Quantum Yields. Samples of phenyl benzoate (0.1 *M*) in various solvents were irradiated by means of the sealed tube technique with a 254-nm "merry-go-round" apparatus. Light intensities of *ca.* 6.1×10^{-8} einstein/min were monitored throughout the irradiation period with potassium ferrioxalate actinometry.[52] Consumption of ester and conversions to nonphenolic products were measured directly by glpc. Phenolic products resulting from the irradiation were analyzed by first converting them quantitatively to their more volatile trimethylsilyl ethers, by the action of bis(trimethylsilyl)acetamide, which were determined by gas chromatography. Measurement of peak areas from the chromatograms was made by means of either the cutting and weighing technique or by using a Disc integrator. Triplicate data points were taken for each value.

The inclusion of an internal standard in the solutions provided accurate values of the amounts of conversion for measured volumes of solution. Comparison of these values with calibration curves for each compound gave the concentration of photoproducts in each sample. By plotting the millimoles of conversion *vs.* millieinsteins of light, extrapolating the curve to zero at zero time, and measuring the slope, we obtained the quantum yields at low conversion.

Silylation of Phenols with Bis(trimethylsilyl)acetamide (BSA).[53] A 2-ml aliquot of the photolyzed solution (typically 0.1 *M* in phenyl benzoate) was placed in a 5-ml serum bottle fitted with a serum cap. To this sample 0.5 ml of purified BSA was introduced through the cap by means of a syringe and needle. (An additional 1 ml of BSA was added to those samples which contained acid.) The bottle was agitated a few seconds and allowed to stand for 24 hr. Independent experiments showed that this period was sufficient to assure quantitative conversion of the sample.

Detection of Gases Resulting from Photodecarbonylation. The hydrocarbon gases resulting from photodecarbonylation in phenyl *n*-butyrate solutions were qualitatively analyzed by coincident injection of authentic gas samples with injections of the solutions containing dissolved gases on a silica gel column. Enhanced peak heights without a change in the shape were taken as strong evidence of the identity of the gas.

Measurement of Carbon Monoxide. Measurement of carbon monoxide produced by irradiation of phenyl acetate vapor in the flow system was made by channeling the effluent gas from the drying tube through a three-necked flask. The center neck of the flask contained a punctured serum cap through which a carbon monoxide analyzer tube could be placed. A Bacharach Universal Gas Sampler No. 1907016 with potassium palladosulfite type carbon monoxide sampling tubes No. 19-0195 permitted measurement of concentrations to 10 ppm. The unit is manufactured by the Bacharach Instrument Co., Pittsburgh, Pa.

Identification of Gas-Phase Photoproducts. All photoproducts were isolated by preparative gas chromatography and compared to authentic samples. Identical nmr, ir, and mass spectra for the isolated materials and an authentic sample along with coincident retention times on three different glpc columns constituted positive identification of the photoproducts.

Acknowledgments. This work was supported by the National Science Foundation, the U. S. Army Research Office-Durham, and by a graduate fellowship awarded to J. W. M. by the National Defense Education Act. We are grateful to Professor Norman Davidson for his helpful suggestions concerning the design of the flow reactor.

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[52] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

[53] E. M. Chambaz and E. C. Horning, *Anal. Lett.*, **1**, 201 (1967).

The E2C Mechanism in Elimination Reactions. III.[1] Dehydrobromination of *tert*-Butyl Bromide in Acetone

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Abstract: Rates of E2C-like dehydrobromination of *tert*-butyl bromide by bases in acetone containing 2,6-lutidine have been studied. The reactions are bimolecular, with both base and *tert*-butyl bromide present in the transition state. This is confirmed by solvent and salt effects on rate and by the dependence of rate on the nature and concentration of the base. Rate constants for elimination decrease in the order of bases: $SC_6H_5 > CH_3CO_2 >$ CN, Cl $> NO_2$, $N_3 > OC_6H_4NO_2$-*p* $> SC_6H_4NO_2$-*p* $>$ Br $>$ I, SCN $> C_5H_5N$, 2,6-lutidine. This order correlates poorly with nucleophilic tendencies toward carbon in a tight transition state, *e.g.*, in the S_N2 reactions of *n*-butyl bromide, nor is there a Brønsted correlation between these elimination rates and the basicity toward hydrogen of these bases. There is a good correlation of rates of elimination from *tert*-butyl bromide with rates of bimolecular substitution in cyclohexyl tosylate by these bases. The effects of ion association on rates of E2 and S_N2 reactions in acetone are different when tetrabutylammonium, rather than lithium salts, are the source of base. Transition-state anions associate with NBu_4^+ to much the same extent as do reactant anions. However, Li^+ associates much more strongly with many reactant anions than with E2C or S_N2 transition-state anions. The initial E2C-like reaction of *tert*-butyl bromide with chloride ion is an endo energetic process.

The pioneering studies of Hughes and Ingold[3] are largely responsible for the interest in the substitution and elimination reactions of *tert*-butyl bromide.[3-11]

This paper describes some bimolecular reactions of *tert*-butyl bromide in the presence of electrolytes in

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[1] Part II: 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).

