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THERMAL DECOMPOSITION OF PYRUVIC ACID AND ITS ESTERS LEADING TO CO_2

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ABSTRACT

The thermal decomposition of butyl pyruvate, ethyl pyruvate, and pyruvic acid has been investigated in the temperature range 110° C to 135° C. The reaction was carried out in the presence and absence of solvents. In all cases the gaseous decomposition product was carbon dioxide. The decomposition was found to be catalyzed by glass powder and pyridine. A preliminary kinetic investigation of the decomposition of pyruvic acid in pyridine showed the reaction to be approximately second order. The results are compared with those in the literature.

THERMAL DECOMPOSITION OF PYRUVIC ACID AND ITS ESTERS LEADING TO CO_2

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In the past decade numerous experiments have been carried out to determine the extent of the "isotope effect" in decompositions involving the rupture of a C^{14}-C^{12} bond. In the last few years much work has been concentrated on determining the ratio of the isotope effect for carbon-14 and carbon-13, since this value can be predicted theoretically. In a large number of these experiments the decompositions studied have involved the decarboxylation of malonic acid or one of its derivatives.[1,2,3] So far as the author was aware, no decarbonylation reaction (i.e., removal of carbon monoxide from a molecule) had been studied in relation to a possible isotope effect. It was therefore decided to attempt to determine the possible existence of an isotope effect, and its magnitude, in a simple decarbonylation reaction.

The thermal decomposition of α-γ diketo esters proceeds with the evolution of carbon monoxide. This reaction has been used as a preparative method for some β-keto esters and acids.[4] Little work has been carried out on the thermal decomposition of α-keto esters; however, the decomposition of the simplest aliphatic α-keto ester, viz., ethyl pyruvate (and pyruvic acid itself), was investigated by Calvin and Lemmon.[5] They showed that both ethyl pyruvate and pyruvic acid underwent thermal decomposition at between 110° and 130° C in the presence of powdered glass, with the evolution of carbon monoxide. With pyruvic acid some 15% of carbon dioxide was also formed. It was shown that the carbon monoxide originated exclusively from the carboxyl group. While these workers did not investigate the kinetics of the reaction, it appeared quite possible that it was first order; the decomposition of several α-γ diketo esters has, for example, been shown to be first order.

A pyruvic ester therefore seemed a suitable material for an isotope decarbonylation study. Owing to its favorable boiling point it was decided to decompose n-butyl pyruvate. A simple synthesis of the required carboxyl-labeled butyl pyruvate was carried out, starting from carboxyl-labeled lactic acid and involving the following steps:

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1 P. E. Yankwich and M. Calvin, J. Chem. Phys. 17, 109 (1949).

2 P. E. Yankwich and A. L. Promislow, J. Am. Chem. Soc. 76, 4648 (1954).

3 P. E. Yankwich, A. L. Promislow, and R. F. Nystrom, J. Am. Chem. Soc. 76, 5893 (1954).

4 Organic Syntheses, edited by A. H. Blatt, Coll. Vol. II, New York, Wiley, 1943, p. 531.

5 M. Calvin and R. M. Lemmon, J. Am. Chem. Soc. 69, 1233 (1947).

$$CH_3CHOHC^{14}OOH \xrightarrow[H^+]{-H_2O} \text{polymer} \xrightarrow[\text{Benzene}]{\text{n-Butyl alcohol}} CH_3CHOHC^{14}OOC_4H_9,$$ [6]

$$CH_3CHOHC^{14}OOC_4H_9 \xrightarrow[H^+]{KMnO_4} CH_3COC^{14}OOC_4H_9.$$ [7]

The thermal decomposition was carried out in a small pear-shaped two-necked flask. The flask was immersed in a heated oil bath, and connected to a water-cooled condenser. Any gases liberated during the decomposition were flushed out of the flask by a slow stream of dry nitrogen. Carbon dioxide was condensed in a trap cooled in liquid oxygen, and carbon monoxide was oxidized to carbon dioxide (using heated copper oxide) and then condensed in another cooled trap.

The ester was heated for several hours at 130°C in the presence of some powdered glass. Almost no carbon monoxide was detected though a considerable quantity of carbon dioxide was evolved. Owing to a tendency for the ester to distill from the flask, condense in the water-cooled condenser, and there remain, an attempt was made to carry out the reaction in the presence of a lower-boiling solvent. Solvents tried included toluene, m-xylene, mesitylene, pyridine, and also quinoline. In all cases the gas evolved was almost exclusively CO_2.

