

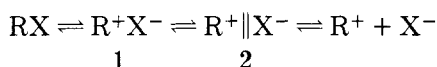
## A Case for the Concerted SN2 Mechanism of Nucleophilic Aliphatic Substitution

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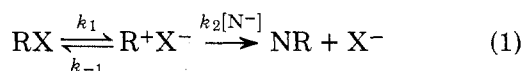
Traditionally the reactions classed as nucleophilic aliphatic substitutions have been described and discussed in terms of a mechanistic dichotomy: either as stepwise processes involving the intermediacy of ionic species (SN1) or as concerted displacements in which a single transition state intervenes between reactants and products (SN2)<sup>1</sup> wherein the energy released in forming the new bond is simultaneously utilized in rupturing the old one.<sup>2</sup> In the 1930's, considerable opposition arose as to the postulation of ionic intermediates in SN1 and similar processes,<sup>3</sup> but no such doubts exist today.<sup>4-7</sup> Carbonium ion chemistry as it pertains to nucleophilic substitution is now largely discussed in terms of intimate or tight ion-pair intermediates (1) and loose or solvent-separated ion pairs (2).



The wheel of mechanistic contention has now turned a full circle, and the most disputed issue in the SN field at this time concerns the reality or otherwise of the concerted SN2 mechanism in which the product precursor is the un-ionized substrate. This Account will examine a counterproposal, most vigorously advocated by Sneen,<sup>8</sup> and will attempt to defend the traditional viewpoint. Recently Bordwell has similarly queried the existence of concerted ionic reactions involving three or more bonds;<sup>9</sup> at issue, therefore, is whether *any* organic ionic reactions are concerted and intermediate free.

### The Sneen Ion-Pair Mechanism

Sneen and his collaborators have contended that, in most, if not all, cases of substitution by an added (nonsolvent) nucleophile N<sup>-</sup> (written as an anion for convenience) nucleophilic attack does not take place until the substrate has ionized, *without nucleophilic assistance*, to at least the intimate ion-pair stage<sup>8,10-12</sup> (eq 1).



The nucleophile is presumably thought to be more strongly attracted to cationic carbon than to "neutral" carbon in RX, and so performs the act of substitution by anion interchange (with inversion) at the ion-pair stage.

When  $[\text{N}^-]_0 \gg [\text{RX}]_0$ , the steady-state rate equation for  $k_{\text{obsd}}$ , the pseudo-first-order rate constant, is given by

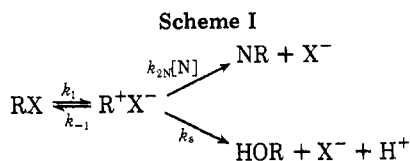
$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{N}^-]}{k_{-1} + k_2 [\text{N}^-]} \quad (2)$$

There are two limiting cases: (i)  $k_2[\text{N}^-] \gg k_{-1}$ , so  $k_{\text{obsd}} = k_1$  and we have rates independent of  $[\text{N}^-]$  and an SN1-like process, and (ii)  $k_{-1} \gg k_2[\text{N}^-]$ ,  $k_{\text{obsd}} = k_1 k_2 [\text{N}^-] / k_{-1}$ , so that the reaction is first order in  $[\text{N}^-]$  and second order overall. These two cases, corresponding respectively to rate-limiting ionization and nucleophilic attack on a preformed ion pair, are thus kinetically indistinguishable from SN1 in the former limit and traditional SN2 in the latter. If, however,  $k_{-1} \approx k_2[\text{N}^-]$ , eq 2 shows that the order with respect to  $[\text{N}^-]$  is between first and second, so that this is a hypothetical borderline region. It is this unique region, and the subsequent saturation kinetics at high  $[\text{N}^-]$ , that the SN1-SN2 dichotomy cannot reproduce, and although various opinions have been expressed on this subject within the traditional framework, none have been completely satisfactory.<sup>13</sup> The unique experimental test

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, G. Bell and Sons, London, 1969, Chapter 7; (b) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom", Elsevier, Amsterdam, 1963.

(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).  
 (3) Reference 1, Chapter 10; C. D. Nenitzescu, *Carbonium Ions*, **1**, 1 (1968).  
 (4) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965); C. J. Collins, *Chem. Soc. Rev.*, **4**, 251 (1975).  
 (5) D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **45**, 60 (1972).  
 (6) J. M. Harris, *Prog. Phys. Org. Chem.*, **11**, 89 (1969).  
 (7) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Interscience, New York, N.Y., 1974, chap. 3.  
 (8) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).  
 (9) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970).  
 (10) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 362 (1969).  
 (11) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 6031 (1969).  
 (12) (a) R. A. Sneen and H. M. Robbins, *J. Am. Chem. Soc.*, **94**, 7868 (1972); (b) R. A. Sneen and W. A. Bradley, *ibid.*, **94**, 6975 (1972); (c) R. A. Sneen, G. R. Felt, and W. C. Dickason, *ibid.*, **95**, 638 (1973).

Duncan McLennan was born in Hastings, New Zealand, in 1940. Undergraduate and graduate studies (with the late B. D. England) at Victoria University of Wellington were followed by postdoctoral work with J. F. Bunnett at Brown University and the University of California, Santa Cruz. He was appointed to the staff at Auckland in 1969 and has there pursued his interests in elimination and substitution mechanisms, free-energy relationships, and isotope effects. He is married, and has a young son and daughter.



of the ion-pair mechanism is then the demonstration of borderline kinetics which can be predictably switched toward first-order or second-order behavior by changes in nucleophile concentration, solvent, nucleophilicity of  $\text{N}^-$ ,<sup>14</sup> leaving group, or structure of R. It is to the delineation of the borderline region that Snee has directed his attention.

For twelve reaction systems where solvolysis competes with attack by external nucleophiles (as in Scheme I), the observation of borderline kinetics has been claimed.<sup>8</sup> Snee's method of testing the rate and product data to confirm the mechanism in Scheme I has been described in detail.<sup>7,8,10-12</sup> It suffices to state that, on the surface, only one adjustable parameter,  $k_{-1}/k_s$  (assumed independent of the identity or concentration of  $\text{N}^-$  for a given  $\text{RX}$ -solvent system) is needed to fit the experimental data to the steady-state rate expression. The solvolysis rate constant for overall formation of ROH (in aqueous solvents) will, however, be affected by increasing the concentration of the nucleophile-supplying salt. If  $k_{\text{NS}}$  is the (hypothetical) rate coefficient for solvolysis in the absence of reaction by  $\text{N}^-$  (but in the presence of  $\text{M}^+\text{N}^-$ ), eq 3 due to Fainberg and Winstein<sup>15</sup> is used to correct the rate constant  $k_s^0$  for solvolysis in the absence of all electrolytes, for the salt effect.

