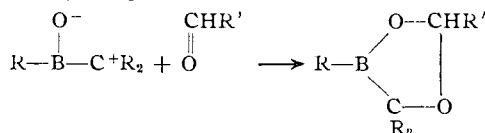


A second possible route could involve rearrangement of a second alkyl group before the reaction with the aldehyde. The intermediate XI could react with the aldehyde by a 1,3-dipolar addition or the intermediate X by a four-center reaction. These latter mechanisms seem highly improbable since the intermediates X



and XI are probably present as the dimeric hexaalkyl-2,5-diboradioxane which did not react with an aldehyde under similar conditions.

The mechanism of the formation of the hexaalkyl-2,5-diboradioxanes was discussed in a preliminary paper.⁴

Experimental

Trialkylboranes.—Triethyl- and tri-*n*-butylborane were obtained from Callery Chemical Co. and were used without further purification. The other alkylboranes were prepared by a procedure described in a previous paper.⁴

4,5,5-Triethyl-4-bora-1,3-dioxolane (Va).—A stainless steel-lined shaker tube (325-ml. capacity) was flushed with nitrogen and charged with aqueous formaldehyde (100 g. of 37%), triethylborane (54.6 g., 0.557 mole) and carbon monoxide (introduced gradually to 700 atmosphere maximum pressure) and heated at 50° for 1 hour. The bomb was agitated in a pendulum shaker under these conditions. After cooling, the layers were separated under nitrogen and the aqueous layer was washed twice with ether. The combined organic layers were washed with water, dried with magnesium sulfate, concentrated, and vacuum distilled to give presumably 4,5,5-triethyl-4-bora-1,3-dioxolane as a clear colorless liquid, b.p. 50° (0.2 mm.) (40.5 g., 48%). This compound deposited a white precipitate on standing under an atmosphere of dry nitrogen so chemical analyses were not possible.

4,5,5-Triisobutyl-4-bora-1,3-dioxolane (Vh).—The bomb was flushed with nitrogen, charged with aqueous formaldehyde (100 ml. of 37%), triisobutylborane (79.0 g., 0.433 mole) and carbon monoxide (700 atmosphere). The bomb was heated at 50° for 1 hour then cooled and washed with ether. The aqueous layer was extracted with ether, and the combined ether layers were washed with water, saturated sodium chloride, and then dried

with magnesium sulfate. Vacuum distillation gave a clear colorless liquid, b.p. 75–85° (0.65 mm.) (54.7 g., 60%, total yield 97%). This solid was recrystallized from ethanol (m.p. 142.4–142.7°) and was shown to be 2,3,3,5,6,6-hexaisobutyl-2,5-dibora-1,4-dioxane, identical (infrared spectrum and mixed m.p.) to the solid obtained by the carbonylation in water⁴ and in ethylene glycol.¹

Anal. Calcd. for C₁₅H₂₇BO: C, 74.29; H, 12.95; B, 5.15. Found: C, 74.16, 73.96; H, 12.78, 12.85; B, 5.01, 5.09.

The liquid from above was redistilled to give 4,5,5-triethyl-4-boradioxolane as a colorless liquid b.p. 68–70° (0.6 mm.) (33.0 g., 86% recovery). For analyses, see Table I.

4,5,5-Triethyl-2-chloromethyl-4-bora-1,3-dioxolane (Vd).—The bomb was flushed with nitrogen and charged with aqueous chloroacetaldehyde (150 ml. of 40%), triethylborane (50.0 g., 0.51 mole) and carbon monoxide (slowly to 500 atmosphere). The bomb was heated at 50° for 1 hour then cooled and extracted with ether. The product was worked up in the usual manner and vacuum distilled to give 4,5,5-triethyl-2-chloromethyl-4-bora-1,3-dioxolane (Vd) as a clear colorless liquid, b.p. 57–65° (0.2 mm.) (96.0 g., 92%). Redistillation gave a constant boiling fraction, b.p. 60° (0.2 mm.) (88% recovery).

4,5,5-Tri-*n*-butyl-2-trichloromethyl-4-bora-1,3-dioxolane (Vg).—The bomb was flushed with nitrogen and charged with chloral hydrate (100 g., 0.6 mole), ethanol (50 ml.), tri-*n*-butylborane (91 g., 0.5 mole) and carbon monoxide (600 atmosphere). The bomb was shaken and heated at 50° for 1 hour then cooled and extracted with ether. The mixture was concentrated then vacuum distilled to give 4,5,5-tri-*n*-butyl-2-trichloromethyl-4-bora-1,3-dioxolane (Vg) as a clear colorless liquid, b.p. 110° (0.1 mm.) (116.5 g., 69%).

4,5,5-Triethyl-2-methyl-4-bora-1,3-dioxolane (Vb).—The bomb was charged with acetaldehyde (75 g., 1.7 moles) and triethylboron (98 g., 1.0 mole). Carbon monoxide was introduced gradually in 20-atmosphere increments (very exothermic) to a maximum pressure of 200 atmosphere. The bomb was shaken for 1 hour at a temperature of 35–55° (no external heat was applied). The contents of the bomb were concentrated and vacuum distilled to give the title compound as a clear colorless mobile liquid, b.p. 35° (0.25 mm.) (135.0 g., 74%). For analyses and a summary of other compounds prepared see Table I.

The Attempted Reaction of 2,3,3,5,6,6-Hexaethyl-2,5-dibora-1,4-dioxane with *n*-Butyraldehyde.—A solution of *n*-butyraldehyde (36 g., 0.5 mole) and 2,3,3,5,6,6-hexaethyl-2,5-diboradioxane (63 g., 0.5 mole) was refluxed for 1.5 hours (pot temperature 90–94°). Vacuum distillation gave *n*-butyraldehyde (30.2 g., 84% recovery) and hexaethyl-2,5-diboradioxane, b.p. 68–70° (0.6 mm.) (60.4 g., 96% recovery). No 4,5,5-triethyl-2-*n*-propyl-4-boradioxolane was detected in the reaction product.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HONG KONG, HONG KONG, BRITISH CROWN COLONY]

The S_N Mechanism in Aromatic Compounds. Part XXVII.¹ A Quantitative Approach to Aromatic Nucleophilic Substitution

By J. MILLER

RECEIVED NOVEMBER 5, 1962

Energy calculations are made for a number of anion-dipole aromatic nucleophilic substitutions utilizing the concept of an intermediate complex. Recorded data, wherever available, for bond energies, electron affinities and solvation energies are used together with an allowance for electronic reorganization, to calculate energies of initial and final states and an intermediate complex. In a consistent way these are related to transition states and activation energies. The results, which are shown to be in accord with experiment, cover several important systems including methanolysis of aryl halides, aryl halide exchange, the formation of stable intermediates, and the change in relationship of reactivity of fluoro— and other halogeno—compounds with change in reagent. Solvent effects are also discussed. A clearer understanding of the factors which influence nucleophilic strength emerges and this is discussed also. The principles involved should permit wider applications than are considered in the present paper.

