Solvolysis of Some Alkyl Esters of Fluorosulphuric Acid in Water and Aqueous Solvents

By **Lázaro F. R. Cafferata,*** **Osvaldo E. Desvard,** and **Juan E. Sicre,** Instituto de Investigaciones Fisicoquimicas Teoricas y Aplicadas–INIFTA–C.C. 16, Suc. 4, 1900 La Plata, República Argentina

The solvolysis of methyl, ethyl, and isopropyl fluorosulphates in pure water and aqueous organic solvents has been studied. The extrapolated reactivity at 25 °C of these compounds is 10^4 to 10^6 times higher than that of halides, alkanesulphonates, and benzenesulphonates but is similar to that shown by chlorosulphates and perfluoroalkanesulphonates.

The kinetics and medium and nucleophile effects have been investigated to establish the mechanism of the reactions. The effect of a variation in the dielectric constant of the medium has also been discussed. The activation parameters of these solvolytic reactions were correlated through a $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ plot.

It is concluded that even when methyl and ethyl fluorosulphates show behaviour typical of compounds reacting by a S_N2-type mechanism, some evidence of a slight difference between both processes was found. The solvolysis of isopropyl fluorosulphate has a high contribution from a unimolecular ionization mechanism.

It has been postulated[1] that the solvolysis of methyl and ethyl fluorosulphates, $ROSO_2F$ (R = Me and Et, respectively), in tetrahydropyran occurs by an S_N2 mechanism. A unimolecular mechanism has been established[2] for some vinyl fluorosulphates. Other reported kinetic data for alkyl fluorosulphates are the first-order rate constants for the reaction of the methyl fluorosulphate with water, methanol, and acetonitrile,[3] but no mechanistic information on the solvolysis of other alkyl esters of fluorosulphuric acid is available. However, it has been suggested[4] that in these compounds the scission of the carbon–oxygen bond may occur. The work of Buncel[5] on the solvolysis of some alkyl chlorosulphates seems to indicate the simultaneous rupture of their C–O and S–Cl bonds. Therefore, the solvolysis of methyl, ethyl, and isopropyl fluorosulphates in water (for the two primary compounds) and in aqueous mixtures of organic solvents was systematically studied in order to compare the pertinent data with the information on the chlorosulphates and to establish the mechanism of their reactions. Unfortunately, tertiary and other alkyl fluorosulphates are too unstable to be handled.

EXPERIMENTAL

Materials.—Methyl fluorosulphate was prepared by the reaction of dimethyl sulphate with fluorosulphuric acid. The ester passes over first when a mixture of the reactants is distilled in glass. Ethyl and isopropyl fluorosulphates were obtained in a glass apparatus by the addition of fluorosulphuric acid to ethylene and propene, respectively. The products were isolated and purified by distillation under reduced pressure and their purity was checked by i.r. and quantitative chemical analysis of their hydrolysis products. Conductivity water was prepared by distillation with potassium permanganate and sodium hydroxide and freed from carbon dioxide by passage of nitrogen. Dioxan was purified employing the Oglukian procedure.[6] Acetone was refluxed with potassium permanganate, distilled, stored over potassium carbonate, and redistilled. The purity of the organic solvents was verified through g.c. analysis. Aqueous mixtures of the organic solvents were prepared by mixing the required volumes of the components at room temperature.

Product Analysis.—The acidity of the solutions was determined by conductimetric titration with aqueous sodium hydroxide. Gas chromatography was used for organic product analysis.

Kinetic Measurements.—The rates of solvolysis were measured conductimetrically in a Tinsley 4896 Conductivity Bridge with an oscilloscope as zero detector. In most of the runs the initial concentration of the alkyl fluorosulphates in the reaction mixtures was *ca.* 0.001M. The first-order rate constants were calculated by Guggenheim's method[7] and the activation parameters according to Huyberechts *et al.*[8]

RESULTS

The solvolysis of methyl, ethyl, and isopropyl fluorosulphates in the media investigated were followed for at least three half-lives and the experimental values fit a first-order kinetic law over the complete range; this behaviour was confirmed by the fact that *k* values were not affected by increasing the initial concentration of the esters by a factor ranging from 2 to 10. One equivalent of acid was produced per equivalent of ester consumed; the corresponding alcohols in quantitative yields were the only organic products found, except for isopropyl fluorosulphate, where small amounts of propene were also detected.

