

KINETICS AND MECHANISM OF THE ALCOHOLYSES OF ETHYL FLUOROSULPHATE

LÁZARO F. R. CAFFERATA AND ESTHER L. SVARTMAN

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, 1900 La Plata, República Argentina

The alcoholyses of ethyl fluorosulphate in methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl and *n*-pentyl alcohols in the initial concentrations and temperature ranges of $(1-10) 10^{-3}$ M and -15.00 to 22.00 °C, respectively, were studied. The reactions follow pseudo-first-order kinetic laws up to at least *ca* 75 per cent ester conversions. At 10 °C the experimental rate constant for ethanolysis is similar to that of ethyl triflate but much smaller than for its hydrolysis. The reactivity of the ester is *ca* 10^4-10^5 times higher than that of alkyl halides and benzenesulphonates. In alcohol-benzene and alcohol-acetone mixtures the ΔH^\ddagger and ΔS^\ddagger activation parameters are only slightly affected by the media composition. The effect of the 'lyate ion' on the kinetics of these reactions were investigated and the effects of changes in the dielectric constant of the media were evaluated. It is concluded that the alcoholyses of the ester fulfil the requirements for predominant S_N2 -type mechanism, where the reaction ground states are more polar than the corresponding transition states.

INTRODUCTION

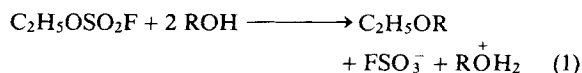
The hydrolysis of ethyl fluorosulphate in aqueous ethanol mixtures¹ gives small amounts of diethyl ether amongst the reaction products, suggesting that ethanolysis is competing with the ester hydrolysis. In this work, the kinetics and mechanism of ethyl fluorosulphate solvolysis in different pure alcohols and their mixtures with benzene or acetone were investigated to elucidate the effects of variations in the structure of the alcohols on the reaction. Thus, valid comparisons of reactivities of ethyl fluorosulphate and related compounds towards alcohols can be evaluated.

RESULTS AND DISCUSSION

The profiles of the kinetics of ethyl fluorosulphate solvolyses in different alcohols, with initial substrate concentrations of $(1-10) 10^{-3}$ M and temperature ranges of -15.00 to 22.00 °C show that all behave very similarly (Figure 1), except for the reaction in *tert*-butyl alcohol where a secondary process can be postulated, resulting in an upward drift of the measured electrical resistance values in the later stages of reaction.

Thus, according to reaction product analyses in terms of ether and acid produced (Table 1), the stoichiometries can be represented by the following general

equation:



where R = CH₃, C₂H₅, *n*-C₃H₇, *i*-C₃H₇, *n*-C₄H₉, *i*-C₄H₉, *tert*-C₄H₉ and *n*-C₅H₁₁.

The RO⁺H₂ oxonium ion species [equation (1)] must be included as a primary reaction product considering the relatively low Lewis base character of the low concentrations of ether products. The signal at $\delta = 9.3$ ppm in the proton NMR analysis of the *tert*-butanolysis reaction products, characteristic of protonated alcohols,² supports the above postulate at least in this solvent. However, the Bu⁺O⁺H₂ ion would probably form the corresponding carbocation which leads to isobutene as a secondary product. The traces of that gaseous compound detected [by gas chromatography (GC)] amongst the reaction products in some of the *tert*-butanolysis experiments support the following consecutive fast decomposition reaction:



For all the alcoholyses investigated, except in *tert*-butyl alcohol solvent, the increases in conductivity follow pseudo-first-order kinetics up to at least *ca* 75 per cent ester conversion, consistent with the lack of any significant differences between the k_{obs} values

