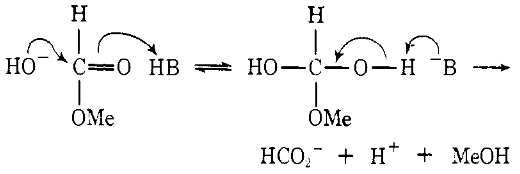
than the first by *ca.* 5 units,[26] the pK_a of V (T$^-$) may be estimated at 16.0. Finally, taking the ΔpK_a between T$^\pm$ and V as equal to that existing between H_3^+O and H_2O gives a pK_a of *ca.* −1 for T$^\pm$. Since this value is considerably less than the pK_2 of succinic acid, the k_2 step in eq 10 should be diffusion controlled. While data sufficient to generate a Brønsted plot for the general base catalyzed hydrolysis of MF do not exist, extrapolations from the literature make it appear unlikely that the coefficient would approach 0. The β value for general base catalyzed hydrolysis of ethyl dichloroacetate, an ester considerably more reactive than MF, in general base catalyzed hydrolysis, is 0.47.[12] The β decreases to $\approx$0.2 for ethyl trifluorothiolacetate which has a much better leaving group than MF, and is equal to 0 only for the hydrolysis reactions of relatively basic catalysts with methyl *S*-trifluoroacetylmercaptoacetate which has an even better leaving group.[23] The mechanism of eq 10 can therefore be ruled out.



$$HO^- \; \overset{H}{\underset{OMe}{C}}{=}O \;\; HB \rightleftharpoons HO{-}\overset{H}{\underset{OMe}{C}}{-}O{-}H \;\; {}^-B \longrightarrow HCO_2^- + H^+ + MeOH + B^- \quad (11)$$

The mechanism of eq 9 is kinetically indistinguishable from that of eq 11 involving specific base, general acid catalysis.[27] Such a mechanism would predict a methoxyl-^{18}O kinetic isotope effect that is less than that obtained for alkaline hydrolysis, since the attack by hydroxide ion on the ester stabilized by proton donation from BH should result in an earlier transition state than in unassisted attack. The observed isotope effect while small is significantly larger for general base catalyzed than for alkaline hydrolysis and thus argues against the mechanism of eq 11. Leaving group kinetic isotope effects thus provide a new means for resolving kinetic ambiguity in general acid–base catalysis reactions.[27]

The remaining mechanism for consideration is that shown in eq 9. The present results provide no information on whether or not the anionic tetrahedral intermediate depicted is stable enough to be at equilibrium with respect to transport processes.[28] They do require that k_1 be rate determining if the intermediate exists, and, in either case, an early transition state involving little C–OMe bond loosening for the rate-determining step.

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(26) Reference 19, p 324.

(27) Reference 22b, p 182.

(28) M. I. Page and W. P. Jencks, *J. Amer. Chem. Soc.*, **94**, 8828 (1972); W. P. Jencks and K. Salvesen, *ibid.*, **93**, 1419 (1971).

Kinetics of the Reaction of Cyclohexyl Bromide with Tetra-*n*-propylammonium Thiophenoxide in Methanol, Dimethylformamide, and Molten Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride

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Abstract: The reaction of cyclohexyl bromide with tetra-*n*-propylammonium thiophenoxide ($N_{3333}SPh$) follows approximately a second-order rate law in each of three solvents. Relative rates as a function of solvent at 25° and 0.1 *M* $N_{3333}SPh$ are: methanol, 1.00; triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$), 41.0; and dimethylformamide (DMF), 492. In DMF at 10–35° and in $N_{2226}B_{2226}$ at 25–45° the reaction products consist of 57 ± 1% cyclohexene and 43 ± 1% cyclohexyl phenyl sulfide. In methanol the per cent elimination ranges from 46% at 24° to 54% at 73°. The insensitivity of product distribution to solvent and temperature suggests that the substitution and elimination transition states are very similar. Mechanisms which may explain this similarity are discussed with emphasis on a possible tight ion pair intermediate.

Preparation of molten tetraalkylammonium tetraalkylborides[1] on a large scale in high purity makes available a totally new class of solvents.[2] These salts may be liquid at or near room temperature and are miscible with most common organic materials. Each ion consists of a charged core surrounded by aliphatic hydrocarbon groups. This character permits electrostatic, ion–dipole, ion-induced dipole, and dispersion interactions but prevents hydrogen bonding or any Lewis acid–base interactions between solvent ions and between solutes and molten salt solvent. We report here the first study of the influence of a molten tetraalkylammonium tetraalkylboride solvent on a chemical reaction.[3]

As a solvent we chose triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) because of its relatively low viscosity at room temperature and its ease of preparation. To test its influence on both the rate and the product distribution of a reaction, we have

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(1) By IUPAC nomenclature these anions are tetraalkylbor*ates*. We prefer tetraalkylbor*ide* because it avoids possible confusion with borate esters.