[2] Deceased Nov 23, 1969.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapters 7 and 8.

[4] S. Winstein, S. G. Smith, and D. Darwish, *Tetrahedron Lett.*, 24 (1959).

[5] L. J. Le Roux and E. R. Swart, *J. Chem. Soc.*, 1475 (1955).

acetone as solvent. Some of the reactions have been studied before,[3–9] but the observed rates have not always been interpreted correctly.[4–8] Cook and Parker,[9] who based part of their paper on the work reported here, discussed some of the difficulties, which include incomplete dissociation of electrolytes,[5] precipitation of electrolytes,[12] and concurrent substitution and elimination.[4] The most serious source of error in earlier work is that 2-methylpropene and hydrogen halides are in an equilibrium (1) which lies well to the right in

$$(CH_3)_2C{=}CH_2 + HX \rightleftharpoons (CH_3)_3CX \qquad (1)$$

weakly basic solvents like acetone, nitromethane, and acetonitrile.[4,8,9] In these solvents, an E2 dehydrobromination of *tert*-butyl bromide followed by Markovnikov addition as in eq 2, appears[6] to be a one-step,

$$\begin{array}{l}(CH_3)_3CBr + Y^- \rightleftharpoons \\ \qquad (CH_3)_2C{=}CH_2 + HY + Br^- \rightleftharpoons (CH_3)_3CY + Br^- \quad (2) \\ \qquad \qquad \Big\downarrow B \\ \qquad (CH_3)_2C{=}CH_2 + BH^+ + Y^- + Br^-\end{array}$$

SN2 reaction, unless efforts are made to trap the intermediate hydrogen halides or 2-methylpropene. Hydrogen halides are trapped by sufficiently basic solvents, like DMF, DMSO, *N*-methylpyrrolidone,[10] water, or alcohols, or by adding bases (B in eq 2), like 2,6-lutidine, pyridine, or excess chloride ion to less basic solvents. Failure to take this precaution led Ingold, de la Mare, and their coworkers[6,7] into the incorrect interpretation that their rates were for SN2 substitutions.

Another question of classical interest is the effect of ion association on rates of bimolecular reactions in acetone, *i.e.*, the reactivity or otherwise of ion pairs *vs.* dissociated ions.[4,5,9,13–19] Some unusual effects are now reported when tetrabutylammonium salts, rather than lithium salts, are the source of base in acetone.

The question of "tight" and "loose" transition states has received some attention recently, as have nucleophilic tendencies in protic and dipolar aprotic solvents.[20,21] We compare nucleophilic tendencies of bases toward carbon in tight SN2 reactions of *n*-butyl bromide and in loose SN2 reactions of cyclohexyl tosylate, in acetone as solvent.

The dehydrobrominations of *tert*-butyl bromide by bases are claimed to be often E2C-like,[1,9,22] *i.e.*, there is some interaction between base and the carbon atom carrying the leaving group in the transition state. We suggest three criteria which must be applied *in conjunction* to distinguish an extremely E2C-like set of reactions of different bases[22] from E2H-like reactions. Firstly, do nucleophilic tendencies in the suspected E2C-like reactions correlate with nucleophilic tendencies toward carbon in a set of bimolecular substitution reactions of a closely related substrate? Secondly, is there *no* Brønsted correlation of nucleophilic tendencies in the suspected E2C-like reaction with base strength toward hydrogen? Thirdly, do nucleophilic tendencies in suspected E2H-like reactions exhibit a Brønsted correlation? The first two criteria have been applied successfully to dehydrotosylations of cyclohexyl tosylate;[22] they are now applied to E2 dehydrobrominations of *tert*-butyl bromide.

Hydrogen bromide reacts slowly with acetone at 50° but lutidinium hydrobromide decomposes much more slowly, so that nearly quantitative acid formation is observed in the presence of 2,6-lutidine, with lithium or tetrabutylammonium perchlorate, chloride, or bromide. The rate of acid formation from *tert*-butyl bromide in acetone is independent of lutidine concentration in the 0.02–0.09 *M* range.[4]

Discussion

In general, the rate of production of bromide ion from reactions of readily ionizable alkyl bromides such as *tert*-butyl bromide, in solutions containing electrolytes MY, and which are sufficiently basic to prevent addition of acid to the product olefin, are given by eq 3. The

$$(d[Br^-]/dt)/[t\text{-BuBr}] = k_1^0(1 + b[MY]_0) + k_E^Y[Y^-] + k_E^{Br}[Br^-] + k_S^Y[Y^-] \quad (3)$$

rates observed and recorded by means of eq 9 and 10 must be interpreted in terms of eq 3. In eq 3 $k_1^0(1 + b \cdot [MY]_0)$ is the rate of a salt-assisted ionization of *tert*-butyl bromide,[4] k_E^Y and k_E^{Br} are second-order rate constants for E2 reactions induced by Y and by the bromide ion produced as reaction proceeds, and k_S^Y is for an SN2 reaction with Y. The concentration terms in eq 3 are the concentration of ions after any necessary allowance has been made for ion association (M^+, Y^-), for protonation (HY), for heteroconjugates (HBrY, R_3NHY), and for homoconjugates (YHY^-).[4,22–26] The terms have varying degrees of importance, depending on the solvent and the base employed. In acetone solvent k_1^0 is relatively small so that the second-order rate constants achieve greater importance, but in DMF,[27] *N*-methylpyrrolidone,[10] DMSO,[28] water, and the alcohols,[3] the ionization rate is often of major importance.