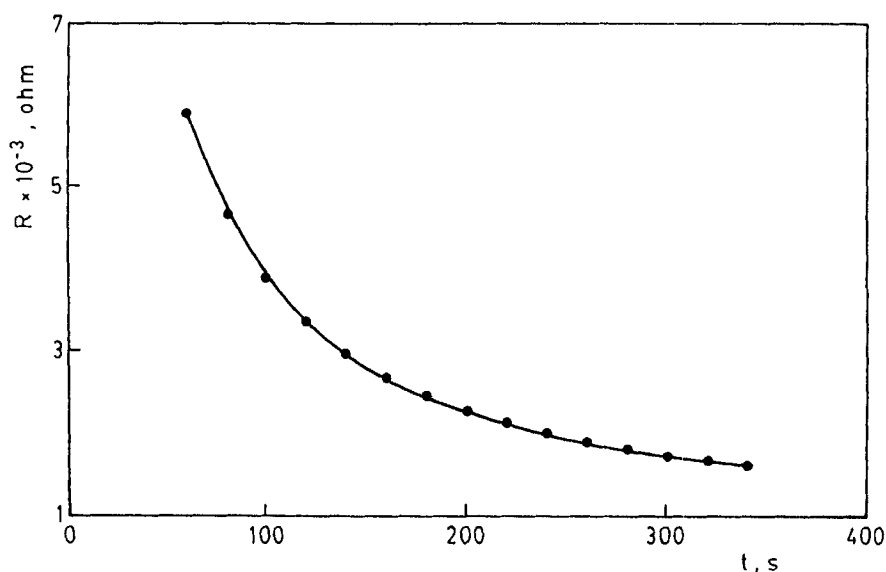


Figure 1. Kinetic profile (electric resistance vs t) for the ethanolysis (at 22.0°C) of ethyl fluorosulphate ($2.0 \times 10^{-3}\text{ M}$). At reaction time of 2400 s the corresponding $R_{\infty} = 1.02 \times 10^3$ ohm

Table 1. Analysis of reaction products of ethyl fluorosulphate solvolyses in pure alcohols and alcohol-benzene mixtures

Solvent	FSO ₃ Et 10 ³ M (10 ³ m) ^d	ROEt ^a 10 ³ m	Acidity ^b 10 ³ M
Methanol	1.8		1.8 ± 0.1
	2.0		2.0
40% Methanol-benzene	2.0		2.0 ± 0.1
Ethanol	5.2 (6.5)	5.7	5.3
	8.2 (10.0)	9.0	
	8.3 (10.0)	8.8	8.3
<i>n</i> -Propanol	1.6		1.6 ± 0.1
40% <i>n</i> -Propanol-benzene	1.5		1.5 ± 0.1
Isopropanol	1.3		1.3 ± 0.1
	2.0 (3.8)	2.9	
	3.3 (4.2)	3.6	
	3.6 (4.5)	3.5	
<i>n</i> -Butanol	2.4		2.4 ± 0.1
40% <i>n</i> -Butanol-benzene	2.2		2.3
Isobutanol	1.2		1.2 ± 0.1
50% Isobutanol-benzene	2.5		2.5 ± 0.1
<i>tert</i> -Butanol ^c	1.3		1.3
	2.5		2.5
	4.0		4.0
	3.6 (4.6)	4.3	
	5.7 (7.2)	6.8	
<i>n</i> -Pentanol	1.6		1.7 ± 0.1
	4.6 (5.6)	5.7	
	5.4 (6.6)	6.4	4.4
	8.0 (9.8)	9.9	

^a Yields of corresponding ethers.

^b Errors as standard deviations of at least three independent determinations.

^c Isobutene was detected as a product (GC).

^d Molality of the solutions.

Table 2. Kinetic parameters of the solvolyses of ethyl fluorosulphate $(1-10) \times 10^{-3}$ M in various alcohols and alcohol-benzene and alcohol-acetone mixtures