$$k_{\text{NS}} = k_s^0(1 + b[\text{salt}]) \quad (3)$$

The  $b$  parameter appropriate to the nucleophilic salt is indeterminable. It is assumed that salt effects are both regular (solvolysis rates linear with respect to [salt]) and nonspecific (i.e.,  $b$  is the same for all salts acting on a given solvolysis). Thus  $b$  is obtained using a model nonnucleophilic salt, usually a perchlorate.<sup>16</sup>

A detailed criticism of this procedure has been given.<sup>7,19</sup> The principal complaint is that  $b$ , like  $k_{-1}/k_s$ , may be an adjustable parameter, and that by a judicious choice of  $b$ , one may correlate experimental data with the predictions of whatever mechanistic model one favors. While a reply has been given,<sup>8,12a</sup> the unarguable fact remains that nonnucleophilic salt effects are both irregular and specific.<sup>15,20-22</sup> Furthermore, nucleophilic

(13) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); M. L. Bird, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 634 (1954); V. Gold, *ibid.*, 4633 (1956).

(14) Equation 2 predicts a decrease in order as  $\text{N}^-$  becomes more nucleophilic. The opposite is generally accepted to be the case. Note too that, in a kinetic run where  $[\text{RX}]_0 \sim [\text{N}^-]_0$  and where solvolytic side reactions do not intrude, the concentration-time data in a borderline process will not be satisfactorily expressed by either the integrated first- or the second-order rate equations. We know of no such unambiguous cases.

(15) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

(16) Note that nucleophilic participation by "inert" anions such as  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  has been proposed.<sup>7,17,18</sup>

(17) B. J. Gregory, G. Kohnstam, A. Queen, and D. J. Reid, *Chem. Commun.*, 797 (1971).

(18) D. G. Graczyk and J. W. Taylor, *J. Am. Chem. Soc.*, **96**, 3255 (1974). See also ref 43.

(19) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 4821 (1971).

(20) J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, **36**, 897 (1971).

(21) P. J. Dais and G. A. Gregoriou, *Tetrahedron Lett.*, 3827 (1974).

(22) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Lett.*, No. 22, 12 (1960); A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956); E. Duynstee, E. Grunwald, and M. L. Kaplan, *ibid.*, **82**, 5654 (1960); P. B. D. de la Mare, D. M. Hall, and E. Manger, *Recl. Trav. Chim. Pays-Bas*, **74**, 1394

salts depress the ionization rates of undoubted  $\text{SN}_1$ -type substrates,<sup>23</sup> which accords with the proposed<sup>7,19</sup> (but disputed<sup>8</sup>) negative salt effect of  $\text{NaN}_3$  on the solvolysis rate of 2-octyl mesylate. A theoretical treatment which uses as a salt effect model the stabilization of an  $\text{SN}_1$  transition-state dipole by an  $\text{M}^+\text{N}^-$  ion pair predicts specific salt effects.<sup>24</sup> Other irregularities may arise as a result of specific salt-induced medium effects on the substrate itself<sup>25</sup> and from opposing salt effects on the pathways producing RN and ROH.<sup>7</sup>

Nevertheless the idea of rate-limiting nucleophilic attack on ion pairs has won some support, generally for specific cases, and usually applying to solvolysis. The various items of evidence in the cited papers are circumstantial, and do not involve borderline kinetics. We merely list the relevant works,<sup>18,26-30</sup> as space does not permit detailed discussion.

Specific mention could, however, be made of a linear free energy relationship (LFER) treatment of displacements on methyl halides and methyl perchlorate, which leads to the espousal of ion-pair processes even for such unlikely substrates.<sup>27d,h</sup> The method uses the reactions of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  with trityl cations as models for nucleophilic attack on  $\text{Me}^+\text{X}^-$  ion pairs, but one could hardly choose less appropriate processes. The water reactions are general base catalyzed<sup>31</sup> and the standard reactions are not unitary processes<sup>31a,32</sup> as is required by the LFER.<sup>27d</sup> The inapplicability of this approach may be easily demonstrated by the fact that  $\text{OH}^- > \text{CN}^-$  in reactivity toward trityl cations, whereas the opposite order pertains for methyl halides in water. In fact, the use of  $\text{OH}^-$  and  $\text{CN}^-$  as model nucleophiles in the calculation leads to the unsupported conclusions that MeCl, MeBr, and MeI are more than 99.9% ionized in aqueous solution, and that nucleophiles react with the ion pairs in processes having rate constants of the order of  $10^{-10}$ – $10^{-16}$  l. mol<sup>-1</sup> s<sup>-1</sup>. Misapplication of the Hammond postulate dominates the argument for methyl perchlorate hydrolysis.<sup>27h</sup>

## The $\text{SN}_2$ Mechanism

An  $\text{SN}_2$  process by definition involves a transition state in which  $\text{N}^-$  and X are partially covalently bound

(1968); C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K. U. Yang, *J. Org. Chem.*, **36**, 887 (1971); C. A. Bunton and L. Robinson, *J. Am. Chem. Soc.*, **90**, 5965 (1968).

(23) C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955); A. Cecon, A. Fava, and I. Papa, *J. Am. Chem. Soc.*, **91**, 5547 (1969); A. Queen and T. C. Matts, *Tetrahedron Lett.*, 1503 (1975); T. Austad and J. Songstad, *Acta Chem. Scand.*, **26**, 3141 (1972).

(24) C. L. Perrin and J. Pressing, *J. Am. Chem. Soc.*, **93**, 5705 (1971).

(25) E. Grunwald and A. Effio, *J. Am. Chem. Soc.*, **96**, 423 (1974).

(26) (a) F. G. Bordwell and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 123 (1975); (b) *ibid.*, **97**, 127 (1975); (c) F. G. Bordwell and G. A. Pagani, *ibid.*, **97**, 118 (1975).

(27) (a) J. A. Cramer and J. G. Jewitt, *J. Am. Chem. Soc.*, **94**, 1377 (1972); (b) C. J. Kim and H. C. Brown, *ibid.*, **94**, 5043, 5051 (1972); (c) R. D. Fischer, R. C. Seib, V. J. Shiner, I. Szele, M. Tomic, and D. E. Sunko, *ibid.*, **97**, 2408 (1975); (d) J. M. W. Scott, *Can. J. Chem.*, **48**, 3807 (1970); (e) A. V. Willi, C. Ho, and A. Ghanbupour, *J. Org. Chem.*, **37**, 1185 (1972); (f) J. M. Harris, D. J. Raber, W. C. Neal, and M. D. Dukes, *Tetrahedron Lett.*, 2331 (1974); (g) V. J. Shiner, W. Dowd, R. D. Fischer, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969); (h) R. E. Robertson, A. Annesa, and J. M. W. Scott, *Can. J. Chem.*, **53**, 3106 (1975). See also D. Farcasiu, *J. Chem. Educ.*, **52**, 76 (1975).

