# The $S_N$ Mechanism in Aromatic Compounds. Part 41.[1] Thermochemical Calculations and Experimental Measurements of Methanolysis of 1-Fluoro-2,4-dinitrobenzene, Picryl Chloride, and Picryl Fluoride

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Rates and Arrhenius parameters for methanolysis of 1-fluoro-2.4-dinitrobenzene, picryl chloride, and picryl fluoride have been determined, and shown to be in satisfactory agreement with the results of a fundamental method of thermochemical calculation successfully applied previously to a wide range of $S_N$Ar reactions. These calculations also shed light on the sources of the large difference in nucleophilic strength of OMe$^-$ and MeOH, selected for the comparison of anionic and neutral forms of a nucleophile. The experimental results also lead to a comparison of the leaving group mobility of F and Cl in reactions with MeOH as nucleophile; as well as the activating power of an *o*-NO$_2$ group, when there is an NO$_2$ group in the other *ortho*-position. In the reaction of picryl chloride, the secondary reaction between product chloride ion and picryl methyl ether (demethylation) was avoided by carrying out the reaction in the presence of silver ion.

In studies of nucleophilic strength, it is of considerable interest to compare directly the reactivity of neutral and anionic forms of a nucleophile (NuH and Nu$^-$). For this $S_N$Ar reactions offer special advantages. Many such reactions are well behaved with bond-breaking and -forming steps separated. It is characteristic of reactions with light nucleophiles in protic solvents that the bond-forming step is rate limiting.[2] A good comparison is of OMe$^-$ and MeOH in the alkaline and neutral methanolysis of 1-fluoro-2,4-dinitrobenzene.

With the weak nucleophile, methanol, we have extended our studies to the more highly activated substrates, picryl chloride and fluoride. This permits quantitative measure and discussion of leaving group mobility of F and Cl with this reagent, and of activation by an *o*-NO$_2$ group when there is an NO$_2$ group in the other *ortho*-position.

The reactivity data have been compared with the results of a method of fundamental thermochemical calculation which has proven consistently successful in its application to a wide range of $S_N$Ar reactions.[2-10]

There are some experimental measurements of limited reliability [11,12] for the methanolysis (solvolysis) of picryl chloride. The authors referred to the difficulties caused by subsequent reaction of the products, chloride ion and 2,4,6-trinitroanisole. We have been able to obtain good results by carrying out the reaction in the presence of silver ion which does not catalyse $S_N2$Ar reactions in which the formation of the first transition state of heavy halide ion displacement is rate limiting.

Murto [13] measured the rate of solvolysis of picryl fluoride in methanol–water (1 : 1 v/v) at 24.8°; and estimated a rate constant for reaction of methanol in that solvent.

## EXPERIMENTAL

*Materials.*—AnalaR methanol was dried by standard procedures and fractionated, collecting the fraction of b.p. 64.3—64.8°. AnalaR 1-fluoro-2,4-dinitrobenzene was distilled under reduced pressure, collecting the fraction of b.p. 163—164° at 11 Torr. This solidified to crystals, m.p. 26° (lit.,[14a] 25.3°).

Picryl chloride was prepared from picric acid (14 g; containing 15% of water) by reaction with POCl$_3$ (40 ml) and pyridine (7 ml). The temperature of the mixture was raised gradually to 120—125°, where it was maintained for 1 h. After cooling and pouring onto ice, crystallisation from EtOH yielded 80% picryl chloride, m.p. 78—80° (lit.,[14b] 83°) (Found: Cl, 14.3. Calc. for $C_6H_2ClN_3O_6$: Cl, 14.3%).

Picryl fluoride was prepared from the chloride by halide exchange without solvent. Picryl chloride (2.48 g) was heated with dried KF (0.7 g) at 185° for 5 h. After extraction with dry benzene picryl fluoride (30%) was recrystallized several times from benzene–light petroleum, m.p. 127—128° (lit.,[15] 122—123, 130—131.5, 131—132°). The fluoride was further characterised by its i.r. spectrum.