(2) W. T. Ford, R. J. Hauri, and D. J. Hart, *J. Org. Chem.*, in press.

(3) For references to previous uses of other kinds of molten salt solvents, see footnotes 1–7 of ref 2.

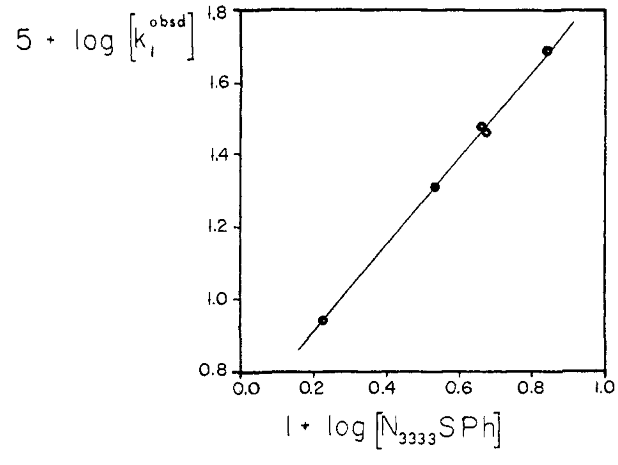
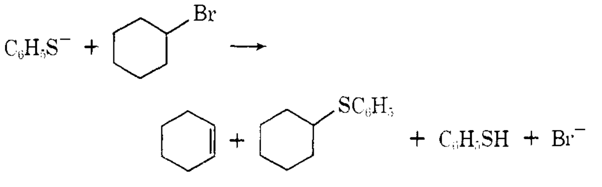


Figure 1. Dependence of pseudo-first-order rate constants on $N_{3333}SPh$ concentration at 59.8° in methanol.

investigated the reaction of thiophenoxide with cyclohexyl bromide (eq 1), which gives both substitution and



(1)

elimination and proceeds at convenient rates near room temperature. Methanol and dimethylformamide (DMF) were selected as typical polar protic and polar aprotic solvents for rate comparisons to the new molten salt solvent.

The mechanisms of elimination reactions catalyzed by weak bases are controversial.[4] The rates and product distributions of the reaction of thiophenoxide with cyclohexyl bromide in three totally different solvents also provide a new variety of experimental evidence to help solve this mechanistic problem.

Results

Rates of reaction of cyclohexyl bromide with thiophenoxide ion were followed by appearance of bromide ion under either second-order or pseudo-first-order conditions. Yields of cyclohexene and cyclohexyl phenyl sulfide determined by glpc accounted quantitatively for the reacted cyclohexyl bromide. Initial attempts to use sodium thiophenoxide failed because of its insolubility in another molten salt ($N_{3333}B_{4446}$), so we switched to the highly soluble tetra-*n*-propylammonium thiophenoxide ($N_{3333}SPh$), in which the cation resembles the molten salt.

Rates and product distributions in methanol were determined at 59.8° over a wide range of $N_{3333}SPh$ concentrations and from 24.9 to 73.2° with *ca.* 0.50 *M* $N_{3333}SPh$. Excess 2,6-lutidine was used to trap liberated acid. Representative results appear in Table I.[5] Control experiments proved that in the absence of $N_{3333}SPh$ under otherwise comparable conditions cyclohexyl bromide did not react, and that the products, cyclohexene and cyclohexyl phenyl sulfide, were stable under the reaction conditions. The fraction of elimination in methanol increased modestly with increases in temperature and slightly with increases in $N_{3333}SPh$ concentration.

Table I. Rate Constants and Product Distributions for Reaction of $N_{3333}SPh$ with Cyclohexyl Bromide in Methanol, DMF, and $N_{2226}B_{2226}$[a]

Initial $N_{3333}SPh$ concn, *M*	Temp, °C	$10^5 k_1^{obsd}$, sec^{-1} [b]	$10^4 k_2^{obsd}$, $M^{-1}\ sec^{-1}$ [b]	% cyclohexene[c]
		Methanol		
0.507	24.90	0.579	0.1142	46
0.497	40.88	3.99	0.803	50
0.0543	59.80		3.96	51
0.1663	59.87		5.26	52
0.467	59.87	29.2	6.58	53
0.693	59.87	51.4	7.70	
0.477	73.22	115.2	24.14	54
		Dimethylformamide		
0.1584	9.80		9.96	56
0.0643	20.07		22.6	
0.0954	20.12		25.1	56
0.1566	20.08		27.9	56
0.1543	34.85		116	57
		Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride		
0.1308	24.90		3.07	58
0.1303	35.06		8.80	58
0.0444	45.24		33.2	58
0.0877	45.24		25.3	59
0.1300	45.25		22.3	57
0.1227[d]	45.27		23.6	

[a] All runs contained 0.075–0.25 *M* 2,6-lutidine and were initially 0.039–0.049 *M* in cyclohexyl bromide. [b] For method of calculation see Experimental Section. [c] ±1%. [d] This run was performed with a completely independent preparation of $N_{2226}B_{2226}$.

