[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SASKATCHEWAN]

THE MECHANISM OF THE KETONIC PYROLYSIS OF CALCIUM CARBOXYLATES[1]

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Received February 17, 1953

The production of ketones by the dry distillation of salts of carboxylic acids has been known for over a century. The mechanism of this reaction, however, has not yet been soundly established. In 1939, Neunhoeffer and Paschke (1) suggested that the first phase of the reaction may be a condensation between two moles of the salts in a manner analogous to the formation of acetoacetic esters. Similarly, Miller, Cook, and Whitmore (2) postulated an aldol-type of condensation as one of the steps leading finally to the ketone. Aside from the objection 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 from the pyrolysis of salts of aromatic acids.

Recently, Bell and Reed (3) observed an exclusive cleavage of the carbon-carbon bond in acetate when a mixture of barium acetate, enriched with C^{13} in the carboxyl group, and barium formate was pyrolyzed to give acetaldehyde. A free radical mechanism was suggested to interpret the results. However, similar tracer studies carried out in our laboratory have revealed certain points of evidence not explainable by the free radical mechanism.

Pyrolyses were carried out using mixtures of calcium acetate, labeled with C^{14} in the carboxyl group, and an equimolar quantity of unlabeled calcium benzoate, *p*-toluate, phenylacetate, or *n*-valerate, as well as carboxyl-labeled calcium benzoate and an equimolar quantity of ordinary calcium formate, acetate, or propionate. The unsymmetrical ketones and benzaldehyde obtained were converted to the corresponding semicarbazones and their radioactivity was determined. The results, shown in Table II, indicate that the ease with which the carboxyl group is lost in forming the ketone follows the order acetate > phenylacetate > valerate > formate > benzoate.

If the reaction mechanism were of the free radical type, one would expect the benzyl radical to be formed more readily than the methyl radical (4). However, the results indicate (Table II) that in the pyrolysis of a mixture of calcium acetate and phenylacetate, two-thirds of the benzyl methyl ketone obtained resulted from the loss of the carboxyl group in acetate.

A free radical mechanism also cannot account for the position of formate and benzoate in the order of ease with which the carboxyl group is lost. Since the energy of the carbon-hydrogen bond is generally known to be greater than that of the carbon-carbon bond (5), one would not expect a preference for the formation of the hydrogen radical over the phenyl radical.

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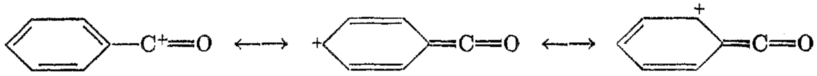
[1] Supported by the Canadian National Research Council. Presented before the Western Regional Conference, The Chemical Institute of Canada, Saskatoon, Saskatchewan, October 24–25, 1952.

It has been suggested (3, 6) that the multitude of products obtained by Miller, *et al.* (2) in the detailed study of the pyrolysis of trimethylacetic acid is evidence that free radicals are involved in the reaction. A large number of these products may be attributed, as pointed out by Miller and co-workers, to the independent decomposition of trimethylacetic acid, which may, indeed, have a free radical mechanism. The major product of the reaction is the unsymmetrical *tert*-butyl isobutyl ketone. If this main product were derived from free radical reactions, a rearrangement of a tertiary carbon radical (*tert*-butyl) to a primary carbon radical (isobutyl) is necessary. Similarly, to account for the appearance of *n*-propyl isopropyl ketone from the pyrolysis of isobutyrate (3), a rearrangement from a secondary to a primary carbon radical is required. Established rearrangements involving free radicals (7, 8), however, indicate an opposite trend in that primary radicals tend to rearrange to the tertiary state.

The great ease with which the carboxyl group is lost from acetate renders improbable any mechanism involving heterolytic cleavage of the carbon-carbon bond as a primary step in the pyrolysis because the predominance of a carbonium ion or a carbanion of the CH_3^+ or CH_3^- type is very unlikely. A carbonium ion arising from the cleavage of the carbon-oxygen bond, analogous to the positive acyl ion originally suggested to account for the cryoscopic behavior of mesitoic acid in sulfuric acid (9, 10), may be worthy of consideration as a reaction intermediate. With an aromatic acyl cation, resonance of the type



would increase the probability of its formation over that of an alkyl acyl cation such as CH_3—C^+=O. This would account for the exclusive carbon-carbon cleavage in acetate or propionate when these salts were pyrolyzed with benzoate or toluate, and the 90% carbon-hydrogen fission in formate when it was pyrolyzed with benzoate. On the basis of hyperconjugation, however, CH_3C^+=O would be expected to have a greater probability of formation than either $C_6H_5CH_2$—C^+=O or $CH_3(CH_2)_3$—C^+=O. An acyl cation intermediate coupled only with resonance interpretations thus fails to account for the preferred cleavage of the carbon-carbon bond of acetate in the pyrolytic production of benzyl methyl ketone and *n*-amyl methyl ketone.

