731. *The Formation of Ketones. Part III.* *The Pyrolysis of Sodium Acetate and Some Sodium Dicarboxylates.*

By R. I. REED and (MISS) M. B. THORNLEY.

Decomposition of the molten sodium salts of acetic and α- and β-methyladipic acid is shown to be of simple, integral kinetic order, suggesting that the reactions proceed by an ionic mechanism. There is evidence for mild catalysis by carbon in all cases. Decomposition of sodium adipate, however, has the kinetic characteristics of an autocatalytic reaction; the presence of carbon, normally a by-product, has a marked effect on the course of the reaction. The distinctive behaviour of this compound is considered to be a consequence of the physical state of the salt which only softens at reaction temperatures. Variations in the velocity constants of the decomposition of the sodium salts of acetic and α- and β-methyladipic acids support a one-stage mechanism.

THE mechanism of the pyrogenic formation of cyclic ketones, as a particular type of Claisen condensation, was proposed by Neunhoeffer and Paschle[1] from a study of the decomposition of barium and calcium adipate, and was supported by Wiberg's investigations.[2] Other theories have been discussed by the above authors, and by Kenner and Morton,[3] and Lee and Spinks.[4] Some evidence in favour of an ionic mechanism of reaction has been adduced from isotopic studies[5] on the formation of ketones by passing the appropriate acids over a suitable catalyst. Recent kinetic studies on systems of this type have led to the conclusion that a salt is first formed,[6] at least in the case of acetic acid passed over heated thoria.

The present studies, which support the view that the reaction proceeds substantially by an ionic mechanism, have been undertaken on sodium acetate and some sodium dicarboxylates. In most cases mild catalysis by carbon was found. Rate constants for sodium acetate were obtained by two methods: first, by measuring the loss in weight of a sample caused by the escape of the reaction product, acetone, and, secondly, by estimating the quantity of sodium acetate remaining at suitable intervals during the reaction (Experiments 6 and 7. Table 1). Substantial agreement was obtained between the two methods.

TABLE 1. *Pyrolysis of sodium acetate.**

No.	Temp.	$10^3 k_2'$ (mole min.$^{-1}$) †	No.	Temp.	$10^3 k_2'$ (mole min.$^{-1}$) †
1 [a]	428°	6·50 ± 0·18	5 [b]	452°	24·39 ± 0·28
2	430	6·32 ± 0·16	6 [c]	429	6·59 ± 1·3
3	440	9·97 ± 0·21	7 [d]	429	9·52 ± 2·1
4	452	15·68 ± 0·24			

* In a platinum vessel, unless otherwise stated.
† The ± figures are standard deviations.
[a] Silica reaction vessel. [b] Platinum vessel, 9·53% by wt. of added carbon. [c] Glass reaction vessel. [d] Glass reaction vessel, 10% by wt. of added carbon.

As these experiments were conducted on melts, in which condition it is not possible to vary the initial concentration of the salt, a full formal examination of the reaction order with respect to the salt was not undertaken. Within any given experiment,

* Part II, *J.*, 1954, 2148.
[1] Neunhoffer and Paschke, *Ber.*, 1939, **72**, 919.
[2] Wiberg, *J. Amer. Chem. Soc.*, 1952, **74**, 4381.
[3] Kenner and Morton, *Ber.*, 1939, **72**, 452.
[4] Lee and Spinks, *J. Org. Chem.*, 1953, **18**, 1079; *Canad. J. Chem.*, 1953, **31**, 103.
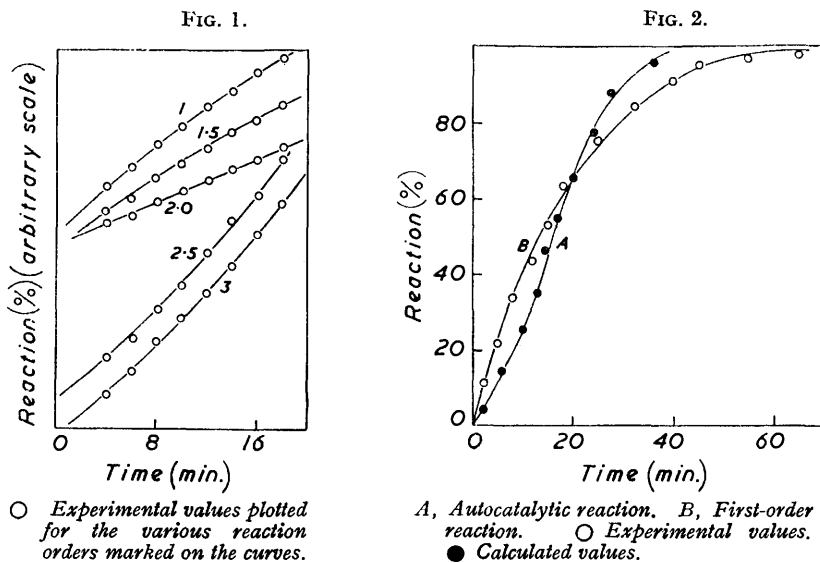[5] Reed, *J.*, 1955, 4423.
[6] Kuriacose and Jungers, *Bull. Soc. chim. belges*, 1955, **64**, 502.

however, the calculated second-order velocity constants showed good agreement with no evidence of a progressive drift in values, as is shown in Fig. 1, where the data are fitted to reaction orders of 1, 1·5, 2, 2·5, and 3 severally.

