and cyclohexene indicate that coupling and disproportionation of geminate cyclohexyl and *t*-butoxy radicals have essentially the same activation free energies at 80°.

Acknowledgments. Support by the National Science Foundation and helpful discussions with Professors G. S. Hammond, C. Walling, and W. Pryor are gratefully acknowledged. The authors especially thank Professor W. Le Noble for his most generous counsel during the early stages of purchase and assembly of the high-pressure apparatus.

Substitution at a Saturated Carbon Atom. XII. The Generality of the Ion-Pair Mechanism of Nucleophilic Substitution[1]

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. *Received May 5, 1969*

Abstract: The competitive reactions of solvent water and sodium azide with *p*-methoxybenzyl chloride in 70 vol % aqueous acetone at 20° [3] and of water and *o*-nitroaniline with benzoyl chloride in 50 wt % aqueous acetone at 0° [4] are shown to proceed *via* the ion-pair mechanism of nucleophilic substitution.[5] This article concludes with some general thoughts about the possible consequences and implications of the ion-pair mechanism.

"The Unification of Mechanisms SN1 and SN2" was the perhaps somewhat pompous-sounding title of a recent publication from these laboratories.[5] To be sure although the theory was therein developed which established that a single mechanism, involving as its most distinguishing feature the intermediacy of a configurationally stable ion pair, could accommodate traditional SN1 and SN2 as well as borderline behavior, the operation of this mechanism was demonstrated unequivocally for only two related sets of conditions.

In brief the competitive reactions of solvent water and added azide ion with 2-octyl mesylate in 25 and 30% aqueous dioxane were shown to possess in common an ion-pair intermediate.

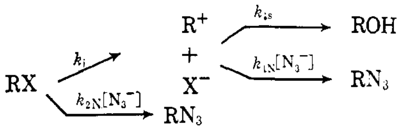
It is of course a rather bold extrapolation, from these limited data, to suggest that all reactions of nucleophilic substitution at a saturated carbon atom proceed *via* an ion-pair mechanism. And yet this is exactly what we would like to suggest. Perhaps data will become available that will require us to modify this view. But we know of none extant to contradict it.

As a further step in establishing the generality of the ion-pair mechanism we herein report reinterpretations of two sets of data taken from the published literature.[3,4]

These additional examples of the ion-pair mechanism not only expand its generality but also serve the rather important ancillary function of providing two new and completely independent methods for the assessment of normal salt effects. This manuscript is concluded with some general thoughts about the possible consequences and implications of the ion-pair mechanism of nucleophilic substitution.

***p*-Methoxybenzyl Chloride.** The competitive reactions of solvent water and azide ion with *p*-methoxybenzyl chloride in 70% aqueous acetone at 20° have been reported by Kohnstam, Queen, and Shillaker.[3] These authors write "sodium azide reduces the rate of hydrolysis (k_h) and increases the rate of ionization (k_i). This . . . demonstrates the unimolecular formation of RN_3. The rate of ionization is, however, always less than the over-all rate of decomposition (k), and it must therefore be concluded that RN_3 is also produced by the alternative, bimolecular mechanism."

Their data are reproduced in Table I. Their presumed reaction scheme can be written



That is, they envisage the operation of distinct competitive uni- and bimolecular reactions.

Table I. Initial First-Order Rate Coefficients (in Sec^{-1}) for the Reaction of 4-Methoxybenzyl Chloride with 70% Aqueous Acetone and Sodium Azide at 20°

$[NaN_3]$		0.0198	0.0312	0.0399
10^4k_h	2.706	2.493	2.427	2.320
10^4k_i[a]	2.706	2.879	2.982	3.063
10^4k	2.706	3.555	4.070	4.336
k_{a1}/k_a		0.363	0.338	0.369

[a] By analogy with experiments on diphenylmethyl chloride.

The data, of course, qualitatively fit this picture; quantitatively they do not, even when the scheme is expanded to allow for a second and bimolecular (k_{2s}) pathway for the formation of solvolysis products.[6] In par-

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(1) Supported in part by the National Science Foundation.

(2) National Institutes of Health predoctoral fellow, 1965–1967.

(3) G. Kohnstam, A. Queen, and B. Shillaker, *Proc. Chem. Soc.*, 157 (1959).

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

(5) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 362 (1969).

