Kinetic and Equilibrium Studies by ^{19}F Nuclear Magnetic Resonance of the Formation of Acetyl Fluoride from Acetyl Chloride and Tetraethylammonium Fluoride in Acetic Acid

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The formation of acetyl fluoride from acetyl chloride and tetraethylammonium fluoride in glacial acetic acid has been studied by ^{19}F n.m.r. The results show that an equilibrium is established slowly at 298 K. For example, a solution initially containing 0.476 mol dm^{-3} each of acetyl chloride and tetraethylammonium fluoride attains 68% conversion into acetyl fluoride after 21 h, whereas the equilibrium position corresponds to 87% conversion. Evidence is provided to show that the reaction involves rapid formation of acetic anhydride and hydrogen fluoride, which then react slowly to give acetyl fluoride.

In recent studies, the unusually low value of the isotopic fractionation factor of acetate ion in acetic acid (φ 0.58) has been used to explain the values of kinetic and equilibrium solvent isotope effects of reactions involving acetate ion in acetic acid.[1] The fractionation factor of fluoride ion in acetic acid has an even lower value[2] (φ 0.55) and it was therefore thought to be of interest to determine kinetic solvent isotope effects for reactions of fluoride ion in acetic acid. Both ions are considered to exist as strongly hydrogen-bonded solvates in this medium.

Previous work has shown that if acetyl chloride is added to a solution of potassium fluoride in acetic acid, immediate and quantitative precipitation of potassium chloride occurs and acetyl fluoride can be distilled from the solution.[3] The observations were thought to be compatible with direct substitution by fluoride. To account for the effect of bromide ions on the rate of reaction between acetyl fluoride and 2-naphthol in acetic acid, halide exchange between acetyl fluoride and bromide ion has also been assumed to occur.[4]

In the present work, direct studies of the reaction between tetraethylammonium fluoride and acetyl chloride in acetic acid show that halide exchange occurs quite slowly and involves intermediate formation and subsequent equilibration of acetic anhydride and hydrogen fluoride to give acetyl fluoride. Direct nucleophilic attack of fluoride ion on acetyl chloride is not the preferred reaction under these conditions.

Experimental

Materials.—Acetic acid, acetic [^{2}H]acid, and tetraethylammonium fluoride were purified and dried as previously described.[1,2] Potassium fluoride was dried at 130 °C under vacuum. Acetyl chloride was distilled at atmospheric pressure, cooled to −78 °C, and pumped under vacuum for several hours to remove hydrogen chloride. Final purification was achieved by distillation under reduced pressure. Acetyl fluoride was prepared by reaction of purified acetyl chloride with potassium fluoride in acetic acid.[3] The product was handled on a vacuum line and distilled before use.

Solutions of tetraethylammonium fluoride in acetic acid were prepared as described previously and subjected to rigorous drying.[2] Solutions were manipulated in a dry box. Water content measured by Mitsubishi moisturemeter (CA-02) was found to be less than 0.01 mol dm^{-3}. The concentration of tetraethylammonium fluoride in the final stock solution was determined by comparison of the methyl integral in the ^{1}H n.m.r. spectrum with that of the solvent.

N.m.r. Spectra.—Spectra for both ^{1}H and ^{19}F were recorded at 298 K with a Bruker WM 250 spectrometer, at 250 and 235 MHz, respectively. A sealed concentric Wilmad tube containing CD_2Cl_2 provided the deuterium lock. Chemical shifts were measured relative to trichlorofluoromethane added as internal standard. Three peaks were observed in the ^{19}F spectrum of Cl_3CF because of different combinations of ^{35}Cl and ^{37}Cl. The most intense peak at lowest field was assigned $\delta = 0.00$. Chemical shifts were considered accurate to within ±0.05 p.p.m. Concentrations of fluorine-containing species in solution were measured by comparison of integrals with signals from a known concentration of added hexafluorobenzene (δ −163.00). ^{1}H N.m.r. spectra were run in [$^2H_4$]acetic acid (99.95 atom %). Chemical shifts were measured relative to the residual C–H peak in acetic acid, and benzene (0.011 mol dm^{-3}; δ 5.29) was added so that concentrations of the species present could be calculated from peak integrals.

Results and Discussion

The ^{19}F spectra of a solution initially made up from tetraethylammonium fluoride (0.476 mol dm^{-3}) and acetyl chloride (0.476 mol dm^{-3}) in acetic acid were recorded at intervals of time and showed that a slow reaction was occurring. A quartet centred at δ 50.4 ($^3J_{HCCF}$ 7.25 Hz) due to acetyl fluoride was observed to increase in intensity, and a broad singlet at δ *ca.* −176 decreased with time. The chemical shifts of these signals did not change as reaction proceeded and no other peaks were found except those due to added markers. After *ca.* 200 h there was no further change in the spectrum. It has previously been observed that the ^{19}F chemical shift of solutions of tetraethylammonium fluoride in acetic acid depends upon concentration,[5] and varies from δ −127.7 at a concentration of tetraethylammonium fluoride of *ca.* 0.7 mol dm^{-3} to δ −135.0 at *ca.* 0.05 mol dm^{-3}. At lower concentrations the chemical shift becomes more strongly negative and at 0.004 mol dm^{-3} the peak appears at δ −164.7. The change in shift is attributed[5] to a change in the proportion of inorganic species thought to be present. These are assumed to be in rapid equilibrium and give rise to an averaged ^{19}F peak. The signal at δ −176 in a solution initially made up from 0.476 mol dm^{-3} acetyl chloride and tetraethylammonium fluoride is seen at this position in all spectra from 1 h up to 240 h after mixing. This cannot be due solely to tetraethylammonium fluoride. The concentrations of acetyl fluoride and the inorganic fluoride species (F_i) giving rise to the peak at δ −176 were calculated from the peak integrals during the reaction and are given in Table 1. The percentage conversion of acetyl chloride into acetyl fluoride after 1 h is 37%; *cf.* 68% after 21 h and 87% at equilibrium.

