	CH ₂ Ph·COEt	(CH ₂ Ph) ₂ CO	Et ₂ CO		
1	0.50	22.14	20.02	40.94	—	58.5	11.0	63.8
2	1.00	32.64	31.60	38.53	2.70	—	5.7	60
3	"	"	31.20	41.40	—	61.8	6.9	64.5
4	2.00	43.15	37.49	40.65	2.56	—	21.0	63.3
5	5.00	11.63	10.03	39.47	1.85	—	23.3	61.5

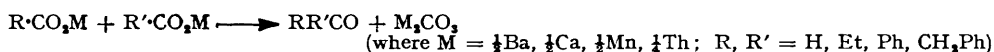
The results for the salt pyrolyses and those of the catalytic method are similar. The enrichment of the carbonyl-carbon from the preparations of propiophenone and propionaldehyde by the latter method is the same as those reported for salt pyrolyses (Lee and Spinks, *loc. cit.*). The percentage of the ketonic carbon derived from the propionyl group in the formation of benzyl ethyl ketone is constant within experimental error, whichever catalyst or method is employed.

Eadie (personal communication) has shown that the percentage of the carbonyl-carbon derived from the acid ion is likewise independent of the metal ion present in pyrolyses of the salts.

These observations, together with the previously established fact that an effective catalyst is one that is capable of forming a salt with the acid (Conroy, *Rev. gen. Sci.*, 1902, **13**, 563; Ipatieff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 514; *Abs.*, 1908, **94**, i, 386), support the view that salt formation is a preliminary step in the reaction. This is supported by the general observation that both modes of reaction occur within a similar temperature range (410–450°). Böeseken (*Rec. Trav. chim.*, 1920, **39**, 621) has reported increased yields of ketones by using the alkaline-earth oxides or carbonates as catalysts instead of the alkali-metal derivatives and this agrees with Krönig's conclusions (*Z. angew. Chem.*, 1924, **37**, 667) for salt decompositions. Bamberger's theory (*Ber.*, 1910, **43**, 3517), that reaction proceeds by alternate formation and decomposition of the anhydride, does not seem well adapted to explain ketone formation, at least in the simple systems here examined; such theories are not further considered here. Two theories have been proposed for the decomposition of salts (Bell and Reed, *loc. cit.*; Lee and Spinks, *loc. cit.*). The latter is principally concerned with ketone formation, for which an ionic mechanism is proposed. Evidence for this view is, in the present study, difficult to obtain. The decomposition of propionic acid over calcium carbonate at 440° yields small quantities of carbon monoxide, ethane, ethylene, and butane in addition to the main products, *viz.*, diethyl ketone, carbon dioxide, and water vapour. These by-products, with the exception of the last which suggests decomposition of the ketone, may be expected from the breakdown of either the acid or the ketone.

Preliminary results in a kinetic study of the formation of ketones by the pyrolysis of the salts of both mono- and di-carboxylic acids indicate mild catalysis by added carbon. A three-fold increase in velocity is the maximum that has been obtained with the catalyst and, with this present, the reactions are of an integral order with respect to the salt (Miss Thornley, personal communication). This supports an ionic mechanism, rather than a free-radical process, and is consistent with the high yield of ketone at 420–460° and with the lack of significant quantities of by-products such as might have been expected with a free-radical mechanism. In particular, no evidence has been obtained for the formation of an oxalate, which might be expected with a reaction mechanism of this type, analogous to that proposed for aldehyde formation (Bell and Reed, *loc. cit.*). Dimerisation of the postulated free radical ·CO₂M would yield oxalate, the more so since in ketone formation there is no strong reducing agent present to destroy it, as might be the case with the formate present in aldehyde formation.

The essential mechanism of the reaction may be written:



in which one molecule provides an acyl and the other an alkyl or an aryl group. In this study it was also possible that one of the reacting molecules would be in the form of a salt,

the other as an acid : this is improbable in view of the similarities already listed. There is moreover no evidence of the increased facility of reaction reported for pyrolyses of dicarboxylic acids and their salts (Kenner and Morton, *Ber.*, 1939, **72**, 452; Neunhoeffer and Paschke, *ibid.*, p. 919); and, with barium oxide as the catalyst, benzoic acid yields only the barium salt (Sabatier and Mailhe, *Compt. rend.*, 1914, **159**, 217) at 450—500°, there being no evidence of any facilitating of the reaction which occurs very slowly with this salt at 450°.