(6) They argue against this mode of solvolysis as follows: "hy-

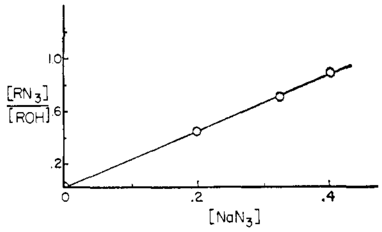


Figure 1. Plot of $[RN_3]/[ROH]$ *vs.* $[NaN_3]$ for *p*-methoxybenzyl chloride in 70% aqueous acetone at 20°.

ticular this scheme of competitive S_N1 and S_N2 reactions predicts that the observed rate constant (k) should be a linear function of azide ion concentration

$$k = k_i + k_{2s} + k_{2N}[N_3^-]$$

It is not, as is evident from Figure 2.

Table II. Comparison of Observed and Predicted Product Distributions and Rate Constants for the Reactions of *p*-Methoxybenzyl Chloride with Water and Sodium Azide in 70% Aqueous Acetone at 20°

$[NaN_3]$, M	% RN_3, exptl	% RN_3,[a] calcd	$k_{\text{exptl}} \times 10^4$, sec^{-1}	k_{ip}[b] $\times 10^4$, sec^{-1}	k_{S_N2}[c] $\times 10^4$, sec^{-1}
			2.71		
0.0198	29.9	29.8	3.56	3.59	4.11
0.0312	40.3	40.2	4.07	4.07	4.99
0.0399	46.3	46.3	4.34	4.39	5.70

[a] Calculated from eq 1 with $m = 21.6$. [b] Calculated from eq 2 with $m = 21.6$ and $x = 1.98$. [c] Calculated from eq 2 with $m = 21.6$ and $x = \infty$.

Furthermore, even assuming a second mode of bimolecular attack, k_{2s}, leading to solvolysis product, the proposed mechanism would be consistent with the observed formation (see Table II and Figure 1) of products in accordance with the linear relationship

$$\frac{[RN_3]}{[ROH]} = m[N_3^-]$$

(m a constant) only in the unlikely event that

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

This condition has been derived previously.[7]

Finally the British authors call attention to their observation that "the fraction of RN_3 formed unimolecularly $k_{a1}/k_a = (k_i - k_h)/(k - k_h)$ is constant." Perhaps it will be intuitively apparent to the reader that such constancy is *not* to be expected if their proposed mechanism be operative. More rigorously it has been established that their mechanism in fact predicts this quantity to be a variable.[8]

The data are beautifully correlated by the unifying ion-pair mechanism of nucleophilic substitution at a saturated carbon atom, the development of which has been previously published.[5] The dominant feature of this mechanism assumes that a common reversibly formed ion-pair intermediate serves as the precursor of both substitution products,[9] alcohol (ROH) and alkyl azide (RN_3).

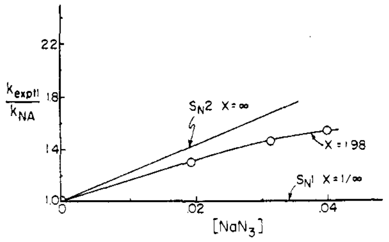
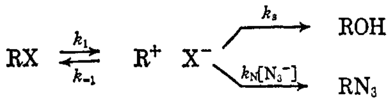


Figure 2. Plot of k_{exptl}/k_{NA} *vs.* $[NaN_3]$ for *p*-methoxybenzyl chloride in 70% aqueous acetone at 20°. The solid curve is that predicted from eq 2 with $m = k_N/k_s = 21.6$ and $x = k_{-1}/k_s = 1.98$. The experimental points are encircled.



Products, according to this scheme, should be formed in accordance with the relationship

$$\frac{[RN_3]}{[ROH]} = \frac{k_N}{k_s}[N_3^-] \qquad (1)$$

and the observed pseudo-first-order rate of reaction (k_{exptl}) should be given by

$$\frac{k_{\text{exptl}}}{k_{NA}} = \frac{(x + 1)(1 + m[N_3^-])}{(x + 1 + m[N_3^-])} \qquad (2)$$

where $x = k_{-1}/k_s$, $m = k_N/k_s$ and is available from product data and eq 1, and k_{NA} is the expected solvolytic rate constant in the absence of azide ion, corrected for normal salt effects.[10] The ability of eq 1, with $m = k_N/k_s = 21.6$, to correlate the product data will be apparent from Table II and Figure 1, while the correspondence of kinetic data to eq 2 will be apparent from Table II and Figure 2 ($m = k_N/k_s = 21.6$ and $x = k_{-1}/k_s = 1.98$).

