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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BROOKLYN COLLEGE]

The Occurrence of Anhydrides in the Pyrolysis of Monocarboxylic Acids[1]

BY DAVID DAVIDSON AND PAUL NEWMAN

A number of monocarboxylic acids have been found to undergo dehydration to the corresponding anhydrides when simply refluxed at 250–350°, a detectable quantity of anhydride being formed within one minute. These results suggest that the known, exothermic hydrolysis of anhydrides is a generally reversible reaction: $(RCO)_2O + H_2O \rightleftarrows 2RCOOH + \text{heat}$.

Although the thermal dehydration of 1,2-dicarboxylic acids to anhydrides has long been a commonplace, only little information concerning a similar dehydration of monocarboxylic acids has previously been available. Thus, in 1929, Hurd[2] stated that while acetic acid is converted to acetic anhydride at elevated temperatures, "no other monobasic acid in organic chemistry behaves in this manner. . . ."

The products of the pyrolysis of monocarboxylic acids which have received frequent mention are hydrocarbons and ketones. These result from the two reactions: (1) $RCOOH \rightarrow RH + CO_2$ and (2) $2RCOOH \rightarrow R_2CO + CO_2 + H_2O$. Each of these reactions is subject to catalysis but both do not necessarily occur under the same conditions. For example, with acetic acid, ketone formation only was noted at 350° in a sealed tube (3% in 50 hours) and the conversion became quantitative when the reaction was catalyzed by sodium acetate.[3] With benzoic acid practically no change was observed at 390° in a sealed glass tube,[4] but with a zinc–copper chromite catalyst,[5] 27% decarboxylation occurred in ten hours at 250°. In quinoline solution with a copper carbonate catalyst, a 94% yield of carbon dioxide was obtained in four hours at the same temperature.[6] In the case of phenylphenylacetic acid, toluene (70% of theory) and dibenzyl ketone (10% of theory) were obtained after 15 hours heating at 340–375° in a sealed tube.[4]

At the time this study was undertaken, acetic acid remained the one case in the literature exclusive of patents in which a pyrolytic dehydration of a monocarboxylic acid to its anhydride had been reported.[7,8] A British patent[9] had also claimed the thermal dehydration of propionic and butyric acids over fireclay at 650° and a number of patents had appeared in which various catalysts, among them phosphoric acid and its salts, were used at 500–1100° for the dehydration of acetic, propionic and butyric acids.[10] Hurd,[2,8] nevertheless, considered acetic acid unique because of the possibility of its dehydration to ketene which could then react with unchanged acetic acid to form the observed anhydride. Since ketene has been obtained by the pyrolysis of acetic anhydride,[11] the assumption that these products appear in the reverse order in the pyrolysis of acetic acid may be open to question.

In the present study it was found that with monocarboxylic acids boiling between 250–350°, anhydrides can be detected[12,13] after refluxing for a minute in a test-tube without added catalysts. This has been verified with a variety of monocarboxylic acids such as benzoic, *p*-chlorobenzoic, anisic, cinnamic, α-amylcinnamic, phenylacetic, capric and myristic acids and with certain dicarboxylic acids which do not form five- or six-membered cyclic anhydrides such as adipic and azelaic acids. It thus appears that the known, exothermic hydrolysis of anhydrides[14] is actually a reversible reaction

$$(RCO)_2O + H_2O \rightleftarrows 2RCOOH + \text{heat}$$

Between room temperature and 300° the equilibrium point in this reaction may generally be so far to the right that the appearance of anhydrides on heating monocarboxylic acids in sealed tubes is likely to be overlooked. Removal of the water formed, however, whether by distillation or by refluxing with an air condenser permits extensive conversion as shown below. One case of a sealed tube experiment which seems to point to anhydride formation is that of trichloroacetic acid.[15] This monocarboxylic acid was smoothly converted to trichloroacetyl chloride in four hours at 300°.

