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ON THE GENERALITY OF THE N_+ CORRELATION: NUCLEOPHILIC ATTACKS ON FLUORENE-9-DINITROMETHYLENE

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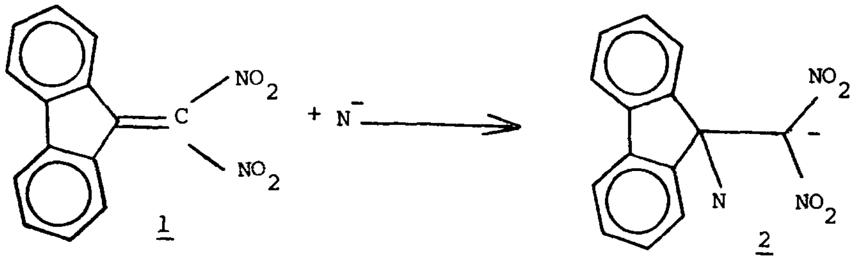
Although nucleophilic reactivity in a substitution reaction at an electrophilic center certainly involves several factors, Ritchie has shown[1] that the reactivity towards cations of a wide range of nucleophiles can be successfully correlated by the single parameter equation (eqn. 1).

$$\log \frac{k}{k_o} = N_+ \qquad (1)$$

where k and k_o are rate constants for the reaction of an electrophile with a given nucleophile and with water, respectively and N_+ is a parameter characteristic of the nucleophilic system and independent of the electrophile.

The order of nucleophilic reactivity according to the N_+ scale differs markedly from that determined by the Swain-Scott[2] equation or by polarizability-basicity considerations. In order to shed some light on this correlation which also seems to violate the reactivity selectivity principle and the Hammond postulate,[3] we decided to investigate the reaction of nucleophiles with fluorene-9-dinitromethylene 1 to give the stable anion 2.



The absence of a leaving group in this electrophile fulfills the condition which, according to Ritchie,[1] is sufficient to correlate its reactions with nucleophiles with N_+ . Since this study was begun, several reports from other laboratories have been published showing that very good correlations with N_+ are obtained for reactions of nucleophiles with the carbonyl group of esters,[4a] with halobenzenes[4b] and with sulfones,[5] and less successful to bad correlations with sulfinyl and sulfonyl sulfur[5] and with ferrocenyl stabilized carbocations.[6] However most of these studies were limited to aqueous solution in which only the lower portion of the N_+ scale could be tested. Working in dipolar aprotic solvents, as well as in protic solvents, enabled us to cover a reactivity range of 11 orders of magnitude. In addition, this reaction unlike the others has the advantage of being a single step reaction uncomplicated by the presence of a leaving group. Kinetic measurements were carried out at 25°C using 2400 Gilford spectrophotometer for the slow reactions and a Durrum stopped-flow spectrophotometer for the faster ones. Both spectrophotometers were interfaced directly to a PDP 11/40 minicomputer for data acquisition and analysis. The results are presented in the table and the log of the second order rate constants (first order for MeOH (MeOH)) vs. N_+ is plotted in the figure. Except for the reaction of N_3^- which subsequently undergoes slow decomposition, all other reaction products were isolated (as 2-H) and identified.

Rate constants for reactions of nucleophiles with 1 at 25°C

No.	Nucleophilic system	N_+	k $M^{-1}sec.^{-1}$	No. of determinations
1	CH_3OH	1.18	$1.8\pm0.2\cdot10^{-4}$ [a]	6
2	$CN^-(H_2O)$	3.67	0.27 ± 0.03	8
3	$CN^-(CH_3OH)$	5.94	318 ± 46	6
4	$CH_3O^-(CH_3OH)$	7.68	426 ± 43	44
5	$CN^-(DMSO)$	8.6	$3.78\pm0.45\cdot10^5$	24
6	$CN^-(DMF)$	9.33	$4.25\pm0.26\cdot10^6$	14
7	$N_3^-(DMSO)$	10.07	$1.06\pm0.3\cdot10^7$	13