In this paper energy calculations are made for some aromatic nucleophilic substitutions involving reactions of anionic reagents with neutral substrates, utilizing the concept of a cyclohexadienide intermediate complex.^{2,3} Meisenheimer,⁴ among early workers, demon-

strated the formation of such compounds, and later workers have confirmed and extended this.^{5–8}

It has been commonly, though not quite universally, accepted practice to extrapolate to less activated systems for which there is much supporting evidence.^{1,9–12}

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(2) (a) J. Miller, *Rev. Pure & Applied Chem.* (Australia), **1**, 171 (1951);

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(4) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(5) O. L. Brady and H. V. Horton, *J. Chem. Soc.*, **127**, 2230 (1925).

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(7) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, 2528 (1956).

(8) R. C. Farmer, *ibid.*, 3425, 3430 (1959).

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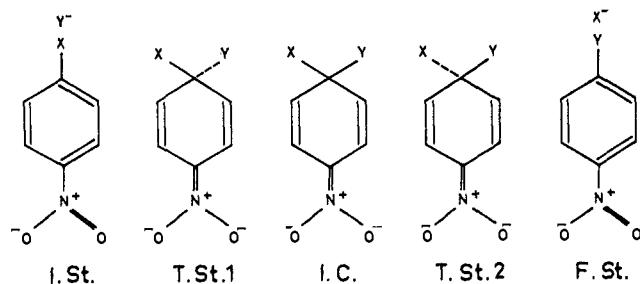


Figure 1.

There is evidence for corresponding intermediates also in aromatic electrophilic substitution.¹³⁻¹⁵

Recorded data, wherever available, for bond and solvation energies and electron affinities, together with an allowance for electronic reorganization, are used to calculate energies of initial and final states (I.St. and F.St.) relative to a cyclohexadienide intermediate complex (I.C.). In a consistent way these are related to transition states (T.St. 1 and 2) and thus activation energies. The structures of these for commonly used *p*-nitro compounds are shown as Fig. 1. The quantities required in calculation are shown in Table I, which gives the numerical values where these do not vary from reaction to reaction. The path used to enable calculations to be made is exemplified in Fig. 2 (I-IV) for the change from I.C. to I.St. or F.St.

TABLE I
ENERGY CHANGES IN PROCEEDING FROM I.C. TO I.St. (OR F.St.)

Term	Exo(-) or endo(+) thermic	Value in kcal.
(i) Heat of dissociation of C-X (or C-Y)	+	Various ^a
(ii) Change in bond energy C=N to C-N	+	74 ^b
(iii) Change in bond energy C-C to C=C	-	63 ^b
(iv) Change in bond energy N-O to N=O	-	57 ^{b,c}
(v) Strengthen C-X (or C-Y)	-	4, 6 or 9 ^u
(vi) Lose electron affinity [$-\ddot{O}:^-$]	+	61 ^d
(vii) Gain electron affinity of X· (or Y·)	-	Various ^d
(viii) Change in delocalization energy from cyclohexadienide to benzenoid system	±	+9, 0, or -9 ^e
(ix) Desolvate I.C.	+	54 ^e
(x) Solvate X ⁻ (or Y ⁻)	-	Various ^u

^a See text. ^b Ref. 16. ^c Ref. 17. ^d Ref. 18 for OH⁻ value. ^e Value for picrate ion—see text.

For term i the carbon at the substitution center is aliphatic. More data are available for Me-X bonds than any other and their values from Cottrell's book¹⁶ or other specified sources are used. They are unlikely to be the correct values but they introduce only a constant error. Values for term ii, iii, and iv are taken also from the same source.¹⁶ For ii the literature values may not be entirely suitable, and another constant error may be involved. For iv, two values are quoted; the lower one is chosen, supported by the estimate of Branch and Calvin.¹⁷ For term v the typical value, about -4 kcal., is used, but when forming ArN₃ as product the value is known to be -6¹⁹ and forming ArOMe it is -9²⁰ and they are then used.

(13) L. Melander, *Acta Chem. Scand.*, **3**, 95 (1949).

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(16) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958, Table 11.5.1, and relevant parts of Chapters 9 and 10.

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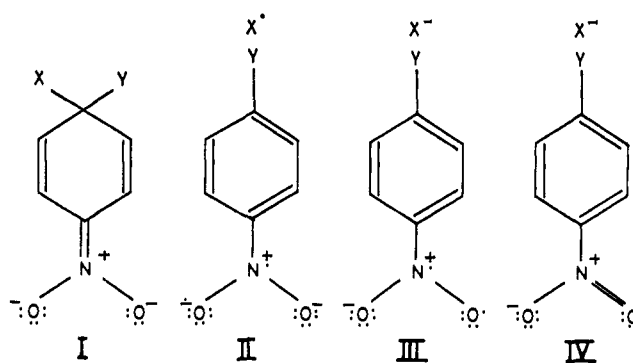


Figure 2.

For term vi the value for OH· + e → OH⁻ is taken as the nearest available. Any error is not likely to be large and is a constant throughout. Term vii varies from reaction to reaction. Where values are not known (and quoted) estimates are made and discussed. Term viii takes into account the delocalization energy differences to be allowed for after bond energy changes have been computed. It is quite likely that for the highly substituted and negatively charged 2,4,6-trinitrocyclohexadienide ion this is higher than that of the 2,4,6-trinitrobenzene system. Bunnett and Zahler³ have suggested that even the *un*substituted system has a delocalization energy approaching that of benzene. Bearing in mind such well known facts as: the pseudo-acid equilibrium in nitro compounds, favoring the *aci*-form in alkaline solution; of nitroso compound-oxime tautomerism; the facile oxidation of polyhydroxybenzenes; and the deep red colors observed in highly activated polynitro and similar aromatic nucleophilic substitutions, as a qualitative basis; and having recourse to experimental data,^{21,22} together with an allowance for a smaller fraction of the bond dissociation energy of more exothermic steps (ref. 23 and see below), values +10, +1, -8 for 2,4,6-trinitro-, 2,4-dinitro- and *p*-nitro- series are suggested for term viii. While the specific figures quoted are inevitably somewhat arbitrary, they are used consistently and form part of a constant term.

Term ix varies only slightly from system to system considered, and may be taken as a constant. Although a value is not known, picrate ion is very similar (see Fig. 3) and its heat of hydration is known^{24,25} (54 kcal.) and is used for the I.C.