A plot of observed pseudo-first-order rate constants at 59.8° against initial $N_{3333}SPh$ concentration over a 0.166–0.693 *M* range is shown in Figure 1. (Initial cyclohexyl bromide concentration was 0.047 *M* in these experiments.) Its slope corresponds to an effective kinetic order of 1.22 in $N_{3333}SPh$. This non-first-order dependence on $N_{3333}SPh$ is probably due to a positive salt effect, although k_1^{obsd} is not quite linearly related to $N_{3333}SPh$ concentration.[6] Most often increases in ion association of a nucleophilic reagent decrease its reactivity, and increases in concentration increase its degree of association. Since second-order rate constants of reactions of $N_{3333}SPh$ with cyclohexyl bromide increase as $N_{3333}SPh$ concentration increases, the degree of association of $N_{3333}SPh$ likely does not change appreciably between 0.05 and 0.7 *M*.

Rate constants and product distributions obtained in DMF appear in Table I. A narrower range of $N_{3333}SPh$ concentrations was used, but k_2^{obsd} increased as $N_{3333}SPh$ concentration increased, just as in methanol. Control experiments showed that cyclohexyl bromide did not react in the absence of $N_{3333}SPh$, and that the products were stable under the reaction conditions.

Rate constants and product distributions obtained in $N_{2226}B_{2226}$ are in Table I. The rate constants are slightly less accurate than those in methanol and in DMF because of difficulties encountered in removal of solvent from aliquots of reaction mixture. Nevertheless,

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(4) For a fresh review of this problem, see W. T. Ford, *Accounts Chem. Res.*, in press.

(5) More complete data will be made available in the Ph.D. Thesis of R. J. H.

(6) Linear dependence on salt concentration is often found in solvolyses[7] and even in bimolecular substitutions.[8]

(7) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. **19**, 109 (1965), and references therein.

(8) R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, **94**, 7868 (1972), and references therein.

k_2^{obsd} clearly decreased as $N_{3333}SPh$ concentration increased. This corresponds to an effective kinetic order in $N_{3333}SPh$ of <1.0, and suggests a rate-retarding salt effect. The question of ion association of $N_{3333}SPh$ in $N_{2226}B_{2226}$ is meaningless because every thiophenoxide ion must have one or more quaternary ammonium ions as nearest neighbors throughout the concentration range studied. The last two lines in Table I show rate constants for runs conducted in two independently prepared batches of $N_{2226}B_{2226}$. The sample of $N_{2226}B_{2226}$ used for the last line of data was over 7 months old. Since the rate constants differ by only 5.8%, we are convinced that unknown impurities in the $N_{2226}B_{2226}$ had little effect on the rate measurements, and that $N_{2226}B_{2226}$ did not decompose significantly during storage.

Activation parameters in all three solvents were calculated from data in Table I and are reported in Table II.

Table II. Activation Parameters for Reaction of Cyclohexyl Bromide with $N_{3333}SPh$ at 25°

Solvent	$N_{3333}SPh$ concn, M^a	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
Methanol	0.5	21.9	−8.3
DMF	0.15	16.2	−15.0
$N_{2226}B_{2226}$	0.13	17.7	−15.1

[a] For exact concentrations used in individual runs see Table I.

For comparison of rates of reaction of cyclohexyl bromide with $N_{3333}SPh$ in the three solvents, data from Tables I and II were used to calculate second-order rate constants at 0.100 *M* $N_{3333}SPh$ assuming that Arrhenius activation energies are independent of $N_{3333}SPh$ concentration and that the rate constant dependence on $N_{3333}SPh$ concentration in each solvent is not dependent on temperature. The results relative to rates in methanol at 25.0 and at 45.0° are in Table III. Relative rates in DMF and methanol are nearly independent of $N_{3333}SPh$ concentration, but rates in $N_{2226}B_{2226}$ relative to methanol or DMF are higher at <0.1 *M* $N_{3333}SPh$ and lower at >0.1 *M* $N_{3333}SPh$ because of the lower effective kinetic order in $N_{2226}B_{2226}$. Since the product distributions are so nearly independent of solvent, the relative overall rate constants in Table III approximate the relative substitution and the relative elimination rate constants.