The equilibrium concentrations ($[AcF]_e$ and $[F_i]_e$) determined for reaction mixtures initially made up to contain tetraethylammonium fluoride at a concentration ($[Et_4NF]_0$) of *ca.* 0.5 mol dm^{-3} and with acetyl chloride concentration $[AcCl]_0$) in the range 0.084—0.483 mol dm^{-3} are given in Table 2. The signal due to acetyl fluoride was always observed at δ −50.4, but the position of the peak due to F_i depends upon the composition of the reaction solution; see Table 2.

A sequence of reactions consistent with the experimental observations is shown as equations (1)—(3), where reactions (1) and (2) represent rapid equilibria strongly in favour of acetic

$$AcCl + AcOH \rightleftharpoons Ac_2O + HCl \qquad (1)$$

$$HCl + F^- \rightleftharpoons HF + Cl^- \qquad (2)$$

$$Ac_2O + HF \underset{k_b}{\overset{k_f}{\rightleftharpoons}} AcF + AcOH \qquad (3)$$

anhydride and hydrogen fluoride. Thus on addition of acetyl chloride to a solution of tetraethylammonium fluoride in acetic acid it is assumed that quantitative formation of acetic anhydride and hydrogen fluoride occurs and that this is followed by slow reaction to give an equilibrium concentration of acetyl fluoride. At equilibrium, the solution contains acetic anhydride and acetyl fluoride together with hydrogen fluoride and unchanged tetraethylammonium fluoride. The values of $[Ac_2O]_e$, $[HF]_e$, $[F^-]_e$, and the equilibrium constant for reaction (3), $K = [AcF]_e/[Ac_2O]_e[HF]_e$, calculated on the basis of this assumption, are given in Table 2. The uncertainty for each value of K corresponds to an uncertainty of ±2% in the measured value of $[AcF]_e$; the average value of K is 75.0 ± 16 dm^3 mol^{-1}. The value calculated for the reaction in AcOD is not significantly different.

If, on the other hand, the halide-exchange equilibrium is assumed to be represented by the stoicheiometry of equation (4), and the equilibrium constant (K') is calculated from equation

$$AcCl + F^- \rightleftharpoons AcF + Cl^- \qquad (4)$$

$$K' = [AcF]_e^2/([AcCl]_0 - [AcF]_e)([Et_4NF]_0 - [AcF]_e) \qquad (5)$$

(5), the values obtained from the results for solutions 2—7 vary from 0.29 to 44.9. The data are more compatible with the equilibrium in reaction (3).

Table 1. Approach to equilibrium for halide exchange in AcOH at 298 K ($[Et_4NF]_0$ 0.476 mol dm^{-3}; $[AcCl]_0$ 0.476 mol dm^{-3})

Time (h)	1	21	51	74	124	192	240
[AcF]/mol dm^{-3}	0.175	0.325	0.375	0.388	0.398	0.412	0.414
[F$_i$]/mol dm^{-3}	0.301	0.151	0.101	0.088	0.078	0.064	0.062

A satisfactory explanation is also provided for the variation in $\delta(F_i)$ with composition. At equilibrium in solutions 2—7, the inorganic fluoride consists of a mixture of hydrogen fluoride ($[HF]_e$) and fluoride ion remaining from the reaction of tetraethylammonium fluoride ($[F^-]_e$). If we assume that proton transfer between these species is rapid, the ^{19}F signal in the n.m.r. spectrum will occur at a chemical shift which is a weighted average of the shifts of HF and F^-. The chemical shift of HF in acetic acid is taken as −175.27, since this is the value observed for solution 7 in which HF is the only inorganic fluorine species present. This result is close to the average value of δ_{HF} in various solvents.[5] The chemical shift of F^- at a particular equilibrium concentration of F^- can be taken from the data obtained previously for solutions of tetraethylammonium fluoride in acetic acid.[5] The weighted average values $\delta(F_i)_{calc.} = \delta_{HF}\cdot[HF]_e/([HF]_e + [F^-]_e) + \delta_{F^-}\cdot[F^-]_e/([HF]_e + [F^-]_e)$ are given in Table 2 for solutions 2—7 and the uncertainties are calculated from an uncertainty of ±2% in $[AcF]_e$.