It might be argued that all the reactions in Table I can be treated as salt-assisted ionizations, some of

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(6) E. D. Hughes, C. K. Ingold, and J. D. H. MacKie, *J. Chem. Soc.*, 3173 (1955).

(7) P. B. D. de la Mare, *ibid.*, 3180 (1955).

(8) P. B. D. de la Mare, E. D. Hughes, C. K. Ingold, and Y. Pocker, *ibid.*, 2930 (1954).

(9) D. Cook and A. J. Parker, *ibid.*, *B*, 142 (1968).

(10) P. O. I. Virtanen, *Suom. Kemistilehti B*, **40**, 1 (1967).

(11) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).

(12) L. Fowden, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 3187 (1955).

(13) W. M. Weaver and J. D. Hutchinson, *J. Amer. Chem. Soc.*, **86**, 261 (1964).

(14) S. F. Acree, *Amer. Chem. J.*, **48**, 353 (1912).

(15) N. N. Lichtin and K. N. Rao, *J. Amer. Chem. Soc.*, **83**, 2417 (1961).

(16) J. L. Kurz, *ibid.*, **85**, 987 (1963).

(17) C. C. Evans and S. Sugden, *J. Chem. Soc.*, 270 (1948).

(18) S. Winstein, L. G. Savedoff, S. G. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, No. 9, 24 (1960).

(19) E. D. Hughes, C. K. Ingold, and A. J. Parker, *J. Chem. Soc.*, 4400 (1960).

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

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

(22) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(23) I. M. Kolthoff, S. Bruckenstein, and M. Chantooni, *J. Amer. Chem. Soc.*, **83**, 3927 (1961).

(24) Y. Pocker, *J. Chem. Soc.*, 1972 (1960); 240 (1958).

(25) H. P. Looy and L. P. Hammett, *J. Amer. Chem. Soc.*, **81**, 3872 (1959).

(26) W. F. K. Wynne-Jones, *J. Chem. Soc.*, 795 (1931).

(27) S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 4155 (1957).

(28) K. Heinonen and E. Tommila, *Suom. Kemistilehti B*, **38**, 9 (1965).

Table I. Rates of Reaction of *tert*-Butyl Bromide[a] in Acetone Containing Basic Anions at 50.0°

Salt X in NBu_4X	[Salt], 10^2 *M*	[Lut],[b] 10^2 *M*	10^2F_E[c]	10^4k_2,[d] M^{-1} sec^{-1}	Salt X in NBu_4X	[Salt], 10^2 *M*	[Lut],[b] 10^2 *M*	10^2F_E[c]	10^4k_2,[d] M^{-1} sec^{-1}
ClO_4	3.00	2.0	88	0.018[j]	N_3	3.36	5.00	82	9.24
SCN	5.20	2.0	97	<0.1[e]			2.0		0.0123[j]
I	4.01	2.0	91	0.16[e]			9.0		0.0123[j]
Br[k]	3.00	2.0		0.88[k]	OAc[b]	3.71	4.00	100	87.5
Br	4.80	4.00	100	1.3[e]	NO_2	5.06		86	6.98[f]
Cl[k]	3.00	2.0		0.70[k]	OAr[b]	5.03	6.33	96	3.90
Cl	4.82	4.12	95	8.80	SAr[b]	4.73	3.64	100	2.85
Cl	4.81	8.83	95	9.34	CN	5.05		100	12.3[f]
Cl	5.31		96	9.00[f]	SC_6H_5[g]	4.0		98	160[g]
Cl	7.15		96	8.80[f]	N_3[g]	3.0		80	1.14[g]
Cl	3.40	1.90	94	9.65	Br[h]	4.0		100	2.6[h]
Cl	5.29	2.00	93	9.00	Br[i]	4.01		100	1.3[i]

[a] *tert*-Butyl bromide at 0.02 *M*. [b] Lut is 2,6-lutidine, Ar is 4-nitrophenyl, and OAc is acetate. [c] F_E is the fraction of acid to bromide ion produced and was effectively constant throughout all stages of reaction. [d] Rate constant calculated from eq 9 unless stated otherwise. [e] Rate constant tabulated is k_E of eq 3, calculated by assuming that the other terms are given by 1.8×10^{-6} sec^{-1}, *i.e.*, rate in presence of 0.03 *M* NBu_4ClO_4 and 0.02 *M* lutidine. *Cf.* ref 4. [f] Rate constant calculated from eq 10. [g] Reaction is at 25.0° with 0.04 *M* *tert*-butyl bromide, in dimethylformamide as solvent; data from ref 20. [h] In dimethylformamide at 50.0°. [i] In nitromethane at 50.0°. [j] First-order rate constant (10^4k_1) in sec^{-1} from ref 4. [k] Lithium salt; the observed first-order rate constant is expressed as an instantaneous initial second-order rate constant for 0.03 *M* base, calculated from data in ref 4.