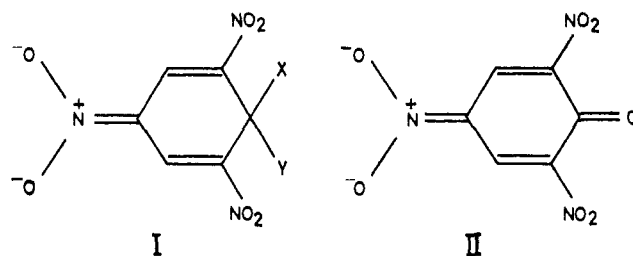


Figure 3.

Term x varies from reaction to reaction and sources are quoted. In both ix and x the approximation is made (any error is a constant throughout) that the heats of solvation in methanol are equal to heats of

(21) (a) A. L. Beckwith, J. Miller and G. D. Leahy, *J. Chem. Soc.*, 3552 (1952); (b) G. L. Briner, J. Miller, M. Liveris and P. G. Iutz, *ibid.*, 1265 (1954).

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TABLE II
 CALCULATION OF ACTIVATION ENERGIES^{a-d}

Reaction	Intermediate complex (I.C.)	Fission	B.D.E., kcal.	$E_{aff.}$ kcal.	$H_{hydr.}$ kcal.	Series term, kcal.	Energy levels kcal.		Less α -subst. effect, kcal.	E_{act} (reagent shown in []), kcal.	
							relative to the I.C. = 0 I.St. (upper value) or F.St. (lower)	% B.D.E. and corresponding value in kcal. from I.C. to T.St.1 (upper value) or T.St. 2 (lower)		Calcd.	Exptl.
1	$p\text{-NO}_2\text{C}_6\text{H}_4$ OMe I	C-OMe	+77 ²⁰	-61 ¹⁸	-83	+56	-11	18% (+14)	0	25 [OMe ⁻]	25 [OMe ⁻]
2	2,4-(NO ₂) ₂ C ₆ H ₃ OMe I	C-I C-OMe	+53 ¹⁶ As 1	-72.5 ³⁴ As 1	-63 ^{24,25} As 1	+51 +65	-31.5 -2	12.5% (+6.5) 22% (+17)	-3 0	19 [OMe ⁻]	19 [OMe ⁻]
3	$p\text{-NO}_2\text{C}_6\text{H}_4$ OMe F	C-I C-OMe	+77 ²⁰	-61 ¹⁸	-83	+60 +56	-22.5 -11	(14.5% (+7.5)) 18% (+14)	-3 -4	21 [OMe ⁻]	21 [OMe ⁻]
4	2,4,6-(NO ₂) ₃ C ₆ H ₂ OMe OMe	C-F C-OMe	+107 ¹⁶ +77 ²⁰	-80.5 ³⁴ -61 ¹⁸	-113 ^{24,25} -83	+51 +69	-35.5 +2	11.5% (+12.5) 25% (+19)	-3 -3	14 [OMe ⁻]	V. fast at room temp.
5	2,4-(NO ₂) ₂ C ₆ H ₃ OMe OMe	C-OMe	As 4	As 4	As 4	+60	+2 -7	25% (+19) 20% (+15.5)	-3	I.C. stable 19.5 [OMe ⁻]	I.C. stable Facile reaction
6	$p\text{-NO}_2\text{C}_6\text{H}_4$ OMe OMe	C-OMe	As 4	As 4	As 4	+51	-7 -16	20% (+15.5) 16.5% (+12.5)	-3	I.C. not stable 25.5 [OMe ⁻]	I.C. not stable Slow reaction
7	2,4,6-(NO ₂) ₃ C ₆ H ₂ OMe N ₃	C-OMe	+77 ²⁰	-61 ¹⁸	-83	+72	-16 +5	16.5% (+12.5) 26.5% (+20.5)	-2	I.C. not stable 13.5 [OMe ⁻]	I.C. not stable V. fast at room temp.
8	$p\text{-NO}_2\text{C}_6\text{H}_4$ OMe N ₃	C-N ₃ C-OMe	+83 ¹⁹ As 7	-73 ¹⁹ As 7	-79 ¹⁹ As 7	+69 +54	0 -13	23.5% (+19.5) 17.5% (+13.5)	-3 -2	I.C. stable 24.5 [OMe ⁻]	I.C. stable 26 [OMe ⁻]
9	2,4,6-(NO ₂) ₃ C ₆ H ₂ OMe Cl	C-N ₃ C-OMe	+77 ²⁰	-61 ¹⁸	-83	+51 +74	-18 +7	15.5% (+13) 28% (+21.5)	-3 -1	I.C. not stable 13.5 [OMe ⁻]	I.C. not stable V. fast at room temp.
10	$p\text{-NO}_2\text{C}_6\text{H}_4$ OMe Cl	C-Cl C-OMe	+80 ³⁴ As 9	-85 ³⁴ As 9	-79 ^{24,25} As 9	+69 +56	-15 -11	17% (+13.5) 18% (+14)	-3 -1	24 [OMe ⁻]	24 [OMe ⁻]
11	$p\text{-NO}_2\text{C}_6\text{H}_4$ Cl N ₃	C-Cl C-N ₃	+83 ¹⁹	-73 ¹⁹	-79 ¹⁹	+51 +56	-33 -13	12% (+9.5) 17.5% (+14.5)	-3 0	27.5 [N ₃ ⁻]	28 [N ₃ ⁻]
12	$p\text{-NO}_2\text{C}_6\text{H}_4$ I N ₃	C-I C-N ₃	+53 ¹⁶ +83 ¹⁹	-72.5 ³⁴ -73 ¹⁹	-63 ^{24,25} -79 ¹⁹	+54 +56	-28.5 -13	13% (+7) 17.5% (+14.5)	-2 -4	24 [N ₃ ⁻]	24 [N ₃ ⁻]
13	2,4-(NO ₂) ₂ C ₆ H ₃ I Br	C-I C-I	+53 ¹⁶	-72.5 ³⁴	-63 ^{24,25}	+65	-17.5	16% (+8.5)	0	27.5 [I ⁻]	25 [I ⁻]
14	2,4-(NO ₂) ₂ C ₆ H ₃ I F	C-Br C-I	+67 ¹⁶ +53 ¹⁶	-79.5 ³⁴ -72.5 ³⁴	-72 ^{24,25} -63 ^{24,25}	+65 +65	-19.5 -17.5	15% (+10) 16% (+8.5)	0 -4	29.5 [Br ⁻]	25 [Br ⁻]
15	$p\text{-NO}_2\text{C}_6\text{H}_4$ SMe I	C-F C-SMe	+107 ¹⁶ +73 ¹⁶	-80.5 ³⁴ -65	-113 ^{24,25} -68	+65 +56	-21.5 -4	14.5% (+15.5) 21.5% (+15.5)	0 0	33 [I ⁻]	No react. at temp. where solvolysis intervenes
16	$p\text{-NO}_2\text{C}_6\text{H}_4$ SMe I	C-SMe C-SMe	+73 ¹⁶	-65	-68	+56	-4	21.5% (+15.5)	-4	19.5 [SMe ⁻]	Ref. 39 and see text
17	2,4-(NO ₂) ₂ C ₆ H ₃ SMe I	C-I C-SMe	+53 ¹⁶ As 15	-72.5 ³⁴ As 15	-63 ^{24,25} As 15	+56 +65	-26.5 +5	13.5% (+7) 26.5 (+19.5)	0 0	14.5 [SM ⁻]	Ref. 39 and see text
17	$p\text{-NO}_2\text{C}_6\text{H}_4$ SMe F	C-I C-SMe	+73 ¹⁶	-65	-68	+65 +56	-17.5 -4	16% (+8.5) 21.5% (+15.5)	0 -4	Ref. 39 and see text	Ref. 39 and see text
17	$p\text{-NO}_2\text{C}_6\text{H}_4$ SMe F	C-SMe C-F	+107 ¹⁶	-80.5 ³⁴	-113 ^{24,25}	+56	-30.5	12.5% (+13.5)	0	17.5 [SMe ⁻]	

