Substitution at a Saturated Carbon Atom. X. The Unification of Mechanisms SN1 and SN2[1]

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Abstract: Evidence is presented that the competitive reactions of 2-octyl mesylate with water and added azide ion in both 25 and 30 vol % aqueous dioxane proceed by way of an ion-pair intermediate. Anomalies of "borderline" behavior of secondary halides and sulfonates thus disappear. It is argued that the corresponding competitive reactions of 2-octyl brosylate with water and azide ion in the less aqueous 75 vol % dioxane, which conform to behavior predicted by a traditional SN2 mechanism, actually react *via* a reversibly formed ion pair, attack on which by nucleophile is rate determining. It is suggested that, perhaps, all nucleophilic substitutions at a saturated carbon atom proceed *via* an ion pair, thus making traditional SN1 and SN2 reactions extremes of a common mechanism which accommodates borderline behavior as well.

In large measure the organic chemist has been well served over the last three decades by the dichotomy of mechanisms of substitution at a saturated carbon atom developed by Ingold and his coworkers.[3] In practice the theory continues to serve admirably as long as attention is restricted to structurally extreme molecules. Thus those molecules with a minimal number of alkyl substituents at the carbon undergoing substitution conform to the operational definitions of mechanism SN2, bimolecularity, and inversion or configuration, while those with considerable substitution at this carbon exhibit the usual characteristics of mechanism SN1, unimolecularity, and racemization.

Between these structural extremes with their associated mechanisms lies a not inconsiderable body of structural types which do not cleanly give rise to the experimental expectations of reaction by either mechanistic extreme.

Traditional explanations for this "borderline" behavior have generally assumed one of two forms: one point of view has been that a new hybrid mechanism is operative, with characteristics intermediate between those of mechanisms SN1 and SN2,[4,5] while others maintain that the facts are better explained by assuming direct competition between distinct SN1 and SN2 processes.[6]

An attractive alternative to either of these rationalizations was suggested to us by some recently reported experiments,[7–9] namely that a single mechanism of nucleophilic substitution at a saturated carbon may be operative over the entire range of substrate types, a mechanism that becomes operationally indistinguishable from mechanisms SN1 and SN2 at the structural extremes. The central feature of the hypothetical unifying mechanism requires the intermediacy of a configurationally stable ion pair whose formation is rate determining at the SN1 end of the mechanistic spectrum and whose destruction by nucleophilic attack is rate determining at the SN2 end. "Borderline" behavior is presumed to result when the rates of formation and destruction of the intermediate are competitive.

The evidence, suggestive rather than conclusive, which led us to formulate this hypothesis included kinetic[8] and stereochemical[7] features of the solvolysis of 2-octyl sulfonates in aqueous dioxane in the presence of added sodium azide. Thus reaction of optically active 2-octyl brosylate in 75 vol % aqueous dioxane (25% water) containing sodium azide gave rise to inverted 2-octyl azide (and inverted 2-octanol), the total rate of destruction of starting material being dependent on the concentration of azide ion. Clearly the reaction exhibits the defining characteristics of an SN2 reaction, bimolecular kinetics, and inversion of configuration. On the other hand, when optically active 2-octyl mesylate was solvolyzed in the more aqueous system, 25 vol % aqueous dioxane (75% water) in the presence of sodium azide, 2-octyl azide was again obtained (along with 2-octanol) but in this solvent system the rate was found to be *nearly independent* of the concentration of sodium azide. Significantly, the 2-octyl azide formed under these conditions proved to be highly inverted. Clearly, in this more aqueous system, an intermediate must be formed in the rate-determining step whose transition state does not include azide ion (kinetic fact) but which must be asymmetric since subsequent attack by azide ion gives rise to optically inverted 2-octyl azide. This intermediate is most reasonably formulated as an ion pair.