them with high *b* values in eq 3.[4,29] However, the need for second-order terms becomes apparent when *b* values for the genuine salt-assisted ionization of *p*-methoxyneophyl tosylate in acetone at 75.0°[30] are compared with *b* values for an assumed salt-assisted ionization of *tert*-butyl bromide in acetone at 50°. The former range between 4 and 50, lithium salts having higher *b* values than tetrabutylammonium salts. The latter range from 12 to 10,000, the tetrabutylammonium salts having higher *b* values than the lithium salts.[4] Some of the *b* values for *tert*-butyl bromide are much too high[10] to reflect a genuine salt-assisted unimolecular ionization of *tert*-butyl bromide in the sense earlier envisaged.[4,30] The *b* value of 12 reported by Winstein, Smith, and Darwish[4] for NBu_4ClO_4 and $LiClO_4$ with *tert*-butyl bromide is thought to be genuine. An average figure of 12 seems reasonable for salts in acetone and this was used in eq 3 to calculate k_E^Y values. The *b* values of >20 for LiCl and LiBr are now thought to be partly a result of a small $k_E^Y[Cl^-]$ and $k_E^{Br}[Br^-]$ term in eq 3.

The rates of reaction of lithium halides with *tert*-butyl bromide in acetone were studied by Ingold and his coworkers.[6,7,12] The reactions are a combination of salt-assisted ionization, bimolecular elimination, addition, and substitution.[4] The lithium salts are extensively ion paired,[18] so that the bimolecular terms in eq 3 are small. We note that lithium halides are much weaker electrolytes and less effective[6,7,12] than the corresponding tetrabutylammonium halides (Table I) in inducing dehydrobromination of *tert*-butyl bromide in acetone. This salt effect is typical of bimolecular reactions, of this charge type, in acetone,[13–19] but is not typical of salt-assisted ionizations, in which lithium salts are more effective than tetrabutylammonium salts.[30]

We wish to emphasize the following points for E2C-like reactions of *tert*-butyl bromide. They are supported by the rate data in Tables I and II.

Neutral Bases Are Ineffective. The dehydrobromination of *tert*-butyl bromide in the presence of 2,6-lutidine in acetone at 50° is a unimolecular reaction, quite independent of the concentration of this strong hydrogen base. 2,6-Lutidine is a very weak carbon nucleophile in acetone. The dehydrobrominations in the presence of 2,6-lutidine are less than one-tenth as rapid as in the presence of NBu_4Cl or NBu_4Br, even though the latter salts are much weaker hydrogen bases than 2,6-lutidine. The latter reactions have the bimolecular components shown in eq 3. Note that the reactions are autocatalytic to the extent that kinetically active bromide ion is produced.

Table II. Rates of SN2 Reactions of *n*-Butyl Bromide[a] in Acetone at 25°

X in NBu_4X	[NBu_4X], 10^2 *M*	$10^3k_2^s$, M^{-1} sec^{-1}	X in NBu_4X	[NBu_4X], 10^2 *M*	$10^3k_2^s$, M^{-1} sec^{-1}
C_5H_5N[f]	4.0[f]	<0.1	SCN	5.20	0.139
OAc[b]	4.41	15.5	OAr[b]	5.03	0.315
Cl	4.82	5.80	SAr[b]	4.64	108
NO_2	4.18	14.9	Br	4	4.0[d]
N_3[c]	2.86	26.7	I	4	1.0[d]
CN	5.00	15.7	SC_6H_5[e]	4.02	5×10^4

[a] *n*-BuBr at 0.01–0.03 *M*. [b] Ar is 4-nitrophenyl, OAc is acetate. [c] NEt_4 salt. [d] Calculated from data in ref 17. [e] Solvent is dimethylformamide and sodium salt was used; data from ref 20. [f] Pyridine with no NBu_4X.

Anions Are in the E2C-Like Transition State. Anions which are sufficiently basic toward carbon or hydrogen promote a dehydrobromination of *tert*-butyl bromide in acetone. The rate depends on the concentration and the nature of the anion, and, in the case of lithium salts, on the extent of ion association of the anion with a cation.[18] The reactions are also considerably faster in dipolar aprotic than in protic solvents,[20] but are much the same rate in acetone, nitromethane, and DMF. These features are all typical of a bimolecular elimination and confirm that both *tert*-butyl bromide and the basic anion are present in the E2 transition state. The solvent cannot be specifically involved in the transition state because rates of dehydrobromination by the same anion are much the same in nitromethane acetone and dimethylformamide, and yet, the former pair are much weaker bases than dimethylformamide toward both carbon and hydrogen.

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(29) S. Winstein, E. C. Freidrich, and S. G. Smith, *J. Amer. Chem. Soc.*, **86**, 305 (1959).

(30) S. Winstein, S. G. Smith, and D. Darwish, *ibid.*, **81**, 5511 (1959).