Particularly noteworthy in the present work are (1) the precision of the data, as evidenced by the close correspondence between the calculated and experimental quantities of Table II; (2) the use of a model substrate, diphenylmethyl chloride, to evaluate salt effects[11] as an alternative to the use of model salts, the method used in our earlier work;[5] (3) the identification of a second sub-

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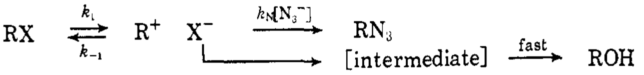
drolysis also occurs, but this side reaction proceeds exclusively by mechanism S_N1.... This conclusion is based on the great similarity of the solvolytic behavior with that of diphenylmethyl chloride, a compound which is known to react unimolecularly in aqueous solvents."

(7) See Appendix, ref 5.

(8) J. W. Larsen, Appendix E, Ph.D. Thesis, Purdue University, 1967.

(9) An alternate scheme, in which a second and irreversibly formed intermediate, perhaps a solvent-separated ion pair, serves as the precursor of solvolysis product, is equally consistent with the experimental data. Stereochemical data might shed light on this interesting possibility.



(10) The quantities k and k_i, as defined by Kohnstam, Queen, and Shillaker,[3] are to be identified with the k_{exptl} and k_{NA}, respectively, of the present treatment. Their $k_h = f_s k$ (where f_s = fraction of solvolysis = $[ROH]/([ROH] + [RN_3])$ can be restated in terms of product distributions; see Table II.

(11) These authors[3] give no experimental details but state that the hydrolysis reactions of both compounds, *p*-methoxybenzyl chloride and diphenylmethyl chloride, "occur at about the same rate and are affected in an almost identical manner by (a) changes in the solvent composition or (b) addition of 'common-ion' salts and 'non-common-ion' salts containing weakly nucleophilic anions.... These results show that the effect of azide ions on the rate of ionization of RCl can be assumed to be the same as their effect on the overall rate of decomposition of diphenylmethyl chloride, since the latter compound is sterically unfavorable to bimolecular attack by nucleophilic reagents."

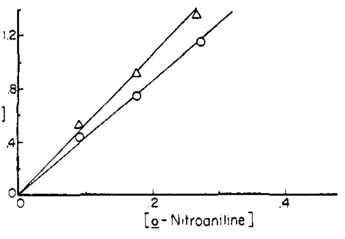
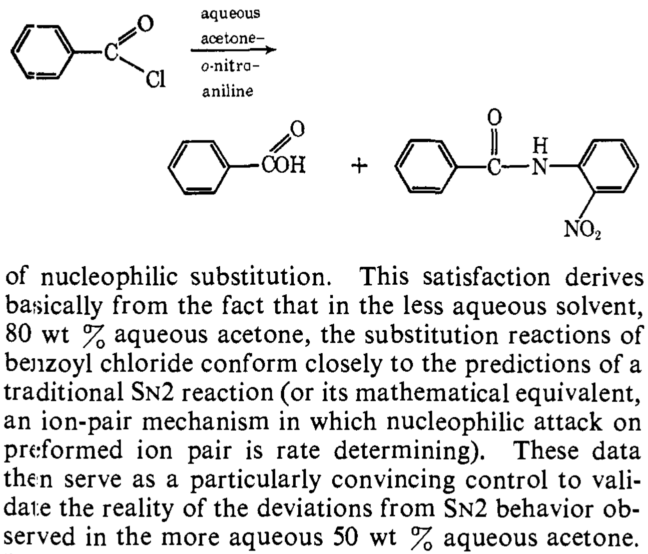


Figure 3. Plot of [anilide]/[acid] *vs.* [*o*-nitroaniline] for benzoyl chloride in 80 (△) and 50 (○) wt % acetone at 0°.

strate, *p*-methoxybenzyl chloride, in addition to the previously reported[5] 2-octyl mesylate, which undergoes competitive reactions with azide ion and solvent to give products in accordance with eq 1, thus rendering virtually inconceivable the fortuity that distinct competitive uni- and bimolecular processes, subject to the necessary condition, $k_{1N}/k_{1s} = k_{2N}/k_{2s}$, can accommodate the data[7]; and (4) the fact that the quantity $k_{a1}/k_a = (k_i - k_h)/(k - k_h)$, "the fraction of RN_3 formed unimolecularly" according to Kohnstam's mechanism,[3] is a constant which, in fact, serves to confirm the ion-pair mechanism since it can be shown[8] that this quantity is equatable with the quantity $k_s/(k_{-1} + k_s)$ of that mechanism, a true constant.