However in view of the demonstration of an ion-pair intermediate in the more aqueous solvent and in the interests of parsimony it seemed of interest to consider the possibility that a configurationally stable, reversibly formed ion pair intervenes in the less aqueous solvent system also, its destruction by nucleophilic attack being rate determining. Such a mechanism would be indistinguishable, with presently available techniques, from the traditional SN2 mechanism, direct attack by nucleophile on covalent starting material.

The experimental results referred to above suggested to us an experimental approach to a solution of the problem at hand: if in fact an intermediate ion pair intervenes in the solvolyses of sulfonate esters in both

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[1] Supported in part by the National Science Foundation.

[2] National Institutes of Health predoctoral fellow, 1965–1967.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., pp 306 ff.

[4] M. L. Bird, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 634 (1954).

[5] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

[6] V. Gold, *J. Chem. Soc.*, 4633 (1956).

[7] H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 287 (1965).

[8] H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965).

[9] R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966).

solvent systems, its formation being rate determining at one extreme (25% dioxane) and its destruction at the other (75% dioxane), then there should exist a solvent system, intermediate in composition between these extremes, in which the rates of formation and of destruction of the intermediate are competitive, neither determining solely the rate. In such a solvent system, as will be established below, a clean experimental distinction can be made between a mechanism involving an ion-pair intermediate and various other conceivable mechanisms. And in fact the evidence presented in this paper will implicate such an intermediate.

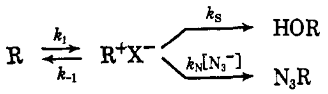
In the development which follows attention will be restricted to the competitive reactions of 2-octyl mesylate with water and azide ion in various dioxane–water mixtures.[10]

To anticipate the results, reaction in both 25[11] and 30 vol % dioxane (75 and 70% water, respectively) exhibits "borderline" behavior, *i.e.*, the total rate of reaction is found to be intermediate between zero and first order in $[N_3^-]$.

It becomes necessary then to establish that conceivable mechanisms, other than one involving an ion-pair intermediate, are inconsistent with the experimental facts.

The experimental approach which will be used to differentiate among the various mechanisms recognizes that in general they require different relationships necessarily to exist between rates of reaction and product distributions as a function of nucleophile concentration $[N_3^-]$. Consider first the ion-pair mechanism shown in Scheme I.

Scheme I



It will be seen that the product distribution is determined solely by the steps with rate constants k_s and k_N in accordance with eq 1a, whereas a simple steady-state

$$\frac{[RN_3]}{[ROH]} = \frac{k_N[N_3^-]}{k_S} \tag{1a}$$

treatment established that the observed pseudo-first-order rate constant (k_{obsd} is a function of all four defined rate constants, k_1, k_{-1}, k_s, and k_N (eq 1b).

$$k_{obsd} = \frac{k_1(k_s + k_N[N_3^-])}{k_{-1} + k_s + k_N[N_3^-]} \tag{1b}$$

In the absence of azide ion (k_{NA}), eq 1b reduces to eq 1c.

$$k_{NA} = \frac{k_1k_s}{k_{-1} + k_s} \tag{1c}$$

Elimination of k_1 between eq 1b and 1c gives eq 1d.

$$\frac{k_{obsd}}{k_{NA}} = \frac{(k_{-1} + k_s)(k_s + k_N[N_3^-])}{k_s(k_{-1} + k_s + k_N[N_3^-])} \tag{1d}$$

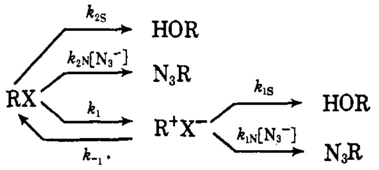
Algebraic simplification (division by k_s) gives

$$\frac{k_{obsd}}{k_{NA}} = \frac{(x + 1)(1 + m[N_3^-])}{(x + 1 + m[N_3^-])} \tag{1e}$$

where $m = k_N/k_s$ and is available experimentally from product distributions (eq 1a); and $x = k_{-1}/k_s$ is a constant independent of azide concentration.[12]