If the reaction is assumed to be between two molecules or acetate ions, its rate will be proportional to the square of the amount of reactant present. This leads to a second-order rate constant. The intramolecular decomposition of a dicarboxylate would give a first-order rate constant.

Sodium carbonate formed in the reaction does not separate, being somewhat soluble in the melt, until after ~10% reaction. When deposition does begin, however, there is no discontinuity in the reaction–time graph until the reaction is at least 75% completed.

The results show mild catalysis by added carbon, the rate being increased 1·45 and 1·56 times respectively. Further large additions of carbon did not affect this value.

FIG. 1.

FIG. 2.

O *Experimental values plotted for the various reaction orders marked on the curves.*

A, Autocatalytic reaction. B, First-order reaction. O *Experimental values.* ● *Calculated values.*

Similar studies on sodium α- and β-methyladipate which, like sodium acetate, melt before decomposition, are reported in Table 2. Arguments analogous to those used above for sodium acetate show these results to represent first-order reactions, and to support an ionic mechanism of reaction. Further it may be expected that molecules of this type would cyclise with great facility. Again mild catalysis by carbon was observed, the maximum rate increases for sodium β-methyladipate being 1·48—1·54 times.

TABLE 2. *Pyrolysis of disodium α- and β-methyladipates.**

| No.	Temp.	$10^2 k_1$ (min.$^{-1}$)	No.	Temp.	$10^2 k_1$ (min.$^{-1}$)	No.	Temp.	$10^2 k_1$ (min.$^{-1}$)
	α-Methyl derivative			β-Methyl derivative			β-Methyl derivative	
8	405°	1·12 †	12	395°	1·06 †	16	427°	8·40 †
9	410	1·67	13	410	2·89	17 ʲ	427	12·44
10	415	2·36	14 ᵉ	427	8·24	18 ʲ	427	13·01
11	419	3·15	15 ᶠ	427	8·35			

* Unless otherwise stated, a platinum bucket was used.
† The standard deviation in all cases is less than ±0·02.
ᵉ Silica vessel. ᶠ Salt mixed with 10% of sodium carbonate. Salt mixed with 11% of carbon.

It is difficult to compare directly the rate constants for the decomposition of these salts and sodium acetate because the reaction orders differ. Some comparison can however be made by deriving an initial rate for sodium acetate as the product of the velocity

constant and the initial concentration of the salt. By comparing the extrapolated value at 410° with velocity constants for the other salts at this temperature the series of relative reactivities β 2·89, α 1·67, Ac 0·42 is obtained, in accord with general theory. The dicarboxylates which yield *cyclo*pentanones are considered to cyclise very easily,[7] and a β-methyl substituent favours the process.[8]

The mechanism most recently proposed, that of Lee and Spinks,[4] seems inadequate to explain these results, depending as it does upon so many particular steric considerations, although its one-stage process seems more probable than a two-stage ionisation process. Accordingly it is suggested that a one-stage reaction of the annexed form is an adequate representation, at least on present evidence. The electron-releasing methyl group will facilitate separation of the O⁻ to complete the reaction. This would lead to a stronger effect by the α- than by the β-Me methyl group, but the influence of the latter on the molecular geometry, favouring closure, outweighs the electronic effects.
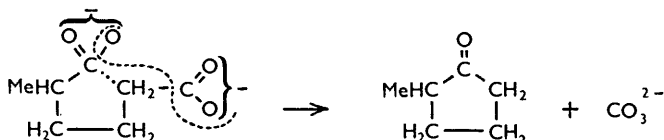
Decomposition of sodium adipate is kinetically more complex. In general the product–time graph is autocatalytic in character (Fig. 2, *A*), although exceptionally first-order graphs were obtained (Fig. 2, *B*). The autocatalytic curve *A* is resolvable into two parts, and is well represented for at least 90% of the reaction as the sum of two first-order velocity graphs, one catalysed, the other not (cf. Table 3). The catalyst, carbon, is assumed proportional to the extent of the reaction. In the presence of excess of carbon, the reaction becomes of the first order (*B*). The reaction rate was also shown to be independent of the surface of the container.