(28) K. Humski, V. Sendjarevic, and V. J. Shiner, *J. Am. Chem. Soc.*, **95**, 7722 (1973); **96**, 6187 (1974).

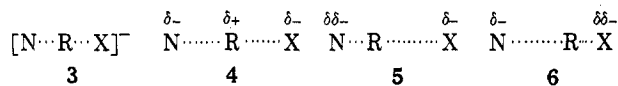
(29) J. Koskikallio, *Acta Chem. Scand.*, **26**, 1201 (1972). See also ref 7, p 365.

(30) W. T. Ford, *Acc. Chem. Res.*, **6**, 410 (1973).

(31) (a) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972); (b) C. D. Ritchie, D. J. Wright, D.-S. Huang, and A. A. Kamego, *J. Am. Chem. Soc.*, **97**, 1163 (1975); C. A. Bunton and S. K. Huang, *ibid.*, **96**, 515 (1974); J. H. Ride, P. A. H. Wyatt, and Z. M. Zochowski, *J. Chem. Soc., Perkin Trans. 2*, 118 (1974).

(32) A. Pross, *J. Am. Chem. Soc.*, **98**, 776 (1976).

to  $C_\alpha$  of R. Some negative charge will remain on N and X, and  $C_\alpha$  may have some positive charge.<sup>33</sup> Bond making and breaking need not be synchronous, and transition states may be tight (3), loose (4), or unsymmetrical (5 or 6).



Thus kinetic responses to changes in molecular and environmental variables in second-order substitutions may be rationalized in terms of the type of transition state involved,<sup>34,35</sup> or by postulating changes in transition-state character.<sup>34-36</sup>

However, the second-order variant of the ion-pair mechanism may also be used to rationalize the effects of various molecular and environmental changes in that such changes may dominate either  $k_1/k_{-1}$ , the equilibrium constant for ion-pair formation, or  $k_2$ , the rate constant for ion-pair destruction at the hands of the nucleophile. Thus, differing kinetic responses may be envisaged for different situations, and the mechanistic interpretation of indirect evidence largely rests on the ingenuity and bias of the individual.

We now cite papers which explicitly or implicitly reassert the conservative SN2 viewpoint. Much of the evidence is inferential, and several attempted rebuttals of the Snee mechanism have themselves attracted criticism. Nonetheless, the universal ion-pair mechanism has not yet won over a majority of adherents,<sup>37</sup> as a reference count shows.<sup>17,19-21,28,38-45</sup>

The loose SN2 transition state (4) resembles the triple ion species  $N^-R^+X^-$  (and thus the transition states flanking it) which, by microscopic reversibility, must lie on an ion-pair pathway. In transition-state theory it matters not at all from the overall rate viewpoint how

(33) C. D. Ritchie and G. A. Chappell, *J. Am. Chem. Soc.*, **92**, 1819 (1970); R. F. Bader, A. J. Duke, and R. R. Messer, *ibid.*, **95**, 7715 (1973); G. Berthier, D. J. David, and A. Viellard, *Theor. Chim. Acta*, **14**, 329 (1969).

(34) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(35) C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951); J. W. Hill and A. Fry, *ibid.*, **84**, 2763 (1962); S. Seltzer and A. A. Zavitsas, *Can. J. Chem.*, **45**, 2023 (1967); D. C. Wigfield, *ibid.*, **48**, 2120 (1970); R. F. Hudson, *Chimia*, **16**, 173 (1962); R. F. Hudson and G. Klopman, *Helv. Chim. Acta*, **44**, 1914 (1961); *J. Chem. Soc.*, 1062 (1962).

(36) B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc. B*, 152 (1966).

(37) A silent majority may exist, but the author, in the relative isolation of his antipodean habitat, is unaware of it.

(38) (a) M. H. Abraham, *J. Chem. Soc. B*, 299 (1971); (b) *J. Chem. Soc., Perkin Trans. 2*, 1893 (1973); (c) P. I. Meikle, J. R. Salmon, and D. Whittaker, *ibid.*, **23** (1972); (d) E. Baciocchi, P. Perucci, and C. Rol, *ibid.*, **329** (1975); (e) H. L. Goering, R. G. Briody, and G. Sandrock, *J. Am. Chem. Soc.*, **92**, 7401 (1970); (f) H. L. Goering and H. Hopf, *ibid.*, **93**, 1224 (1971); (g) U. Miotti and A. Fava, *ibid.*, **88**, 4274 (1966); (h) V. J. Shiner, M. W. Rapp, and H. R. Pinnick, *ibid.*, **92**, 232 (1970); (i) J. Hayami, N. Tanaka, S. Kurabayashi, Y. Kotani, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **44**, 3091 (1971); (j) O. E. Edwards and C. Grieco, *Can. J. Chem.*, **52**, 3561 (1974); (k) A. Loupy and J. Seyden-Penne, *C. R. Hebd. Seances Acad. Sci.*, **272**, 1665 (1971); *Tetrahedron*, **29**, 1015 (1973); (l) H. Meislich and S. Jasne, *J. Org. Chem.*, **40**, 2662 (1975); (m) A. Pross and R. Koren, *Tetrahedron Lett.*, **3613** (1975); (n) K. C. Westaway, *ibid.*, **4229** (1975); K. C. Westaway and R. Poirier, *Can. J. Chem.*, **53**, 3216 (1975).

(39) J. F. Bunnett and D. L. Eck, *J. Am. Chem. Soc.*, **94**, 1900 (1972). See also ref 30.

(40) A. Ceccon, I. Papa, and A. Fava, *J. Am. Chem. Soc.*, **88**, 4643 (1966). See also ref 7, p 343.

(41) G. A. Gregoriou, *Tetrahedron Lett.*, **233** (1974). See also ref 7, p 341.

(42) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *Chem. Commun.*, 1032 (1970). See also ref 7 and 11.

(43) K. M. Koshy, R. E. Robertson, and W. J. M. Strachan, *Can. J. Chem.*, **51**, 2958 (1973).

(44) J. L. Kurz and J. C. Harris, *J. Am. Chem. Soc.*, **92**, 4117 (1970). See also ref 8.

(45) V. F. Raean, T. Juhlke, F. J. Brown, and C. J. Collins, *J. Am. Chem. Soc.*, **96**, 5928 (1974); M. P. Freidberger and E. R. Thornton, *ibid.*, **98**, 2861 (1976); see also ref 18.

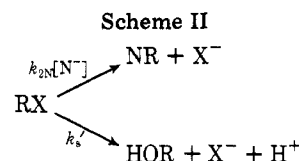
a system attains the configuration of highest energy on the reaction coordinate, so what then is the present argument about?