Perhaps the most reasonable alternative to an ion-pair mechanism is one requiring simultaneous competitive SN1 and SN2 processes (Scheme II). It can be

Scheme II



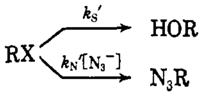
shown (Appendix) that such a scheme will give rise to products in accordance with a rate law of the form of eq 1a (in the borderline region) only in the unlikely event that

$$k_{1N}/k_{1s} = k_{2N}/k_{2s} \tag{2a}$$

It can furthermore be shown that the rate of reaction, assuming Scheme II, will approach second-order behavior as the concentration of nucleophile $[N_3^-]$ becomes large.

It is further instructive to consider the consequences of a true SN2 mechanism (Scheme III).

Scheme III



Here, since rates and products are determined in the same steps, there will necessarily be a direct correspondence (eq 3a and 3b).

$$\frac{[N_3R]}{[HOR]} = \frac{k_N'[N_3^-]}{k_s'} \tag{3a}$$

$$k_{obsd} = k_s' + k_N'[N_3^-] \tag{3b}$$

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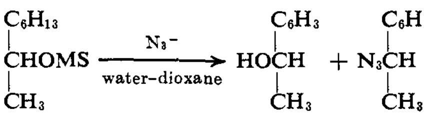
(10) That these are not reactions of carbonium ions is evidenced by the inverted configuration of the products.[7]



$$\underset{CH_3}{\overset{C_6H_{13}}{CHOMS}} \xrightarrow[\text{water-dioxane}]{N_3^-} HO\underset{CH_3}{\overset{C_6H_3}{CH}} + N_3\underset{CH_3}{\overset{C_6H_3}{CH}}$$

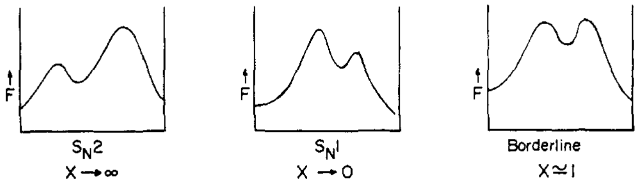
$$RX \longrightarrow HOR + N_3R$$

(11) An earlier report[8] had indicated that reaction in this solvent system gave rise to pure SN1 behavior. But at higher concentrations of azide ion than used in these preliminary studies a small dependence of rate on azide concentration was noted.

(12) It is instructive to consider the limits of this expression, as $x = k_{-1}/k_s \rightarrow \infty$, on the one hand

$$\lim_{x\rightarrow\infty} k_{obsd}/k_{NA} = 1 + m[N_3^-]$$

or typical SN2 kinetic behavior is predicted (see eq 3d). As $x \rightarrow 0$, $\lim_{x\rightarrow 0} k_{obsd}/k_{NA} = 1$, or one expects typical SN1 behavior. Intermediate values of x (realistically $10 > x > 1/2$) give rise to "borderline" behavior. These three situations can be diagrammed energetically as



It will further be seen that, for intermediate values of x, the rate constant, k_{obsd}, approaches asymptotically a limit as the concentration of nucleophile, $[N_3^-]$, is increased. (Thus for $x = 2.00$, $\lim_{[N]\rightarrow\infty} k_{obsd}/k_{NA} = 3$.) This is in direct contrast to the predictions of reaction either by competitive SN1 and SN2 reactions or by mechanism SN2 either of these two situations predicting no such limit (*vide infra*).

In the absence of azide ion, eq 3b reduces to eq 3c

$$k_{NA} = k_s' \qquad (3c)$$

$$\frac{k_{obsd}}{k_{NA}} = 1 + m'[N_3^-] \qquad (3d)$$

where $m' = k_N'/k_s'$, and is available from product data, eq 3a.

The "merged" mechanism concept,[4,5] being rather nebulous in character, is both more difficult to credit as well as to disprove. Suffice it to say that a single-stage reaction whose rate (*vide infra*) is less than first order in nucleophile could hardly be expected to give rise to products in accordance with a first-order rate law.

