

Halogen Mobility in S_N2 Reactions of Carbonyl Compounds. Comparisons with Aromatic Halogen Mobility †

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Kinetic studies, using conductimetric techniques, have been carried out for isopropanolysis (solvolysis) reactions of some alkanoyl, benzoyl, and perfluoroalkanoyl halides, *viz.* butanoyl and benzoyl fluorides, chlorides, and bromides and perfluoropentanoyl fluoride and chloride. The halogen mobility orders, $F \ll Cl < Br$, have been compared with mobility patterns recognised for S_N reactions at saturated and aromatic carbon, and have been discussed in mechanistic terms. The substrate class reactivity order is perfluoroalkanoyl \gg benzoyl, alkanoyl. The actual ratios depend on which halogen is displaced, the ratios being larger in displacement of fluorine.

Halogen mobility can be highly indicative of details of mechanism. Our long-term studies of this in S_NAr reactions¹⁻⁵ are relevant to the present discussion and can be summarised as follows. (i) The addition-elimination S_N2 mechanism *via* a σ -complex is the principal mechanism, with reaction profiles in which there is a *deep* potential energy well. Thus, even in displacement of fluorine the formation of the first or second transition state may be rate limiting. (ii) There is an electronegativity factor favouring displacement of fluorine, compared with the heavy halogens, which the depth of the potential energy well allows to be kinetically significant in many reactions.

As a result, the halogen mobility orders $F \gg Cl, Br, I$, $F \ll Cl, Br, I$, and a few intermediate cases are well known. The high fluorine mobility pattern, observed for example in alcoholysis (solvolysis), is illustrated by curves A and B of Figure 1, and is based on ref. 5.

Our key suggestion for interpreting the acyl halide alcoholyses (solvolyses), studied by us, is that these reactions also proceed by an addition-elimination S_N2 -type mechanism, but with a *shallower* potential energy well.

This suggestion and its consequences are elaborated and discussed below, but it is convenient to present at this point a pair of reaction profiles for acyl fluoride and chloride alcoholysis (solvolysis) (curves C and D of Figure 1) which correspond to our suggestion, while maintaining the general character of addition-elimination S_N2 displacement of halogens.

In Figure 1 the differences in heights of transition state 1 of curves A and B and of curves C and D correspond to the electronegativity factor mentioned above. Differences in heights of transition state 2 of curves A and B and of curves C and D correspond to the differences in *intrinsic* mobility of fluorine and chlorine in corresponding situations.

It is also convenient, however, to recall that S_N1 reactions of $RCOLG^N$ compounds (LG^N = nucleofugal group) are known.⁶⁻⁹ It is accepted that such reactions, of *e.g.* acyl halides, occur only in propitious circumstances, including the structure of R such that it lends additional stabilisation to the forming acylium ion $[RC\equiv O]^+$. It is also convenient to add that various authors (*e.g.* see ref. 10 and papers cited therein) assert that a synchronous S_N2 mechanism, analogous to that at saturated carbon, may be utilised.

It is surprising how little serious attention has been directed to halogen mobility (or indeed that of other nucleofugal groups) in S_N reactions of carbonyl compounds.⁹⁻¹¹

In virtually all cases which include the mobility of fluorine, the reactions studied are of hydrolysis, and show fluorine as much less mobile than the heavy halogens, where the mobility order is $I > Br > Cl$. There is however one report¹² of the reactions of benzoyl chloride and fluoride with OH^- in 50% ethanol-water in which the F:Cl mobility ratio is 1.4:1 at 0 °C.

Though the experimental work now reported was carried out a considerable time ago¹³ its purpose still stands, *viz.*, to contribute to knowledge of leaving group, especially halogen, mobility in S_N reactions at heteropolar unsaturated carbon and to discuss the relation to the mechanism probably involved. In addition, the work was conceived for the purpose of extending our knowledge of the reactivity of electrophilic carbon centres.

We selected as substrates butanoyl fluoride, chloride, and bromide, benzoyl fluoride, chloride, and bromide, and perfluoropentanoyl fluoride and chloride. The reaction selected for study was isopropanolysis (solvolysis) in anhydrous conditions, and we followed rates by measuring conductivity changes.

The choice of isopropanolysis was based on the following considerations. (i) We could follow the reactions using conventional equipment; (ii) the conductivity values were adequate; (iii) we judged that there would be no possibility of an S_N1 reaction.