Innate curiosity as to intimate details of the reaction coordinate and in the spirit of Bordwell's query mentioned above is a motivating factor. Are there any potential wells on the way to the transition state and are they significant in permitting a diversity of products? Must the transition state always be mainly ionic in character or are tighter covalent-like species such as 3 possible? One has only to consider the number of times second-order nucleophilic substitutions have been used as model processes for investigating isotope, substituent, and solvent effects to realize the importance of understanding (with more than the usual degree of certainty) just what the model reaction is. One has only to consider the importance of alkylation, especially of ambident nucleophiles, in organic synthesis to appreciate the importance of ionic vs. covalent character of transition states.

But before unequivocal evidence for or against specific or general cases of ion-pair mechanisms can be adduced, the evidence for the purported borderline region must be examined. The aforementioned pernicious salt effects must be gotten rid of, and we now discuss some approaches to this end.

### An SN2 Reinterpretation of Literature Results

Consider the reaction system in Scheme II. Without



commitment as to mechanism we assume (i) that the formation of ROH is first order within a kinetic run, with  $k_s'$  perhaps being dependent on  $[N^-]$  in some way, and (ii) that formation of RN is second order, with  $k_{2N}$  being independent of  $[N^-]$ . In a given kinetic run with  $[N^-]_0 \gg [RX]_0$ , eq 4 and 5 apply.

$$k_{\text{obsd}} = k_s' + k_{2N}[N^-] \quad (4)$$

$$\begin{aligned}
 f_N &= [\text{RN}]_\infty / ([\text{RN}]_\infty + [\text{ROH}]_\infty) \\
 &= k_{2N}[N^-] / (k_s' + k_{2N}[N^-]) \quad (5)
 \end{aligned}$$

Here,  $f_N$  is the fraction of RN in the product mixture. We now eliminate  $k_s'$  from eq 4 and 5, which is perfectly valid since  $[N^-]$ , and hence  $k_s'$ , is the same in both. The simple result is eq 6.

$$f_N k_{\text{obsd}} = k_{2N}[N^-] \quad (6)$$

Raw rate and product data for Snee's twelve reactions and one other<sup>46</sup> are analyzed by examining plots of  $f_N k_{\text{obsd}}$  (unadjusted experimental values) against  $[N^-]$ . Typical plots are shown in Figure 1, and the resultant data (including standard deviations and correlation coefficients) are displayed in Table I. In 12 out of 13 cases, good straight lines are obtained. Some of the data sets have too few points for  $r$  to be of much significance, and two experimental points (out of 67) have been rejected as being obviously out of line.

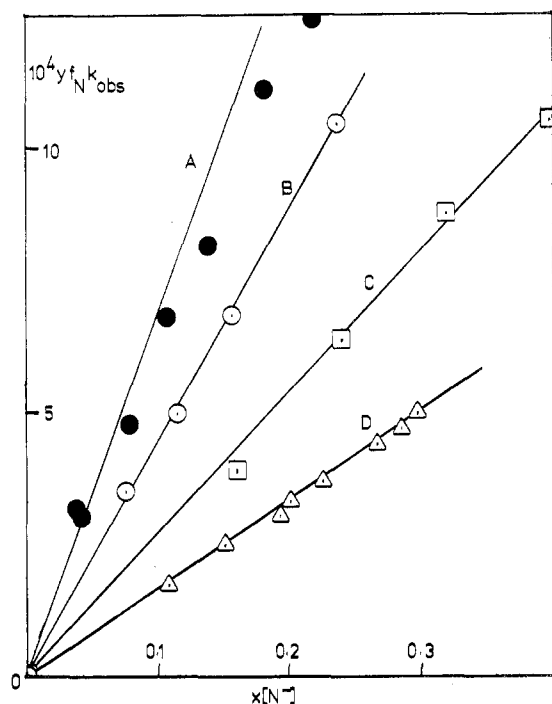
Data from Figure 1D are shown in detail in Table II. It is seen that  $k_{2N}$  and  $m$ , the latter equal to  $[\text{RN}]/$

(46) D. J. McLennan, *J. Chem. Soc., Perkin Trans. 2*, 481 (1974).

**Table I**  
Analysis of "Borderline" Reactions in Terms of Scheme I and Equation 3

Substrate	Salt	Solvent	Temp, °C	$r^h$	$10^4 k_{2N}$ , l. mol <sup>-1</sup> s <sup>-1</sup>	$m^l$	Ref
1. ROMs <sup>a</sup>	NaN <sub>3</sub>	25% D-W <sup>f</sup>	36.2	0.999 (5)	14.5 ± 0.3	7.4 ± 0.6	8, 13
2. ROMs <sup>a</sup>	NaN <sub>3</sub>	30% D-W	36.2	0.998 (8)	13.8 ± 2.0 <sup>k</sup>	9.9 ± 1.2	8, 13
3. ArCH <sub>2</sub> Cl <sup>b</sup>	NaN <sub>3</sub>	70% Me <sub>2</sub> CO-H <sub>2</sub> O	20	0.999 (4)	50.7 ± 1.2 <sup>k</sup>	21.6 ± 0.1	8, 14
4. MeCH=CH(Cl)Me	Pr <sub>4</sub> NN <sub>3</sub>	EtOH	36	0.999 (5) <sup>i</sup>	43.5 ± 1.0	34.7 ± 1.3	8, 15b
5. MeCH=CH(Cl)Me	NaSCN	EtOH	36	0.999 (6) <sup>i</sup>	10.4 ± 0.3	7.5 ± 0.6	8, 15b
6. MeCH=CH(Cl)Me	NaN <sub>3</sub>	90% E-W <sup>g</sup>	36	0.998 (5)	107 ± 5	11.8 ± 0.3	8, 15b
7. PhCH(Br)Me	Pr <sub>4</sub> NN <sub>3</sub>	EtOH	50	0.995 (9)	115 ± 8	124 ± 8	8, 15a
8. PhCH(Br)Me	NaSCN	EtOH	50	0.999 (9)	32.5 ± 0.7	27.0 ± 0.6	8, 15a
9. ArCH(Cl)Me <sup>c</sup>	Pr <sub>4</sub> NN <sub>3</sub>	EtOH	50	0.999 (5)	18.8 ± 1.1	10.7 ± 1.0	8, 15a
10. ArCH(Cl)Me <sup>c</sup>	NaSCN	EtOH	50	0.997 (7)	9.2 ± 0.3	4.44 ± 0.17	8, 15a
11. ROMs <sup>a</sup>	NaN <sub>3</sub> <sup>d</sup>	25% D-W	35	0.999 (8)	24.5 ± 0.7	12.1 ± 0.3	46
12. PhCOCl	ArNH <sub>2</sub> <sup>e</sup>	80% Me <sub>2</sub> CO-H <sub>2</sub> O	0	0.999 (4)	2.02 ± 0.2 <sup>k</sup>	5.27 ± 0.37	8, 14, 52
13. PhCOCl	ArNH <sub>2</sub> <sup>e</sup>	50% Me <sub>2</sub> CO-H <sub>2</sub> O	0	0.984 (4) <sup>j</sup>		4.45 ± 0.32	8, 14, 52