The reaction of 2-octyl mesylate on solvolysis in 25 and 30 vol % aqueous dioxane does in fact give rise to borderline behavior. The total rate of destruction of starting material is intermediate between zero and first order in azide concentration; at the same time the products are determined in accordance with eq 1a. It can be shown that the latter correlation can be achieved assuming a mechanism of competitive SN1 and SN2 reactions, only in the unlikely event that $k_{1N}/k_{1S} = k_{2N}/k_{2S}$ (see Appendix).

Product and kinetic data were obtained tritrimetrically, the difference between theoretical and observed liberated acid being used as a measure of incorporated azide ion. A sufficiently large excess of nucleophile assured pseudo-first-order kinetics.

Normal salt effects were compensated for by assuming them to be linear in azide concentration, independent of the nature of the salt and equal in magnitude to those of nonnucleophilic salts.[13] Justification for these assumptions will be seen in the data of Tables I and II.

Table I. Salt Effects in 30% Aqueous Dioxane at 36.2°

Salt	b^a	$k_{obsd} \times 10^4$, sec^{-1}	$k_{calcd}^a \times 10^4$, sec^{-1}
0	. . .	1.74 ± 0.04	. . .
$LiClO_4$	1.04	. . .	. . .
0.108		1.92 ± 0.09	1.93
0.09868		1.93 ± 0.04	1.92
$NaNO_3$	0.73		
0.113		1.91 ± 0.03	1.88
0.234		1.98 ± 0.04	2.03
NaBr	0.73		
0.104		1.88	1.87
0.205		1.99	2.00

[a] Calculated from the Winstein equation:[13] $K_{NA} = k^0(1 + b[\text{salt}])$, where k_{NA} is the rate constant in the absence of azide but in the presence of nonnucleophilic salt and k^0 is the rate constant in the absence of all salts.

Table II. Salt Effects in 25% Aqueous Dioxane at 36.2°

$LiClO_4$	$k_{obsd} \times 10^4$, sec^{-1}	$k_{calcd}^a \times 10^4$, sec$^-$
0	2.21 ± 0.08	
0.015	2.25 ± 0.05	2.25
0.0916	2.40 ± 0.05	2.44
0.102	2.47 ± 0.04	2.47
0.175	2.64 ± 0.12	2.65

[a] Calculated from the Winstein equation[13] with $b = 1.15$.

Table III. Comparison of Observed and Predicted Rate Constants in 25% Aqueous Dioxane at 36.2°

$[NaN_3]$, M	% $RN_{3(exptl)}$	% $RN_{3(calcd)}$	$k_{exptl} \times 10^4$, sec^{-1}	$k_{SN_2}^b \times 10^4$, sec^{-1}	$k_{ip}^c \times 10^4$, sec^{-1}
0	0	0	2.21 ± 0.08	. . .	. . .
0.0758	36.6	38.3	3.18 ± 0.12	3.98	3.28
0.113	44.0	48.1	3.76 ± 0.07	4.80	3.76
0.156	52.2	57.7	4.34 ± 0.17	5.90	4.28
0.237	67.1	66.1	5.18 ± 0.22	8.21	5.19

[a] Calculated from eq 1a with $m = 8.22$. [b] Rate constant calculated from eq 3d with $m' = 8.22$ and $k_{NA} = 2.21 \times 10^{-4}(1 + 1.08[N_3^-])$. [c] Rate constant calculated from eq 1e assuming an ion-pair mechanism with $m = 8.22$, $x = 2.33$, $k_{NA} = 2.21 \times 10^{-4}(1 + 1.08[N_3^-])$.