It is worth recalling that in some recent work^{7,8} we showed that benzoyl chloride follows an S_N2 mechanism even in methanolysis (solvolysis), while alkanoyl and perfluoroalkanoyl chlorides would be less susceptible to reaction by an S_N1 mechanism.

Experimental

Preparation of Materials and Solvents.—Butanoyl chloride was the commercial product redistilled twice to b.p. 100–101 °C (lit.,¹⁴ 101–101.5 °C). Butanoyl fluoride was prepared by reaction of anhydrous butanoic acid with oven-dried KHF_2 under reflux (3 h). After two distillations it had b.p. 66–67 °C (lit.,¹⁵ 67 °C). Butanoyl bromide was prepared by reacting anhydrous butanoic acid with PBr_3 at ambient temperature. After two distillations it had b.p. 127 °C (lit.,¹⁶ 128 °C). Benzoyl chloride was the commercial product redistilled several times to b.p. 196 °C (lit.,¹⁷ 196.2–196.5 °C). Benzoyl fluoride was prepared from the purified chloride by reaction with oven-dried KHF_2 under reflux (3 h). After three fractional distillations it had b.p. 154 °C (lit.,¹⁷ 155–156 °C). Benzoyl bromide was prepared by reacting dried benzoic acid with PBr_3 at ambient temperature. After distillation several times at reduced pressure,

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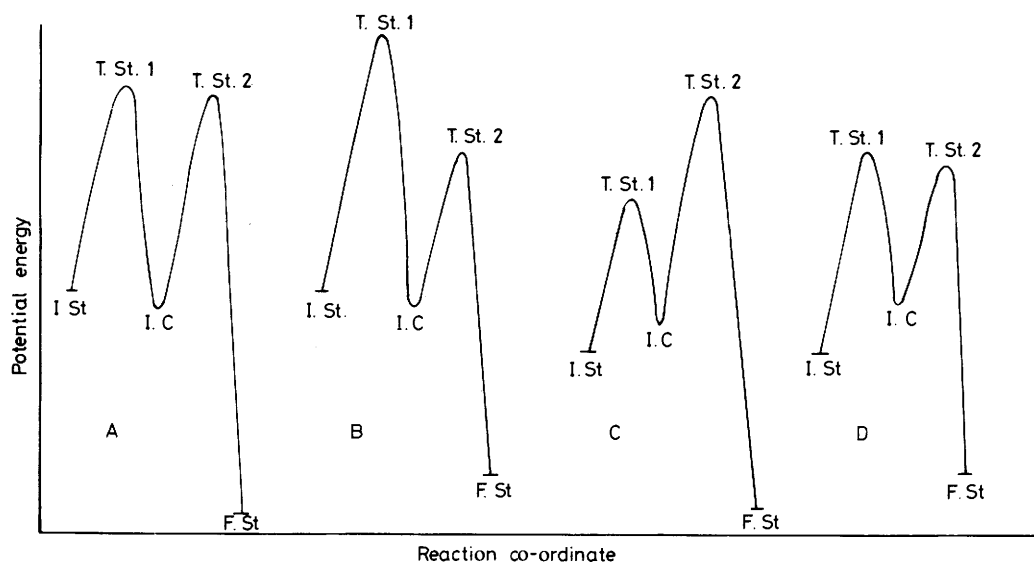


Figure 1. Types of reaction profile suggested for alcoholysis (solvolysis): A, displacement of fluorine from an activated aryl fluoride; B, displacement of chlorine from the corresponding chloride; C, displacement of fluorine from an acyl fluoride; D, displacement of chlorine from the corresponding chloride. I.St. = Initial state; I.C. = intermediate complex; F.St. = Final state; T.St. 1 and T.St. 2 = transition states 1 and 2

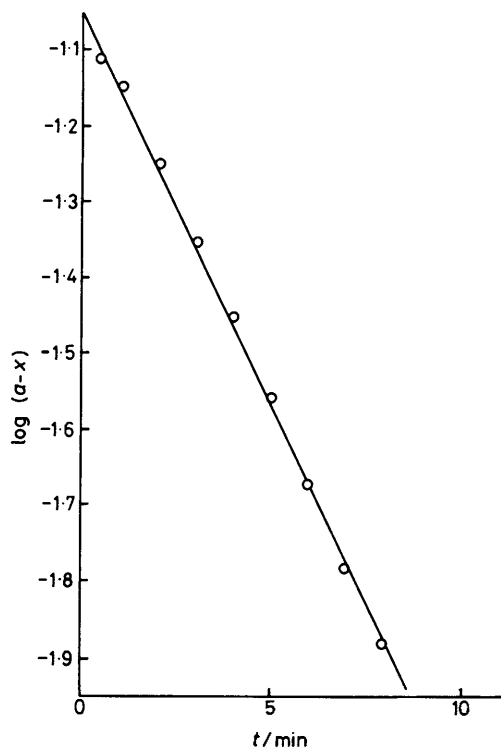


Figure 2. First-order plot for reaction of perfluoropentanoyl chloride in absolute propan-2-ol at -52°C