In Table 1 the average rate constant values for the solvolysis in pure water and in aqueous acetone and dioxan, together with the corresponding activation parameters, are given. The extrapolation of these *k* values at 25 °C and their comparison with that existing in the literature for other alkyl derivatives, established that, at the same temperature, alkyl fluorosulphates are 10^4 to 10^6 more reactive than substrates having a ' leaving group ' related to acids that are not ' very strong ', *i.e.* halides,[9] alkanesulphonates,[10,11] and benzenesulphonates;[12-14] the reactivity of the fluorosulphates is similar to that shown by the chlorosulphates[5] and perfluoroalkanesulphonates,[15] in which the ' leaving group ' is related to a ' very strong ' acid.

For the methyl and ethyl fluorosulphates an acid catalysis effect was not observed when perchloric or fluorosulphuric acid (0.001M) were added. The alkaline hydrolysis of these two compounds was also measured in an aqueous solution of sodium hydroxide (0.004M) at 1.90 °C; the experimental data followed a second-order equation for at least three half-lives. The ratio of the bimolecular rate constant thus

TABLE 1

Solvolysis of alkyl fluorosulphates

Compound	Solvent [a]	$k_{obs.}10^4/s^{-1}$ [b] −3.20°	$k_{obs.}10^4/s^{-1}$ [b] 1.90°	$k_{obs.}10^4/s^{-1}$ [b] 7.00°	$k_{obs.}10^4/s^{-1}$ [b] 12.20°	$\Delta H^\ddagger$ [c] kcal mol^{-1}	$\Delta S^\ddagger$ [c] cal K^{-1} mol^{-1}
$MeOSO_2F$	Water		23.8 ± 1.4		76.1 ± 0.6	16.4 ± 0.4	−29.9 ± 1.3
	40% Dioxan		41.1 ± 1.2				
	60% Dioxan		50.0 ± 1.7				
	70% Dioxan		44.7 ± 0.5				
	80% Dioxan		34.2 ± 1.4		80.6 ± 0.2	11.8 ± 0.7	−42.2 ± 2.5
$EtOSO_2F$	Water		21.3 ± 1.2	42.8 ± 0.5	75.8 ± 0.9	17.4 ± 1.1	−26.3 ± 4.0
	30% Dioxan		22.5 ± 0.4	45.7 ± 0.5	81.2 ± 3.0	19.3 ± 0.5	−18.5 ± 1.7
	40% Dioxan		22.6 ± 0.4	43.6 ± 0.6	78.7 ± 1.0	17.7 ± 0.2	−24.0 ± 0.7
	60% Dioxan		17.3 ± 0.5	34.2 ± 0.7	54.9 ± 2.3	17.2 ± 0.8	−25.5 ± 3.0
	70% Dioxan		13.8 ± 0.2	24.3 ± 0.2	40.2 ± 1.3	15.6 ± 0.4	−31.0 ± 1.4
	80% Dioxan		10.4 ± 0.4	19.5 ± 0.3	27.3 ± 0.7	13.8 ± 1.1	−37.2 ± 4.1
	25% Acetone	12.1 ± 0.4	22.9 ± 1.1	47.9 ± 0.4	79.9 ± 1.5	17.7 ± 0.7	−24.4 ± 2.7
	40% Acetone	14.5 ± 0.5	25.0 ± 1.4	47.6 ± 0.3	73.6 ± 1.2	14.5 ± 0.7	−35.5 ± 2.6
	60% Acetone	14.2 ± 0.5	20.9 ± 0.3	33.9 ± 0.5	48.6 ± 2.0	12.1 ± 0.5	−44.2 ± 1.6
	70% Acetone	9.87 ± 0.1	16.7 ± 0.2	31.6 ± 1.2	48.3 ± 0.2	14.7 ± 0.1	−34.7 ± 0.4
	80% Acetone	8.24 ± 0.1	12.6 ± 0.5	23.6 ± 1.4	32.9 ± 0.2	12.7 ± 0.2	−42.3 ± 0.6
	90% Acetone	5.49 ± 0.1	8.99 ± 0.5	18.1 ± 0.1	25.9 ± 1.0	16.2 ± 0.5	−29.3 ± 1.9