Table III. Relative Rates of Reaction of Cyclohexyl Bromide with 0.100 *M* $N_{3333}SPh$ in Methanol, $N_{2226}B_{2226}$, and DMF

Solvent	k_{rel} (25°)	k_{rel} (45°)
Methanol	1.00^a	1.00^b
$N_{2226}B_{2226}$	41.0	26.2
DMF	492	271

[a] $k_2 = 8.41 \times 10^{-6}\ M^{-1}\ sec^{-1}$. [b] $k_2 = 9.16 \times 10^{-5}\ M^{-1}\ sec^{-1}$.

Discussion

Measurement of reaction rates in $N_{2226}B_{2226}$ demonstrates that molten salts may be viable solvents for some organic reactions. However, $N_{2226}B_{2226}$ offers no advantage over other solvents either in rate or in product distribution for reaction of cyclohexyl bromide with $N_{3333}SPh$, which is less sensitive to solvent effects than most ionic reactions.

The reaction of cyclohexyl bromide with thiophenoxide ion was investigated earlier in ethanol and in DMF. At 55° our k_2 for reaction with 0.5 *M* $N_{3333}SPh$ in methanol is about 0.5 times as large as k_2 for reaction with NaSPh in ethanol.[9] This rate difference might be attributed to different degrees of ion pairing in the two alcohols, or to another solvent effect. McLennan[9] found 55% elimination in ethanol, in reasonable agreement with our results. A similar rate comparison between our data and that of Ko and Parker[10] for reaction of NaSPh with cyclohexyl bromide in ethanol at 76.4° shows our reaction to be 0.45 times as fast as theirs.[11] They[10] found 60% elimination. At 25° with cyclohexyl bromide in DMF our rate with $N_{3333}SPh$ is 0.38 times as fast as that of Ko and Parker[10] with NaSPh in DMF. They[10] found 60% elimination in DMF. If the rate difference between $N_{3333}SPh$ and NaSPh obtained from results in different laboratories is real, it could be due to different degrees of dissociation of $N_{3333}SPh$ and NaSPh or to different reactivities of their respective ion pairs (or other aggregates). Increases in our observed k_2 values in DMF and in methanol with increases in $N_{3333}SPh$ concentration from 0.05 to 0.7 *M* suggest either that $N_{3333}SPh$ is completely dissociated over this range of concentration and the activity of thiophenoxide ion increases with increasing concentration, or that $N_{3333}SPh$ ion pairs are more reactive than free thiophenoxide ions. Since neither we nor Ko and Parker[10] have actually measured ion pair dissociation constants for $N_{3333}SPh$ or NaSPh, and they did not investigate rate dependence on initial NaSPh concentration, we cannot determine whether free ions, ion pairs, or both are the reactive species in reactions of $N_{3333}SPh$ and NaSPh with cyclohexyl bromide in DMF, methanol, and ethanol.

The factors contributing to the faster rate of reaction of NaSPh and cyclohexyl bromide in DMF than in methanol have been analyzed by Ko and Parker[10] in terms of solvent activity coefficients.[12] From rates of reaction in two solvents and solvent activity coefficients of reactants, the solvent activity coefficient of the transition state of the reaction can be calculated by eq 2.[12] The solvent activity coefficient for cyclohexyl bromide has been measured ($\log {}^{CH_3OH}\gamma^{DMF}{}_{C_6H_{11}Br} = 0.1$),[13] but the solvent activity coefficient for our reactive base, SPh^- or $N_{3333}SPh$, is unknown. From

$$\log (k^{DMF}/k^{CH_3OH}) = \log {}^{CH_3OH}\gamma^{DMF}{}_{SPh^-} + \log {}^{CH_3OH}\gamma^{DMF}{}_{C_6H_{11}Br} - \log {}^{CH_3OH}\gamma^{DMF}{}_{\ddagger} \quad (2)$$

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(9) D. J. McLennan, *J. Chem. Soc. B*, 705 (1966).

(10) E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90**, 6447 (1968).

(11) The data of Ko and Parker[10] for rates of reaction of cyclohexyl bromide with NaSPh in ethanol at 76–100° do not form a linear Arrhenius plot.

(12) The solvent activity coefficient ${}^{O}\gamma_i{}^{S}$ for transfer of solute i from reference solvent O to solvent S is proportional to the change in standard chemical potential μ_i

$$\bar{\mu}_i{}^{S} = \bar{\mu}_i{}^{O} + RT \ln {}^{O}\gamma_i{}^{S}$$

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

(13) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968).