Benzoyl Chloride. The published data of Gold, Hilton, and Jefferson,[4] describing the competitive reactions of solvent water and *o*-nitroaniline with 80 and 50 wt % aqueous acetone at 0°, provide a particularly satisfying additional example of the ion-pair mechanism



of nucleophilic substitution. This satisfaction derives basically from the fact that in the less aqueous solvent, 80 wt % aqueous acetone, the substitution reactions of benzoyl chloride conform closely to the predictions of a traditional SN2 reaction (or its mathematical equivalent, an ion-pair mechanism in which nucleophilic attack on preformed ion pair is rate determining). These data then serve as a particularly convincing control to validate the reality of the deviations from SN2 behavior observed in the more aqueous 50 wt % aqueous acetone. In particular "salt effect" corrections, in the first approximation, for the neutral "salt," *o*-nitroaniline, are shown to be unnecessary.

That the "borderline" behavior observed in the more aqueous system cannot be attributed to distinct and competitive uni- and bimolecular reactions, the proposal advanced by Gold, Hilton, and Jefferson[4] is confirmed (1) by the nonlinearity of a k_{exptl} *vs.* [*o*-nitroaniline] plot (Figure 5) and (2) more convincingly, by the linearity of a plot of [anilide]/[benzoic acid] *vs.* [*o*-nitroaniline][12] (Figure 3). This latter condition could be achieved, assuming a mechanism of competitive SN1 and SN2 reactions, only in the unlikely event that the ratio of rates of bi- and unimolecular aniline attack, k_{2N}/k_{1N}, is equal to the corresponding ratio of rates of solvent attack, k_{2s}/k_{1s}.[7]

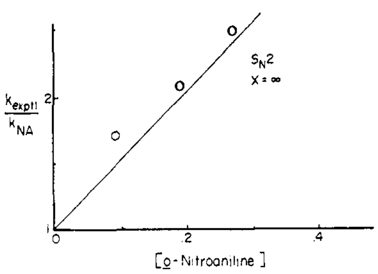


Figure 4. Plot of $k_{\mathrm{exptl}}/k_{\mathrm{NA}}$ *vs.* [*o*-nitroaniline] in 80 wt % aqueous acetone at 0°. The solid line is that predicted from eq 2 with $m = 5.33$ and $x = \infty$. The experimental points are encircled.

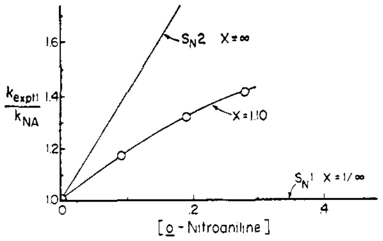


Figure 5. Plot of $k_{\mathrm{exptl}}/k_{\mathrm{NA}}$ *vs.* [*o*-nitroaniline] in 50 wt % aqueous acetone at 0°. The solid curve is that predicted by eq 2 with $m = 4.42$ and $x = 1.10$. The experimental points are encircled.

The data are given in Table III (80 wt % acetone) and Table IV (50 wt % acetone). Product data, plotted according to eq 1,[12] are given graphically in Figure 3 for both solvent systems. The slopes of these plots ($k_N/k_s = m$) are 5.33 (80% acetone) and 4.42 (50% acetone). Kinetic data for the reactions in 80% acetone are plotted *vs.* [*o*-nitroaniline] in Figure 4 ($m = k_N/k_s = 5.33$; $x = k_{-1}/k_s = \infty$) and for 50% acetone in Figure 5 ($m = k_N/k_s = 4.42$; $x = k_{-1}/k_s = 1.10$).