		$k_{obs.}10^4/s^{-1}$ [b] −17.4°	$k_{obs.}10^4/s^{-1}$ [b] −5.5°	$\Delta H^\ddagger$ [c] kcal mol^{-1}	$\Delta S^\ddagger$ [c] cal K^{-1} mol^{-1}
Pr^iOSO_2F	80% Acetone	30.6 ± 1.3			
	95% Acetone	3.97 ± 0.3	20.0 ± 0.2	17.2 ± 0.4	−21.5 ± 1.0

[a] x% A means x volumes of A plus $(100 - x)$ volumes of water. [b] Errors in $k_{obs.}$ are expressed as standard deviations of at least three independent runs. [c] Activation parameters and corresponding errors calculated from the log (k_2/T) *vs.* $1/T$ plot, where $k_2 = k_{obs.}/a_{H_2O}$ (see below).

obtained to that corresponding to the neutral hydrolysis at the same temperature, *e.g.* the ' lyate ion effect ', were 248 and 275 (l mol^{-1}) for the methyl and ethyl fluorosulphates, respectively. These values suggest a nucleophilic attack on the substrates as the rate-determining stage of their reactions.[16–19]

For the hydrolysis of ethyl fluorosulphate in pure water the kinetic effect of added sodium iodide (0.004M) was almost negligible. This absence of rate acceleration by a nucleophile was in contrast with the observation in the same media for the methyl ester, where a 30% change was noticed. These results suggest a slight difference in the character of the hydrolysis of the two primary esters.

The k values for the solvolysis in aqueous dioxan and acetone mixtures were well correlated by the Grunwald–Winstein equation,[20] $\log (k/k_0) = mY$, even though the points corresponding to mixtures with a high proportion of water showed certain deviations, a fact that has already been mentioned [21] in the literature for this kind of plot. The resulting m values for the methyl and ethyl fluorosulphates range from 0.11 to 0.13, which represent the typical behaviour of compounds reacting by a bimolecular mechanism.[16,22] The data obtained for the isopropyl fluorosulphate indicated an m value of *ca.* 0.4, which suggests that its solvolysis has more S_N1 character.

The sensitivity of the rate of solvolysis to a change in the solvent nucleophilic character N was evaluated by performing the reactions in aqueous mixtures of ethanol and trifluoroethanol (TFE) with the same ionizing power (Y = 1.894); the values obtained for the ratio ($k_{aq.\ EtOH}/k_{aq.\ TFE}$) were 19, 20, and 4, for the methyl, ethyl and isopropyl esters, respectively, which show that for the primary compounds the reactivity is strongly influenced by the nucleophilicity of the medium, whereas for the secondary compound the dependence is less noticeable and approaches the values found in substrates with a unimolecular, type S_N1 mechanism, when this kind of comparison is made.[16,23–25]

The ' solvation number ' n (*i.e.* the number of water molecules needed for the transition-state formation [12,26]) for the solvolysis of the alkyl fluorosulphates has been determined graphically (Figure 1). These values are similar to those found for the chlorosulphates but lower than those for other compounds (Table 2), which is an indication of the polar character of those molecules.[26] The

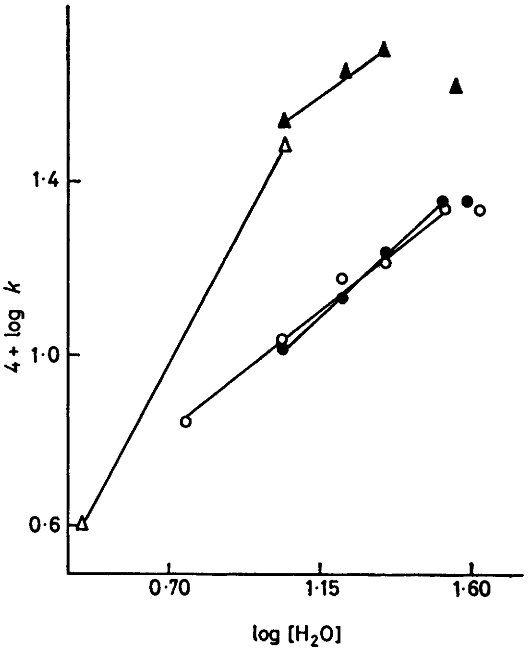

FIGURE 1 log $k_{obs.}$ *vs.* log $[H_2O]$ plot for the solvolysis of alkyl fluorosulphates: ▲, $MeOSO_2F$ in aqueous dioxan; ●, $EtOSO_3F$ in aqueous dioxan; ○, $EtOSO_2F$ in aqueous acetone; △, Pr^iOSO_2F in aqueous acetone order of the corresponding solvation numbers, isopropyl > ethyl > methyl, suggests a more S_N1 character for the isopropyl solvolysis than for the other two esters.