*Kinetics.*—With 1-fluoro-2,4-dinitrobenzene, rates of solvolysis were measured by estimation of product fluoride ion against buffered standard thorium nitrate with Alizarin S indicator.

The solvolysis of picryl chloride was carried out in the presence of excess of Ag$^+$ and potentiometric back-titration of Ag$^+$ against standard Cl$^-$. The side reaction of demethylation by Cl$^-$ produced in the reaction was thus avoided.

The solvolysis of picryl fluoride was measured by following changes in u.v. absorption at 327 nm. Guggenheim analysis was used to obtain the $\psi$-$k$ values. In all the reactions the $\psi$-$k$ values obtained were converted to $k_2$ before estimating the Arrhenius parameters. These and rate constants were evaluated by computer analysis of experimental data. The following are typical results: picryl fluoride at 21.3°, $\psi$-$k$ $5.21 \times 10^{-3}$ s$^{-1}$, percentage error ±1.1%, correlation coefficient 0.999 7; picryl chloride

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at 101.0°, ψ–$k$ $9.63 \times 10^{-5}$ s$^{-1}$, percentage error ±0.56%, correlation coefficient 0.999 9. From all the rate data for picryl chloride, $\Delta E^{\ddagger} = 71.2$ kJ mol$^{-1}$, percentage error ±1.1%, correlation coefficient 0.999 7. The corresponding value of log $B$ is 4.58. As a matter of interest we attempted to get values of ψ–$k$ with picryl chloride in the absence of Ag$^+$. At 101.0°, for example, though we were able to use only the first 10% of reaction with any reasonable confidence, we obtained a ψ–$k$ value of $9.96 \times 10^{-5}$ s$^{-1}$. This is in quite good agreement with the reliable value obtained in the presence of Ag$^+$.

Solvolyses of 1-fluoro-2,4-dinitrobenzene and picryl chloride were carried out with samples sealed in glass ampoules. Table 1 gives all experimental rate measurements. Table 2 gives derived kinetic data, including alkaline methanolysis of 1-fluoro-2,4-dinitrobenzene, previously recorded.[16] Table 3 sets out the thermochemical calculations. The Figure shows calculated potential energy–reaction co-ordinate profiles.

TABLE 1

Experimental kinetic data for the methanolysis (solvolysis) of 1-fluoro-2,4-dinitrobenzene (A), picryl chloride (B), and picryl fluoride (C). ψ–$k_1$/s$^{-1}$ and $k_2$/l mol$^{-1}$ s$^{-1}$ at temperatures shown in parentheses