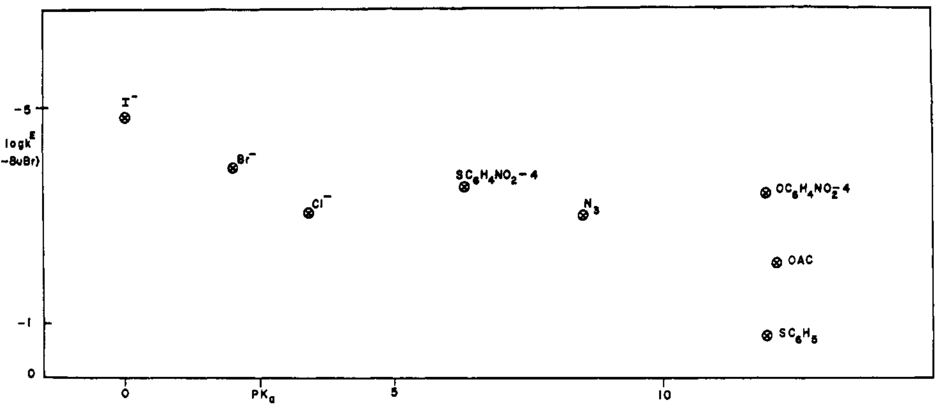

Figure 1. Brønsted plot, eq 1, of rates of dehydrobromination (log K^E) of *tert*-butyl bromide by bases B^- in acetone (thiophenoxide in DMF) at 50° (Table I) *vs.* pK_a of acids HB in dimethylformamide[31] at 25°.

No Brønsted Correlation. The rates of E2C-like dehydrobromination of *tert*-butyl bromide, like E2C-like dehydrotosylation of cyclohexyl tosylate, by a series of bases in acetone, do not correlate with their base strengths toward hydrogen (*cf.* Figure 1) in dipolar aprotic solvents.[31] The Brønsted equation (4) is *not*

$$\log k_E^Y = \beta pK_a[HY] + \text{constant} \qquad (4)$$

followed.[22] Of particular significance in Figure 1 is $Cl^- > OC_6H_4NO_2^-$-*p* for k_E^Y of eq 3 despite the fact that *p*-nitrophenoxide is at least 10^{10} times more basic than chloride ion toward hydrogen, in dipolar aprotic solvents.[31] Furthermore, the thiophenoxide is 200 times *more* effective than azide ion in the E2 dehydrobromination of *tert*-butyl bromide in DMF at 25°, but azide and thiophenoxide ions are of comparable base strength toward hydrogen in DMF.[31]

No Correlation with C Nucleophilicity in a Tight Transition State. Rates of the E2 dehydrobrominations of *tert*-butyl bromide (Table I) by a set of bases do not correlate with rates (Table II) of the SN2 reactions of *n*-butyl bromide with the same bases, in solvent acetone, at virtually the same concentration (*cf.* Figure 2). E2-nucleophilic tendencies toward *tert*-butyl bromide decrease in the order: $C_6H_5S \gg OAc > CN > Cl$, $N_3 > NO_2 > OC_6H_4NO_2$-*p*, $SC_6H_4NO_2$-*p* $> Br > I$, SCN ≫ lutidine (Table I), whereas SN2 nucleophilic tendencies toward *n*-butyl bromide decrease in the order: $C_6H_5S > SC_6H_4NO_2$-*p* $> N_3 > CN$, NO_2, OAc, $> Cl > Br > I > OC_6H_4NO_2$-*p* > SCN > pyridine (Table II). The different position of *p*-nitrothiophenoxide and *p*-nitrophenoxide in the two reactions is striking. Pyridine and lutidine, although strong hydrogen bases, are weak carbon nucleophiles.

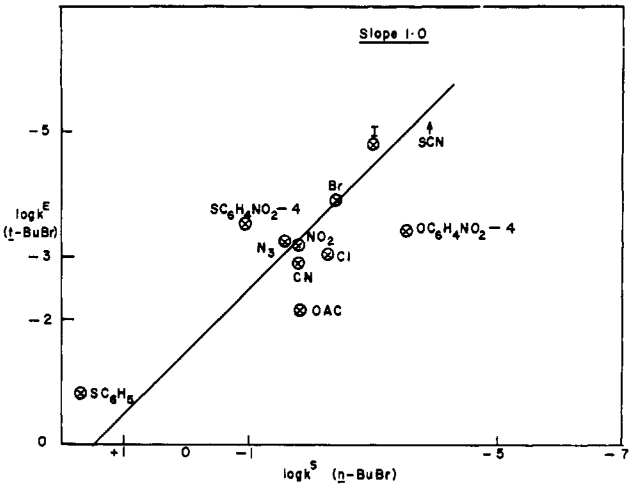

Figure 2. Swain and Scott plot, eq 5, of rates of dehydrobromination (log k^E) of *tert*-butyl bromide in acetone at 50° (Table I) *vs.* rates of substitution (log k^S) of *n*-butyl bromide in acetone at 25° (Table II).

The rates of E2 dehydrobromination of *tert*-butyl bromide (Table I) are much less responsive to change of base than are SN2 reactions of *n*-butyl bromide (Table II). One reason for this and the resulting lack of correlation in Figure 2, seems to be that SN2 reactions of *n*-butyl bromide, a primary alkyl halide, proceed through much "tighter" transition states than do E2C-like reactions of *tert*-butyl bromide, a tertiary alkyl halide.[20,21] The loosening of E2C-like and of SN2 transition states, as the reaction center changes from primary alkyl halide to tertiary alkyl halide, is now well established, following the work of Ko and Parker.[20] They discussed the leveling effect on nucleophilic tendencies as transition states loosen.

