

### 54. Studies of Trifluoroacetic Acid. Part XIII.\* Cryoscopic Measurements on Trifluoroacetic Anhydride-Acetic Acid Systems.

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Cryoscopic measurements have been made on solutions of trifluoroacetic anhydride, acetyl trifluoroacetate, trifluoroacetic acid, and acetic anhydride, in acetic acid as solvent. They indicate that, contrary to earlier ideas,<sup>1</sup> acetyl trifluoroacetate reacts almost completely with an excess of acetic acid to give acetic anhydride and trifluoroacetic acid.

THE discovery<sup>2</sup> of the acylating activity of carboxylic acid-trifluoroacetic anhydride mixtures was followed by formulation<sup>3,4</sup> of a reaction mechanism in which it was postulated that, in these systems, there were present unsymmetric anhydrides (acyl trifluoroacetates) which were the reactive intermediates. Thus, in the case of acetic acid, it was assumed that the formation of acetyl trifluoroacetate and trifluoroacetic acid was favoured in equilibrium (1).

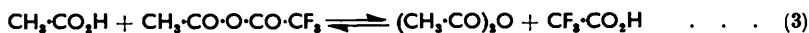


Important evidence in support was provided by Morgan,<sup>1</sup> who carried out cryoscopic measurements on dilute solutions of trifluoroacetic anhydride in acetic acid. Each anhydride molecule apparently reacted to give two particles, indicating that the overall reaction was not represented by equation (2) which, if operative, would give rise to three particles.



Hence, it was concluded that acetic anhydride was not present to any great extent in acetic acid to which small proportions of trifluoroacetic anhydride had been added. Thus, it was most unlikely to be the active acylating species in the approximately equimolar systems used for esterification, etc. Accordingly, support was given to the idea that acetyl trifluoroacetate was the active intermediate.

Later work<sup>5</sup> has amply confirmed these early ideas. The presence of appreciable proportions of acyl trifluoroacetates in equimolar carboxylic acid-trifluoroacetic anhydride systems was demonstrated by infrared spectroscopy, and they were isolated from such mixtures and characterised completely. However, one discrepancy was found between the early postulates<sup>3,4</sup> and this later work,<sup>5</sup> involving, strangely enough, Morgan's cryoscopic results<sup>1</sup> which had been utilised to support the original ideas. Infrared examination of the various systems<sup>5</sup> indicated that acetyl trifluoroacetate was formed to the extent of about 95% from an equimolar mixture of acetic acid and trifluoroacetic anhydride as represented by equilibrium (1). However, acetic anhydride was formed to the extent of about 60% from an equimolar mixture of acetic acid and acetyl trifluoroacetate [equilibrium (3)]:



This suggested that, in a large excess of acetic acid, trifluoroacetic anhydride should give rise mainly to acetic anhydride and not to acetyl trifluoroacetate. Hence, it appeared that, under the conditions used by Morgan,<sup>1</sup> with acetic acid as the cryoscopic solvent, the net reaction should in fact have been that represented by equilibrium (2). Though, with the independent establishment<sup>5</sup> of the presence of acetyl trifluoroacetate in equimolar systems,

\* Part XII, *J.*, 1954, 2006.

<sup>1</sup> Morgan, *J. Amer. Chem. Soc.*, 1951, **73**, 860.

<sup>2</sup> Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976; 1951, 718.

<sup>3</sup> Bourne, Randles, Tatlow, and Tedder, *Nature*, 1951, **163**, 942.

<sup>4</sup> Bourne, Randles, Stacey, Tatlow, and Tedder, *J. Amer. Chem. Soc.*, 1954, **76**, 3206.

<sup>5</sup> Bourne, Stacey, Tatlow, and Worrall, *J.*, 1954, 2006.

the doubt about Morgan's results no longer affected the broad aspects of the reaction scheme, a further study of the cryoscopy of these solutions appeared to be desirable.

Preliminary attempts to repeat Morgan's work, using carefully purified materials and a conventional apparatus, purported to show that, in acetic acid, each molecule of trifluoroacetic anhydride gave rise to 2.5 particles. However, a rise in the freezing points of the solutions was noted after they had been kept for some hours, and, after 78 hr., the calculated value of the number of particles had fallen to about 2. Ingress of atmospheric moisture with hydrolysis of anhydrides to give acetic acid was probably responsible for this effect. Further troubles arose from the variations of the freezing points with fluctuations of room temperature.