| Compound | ψ–$k_1$ | $k_2$ | Compound | ψ–$k_1$ | $k_2$ | Compound | ψ–$k_1$ | $k_2$ |
|---|---|---|---|---|---|---|---|---|
| A | $4.6_0 \times 10^{-6}$ (86.0) | $2.0_1 \times 10^{-7}$ | B | $3.7_7 \times 10^{-5}$ (85.6) | $1.6_6 \times 10^{-6}$ | C | $1.5_7 \times 10^{-3}$ (7.7) | $6.2_7 \times 10^{-5}$ |
| | $1.0_1 \times 10^{-5}$ (90.0) | $4.4_7 \times 10^{-7}$ | | $3.7_4 \times 10^{-5}$ (85.6) | $1.6_5 \times 10^{-6}$ | | $2.1_5 \times 10^{-3}$ (10.7) | $8.6_1 \times 10^{-5}$ |
| | $2.1_4 \times 10^{-5}$ (100.0) | $9.6_1 \times 10^{-7}$ | | $3.6_0 \times 10^{-5}$ (85.6) | $1.5_9 \times 10^{-6}$ | | $2.1_8 \times 10^{-3}$ (10.8) | $8.7_3 \times 10^{-5}$ |
| | $4.3_4 \times 10^{-5}$ (110.0) | $1.9_8 \times 10^{-6}$ | | $9.3_1 \times 10^{-5}$ (101.0) | $4.1_9 \times 10^{-6}$ | | $5.0_0 \times 10^{-3}$ (21.1) | $2.0_3 \times 10^{-4}$ |
| | $8.9_8 \times 10^{-5}$ (120.0) | $4.1_5 \times 10^{-6}$ | | $9.6_3 \times 10^{-5}$ (101.0) | $4.3_3 \times 10^{-6}$ | | $5.0_3 \times 10^{-3}$ (21.1) | $2.0_4 \times 10^{-4}$ |
| | $1.9 \times 10^{-4}$ (130.0) | $9.0_1 \times 10^{-6}$ | | $2.9_0 \times 10^{-4}$ (119.9) | $1.3_4 \times 10^{-5}$ | | $5.2_1 \times 10^{-3}$ (21.3) | $2.1_1 \times 10^{-4}$ |
| | | | | $2.7_8 \times 10^{-4}$ (119.9) | $1.2_9 \times 10^{-5}$ | | $7.9_2 \times 10^{-3}$ (26.5) | $3.2_3 \times 10^{-4}$ |

TABLE 2

Derived kinetic data for methanolysis of some halogenonitro-aromatic substrates at 100° (A, 1-fluoro-2,4-dinitrobenzene; B, picryl chloride; C, picryl fluoride)

| Substrate | Reagent | Rate constant $k_2$/l mol$^{-1}$ s$^{-1}$ | Activation energy * $\Delta E^{\ddagger}$/kJ mol$^{-1}$ | Frequency factor log ($B$/l mol$^{-1}$ s$^{-1}$) and activation entropy $\Delta S^{\ddagger}$/J mol$^{-1}$ K$^{-1}$ | Activation free energy $\Delta E^{\ddagger} - RT - T\Delta S^{\ddagger}$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| A | OMe$^-$ | $1.37 \times 10^{3}$ | $56._5$ (62) | $11.0_5$ −43.5 | $67._5$ |
| | MeOH | $9.61 \times 10^{-7}$ | 89.0 (80) | $6.4_5$ −127 | 133 |
| B | MeOH | $4.08 \times 10^{-6}$ | $71._2$ (69) | 4.6 −157 | 118 |
| C | MeOH | $3.57 \times 10^{-2}$ | $59._6$ (56) | 6.9 −113 | $93._5$ |

* Values calculated by thermochemical procedures are in parentheses (see also Table 3).

TABLE 3

Thermochemical estimates of activation energy for reactions in MeOH of OMe$^-$ and MeOH with 1-fluoro-2,4-dinitrobenzene (DNF), picryl chloride (PicCl), and picryl fluoride (PicF). All energy terms in kJ mol$^{-1}$. For fuller discussion of the method, see especially refs. 3 and 8

| Substrate | Reagent | Bond broken in σ-complex | Bond dissociation energy (BDE) | Ionisation energy | Solvation energy | Series term | Relative * energy levels | Corresponding % BDE and energy levels | | α-Substituent effect | Transition state energy levels | $\Delta E^{\ddagger}$ forward | $\Delta E^{\ddagger}$ reverse |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DNF [a] | MeO$^-$ | C–OMe | +322 | −255 | −347 | +272 | −8 | 22 | +71 | −17 | +54 | 62 | 165 |
| | | C–F | +448 | −337 | −473 | +251 [b] | −111 | 13.5 | +60 | −13 | +47 | | |
| DNF | MeOH | C–$\overset{+}{\mathrm{O}}$HMe | +322 | −1 042 | 0 | +686 | −34 | 19.5 | +63 | −17 | +46 | 80 | 136 |
| | | C–F | +448 | −337 | −473 | +272 | −90 | 14.5 | +65 | −21 | +44 | | |
| PicF | MeOH | C–$\overset{+}{\mathrm{O}}$HMe | +322 | −1 042 | 0 | +724 | +4 | 24 | +77 | −17 | +60 | 56 | 112 |
| | | C–F | +448 | −337 | −473 | +310 | −52 | 17.5 | +78 | −21 | +57 | | |
| PicCl | MeOH | C–$\overset{+}{\mathrm{O}}$HMe | +322 | −1 042 | 0 | +724 | +4 | 24 | +77 | −4 | +73 | 69 | 115 |
| | | C–Cl | +335 | −356 | −331 | +310 | −42 | 18.5 | +62 | −21 | +41 | | |