Table IV. Comparison of Observed and Predicted Rate Constants in 30% Aqueous Dioxane at 36.2°

$[NaN_3]$, M	% $RN_{3(exptl)}$	% $RN_{3(calcd)}^a$	$k_{exptl} \times 10^4$, sec^{-1}	$k_{SN_2}^b \times 10^4$, sec^{-1}	$k_{ip}^c \times 10^4$, sec^{-1}
0	0	0	1.74 ± 0.04	. . .	. . .
0.0543	38.4	32.3	2.43 ± 0.08	2.74	2.41
0.0571	39.3	34.1	2.26 ± 0.11	2.80	2.43
0.0979	52.5	47.0	2.67 ± 0.14	3.61	2.90
0.152	54.5	57.8	3.65 ± 0.14	4.84	3.50
0.199	64.0	64.3	3.73 ± 0.12	5.88	3.92
0.258	69.3	70.0	4.71 ± 0.08	7.36	4.47
0.311	74.6	73.8	4.91 ± 0.15	8.77	4.92

[a] Calculated from eq 1a with $m = 9.04$. [b] Rate constant calculated from eq 3d with $m' = 9.04$ and $k_{NA} = 1.74 \times 10^{-4}(1 + 1.04\,N_3^-])$. [c] Rate constant calculated from eq 1e assuming an ion-pair mechanism with $m = 9.04$, $x = 2.59$, and $k_{NA} = 1.74 \times 10^{-4}(1 + 1.04[N_3^-])$.

The data are presented in Tables III and IV for the solvolyses of 2-octyl mesylate with added sodium azide in 25 and 30 vol % aqueous dioxane, respectively. The product data, as a function of azide concentration, are shown graphically in Figures 1 and 2. The linearity of the plot will be recognized. And the kinetic data are plotted *vs.* the concentration of azide ion in Figures 3 and 4. It will be apparent that the ion-pair mechanism is able to accommodate both product and kinetic data; other conceivable mechanisms are not.

It is of interest to consider the effect of solvent on various rate ratios. From earlier work[8] the ratio k_N/k_s in 75% aqueous dioxane is 50. From this work that ratio in the more aqueous 25% dioxane is 8. Since the m value for the substrate has been found to be 0.53, it follows that the rate of azide substitution is some six times faster in the more aqueous solvent, contrary to Ingoldian predictions. Thus the reaction between charged nucleophile, N_3^-, and uncharged substrate is faster in the more aqueous solvent. This is apparently a consequence of reaction *via* an ion-pair mechanism.

Some intriguing questions are posed by the observance of the ion-pair mechanism. In particular how general is it? Obviously it can accommodate borderline behavior. Theoretically it can also accommodate traditional SN1 and SN2 behavior; and in fact there seems to be good evidence that the former systems react *via* pairs, on occasion dissociating to free ions. The question remains, are traditional SN2 reactions the result of rate-determining attack by nucleophile on reversibly formed ion pair? If so the dichotomy of nucleophilic substitution by mechanisms SN1 and SN2 disappears.

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[13] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).

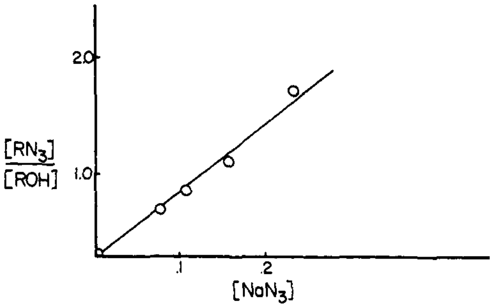

Figure 1. Plot of $[RN_3]/[ROH]$ *vs.* $[NaN_3]$ for the reaction of 2-octyl mesylate with sodium azide and water in 25 vol % aqueous dioxane. The solid line is a theoretical plot from eq 1a with slope = $m = k_N/k_s = 8.22$.