The use of an apparatus entirely closed to the atmosphere and assembled in a room maintained at a constant temperature overcame these difficulties. The freezing points, both of the cryoscopic solvent and of a solution containing trifluoroacetic anhydride, remained reasonably constant for 48 hr. Further, the molar depressions resulting from consecutive additions of two portions of acetic anhydride (and also of trifluoroacetic anhydride) to one charge of the solvent were within reasonable agreement, showing that only very little water could have been present initially. However, no very great accuracy is claimed for the results, which were calculated conventionally, since our main concern was simply to establish the general pattern of behaviour of the system.

Diphenyl and naphthalene gave molar depressions of 3.67 and 3.65 respectively in acetic acid. The average of these values (3.66) was used in the calculations on the trifluoroacetic anhydride systems. This cryoscopic constant is appreciably lower than that

Wt. of acetic acid solvent used (g.) ( $w_1$ )	Solute			Total depression of f. p. ( $\Delta t$ )	Molar depression ( $d$ ) ( $\frac{\Delta t \cdot w_1 M}{w_2 \cdot 1000}$ )	Spectroscopic determ.	
	Formula	Mol. wt. ( $M$ )	Wt. used (g.) ( $w_2$ )			Ac <sub>2</sub> O found (mol.)	Resultant total no. of particles
16.66	C <sub>10</sub> H <sub>8</sub>	128.2	0.221	0.380	3.67	—	—
20.23	"	—	0.207	0.290	3.63	—	—
18.35	"	—	0.330	0.510	3.64	—	—
19.34	C <sub>11</sub> H <sub>10</sub>	154.2	0.270	0.332	3.67	—	—
	"	—	0.462	0.568	3.67	—	—
18.95	Ac <sub>2</sub> O	102.1	0.220	0.375	3.30	0.90	—
	"	—	0.386	0.663	3.32	0.91	1.0
17.91	CF <sub>3</sub> ·CO <sub>2</sub> H	114.0	0.225	0.396	3.59	0.98	—
17.96	"	—	0.217	0.380	3.59	—	—
	"	—	0.437	0.757	3.55	0.97	—
17.10	(CF <sub>3</sub> ·CO) <sub>2</sub> O	210.0	0.302	0.825	9.81	2.68	0.9
15.11	"	—	0.283	0.872	9.78	2.67	0.9
15.52	"	—	0.154	0.460	9.74	2.66	—
	"	—	0.311	0.940	9.85	2.69	0.9
15.54	Ac·O·CO·CF <sub>3</sub>	156.1	0.276	0.728	6.40	1.75	1.0
16.66	"	—	0.140	0.343	6.37	1.74	0.9
18.98	Ac <sub>2</sub> O	102.1	0.204	0.358	3.40	—	1.0
	CF <sub>3</sub> ·CO <sub>2</sub> H	114.0	0.216	0.706	3.49	—	—
	"	—	0.432	1.050	3.47	—	—

\* In these experiments more solute was added to the previous solution.

(3.90) obtained by Raoult,<sup>6</sup> which is usually quoted in text-books and was used by Morgan. However, our value agrees better with those of Meyer<sup>7</sup> (3.62) and Eichelberger<sup>8</sup> (3.59) calculated from the latent heat of fusion of acetic acid. The results obtained from the solutes investigated in the present work are given in the Table. Determinations on trifluoroacetic anhydride and acetyl trifluoroacetate in acetic acid gave average molar depressions of 9.80 and 6.39 respectively, and, if  $K = 3.66$ , then 2.68 and 1.75 particles

<sup>6</sup> Raoult, *Ann. Chim. Phys.*, 1884, 2, 66.

<sup>7</sup> Meyer, "Festschrift Otto Wallach," 1909, p. 540; *Chem. Zentr.*, 1909, 2, 1842.

<sup>8</sup> Eichelberger, *J. Amer. Chem. Soc.*, 1934, 56, 799.

respectively resulted from one molecule of each. An investigation of a system to which both acetic anhydride and trifluoroacetic acid were added revealed no abnormal effects. If allowance is made for the somewhat low values for the molar depressions of acetic anhydride and trifluoroacetic acid (see Table), the numbers of particles obtained from trifluoroacetic anhydride and acetyl trifluoroacetate are about 2.8 and 1.9 respectively. All these results are in general accord with infrared spectroscopic determinations, using the band at 1121  $\text{cm.}^{-1}$ , of the amounts of acetic anhydride in the cryoscopic solutions. The absorption bands previously used <sup>5</sup> for acetyl trifluoroacetate (1072  $\text{cm.}^{-1}$ ) and trifluoroacetic anhydride (1041  $\text{cm.}^{-1}$ ) were masked by the absorptions due to the large concentrations of acetic acid, so that only acetic anhydride could be estimated.