we recorded b.p. 218°C (lit.,¹⁸ 218 – 219°C). Perfluoropentanoyl chloride was the commercial product redistilled twice to b.p. 67 – 68°C (lit.,¹⁹ 67.5 – 68°C). Perfluoropentanoyl fluoride was obtained from the purified chloride by reaction with oven-dried KHF_2 under reflux (3 h). After two fractional distillations it had b.p. 45 – 47°C (lit.,²⁰ b.p. not recorded). For all these preparations oven-dried glassware was used and

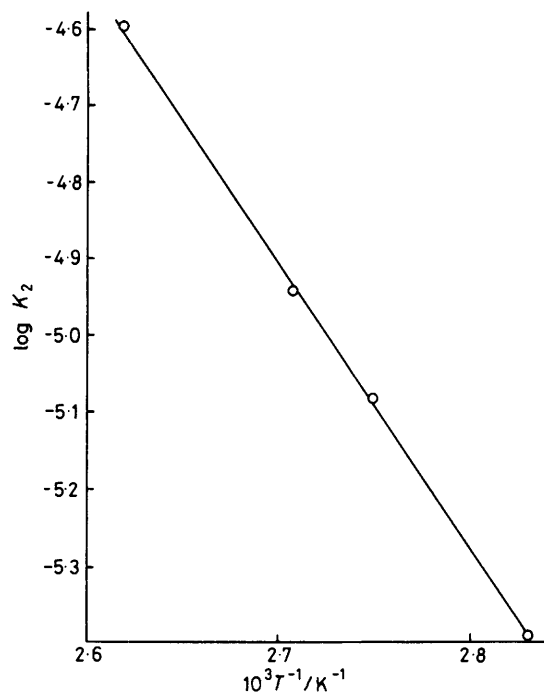


Figure 3. Arrhenius plot for reaction of benzoyl fluoride in absolute propan-2-ol

precautions taken to avoid entrance of moisture. Propan-2-ol was purified according to Vogel.²¹ Conductivity water was prepared from distilled water by reflux with KMnO_4 and KOH and re-distillation. Entrance of CO_2 to the receiver was avoided.

Thermostats.—Below -20°C , dry-ice-ethanol mixtures in a Dewar flask were used. This gave acceptable temperature control ($\pm 0.3^{\circ}\text{C}$) for the reaction times used. For other

Table 1. Experimental rate coefficients ($k_2/\text{mol}^{-1} \text{s}^{-1}$) for the isopropanolysis (solvolysis) of some carbonyl halides (logarithmic exponents in parentheses)

Groups linked to CO		Rate coefficient	$T/^\circ\text{C}$	Group linked to CO		Rate coefficient	$T/^\circ\text{C}$
C ₃ H ₇	F	1.31 (-6)	110.0	C ₆ H ₅	Cl	7.27 (-6)	25.0
		1.84 (-6)	115.0			8.39 (-6)	27.0
		2.44 (-6)	120.0			9.81 (-6)	29.6
		3.40 (-6)	125.0			1.50 (-5)	35.0
C ₃ H ₇	Cl	5.17 (-6)	25.0	C ₆ H ₅	Br	5.12 (-6)	-23.0
		5.22 (-6)	25.1			1.04 (-5)	-16.0
		7.55 (-6)	30.0			2.09 (-5)	-6.0
		1.10 (-5)	34.8			4.02 (-5)	+0.5
		1.48 (-5)	39.4			C ₄ F ₉	F
1.38 (-4)	-20.0	7.34 (-5)	-20.0				
2.01 (-4)	-15.0	1.61 (-4)	-10.0				
C ₃ H ₇	Br	2.93 (-4)	-10.0	C ₄ F ₉	Cl	3.33 (-4)	+0.1
		5.83 (-4)	0.0			1.26 (-4)	-61.0
		4.11 (-6)	80.0			1.76 (-4)	-57.0
		8.60 (-6)	90.8			2.82 (-4)	-52.0
C ₆ H ₅	F	1.20 (-5)	96.3			4.11 (-4)	-47.0
		2.68 (-5)	109.1			6.38 (-4)	-42.0