For formation of acetone from acetic acid vapour in the presence of barium or calcium carbonate, Rubinshtein and Pribythkova (*Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 917; *Chem. Abs.*, 1952, **46**, 33) adduced evidence for the intermediate formation of the appropriate salt.

EXPERIMENTAL

Barium [*carboxy*-¹³C]propionate was prepared by the method used for the acetate (Bell and Reed, *J.*, 1952, 1383) with an overall yield of 86%. The salt was mixed with an equimolecular quantity of propionic acid which was subsequently removed by distillation, providing enriched samples of both the acid and the salt.

The pyrolyses were carried out in a tube loosely filled throughout its length (7") with the catalyst. The temperature of the furnace, measured by a thermocouple in the tube, was controlled manually. The two acids were separately introduced into the tube, from small reservoirs, and allowed to mix immediately on entry. In some cases dry nitrogen was used as carrier, and in others the experiment was carried out at about 11 mm. pressure. No attempt was made to control exactly the relative amounts of each acid used; an approximate ratio was obtained by adjusting the temperature of the separate reservoirs which controlled the vapour pressure of each species. The condensable products were trapped in liquid air immediately on leaving the reaction vessel and, except in certain experiments, subsequently allowed to warm to room temperature, with the escape of the volatile material. The remaining liquid which frequently contained water was transferred to a small tube, then dried by mixing it with dry benzene and distilling this away. The residue was heated on a water-bath at 11 mm., whereupon a liquid distilled and condensed on the upper parts of the tube. This was converted into the semicarbazone which on recrystallisation yielded a pure sample of this derivative of benzyl ethyl ketone (m. p. 142—143°). In two favourable cases a preliminary distillation was carried out at normal pressures and a sample of diethyl ketone was obtained, which was converted into the semicarbazone which, on recrystallisation, had m. p. 137—138°. The residue from the reduced-pressure distillations, in nearly every case, solidified, and on recrystallisation gave pure dibenzyl ketone, m. p. 32°.

All the products were oxidised by Van Slyke and Folch's method (*J. Biol. Chem.*, 1940, **136**, 509) to carbon dioxide, which was analysed mass-spectrometrically in a Metropolitan-Vickers Ltd. Type M.S. 2 instrument.

In particular cases, by-products were analysed. Samples of propionic acid were passed over heated barium carbonate, and the issuing gases passed through a spiral trap immersed in liquid air and then into the mass-spectrometer. Under these conditions only carbon monoxide was detected. The pyrolyses were stopped, the contents of the trap warmed to the temperature of an acetone—solid carbon dioxide bath, and the liberated gases examined. Ethane was identified by the appearance of the characteristic mass spectrum (masses 26—30) together with some evidence for ethylene (26—28). On further warming of the trap in ice-salt (~ -10°), butane was also detected (masses 27, 28, 29, 41, 43). In general the quantity of by-products was small, particularly when the pyrolysis was slow. Significant concentrations occurred in the range 480—520°, and at 520° extensive decomposition of the ketone occurred.

Similar isotopic experiments were made at 500—540° to examine the possibility that a definite free-radical process might be demonstrated. The yield of ketone was however very small, that of the by-products large. Examination of the ¹³C content of the carbonyl group showed about 20% to have been derived from the propionic acid. However, in view of the multiplicity of other products, and the absence of a knowledge of the kinetic factors involved in the reaction, these results are of doubtful significance.

Materials.—Formic acid (98—100%; from B.D.H.) was dried (MgSO₄) and distilled, large head and tail fractions being rejected. Propionic acid was treated similarly, the sample collected having b. p. 139—140°/764 mm. B.D.H. samples of benzoic and phenylacetic acids were recrystallised from aqueous ethanol, acids having m. p.s 120° and 76° respectively being retained.

Barium carbonate ("AnalaR ") and calcium carbonate (powdered Iceland spar) were used as obtained. Manganous oxide was prepared from the carbonate by Vogel's method (" Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 337). Thorium oxide was prepared by heating a Hopkin and Williams sample of the hydroxide at 1100° for 3 hr.

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THE UNIVERSITY, GLASGOW.

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