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THE INTERACTION OF ACETIC AND TRIFLUOROACETIC ANHYDRIDES IN CARBON TETRACHLORIDE

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Abstract—The reaction of acetic and trifluoroacetic anhydrides in carbon tetrachloride to form acetyl trifluoroacetate does not proceed at a measurable rate under anhydrous conditions. Small quantities of either acetic or trifluoroacetic acid catalyse the reaction equally effectively and with both a zeroth order kinetic rate law is found. An interpretation of these results is given.

The preparation of acetyl trifluoroacetate by distillation methods based on the reaction of acetic acid or anhydride with trifluoroacetic anhydride[1] is unreliable. Wherever possible it is preferable to use equimolecular quantities of the simple anhydrides *in situ*[1–3] and to follow the formation of the unsymmetrical anhydride(1) by the changing IR absorption spectrum. The time required to reach equilibrium (corresponding to 95% reaction) is however unpredictable and in carbon tetrachloride has been found to vary from a few hours to several days.[4] The presence of small catalytic quantities of acetic or trifluoroacetic acid has now been shown to be a time controlling factor for the reaction.

Solutions (0·10–0·20 M) of the simple anhydrides in dry carbon tetrachloride were mixed and introduced into a suitable cell in a 'drybox'. The cell was immediately transferred to an IR spectrometer set to a frequency of 661 cm^{-1}, at which a sharp band has been found characteristic of trifluoroacetic anhydride. No significant change in absorbance was observed over a period of some hours with the anhydrous solutions; the addition of either acetic or trifluoroacetic acid (0·005–0·05 M in the reaction solution) however resulted in a gradual decrease in absorbance at 661 cm^{-1} recorded continuously as reaction proceeded.

Measurements of the absorbance of standard solutions of different known concentrations of trifluoroacetic anhydride in carbon tetrachloride at 661 cm^{-1} showed a reasonably linear correspondence with concentration in accordance with Beer's law, which made possible the evaluation of rate constants from the absorption data on the reacting solutions. The rate of fall of concentration of trifluoroacetic anhydride in either acid-catalysed reaction consistently showed a zeroth order form. A typical plot is shown in Fig. 1. A straight line dependence of the zeroth order rate constant on the concentration of added carboxylic acid was found with closely similar gradients for the two acids (Fig. 2). The rate constants for a fixed concentration of added acid had the same value for either 0·1 M or 0·2 M initial anhydride

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[1] E. J. Bourne, M. Stacey, J. C. Tatlow and R. Worrall, *J. Chem. Soc.* 2006 (1954).
[2] L. J. Bellamy, B. R. Connelly, A. R. Philpotts and R. L. Williams, *Z. Elektrochem.* **64**, 563 (1960).
[3] T. G. Bonner and E. G. Gabb, *J. Chem. Soc.* 3291 (1963).
[4] E. G. Gabb, *Ph.D. Thesis* University of London (1963).

concentrations and the rate constants were also found to be closely similar for the same concentration of either acid (Table 1). The higher rate constants for trifluoroacetic acid catalysis at 19·0° compared with those at 20·2° are attributed to the considerable hygroscopity of trifluoroacetic acid. Any water present in a particular specimen would be rapidly converted on mixing with the anhydrides into an additional amount of acid with a consequent enhanced catalytic effect. The rate of change of rate constant with concentration of added acid should however not be affected by the acid increment introduced by the water present. In accordance with this conclusion the gradients of the plots of the rate constant k against molarity of initially added acid were found to be practically the same for the results at two temperatures.

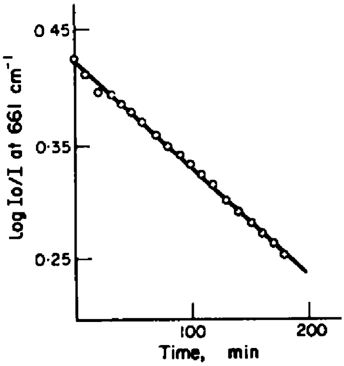

Fig. 1. Rate of change of trifluoroacetic anhydride with time at 29·7°

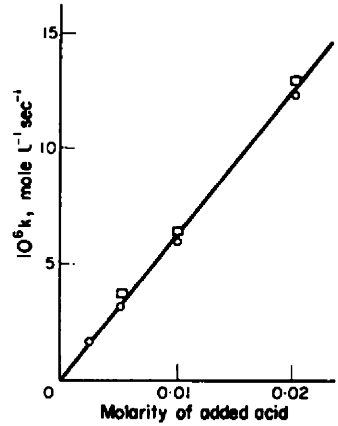

Fig. 2. Dependence of zeroth order rate constant, k, on concentration of acid catalyst at 29·7°
○ CH_3CO_2H □ CF_3CO_2H

Since acetyl trifluoroacetate is formed readily from either acetic acid and trifluoroacetic anhydride (2) or trifluoroacetic acid and acetic anhydride (3) in carbon tetrachloride,[1] the rate at which these equilibria were established was measured approximately. Using 0·1–0·2 M concentrations of the reactants it was found that reaction (2) was too rapid for measurement while reactant (3) required 1–2 hr to attain equilibrium.