[a] Previously included in ref. 6 (non-SI units). [b] For the lower value of the series term in this case, see ref. 3 [item (v) of Table 1].

* Of initial and final states relative to the σ-complex.

DISCUSSION

The experimental results demonstrate and quantify the large difference in reactivity of OMe$^-$ and MeOH (examples of anionic and neutral forms of a nucleophile) in their reactions with 1-fluoro-2,4-dinitrobenzene in MeOH. Rate ratios (OMe$^-$ : MeOH) are $6.59 \times 10^{10}$ and $1.43 \times 10^{9}$ at 0 and 100° respectively.

The values of $\Delta E^{\ddagger}$ (kJ mol$^{-1}$) are 56.5 (OMe$^-$) and 89.0 (MeOH). The thermochemical estimates are 62 and 80, in acceptable agreement. The values of log $B$ (11.05 and 6.45) are in the range normally found for anion–neutral and neutral–neutral reactants respectively in methanol.

The thermochemical estimates relate intrinsic donating power of a nucleophile to its ionization energy. In the present comparison (and generally in comparing anionic

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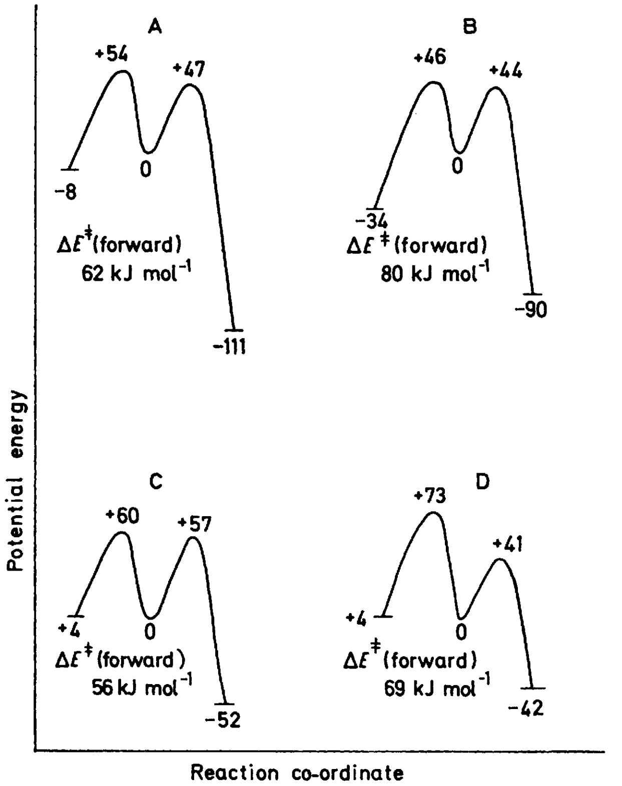
[16] J. Miller and K. W. Wong, *Austral. J. Chem.*, 1965, **18**, 117.

and neutral nucleophiles) the difference in ionization energy is much larger than the experimental reactivity difference. Some large favourable counterbalancing energy term must therefore be involved. In this case it is seen to be the large increase in solvation energy when the neutral–neutral reaction proceeds from the initial state to highly polar intermediates. In contrast, there is a diminution in solvation energy in the corresponding phases of the anion–neutral reaction.