Solvolytic reactions usually fit first-order kinetic laws, even where the actual mechanism is a bimolecular one, which makes it necessary to normalize the experimentally observed rate constant values to obtain valid comparisons between the data from different media. In this work $k_{obs.}$ was divided by the activity of the reactant in excess, a unitary order with respect to it being assumed.

TABLE 2

Solvation numbers for the solvolysis of different compounds

Compound	*n*	Solvent	Ref.
Methyl fluorosulphate	0.2	Aq. dioxan	This work
Ethyl fluorosulphate	0.6	Aq. dioxan	This work
Ethyl fluorosulphate	0.6	Aq. acetone	This work
Ethyl chlorosulphate	1.0	Aq. dioxan	26
Ethyl bromide	2.3	Aq. acetone	12
n-Propyl chlorosulphate	1.1	Aq. dioxan	26
Isopropyl fluorosulphate	1.5	Aq. acetone	This work
Neopentyl chlorosulphate	1.8	Aq. dioxan	26
Isopropyl benzenesulphonate	4.3	Aq. dioxan	12
t-Butyl bromide	5.7	Aq. acetone	*a*
t-Butyl chloride	6.7	Aq. dioxan	*b*

[a] E. Tommila, M. Tiilikainen, and A. Voipio, *Ann. Acad. Sci. Fenn. Sect. AII*, 1955, 65. [b] A. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.

Employing Kirkwood's treatment[27] for the free energy needed to transfer a dipole from a vacuum to a medium of dielectric constant ε, the following equation results[28] where

$$ln\ k = \ln k_0 - \frac{1}{kT}\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_M^2}{r_M^3}\right]\frac{\varepsilon - 1}{2\varepsilon + 1}$$

k_0 is the reaction rate constant in the reference medium ($\varepsilon = 1$); μ_A, μ_B, and μ_M are dipolar moments of the reacting particles A and B and of the transition state M, considered as rigid spheres, respectively; r_A, r_B, and r_M are the radii of these spheres, which in this work have been taken as the corresponding molecular radii. In Figure 2 the plot of log k_2 *vs.* $(\varepsilon - 1)/(2\varepsilon + 1)$ is shown, where $k_2 = k_{obs.}/a_{H_2O}$ (a_{H_2O} is the water activity), for the fluorosulphates studied in this work. The activity coefficient of the esters was considered constant for the different mixtures in which the reactions were investigated. (The assumption of first order in water for the solvolysis of isopropyl fluorosulphate could be criticized because of its high S_N1 character, but the tendency observed in Figure 2 remained unchanged even though a zero order was considered.)

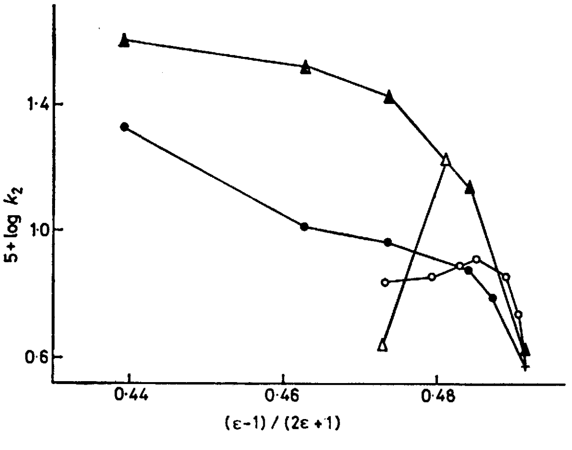

FIGURE 2 log k_2 *vs.* $(\epsilon - 1)/(2\epsilon + 1)$ plot for the solvolysis of alkyl fluorosulphates: ▲, $MeOSO_2F$ in aqueous dioxan; +, $EtOSO_2F$ in water; ●, $EtOSO_2F$ in aqueous dioxan; ○, $EtOSO_2F$ in aqueous acetone; △, Pr^iOSO_2F in aqueous acetone

In Figure 2 the isopropyl fluorosulphate data, in spite of the limited number of rate constant values obtained, show the usual behaviour observed in nucleophilic substitution reactions of the dipole–dipole type. Instead the rate constant values for the methyl and ethyl fluorosulphates do not increase on increasing ε.