<sup>a</sup> R = 2-octyl. <sup>b</sup> Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>. <sup>c</sup> Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>. <sup>d</sup> Total salt concentration maintained at 2 M by NaClO<sub>4</sub>. <sup>e</sup> Ar = *o*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. <sup>f</sup> Dioxane-water. <sup>g</sup> Ethanol-water. <sup>h</sup> Correlation coefficient of  $f_N k_{\text{obsd}}$  vs.  $[N^-]$  plot. Number of points in parentheses. <sup>i</sup> One deviant data point omitted. <sup>j</sup> Smooth curve, see text. <sup>k</sup> Slight curvature evident. <sup>l</sup> Average of  $m$  values from individual data points. Uncertainty is standard or mean deviation.



**Figure 1.** Plots of  $f_N k_{\text{obsd}}$  vs.  $[N^-]$  for representative reactions from Table I. (A) Reaction 2, solid circles,  $y = 3.4$ ,  $x = 0.7$ . (B) Reaction 1, open circles,  $y = 3.0$ ,  $x = 1.0$ . (C) Reaction 6, squares,  $y = 1.0$ ,  $x = 4.0$ . (D) Reaction 8, triangles,  $y = 2.0$ ,  $x = 4.0$ .

$[ROH][N^-]$ , are constant. Values of  $k_s'$  are also constant,<sup>47</sup> so  $b = 0$  for NaSCN as added salt in the ethanolysis of PhCH(Br)CH<sub>3</sub>. In contrast, Table III gives detailed data from Figure 1C, wherein it is seen that  $m$  is not constant and  $k_s'$  is subject to an overall positive salt effect. In other reaction systems, negative salt effects, maxima, or minima are seen. The behavior of  $k_s'$  is unpredictable.<sup>48</sup> The important point is that  $k_{2N}$  is constant, as required, within each reaction series, over a range of nucleophile concentrations.<sup>49</sup> Note that the

(47) Equations 5 and 6 predict a linear relationship between  $[RN]/[ROH]$  and  $[N^-]$  over a range of nucleophile concentrations (i.e., constant  $m$ ) only if  $k_s'$  and  $k_{2N}$  have identical dependence on  $[N^-]$ .

(48) We will never know for sure what the effect of a given nucleophilic salt is on the rates of competitive solvolysis, so no standards of behavior are available. One could assume a kinetic form for the nucleophile-induced reaction and deduce the salt effect, but such an assumption is central to the present controversy.

**Table II**  
Reaction of 1-Phenylethyl Bromide with NaSCN in EtOH at 50 °C<sup>15a</sup>

[NaSCN], M	$10^4 k_{\text{obsd}}^a$	$f_N$	$m$	$10^4 k_{2N}^b$	$10^4 k_s'^a$
0	1.13				1.13
0.0273	2.02	0.426	27.2	31.5	1.16
0.0381	2.47	0.501	26.3	32.5	1.23
0.0482	2.67	0.565	26.9	31.3	1.16
0.0502	2.88	0.573	26.7	32.9	1.23
0.0564	3.07	0.604	27.0	32.8	1.22
0.0667	3.40	0.643	27.0	32.8	1.21
0.0716	3.54	0.660	27.1	32.7	1.20
0.0744	3.65	0.676	28.0	33.2	1.18

<sup>a</sup> In s<sup>-1</sup>. <sup>b</sup> In l. mol<sup>-1</sup> s<sup>-1</sup>.

**Table III**  
Reaction of  $\alpha,\gamma$ -Dimethylallyl Chloride with NaN<sub>3</sub> in 90% EtOH-H<sub>2</sub>O at 36 °C<sup>15b</sup>

[NaN <sub>3</sub> ], M	$10^4 k_{\text{obsd}}^a$	$f_N$	$m$	$10^4 k_{2N}^b$	$10^4 k_s'^a$
0	8.40				8.4
0.04	11.9	0.325	13.0	97	8.0
0.06	15.0	0.423	12.2	106	8.7
0.08	17.7	0.492	12.1	109	9.0
0.10	19.5	0.536	11.5	104	9.0

<sup>a</sup> In s<sup>-1</sup>. <sup>b</sup> In l. mol<sup>-1</sup> s<sup>-1</sup>.

rate of the  $\alpha,\gamma$ -dimethylallyl chloride-N<sub>3</sub><sup>-</sup>-EtOH reaction is increased by the addition of water, contrary to the predictions of simple solvation theory.<sup>50</sup> However, several other aberrant examples are available,<sup>26a,51</sup> and

(49) The slight curvature seen in three plots, curved in the sense of Figure 1A, can be understood in terms of variation of the degree of dissociation of M<sup>+</sup>N<sup>-</sup> ion pairs, with free N<sup>-</sup> being more nucleophilic than the ion pair. For other work on the effect of nucleophilic salt association on substitution kinetics, see A. R. Stein, *J. Org. Chem.*, **38**, 4022 (1973); **41**, 519 (1976); *J. Chem. Educ.*, **52**, 303 (1975); P. Baronius, A.-M. Nilsson, and A. Holmgren, *Acta Chem. Scand.*, **26**, 3173 (1972). It is therefore significant that, while a curved plot is obtained for the 2-octyl mesylate-Na<sub>3</sub> system in 30% dioxane-water (Figure 1A), the plot for the same reaction in 25% dioxane-water, where Na<sub>3</sub> would be expected to be more extensively dissociated, is linear (Figure 1B).

(50) Reference 1a, p 457.