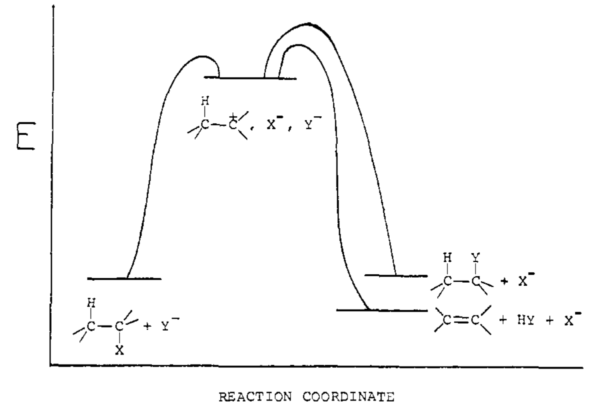

Figure 2.

relative rates at 25° the difference in solvent activity coefficients of the base and the transition state is $\log {}^{\mathrm{CH_3OH}}\gamma^{\mathrm{DMF}}{}_{\mathrm{SPh^-}} - \log {}^{\mathrm{CH_3OH}}\gamma^{\mathrm{DMF}}{}_{\ddagger} = 2.6$. Ko and Parker[10] calculated a value of 2.9 for this same quantity from their data with NaSPh in ethanol and DMF, estimated that $\log {}^{\mathrm{C_2H_5OH}}\gamma^{\mathrm{DMF}}{}_{\mathrm{SPh^-}} \approx +5$, and concluded that thiophenoxide ion and the substitution and elimination transition states all were solvated more strongly in ethanol than in DMF. Recently, measurements of heats of solution of reactants have also enabled determination of enthalpies of transfer of some S_N2 transition states from methanol to DMF,[14] but the reaction of cyclohexyl bromide with thiophenoxide was not studied. Analysis of our rate data in N_{2226}-B_{2226} in a similar manner would require measurement of solvent activity coefficients and/or heats of solution of cyclohexyl bromide and N_{3333}SPh in methanol, DMF, and $N_{2226}B_{2226}$.

Because the fraction of cyclohexene formed from N_{3333}SPh and cyclohexyl bromide is so nearly the same in three solvents with markedly different solvating properties, each solvent must either not be involved in the product-determining steps, or solvate the transition states for substitution and elimination equally well. If solvent is not involved in the rate-limiting steps, the substantial rate differences in the three solvents are due solely to differences in reactant solvation. Since thiophenoxide appears in the rate law, the rate-determining and product-determining steps are most likely bond formation between thiophenoxide and either carbon or hydrogen.

The lack of dependence of product distribution on solvent and temperature is strong evidence that the transition states for a weak base-catalyzed elimination reaction and concurrent nucleophilic substitution are very similar. That the two transition states are not identical in related reactions has been proved by the formation of different olefins in tetra-*n*-butylammonium chloride induced elimination from *threo*- and *erythro*-3-*p*-anisyl-2-butyl chlorides,[15] and by measurement of different hydrogen/deuterium isotope effects for substitution and elimination reactions of tetra-*n*-butylammonium chloride with 3-methyl-2-butyl tosylate and with *trans*-4-*tert*-butylcyclohexyl tosylate.[16] There are other indications of great similarity between substitution and weak base-catalyzed elimination transition states. For example, a plot of log k_2 for base-catalyzed elimination of HBr from *tert*-butyl bromide in acetone against log k_2 for nucleophilic substitution with cyclohexyl tosylate in acetone is reasonably linear.[17] However, this type of rate correlation fails with some other substitution and weak base-catalyzed elimination rates for which it would be expected by analogy to work well.[4,17] Another striking similarity between the substitution and elimination reactions of cyclohexyl derivatives is that the amount of cyclohexene formed in reaction with tetra-*n*-butylammonium chloride varies over only 50–73% for five different leaving groups (Br^- and OTs^- in acetone, and Cl^-, I^-, and $S(CH_3)_2$ in DMF).[17]

The similarity between substitution and weak base-catalyzed elimination transition states has been explained by Parker with an "E2C" transition state in which base interacts with carbon almost as in an S_N2 transition state.[15–18] The E2C transition state has been criticized by Bunnett[19] because highly hindered secondary and tertiary alkyl bromides and secondary alkyl tosylates undergo elimination just as readily as unhindered ones. Bunnett[19] argues that if the elimination transition state resembles an S_N2 transition state, elimination rates should be retarded severely by steric hindrance, which they are not. Therefore, he suggests that weak base-catalyzed eliminations proceed *via* concerted E2 transition states. However, the similarities between substitution and elimination reactions and the lack of correlation between elimination rates and the proton basicity of the catalyst (in many eliminations halide and thioalkoxide ions are more effective catalysts than alkoxide ions) may be more difficult to explain with a conventional E2 transition state.