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(1) Abstracted from a thesis by Paul Newman submitted to the Faculty of Brooklyn College in partial fulfillment of the requirements for the degree of Master of Arts, 1951.

(2) C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 333.

(3) O. Neunhoffer and P. Paschke, *Ber.*, **72**, 919 (1939).

(4) C. Engler and E. Löw, *ibid.*, **26**, 1439 (1893).

(5) C. R. Kinney and D. P. Langlois, THIS JOURNAL, **53**, 2189 (1931).

(6) M. H. Hubacher, *Anal. Chem.*, **21**, 945 (1949).

(7) E. Peytral, *Bull. soc. chim.*, **31**, 113 (1922).

(8) C. D. Hurd and K. E. Martin, THIS JOURNAL, **51**, 3614 (1929).

(9) R. Meingast and M. Mugdan, British Patent 194,719 (1923).

(10) R. Meingast and M. Mugdan, German Patents 408,715; 410,363; 417,731; 442,256 (1925); 475,885; 488,157 (1929); U. S. patent 1,570,514 (1926); H, Dreyfus, British Patents 462,714 (1937); 478,303; 478,213; 478,325 (1938); French Patents 737,610; 740,912 (1932); U. S. Patents 2,075,889; 2,081,988 (1937); 2,098,334 (1938); 2,160,840; 2,160,841 (1939); 2,202,046 (1940); 2,278,537 (1942); D. C. Hull, U. S. Patent 2,249,527 (1941); J. Maseré and A. Krawezinski, German Patent 742,244 (1943); J. E. Bludworth, M. O. Robeson and H. A. Truby, U. S. Patent 2,439,416 (1948).

(11) N. T. M. Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907).

(12) α-(*p*-Nitrobenzoyl)-amino-α-toluic acid in pyridine solution gives a blue color with anhydrides (other than five- or six-membered cyclic anhydrides) due to its conversion to the corresponding azlactone.

(13) A. W. Ingersoll and R. Adams, THIS JOURNAL, **44**, 2930 (1922).

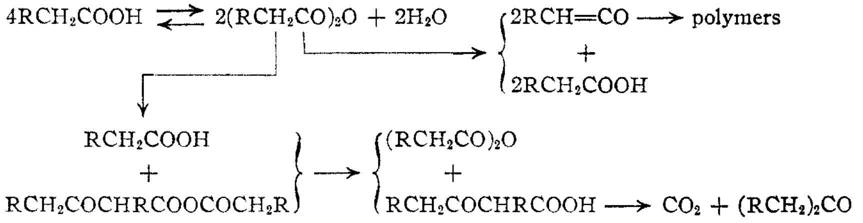
(14) J. B. Conn, G. B. Kistiakowsky, R. M. Roberts and E. A. Smith, THIS JOURNAL, **64**, 1747 (1942).

(15) C. Engler and M. Steude, *Ber.*, **26**, 1443 (1893).

The over-all reaction was confirmed to be: $2CCl_3COOH \rightarrow CCl_3COCl + CO_2 + CO + 2HCl$. In the light of the results reported in this paper the following course of events may be suggested.

$$2CCl_3COOH \rightleftarrows (CCl_3CO)_2O + H_2O$$
$$H_2O + CCl_3COOH \longrightarrow 2HCl + ClCOCOOH$$
$$ClCOCOOH \longrightarrow CO + CO_2 + HCl$$
$$(CCl_3CO)_2O + HCl \rightleftarrows CCl_3COOH + CCl_3COCl$$

Since benzoic acid, for which there is no related ketene, readily undergoes thermal dehydration to its anhydride, ketene need no longer be considered a necessary intermediate in the conversion of acetic acid to acetic anhydride. Furthermore, the case of phenylacetic acid appears to indicate the contrary; *i.e.*, that ketenes are formed, where possible, as a secondary product resulting from the pyrolysis of the anhydride.[16-18] Another possible fate of the anhydride may be its conversion to a ketone, presumably through an aldol condensation which is catalyzed by bases[4,19,20] or acids.[21] The related ketones could not be detected on heating monocarboxylic acids under the conditions employed in the present study but in the case of adipic acid, polymeric anhydride and ketone (cyclopentanone) appeared simultaneously although ultimately ketone formation is said to be practically quantitative.[3] The several transformations mentioned above are summarized in the scheme.



