290. *Quantitative Studies of the Reactivities of Mixed Carboxylic Anhydrides. Part IV.* The Hydrolysis and Decomposition of Acetic Formic Anhydride.*

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The hydrolysis of acetic formic anhydride in acetone–water and its decomposition into acetic acid and carbon monoxide in toluene have been studied kinetically. The hydrolysis is over 100 times faster than that of acetic anhydride in the same medium, in agreement with the principles previously established concerning the effect of structure on the reactivity of mixed carboxylic anhydrides (Part III). The hydrolysis is catalysed by pyridine. The decomposition of acetic formic anhydride is catalysed by heterocyclic tertiary amines, the order of their activity being the same as that for the catalysed hydrolysis of acetic anhydride. The mechanism of the reactions is discussed.

ACETIC FORMIC ANHYDRIDE was first reported and studied by Béhal (*Compt. rend.*, 1899, **128**, 1460; *Ann. Chim. Phys.*, 1900, **20**, 417) who found that it acted as formylating agent towards alcohols and ammonia. It has recently been shown that reaction with aniline (Hurd and Roe, *J. Amer. Chem. Soc.*, 1939, **61**, 3355) and with nitro-alcohols (Hurd, Drake, and Fancher, *ibid.*, 1946, **68**, 789) under mild conditions also leads to the exclusive formation of formyl derivatives. At elevated temperatures (above 50—60°), or in the presence of sulphuric acid, acetyl derivatives are obtained but it seems possible that reaction under these conditions involves decomposition of the mixed anhydride. The formation, under normal conditions, of formyl rather than acetyl derivatives is in accord with the analysis of the factors governing the acylation product ratio given in connection with the study of mixed anhydrides of acetic acid and chloro-aliphatic acids, according to which electronic and steric effects play rôles of comparable importance (Part III *). This analysis has more recently been shown to predict correctly the acylating action of mixed anhydrides of *N*-substituted amino-acids with aliphatic acids (Vaughan and Osato, *ibid.*, 1951, **73**, 5553). In the case of acetic formic anhydride the electronic and steric effects should reinforce each other in favouring formylation relative to acetylation, as is indeed found. The above principles also predict that acetic formic anhydride should be more reactive towards water, amines, and alcohols. This is now confirmed experimentally for the hydrolysis. Acetic formic anhydride is found to hydrolyse over 100 times more rapidly than acetic anhydride in 80% acetone–water. In a dilatometric study of the effects of salts of aliphatic acids on the rate of hydrolysis of acetic anhydride Kilpatrick (*ibid.*, 1928, **50**, 2891) discovered an abnormally large positive catalysis by formate ions and suggested that this was due to the intermediate formation of acetic formic anhydride. Our observation on the reactivity of this substance towards water are not compatible with this hypothesis.

Mixed anhydrides of formic acid are in a special position with regard to the disproportionation reaction (formation of the two symmetrical anhydrides from a mixed anhydride). Since the anhydride of formic acid—if it exists under any feasible conditions—is not stable by itself or in solution at room temperature, the disproportionation is not detectable as such but instead carbon monoxide is formed. A study of this reaction seemed relevant to the elucidation of the problems discussed in the preceding paper. Several qualitative observations are on record that some of the amines which we have found to be catalytically active for acylation reactions of acetic anhydride will also catalyse this decomposition. This seems to be a catalysed reaction of an acid anhydride which does not involve another reagent molecule and indirectly supports the hypothesis that the operation of catalysis in acylation by anhydrides is concerned with action on the anhydride rather than on the water or amine molecule being acylated. However, the observations in the literature (Béhal, *loc. cit.*; Schierz, *J. Amer. Chem. Soc.*, 1923, **45**, 455) are slightly contradictory and

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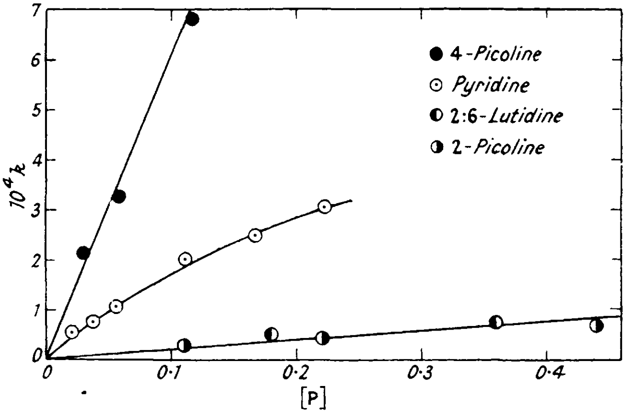
* Part III, *J.*, 1950, 1455.

altogether insufficient to assess the extent of the suspected parallelism between the catalyses in the two reactions.

The results now reported demonstrate that—within the experimental limits—the order of efficiency of pyridine and its homologues in catalysing the decomposition of acetic formic anhydride (see Figure and Table 3) is also the order for the catalysis of the hydrolysis of acetic anhydride. This sequence of catalytic efficiencies differs from the order of the basic dissociation constants of the amines or from the sequence of their catalytic efficiencies for reactions initiated by a rate-determining proton transfer from the substrate to the catalyst (such as the decomposition of nitramide). It has been suggested (preceding paper) that the catalytic efficiency of the amines in the hydrolysis reaction is markedly affected by the steric requirements of a reaction of the catalyst molecule. In view of the close similarity of the results for the hydrolysis and the decomposition it seems reasonable to infer that the catalytic action is similar in the two cases and that it consists in an association between the amine and the whole or part of an anhydride molecule.

