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## The Occurrence of Anhydrides in the Pyrolysis of Monocarboxylic Acids<sup>1</sup>

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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:  $(\text{RCO})_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{RCOOH} + \text{heat}$ .

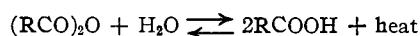
Although the thermal dehydration of 1,2-dicarboxylic acids to anhydrides has long been a commonplace, only little information concerning a similar dehydration of monocarboxylic acids has previously been available. Thus, in 1929, Hurd<sup>2</sup> stated that while acetic acid is converted to acetic anhydride 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)  $\text{RCOOH} \rightarrow \text{RH} + \text{CO}_2$  and (2)  $2\text{RCOOH} \rightarrow \text{R}_2\text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ . 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.<sup>3</sup> With benzoic acid practically no change was observed at 390° in a sealed glass tube,<sup>4</sup> but with a zinc-copper chromite catalyst,<sup>5</sup> 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.<sup>6</sup> 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.<sup>4</sup>

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.<sup>7,8</sup> A British patent<sup>9</sup> 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.<sup>10</sup> Hurd,<sup>2,8</sup> 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,<sup>11</sup> 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<sup>12,13</sup> 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,  $\alpha$ -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<sup>14</sup> is actually a reversible reaction



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.<sup>15</sup> 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.

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

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(9) R. Meingast and M. Mugdan, *British Patent* 194,719 (1928).