A two-step mechanism in which an acyl cation is produced by a fairly rapid reversible process followed by a rate-controlling S_E2 type of decarboxylation (6, 11), with the acyl cation acting as the electrophilic component, may be considered.

$$\text{RCOOM} \rightarrow \text{R—C}^+\text{=O} + \text{MO}^-$$

$$\text{R—C}^+\text{=O} + \text{R'COOM} \xrightarrow{\text{slow}} \text{RCOR'} + \text{M}^+ + \text{CO}_2$$

where R and R′ may be the same or different, aliphatic or aromatic and M a metal such as calcium, barium, etc.

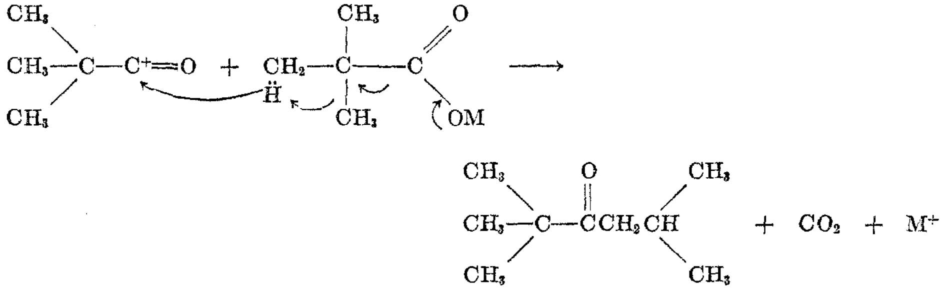
Considering first the pyrolysis of calcium acetate with calcium benzoate or toluate, it is seen that the S_E2 displacement of C_6H_5—C^+=O on calcium acetate would involve a backside attack on the methyl carbon with Walden inversion; whereas the displacement of $CH_3-C^+=O$ on calcium benzoate or toluate would, of necessity, proceed by a frontal attack on a carbon of the nucleus. These two reactions, being quite different in nature, might be expected to proceed at very different rates, and this, rather than the relative probability of formation of the two onium ions in the first step, might account for the observed exclusive carbon-carbon cleavage in acetate.

The preferred cleavage of the carbon-carbon bond of acetate in the pyrolysis with phenylacetate and *n*-valerate might be explained in terms of this mechanism on the basis of a difference in the steric factor. The attack of $CH_3-C^+=O$ on phenylacetate or *n*-valerate would be expected to have a lower entropy of activation than the alternative process involving the attack of $C_6H_5-CH_2-C^+=O$ or $CH_3(CH_2)_3-C^+=O$ on acetate, thus giving a greater rate of reaction for the latter process.

The difference in the extent of carbon-carbon cleavage of acetate in its pyrolysis with phenylacetate and *n*-valerate could be attributed to a difference in activation energy. The fission of the carbon-carbon bond in phenylacetate would be expected to require a lower energy of activation than carbon-carbon cleavage in *n*-valerate since this bond in phenylacetate is one carbon atom removed from an aromatic nucleus.[2] Moreover, the observation of Bell and Reed (3) might be similarly explained for the activation energy required for carbon-carbon cleavage in barium acetate should be lower than that for carbon-hydrogen cleavage in barium formate.

Finally, the preferred carbon-hydrogen fission in formate in the production of benzaldehyde might be attributed to the predominance of the steric factor. The favorable backside attack by $C_6H_5-C^+=O$ on formate could be of sufficient importance to overcome the greater activation energy required in breaking the carbon-hydrogen bond.

Steric considerations would also render an interpretation for the formation of the major product in the pyrolysis of trimethylacetic acid. The *tert*-butyl group may hinder the approach of the acyl cation in the S_E2 decarboxylation. A carbon atom β to the carboxyl instead of the α-carbon atom is attacked.



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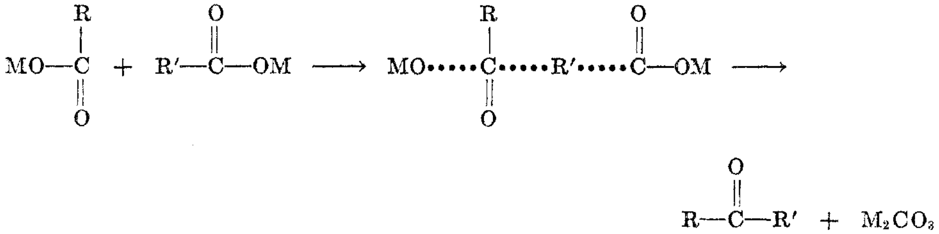
[2] *Cf.* Johnson and Heinz (12) on the effect of the aromatic nucleus on the ease of S_E2 decarboxylation.