Table III. Comparison of Observed and Predicted Product Distributions and Rate Constants for the Reactions of Benzoyl Chloride with Water and *o*-Nitroaniline in 80 Wt % Aqueous Acetone at 0°

[*o*-Nitroaniline], *M*	% anilide, exptl	% anilide, calcd[a]	$k_{\mathrm{exptl}} \times 10^5$, sec^{-1}	k_{ip}[b] $\times 10^5$, sec^{-1}
			3.9	3.9
0.091	34.7	32.6	6.5	5.9
0.187	49.0	49.9	8.0	7.7
0.285	58.0	59.0	10.0	9.3

[a] Calculated from eq 1 with $m = 5.33$. [b] Calculated from eq 2 with $m = 5.33$ and $x = \infty$.

The correspondence of the experimental data with those predicted by the ion-pair mechanism will be seen to be excellent.

The significance of the fact that both product and kinetic data in 80 wt % aqueous acetone conform to traditional SN2 behavior (ion-pair behavior with $x = k_{-1}/k_s = \infty$) should not be minimized. Not only does it serve the function of establishing that "salt" effect corrections are unnecessary but it is consistent with the notion that there is a single mechanism of nucleophilic substitution,

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[12] Equations 1 and 2 are applicable with the obvious substitutions of *o*-nitroaniline for N_3^-, benzoic acid for ROH, and benzoyl chloride for RX.

Table IV. Comparison of Observed and Predicted Product Distributions and Rate Constants for the Reactions of Benzoyl Chloride with Water and *o*-Nitroaniline in 50 Wt % Aqueous Acetone at 0°

[*o*-Nitroaniline], *M*	% anilide, exptl	% anilide,[a] calcd	$k_{\text{exptl}} \times 10^5$, sec^{-1}	k_{ip}[b] $\times 10^5$, sec^{-1}	k_{SN2}[c] $\times 10^5$, sec^{-1}
			27.7	27.7	27.7
0.092	31.2	28.9	32.1	32.7	40.2
0.188	45.0	45.4	36.3	36.3	49.9
0.286	53.8	55.8	39.6	39.2	59.9

[a] Calculated from eq 1 with $m = 4.42$. [b] Calculated from eq 2 with $m = 4.42$ and $x = 1.10$. [c] Calculated from eq 2 with $m = 4.42$ and $x = \infty$.

the ion-pair mechanism, which, however, can show a continuous change in the apparent kinetic order of reaction from second (80% acetone) to "borderline" (50% acetone) to, presumably, first (<50% acetone).[13] This results, of course, not from any basic change in the reaction mechanism but from a gradual inversion of the relative heights of the energy barriers to destruction and formation of the ion-pair intermediate.

Discussion

It is becoming increasingly apparent that the ion-pair mechanism of nucleophilic substitution at a saturated carbon atom is of some generality. Details of the reactions of three rather diverse types of substrates have now been published: in an earlier publication[5] substitution reactions of the secondary system, 2-octyl mesylate, in 25 and 30% aqueous dioxane were shown to share a common ion-pair intermediate; and in the present manuscript such an intermediate has been implicated in the reactions of both a primary benzylic system, *p*-methoxybenzyl chloride in 70% aqueous acetone,[3] as well as in the reactions of an acylium system, benzoyl chloride in 50 wt % acetone.[4]

In addition, as yet unpublished work from these laboratories has implicated a common ion-pair intermediate in the substitution reactions of the secondary benzylic systems, α-phenylethyl bromide[14] and α-*p*-tolylethyl chloride[14] in solvent enthanol, and of the allylic system, α,γ-dimethylallyl chloride[15] in ethanol.

This spectrum of substrates, all of which have been shown to undergo substitution reactions exclusively at an ion-pair stage, encompasses structural types traditionally considered limiting or typical SN1 substrates (α-phenylethyl bromide, α-*p*-tolylethyl chloride, α,γ-dimethylallyl chloride, and, perhaps, *p*-methoxybenzyl chloride) as well as the typical borderline compound, 2-octyl mesylate.

As yet missing from the list, obviously, are typical SN2 substrates, such as primary and methyl systems. We shall temporarily defer a discussion of this subject.

It should be emphasized that *with those substrates* and *under those conditions* where ion-pair intermediates have been implicated as precursors of products, it is equally firmly established that *neither solvent nor added external nucleophile attacks covalent substrate*. Under all conditions, then, that permit the identification of an intermediate,[16] and with all substrates investigated, nucleophilic attack on covalent substrate was not observed.