$$(CH_3CO)_2O + (CF_3CO)_2O \rightleftharpoons 2CH_3COOCOCF_3 \qquad (1)$$

$$(CF_3CO)_2O + CH_3CO_2H \rightleftharpoons CH_3COOCOCF_3 + CF_3CO_2H \qquad (2)$$

$$(CH_3CO)_2O + CF_3CO_2H \rightleftharpoons CH_3COOCOCF_3 + CH_3CO_2H \qquad (3)$$

The formation of acetyl trifluoroacetate from the symmetrical anhydrides can therefore be interpreted in the following way: in catalysing reaction (1) either acid probably reacts with its appropriate anhydride to form the unsymmetrical anhydride and the other acid. The rate-limiting step will be reaction (3) and this could result in a zeroth order reaction if reaction (3) proceeds through a complex formed rapidly and completely by trifluoroacetic acid and acetic anhydride. Since the rapidity of reaction (2) ensures that the free acid present is always trifluoroacetic acid (even when the added catalyst is acetic acid), the amount of either anhydride undergoing change in unit time will be constant.

TABLE 1. ZEROTH ORDER RATE CONSTANTS (k) FOR THE INTERACTION OF ACETIC AND TRIFLUOROACETIC ANHYDRIDE IN CARBON TETRACHLORIDE

Initial conc. Temp.	$[(CH_3CO)_2O] = [(CF_3CO)_2O] = [A]$ [A] M	$[CF_3CO_2H]$ M	$[CH_3CO_2H]$ M	10^6k mole litre^{-1} sec^{-1}
19·0	0·2	0·005	—	7·0
19·0	0·1	0·005	—	7·2
20·2	0·1	—	0·01	2·9
20·2	0·1	—	0·03	12·7
20·2	0·1	—	0·04	15·7
20·2	0·1	—	0·05	19·4
20·2	0·1	0·0095	—	3·7
20·2	0·1	0·038	—	14·9
20·2	0·1	0·057	—	22·5
29·7	0·1	—	0·0025	1·7
29·7	0·1	—	0·005	3·0
29·7	0·1	—	0·01	6·0
29·7	0·1	—	0·02	12·3
29·7	0·1	0·005	—	3·7
29·7	0·1	0·01	—	6·4
29·7	0·1	0·02	—	12·8

The formation of acetyl trifluoroacetate from the simple anhydrides accordingly proceeds by reactions (2) and (3) only and not by (1). In the absence of added acids reaction can presumably only occur by ingress of extraneous moisture. Hydrolysis of trifluoroacetic anhydride by water is extremely rapid and the trifluoroacetic acid formed would then initiate the cycle of alternating acid-anhydride reactions as described above.

The mechanism is one which probably operates in other similar equilibria involving acylating species.[5]

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[5] D. P. N. Satchell, *Quart. Rev.* **17**, 178 (1963).

EXPERIMENTAL

Materials. 'AnalaR' CCl_4 was dried by treatment with CaH_2 followed by passage through a molecular sieve column. Trifluoroacetic anhydride (b.p. 38–39°) was dried with P_2O_5 and distilled in a vacuum line as required. Trifluoroacetic acid (b.p. 72–74°) and 'AnalaR' acetic anhydride (b.p. 139–140°) were both redistilled. All solutions were made up in a dry box. The trifluoroacetic anhydride solution was stored at 0° over a drying agent.

IR absorption spectra. The two single anhydrides and acetyl trifluoroacetate have readily distinguishable absorption spectra. Very strong absorptions occur between 990 cm^{-1} and 1900 cm^{-1} and the six strongest absorptions for each anhydride (0·1 M–0·2 M) in this range are set out in Table 2. Trifluoroacetic anhydride alone had a less intense but sharp and characteristic peak at 661 cm^{-1} which was used for preparing a calibration curve of the variation of absorbance with concentration for this anhydride.

TABLE 2. STRONGEST ABSORPTIONS IN THE RANGE 990–1900 CM^{-1} IN CCl_4 SOLUTION

Compound	Frequency (cm^{-1})						
$(CH_3CO)_2O$	1825^2	1755^3	1365^5	1220^6	1120^1	—	990^4
$(CF_3CO)_2O$	1870^4	1800^5	1325^6	1240^3	1190^2	1045^1	—
$CH_3COOCOCF_3$	1860^4	1785^5	—	1230^2	1180^3	1075^1	995^6

The superscripts indicate the order of intensity of the absorbance for each anhydride.

Rate measurements. Mixtures of the reactants giving solutions always equimolecular in concentrations of the two anhydrides were prepared and transferred to a KBr cell (0·2 mm) in the dry box. The cell was transferred to the jacketed cell-holder in a SP 100 IR spectrometer set to a frequency of 661 cm^{-1}. Temp control was maintained by circulating water from a constant temp bath. The temp was continuously recorded by means of a Pt resistance thermometer and apart from the time required to attain thermal equilibrium (ca. 10 min) the temp remained constant to within 0·1°.

In the experiments in which an acid catalyst was present, the gradual decrease in absorbance at 661 cm^{-1} was continuously recorded until no further change occurred. The same rate of change of absorbance at 661 cm^{-1} was evident when measurements were made with brief exposure to the IR beam at 10 min intervals; this demonstrated that no initiation of reaction or rate variation occurred as a result of continuous exposure to the radiation.

The plot of absorbance at 661 cm^{-1} against time showed a constant rate of disappearance of trifluoroacetic anhydride throughout the reaction (Fig. 1). Rate constants were evaluated from the gradients of these graphs and the calibration curve obtained for trifluoroacetic anhydride.

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