The approach to equilibrium for reaction (3) is given by equations (6) and (7), assuming that the reactions in equations

$$d[AcF]/dt = k_f\{([AcCl]_0 - [AcF])^2 - [AcF]([AcCl]_0 - [AcF]_e)^2/[AcF]_e\} \qquad (6)$$

$$[AcF]_e/([AcCl]_0^2 - [AcF]_e^2)\ln\{([AcF][AcF]_e - [AcCl]_0^2)/([AcF][AcF]_e - [AcF]_e^2)\} = k_f t \qquad (7)$$

(1) and (2) occur rapidly. A plot of equation (7) using the data in Table 1 was treated by linear regression analysis (correlation coefficient 0.98; six data points) and gave k_f (3.9 ± 0.5) × 10^{-5} dm^3 mol^{-1} s^{-1} and k_b (5.2 ± 1) × 10^{-7} s^{-1}.

In the preparation of acetyl fluoride, addition of acetyl chloride to a solution of potassium fluoride in acetic acid results in the immediate quantitative precipitation of potassium chloride.[3] This is compatible with rapid and complete reaction according to equations (1) and (2). Although the present results show that the subsequent reaction of acetic anhydride with hydrogen fluoride occurs slowly, under preparative conditions the solution is warmed and acetyl fluoride is distilled from solution. The rate of reaction (3) would be increased by the higher temperature and the equilibrium would be displaced to products by removal of acetyl fluoride.

To confirm that acetic anhydride is formed, the reaction was

Table 2. Equilibrium position for halide exchange in AcOH and AcOD at 298 K

	Solution no.								
	1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[a]	8[b]	9[b]
$[Et_4NF]_0$/mol dm^{-3}	0.500	0.497	0.494	0.491	0.489	0.486	0.483	0.412	0.416
$[AcCl]_0$/mol dm^{-3}	0.0	0.084	0.167	0.249	0.323	0.403	0.483	0.461	0.445
$-\delta(F_i)$	128.28	129.93	131.90	134.54	138.53	147.66	175.27	158.61	156.40
$[AcF]_e$/mol dm^{-3}	0.0	0.058	0.121	0.194	0.256	0.338	0.420	0.360	0.358
$[F_i]_e$/mol dm^{-3}	0.500	0.439	0.373	0.298	0.233	0.148	0.063	0.052	0.058
$[HF]_e$/mol dm^{-3}	0.0	0.016	0.046	0.055	0.067	0.065	0.063	0.052	0.058
$[Ac_2O]_e$/mol dm^{-3}	0.0	0.016	0.046	0.055	0.067	0.065	0.063	0.101	0.087
$[F^-]_e$/mol dm^{-3}	0.500	0.423	0.327	0.243	0.166	0.083	0.00	0.00	0.00
K/dm^3 mol^{-1}		85.8 ± 8	57.2 ± 9	64.1 ± 11	57.0 ± 12	80.0 ± 19	105.8 ± 30	68.5 ± 16	70.9 ± 16
$-\delta(F_i)_{calc.}$	128.1	131.1 ± 0.3	134.6 ± 0.8	138.2 ± 2	143.7 ± 3	150.0 ± 3	175.27		

[a] Solvent AcOH. [b] Solvent 97% AcOD/3% AcOH.

carried out under slightly different conditions. Potassium fluoride (1.16 g, 0.02 mol) was partly dissolved in glacial acetic acid (4.82 g, 0.06 mol). Benzene was added and the mixture was heated to remove the water–benzene azeotrope. The mixture solidified on cooling and further benzene (20 g) was added to dissolve the solid. Addition of acetyl chloride (1.56 g, 0.02 mol) resulted in the immediate precipitation of potassium chloride. Anhydrous sodium carbonate (10 g) was added and the solution was filtered through sodium carbonate. The ^{1}H n.m.r. spectrum of the filtrate showed the presence of acetic anhydride (δ 1.72 relative to Me_4Si) with no other products in detectable amounts. It follows that under these experimental conditions reactions (1) and (2) occur, but the anhydride is prevented from further reaction because HF is removed by neutralisation.

Further evidence for the intermediate formation of acetic anhydride was provided by direct observation of the reaction using ^{1}H n.m.r. The spectrum of a solution of acetyl chloride (0.011 mol dm^{-3}) and potassium fluoride (0.103 mol dm^{-3}) in [$^2H_4$]acetic acid was recorded immediately after mixing. A singlet due to acetyl chloride was observed at δ 0.152 (relative to the residual C–H in [$^2H_4$]acetic acid), and a singlet at δ 0.025 for acetic anhydride and a doublet (J 7.2 Hz) centred at δ 0.188 for acetyl fluoride were present. After 2 h the major peak in the spectrum was that of acetic anhydride and the signal due to acetyl fluoride had increased, whereas that for acetyl chloride had decreased.

The halide exchange between acetyl chloride and tetraethylammonium fluoride in acetic acid involves intermediate formation of acetic anhydride and hydrogen fluoride which then react to give acetyl fluoride. In acetic acid, fluoride ion exists as a strongly hydrogen-bonded complex and this may explain why direct nucleophilic displacement of chloride by fluoride is unfavourable under these conditions.

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