Table 2. Rate coefficients and Arrhenius parameters for the isopropanolysis (solvolysis) of some carbonyl halides at 25 °C (logarithmic exponents in parentheses)

Groups linked to C=O		Rate coefficient k_2 (l mol ⁻¹ s ⁻¹)	Halogen mobility ratio Cl = 1	Activation energy (ΔE^\ddagger / kJ mol ⁻¹)	Frequency factor log ₁₀ ($A/\text{mol}^{-1} \text{s}^{-1}$)	Substrate reactivity ratios displacing		
						F	Cl	Br
C ₃ H ₇	F	8.4 ₇ (-10)	1.6 ₄ (-4)	80.1	5.2 ₉	1		
C ₃ H ₇	Cl	5.1 ₇ (-6)	1 (0)	57.5	4.8 ₀		1	
C ₃ H ₇	Br	2.7 ₁ (-3)	5.2 ₄ (2)	41.5	4.7 ₁			1
C ₆ H ₅	F	4.2 ₈ (-8)	5.9 ₈ (-4)	72.4	5.3 ₄	5.0 ₅ (1)		
C ₆ H ₅	Cl	7.1 ₆ (-6)	1 (0)	56.5	4.7 ₇		1.3 ₉	
C ₆ H ₅	Br	2.7 ₂ (-4)	3.8 (1)	49.8	5.1 ₆			1.00 (-1)
C ₄ F ₉	F	1.6 ₃ (-3)	4.6 (-2)	43.1	4.7 ₆	1.9 ₂ (6)		
C ₄ F ₉	Cl	3.5 ₉ (-2)	1 (0)	34.5	4.9 ₄		6.9 ₄ (3)	

temperatures standard water- or oil-bath thermostats were used with temperature control to better than $\pm 0.1^\circ\text{C}$.

Conductivity Measurements and Rate Constants.—Conductivity measurements were made with an LKB 3216B conductivity bridge, and related to concentrations of products by prior calibration. Above 40 °C a sealed conductivity tube was used, allowing 15 min for it to attain thermostat temperature. For lower temperatures a cell with main and subsidiary containers was used which permitted the thermostat temperature to be attained before mixing.

The second-order rate coefficients were obtained from the solvolysis (first order) rate coefficients, dividing them by the molar concentration of solvent. The first-order rate coefficients were obtained graphically. Experimental rate coefficients are given as Table 1. Examples of determinations are given as Figures 2 and 3, *viz.*, the first-order rate plot for isopropanolysis of perfluoropentanoyl chloride at -52°C and the Arrhenius plot for benzoyl fluoride. Estimated errors in k_2 are *ca.* 1%.

Discussion

The halogen mobilities encountered in our studies are consistent with the limited number of studies reported in the literature.⁹⁻¹²

Analysing the kinetic data in detail (see Table 2), a number of very interesting features emerge.

In the three series studied, the order of mobility $\text{F} < \text{Cl}$ is clearly evident. In two of the series, in which the mobility of bromine was also determined, the extended order $\text{F} < \text{Cl} < \text{Br}$ is evident. The detailed analysis shows however that the relative fluorine:chlorine mobilities increase sequentially in the series RCOHal , PhCOHal , $\text{R}^{\text{F}}\text{COHal}$ for which $\text{F}:\text{Cl}$ mobility ratios are 1.64×10^{-4} , 5.98×10^{-3} , and 4.6×10^{-2} respectively.

In the change from RCOHal to PhCOHal the $\text{Br}:\text{Cl}$ mobility ratio decreases substantially, from 524 to 38.

Because of these changes the substrate reactivity ratios depend on which halogen is displaced. In displacement of fluorine, the perfluoroalkanoyl compound is over 10^6 times more reactive than the alkanoyl compound whereas it is only *ca.* 7×10^3 times more reactive in displacement of chlorine. In the intermediate position, benzoyl fluoride is *ca.* 50 times more reactive than butanoyl fluoride whereas the benzoyl and butanoyl chlorides have about equal reactivity. In displacement of bromine the benzoyl compound is *ca.* 10 times less reactive.

The substrate reactivity ratios, $\text{RCOHal} \sim \text{PhCOHal} \ll \text{R}^{\text{F}}\text{COHal}$, are what one would expect in relation to electron deficiency at carbonyl carbon, and to conjugative interactions.