That part of the scheme which involves mixed anhydrides of β-ketoacids is supported by a recent patent.[22]

Experimental

The Pyrolysis of Monocarboxylic Acids.—A known weight (2.5–10.0 g.) of the carboxylic acid was refluxed in an 8 × 1-inch test-tube clamped vertically over a small gas flame. A constant immersion thermometer was placed in the liquid. At the end of the desired heating period the residue was cooled, dissolved in a minimum amount of methanol and the resulting solution treated successively with half an equivalent of aniline, a sufficient amount of 3 *M* sodium hydroxide to render the mixture basic to litmus and finally with water until no further precipitation occurred. If the anilide appeared as an oil, the mixture was chilled for several hours or allowed to stand overnight. The precipitate was then filtered by suction, washed with water and air dried. When tested with pure benzoic anhydride this method gave a 95% yield of benzanilide. The results obtained with several acids are given in Table I. In all cases the anilides had melting points corresponding with the literature. Adipic acid, under these conditions, yielded the dianilide, indicating the formation of polymeric adipic anhydride.[23]

TABLE I

THE CONVERSION OF CARBOXYLIC ACIDS TO ANHYDRIDES BY HEATING

Acid employed	Boiling time, min.	B.p., °C.	Conversion to anhydride, %
Cinnamic	1	297	2
	2	299	4
	4	301	5
Hydrocinnamic	15	301	8
	30	305	20
	60	310	30
Phenylacetic	15	264	5
	30	265	17
	60	266	19
Myristic	3	332	4
(Armour's	6	337	19
Neo Fat 13)	12	343	30
Benzoic	720	262	17
	1440	267	38
	2880	278	50
Adipic	1	334	5
	2	336	7
	4	338	6

Discussion

The ease with which most of the carboxylic acids mentioned above undergo thermal dehydration appears astonishing in view of the generally existing impression of the stability of these substances. Two types of behavior may be differentiated. One type is exemplified by phenylacetic acid in which the yield of anhydride appears to pass through a maximum well below 100%. This may be ascribed to the known instability of phenylacetic anhydride[16,19] at the prevailing temperatures. If the heating is continued beyond the time given in Table I, dark, oily, neutral decomposition products interfere with the anilide method of determining the anhydride content, but the maximum appears after about two hours heating at about 25% of theory of anhydride. The second type is exemplified by benzoic acid, the anhydride of which is sufficiently stable so that almost complete conversion to the anhydride may be effected.

The mechanism of this dehydration of carboxylic acids to anhydrides is likely to be analogous to the esterification of a carboxylic acid by an alcohol.[24] The relatively slow rate of dehydration of benzoic acid as compared with phenylacetic acid is consistent with such an hypothesis.

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[16] P. Kalnin, *C. A.*, **26**, 1806 (1932).

[17] C. D. Hurd, R. Christ and C. L. Thomas, THIS JOURNAL, **55**, 2589 (1933).

[18] C. J. Miller and B. E. Sorenson, U. S. Patent 2,465,337 (1949).

[19] C. D. Hurd and C. L. Thomas, THIS JOURNAL, **58**, 1240 (1936).

[20] R. G. Curtis, A. G. Dobson and H. H. Hatt, *J. Soc. Chem. Ind.*, **66**, 402 (1947).

[21] F. S. Kipping, *J. Chem. Soc.*, **57**, 532, 980 (1890).

[22] H. J. Hagemeyer, U. S. Patent 2,476,859 (1949).

[23] J. W. Hill, THIS JOURNAL, **52**, 4110 (1930). The quantity of dianilide obtained corresponds to one-fourth of the adipic anhydride units in the polymer.

[24] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 357.