Ko and Parker[20] showed that behavior in a tight SN2 transition state was not a good model for behavior in a loose SN2 transition state; it should be an even worse model for behavior in a loose E2C-like transition state. Eck and Bunnett,[11] for example, suggested using the response to steric effects of a tight SN2 transition state as a model for expected steric effects in a loose E2C transition state. Just as the failure of their model gives no justification for discarding the concept of E2C-like transition states[32] so the lack of correlation in Figure 2 is not necessarily evidence against the E2C mechanism.

Correlation with C Nucleophilicity in a Loose Transition State. Rates of E2C-like dehydrobrominations of *tert*-butyl bromide (Table I) by a set of bases do correlate reasonably with rates of bimolecular substitution reactions of cyclohexyl tosylate[22] with the same bases, at the same concentration, in acetone (Figure 3). Ideally we would like to test whether the E2C-like reactions of *tert*-butyl bromide respond to a change of base in much the same way as do SN2 reactions of *tert*-butyl

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(31) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966); C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 3415, (1968).

(32) D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969).

Table III. Ion Pair Association Constants in Acetone at 25°

$$\log K_A = \log \frac{[MY]}{[M^+]}[Y^-]\gamma\pm^2$$

Salt MY	LiCl	LiBr	LiI	LiPic	NEt_4Cl	NBu_4Cl	NBu_4Br	NBu_4I
Log K_A	5.48[a]	3.66[a]	2.15[a]	2.91[b]	2.57[c]	2.78[a]	2.69[d]	2.37[d]
Salt MY	NBu_4ClO_4		$NBu_4OC_6H_4NO_2$-4		NBu_4NO_3	NBu_4Pic	NBu_4I_3	
Log K_A	2.06[b]		2.08[d]		2.26[b]	1.65[b]	2.30[d]	

[a] Reference 39. [b] Reference 38. [c] P. Walden, H. Ulick, and G. Busch, *Z. Phys. Chem.*, 429 (1926). [d] This work.

bromide; however, the latter reactions are usually too slow to be observed in competition with E2 reactions. The SN2 reactions of cyclohexyl tosylate are a better model than are those of *n*-butyl bromide for the SN2 reactions of *tert*-butyl bromide. The SN2 reactions of cyclohexyl tosylate, like those of *tert*-butyl bromide, proceed through very loose transition states, because the leaving group is tosylate and because the reaction center is a secondary carbon atom in a crowded cyclic structure. Thus, it is difficult to achieve a tight SN2 transition-state geometry. A plot of the Swain–Scott[33]-like linear free-energy relationship (eq 5), as in Figure 3, is a reasonable test of whether E2C-like rates $k_E{}^Y$ correlate with C nucleophilicity ($k_S{}^Y$) in reactions proceeding through a loose transition state.[22]

$$\log k_E{}^Y(t\text{-BuBr}) = S \log k_S{}^Y[C_6H_{11}OTs] + C \quad (5)$$

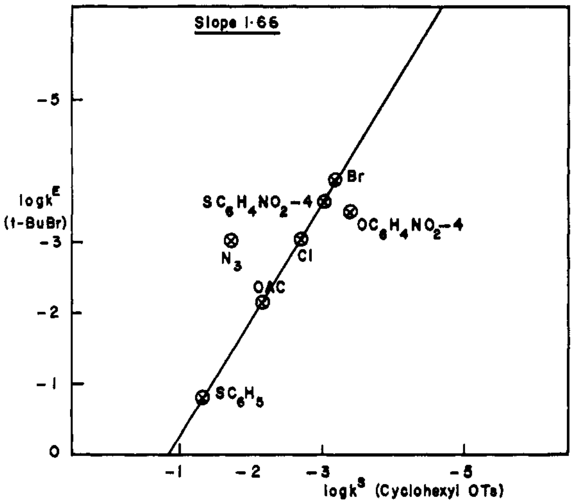

Figure 3. Swain and Scott plot, eq 5, of rates of dehydrobromination of *tert*-butyl bromide (log k^E) in acetone at 50° (Table I) *vs.* rates of substitution (log k^S) of cyclohexyl tosylate[22] in acetone at 75°.

It is clear that E2C-like reactions of *tert*-butyl bromide respond to the C nucleophilicity toward "loose" carbon (Figure 3) rather than to the H basicity of the bases (Figure 1). We note that the slope *S* of eq 5 is 1.66. Reactions of cyclohexyl tosylate are of lower sensitivity to change of base. This suggests that SN2 transition states for reaction of cyclohexyl tosylate are looser than E2C-like transition states for reactions of *tert*-butyl bromide. This agrees with conclusions drawn from the solvent activity coefficients of these transition states.[21] We note that, as usual,[9,22] azide ion is more effective in SN2 reactions than predicted by eq 5 and that alkoxides are more effective in elimination than predicted by eq 5. Reactions of alkoxides are more E2H-like than are E2 reactions of the other bases in Table I.