The polar mechanism involving an acyl cation may further afford at least one explanation for the well-known fact that in the ketonic pyrolysis of salts of carboxylic acids, lithium, barium, and calcium salts proceed more smoothly than sodium or potassium salts. Relatively speaking, metals of the first group have a greater affinity for electrons than those of the latter group. The splitting off of MO^-, and hence the production of the acyl cation, is thus favored when M is one of the less basic metals.

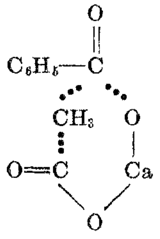
The ionic mechanism just outlined thus explains quite satisfactorily the observed experimental facts. One may, however, still be critical of it on the ground that the formation of an onium ion usually is slow compared to its subsequent reaction to give the final product. Instead of a two-stage reaction, the decarboxylation might be represented by a concerted process with the structure of the transition state shown below.



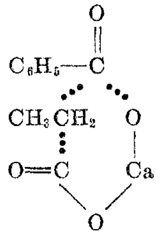
$$MO-\overset{R}{\underset{O}{C}} + R'-\overset{O}{C}-OM \longrightarrow MO\cdots\cdots\overset{R}{\underset{O}{C}}\cdots\cdots R'\cdots\cdots\overset{O}{C}-OM \longrightarrow R-\overset{O}{C}-R' + M_2CO_3$$

The reaction may involve either heterolytic or homolytic leavage of the bonds concerned.

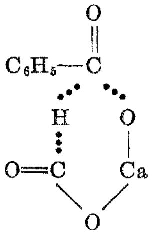
In accounting for the order of ease with which the carboxyl group is lost, the arguments presented above, based on the two-step mechanism should apply equally well to the one-step interpretation. Steric considerations would play a prominant role in the location of R and R′ in the transition state. For reactions between mixtures of aromatic and aliphatic salts of bivalent metals, an intramolecular concerted process involving transition states such as I, II, or



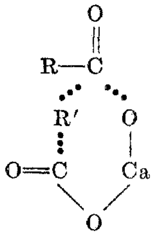
I



II



III



IV

III is particularly attractive. Similarly, steric factors would account for a predominance of CH_3 occupying the R′ position in IV in the reaction between acetate and phenylacetate or valerate. It is our belief that this intramolecular concerted process may be the most probable representation of the mechanism for the pyrolysis of calcium carboxylates.

EXPERIMENTAL

Carboxyl-labeled acetic and benzoic acids were prepared by carbonation of the corresponding Grignards with $C^{14}O_2$ (13). The calcium salts were prepared by evaporating to dryness mixtures of aqueous solutions of equivalent quantities of acid and calcium hydroxide. The pyrolyses of the mixtures of calcium salts were effected by simple dry distillation since the use of an electric furnace (3) was found to give little, if any, advantage with respect to the yield of the desired unsymmetrical ketones.

General procedure. Equimolar quantities of two calcium salts (Salt I and Salt II) were dissolved in distilled water and then evaporated to dryness to give an intimate mixture. A weighed quantity of the mixture was placed in a small distillation flask connected to an efficient condenser for downward distillation. Heat was applied by the strong flame of a Bunsen burner until no more liquid distillate was obtainable. The residual calcium carbonate was generally admixed with black carbonaceous material of decomposition. The distillate was taken up in ether, washed thoroughly with distilled water to remove acetone, dried over sodium sulfate, and treated with decolorizing charcoal. After removal of the ether, the residue was fractionated. The desired unsymmetrical ketone was collected over the accepted boiling point range, the forerun and residue being discarded. The yields are summarized in Table I.

TABLE I

YIELDS OF UNSYMMETRICAL KETONES

REACTANTS		WT. OF MIXTURE PYROLYZED, g.		TOTAL WT. OF DISTILLATE, g.		WT. OF UNSYMMETRICAL KETONE, g.	
Salt I	Salt II	Run I	Run II	Run I	Run II	Run I	Run II
$CH_3C^{14}OOM$[a]	C_6H_5COOM	4.00	4.00	1.52	1.60	0.40	0.37
$CH_3C^{14}OOM$	p-$CH_3C_6H_4COOM$	4.00	4.00	1.59	1.65	.38	.39
$CH_3C^{14}OOM$	$C_6H_5CH_2COOM$	4.00	4.00	1.88	1.92	.69	.70
$CH_3C^{14}OOM$	$CH_3(CH_2)_3COOM$	4.00	4.00	1.30	1.44	.47	.51
$C_6H_5C^{14}OOM$	$HCOOM$	6.00	6.00	1.84	2.10	.49	.52
$C_6H_5C^{14}OOM$	CH_3COOM	4.00	4.00	1.64	1.60	.58	.62
$C_6H_5C^{14}OOM$	CH_3CH_2COOM	4.00	4.00	1.88	1.86	.60	.57

[a] M = ½Ca.