The formation of symmetrical formic anhydride, or its catalysed decomposition, is unlikely to be a slow step in the reaction scheme, since the reaction would then have to follow second-order kinetics with respect to anhydride. The range of initial concentration of anhydride over which the reaction has been studied is not extensive but the experiments give no indication of a reaction order greater than unity with respect to acetic formic anhydride. The simplest mechanism in accord with these observations is closely analogous to that suggested for the catalysed hydrolysis of acetic anhydride, involving a rate-determining acylium-group transfer from anhydride to base followed by breakdown of the complex formed :



Catalytic effect of tertiary amines on the decomposition of acetic formic anhydride.

$$CH_3{\cdot}CO{\cdot}O{\cdot}CHO + P \longrightarrow [P{\cdot}CHO]^+ + OAc^- \longrightarrow PH^+ + CO + OAc^-$$

The second reaction in this scheme may be the unimolecular decomposition of $[P{\cdot}CHO]^+$ or involve more complicated steps. However, the reaction order requires that these cannot be kinetically significant.

The absence of detectable formation of carbon monoxide during the catalysed hydrolysis of acetic formic anhydride indicates that, in 80% acetone–water, the reaction of the complex with water is much more rapid than its decomposition.

EXPERIMENTAL

Acetic formic anhydride was prepared by passing excess of keten into pure formic acid (100 g.) at ~ −10° (Hurd and Roe, *loc. cit.*). The product was twice fractionated under reduced pressure, and 41 g. of a middle fraction (b. p. 25·5—26·5°/10 mm.) were collected for kinetic experiments and stored at a temperature of 0°. The following determinations were carried out: (1) the acid produced on complete hydrolysis; (2) the acid produced on reaction with dry aniline at 0°; (3) the volume of carbon monoxide evolved on catalysed decomposition with pyridine. From these analyses it was found that the product was 95—96% pure, the most likely impurity remaining after careful fractionation being acetic acid.

The catalytic amines were the specimens used in the work of the preceding paper. "AnalaR" toluene was used as solvent without further purification.

The purification and preparation of the other solvents and reagents have been described in the preceding paper.

Hydrolysis velocities were determined chemically by adaptation of the method previously described (Emery and Gold, *J.*, 1950, 1447; Bafna and Gold, *J.*, 1953, 1406). The uncatalysed hydrolyses strictly obeyed a first-order law. First-order rate coefficients for the catalysed reactions varied with time, and the values quoted refer to the rate after one half-life of reaction. Evolution of carbon monoxide was not observed in any of these experiments.

The velocity of the catalysed decomposition was determined by measuring the rate of evolution of carbon monoxide from the solution. The anhydride was weighed into a solution of the catalyst which was contained in a cylindrical Pyrex vessel (100 ml.). The vessel was vigorously shaken at a constant rate throughout the reaction and was connected to a nitrometer in which the volume of liberated carbon monoxide was measured. For the more rapid decompositions the anhydride was added to the solvent in a sealed capsule which was broken by shaking after isolation of the apparatus from the atmosphere.

The results are tabulated.

TABLE 1. *Spontaneous hydrolysis of acetic formic anhydride.* [Anhydride]$_0$ ~0·06M.

Solvent	Temp.	10^4k_1 (sec.$^{-1}$)	E (kcal.)	Frequency factor (sec.$^{-1}$)
80% Acetone–water (w/w) ...	0·00°	1·91	10·8	8·1 × 10^4
	20·01	7·52		
50% Acetone–water (w/w) ...	0·00	38·7		

TABLE 2. *Pyridine catalysis of the hydrolysis of acetic formic anhydride.*

Temp. = 0·00°. Solvent = 80% acetone–water (w/w)

[Anhydride]$_0$ (M)	0·0607	0·0601	0·0606	0·0611	0·0603
10^3 [Pyridine] (M)	—	1·66	3·32	5·38	8·50
10^4k_{HL} (sec.$^{-1}$)	1·91	5·41	8·60	11·7	14·3

TABLE 3. *Rate coefficients for the catalysed decomposition of acetic formic anhydride in toluene at* 39·92°.

10^2 [Anhydride]$_0$ (M)	10^2[P]$_0$ (M)	10^5k (sec.$^{-1}$)	10^2 [Anhydride]$_0$ (M)	10^2[P]$_0$ (M)	10^5k (sec.$^{-1}$)	10^2 [Anhydride]$_0$ (M)	10^2[P]$_0$ (M)	10^5k (sec.$^{-1}$)
~5	—	I.s.*	P = 4-*Picoline*			P = 2-*Picoline*		
P = *Pyridine*			4·50	2·87	21·5	4·51	11·02	2·90
4·62	2·21	5·56	4·31	5·74	32·8	4·62	22·04	4·28
5·21	3·69	7·60	4·23	11·47	68·3	4·70	44·07	6·56
6·04	5·53	10·6	4·22	22·94	137			
5·98	11·07	20·2	4·46	45·37	223	P = 2 : 6-*Lutidine*		
4·51	16·59	24·9				4·73	18·01	5·01
6·43	22·13	30·5				4·63	36·03	7·31

* Imperceptibly slow.

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