Solvent ^a	Temperature (°C)	$k_{\text{obs}} \times 10^4$ (s ⁻¹) ^b	n^c	ΔH^\ddagger (kcal mol ⁻¹) ^d	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹) ^d	
Methanol	-15.00	0.662 ± 0.034	3			
	1.90	4.84 ± 0.02	3			
	12.20	15.2 ± 0.5	4			
	22.00	38.3 ± 1.0	3	16.1 ± 0.1	-19.4 ± 0.4	
80% Methanol-benzene	1.90	3.77 ± 0.08	3			
	22.00	30.4 ± 1.2	3	16.2 ± 0.2	-17.7 ± 0.8	
60% Methanol-benzene	1.90	3.16 ± 0.08	3			
	22.00	23.9 ± 1.2	3	15.7 ± 0.3	-20.0 ± 0.9	
50% Methanol-benzene	1.90	2.92 ± 0.06	3			
	22.00	21.0 ± 0.1	3	15.3 ± 0.1	-21.6 ± 0.4	
40% Methanol-benzene	1.90	2.44 ± 0.21	3			
	22.00	20.9 ± 0.70	3	16.7 ± 0.4	-16.7 ± 1.5	
80% Methanol-acetone	1.90	4.94 ± 0.08	3			
	22.00	52.4 ± 3.8	6	18.4 ± 0.2	-9.2 ± 0.9	
60% Methanol-acetone	1.90	5.10 ± 0.05	4			
	22.00	44.7 ± 3.2	5	16.8 ± 0.3	-14.8 ± 1.0	
40% Methanol-acetone	1.90	4.65 ± 0.25	4			
	22.00	38.8 ± 3.2	5	16.4 ± 0.3	-16.4 ± 1.3	
20% Methanol-acetone	1.90	2.81 ± 0.09	5			
	22.00	22.2 ± 1.8	7	16.0 ± 0.3	-19.1 ± 0.9	
Ethanol	-15.00	0.266 ± 0.003	3			
	1.90	2.81 ± 0.26	2			
	2.18	3.15 ± 0.36	3			
	4.58	4.16 ± 0.20	2			
	12.18	9.73 ± 0.26	2			
	12.18	10.6 ± 0.1 ^e	2			
	12.20	11.3 ± 0.1	2			
	17.69	18.3 ± 0.1	2			
	22.00	29.0 ± 0.1	3	18.1 ± 0.2	-14.5 ± 0.8	
	90% Ethanol-benzene	1.90	2.80 ± 0.01	2		
		12.20	10.0 ± 0.1	2		
22.00		27.3 ± 1.0	3	18.4 ± 0.1	-13.1 ± 0.8	
80% Ethanol-benzene	1.90	2.87 ± 0.10	2			
	12.20	9.55 ± 0.10	2			
	17.69	15.5 ± 0.2	2			
	22.00	25.5 ± 0.1	3	17.0 ± 0.4	-18.0 ± 1.3	
70% Ethanol-benzene	1.90	2.40 ± 0.02	2			
	12.20	8.39 ± 0.06	2			
	22.00	22.3 ± 0.4	3	17.4 ± 0.3	-16.5 ± 1.0	
60% Ethanol-benzene	1.90	2.04 ± 0.10	2			
	12.20	7.77 ± 0.06	2			
	22.00	20.3 ± 0.3	3	16.1 ± 0.4	-20.9 ± 1.4	
50% Ethanol-benzene	1.90	1.59 ± 0.03	2			
	12.20	6.57 ± 0.10	2			
	22.00	17.1 ± 0.6	3	19.1 ± 0.9	-10.5 ± 3.1	
40% Ethanol-benzene	12.20	5.46 ± 0.23	2			
	22.00	12.6 ± 0.13	2	17.9	-16.2	
30% Ethanol-benzene	1.90	1.28 ± 0.04	2			
	12.20	4.32 ± 0.10	2			
	22.00	11.9 ± 0.2	3	17.2 ± 0.3	-16.7 ± 0.8	
90% Ethanol-acetone	1.00	3.21 ± 0.13	3			
	12.20	12.5 ± 0.3	2			
	22.00	33.1 ± 0.6	3	17.6 ± 0.5	-13.8 ± 1.6	
70% Ethanol-acetone	1.90	3.71 ± 0.04	2			
	12.20	13.7 ± 0.1	2			
	22.00	35.5 ± 1.0	3	18.8 ± 0.4	-8.4 ± 1.4	

(Continued)

Table 2. (Continued)