Perhaps this is fortuitous? Hardly. It would seem much more probable that direct attack by nucleophile on covalent carbon seldom, if ever, occurs. Not only does this suggestion have the virtue of simplicity, allowing all substitutions at a saturated carbon atom to be mechanistically of one kind, but it does away with the need to postulate a pentacovalent carbon atom in the traditional picture of the transition state of an SN2 substitution.[17]

This suggestion is too important not to merit amplification: under no set of conditions which allow experimental differentiation between a traditional SN2 mechanism and the ion-pair mechanism has attack by nucleophile, whether solvent or added anion, on covalent substrate been observed; attack by nucleophiles on preformed ion pair is proving to be quite general but in no instance has attack on covalent substrate proved to be competitive.

We would suggest that the burden of proof has shifted. Ion pairs have been established as substrates for nucleophilic attack; covalent, saturated carbon has not.

It is perhaps appropriate here to attempt to bring into perspective some of the features of solvolysis reactions which, before the importance of ion pairs as reactive intermediates were appreciated, required a variety of not always internally consistent explanations.

In the first place very few secondary systems have been established to give rise to products *via* dissociated carbonium ions.[19] It is true of course that the only available kinetic technique for the detection of dissociation, common-ion depression, fails if the dissociation is irreversible. Nonetheless evidence, particularly stereochemical,[21] is accumulating that solvolysis products arise by solvent attack on a preformed ion pair. It would seem that an intimate ion pair reacts with inversion; the stereochemical course of solvolysis product formation from solvent-separated ion pair is not clear but retention, perhaps competitive with inversion, would seem a reasonable hypothesis.

At all events the prevailing textbook notion that, in general, reactions of secondary systems are those of carbonium ions must be disavowed. To disregard the role of the counteranion, even in many so-called nonclassical carbonium ion systems, can be and frequently has been dangerously misleading.[22]

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(13) Note that the change in other measured rate quantities is also gradual: $m = k_{\text{N}}/k_{\text{s}} = 5.33$ (80%) → $m = 4.42$ (50%); $k_{\text{NA}} = 3.9 \times 10^{-5}$ sec^{-1} (80%) → $k_{\text{NA}} = 27.7 \times 10^{-5}$ sec^{-1} (50%).

(14) H. M. Robbins, Ph.D. Thesis, Purdue University, 1969.

(15) W. A. Bradley.

(16) It will be seen that as $x = k_{-1}/k_{\text{s}}$ becomes large, eq 2 reduces to $k_{\text{exptl}}/k_{\text{NA}} = 1 + m\,[\text{N}_3^-]$, typical SN2 behavior; as x becomes small, eq 2 reduces to $k_{\text{exptl}}/k_{\text{NA}} = 1$, typical SN1 behavior. Only when x is of intermediate values ($10 \geq x \geq 1/2$) is the ion-pair picture experimentally distinguishable, by the present technique, from the SN2 and SN1 extremes. See ref 5.

(17) This view also leads to a new view of the SN2′ reaction, one in which reaction is initiated, not by nucleophilic attack, but by ionization of a C–X bond. See ref 18.

(18) J. V. Carter, Ph.D. Thesis, Purdue University, 1967.

(19) The acetolysis of cholesteryl tosylate at 50° provides a notable exception.[20] However, even here only ~25% of the solvolysis product arises from dissociated carbonium ion. Note that this system is stabilized by homoallylic resonance and that the solvent, acetic acid, is quite nonnucleophilic.

(20) S. Winstein and E. Clippinger, *J. Am. Chem. Soc.*, 78, 2784 (1956).

(21) (a) H. Weiner and R. A. Sneen, *ibid.*, 87, 287, 292 (1965); (b) A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.*, 27, 290 (1962); A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, 87, 3682 (1965); A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, 87, 3686 (1965).

(22) Note in particular that solvent collapse from an intervening

As unstable intermediates, ion pairs of course can serve in many of the roles historically played by dissociated ions. In particular their relative instabilities should make them relatively unselective in their subsequent reactions, thus accounting for the diversity of products and reactions modes frequently observed under solvolytic conditions. Among the reactions which might reasonably be expected of an unstable ion pair (other than return to covalent starting material) are (1) attack by nucleophile (solvent and/or external nucleophile) to give substitution product,[5] (2) attack by base and/or solvent to give olefin,[23] (3) further charge separation to a solvent-separated ion pair,[20] (4) oxygen scrambling in, *e.g.*, sulfonates and *p*-nitrobenzoates,[24] (5) racemization,[25] and (6) rearrangement *via* neighboring group intervention.