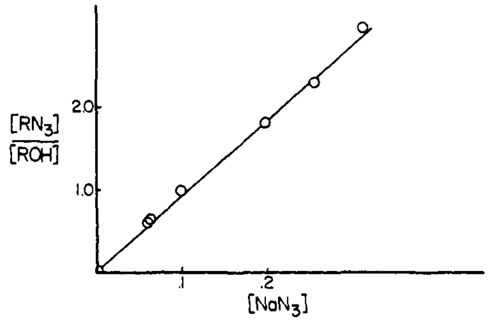

Figure 2. Plot of $[RN_3]/[ROH]$ *vs.* $[NaN_3]$ for the reaction of 2-octyl mesylate with sodium azide and water in 25 vol % aqueous dioxane. The solid line is a theoretical plot from eq 1a with slope = $m = k_N/k_s = 9.04$.

The technique used to discern the intervention of ion pairs in the borderline region does not lend itself to traditional SN2 systems, both SN2 and ion-pair mechanisms make the same kinetic predictions. But the continuity of functions (such as k_{exptl} and k_N/k_s ratios) bespeaks a continuum of mechanism.

If in fact SN2 reactions should generally fit into the ion-pair picture it becomes necessary to question whether the carbonium ion parts of ion pairs parallel in stability carbonium ions; the scale would appear to be compressed. We intend to pursue this question.

Experimental Section

Preparation and Purification of Chemicals 2-Octyl Methanesulfonate. In a 50-ml, stoppered erlenmeyer flask were placed 25 ml of dry pyridine and 5 ml of 2-octanol (Eastman). The mixture was cooled to 0°, 3 ml of methanesulfonyl chloride (Eastman) was added, and the mixture was stirred at 0° for *ca.* 3 hr. The reaction mixture was then poured into a mixture of 100 ml of cold 6 *N* hydrochloric acid and 75 ml of ether. The water layer was extracted twice with 50-ml portions of ether. The ether fractions were combined and washed consecutively with two 50-ml portions of water, *ca.* 20 ml of a 10% cadmium chloride solution, and 20 ml of water. After drying over anhydrous sodium sulfate, the ether was removed at room temperature under reduced pressure, and the resulting oil crystallized from pentane at *ca.* −7°. The solid was dried under vacuum (1-2 mm) at −78° for 2-3 days and was stored at −78°. The infrared spectrum was identical with that of an authentic sample.[14]

Dioxane. Dioxane was purified by the method of Fieser.[15] It proved necessary to store the purified solvent over sodium and to distill it immediately before use.

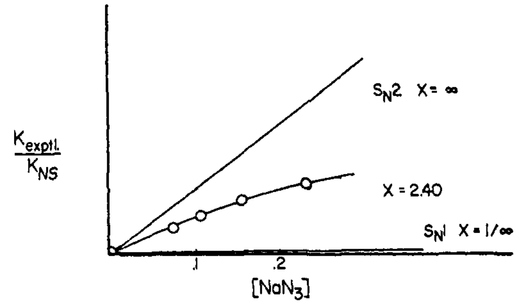

Figure 3. Plot of k_{exptl}/k_{NA} *vs.* $[N_3^-]$ for the reaction of 2-octyl mesylate with sodium azide and water in 25 vol % aqueous dioxane. The solid line is a theoretical plot from eq 1d with $k_N/k_s = 8.22$ and $x = k_{-1}/k_s = 2.40$. The experimental points are encircled.

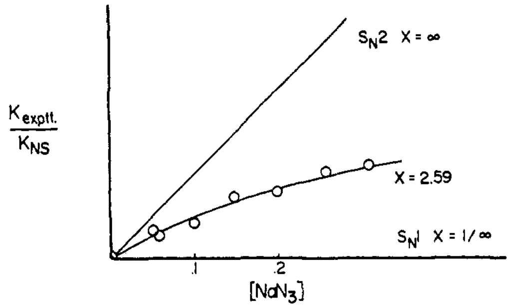

Figure 4. Plot of k_{exptl}/k_{NA} *vs.* $[N_3^-]$ for the reaction of 2-octyl mesylate with sodium azide and water in 30 vol % aqueous dioxane. The solid line is a theoretical plot from eq 1d with $k_N/k_s = 9.04$ and $x = k_{-1}/k_s = 2.59$. The experimental points are encircled.