Solvent ^a	Temperature (°C)	$k_{\text{obs}} \times 10^4$ (s ⁻¹) ^b	n^c	ΔH^\ddagger (kcal mol ⁻¹) ^d	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹) ^d
50% Ethanol-acetone	1.90	3.95 ± 0.18	2	14.9 ± 0.1	-21.6 ± 0.5
	12.20	13.3 ± 0.1	2		
	22.00	32.8 ± 0.1	3		
30% Ethanol-acetone	1.90	3.38 ± 0.04	2	15.6 ± 0.3	-18.7 ± 1.1
	12.20	10.4 ± 0.01	2		
	22.00	25.0 ± 0.2	3		
10% Ethanol-acetone	1.90	2.39 ± 0.10	2	14.6 ± 0.3	-20.9 ± 1.2
	12.20	6.07 ± 0.22	2		
	22.00	15.5 ± 0.5	3		
<i>n</i> -Propanol	-15.00	0.240 ± 0.025	3	16.5 ± 0.2	-18.2 ± 0.8
	-10.00	0.448 ± 0.047	2		
	1.90	2.18 ± 0.04	3		
Isopropanol	12.20	6.41 ± 0.13	4	16.0 ± 0.2	-20.1 ± 0.6
	22.00	18.2 ± 0.7	3		
	1.90	1.57 ± 0.03	3		
80% Isopropanol-benzene	12.20	4.69 ± 0.16	3	16.5 ± 0.2	-18.4 ± 0.5
	22.00	12.4 ± 0.8	6		
	1.90	1.39 ± 0.06	3		
60% Isopropanol-benzene	22.00	11.7 ± 0.32	6	17.4 ± 0.2	-15.4 ± 0.5
	1.90	1.21 ± 0.04	3		
	22.00	11.4 ± 0.4	6		
50% Isopropanol-benzene	1.90	1.06 ± 0.05	3	19.0 ± 0.2	-10.1 ± 0.8
	22.00	12.1 ± 0.7	6		
	1.90	1.02 ± 0.06	3		
40% Isopropanol-benzene	22.00	9.7 ± 0.4	4	17.5 ± 0.3	-15.6 ± 1.1
	1.90	1.67 ± 0.06	3		
	12.20	5.32 ± 0.03	3		
<i>n</i> -Butanol	22.00	15.2 ± 0.4	5	17.2 ± 0.2	-15.8 ± 0.6
	1.90	1.69 ± 0.01	3		
	12.20	17.6 ± 0.4	2		
80% <i>n</i> -Butanol-benzene	22.00	16.6 ± 0.3	2	16.0 ± 0.2	-20.0 ± 0.6
60% <i>n</i> -Butanol-benzene	22.00	16.5 ± 2.1	3		
40% <i>n</i> -Butanol-benzene	22.00	16.5 ± 0.06	3		
Isobutanol	1.90	1.69 ± 0.01	3	15.4 ± 0.5	-21.6 ± 1.8
	12.20	4.98 ± 0.06	3		
	22.00	14.8 ± 0.7	3		
80% Isobutanol-benzene	1.90	1.90 ± 0.18	2	15.9 ± 0.5	-18.9 ± 1.8
	12.20	5.16 ± 0.16	2		
	22.00	13.7 ± 0.81	3		
60% Isobutanol-benzene	1.90	2.42 ± 0.15	2	17.9 ± 0.8	-11.6 ± 2.7
	12.20	5.42 ± 0.40	2		
	22.00	18.8 ± 1.03	6		
50% Isobutanol-benzene	1.90	2.41 ± 0.22	4	18.5 ± 0.5	-11.1 ± 1.8
	12.20	5.67 ± 0.64	2		
	22.00	21.1 ± 0.3	3		
<i>n</i> -Pentanol	1.90	1.43 ± 0.01	3	21.4 ± 1.0	-1.1 ± 3.5
	12.20	4.70 ± 0.04	3		
	22.00	17.6 ± 0.4	3		
80% <i>n</i> -Pentanol-benzene	22.00	17.9 ^e	1	15.4 ± 0.1	-21.4 ± 0.5
	1.90	1.27 ± 0.05	3		
	22.00	19.6 ± 3.6	2		
60% <i>n</i> -Pentanol-benzene	1.90	1.90 ± 0.07	3	17.4 ± 0.3	-14.2 ± 1.3
50% <i>n</i> -Pentanol-benzene	1.90	1.79 ± 0.10	3		
80% <i>n</i> -Pentanol-acetone	1.90	2.46 ± 0.04	3		
60% <i>n</i> -Pentanol-acetone	22.00	18.0 ± 0.5	3	17.8 ± 0.1	-12.6 ± 0.5
	1.90	2.35 ± 0.01	3		
	22.00	22.2 ± 1.9	4		
40% <i>n</i> -Pentanol-acetone	1.90	2.35 ± 0.05	3	17.8 ± 0.1	-12.6 ± 0.5
	22.00	23.3 ± 0.4	3		

(Continued)

Table 2. (Continued)

Solvent ^a	Temperature (°C)	$k_{\text{obs}} \times 10^4$ (s ⁻¹) ^b	n^c	ΔH^\ddagger (kcal mol ⁻¹) ^d	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹) ^d
<i>tert</i> -Butanol	28.50	26.2 ± 1.27	2		
	30.50	29.7 ± 0.8	2		
	32.00	33.7 ± 0.3	2		
	35.00	47.7 ± 4.4	3		
	36.50	54.9 ± 0.1	2		
	39.00	72.6	1		
	39.00	72.1 ^e	1	19.9 ± 0.3	- 7.2 ± 0.9
80% <i>tert</i> -Butanol-benzene	30.20	44.7 ± 6.3	11		

^a $x\%$ means x volumes of alcohol plus $100 - x$ volumes of benzene at 25 °C.

^b Errors expressed as mean standard deviations.

^c Number of individual kinetic determinations.

^d Activation parameters at 10.0 °C calculated with normalized values of k ($k = k_{\text{obs}}/[ROH]$); errors obtained as in Ref. 20.

^e Value obtained in the presence of the products of a previous alcoholysis run.

obtained at one temperature in experiments where the initial ester concentration was changed by nearly tenfold (Table 2).