Weak base-catalyzed eliminations have many characteristics in common with carbonium ion pair reactions. Reversible ionization of the alkyl halide or tosylate to a tight ion pair, which is captured by the base at either carbon or hydrogen in steps which are both rate determining and product determining, is illustrated in Figure 2. In this mechanism most of the activation energy is required in an ionization step. If the subsequent formation of a covalent bond between base and carbon or base and hydrogen requires little additional activation energy, little selectivity between substitution and elimination should be expected. Ritchie[20] recently has explored the rates of reaction of nucleophiles with cations in a variety of solvents and found them to be dependent on the structure of the nucleophile and on the solvent, but independent of

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(14) (a) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, and P. Steinherz, *Chem. Commun.*, 194 (1968); (b) P. Haberfield, L. Clayman, and J. S. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 (1969); (c) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and G. Ginsberg, *J. Org. Chem.*, **36**, 1792 (1971).

(15) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(16) G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **94**, 2235 (1972).

(17) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, **94**, 2240 (1972). Each point in the plot represents the rates of reaction of a single base (nucleophile).

(18) (a) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968); (b) D. J. Lloyd and A. J. Parker, *ibid.*, 5029 (1970); (c) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 4735 (1971); (d) A. J. Parker, *Chem. Technol.*, 297 (1971); (e) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2228 (1972).

(19) (a) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969); (b) J. F. Bunnett and D. L. Eck, *ibid.*, **95**, 1897, 1900, 4473 (1973).

(20) C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972), and references therein.

the basicity of the nucleophile. Moreover, he found that relative nucleophilicities of various nucleophile–solvent combinations were independent of cation structure. His cation–nucleophile reactions are similar to weak base-catalyzed eliminations in two ways: rates do not depend on the proton basicity of the nucleophile, and rates are faster in polar aprotic solvents than in polar protic solvents. The relative rates of reaction of thiophenoxide ion with a triarylmethyl cation in methanol and in dimethyl sulfoxide (a polar aprotic solvent with properties not unlike those of DMF) are 1.0:250 at 23°, a difference of the same order of magnitude as our relative rates of reaction of thiophenoxide with cyclohexyl bromide in methanol and in DMF. Although most of Ritchie's work involves rates of reaction of nucleophiles with free cations, azide–ether product distributions in methanolyses of *p,p'*-dimethoxybenzhydryl mesitoate with added sodium azide suggest that the dissociated *p,p'*-dimethoxybenzhydryl cation exhibits greater azide–methanol selectivity than the *p,p'*-dimethoxybenzhydryl mesitoate ion pair.[21] If the rate-limiting steps of weak base-catalyzed elimination and concurrent nucleophilic substitution resemble those of nucleophile–cation reactions, little or no substitution–elimination selectivity should result.

In spite of these arguments for an ion-pair mechanism of weak base-catalyzed elimination, one major class of evidence rules against it: substituent effects at the carbon atom which should be positively charged in the transition state of an ion-pair mechanism (Figure 2) fail to indicate appreciable charge.[18b,d] Since major objections to all three mechanisms, E2C, E2, and ion pair, can be raised, a compromise between them comes closest to fitting all the data available.[4]

Experimental Section

Materials. Cyclohexyl bromide was vacuum distilled and contained no impurities detectable by glpc on five different columns. 2,6-Lutidine was vacuum distilled from barium oxide. Methanol was distilled from freshly prepared magnesium methoxide. Dimethylformamide was dried over 4-Å molecular sieves and vacuum distilled from anhydrous $MgSO_4$ at 65° (28 Torr). Triethyl-*n*-hexylammonium triethyl-*n*-hexylboride was prepared as described elsewhere[2] and dried at 10^{-5} Torr and 50–60° before use.

Tetra-*n*-propylammonium Thiophenoxide ($N_{3333}SPh$). All operations were performed in an inert atmosphere. A slurry of 0.372 mol of freshly prepared silver oxide in 200 ml of water and 60 ml of ethanol was combined with a solution of 0.33 mol of tetra-*n*-propylammonium bromide (recrystallized from chloroform–ethyl ether) in 200 ml of water in the dark and shaken 2 hr. The mixture was filtered rapidly and 0.388 mol of thiophenol (>99% pure by glpc) was added to the filtrate. Removal of water at 35–40° and reduced pressure left a viscous yellow oil which was dissolved in methanol and filtered. Addition of diethyl ether caused separation of an oil which crystallized upon cooling to −20° for 12 hr. The white crystals were recrystallized twice from methanol–ethyl ether and dried at 10^{-4} Torr and 25° to give 78.1 g of $N_{3333}SPh$ (87.5%) with a neut equiv of 296.5 (calcd, 295.6). The solid is hygroscopic and turns yellow in dry air. Consequently, it was always stored and handled in an inert atmosphere.