TABLE II (continued)

Reaction	Intermediate complex (I.C.)	Fission	B. D. E., kcal.	E_{act} , kcal.	H_{hydr} , kcal.	Series term, kcal.	Energy levels relative to the I.C. = 0		% B. D. E. and corresponding value in kcal. from I.C. to T.St.1 (upper value) or T.St.2 (lower)	Less α -subst. effect, kcal.	E_{act} (reagent shown in []), kcal	Exptl.
							I. St. (upper value of F. St.)	F. St. (lower)				
18	<chem>CC1(C)C(C)C(C)C1</chem> with <chem>SMe</chem> and <chem>F</chem> substituents	C-SMe	As 17	As 17	As 17	+65	+5	26.5% (+19.5)	-4	10.5 [SMe ⁻]	Ref. 39 and see text	
19	<chem>CC1(C)C(C)C(C)C1</chem> with <chem>SCN</chem> and <chem>I</chem> substituents	C-F	+73	-76	-72 ^{24,25}	+65	-21.5	14.5% (+15.5)	0	23.5 [SCN ⁻]	20 [SCN ⁻]	
		C-SCN	+73	-76	-72 ^{24,25}	+65	-17.5	16% (+8.5)	0			
20	<chem>CC1(C)C(C)C(C)C1</chem> with <chem>SCN</chem> and <chem>F</chem> substituents	C-I	+53 ¹⁶	-76	-63 ^{24,25}	+65	-10	18.5% (+13.5)	-4			
		C-SCN	+73	-76	-72 ^{24,25}	+65	-10	18.5% (+13.5)	-4			
		C-F	+107 ¹⁶	-80.5 ²⁴	-113 ^{24,25}	+65	-21.5	14.5% (+15.5)	0	25.5 [SCN ⁻]		

^a I. St. corresponds to the compound with the upper group as substituent, and the F. St. to that with the lower group. ^b Energy levels of I. St. and T. St. 1 are shown on the upper line, and F. St. and T. St. 2 on the lower line. ^c The α -substituent effect is shown on the line corresponding to the reaction direction (*i.e.* to I. St. or F. St.) in which it is effective. ^d E_{act} calculated is shown on the line corresponding to whichever T. St. is rate determining for the reaction. In one case (reaction 18) where T. St. 1 = T. St. 2 it is shown in-between.

Slow with side reagents of init. prod., and accompanied by much solvol.

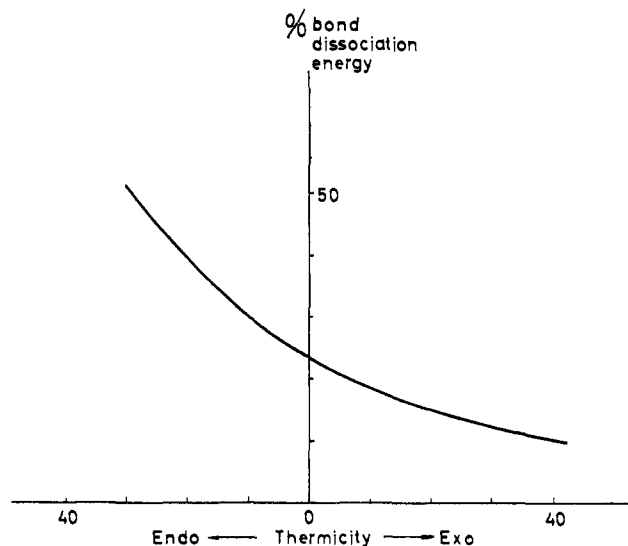


Figure 4.

hydration,^{26,27} while results are taken as giving a general indication for protic solvents. Except where specified, heats of hydration are those of Yatsimirskii²⁴ reduced by 6 kcal., or those of Mischenko²⁵ which are consistent. The latter are based on "best values" of total heats of hydration separated into individual heats on the basis of equality of Cs⁺ and I⁻; on the assumption that the difference in their radii is compensated by the H₂O dipole moment dissymmetry. One desired value is not available, *viz.*, for OMe⁻. Since the heats of hydration of HCO₂⁻ and CH₃CO₂⁻ are quoted as 99 and 66 kcal., respectively,²⁸ this difference applied to the value for OH⁻ = 116 kcal., leads to the value 83 kcal. for OMe⁻.

Terms ii-iv, vi and ix are constant; v is a small constant modified in two cases (*g.v.*); and viii has a fixed value for each of the three nitro series considered. Corresponding totals of these terms are +56, +65 and +74 for *p*-nitro-, 2,4-dinitro- and 2,4,6-trinitro- series, respectively.

There are surely some constant errors, due to uncertainty in some values and the need for one or two estimates, sometimes rather arbitrary, and one would expect to have to introduce an empirical correction to bring levels of I. St. and F. St. into correct relationship with the I.C. This would be legitimate provided only one correction were used throughout. It must be regarded therefore as fortuitous that the estimates and the values from the literature give satisfactory results without such a correction, and this indicates a cancellation of errors, including any divergence of aqueous and methanolic heats of solvation.

For full use to be made of these calculations estimates of T. St. 1 and 2 are required. They are obtained by the use of Hammond's postulates²³ and a curve discussed below. The postulates are a reduction or increase in the bond energy term according to the degree of exo- or endothermicity of reaction, with which is associated a corresponding shift in the reaction coordinate of the transition state.

The application here requires a curve relating a fraction of the bond dissociation energy (% B. D. E.) with the degree of thermicity. Even a purely speculative curve would be acceptable if only one such curve were used and applied objectively. However, apart from general guidance from the recorded body of kinetic data, some specific if crude guidance is obtainable.