In the experiments performed in the presence of the products of previous solvolytic reactions (fluoro-sulphuric acid being one of those substances), acid catalysis was not observed (Table 2). This suggests that S_N2 -type nucleophilic substitution mechanisms without specific electrophilic assistance from added acids are predominant for the ethyl fluorosulphate alcoholyses.³

The comparison of the k_{obs} values in all of the pure alcohols investigated shows that, in general, the alcoholyses of ethyl fluorosulphate are slower than that of its hydrolysis.⁴ The reactivity of the ester (calculated at 10 °C using the data in Table 2) is *ca* 10^4 – 10^5 times higher than those of substrates related to moderate acids, such as ethyl bromide⁵ and ethyl benzene-sulphonate⁶ (Table 3). However, it is similar to that of ethyl triflate,⁷ both compounds being derived from 'very strong acids', an observation in accord with the behaviour of the corresponding methyl esters.⁸

The k_{obs} values in the alcohols and in the mixtures of the alcohols with benzene or acetone (Table 2) show that, at constant temperature, the rates of solvolyses of the ester decrease as the alcohol concentration is lowered. This effect can be evaluated by the Kirkwood treatment⁹ of the free energy needed to transfer a dipole from the vacuum to a medium of dielectric constant ϵ , represented by the equation

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

where k_0 is the solvolysis rate constant in a reference medium ($\epsilon = 1$), μ_A , μ_B and μ_M are the dipole moments of the reactive particles A, B and the 'transition state' M, considered as rigid spheres with the corresponding molecular radii, and k is the Boltzman constant. The $\log k$ vs $(\epsilon - 1)/(2\epsilon + 1)$ plot for all the alcohol-benzene mixtures (Figure 2), where $k = k_{\text{obs}}/C_{\text{ROH}}$ (C_{ROH} is the molar alcohol concentration) indicate a nonlinear decrease in $\log k$ values as ϵ of the media increases. Thus, the data shown in Figure 2 clearly show that the

Table 3. Kinetic parameters for the solvolysis of some structurally related esters at 10 °C

Compound	Solvent	$k_{\text{obs}} \times 10^8$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal K ⁻¹ mol ⁻¹)	Ref.
BrEt	80% Ethanol-water	0.599	23.3	- 11.95	5
C ₆ H ₅ SO ₂ OEt	Ethanol	3.29	21.4	- 17.0	6
<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ OEt	Ethanol	1.95	21.5	- 16.9	6
<i>p</i> -ClC ₆ H ₄ SO ₂ OEt	Ethanol	6.47	22.1	- 13.2	6
CF ₃ SO ₂ OEt	Ethanol	108000	13.2	- 25.5	7
FSO ₂ OEt	Methanol	115000	16.1	- 19.4	This work
FSO ₂ OEt	Ethanol	26800	18.1	- 14.5	This work
FSO ₂ OEt	<i>n</i> -Propanol	56000	16.5	- 18.2	This work
FSO ₂ OEt	Isopropanol	51200	16.0	- 20.1	This work
FSO ₂ OEt	<i>n</i> -Butanol	44100	17.2	- 15.8	This work
FSO ₂ OEt	<i>sec</i> -Butanol	44600	16.0	- 20.0	This work
FSO ₂ OEt	<i>tert</i> -Butanol	26800	19.9	- 7.2	This work
FSO ₂ OEt	<i>n</i> -Pentanol	39600	18.5	- 11.1	This work

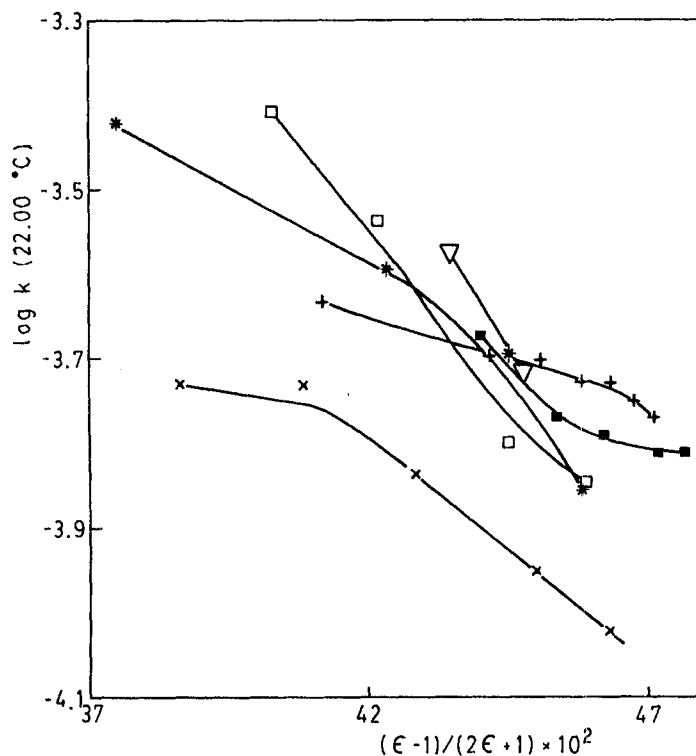


Figure 2. Kirkwood equation plot (at 22.00 °C) for alcoholysis of ethyl fluorosulphate in alcohol-benzene mixtures: ■, methanol-benzene; +, ethanol-benzene; ×, isopropanol-benzene; □, isobutanol-benzene; *, *n*-butanol-benzene; ▽, *n*-pentanol-benzene

Kirwood treatment is not applicable to the alcoholyses of ethyl fluorosulphate, which represent typical examples of S_N2 solvolyses where the solvent is also a reactant.