Water. Water was purified by distillation, passage through a Barnstead oxygen-removing column, followed by passage through a Barnstead mixed-ion-exchange bed.

Sodium Azide. The commercial salt (Fisher) was dissolved in hot water, and the solution was filtered. The salt precipitated after the solution, cooled to *ca.* 0°, was diluted with ethanol. This material was filtered, washed five or six times with acetone, and dried over Drierite in a desiccator.

Lithium Perchlorate. An aqueous solution of lithium carbonate (Baker and Adamson) was neutralized with perchloric acid (G. Fredrich Smith Chemical Co.). The water was evaporated leaving the trihydrate, mp 96°.

Sodium Bromide. Commercial material (Mallinckrodt) was used without further purification.

Sodium Nitrate. Commercial material (Baker) was used without further purification.

Equipment. Glassware. All glassware was washed with hot soapy water, rinsed with distilled water, and again with distilled deionized, deoxygenated water, and dried overnight at 110°. Ampoules were prepared by constricting new, dust-free, 6-in. test tubes.

Kinetic Procedure. Solutions were prepared by pipetting the approprirate amounts of freshly distilled dioxane and distilled, deionized, deoxygenated water into an erlenmeyer flask. To a weighed amount of the necessary salts in an erlenmeyer flask was added 125 ml of the above solution. The ester was weighed into a 100-ml volumetric flask, and the salt solution was added. The ampoules were then charged with *ca.* 8 ml of the reaction mixture and were stoppered quickly. The excess salt solution was used for blanks. The ampoules were then immersed in an ice bath, flushed with nitrogen, and sealed. They were dropped simultaneously into a rate bath. Each ampoule was withdrawn and opened, and a known volume (*ca.* 5 ml) was pipetted into 10 ml of acetone. The acetone solution was titrated with a standard sodium hydroxide solution using bromothymol blue or, preferably, a 1:1 mixture of bromothymol blue-phenol red solutions as an indicator. The time of addition to the acetone quench was recorded.

Calculations. The pseudo-first-order rate constants were calculated using the formula

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

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(14) H. Weiner, Ph.D. Thesis, Purdue University, 1963, p 23.

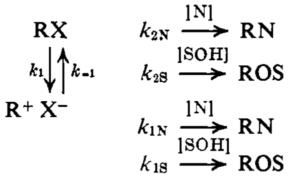
(15) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941.

The experimental infinity titer is V_∞, the initial titer ($t = 0$) is V_0, and V_t is the titer at any time, t.

Appendix

Demonstration that $k_{1N}/k_{1S} = k_{2N}/k_{2S}$ for Simultaneous SN1 and SN2 Reactions. It can be shown that $k_{1N}/k_{1S} = k_{2N}/k_{2S}$ if a plot of [RN]/[ROS] *vs.* [N] is linear and if simultaneous SN1 and SN2 mechanisms are operative. The reaction scheme for simultaneous SN1 and SN2 reactions is shown in Scheme IA.

Scheme IA



The ratio [ROS]/[RN] is shown in eq A.

$$\frac{[\mathrm{ROS}]}{[\mathrm{RN}]} = \frac{k_{2S} + \dfrac{k_1k_{1S}}{k_{1S} + k_{1N}[\mathrm{N}] + k_{-1}}}{k_{2N}[\mathrm{N}] + \dfrac{k_1k_{1N}[\mathrm{N}]}{k_{1S} + k_{1N}[\mathrm{N}] + k_{-1}}} \qquad \text{(A)}$$

$$\frac{[\mathrm{ROS}]}{[\mathrm{RN}]} = \frac{k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S}}{k_{2N}[\mathrm{N}]k_{1S} + k_{2N}k_{1N}[\mathrm{N}]^2 + k_{2N}k_{-1}[\mathrm{N}] + k_1k_{1N}[\mathrm{N}]} \qquad \text{(B)}$$