Endoenergetic Reactions. 2-Methylpropene and hydrogen halides react to give *tert*-butyl halides in acetone, unless another base is present to trap the hydrogen halide (*cf.* discussion of eq 2). The second base is not present in the E2C-like transition state. Thus, the first step of a halide ion induced dehydrobromination of *tert*-butyl bromide is an endoenergetic reaction. Application of Hammond's postulate[34] would suggest that these E2C-like transition states have structures resembling products, *i.e.*, they are like an anion, 2-methylpropene, and hydrogen halide. This is in accord with our earlier conclusions that the double bond is well developed at the transition state of E2C-like reactions.

Ion Association. Electrolytes are weak in acetone[35] and since this is the solvent of choice for most of the reactions studied in this series the kinetic implications[18,35] must be considered. Some association constants are in Table III. The effects of ion association on rates in acetone are well known.[4,5,13–19] De la Mare, Ingold, and their coworkers[6,7,19] aroused criticism when they chose not to apply eq 6 to their rate data for Finkelstein substitutions in acetone. The criticism has been examined by Cook and Parker.[9] In eq 6 $k_2{}^\mu$ is

$$k_2{}^\mu = k_2{}^0\alpha \quad (6)$$

the rate constant for reaction of the electrolyte at ionic strength μ, $k_2{}^0$ is the concentration at infinite dilution, and α is the degree of dissociation at ionic strength μ. This "Acree treatment" appears to deal satisfactorily with rates of reaction of lithium halides in acetone.[17] The important question arises, is eq 6 applicable to SN2 and E2 reactions of tetrabutylammonium salts with alkyl halides in solvents of low dielectric constant, like acetone?

As shown in Table III, lithium forms very stable ion pairs with small anions like chloride and bromide, but forms much weaker ion pairs with larger, more polarizable anions like iodide, triiodide, and picrate. If the large polarizable SN2 or E2 transition-state anion forms weak ion pairs with lithium just like iodide ion, then the reactant anion (*e.g.*, Cl^-) is much more strongly associated with Li^+ than is the transition-state anion (*e.g.*, $ClBuBr^{-\ddagger}$). Turning now to the tetrabutylammonium salts, NBu_4Y in acetone, we see in Table III that their association constants vary by no more than one power of ten for a variety of anions. We therefore expect that transition-state anions and reactant anions will

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[33] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

[34] G. S. Hammond, *ibid.*, 77, 334 (1955).

[35] C. W. Davies, "Ion Association," Butterworths, London, England, 1962.

Table IV. Effects of Ion Association on S_N2 and E2 Rates at 25° [a]

$$\mathrm{RX} + \mathrm{M^+Y^-} \rightleftharpoons \mathrm{YRX^{-\ddagger}\ M^+} \longrightarrow \text{products}$$

[MY], $10^3 M$,	$10^2 k_2^{\mu}$, M^{-1} sec^{-1}	α [b]	$10^2 k_2 \mu/\alpha$, M^{-1} sec^{-1}
(a) CH_3I + NBu_4Cl in 1,2-Dichloroethane, $K_A > 10^3$,[c] S_N2 Reaction			
3.15	9.69		
28.6	10.43		
(b) CH_3I + NEt_4Cl in 1,2-Dichloroethane, K_A = 19,600,[d] S_N2 Reaction			
3.09	6.50	0.204	31.7
32.8	6.84	0.130	52.6
(c) CH_3I + LiCl in Acetonitrile, K_A = 6110,[e] S_N2 Reaction			
1.93	2.75	0.269	10.2
15.0	0.89	0.114	7.84
(d) CH_3I + NEt_4Cl in Acetonitrile, K_A = 14,[f] S_N2 Reaction			
4.01	11.2	0.96	11.7
45.0	10.4	0.77	13.5
(e) CH_3I + LiCl in Acetone, $K_A = 3 \times 10^5$,[g] S_N2 Reaction			
7.40	5.50	0.0235	234
14.80	3.80	0.0170	223
29.60	1.87	0.0124	151
49.33	1.72	0.0098	175
(f) *t*-BuBr + NBu_4Cl in Acetone, K_A = 602,[g] E2C Reaction			
20.6	0.00651	0.444	0.0146
48.1	0.00577	0.392	0.0147
174	0.00539	0.380	0.0142
(g) CH_3I + $NBu_4OC_6H_4NO_2$-4 in Acetone, K_A = 120,[e] S_N2 Reaction			
0.0137	2.83	0.998	2.84
0.0683	2.34	0.939	2.50
0.956	2.35	0.939	2.50
10.4	1.93	0.804	2.40
31.5	1.56	0.759	2.06
(h) *n*-BuBr + NBu_4OAc in Acetone, $K_A > 200$,[c] S_N2 Reaction			
8.8	154		
44.1	155		
(i) *n*-BuBr + NBu_4Cl in Acetone, K_A = 602,[g] S_N2 Reaction			
19.6	0.504	0.444	1.14
48.2	0.580	0.392	1.18
452	0.648	0.386	1.68