We did not need, nor seek, kinetic data of high precision. It is gratifying therefore that the Arrhenius parameters are so well behaved. The values of the frequency factor, given as $\log_{10} A$,

are all virtually identical, falling in the range 5.03 ± 0.32 . They are what one might expect for a reaction between neutral substrates forming ions in a protic solvent.⁵

As a consequence reactivity differences are enthalpy-dependent. In displacement of fluorine ΔE^\ddagger values are 80.1, 72.4, and 42.1 kJ mol⁻¹ (alkanoyl, benzoyl, perfluoroalkanoyl). In displacement of chlorine the lower ΔE^\ddagger values are 57.5, 56.5, and 34.5 kJ mol⁻¹ respectively. The differing F:Cl mobility ratios correspond to $\Delta\Delta E^\ddagger$ values of 38.6, 22.6, and 8.6 kJ mol⁻¹. ΔE^\ddagger Values are lowest with the bromo compounds, varying from 41.5 (alkanoyl) to 49.8 kJ mol⁻¹ (benzoyl).

In discussing our results, we feel it necessary to make a number of general comments, making comparisons especially with halogen mobilities in S_NAr reactions, which we have studied in considerable depth.¹

We put forward and comment on the following mechanistic possibilities, and their ability or otherwise to explain the experimental results.

The first of these is that the reactions proceed by a synchronous S_N2 mechanism, which excludes any change in the bond order of the carbon-oxygen double bond and thus corresponds to the S_N2 mechanism at saturated carbon.

The second proposition is that the reactions proceed by a pure addition-elimination S_N2 mechanism, passing through a fully bonded tetrahedral intermediate which corresponds to a minimum in the reaction profile [analogous to the normal (activated) S_NAr mechanism] but differing from it in having a relatively shallow potential well.

The third proposition is that the reactions proceed by a 'mixed' addition-elimination S_N2 mechanism, corresponding to that suggested by Ingold²² for carboxy and amide reactions.

This also passes through a tetrahedral intermediate, which corresponds to a minimum in the reaction profile. The difference from the pure mechanism is the suggestion that in the intermediate, and in the first, as well as second, transition states there is some degree of rupture of the carbonyl-halogen bond. In these circumstances it seems reasonable to assume that the isopropoxy-carbon bond is not fully formed, at least in the first transition state and perhaps in the tetrahedral intermediate also.

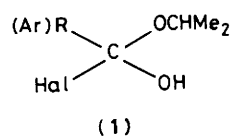
It seems to us extremely improbable that the carbonyl halide solvolyses follow a synchronous S_N mechanism, when one bears in mind that there is a polarisable π -bond at the electrophilic reaction centre linking carbon to the very electronegative oxygen atom. Further, this bond, though quite strong, is considerably weaker than the C-F bond and about equal in strength to the C-Cl bond. The mechanism seems to us incompatible with the F:Cl mobilities encountered in alkaline hydrolysis of benzoyl chloride and fluoride,¹² bearing in mind that there is no record in the literature of synchronous S_N2 reactions in which fluorine is not substantially *less* mobile than the heavy halogens.

The synchronous mechanism is not needed to explain the lower mobility of fluorine than of the heavy halogens (see below) and we regard it as incompatible with the much higher reactivity of perfluoroalkanoyl than of alkanoyl halides. It is also inconsistent with oxygen-exchange data.¹⁰

Furthermore, the very large differences in bond order necessary for the synchronous S_N2 mechanism to explain our results, even in part, are inconsistent with the near constancy of the log *A* term.

In relation to the addition-elimination S_N2 mechanism for the S_N2 carbonyl substitutions we make the following comments on our suggestion of a shallower potential well, when compared with S_NAr reactions.

The tetrahedral S_NAr intermediates (benzenide or σ -complex) are species which are highly conjugated; and this is much enhanced when suitably placed conjugative electron-withdrawing groups are present. This concept, which suggests



as an example equal levels of conjugative stabilisation of 2,4-dinitrobenzenoid and 2,4-dinitrobenzenide systems, gains strong support from the agreement with experiment of numerous thermochemical calculations of S_NAr reactions,^{1,23} which incorporate it.

In contrast, as the acyl halide reactions proceed, positive charge begins to develop on the isopropoxy oxygen ($\text{Me}_2\text{CH}-\text{OH}^{\delta+}$ ---), while negative charge begins to develop on the erstwhile carbonyl oxygen ($\text{C}^{\delta-}=\overset{\delta-}{\text{O}}$). These are highly acidic and basic centres respectively, and we suggest that there is an early proton transfer, essentially complete by the formation of the first transition-state. For simplicity, we present the subsequent tetrahedral intermediate in the fully-bonded form (1).