(51) J. W. Hackett and H. C. Thomas, *J. Am. Chem. Soc.*, **72**, 4962 (1950); R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968); R. G. Burns and B. D. England, *Tetrahedron Lett.*, No. 24, 1 (1960); *J. Chem. Soc. B*, 864 (1966); R. J. Anderson, P. Ang, B. D. England, V. H. McCann, and D. J. McLennan, *Aust. J. Chem.*, **22**, 1427 (1969); E. Tommila and M.-J. Savolainen, *Suom. Kemistil.*, **42**, 111 (1969); E. Tommila and I. P. Pitkainen, *Acta Chem. Scand.*, **20**, 937 (1966).

may be understood in one of two ways. Unreactive associated nucleophilic salts may be progressively dissociated as the solvent is rendered more polar. Secondly, loose transition states such as 4 or 5 may be better H-bond acceptors than the nucleophilic anion itself, as solvent activity coefficients for  $\text{Cl}^-$  and the delocalized azide ion suggest.<sup>34</sup>

The decomposition of benzoyl chloride in 50% acetone–water solvent containing the neutral nucleophile *o*-nitroaniline does not fit Scheme II kinetics, but does correlate with the predictions of Scheme I.<sup>11,52</sup> Borderline ion-pair kinetics are indicated, since no salt effect can arise. A predictable switch to second-order behavior ( $k_{-1} \gg k_s$ ) occurs when the solvent is the less polar 80% acetone–water mixture. Mechanisms of hydrolysis of, and nucleophilic attack on, acyl halides are by no means well understood,<sup>53</sup> although the acylium cation as an ion-pair partner is not inconceivable. Far less likely are ion pairs of the type  $\text{RCOCH}_2^+\text{X}^-$  from  $\alpha$ -halo ketones. Yet nucleophilic substitution for  $\text{R} = \textit{tert}$ -butyl occurs readily in comparison with suitable reference cases,<sup>54</sup> and this is clearly not due to nucleophilic attack on, or coordination to, carbonyl carbon (steric hindrance) or to formation of an allylic system by enolization (impossible).

### Swamping the Salt Effect

We have shown above that, by treating  $k_s'$  as a floating disposable parameter, uncertainties as to its behavior can be avoided. In an experimental attempt to control salt effects on concurrent solvolysis we have reinvestigated the decomposition of 2-octyl mesylate in 25% dioxane–water containing varying amounts of  $\text{NaN}_3$  (0–0.3 M) and sufficient  $\text{NaClO}_4$  to maintain the ionic strength at 2.0 M.<sup>46</sup> It was hoped that the  $\text{NaClO}_4$  salt effect would dominate, thus keeping  $k_s'$  constant as  $[\text{NaN}_3]$  was varied over a relatively small range. Indeed, the solvolysis rate was constant between  $[\text{NaClO}_4] = 1.7 \text{ M}$  and  $2.0 \text{ M}$  in the absence of  $\text{NaN}_3$ , suggesting kinetic salt saturation. Treatment according to eq 6 yielded good second-order rate constants for formation of 2-octyl azide, as is shown in Table I. The same reaction in the same solvent with 0–0.3 M  $[\text{NaN}_3]$  but with the ionic strength unbuffered exhibits apparent borderline kinetics when the rate and product data are empirically “corrected” via eq 3.<sup>10</sup> Our work suggests that the kinetics are not truly borderline, and that the salt effect correction is misleading.

Sneen has challenged this view<sup>55</sup> and has reckoned that 2.0 M  $\text{NaClO}_4$  will “dry out” a 25% dioxane–water mixture to such an extent that it behaves like a 60% dioxane–water mixture, where nonborderline kinetics are observed.<sup>56</sup> Note too that the addition of  $\text{NaClO}_4$  increases  $k_{2\text{N}}$  (Table I), a medium effect expected when solvent polarity is decreased.<sup>50</sup> However,  $\text{NaClO}_4$  may also “dedioxanate” the solvent.<sup>57</sup> While we can quibble a little at Sneen’s method of arriving at his conclusion

(52) V. Gold, J. Hilton, and E. G. Jefferson, *J. Chem. Soc.*, 2756 (1954).

(53) A. Kivinen in “The Chemistry of Acyl Halides”, S. Patai, Ed., Interscience, London, 1972, Chapter 6; D. N. Kevill, P. H. Daum, and R. Sapre, *J. Chem. Soc., Perkin Trans. 2*, 963 (1975).

(54) J. W. Thorpe and J. Warkentin, *Can. J. Chem.*, 51, 927 (1973).

(55) R. A. Sneen, private communication.

(56) R. A. Sneen and J. W. Larsen, unpublished results communicated by Dr. Sneen.

(57) E. Grunwald, G. Baugham, and G. Kohnstam, *J. Am. Chem. Soc.*, 82, 5801 (1960); J. F. Hinton, L. S. McDowell, and E. S. Amis, *Chem. Commun.*, 776 (1966).

**Table IV**  
Reaction of 2-Octyl Mesylate with Thiourea in 30%  
Dioxane–Water at 36.2 °C<sup>60</sup>

[Thiourea], M	$10^4 k_{\text{obsd}}^a$	$m$	$10^4 k_{\text{ip}}^{a,b}$	$10^4 k_{\text{SN2}}^{a,c}$	$10^4 k_{2\text{N}}^{d,e}$
0	1.74 <sup>f</sup>		1.74	1.74	
0.0808	4.35	17.8	3.02	4.24	31.8
0.163	7.40	18.8	3.82	7.07	34.2
0.194	8.2	19.0	4.02	8.15	33.3
0.236	9.0	18.2	4.19	9.21	30.9
0.270	10.2	18.6	4.38	10.5	32.4
0.318	12.1	18.7	4.55	12.1	32.6

<sup>a</sup> In  $\text{s}^{-1}$ . <sup>b</sup> Prediction based on Scheme I mechanism with  $k_{-1}/k_s = 2.59$  and  $b = 0$ . <sup>c</sup> Prediction based on product results alone in terms of Scheme II process, with  $b = 0$ . <sup>d</sup> In  $\text{l. mol}^{-1} \text{s}^{-1}$ . <sup>e</sup> From eq 7. <sup>f</sup> From ref 13.

(and we choose not to do so here), the fact remains that we may have been wading in waters of uncomfortably high salinity for an extrapolation from the buffered to the unbuffered system to be made with certainty.

### The Neutral Nucleophile Stratagem

Thiourea is a strong carbon nucleophile, it is weakly basic,<sup>58</sup> and most importantly, it is neutral although highly dipolar.<sup>59</sup> Results for the 2-octyl mesylate decomposition in 30% dioxane–water containing thiourea are shown in Table IV. Equation 6 correlates the data perfectly satisfactorily, and  $k_s'$  is apparently not subject to a nonelectrolyte effect (constant  $m$ ). Also shown are  $k_{\text{ip}}$  values calculated using  $k_{-1}/k_s = 2.59$  (Scheme I), a value which Sneen has used to correlate data from the ROMs– $\text{NaN}_3$  reaction with borderline kinetics predicted by Scheme I. There is clearly no correlation between the experimental  $k_{\text{obsd}}$  and the calculated  $k_{\text{ip}}$  values. Note that the latter are predicted to level off to a plateau in SN1 fashion as  $[\text{thiourea}]$  increases.<sup>14</sup> The implication is that, if Sneen’s mechanism and adjustable parameters are correct,  $k_{\text{obsd}}/k_{\text{NS}}$  can have no value greater than  $(1 + x)$ , equal to 3.59 for the present system. However, if the  $k_{\text{NS}} = k_s^0$  assumption for thiourea is correct, the absurd situation arises in which the products must form faster than ion pairs are supplied by the substrate for nucleophile concentrations greater than 0.15 M. Urea was used as a model, nonnucleophilic nonelectrolyte and, somewhat surprisingly, in view of the unusual properties of urea–water mixtures, the solvolysis rate coefficient remained almost constant in the 0–0.3 M range. We have assumed, therefore, that thiourea behaves similarly.<sup>60</sup>

These results constitute the most conclusive and unambiguous rebuttal of the Sneen borderline formulation available to date, and indeed point to the misuse of eq 4 as the origin of the claimed borderline behavior in this example at least.