The first five of these reactions have been documented; the sixth, rearrangements, and the related phenomenon of anchimeric assistance may well follow upon the initial formation of an unrearranged ion pair. The

$$\begin{tikzcd}
RX \arrow[r, shift left, "k_1"] & R^+X^- \arrow[l, shift left, "k_{-1}"] \arrow[r, "\text{rearrangement}"] & R'^+X^- \arrow[d] \\
 & & \text{products}
\end{tikzcd}$$

rate enhancements generally associated with anchimeric assistance, then, may result from an increased rate of rearrangement of the ion pair, competitive with k_{-1}, rather than from any enhancement of its rate of formation from covalent starting material.

Finally we return to the question of the role of ion pairs, if any, in the reactions of primary and methyl systems. One's *a priori* thinking about ion-pair stabilities, of course, is inevitably conditioned by his knowledge of the literature of dissociated carbonium ions. If in fact the parallel is complete it is difficult to credit the suggestion that ion pairs intervene in the substitution reactions of these precursors of notoriously unstable carbonium ions.

It then follows either (1) that primary and methyl compounds choose an alternate mechanism (traditional SN2?) of substitution, bypassing the unstable ion pair, or (2) that the ion pairs derived from primary and methyl substrates do not in fact parallel, at least quantitatively, in stability the corresponding dissociated carbonium ions; the energy differences are attenuated.

The latter alternative seems to us, at least aesthetically, the more satisfying, and one can make a quite reasonable argument in its defense. In particular because of the nature of the electrostatic stabilization in an ion pair the positive charge in the alkyl moiety should resist dispersal by any mechanism away from the negative counteranion. Thus the usual mechanisms of charge dispersal, generally considered to be of great importance in stabilizing dissociated carbonium ions, such as polarization and resonance, may be of considerably lesser importance with the corresponding ion pairs.

If this be the case it follows that ion pairs should be less sensitive to substituent effects than are the corresponding dissociated carbonium ions and makes credible the suggestion that even primary and methyl systems undergo substitution reactions *via* the ion-pair mechanism. Definitive experiments are under way.

solvent molecule of a solvent-separated ion pair might be expected to take place with retention, thus providing an alternative explanation to nonclassical bonding for the frequently observed examples of retention.

[23] R. A. Sneen and H. M. Robbins, *J. Am. Chem. Soc.*, **91**, 3100 (1969).

[24] H. L. Goering and R. W. Thies, *ibid.*, **90**, 2967, 2968 (1968).

[25] S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, 12 (1960).

Dichlorocarbene, Free or Complexed? Relative Reactivities of Free CCl_2

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Abstract: High-temperature pyrolysis of $CHCl_3$ or CCl_4 produces CCl_2. Dichlorocarbene molecules issuing from a 1500° furnace zone into a high vacuum chamber experience collisionless flight to the wall. Wescott demonstrated that this free CCl_2 reacts stereospecifically with *cis*- and *trans*-2-butene when it is cocondensed with the cold olefin. Since the graphite furnace provides a surface for spin equilibration, it was concluded that the ground state of CCl_2 is singlet. This same technique has been employed to determine the relative reactivities of olefins in reaction with this variety of CCl_2. Dichlorocarbene intermediates generated from MCX_3 in similar media[18] show the same relative reactivities, suggesting that free CCl_2 is the active reagent in dichlorocyclopropanation of olefins.

The direct observation of carbenes by optical and electron spin resonance spectroscopies leaves little doubt regarding the independent existence of these species.[1] However, in the usual chemical experiments it is not apparent that the free carbenes are intermediates. It is conceivable that excited states of diazo compounds and ketenes eliminate nitrogen or carbon monoxide as they react with substrates. Further, carbenes may form complexes with ligands which can transfer the carbene moiety directly to an olefin.

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[1] R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965); D. E. Milligan and M. E. Jacox, *ibid.*, **47**, 703 (1967); L. Andrews, *Tetrahedron Letters*, 1968; A. M. Trozzolo, *Accounts Chem. Res.*, **1**, 529 (1968), footnote 7.