We surmise that this intermediate is less stable than the reactant, as is ester hydrolysis. One can speculate on loss of conjugation (ArCO case), or of polarisation-hyperconjugation (RCO case) as factors involved while it is reasonable to speculate that solvation factors favour the S_NAr intermediate in comparison with the acyl halide intermediate.

With a shallow potential energy well it would not be possible to have reactions in which the formation of transition state 1 is rate-limiting in displacement of fluorine. With a powerful reagent one might, as an exceptional case, have a reaction displacing fluorine in which although the formation of transition state 2 is rate-limiting the difference in energy transition state 2 - transition state 1 is less than the electronegativity effect discussed below. Thus the pure addition-elimination S_N2 mechanism is adequate to explain F:Cl mobility ratios considerably less than unity, as well as the F:Cl mobility ratio of 1.4, obtained in an alkaline hydrolysis reaction.^{1,2-5,12}

This brings forward the necessity to comment on the electronegativity effect so important in S_NAr reactions^{1,23-25} and which should be involved in the details of the reaction profiles of addition-elimination S_N2 reactions in general. An electronegative group reduces electron density on the electrophilic carbon to which it is attached and thus facilitates nucleophilic attack. This has an observable kinetic effect only when (i) the formation of transition state 1 is rate-limiting or (ii) in those cases in which the formation of transition state 2 is rate-limiting, where the difference of energy transition state 2 - transition state 1 does not exceed the amount by which the electronegativity effect reduces transition state 1. Examples are shown in ref. 4. As regards displacement of fluorine and chlorine we have suggested that the electronegativity difference between F and Cl causes a reduction in transition state 1 in displacement of fluorine approximately equal to 13 kJ mol⁻¹ (see particularly refs. 1, 2, and 23). The results of Swain and Scott¹² with F:Cl 1.4 correspond closely to this difference between transition states 1 and 2.

The pure addition-elimination S_N mechanism fails in not explaining the quite high Br:Cl mobility ratios observed in the carbonyl reactions (some high I:Cl ratios have also been observed¹⁰). We stress that in S_NAr reactions which proceed by the addition-elimination S_N2 (principal) mechanism, there is no known case where bromine is substantially more mobile than is chlorine and never even approaches the values shown by our work. Bromine is normally less mobile than chlorine.¹

On the basis of the preceding comments we suggest therefore that the reactions of the chlorides and bromides occur *via* the

'mixed' addition-elimination S_N2 mechanism, mentioned earlier. Since all the intermediates involve carbonyl-halogen bond rupture, it is difficult to conclude with any certainty which is the rate-limiting step formation of the first or second transition state. It does seem however that there is more carbonyl-halogen bond rupture in the alkanoyl than in the benzoyl series (see below). We consider that the fluorides react by the pure addition-elimination S_N2 mechanism, with the formation of the second transition state as the rate-limiting step (see above).

We believe that our comments are equally valid for other solvolytic reactions in hydroxylic solvents.

The reactions with OH^- , already mentioned, and reactions of strong nucleophiles in general, probably follow our version of the pure addition-elimination S_N2 mechanism.

We do not consider that our comments are in any way weakened by the occurrence of the halogen mobility order $\text{F} \ll \text{Cl} < \text{Br} < \text{I}$ in S_N2 reactions at saturated carbon, nor that the mobility order $\text{F} \ll \text{Cl}, \text{Br}, \text{I}$ is encountered in $S_N\text{Ar}$ reactions with many heavy nucleophiles* and/or in poorly ionising solvents. The spectrum of halogen mobilities in $S_N\text{Ar}$ reactions has been fully rationalised.¹

One additional point needs to be made abundantly clear. We recognise that the relatively low dielectric constant of propan-2-ol compared with water and methanol, or even ethanol, should reduce its ability to solvate ions in preference to interactions leading to formation of ion-pairs or multiplets or a crystal lattice. This cannot, however, be responsible for the halogen mobility order (especially $\text{F} \ll \text{Cl}$) encountered in our work. This is amply demonstrated by our other studies on solvolytic hydrolysis and alcoholysis, including isopropanolysis, of picryl chloride and fluoride. In all these reactions fluorine is much more mobile, and $\text{F}:\text{Cl}$ mobility ratios differ little from each other.^{5,26}

* Nucleophiles whose reactive centre is an atom of the second or higher row of the Periodic Table.

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