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(27) J. O'M. Bockris, "Modern Aspects of Electrochemistry," Butterworths Scientific Publications, London, 1954, pp. 49, 53-54.

(28) D. F. C. Morris, *Rec. trav. chim.*, **78**, 150 (1959).

Streitwieser²⁹ quotes Stevenson's computations for the gas phase dissociation into carbonium ion and anion of *inter alia* *t*-butyl bromide and iodide, both = 132 kcal. Franklin³⁰ has calculated the heat of hydration of *t*-Bu⁺ as 40 kcal., and with the heats of hydration of Br⁻ and I⁻ = 72, 63 kcal., respectively,^{24,25} these SN1 solvolyses are then 20 and 29 kcal. endothermic, respectively. He quotes corresponding activation energies as 22.8 and 22.4 kcal. Frequency factors for these two are about the same and have a typical value, and therefore do not complicate the situation. Bond dissociation energies of *t*-butyl are about 5–10 kcal. less than methyl compounds.¹⁶ Using -8 as an average, values for dissociation of *t*-BuBr and *t*-BuI are then 59 and 45 kcal., respectively.

Thus a reaction 20 kcal. endothermic requires 39% of the bond dissociation energy in its transition state, and another 29 kcal. endothermic requires 50%. A plot of such % bond dissociation energies against thermicity should in the exothermic direction be asymptotic to the axis, though practically chemical bond energies would not in fact extend it very far. Such a curve drawn through the two fixed points and extended in this way is shown as Fig. 4. Though its exact curvature is thereafter drawn arbitrarily, the complete curve is not entirely so and it is used consistently and objectively. The main guidance from the two points is in fact the intercept for an athermal reaction, since the endothermic side is hardly used. On that side the curve is steeper, and a small error there would produce relatively greater error in calculation. On the exothermic side mainly used the curve is relatively flat.

It should be noted that the percentage B.D.E. is not strictly a bond energy term alone. It represents the point where increase in energy due to further bond dissociation is just counteracted by the decrease due to the further effect of electron affinity and any solvation energy which has commenced to be effective. The actual percentage of bond dissociation is thus larger than the percentage B.D.E.

One additional factor must be considered, *viz.*, the effect of X and Y, on each other (the α -substituent effect), in forming and dissociating the I.C. Miller and co-workers,^{2h,31,32} commenting on aromatic SN reactions giving the replacement order F > I and X⁺ > X⁺-Y⁻ > X^o, suggested it is a result of the decisive importance there of the electronegativity of the attached group as compared with the bond strength factor, *i.e.*, the electron deficiency which can be sustained at a carbon atom to which an electronegative atom or group is attached lowers the energy of the T.St. for attachment of a nucleophile to the carbon. The energy-reaction coordinate curve is the same for reaction in either direction.

It is known experimentally that for replacement of F in relation to I the result is a reduction of about 4 kcal. for the T.St. From the known order of electronegativities of the groups in the Periodic Table, and Pauling's electronegativity indices³³ may also be used, the values 3 kcal. for OMe and 2 for N₃ (allowing a slightly higher value for this than would be given for NR₂) and 1 for Cl may be estimated. This factor would thus amount to less than 1 kcal. for other second row and for higher row elements and it is therefore ignored for them.

(29) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(30) J. L. Franklin, *Trans. Faraday Soc.*, **48**, 443 (1952).

(31) (a) J. Miller, *J. Chem. Soc.*, 3550 (1952); (b) M. Liveris and J. Miller, *Chem. Ind. (London)*, 954 (1957); (c) R. Bolton, J. Miller and A. J. Parker, *ibid.*, 1026 (1960).

(32) R. E. Parker and T. O. Read, *J. Chem. Soc.*, 9 (1962).

(33) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 93.

The detailed calculations all have a standard pattern, *viz.*: (a) values of terms i, vii and x appropriate to the particular bond fission are given; (b) the sum of the rest of the terms is added. These are the appropriate series term +56, +65 or +74 with the small difference when ArN₃ or ArOMe is formed, as already explained. From a and b the energy levels of I.St. and F.St. relative to the I.C. are obtained. Then (c) T.St. 1 and 2 are computed from the curve given (Fig. 4), incorporating the α -substituent effect where applicable.

The calculations cover a variety of reactions, the majority already measured experimentally—many by the author and co-workers—and are given in Table II, in which energy values are in kcal.

Entropy factors have been excluded, partly because necessary data are even scarcer than those already discussed, but mainly because in these anion-dipole reactions the frequency factors (which contain the entropy terms) vary little; however, see comments later.

One of the common reagents is methoxide ion. The detailed calculation for reaction of methoxide ion with *p*-iodonitrobenzene follows as an example. The I.C. is as in Fig. 1 with X = OMe, Y = I. For fission of C-OMe, *i.e.*, back to the I.St., values of bond dissociation energy (B.D.E.), electron affinity (E_{aff}), and heat of hydration (H_{hydr}) are +77,²⁰ -61 (as for OH¹⁸) and -83 (see earlier). For C-I fission (*i.e.*, forward to F.St.) values are +53,¹⁶ -72.5,³⁴ -63.^{24,25}

Adding the *p*-nitro series constant = 56 (but reduced to 51 when ArOMe is the product) one obtains energy levels (I.St., I.C., F.St.) -11, 0, -31.5. T.St. 1 read off from the % B.D.E. curve (Fig. 4) is at 18% of the C-OMe bond dissociation energy = +14 kcal. T.St. 2 is correspondingly at 12.5% of the C-I bond dissociation energy less 3 for the α -substituent effect of OMe = +6.5 - 3 = +3.5 kcal. The energy-reaction coordinate curve is shown as Fig. 5; E_{act} calculated = 25 kcal.; experimental value 21b = 25 kcal.

From Table II it is clearly seen that the calculations agree satisfactorily, and in the majority of cases extremely well, with experiment. Short notes on each follow.

Reactions 1-3 are typical activated aromatic SN reactions and agree very well with experiment. The closeness of energy of T.St.1 and 2 for the fluoro compound should be noted, however (Fig. 6).

The formation in some cases of a stable I.C. in protic solvents has been known for over 60 years⁴ and has been further investigated recently. It is a crucial test of these calculations that such reactions, *e.g.*, of methoxide ion with picryl methyl ether, should be predictable. Reaction 4 (Fig. 7) shows this very satisfactorily; an E_{act} of 14 kcal. as calculated, with normal (entropy) frequency factor, is indeed very fast at room temperature as is observed, and the stability of the I.C. is predicted. Calculation of reactions 5 and 6 predicts correctly that I.C.'s are not stable there, and that reaction is facile for the 2,4-dinitro- but slow for the *p*-nitro-compound as is known^{35,36}; the latter is accompanied by reductive side reactions at the elevated temperatures necessary.