The behaviour of the primary esters may be due to the high polarity of these compounds, which means that not only the transition state, but the reacting dipoles too would be affected by the dielectric constant of the medium. If in equation (1) the following numerical values are given: $r_{H_2O} = 1.93$ A; $r_{EtOSO_2F} = 3.42$ A (both obtained by consideration of the corresponding molar volumes); r_M is taken as 10% higher than r_{EtOSO_2F} (*e.g.* $r_M = 3.76$ A); $\mu_{H_2O} = 1.84$ D and $\mu_{EtOSO_2F} = 4$ D (which is a reasonable estimation), the term $[(\mu_A^2/r_A^3) + (\mu_B^2/r_B^3) - (\mu_M^2/r_M^3)]$ becomes positive when $\mu_M < 6.8$ D, which makes the rate constant decrease when the dielectric constant is increased. This μ_M limiting value could be still lower where specific solvation contributions affect the solvolysis transition state more than the reactants. The behaviour was not modified when concentration was employed instead of activity in the reaction rate constants normalization.

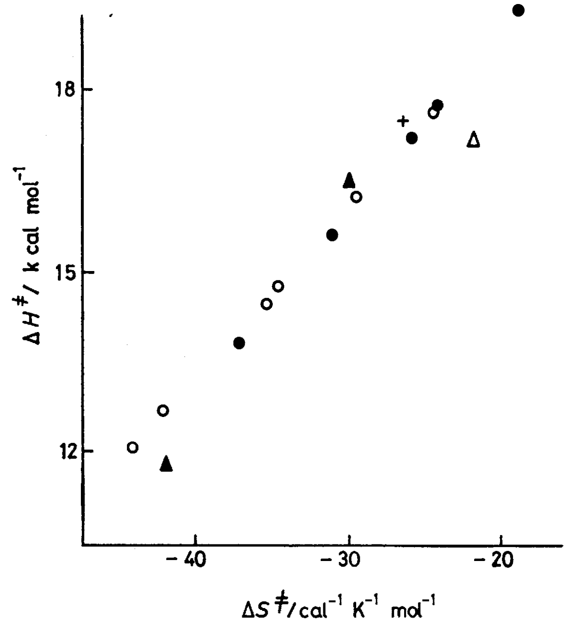

FIGURE 3 $\Delta H^‡$ *vs.* $\Delta S^‡$ Plot for the solvolysis of alkyl fluorosulphates: ▲, $MeOSO_2F$ in aqueous dioxan; +, $EtOSO_2F$ in water; ●, $EtOSO_2F$ in aqueous dioxan; ○, $EtOSO_2F$ in aqueous acetone; △, Pr^iOSO_2F in aqueous acetone

The activation parameters for the solvolysis of alkyl fluorosulphates in water and aqueous solvents are shown in Table 1. These values could be correlated ($r = 0.99$) through a $\Delta H^‡$ *vs.* $\Delta S^‡$ representation (Figure 3), resulting in an isokinetic temperature of 294 K. The data corresponding to the methyl and isopropyl fluorosulphates show some departure from linearity.

Conclusions.—The results of this kinetic study indicate than an S_N2 mechanism rather than a unimolecular ionization process occur for the methyl and ethyl fluorosulphate solvolysis in water and aqueous acetone or dioxan. The non-existence of an acid-catalysis effect, the rate constant increase in the presence of strong nucleophiles, and the sensitivity of the reactions to the solvent ionizing power and nucleophilic character are also consistent with a bimolecular nucleophilic substitution mechanism. Although in pure water the two primary esters seem to solvolyse by the same type of mechanism, differences do exist in the character of their reactions, as shown by the added iodide effect.

For the solvolysis of isopropyl fluorosulphate in aqueous acetone, evidence of a unimolecular ionization process was found, from the large difference in the sensitivity to the solvent nucleophilicity and ionizing power, and the ' solvation number ' values; the presence of propene among the products of this reaction support the occurrence of this type of mechanism.

The influence of the dielectric constant of the medium on the rate constant values has also been discussed.

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