However, these results for the ethyl fluorosulphate reactions are similar to the behaviour shown by the same ester in its hydrolysis in aqueous-organic solvents.⁴ This can be explained if the reaction ground states were more polar than the corresponding transition states because the former turns out to be more stabilized when the dielectric constant of the media is increased. The sequence of the decrease in Figure 2 can also be related to the chain length of the alcohol molecules: those with longer carbon atom chains are the best solvents because the self-association by hydrogen bonding in the liquid state decreases with the increase in the molecular weight of the alcohol molecules.¹⁰

The 'solvation number plot'¹¹ (Figure 3) gives values ranging from -1.8 to 0.7 for the solvolytic reactions in the different alcohols. These extremely low values (usually near 2 for an S_N2 -type and 6-7 for an S_N1 -type reaction) resembles those for the alkyl chlorosulphate reactions in aqueous mixtures.¹² Further, the values

will be related to variations in the nucleophilicities of the different solvents according to their composition (in some cases the negative parameters suggest a desolvation of a relatively polar ground state). However, the results are as expected, considering the strongly polar character of the substrate molecule, which should in general be relatively more solvated at the initial state of the reactions.

The 'lyate ion effect',¹³ i.e. the k_{RO^-}/k_{ROH} ratio values (Table 4), a useful parameter for mechanistic determination of nucleophilic substitution reactions, turns out to be similar to values observed for other S_N2 -type reactions.^{6,14}

The low enthalpies of activation for the alcoholyses (Table 2) can be rationalized considering the strong leaving character of the FSO_3 group of the substrate molecule. The variations in the entropies of activation almost compensate those of the enthalpies, rendering the alcoholysis of ethyl fluorosulphate a process with a nearly constant free energy of activation. Following a treatment applied to the reactions of some aryl sulphonic esters,¹⁵ the initial and transition states of the solvolyses of ethyl fluorosulphate in methyl, ethyl,

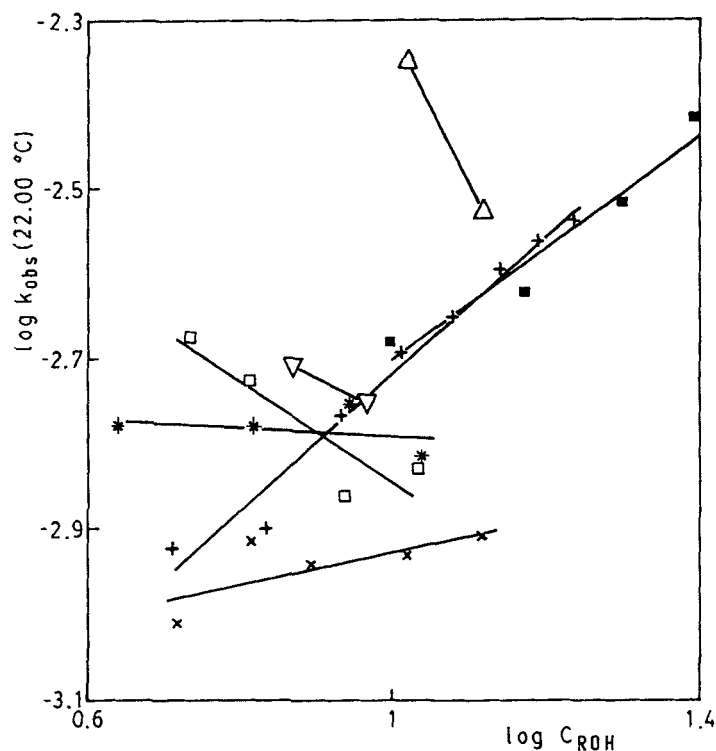


Figure 3. 'Solvation number plot' for alcoholysis (at 22.00 °C) of ethyl fluorosulphate in alcohol-benzene mixtures: ■, methanol-benzene ($n=0.7$); +, ethanol-benzene ($n=0.7$); ×, isopropanol-benzene ($n=0.3$); □, isobutanol-benzene ($n=-0.6$); *, *n*-butanol-benzene ($n=-0.05$); Δ, *tert*-butanol-benzene ($n=-1.8$); ▽, *n*-pentanol-benzene ($n=-0.5$)