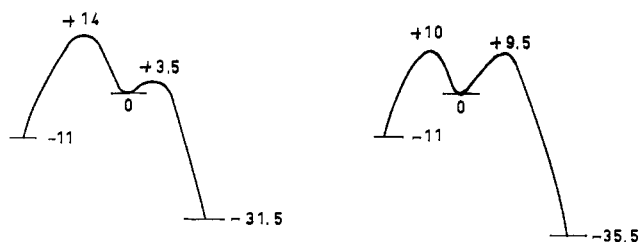
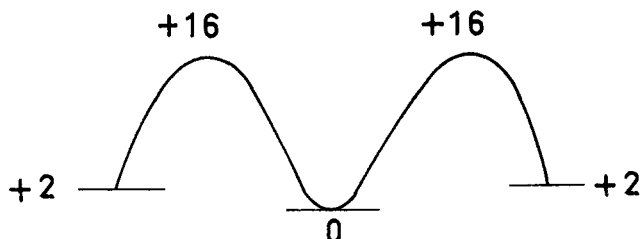
The colors observed by Miller^{37a} in some reactions of methoxide ion with 1-chloro-2,6-dinitro-4-X-benzenes, where X is an activating group, so that these resemble picryl compounds, and the absence of color with the less reactive 1-chloro-2-nitro-4-X-benzenes,^{37b} supports the above distinction of complex stability.

(34) D. D. Cubicciotti, Jr., *J. Chem. Phys.*, **31**, 1846 (1959).

(35) J. J. Blanksma, *Chem. Weekblad*, **6**, 313 (1909).

(36) L. Gattermann and A. Ritschke, *Ber.*, **23**, 1738 (1890).

(37) (a) J. Miller, *J. Am. Chem. Soc.*, **77**, 180 (1955); (b) **76**, 448 (1954).

Fig. 5.—*p*-NO₂C₆H₄I with OMe⁻/MeOH.Fig. 6.—*p*-NO₂C₆H₄F with OMe⁻/MeOH.Fig. 7.—Picryl methyl ether with OMe⁻/MeOH.

The recent report³⁸ of a similar complex in protic solvent with methoxide ion and picryl azide led to calculation of reaction 7 and here too there is good agreement.

Calculation of reaction 8 showed that azide should be displaced simply by methoxide ion in the *p*-nitro series, and the predicted E_{act} is in good agreement with experiments then made to confirm it.³⁹

Farmer⁸ mentions the similarity of reaction of picryl chloride and the ether, but that the former then gives the picryl ether, and dimethoxy I.C. as in reaction 4 and also by a direct aliphatic type substitution of Cl by OMe in the methoxychloro-I.C. Calculation of reaction 9 agrees with this.

Calculation of reaction 10 gives E_{act} correctly, and it can be seen that similarity in rates of I, Cl and N₃ replacement is correctly predicted.

Calculation of reactions 11 and 12 shows that substitution by azide ion is also typical and the reagent a strong one, though weaker than methoxide. The reaction with the fluoro compound has T.St. 2 rate determining but by so small a difference from T.St. 1 (0.5 kcal.) that the normal pattern of relative ease of replacement of fluorine and other halogens is essentially unaffected. Nevertheless the very close margin on which the high F/Hal replacement rate ratio depends for its existence^{23,31,40} is further clearly demonstrated. It depends on a 2-stage mechanism but is not characteristic of all aromatic nucleophilic substitutions. It is generally confined in these to reactions, in protic solvents, with first-row reagents which combine a sufficiently high energy of bond formed, and T.St. energy level, with an α -substituent effect.

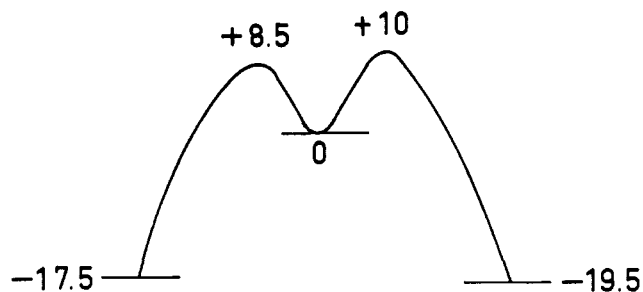
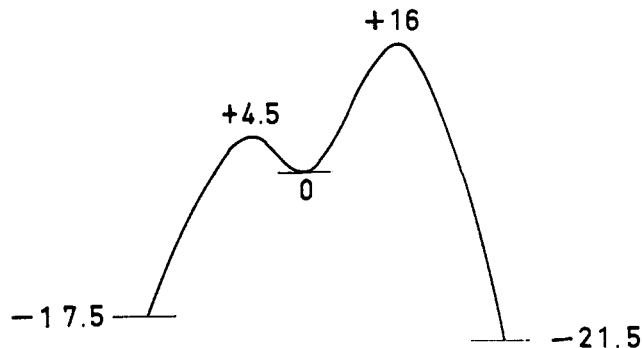
Reaction 13 is of interest because it is known that such inter-halide reactions are slow and reversible. This is exactly what is predicted by calculation, though the predicted E_{act} value is somewhat high. Actual rates correspond well to predictions, however, since the heavy nucleophiles also have low values of S_{act} (and $\log B$). See Fig. 8.

Reaction 14 is of special interest since calculation predicts that T.St. 2 is much higher than T.St. 1 and the C-F bond strength thus controls the situation (Fig. 9). This resembles the situation in saturated aliphatic compounds. The calculated E_{act} is 33 kcal., a value so high that solvolysis occurs instead^{1a,41} even though this does

(38) R. Andrisano and D. Dalmarte Casoni, *Chem. Abstr.*, **41**, 723d (1947).

(39) J. Miller and K. W. Wong, unpublished work.

(40) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957).

Fig. 8.—1-Bromo-2,4-dinitrobenzene with I⁻/MeOH.Fig. 9.—1-Fluoro-2,4-dinitrobenzene with I⁻/MeOH.

not begin effectively below 100°. The reverse reaction has even higher E_{act} . The product ether can itself be demethylated by I⁻ so that eventually some I⁻ is consumed. The weak nucleophilicity of halide ions in protic solvents in the simple order I⁻ > Br⁻ > F⁻ is seen (and Cl⁻ could be inserted in its appropriate place).

Reactions of nucleophiles involving higher row elements are seen to be of particular interest and the values for second row methyl mercaptide ion have therefore been calculated in reactions 15-18. The value of the electron affinity of SMe (SH) is obtained by applying the Cl-F difference to the OMe (OH) value already quoted; the increase of 4 kcal. is supported by the work of Evans, *et al.*⁴² The value of the solvation energy of SMe⁻ is found by applying the OCN⁻ - SCN⁻ difference = 15 kcal. to the OMe⁻ value, giving that for SMe⁻ as 68.