### The Fate of a Model Ion Pair

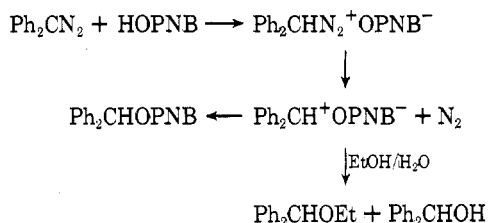
The decomposition of diphenyldiazomethane (DDM) in a hydroxylic solvent mixture containing *p*- $\text{NO}_2$ - $\text{C}_6\text{H}_4\text{CO}_2\text{H}$  (HOPNB) probably proceeds by the mechanism in Scheme III.<sup>61</sup> The species  $\text{Ph}_2\text{CH}^+\text{OPNB}^-$  may be an ion-pair spectrum, but only

(58) R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, 90, 319 (1968).

(59) G. K. Estok and S. P. Sood, *J. Phys. Chem.*, 66, 1372 (1962).

(60) D. J. McLennan, *Tetrahedron Lett.*, 4689 (1975).

## Scheme III



the intimate ion pair yields covalent ester, which is stable in solution around room temperature. Ion-pair formation is most likely unassisted by nucleophilic solvent components for the reason that, if unstable phenyl cations are formed from stable  $\text{PhN}_2^+$  without solvent assistance,<sup>62</sup> it is unlikely that the unstable  $\text{Ph}_2\text{CHN}_2^+$  ion would require solvent assistance in decomposing to relatively stable benzhydryl cations. It follows that, if the solvolysis of  $\text{Ph}_2\text{CHOPNB}$  in the same solvent mixtures at higher temperatures<sup>63</sup> involves nucleophilic attack on the  $\text{Ph}_2\text{CH}^+\text{OPNB}^-$  ion pair which is formed without assistance, the same  $\text{Ph}_2\text{CHOEt}:\text{Ph}_2\text{CHOH}$  product ratio should be obtained as in the DDM-HOPNB reaction. This expectation is not realized.<sup>64</sup> We therefore conclude that the ester solvolysis involves at least some solvent assistance to ion-pair formation and even an  $\text{S}_\text{N}2$  pathway, in that a stable product precursor is suggested.<sup>64</sup>

A Grunwald-Winstein  $m$  value of 0.62 for the solvolysis in ethanol-water mixtures is obtained.<sup>64b</sup> This is surprisingly low for benzhydryl solvolyses, and is further testimony to solvent participation. It follows that, if some type of nucleophilic solvent participation is necessary when a relatively stable ion pair is formed, it is very unlikely that more unstable ion pairs arising from primary and simple secondary substrates can be formed without assistance, as the Snee mechanism requires. Studies in this area are continuing, and experiments designed to test the suggestion of Harris<sup>65</sup> that solvent sorting may be responsible for the different product ratios in the two systems are planned. Harris has raised the possibility that the solvation shell of  $\text{Ph}_2\text{CH}^+\text{OPNB}^-$  arising from the DDM-HOPNB reaction may in fact be appropriate to the unstable diazonium ion-pair precursor and so may differ in composition<sup>66</sup> from the equilibrated solvation shell of the ion pair from the ester solvolysis. This cannot be lightly dismissed, but we note that the solvent-separated rather than the intimate ion pair is likely to be the intermediate in the stepwise pathway leading to solvolysis products in both systems,<sup>38e,f,66,67</sup> and it is possible that the solvent shells will have relaxed into equilibrated states by the time that this has formed.

The question of stepwise vs. concerted  $\beta$  eliminations

(61) R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Am. Chem. Soc.*, **86**, 5553 (1964); A. Diaz and S. Winstein, *ibid.*, **88**, 1316 (1966); E. R. Stedronsky, J. Gal, R. A. More O'Ferrall, and S. I. Miller, *ibid.*, **90**, 993 (1969); R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, **5**, 331 (1967).

(62) C. G. Swain, J. E. Sheats, D. J. Gorenstein, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 791 (1975); C. G. Swain, J. E. Sheats, and K. G. Harbison, *ibid.*, **97**, 783 (1975); R. G. Bergstrom, G. H. Wahl, and H. Zollinger, *Tetrahedron Lett.*, 2795 (1974).

(63) The  $\text{Ph}_2\text{CHOEt}:\text{Ph}_2\text{CHOH}$  product ratio in the DDM-HOPNB reaction is temperature independent.

(64) (a) D. J. McLennan and P. L. Martin, *Tetrahedron Lett.*, 4215 (1973); (b) unpublished results.

(65) J. M. Harris, private communication.

(66) J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Am. Chem. Soc.*, **96**, 4484 (1974).

(67) A. Pross, *Tetrahedron Lett.*, 637 (1975).

has been argued within these pages;<sup>68,69</sup> we merely note that a claim of borderline kinetics in the  $\text{PhCH}(\text{Me})\text{Br}-\text{OEt}^- - \text{EtOH}$  reaction<sup>70</sup> has been reinterpreted in terms of competing first- and second-order reactions.<sup>71</sup>

## General Remarks

Let us examine in a little detail one of the consequences of a second-order ion-pair process, eq 1 with  $k_{-1} \gg k_2[\text{N}^-]$ . Initial ionization to  $\text{R}^+\text{X}^-$  must by definition be unassisted except by interaction between the  $\text{R}^{\delta+} \dots \text{X}^{\delta-}$  transition-state dipole and the salt and solvent dipoles. The proposition that must be accepted is that, although the magnitude of the attractive forces between  $\text{N}^-$  and  $\text{R}^{\delta+}$  increases with passage along the reaction coordinate,  $\text{N}^-$  cannot be drawn by these forces sufficiently close to R to effect a significant degree of orbital overlap until the full ion-pair charge has developed. This must apply irrespective of the identity of R and of the magnitude of repulsive steric interactions between  $\text{N}^-$  and R, whether they be relatively strong (tertiary  $\text{C}_\alpha$ ) or weak (primary  $\text{C}_\alpha$ ). Thus, in the absence of steric hindrance or charge delocalization, a severe discontinuity in the magnitude of attractive intermolecular interactions is called for. In other words,  $\text{N}^-$  must act as a spectator to ionization.