a. Units are sec^{-1}

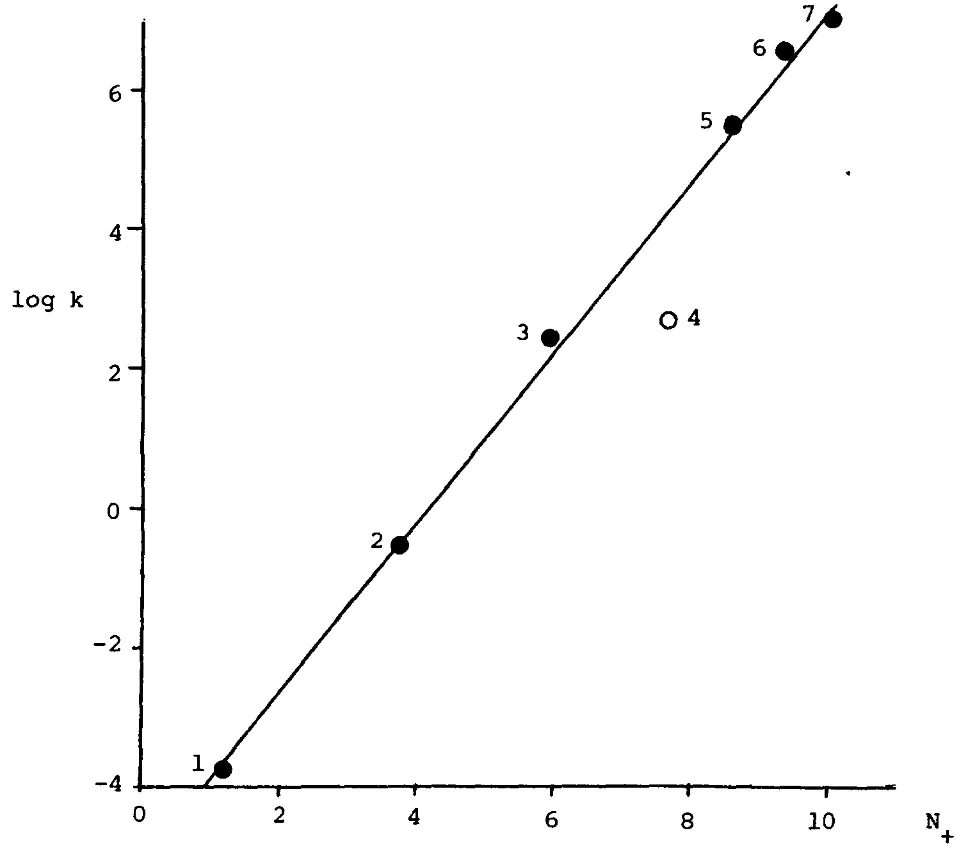
As can be seen from the figure, except for the single deviating point due to $MeO^-(MeOH)$, there is an excellent correlation with the N_+ scale (r = 0.998). This remarkably good correlation once again supports the generality of Ritchie's N_+ equation.

One of the most interesting features of Ritchie's correlation is that all the reactions studied by him are correlated to N_+ with a unit slope. As the slope is a measure of selectivity one can see that although the substrate reactivity is varied by several orders of magnitude, the selectivity, in contrast to the reactivity-selectivity principle, remains constant.[3] Recently a non-unit slope for the reaction of TAM with nucleophiles was observed by Scott[7] who suggested a modified two parameter equation (eqn. 2) which includes a selectivity parameter S_+ .

$$\log \frac{k}{k_o} = S_+N_+ \qquad (2)$$

The reaction of 1 with nucleophiles in our case also resulted in a non-unit slope of magnitude 1.23 (1.20 if $MeO^-(MeOH)$ is included). As predicted by the reactivity-selectivity principle, our substrate which is less reactive than some of the cations studied by Ritchie, is also more selective.

Although it does not explain the unit slope obtained for other substrates, it clearly indicates that the reactivity-selectivity principle cannot be totally ignored and it furthermore supports Scott's suggestion to modify Ritchie's equation to a two parameter one.



Log k for reactions of nucleophiles with 1 vs. N_+ . r = 0.998 ; slope is 1.23. Identification numbers on the plots correspond to those in the table.

The location of the transition state along the reaction coordinate of these reactions is a matter of uncertainty. Based on cation-anion combination reactions, Ritchie has concluded that the transition state for the rate determining step is between the intimate and solvent separated ion pairs.[1] However evidence of intervening steric factors[8] and the observation of fairly large Brønsted slopes for reactions of amino nucleophiles with esters[4a] caused him to change his mind and to assume higher degree of interaction between the nucleophile and the electrophilic center at the transition state.

One of the probes available for determining the extent of bond formation between a nucleophile and a substrate at the transition state is by comparing the acidity of transition state with that of the nucleophile and the product.[9] The transition state acidity (pKa(‡)) for the reaction of MeOH with 1 can be calculated from the equation (eqn. 3) developed by Kurz.[9]

$$pKa(\ddagger) = \log \frac{k_1}{k_2} + pKa(MeOH) \qquad (3)$$

where k_1 and k_2 are the pseudo-first order rate constant for the reaction of MeOH(MeOH) and the second order rate constant for the reaction of MeO^-(MeOH) with FDN respectively. Using the value of 16.92 for the pKa of MeOH[10] one obtains a value of 10.4 for the acidity of the methanolic proton in the transition state. The pKa of diethyl ether is -4.13,[11] and in using it as an approximation for the pKa of the product, one can see that about one third of the bond between the nucleophile and the substrate is formed. This is only an average value for the degree of bond formation for MeOH and MeO^-, however it supports the assumption of a covalent interaction between the nucleophile and the substrate in transition states of reactions which obey the N_+ correlation.

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