From the calculation of reaction 17, T.St. 2 is seen to be rate determining but the difference between T.St. 2 and T.St. 1 is only half that of that α -substituent effect of F so that by comparison with reaction 15 a substantial F/I replacement rate ratio is still expected. Experiment suggests, however, that in reactions where neither entering nor replaced groups are first-row nucleophiles, as in reaction 15, the entropy of activation is low, so that the F/I ratio might after all be as high as for first row reagents but here only partly energetic in origin.

In reaction 18 (in the 2,4-dinitro series), T.St. 2 = T.St. 1 so that the energetic pattern of first-row reagents is retained, but since the comments about S_{act} still apply one might then expect to find an unusually high F/I replacement rate ratio. Another interesting point that emerges is that as far as E_{act} values are concerned, a lower SMe⁻/OMe⁻ nucleophilicity ratio is expected for reaction with *p*-fluoronitrobenzene (reaction 17) than the other three substrates of reactions 15-18. There are a number of difficulties in measuring these four reactions experimentally, but the work is now proceeding³⁹ and so far supports the above conclusions.

It is regrettable that values for calculation of *p*-nitro- and 2,4-dinitro compounds with SPh⁻ as reagent are not

(41) P. J. C. Fierens and A. Halleux, *Bull. soc. chim. Belges.*, **64**, 717 (1955).

(42) M. G. Evans, E. Warhurst and E. Whittle, *J. Chem. Soc.*, 1524 (1950).

available because the situation there is known experimentally^{43,44} to be similar but more conspicuously corresponding to a greater shift to T.St. 2 rate determining. This is an alternative explanation to that given by Bunnett.^{43b}

Calculation of reaction 19 for thiocyanate ion is made, though necessary data are less reliable. For want of a better value the C-SCN dissociation energy is taken as equal to that of C-SMe. The electron affinity of SCN is likely to be higher than that of SMe(SH). The value 76 kcal. intermediate between the values of I and Br is taken and fits the properties of thiocyanate compounds. Calculation shows the reagent is weaker than SMe⁻, OMe⁻ and N₃⁻ but stronger than I⁻ and that reaction should proceed to completion. The calculated E_{act} value is also found to be somewhat high but again a low S_{act} means that the predicted rate is in better agreement. Reaction does proceed to completion.

Calculation of reaction 20 shows that thiocyanate ion behaves as a typical heavy nucleophile in reaction with an aromatic fluoro compound, with T.St. 2 rate determining. E_{act} calculated is 25.5 kcal., a value such that reaction would only take place at a reasonable rate above 100° where solvolysis also occurs and where side reactions^{45,46} involving S-CN fission play a major part. This is just what is found experimentally: some SCN⁻ is consumed above 100°, but the product consists largely of the anisole and diaryl sulfide.^{45,46}

We find a tendency to reduced reactivity consequent upon a low entropy of activation, particularly when neither entering nor replaced group is first-row nucleophiles. This may be due to steric factors. Courtauld models of the I.C. indicate some steric hindrance in these cases with the π -electrons of the ring, but at a level which is more likely to affect entropy than energy of activation. In contrast, the experimental E_{act} values tend to be lower than calculated ones for heavy nucleophiles, and this is likely to be a direct result of their polarizability, permitting more facile bond formation at relatively large distances. The experiments and their interpretation do not lend support to any special polarizability effect such as has been discussed by Bunnett.^{43b}

Miller and Parker^{1a} have discussed solvent effects in SN₂ reactions, mainly in the aromatic series and Parker⁴⁷ has now extended this to aliphatic compounds. Some elaboration of their comments is valuable even at the risk of some repetition. Water and hydroxylic solvents generally (except for a few highly hindered species) have both ends of the OH dipole readily accessible and thus solvate both anions and cations well. Other protic solvents are quite comparable except the main alternative NH solvents are more likely to be hindered in view of the higher valency of nitrogen. Protic solvents, with hydrogen attached to an electronegative element, are in fact particularly good anion solvents.

Dipolar aprotic solvents, *e.g.*, acetone, dimethyl sulfoxide (DMSO), sulfolane, nitrobenzene and dimethylformamide (DMF), have the negative ends of their dipoles readily accessible and thus can solvate cations well. However, in the great majority of such solvents the positive ends of their dipoles are considerably hindered and anion solvation is reduced. Substances such as liquid SO₂ are clearly an exception, while this deficiency is presumably less severe in aprotic amides where a fractional positive charge resides also on nitrogen.⁴⁸

Whereas too normal protic solvents can form a close solvation sheath around anions, even small ones, the minimum sized anion solvation sheath of dipolar aprotic solvents may be too large for a close sheath around the smaller anions. Thus anion solvation in such solvents suffers, especially for small ions below 2 Å., and could possibly even reverse the normal size order of solvation for the common ions which are generally less than this. Solubility data above must naturally be treated with much caution since they involve cations as well as anions, but the body of data quoted by Miller and Parker^{1a} gives general support for reduced anion solvation though a fully reversed order of solvation must be regarded as speculative.

An interesting possibility with the smallest anions is that where such an ion is produced *in situ* a dipolar aprotic solvent might be able to form a single solvation sheath around an ion pair formed from the anion and cation in contact.

In such circumstances a very high degree of supersaturation might occur and may be the explanation for such a phenomenon observed in the azide ion reaction with *p*-fluoronitrobenzene^{1a,31c} where sodium fluoride often fails to precipitate, although its solubility is extremely small. Such solvation sheaths would tend to increase the viscosity and decrease the conductivity of the solution.

Because of the lack of quantitative data, satisfactory calculations for reactions in dipolar aprotic solvents cannot be made. Nevertheless, from what has been said, the I.St. and F.St. of the anion-dipole reactions are expected to suffer a greater solvation loss than the I.C. It is important to note that it is unnecessary to assume reverse order of solvation for this. It is sufficient that the differences in solvation energy between small and large anions should be less in dipolar aprotic than in protic solvents.

The single qualitative concept of raising the I.St. and F.St. relative to the I.C. leads at once to a number of important conclusions: (a) reaction will be substantially faster in dipolar aprotic than in protic solvents, particularly for the small first-row nucleophiles; (b) usual orders of nucleophilic strength such as I⁻ > Br⁻ > Cl⁻ > F⁻ tend to be reversed in changing from protic to dipolar aprotic solvents; (c) reactions which go to completion in protic solvents—the products involving the smaller anion being called the F.St.—may become reversible in dipolar aprotic solvents or even become one-way reactions in the reverse direction; (d) reactions which are reversible in protic solvents have the equilibrium changed in dipolar aprotic solvents in the direction favoring the production of the larger anion; (e) a situation may occur when the energy level of I.St. (or F.St.) rises so far above the I.C. in a dipolar aprotic solvent that reaction stops at the I.C.