Table 4. 'Lyate ion effect' for ethyl fluorosulphate solvolyses in ethyl, methyl and isopropyl alcohols (ROH)

R	Temperature (°C)	$10^2 k_{RO^-}$ (l mol ⁻¹ s ⁻¹) ^a	k_{RO^-}/k_{ROH} (l mol ⁻¹)
Et	-15.00	2.85 ± 0.28	1071
	-6.30	7.38 ± 0.54	
	1.90	21.7 ± 3.3	772
	12.20	41.8 ± 3.0	370
Me	1.90	13.0 ± 2.3	268
	22.00	0.35 ± 0.10	3

^a Values obtained with a second-order kinetic equation; errors as mean standard deviations.

n-propyl, *n*-butyl and *n*-pentyl alcohols can exhibit differences in their degree of order, which would be reflected in the corresponding ΔS^\ddagger values (Figure 4).

The behaviour can be interpreted by the formation of solvation shells of variable rigidity owing to intermolecular hydrogen bonding between the alcohol solvents and the ethyl fluorosulphate molecules or the corres-

ponding transition states of the reactions. In the alcoholyses the charges of both states are more dispersed as the hydrocarbon residue of the alcohol molecule increases in size, leading to increasing difficulties in ordering progressively larger solvent molecules around the solvation shell. However, the entropies of the more polar initial states might be expected to decrease more rapidly through the series of alcohols than in the corresponding transition states, as the hydrocarbon chain of the alcohol molecules increases in length. It can also be proposed that the entropies of the reaction initial states in methanol and ethanol have smaller values than expected because in these solvents the smaller molecular volume and the hydrogen bonding self-association are more important; the corresponding enthalpies of activation have larger values than the expected, reflecting the importance of these effects.

Further, the entropies of activation of the solvolyses in the alcohols with branched hydrocarbon chains, such as isopropyl and isobutyl alcohols, are in accord with the above postulate, but the reaction in *tert*-butyl alcohol exhibits a more disordered transition state,

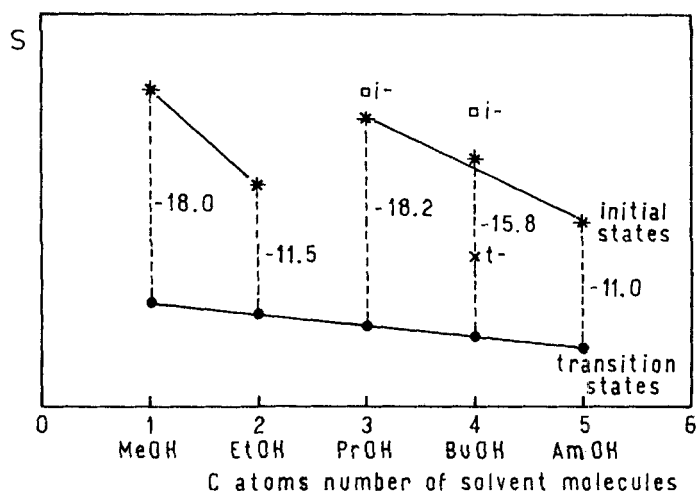
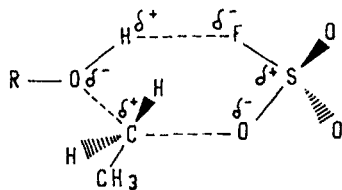


Figure 4. Entropy values for alcoholysis of ethylfluorosulphate in pure alcohol solvents. The symbols i- and t- refer to iso- and tert-alcohols, respectively; numerical values correspond to the ΔS^\ddagger of the reactions

probably owing to steric hindrance by the substituent methyl groups. Certainly, the relative effect of the variation of the entropies of activation on the rate constants is larger than that of the corresponding enthalpies.

A six-centred cyclic transition state (Scheme 1) could be postulated for the alcoholyses of ethyl fluorosulphate where the corresponding charge dispersion is increased with increasing complexity of the substituent R atomic groups.