Experimentally, a plot of [RN]/[ROS] vs. N is a straight line. Therefore

$$C_1 = \frac{k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S}}{k_{2N}k_{1S} + k_{2N}k_{1N}[\mathrm{N}] + k_{2N}k_{-1} + k_1k_{1N}} \qquad \text{(C)}$$

where C_1 is a constant.

$$k_{1S}k_{2S} + k_{2S}k_{1N}[\mathrm{N}] + k_{2S}k_{-1} + k_1k_{1S} = C_1(k_{2N}k_{1S} + k_{2N}k_{1N}[\mathrm{N}] + k_{2N}k_{-1} + k_1k_{1N}) \qquad \text{(D)}$$

$$[\mathrm{N}](k_{2S}k_{1N} - C_1k_{2N}k_{1N}) = C_1k_{2N}k_{1S} + C_1k_{2N}k_{-1} + C_1k_1k_{1N} - k_{1S}k_{2S} - k_{2S}k_{-1} - k_1k_{1S} \qquad \text{(E)}$$

The right side of eq E is a constant.

$$[\mathrm{N}](k_{2S}k_{1N} - C_1k_{2N}k_{1N}) = C_2 \qquad \text{(F)}$$

Since [N] is a variable and C_2 is a constant

$$k_{2S}k_{1N} - C_1k_{2N}k_{1N} = 0 \qquad \text{(G)}$$

Solving eq 6 for C_1 and substituting this value into eq D gives

$$k_{1S}k_{2S}k_{2N} + k_{2S}k_{1N}k_{2N}[\mathrm{N}] + k_{2S}k_{-1}k_{2N} + k_1k_{1S}k_{2N} = k_{2N}k_{1S}k_{2S} + k_{2N}k_{1N}k_{2S}[\mathrm{N}] + k_{2N}k_{-1}k_{2S} + k_1k_{1N}k_{2S} \qquad \text{(H)}$$

Rearranging and simplifying this equation gives

$$k_{1S}/k_{1N} = k_{2S}k_{2N} \qquad \text{(I)}$$

Thus if simultaneous SN1 and SN2 reactions are operating, a linear plot of [RN]/[ROS] *vs.* [N] leads directly to the condition

$$k_{1N}/k_{1S} = k_{2N}/k_{2S}$$

The Effect of Solvents on Anion Structure[1]

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Abstract: The nmr and electronic spectra of salts of 1-nitroindene and 9-nitrofluorene show significant changes between hydroxylic and nonhydroxylic solvents. These changes demonstrate that hydrogen bonding to the oxygens of the anions tends to localize the charge on the oxygens, and thereby causes alterations in the structure of the anions. Cation coordination to the oxygens in nonpolar aprotic solvents produces similar effects, but of smaller magnitude. Analogous effects are observed for some phenoxide salts.

Our interest in the equilibria between 9-*aci*-nitrofluorene and 1-*aci*-nitroindene and their tautomers[2] led us to prepare the potassium salts of these compounds.[3] In the process of confirming the identity of these salts, we observed that their spectra showed substantial differences when measured in different solvents. Since a search of the literature failed to reveal any unequivocal examples of the effect of solvents on anion *structure* as revealed by spectra or other means, we undertook an investigation of this phenomenon, for the cases of these nitro salts and a pair of substituted phenoxide salts.

Nitro Salts. The potassium salts of 1-nitroindene (**1**) and 9-nitrofluorene (**2**) are high-melting, relatively stable solids, soluble in hydroxylic and in polar aprotic solvents but not very soluble in nonpolar solvents. Aqueous solutions are essentially neutral to pH paper, indicating the high acidity of the conjugate nitro compounds.

The infrared spectra of salts **1** and **2** in Nujol or hexachlorobutadiene mulls show lower C=N stretching frequencies (1527 and 1504 cm^{-1}, respectively) than typical secondary nitroalkane salts (1579–1603 cm^{-1}).[4]

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(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 3, 1968, Abstract P-130.

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