The rate increase in dipolar aprotic solvents, (a) above, is fully supported for example by the results of Miller and Parker.^{1a}

The reversal of reactivity order, (b) above, is clearly seen for Group VII nucleophiles in the synthesis of aromatic fluoro compounds by the method of Finger and Kruse⁴⁹ involving F/Hal interchange. Its theoretical basis is now evident. Results of Miller and co-workers confirm and extend this.^{46,50}

The reversibility of some reactions in dipolar aprotic solvents, (c) above, which go to completion in protic solvents has not yet been confirmed.

(43) (a) J. F. Bunnett and W. D. Merritt, Jr., *J. Am. Chem. Soc.*, **79**, 5967 (1957); (b) J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

(44) C. W. L. Bevan and J. Hirst, *J. Chem. Soc.*, 254 (1956).

(45) F. Challenger and A. D. Collins, *ibid.*, **125**, 1377 (1925).

(46) (a) B. A. Bolto and J. Miller, unpublished work; (b) J. Miller and A. J. Parker, unpublished work.

(47) A. J. Parker, *Quart. Rev.*, **16**, 163 (1962).

(48) A. Eucken, *Z. Elektrochem.*, **52**, 225 (1948).

(49) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956), and subsequent papers.

(50) R. Bolton and J. Miller, unpublished work.

The shift of equilibrium, (d) above, is shown for example in the I/Br exchange reaction in the 2,4-dinitro series.^{1a}

The reaction of azide ion with *p*-fluoronitrobenzene in DMF^{1a, 31b} was thought to be a reaction which stopped at the I.C., (e) above, but this is now known not to be so.^{46, 51} However, several 2,4,6-trinitrobenzene reactions are examples.

The calculations and observation already given permit consideration to be given to nucleophilicity in aromatic S_N reactions relevant to the general problem of nucleophilicity.⁵²⁻⁵⁴

Toward aromatic compounds the situation in a sense is more complicated than in the simple aliphatic substitutions because in the former either T.St. 1 or T.St. 2 may determine the reactivity, depending on the nature of the entering and expelled groups as calculated above. The examples of reactivity of large nucleophiles for displacement of fluorine are the obvious examples.

A further complication exists when reaction stops at the I.C.

In contrast, when T.St. 1 is rate determining a general enhanced reactivity occurs when replacing fluorine.

At any rate, the picture, if complex, can be explained and understood.

In general terms it is readily seen that nucleophilicity increases with strength of the bond formed and decreases as electron affinity and solvation energy increase. In terms of E_{act} , nucleophilicity is the difference in energy level of I.St. of the reaction considered, and whichever T.St. is rate determining. In calculating the I.St. relative to the I.C., the whole of (a) the bond dissociation energy, (b) electron affinity, (c) the difference in solvation energy of I.C. and I.St., and (d) a residue of terms (*q.v.*) which might be bulked together as the system term, have been used.

In calculating the T.St. relative to the I.C. which it structurally resembles much more closely than the I.St.,^{22, 55} (e) a fraction of the bond dissociation energy has been used, though recognizing (see earlier) that it is the resultant of this and other terms and also had to allow for complicating factors already explained.

Nucleophilicity is then the algebraic sum of b, c, d, e and part of a; or in the complicating case when T.St. 2 is rate determining the algebraic sum of b, c, d, e, with a and a new bond energy term, but the two latter are still less than a. This is, however, the nucleophilicity in protic solvents. Information on nucleophilicity in dipolar aprotic solvents would be valuable for both practical and theoretical reasons. Regrettably the

data are not available but, as has been suggested already, a change from protic to dipolar aprotic solvents causes an enhancement of nucleophilic strength, greatest for the anions which are most solvated in protic solvents, and for halide ions at least seems to be sufficient to reverse the usual reactivity order.

In protic solvents a table (Table III) may be obtained by calculating the activation energies for reactions with *p*-iodonitrobenzene in which it is known that T.St. 1 is rate determining. Since the values do not involve any bond breaking of the replaced group these values would appear to be a more fundamental characteristic of the reaction of the nucleophile with carbon than those from aliphatic S_N and other one-stage reactions.

TABLE III
NUCLEOPHILICITY VALUES^a

Reagent	SMe ⁻	OMe	N ₃ ⁻	SCN ⁻	I ⁻	Br ⁻	Cl ⁻	F ⁻
Nucleophilicity ^b	19.5	25	27.5	30.5	33.5	37	38.5	44

^a For substitution on aromatic carbon in protic solvents.

^b In terms of activation energy, thus the most reactive have the lowest values. Entropy considerations do not in fact change the order.

In aliphatic one-stage substitutions, less bond making is involved, as well as a substantial element of bond breaking. Since the high reactivity of first-row elements given above depends on the strength of the bond formed, the larger nucleophiles will be relatively more effective in aliphatic than in aromatic S_N reactions. This is probably why thiocyanate ion was observed to demethylate *p*-nitro-N,N,N-trimethylanilinium ion,⁵⁶ whereas methoxide ion replaced the whole -NMe₃⁺ group in an aromatic substitution.^{2b}

Since actual and relative strengths of bonds to other atoms are different from those to carbon, it is clear that nucleophilic strengths there will also differ correspondingly. We would expect first-row nucleophiles, for example, to be relatively less effective for S_N reactions on nitrogen and oxygen.

Calculations for such well known nucleophiles as OH⁻ and SH⁻ are not attempted for the present. The complications that there is an extra mole of nucleophile in the I.St. and that both nucleophile and aromatic substrate of the F.St. are charged should be manageable, but reliable data for handling a large I.C. in which there is an unknown equilibrium between an initially unit charged I.C. and a second mole of nucleophile to give a doubly charged form (alcohol-hydroxide type equilibrium) are lacking. The use of charged aromatic substrates in the I.St.,^{2b, 57} is a further complication.

It is hoped to extend this work both within the aromatic series and beyond it.

Acknowledgment.—The author thanks Sir Christopher Ingold, F.R.S., for his interest and helpful comment.

(56) B. A. Bolto and J. Miller, *J. Org. Chem.*, **20**, 558 (1955).

(57) G. P. Briner and J. Miller, *J. Chem. Soc.*, 4682 (1954).

(51) R. Bolton, J. Miller and A. J. Parker, *Chem. Ind. (London)* 492, (1963).

(52) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(53) (a) J. O. Edwards, *ibid.*, **76**, 1540 (1954); (b) **78**, 1819 (1956).

(54) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(55) J. R. Knowles, R. O. C. Norman and J. H. Prosser, *Proc. Chem. Soc.*, 341 (1961).