Kinetics in Methanol. Standard solutions of 0.054–0.69 *M* $N_{3333}SPh$, 0.045–0.049 *M* cyclohexyl bromide, and 0.086–0.25 *M* 2,6-lutidine were prepared in an inert atmosphere, sealed in ampoules, and placed in a bath whose temperature was known to ±0.01°. Concentrations were corrected for volume expansion of the solvent. For each data point the solution in the ampoule was quenched with 1–2 ml of 1 *N* sulfuric acid and extracted four times with 3–4 ml of pentane to remove thiophenol and cyclohexene. The remaining aqueous methanol solution was diluted with 30 ml of 2-propanol and titrated for bromide ion to the diphenylcarbazone end point with standard 0.01 *N* aqueous mercuric nitrate.[22] Control experiments demonstrated that this extraction–titration procedure was accurate for bromide ion to ±0.3%. Each kinetic run consisted of 5–8 data points taken up to at least 66% consumption of cyclohexyl bromide. The data points fit the first-order rate equation (3)[23] at ≥0.166 *M* initial concentrations of $N_{3333}SPh$ and the second-order rate equation (4)[23] at all initial concentrations of $N_{3333}SPh$. In eq 3 and 4, x is the quantity of cyclohexyl bromide reacted at time t, a and b are the initial quantities of cyclohexyl bromide and $N_{3333}SPh$, respectively, and c is a constant.

$$\ln\left(\frac{a}{a-x}\right) = k_1t + c \tag{3}$$

$$\left(\frac{1}{b-a}\right)\ln\frac{a(b-x)}{b(a-x)} = k_2t + c \tag{4}$$

Rate constants in Table I are slopes of least-squares lines of data fitted to eq 3 and 4. In independent experiments, second-order rate constants for two runs at 0.45–0.47 *M* $N_{3333}SPh$ and 59.8° differed by 1.8%.

Product distributions were determined by glpc on a Hewlett-Packard Model 700 thermal conductivity instrument using a 9 ft × 0.25 in. column of 14% FFAP on Aeropak 30 at 50° with hexane internal standard to analyze cyclohexene and a 6.5 ft × 0.25 in. column of 11% Apiezon L on acid-washed Chromosorb G at 220° with tetradecane internal standard to analyze cyclohexyl phenyl sulfide. The sum of these determinations accounted for 100 ± 2% of the initial cyclohexyl bromide after >99% reaction.

In a control experiment a sample containing all reagents used in kinetic runs except $N_{3333}SPh$, which was replaced by 0.65 *M* sodium tetraphenylboride to mimic the ionic strength of kinetic runs, was held 40 hr at 60°. No cyclohexene was formed by glpc analysis, and the solution contained no bromide ion by titration.

Similarly, two control solutions, the first containing cyclohexene, thiophenol, $N_{3333}SPh$, and 2,6-lutidine, and the second containing cyclohexyl phenyl sulfide, thiophenol, $N_{3333}SPh$, and 2,6-lutidine, were completely stable according to glpc analyses for times corresponding to those required for >99% reaction of cyclohexyl bromide at 60°. These controls demonstrate that the substitution and elimination products are stable under kinetic conditions.

Kinetics in DMF. A solution containing all reagents except cyclohexyl bromide was prepared at room temperature under nitrogen. Aliquots were transferred to serum-capped test tubes. To each tube at −78° a fixed amount of cyclohexyl bromide was added with a 10-μl Hamilton syringe fitted with a Chaney adapter. Bromide determination for each data point, treatment of data, and product distributions were done by the methods described for kinetics in methanol. Control experiments analogous to those run in methanol demonstrated that cyclohexyl bromide did not solvolyze and that cyclohexene and cyclohexyl phenyl sulfide were stable under the reaction conditions. In independent experiments second-order rate constants for two runs at 20.1° and 0.095–0.099 *M* $N_{3333}SPh$ differed by 1.6%.

Kinetics in $N_{2226}B_{2226}$. For each kinetic run a solution containing all reactants except cyclohexyl bromide was prepared in an inert atmosphere in a flask fitted with a silicone rubber septum. The solution was equilibrated at the desired temperature, and cyclohexyl bromide was added by syringe with magnetic stirring. Aliquots were withdrawn with a gas-tight syringe, and bromide ion content for each data point was determined by a method modified from that described for kinetics in methanol. $N_{2226}B_{2226}$ interfered with the diphenylcarbazone–mercuric nitrate titration. Consequently, each molten salt aliquot was quenched in 4 ml of 0.25 *M* sulfuric acid and the mixture was extracted four times with benzene and three times with chloroform. The resulting aqueous solution was free of $N_{2226}B_{2226}$ and contained all the bromide ion according to control experiments which simulated kinetic conditions. Rate constants were determined by the method described for kinetics in methanol, but data points were slightly more scattered from the least-squares lines than in methanol or DMF experiments. However, rate constants obtained at 45.25° and 0.12–0.13 *M* $N_{3333}SPh$ in two batches of $N_{2226}B_{2226}$ prepared over 7 months apart differed by only 5.8% (see the last two lines of Table I).