Scheme 1

EXPERIMENTAL

Materials. Ethyl fluorosulphate was obtained¹⁶ using a Pyrex flow apparatus by reaction of fluorosulphuric acid with ethylene at 0°C. The reaction product was isolated and purified by several bulb-to-bulb distillations from 0 to -78°C under reduced pressure and its purity was checked by IR and quantitative chemical analysis of alcoholysis products. Reagent-grade methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and isobutyl alcohol were refluxed with magnesium cuttings activated with mercury(II) chloride and then distilled.¹⁷ Tert-Butyl alcohol was refluxed with calcium hydride and distilled.¹⁸ *n*-Pentyl alcohol was dried with sodium and diethyl phthalate and then

distilled.¹⁷ Benzene was dried by refluxing with sodium and distilled.¹⁷ Acetone was purified by refluxing with potassium permanganate and dried with anhydrous potassium carbonate.¹⁸ The purity of the organic solvents was verified by GC analysis and the water contents (less than 100 ppm) were checked by Karl Fisher titration.

Quantitative product analyses. Gas chromatography with flame ionization detection was employed for the determination of the alkyl ethyl ether products (6 ft × $\frac{1}{8}$ in i.d. stainless-steel column at 50°C filled with Chromosorb W AW DMCS impregnated with 25 per cent β, β' -oxydipropionitrile). The internal standard method was used with ethyl pentyl ether as the internal standard (diethyl ether was used when the ether analysed was ethyl pentyl ether). The acidity of the reaction solutions after the kinetic experiments was determined by conductimetric titration against ethanolic potassium hydroxide.

Kinetic measurements. The reaction rates of the alcoholyses were measured conductimetrically (cell constant 0.4 cm⁻¹) using a Tinsley Model 4896 conductivity bridge with an oscilloscope as zero detector. In most of the runs the initial concentration of the ester in the reaction media was ca 0.001 M. Pseudo-first-order rate constants (k_{obs}) were calculated by least mean square data treatments, plotting $-\ln(1/R_{t'} - 1/R_t)$ vs t , where R_t and $R_{t'}$ are the electric resistances of the solutions measured at times t and t' , respectively, in a constant period of time.¹⁹ The activation parameters of the reactions were calculated according to the method of Huyberechts *et al.*²⁰ In the

alcoholysis experiments with the corresponding alkoxide ions added, the reaction constant values (k_{RO^-}) were calculated with a second-order kinetic equation using calibration plots which related the electric resistance measurements with the actual concentration of the reaction products in the corresponding solutions.

ACKNOWLEDGEMENTS

INIFTA is sponsored by Consejo Nacional de Investigaciones Científicas y Técnicas, the Universidad Nacional de La Plata and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

REFERENCES

1. O. E. Desvard and L. F. R. Cafferata, *An. Asoc. Quím. Argent.* **67**, 9 (1979).
2. G. A. Olah, J. Sommer and E. Namanworth, *J. Am. Chem. Soc.* **89**, 3576 (1967).
3. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Chapt. 7. Cornell University Press, Ithaca, NY (1953).
4. L. F. R. Cafferata, O. E. Desvard and J. E. Sicre, *J. Chem. Soc., Perkin Trans.* **2** 940 (1981).
5. W. Taylor, *J. Chem. Soc.* 992 (1937).
6. E. Tommila and M. Lindholm, *Acta Chem. Scand.* **5**, 647 (1951).
7. A. Streitwieser, Jr, C. L. Wilkins and E. Kiehlmann, *J. Am. Chem. Soc.* **90**, 1598 (1968).
8. D. N. Kevill and G. M. L. Lin, *Tetrahedron Lett.* 949 (1978).
9. J. K. Kirkwood, *J. Chem. Phys.* **2**, 531 (1934).
10. B. Singh and J. K. Vij, *Bull. Chem. Soc. Jpn.* **49**, 1824 (1976).
11. E. Tommila and A. Nieminen, *Acta Chem. Scand. Ser. A* **9**, 989 (1955).
12. E. Buncl, J. P. Millington and J. F. Wiltshire, *Can. J. Chem.* **55**, 1401 (1977).
13. A. Streitwieser, Jr, *Chem. Rev.* **56**, 571 (1956).
14. E. Buncl and J. P. Millington, *Can. J. Chem.* **43**, 556 (1965).
15. J. B. Hyne and R. E. Robertson, *Can. J. Chem.* **34**, 863 (1956).
16. G. A. Olah, J. Nishimura and Y. K. Mo, *Synthesis* 661 (1973).
17. A. I. Vogel, *A Text-Book of Practical Organic Chemistry*, Chapt. II. Longmans Green, London (1948).
18. J. A. Riddick and W. B. Bunger, *Organic Solvents*, Vol. 2 of *Techniques of Chemistry*, edited by A. Weissberger, Chapt. V. Wiley, New York (1970).
19. E. Guggenheim, *Philos. Mag.* **2**, 538 (1926).
20. S. Huyberechts, A. Halleux and R. Kruys, *Bull. Soc. Chim. Belg.* **64**, 203 (1955).