TABLE 3. *Pyrolysis of sodium adipate.**

No.	Temp.	$10^2 k_1$ (min.$^{-1}$) (uncat.) †	$10^2 k_1$ (min.$^{-1}$) (cat.) †	No.	Temp.	$10^2 k_1$ (min.$^{-1}$) (uncat.) †	$10^2 k_1$ (min.$^{-1}$) (cat.) †
19	430°	0·16	—	23	440°	1·34	4·38
20	440	1·34	3·88	24 [h]	440	1·50	3·84
21	449	3·90	7·08	25 [i]	440	1·39	3·43
22	464	6·96	14·76	26 [j]	440	—	3·08

* Unless otherwise stated, the reactions were carried out in a platinum vessel.
† Standard deviations in all cases, except No. 19 (±0·04), were less than ±0·02.
[h] Silica vessel. [i] Pyrex vessel. [j] Pyrex vessel coated with carbon.

Catalysis is rather greater than that in the previous examples and is considered a consequence of the physical state of the reacting material. Sodium adipate does not melt below the temperature of decomposition and examination of the crystals supports the conclusion that during reaction there is at most some softening, the crystals nevertheless retaining their shape. Consequently, it is considered that at least one function of the carbon present is to lower the energy necessary for the escape of the ketone from the crystal. It has not, as yet, been possible to demonstrate any other function of the carbon. Some mobility of reacting entities within crystals and across their boundaries seems necessary, however, to account for the observation that a layer of carbon on the walls of the vessel is as efficient a catalyst as a sample intimately mixed with the solid adipate.

EXPERIMENTAL

These experiments were conducted in a sodium nitrate–potassium nitrate melt, the temperature of which was thermostatically controlled. The appropriate salt was put in the bucket

[7] Bennett, *Trans. Faraday Soc.*, 1941, **37**, 794.
[8] Reed and Thornley, *J.*, 1954, 2150.

of a modified sorption balance [9] and there pyrolysed. The temperature control was based upon a mechanical lever operated by the expansion of a metal rod, and preliminary experiments showed that the temperature at the centre of the bath was constant within $0.5°$ provided the bath-liquid was rapidly stirred and the rate of heating about balanced the heat loss. The salt was contained in a shallow boat of platinum, Pyrex, or silica, and heated by a stream of nitrogen, preheated by passage through a spiral immersed in the thermostat. The progress of the reaction was followed by measuring the loss in weight of the bucket determined by the extension of a spring, which had previously been calibrated at the temperature of the experiment and was further checked by weighing the boat and contents before and after reaction. The extent of reaction was determined by titrating the residual carbonate and weighing the carbon formed.

Preliminary examination of the apparatus for heat-transport effects suggested that, provided less than 0.3 g. of material was taken, these were without effect upon the reaction velocity. Usually less than half this quantity of salt was used.

Mixtures of sodium adipate and carbonate were obtained by evaporating a solution of the mixture, drying the residue, and grinding it to a fine powder. In the case of the carbon catalyst, the required quantity of this and the salt were ground together to a fine powder.

In addition to experiments with the sorption balance, some on sodium acetate were carried out as follows.

Equal quantities of about 0.1 g. of sodium acetate were weighed out, and some samples were mixed with 10% of their weight of carbon. The samples were placed in Pyrex tubes, dried at $110°$, and sealed under a oil-pump vacuum. The pyrolyses were carried out at $428°$, tubes being withdrawn at suitable time intervals and quenched in water. This solution was made up to 100 ml. and analysed by the method of Hutchen and Kass,[10] using a Hilger " Spekker " absorptiometer: comparison of the unknown with known standards of about the same concentration was necessary for reliable results.

The results were in good agreement. Product analyses were also carried out by trapping the ketone evolved in certain experiments and preparing the 2 : 4-dinitrophenylhydrazone [11] which was then weighed. Yields of over 98% were obtained in all cases.

Materials.—Sodium adipate. Adipic acid (British Drug Houses Ltd.) recrystallised twice from water had m. p. $150°$. An aqueous solution was neutralised with a calculated amount of " AnalaR " sodium hydroxide and evaporated to dryness, the residue being powdered.

Sodium α-methyladipate. α-Methyladipic acid, the minor product from the oxidation of 3-methyl*cyclo*hexanone,[12] was repeatedly recrystallised from water (m. p. $59°$), and made into the salt as above.

Sodium β-methyladipate. β-Methyladipic acid, the major product from the above oxidation, was salted out by ammonium nitrate, repeatedly recrystallised from water (m. p. $94.5°$), and treated as above.

Carbon. Sugar charcoal was finely ground, boiled with water, filtered off, and dried. Other materials used were of the highest possible purity, " AnalaR " where possible.

[9] Reilly and Rae, " Physico-Chemical Methods," Methuen and Co., 1948, Vol. III (Supplementary), p. 267.
[10] Hutchen and Kass, *J. Biol. Chem.*, 1949, **177**, 571.
[11] Iddles and Jackson, *Ind. Eng. Chem. Anal.*, 1934, **6**, 456; Iddles, Low, Rosen, and Hart, *ibid.*, 1939, **11**, 102.
[12] Markovnikoff, *Chem. Zentr.*, 1903, **2**, 289.