This is unrealistic. It is better to suppose that the growth of charge on R and the increase in the magnitude of attractive interactions between  $\text{R}^{\delta+}$  and  $\text{N}^-$  are accompanied by a monotonic decrease in the N-R distance, to the point where significant covalent overlap occurs. Energy loss arising from primary N-R repulsive interactions may be offset to some extent by the relief of steric compressions between groups bonded to  $\text{C}_\alpha$  as hybridization shifts from  $\text{sp}^3$  toward  $\text{sp}^2$ .<sup>72</sup> From the point of view of the nucleophile, the approach of  $\text{N}^-$  to the polar substrate may assist the stretching of the  $\text{C}_\alpha-\text{X}$  bond and, by electron-repulsion effects, ensure that it is heterolytic stretching. There will not only be assistance to ion-pair formation, but assistance to the extent that in many cases an ion-pair intermediate may never form. The idea that a nucleophile attacks neutral "covalent carbon" in  $\text{S}_\text{N}2$  reactions is thus erroneous in these terms. Furthermore the difference between a nucleophilic and a nonnucleophilic anion can be clearly seen in that, while both can provide electrostatic assistance to heterolytic  $\text{C}_\alpha-\text{X}$  stretching, the former can covalently consummate the attraction while the latter cannot do so.

But if ion pairs are intermediates in the reactions in question, they must be strange ion pairs indeed. Even though their formation must be solvent assisted,<sup>73</sup> no concurrent or competitive assistance by added nucleophiles is permitted until the intermediate is fully formed. If the leaving group is sulfonate (or carboxyl-

(68) F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374 (1972).

(69) W. H. Saunders, *Acc. Chem. Res.*, **9**, 19 (1976).

(70) R. A. Snee and H. M. Robbins, *J. Am. Chem. Soc.*, **91**, 3100 (1969).

(71) D. J. McLennan, *J. Chem. Soc., Perkin Trans. 2*, 1577 (1972). Solvolysis rate constants from here and ref 12a show that the ethanolysis of  $\text{PhCH}(\text{Me})\text{Br}$  also exhibits irregular salt effects.

(72) Reference 1a, pp 544-559; P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *J. Chem. Soc.*, 3200 (1955).

(73) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970); J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971).

ate), the necessary internal return results in insignificant oxygen scrambling.<sup>74</sup> If ion pairs formed under solvolytic conditions undergo rearrangement, attack by an added nucleophile, although rate limiting, must *always* suppress rearrangement<sup>20,38k,39</sup> since no example of skeletal rearrangement accompanying second-order substitution has ever been reported, even for the potentially favorable neopentyl case.<sup>75</sup>

These ion pairs must be "more intimate than intimate",<sup>76</sup> and must thus behave like polarized RX molecules. This is what we believe they are, but we see no reason to call them ion pairs, for in such terms a methyl iodide molecule could be regarded as an ion pair by virtue of the C-I bond polarity.<sup>43</sup> This would be fine in the present context since mechanistic distinction would be lost, but chemical problems cannot be solved by such semantic extensions, although we agree with the view that genuine ion pairs may possess a degree of covalent character. In fact, the postulation of ion-pair intermediates (and their formation with solvent assistance) in simple primary and secondary substrate solvolysis in reasonably nucleophilic solvents may be incorrect, and SN2 solvent attack may be the favored mode. We know of no evidence that demands *intermediates* in such simple solvolyses, and specifically intermediates formed without solvent or neighboring group assistance. If so,

(74) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1904 (1968). If such scrambling were detected it would still be difficult to prove that it did not occur in a mechanistic blind alley (see also ref 5).

(75) Reference 1, p 742. See also G. M. Fraser and H. M. R. Hoffmann, *Chem. Commun.*, 561 (1967).

(76) Reference 7, p 366.

there is no reason why they should intervene in non-solvolytic substitutions with stronger nucleophiles.

In summary, the "extra-intimate ion pair" is in our opinion a polarized RX molecule. The polarization arises from approach of N<sup>-</sup>, and the energy buildup needed to cross the SN2 potential barrier arises largely from solvent reorganization<sup>77</sup> attendant on the merging of the original N<sup>-</sup> and RX solvation shells. We deliberately choose these words to mimic Bordwell's description of an ion-sandwich intermediate,<sup>26</sup> noting that Bordwell himself has not been definite in postulating actual intermediacy. His results could equally well be rationalized in terms of a loose SN2 transition state (4) for his tertiary substrate and a tighter transition state (3) for the model primary system.

In conclusion, the verdict which must be passed on Snee's proposed universal unification of SN1 and SN2 mechanisms is one which is unique to the Scottish legal system, and so I turn to the words of my forbears in stating "not proven". A more positive conclusion is not presently available, but we note that strides in this direction are being made through heavy atom isotope effect studies.<sup>45</sup>

*I warmly thank Professors P. B. D. de la Mare, J. M. Harris, P. v. R. Schleyer, J. Seyden-Penne, R. A. Snee, and J. Warkentin for exchanges of information and (often provocative but invariably helpful) views. I appreciate the continuing attention of Peter Martin to experimental problems.*

(77) E. D. German and R. R. Dogonadze, *Int. J. Chem. Kinetics*, **6**, 467 (1974).

## Ipsso Attack in Aromatic Nitration

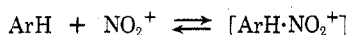
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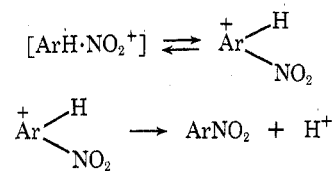
The mechanism of aromatic nitration was admirably discussed<sup>1</sup> by J. H. Ridd in 1971, and it might be doubted that in 4 years the subject could develop enough to justify another Account. There is, however, a protean quality about this reaction, and we hope to show that there is indeed more to be said.

Ridd showed<sup>1</sup> that the major mechanism of nitration in solutions of nitric acid in sulfuric or perchloric acid and in inert organic solvents is as follows.



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The nitronium ion and the aromatic diffuse together to give an "encounter pair", represented by [ArH·NO<sub>2</sub><sup>+</sup>] but of undefined structure. The encounter pair produces Wheland intermediates (W's) which, by loss of proton, generate nitro compounds. Depending on the conditions and the aromatic any of the steps (or the one which produces the nitronium ion) may be rate determining. Recently studies of positional selectivity in the nitration of 1,2,4-trimethylbenzene, taking into account the possible fates of W's (see below), support the view

(1) J. H. Ridd, *Acc. Chem. Res.*, **4**, 248 (1971).