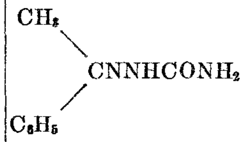
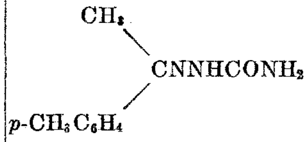
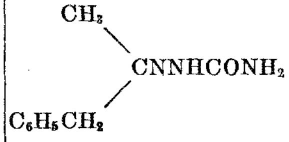
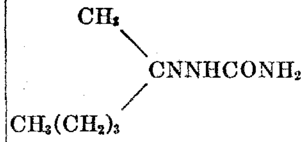
The *semicarbazones* of the various ketones obtained from the pyrolyses were prepared by treating an aqueous alcoholic solution of the ketone with a 10% excess of semicarbazide hydrochloride. After heating on the steam-bath for about 15 minutes, potassium acetate was added and the semicarbazone crystallized on cooling. After recrystallization from aqueous alcohol, the radioactivity was measured using "infinitely thick" samples of the semicarbazone with a constant geometry in a windowless gas flow counter. The radioactivity data are given in Table II.

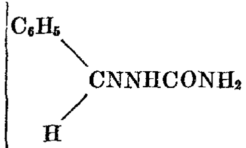
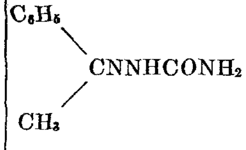
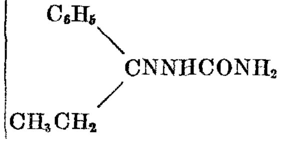
SUMMARY

The tracer technique has been applied to a study of the production of ketones from the dry distillation of calcium carboxylates. For the general reaction $RCOOM + R'COOM \rightarrow RCOR' + M_2CO_3$, the ease with which the carboxyl group is lost follows the order acetate > phenylacetate > n-valerate > formate> benzoate. A possible mechanism involving a fairly rapid formation of an inter-

TABLE II

RADIOACTIVITY OF SEMICARBAZONES

REACTANTS	COMPOUND	OBSERVED ACTIVITY,[a] counts/minute		CORRECTED ACTIVITY,[b] counts/min./mmole		% OF ORIGINAL ACTIVITY IN KETONE	
		Run I	Run II	Run I	Run II	Run I	Run II
	$CH_3C^{14}OONa$	3390 ± 22	3366 ± 22	278	276		
Acetate-C^{14} + benzoate		22.2 ± 3.8	22.8 ± 3.8	3.93	4.03	1.4	1.5
Acetate-C^{14} + *p*-toluate		19.2 ± 3.7	22.8 ± 3.8	3.67	4.36	1.3	1.6
Acetate-C^{14} + phenylacetate		484 ± 8.5	483 ± 8.5	92.5	92.3	33.3	33.4
Acetate-C^{14} + valerate		335 ± 7.2	327 ± 7.1	53.0	51.7	19.1	18.7
	$C_6H_5C^{14}OOH$	15690 ± 72	15693 ± 72	1913	1913		

Benzoate-C^{14} + formate		10630 ± 40	10880 ± 41	1732	1771	90.7	92.6
Benzoate-C^{14} + acetate		10970 ± 41	10980 ± 41	1940	1940	101.4	101.4
Benzoate-C^{14} + propionate		10100 ± 39	10190 ± 39	1930	1942	100.9	101.6

[a] At "infinite thickness". [b] Observed activity × Molecular Wt. × 10^{-3}

mediate acyl cation followed by a rate-controlling S_E2 decarboxylation between the acyl cation and a second mole of carboxylate to produce the ketone is discussed. Though the ionic mechanism explains satisfactorily the observed results, an alternative intramolecular concerted process, which also accounts for the experimental facts but without assuming the formation of any free cation, is presented as a more probable representation of the mechanism for the ketonic pyrolysis. Possible structures of the transition state, in which steric factors play a prominant role, for the concerted process are also given.

SASKATOON, SASKATCHEWAN, CANADA.

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