Thus, these experiments have shown that, in a large excess of acetic acid, equilibria (2) and (3) largely favour the formation of acetic anhydride and trifluoroacetic acid. Recalculation of Morgan's results using the amended molar depression constant still gives values appreciably lower than ours for the number of particles produced by trifluoroacetic anhydride in acetic acid, and it seems possible that these determinations were affected by atmospheric moisture, as were our preliminary experiments.

Thus, acetyl trifluoroacetate apparently is able to acetylate the hydroxyl group of acetic acid. In carrying out an acylation with trifluoroacetic anhydride and a carboxylic acid it is important to avoid using an excess of the acid, so that the maximum concentration of acyl trifluoroacetate is present in the equilibrium system. Trifluoroacetic acid should also be present. It definitely enhances the acetylating activity of acetyl trifluoroacetate (and also of acetic anhydride <sup>9</sup>).

#### EXPERIMENTAL

*Cryoscopic Apparatus and Experimental Technique.*—A tube [160 cm.  $\times$  2.7 cm. (i.d.)] with a standard B29 ground socket was closed by a Polythene plug which had been accurately machined to fit the socket. The plug was bored to accommodate a Beckmann thermometer and a glass stirrer-housing which were then sealed to the plug with paraffin wax. A length of tubular glass to which had been sealed two loops to act as stirrers and, near the top, a core of soft iron enclosed in glass, was raised 80 times per min. by a water-cooled solenoid. The intermittent current which actuated the solenoid was fed through contacts which were opened and closed by a rotating toothed wheel. Liquid samples could be introduced through a self-sealing rubber serum cap on an inclined side-arm near the glass socket. The apparatus was broadly similar to those of Treffers and Hammett,<sup>10</sup> and Gillespie, Hughes, and Ingold.<sup>11</sup>

Acetic acid (15–20 g.) was weighed into the cryoscopic apparatus and a seal was made between the plug and socket with silicone high-vacuum grease. The apparatus was then assembled in a room controlled at  $20^\circ \pm 0.2^\circ$  and allowed to stand for 16 hr. to attain equilibrium conditions. The tube of the cryoscopic apparatus was then centred in a second tube (which left an 8 mm. air-jacket) and this was immersed in a freezing bath ( $1^\circ \pm 0.1^\circ$  below the f. p. of the solvent) contained in a silvered Dewar vessel. Nucleation was effected after removal of the freezing bath by touching the side of the inner tube with a lump of solid carbon dioxide, after which the temperature of the solvent was allowed to rise above its freezing point. The cooling bath was then replaced for the actual determination of the freezing point. The solvent would supercool *ca.*  $0.1^\circ$  and then rise to its freezing point which remained constant for *ca.* 20 min.; determinations of the freezing point agreed within  $0.003^\circ$  and no appreciable variations were observed during 24 hr.

Liquid samples were introduced through the serum cap from a weighed micrometer syringe; solid samples were added by removing momentarily the Polythene plug. Negligible variation of freezing point of the solutions was observed during 24 hr. The experimental observations are recorded in the Table.

On completion of experiments with acetic anhydride, acetyl trifluoroacetate, and trifluoroacetic anhydride, a sample (*ca.* 3 g.) of the cryoscopic solution was diluted to 10 c.c. with dry

<sup>9</sup> Morgan, *Ind. Eng. Chem.*, 1951, **43**, 2575.

<sup>10</sup> Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.

<sup>11</sup> Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

carbon tetrachloride, and the acetic anhydride was determined by infrared spectroscopic analysis, with comparative measurements of optical density of the absorption band at  $1121\text{ cm}^{-1}$ . The absorption bands of acetyl trifluoroacetate ( $1072\text{ cm}^{-1}$ ) and trifluoroacetic anhydride ( $1041\text{ cm}^{-1}$ ) were masked by the heavy absorption of the high concentrations of acetic acid. The accuracy of the infrared analysis is estimated as  $\pm 10\%$  under these conditions.

*Purification of Materials.*—The materials used in the cryoscopic determinations were purified by methods described by Randles, Tatlow, and Tedder.<sup>12</sup> Acetic acid, purified by fractional recrystallisation, had m. p.  $16\cdot70^\circ$ .

Trifluoroacetic acid, purified by treatment with trifluoroacetic anhydride followed by fractional distillation, had b. p.  $70\cdot5^\circ$ . Acetic anhydride, fractionally distilled, had b. p.  $137\cdot5\text{--}137\cdot9^\circ$ . Trifluoroacetic anhydride, fractionally distilled, had b. p.  $38\cdot7^\circ$ . Acetyl trifluoroacetate was prepared by allowing an equimolecular mixture of the above anhydrides to remain at *ca.*  $20^\circ$  for 3 days.

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<sup>12</sup> Randles, Tatlow, and Tedder, *J.*, 1954, 436.

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