More specifically it is seen that these two large energy terms when combined, produce somewhat more than half the free energy difference favouring $OMe^-$. The rest is associated with the much more negative entropy of activation accompanying the large increase in solvation energy in the neutral–neutral reaction.



Potential energy–reaction co-ordinate profiles: A, $OMe^-$; B, MeOH with 1-fluoro-2,4-dinitrobenzene; C, MeOH with picryl fluoride; D, MeOH with picryl chloride

Some detailed comment is required on the methanol calculations, even though they parallel closely the considerable number of amine calculations previously recorded.[8] Like these, the main uncertainty is the solvation energy of the highly polar σ-complex. The problem with the larger amines was solved on a reasoned, consistent semi-empirical basis. Since it worked well with ammonia, primary, secondary, and tertiary amines, we felt justified in using those values to estimate a value for the $-\overset{+}{O}HMe$ σ-complex. This was done by adding to the value used for the $-NH_2{}^+Me$ complex, the difference in solvation energy of $NH_4{}^+$ and $H_3O^+$ ions, *viz.* 92 kJ mol$^{-1}$.[17,18]

It should be noted that the values of solvation energy of σ-complexes are included in the ' series term ' in these calculations. Thus the series term for the $-NH_2{}^+Me$ complex, which is 594 kJ mol$^{-1}$ becomes 686 kJ mol$^{-1}$ for the $-\overset{+}{O}HMe$ complex.

The strength of a $C-\overset{+}{O}HMe$ bond was taken as equal to that of C–OMe, analogous to the assumed equality of the various $C-NR_3{}^+$ and $C-NR_2$ bonds[8] (R = H or Me).

A value was also needed for the electronegativity (α-substituent) effect.[3,8] In relation to the value 17 kJ mol$^{-1}$ used consistently for –F and $-NR_3{}^+$ species, we have used 21 kJ mol$^{-1}$ for $-OHMe^+$.

Comparison of methanolysis of picryl chloride and fluoride leads to an F : Cl mobility ratio of $8.75 \times 10^3$ at 100°. A large value is characteristic of the reactions of aromatic substrates with first row nucleophiles in protic solvents.[2] Our value is in fact >10 times the value at 0° found for the alkaline methanolysis and in each case the temperature for comparison approximates to the range used in experimental measurements.

The enthalpy contributions to these ratios are however about the same in both, *viz.* $\Delta\Delta E^\ddagger$ *ca.* 12 kJ mol$^{-1}$. It is readily seen that the *increase* in the ratio is entropy dependent: $\Delta\log (B/\text{l mol}^{-1}\text{ s}^{-1})$ 2.3; $\Delta\Delta S^\ddagger$ 44 kJ mol$^{-1}$ K$^{-1}$.

Acid and hydrogen bonding catalysis of fluorine but not chlorine displacement is a well accepted concept, and we link the higher F : Cl ratio with this. Specifically we speculate that a methanol molecule in the solvent shell around the positively charged oxygen of the forming σ-complex is conveniently intercalated between the $-\overset{+}{O}HMe$ and F to form a six-membered ring in which its hydrogen assists the displacement of fluorine. We prefer this to direct interaction between the hydrogen of the $-\overset{+}{O}HMe$ and F.

Comparisons of neutral methanolysis of 1-fluoro-2,4-dinitrobenzene and picryl fluoride leads to the activating power of an *o*-nitro-group when there is a nitro-group in the other *ortho*-position (*cf.* ref. 19). At 100° the rate ratio is $3.7 \times 10^4$. A similar comparison[20] in alkaline methanolysis is of *o*-fluoronitrobenzene and 1-fluoro-2,6-dinitrobenzene at 50°. In this case the rate ratio is $2.8_5 \times 10^4$. It is relevant that the latter result forms part of a series in which it was shown that steric effects are unimportant in displacement of fluorine, but are significant and increase in the order Cl, Br, I.

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