An attempt was made to repeat the decarbonylation reported by Calvin and Lemmon (for pyruvic acid and ethyl pyruvate). Ethyl pyruvate was heated at between 120°and 130°C in the presence of powdered glass, either alone or with a solvent. In no case did the amount of carbon monoxide produced exceed a few percent of the amount of carbon dioxide evolved.

Pyruvic acid was heated in the presence of powdered glass at temperatures between 115° and 130°C. Once again, by far the major gaseous product was carbon dioxide. Decomposition of pyruvic acid was then investigated more thoroughly in the presence of pyridine as a solvent. The temperature was adjusted so that the pyridine just refluxed (about 120°C). The decomposition was carried out both in the presence and in the absence of powdered glass, and with various initial concentrations of the acid in the pyridine.

It was found that (a) the decarboxylation was catalyzed by the glass powder; (b) the decarboxylation was catalyzed by the pyridine; and (c) the initial rate of the reaction and the half-life of the reaction were dependent on the initial concentration of the acid in the pyridine.

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[6] Organic Syntheses, edited by E. C. Horning, Col. Vol. III, New York, Wiley, 1955, p. 46.

[7] W. Sakami, W. E. Evans and S. Gurin, J. Am. Chem. Soc. 69, 1110 (1947).

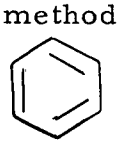
Finding (c) indicates that the reaction cannot be first order and, in fact, the dependence of the half-life of the reaction on the initial concentration was approximately that which would be expected for a second-order reaction.

In some of the pyrolyses the quantity of carbon dioxide collected corresponded to 90% decomposition of the pyruvic acid used.

It has been reported that the decarbonylation of α-γ diketo esters is catalyzed by the presence of powdered soft glass and iron powder. Accordingly pyruvic acid was heated with both powdered soft glass and iron powder (separately and together), but once again only carbon dioxide was evolved. Ethyl pyruvate behaved in a similar manner.

It has been shown that the decomposition of diphenyl triketone (diphenylpropane-1, 2, 3-trione) in the presence of aluminum trichloride gives rise to carbon dioxide unless water is rigorously excluded from the system. Under completely dry conditions carbon monoxide is produced.[8] In order to determine whether a similar effect could occur in the decomposition of ethyl pyruvate a small sample of the ester was carefully dried and placed in a pear-shaped flask. The flask had previously been dried by heating to 120°C and allowing a stream of dry nitrogen to flow through it for several hours. Under these anhydrous conditions no difference in the decomposition of either ethyl pyruvate or pyruvic acid could be detected, and again only CO_2 was evolved.

It is difficult to reconcile the results presented here with those of Calvin and Lemmon for ethyl pyruvate and pyruvic acid. Little work is reported in the literature for the thermal decomposition of simple α-keto esters. As has been mentioned, most of the work recorded is concerned with α-γ diketo esters where carbon monoxide is always evolved (though difficulty has been reported when a catalyst has not been employed). Rather more information is available for the thermal decomposition of α-keto acids themselves. Here most of the work has shown CO_2 to be the only or major gaseous product. Bouveault (1896) stated that most α-ketonic acids give good enough yields of aldehydes (by loss of carbon dioxide) on pyrolysis to make it a satisfactory method for their preparation. $\phi COCOOH$, $\phi CH_2COCOOH$, and



all lose carbon dioxide on heating.[9] An exception seems to be $(CH_3)_2CH$ COCOOH, which is reported to give rise to carbon monoxide. Pyruvic acid itself is reported to decompose slowly on boiling, with evolution of CO_2.[10] This reaction occurs much more readily in the presence of amines.[11]

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[8] J. D. Roberts, D. R. Smith, and C. C. Lee, J. Am. Chem. Soc. 73, 618(1951).

[9] C. D. Hurd, Pyrolysis of Carbon Compounds, American Chemical Monograph Series, 1929.

[10] Chemistry of Carbon Compounds, edited by E. H. Rodd, New York, Elsevier, 1951.

[11] H. Euler, H. Hasselquist, and E. Eriksson, Ann. 578, 188 (1952).

It will be seen that the results obtained in this work for pyruvic acid are in general agreement with the literature. Those obtained for ethyl pyruvate do not agree with the only reported work.[5] It appears that in the work of Calvin and Lemmon a catalyst for the decarbonylation reaction was present which did not occur in the work described herein.

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