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Product distributions were determined after >99% disappearance of cyclohexyl bromide by extraction of the $N_{2226}B_{2226}$ solution with 5–6 portions of 1–2 ml of pentane and glpc analysis of the pentane extracts. Cyclohexene and cyclohexyl phenyl sulfide were determined using octane and tetradecane as internal standards on matched 6.5 ft × 0.25 in. 11% Apiezon L columns with temperature programming to obtain both analyses from a single injection. In control experiments the sum of products determined by this method accounted for 97% of the initial cyclohexyl bromide when the reaction was carried out in sealed glass ampoules, but some cyclohexene was lost when the reaction was carried out in septum-capped flasks. In the latter cases cyclohexyl phenyl sulfide was determined by the glpc method and the cyclohexene was assumed to account for the remainder of the cyclohexyl bromide consumed. Control experiments showed that this assumption gave results within 2% of those obtained by glpc analysis of both products.

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Mercury ($^3P_1$)-Sensitized Decomposition of *cis*- and *trans*-3,4-Dimethyl-1-pyrazoline. The Kinetics of Highly Vibrationally Excited Triplet 1,2-Dimethyltrimethylene Biradicals

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Abstract: The Hg($^3P_1$)-photosensitized decomposition of both *cis*- and *trans*-3,4-dimethyl-1-pyrazoline was studied from 0.2 to 4 and 5 Torr, respectively, and in the presence of Ar at pressures up to 1 atm. The major products are nitrogen, *cis*- and *trans*-dimethylcyclopropane, *cis*- and *trans*-2-pentene, 3-methyl-1-butene, and ethane. The product distributions from both reactant isomers are nearly identical. For the cis reactant $\Phi_{N_2} = 0.93 \pm 0.05$ at 4 Torr, and for the trans reactant $\Phi_{N_2} = 0.95 \pm 0.05$ at 5 Torr. Total hydrocarbon quantum yields are independent of pressure from ~1 to 760 Torr (pressurized with Ar). Highly vibrationally excited triplet 1,2-dimethyltrimethylene biradicals are formed by N_2 elimination from both pyrazolines. The hot biradicals either dissociate to methyl and methallyl radicals or cyclize to dimethylcyclopropanes, which are also sufficiently excited to experience geometrical and structural isomerization, the latter only being observed at pressures below about 1 Torr. Pentenes and ethane are formed by radical–radical combination reactions.

Direct and triplet-sensitized photodecomposition of 1-pyrazolines has frequently been postulated to proceed *via* nitrogen elimination to yield 1,3 biradicals.[1–9] The spin multiplicity of the intermediates and their subsequent reactions depend on the primary photophysical processes occurring in the precursor, though in general direct photolysis is thought to yield singlet biradicals while triplet photosensitizers are thought to produce triplet biradicals.

Direct photolysis of 1-pyrazolines yields cyclopropanes, presumably *via* biradical cyclization, and olefins as the major products both in vapor and condensed phases.[3,7,9] Olefins and cyclopropanes are also formed in two vapor phase systems which are thought to involve triplet 1,3 biradicals as the olefin precursor. These are the addition of $CH_2(^3B_1)$ to double bonds[10,11] and the triplet photosensitization of dimethylcyclobutanone vapors.[12,13] In contrast, triplet photosensitization of 1-pyrazolines in solution yields cyclopropanes but no olefins.[3,8,9] If triplet biradicals are important intermediates in these reactions, there is an unexplained effect of phase on the reaction products. On the other hand, triplet biradicals may not be involved in all cases, or the biradicals may have different properties, dependent upon their mode of formation. In this work we have investigated the reasons for the above noted differences in behavior.

No one mechanism can explain the results of the photolytic or pyrolytic decomposition of all the compounds in which diradical intermediates are thought to play a role. The diverse modes of reaction can be attributed to different structures and/or electronic states of the intermediates. We initiated an investigation of the vapor phase triplet-sensitized decomposition of 1-pyrazolines in order to compare and contrast behavior with that obtained by triplet sensitization in solution and with direct photolysis. *cis*- and *trans*-3,4-dimethyl-1-pyrazoline were chosen for study since the expected triplet biradicals would be similar to those obtained by adding $CH_2(^3B_1)$ to *cis*- or *trans*-2-butene[10,11] or by the triplet-sensitized decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanone.[12,13] The investigation was expected to reveal whether the triplet biradicals produced

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