[a] k_2^{μ} is the rate constant at ionic strength μ corresponding to the concentration of MY. [b] The degree of dissociation of MY is calculated from $K_A = (1 - \alpha)/\alpha^2 C\gamma_{\pm}^2$, using for acetone $\log \gamma_{\pm} = -3.760\,[\sqrt{\mu}/(1 + \sqrt{\mu}) - \mu/3]$ and $\mu = \alpha c$ in an iterative computer program. [c] Based on K_A for related salts. [d] W. E. Thompson and C. A. Kraus, *J. Amer. Chem. Soc.*, **69**, 1016 (1947). [e] This work. [f] A. C. Harkness and H. M. Daggett, *Can. J. Chem.*, **43**, 1215 (1965). [g] Reference 39.

form ion pairs of comparable stability ($\log K_A \approx 2.2$) with NBu_4^+ in acetone. Similar behavior is expected in 1,2-dichloroethane with $\log K_A$ remaining much the same (3.8)[35] for different anions. Thus, we have two different types of behavior: reactions of lithium chloride and lithium bromide have reactant anion much more strongly ion paired than the transition-state anions, but reactions of tetrabutylammonium salts have reactant anion and transition-state anion ion paired to much the same extent. The situation can be expressed as in eq 7 and 8, following a procedure suggested

$$\begin{array}{ccccr} \mathrm{RX} + \mathrm{Y^-} + \mathrm{M^+} & \rightleftharpoons & \mathrm{YRX^-} + \mathrm{M^+} & & \\ \downarrow\uparrow K_1 & & \downarrow\uparrow K_3 & \longrightarrow \text{products} & (7) \\ \mathrm{RX} + \mathrm{M^+\cdot Y^-} & \overset{K_4}{\rightleftharpoons} & \mathrm{YRX^-\cdot M^+} & & \end{array}$$

$$\text{rate} = k_2^0[\mathrm{RX}]([\mathrm{Y^-}] + (K_3/K_1)[\mathrm{M^+\cdot Y^-}]) \qquad (8)$$

by Kurz.[16] In eq 8 $[\mathrm{M^+\cdot Y^-}]$ and $[\mathrm{Y^-}]$ represent the concentrations of ion pairs and dissociated ions, respectively, and [MY] represents the formal concentration of MY, whether present as ions or ion pairs or both. In eq 8, if $K_3 \approx K_1$, as for NBu_4Y salts, then rate $= k_2^0[\mathrm{RX}]([\mathrm{Y^-}] + [\mathrm{N^+Bu_4\cdot Y^-}]) = k_2^0[\mathrm{RX}][\mathrm{NBu_4Y}]$, *i.e.*, $k_2^{\mu} = k_2^0$. However, if $K_3 \ll K_1$, and $[\mathrm{M^+\cdot Y^-}]$ is not $\gg [\mathrm{Y^-}]$, as for lithium chloride and lithium bromide, then rate $= k_2^0[\mathrm{RX}][\mathrm{Y^-}] = k_2^0[\mathrm{RX}]\alpha[\mathrm{LiY}]$ or $k_2^{\mu} = k_2^0\alpha$ (where α is the degree of dissociation of LiY). Intermediate behavior will be observed depending on the significance of the last term in eq 8.

Thus, reactions of lithium chloride and of lithium bromide in solvents of low dielectric constant are expected to roughly obey the Acree equation (6), but k_2^{μ} is likely to remain fairly constant at different μ, for reactions of tetrabutylammonium salts, provided that our assumption of $K_3 \approx K_1$ in eq 7 is approximately correct.

Some rate constants observed for S_N2 and E2 reactions of lithium chloride and of tetraalkylammonium salts in solvents of low dielectric constant are in Table IV. Degrees of dissociation, α, were calculated from K_A and Debye–Hückel activity coefficients, using an iterative procedure and the equation of Davies.[35] It can be seen that k_2^{μ} is more or less constant for reactions of any NR_4Y species over a considerable range of ionic strength. Particularly striking is the constancy of k_2^{μ} for the reaction of NEt_4Cl (K_A = 19,600) in 1,2-dichloroethane (Σ = 10.2) with methyl iodide. This should be compared with the substantial decrease in k_2^{μ} as μ increases, for the reaction of a stronger electrolyte, lithium chloride (K_A = 6110), in acetonitrile (Σ = 37.5) with methyl iodide.

In some cases k_2^{μ} increases slightly with increasing ionic strength; in other reactions k_2^{μ} decreases. We have not been able to analyze satisfactorily the rate data in Table IV in terms of eq 8, possibly because unknown changes in the activity coefficients of alkyl halides and of ion pairs, and unknown differences between the activity coefficients of reactant anions and transition-state anions at different ionic strengths, need to be considered in the derivation of eq 8. Sneen and Rolle have demonstrated the difficulties.[36] We merely note that k_2^{μ} does not change substantially with changes of μ, nor would we expect it to for reactions of tetraalkylammonium salts in acetone or in 1,2-dichloroethane (this despite significant ion pairing of the salts, in these solvents). For this reason, in this series of papers we have not applied the Acree eq 6 to our observed rates, but have chosen to make measurements on reactions of 0.01–0.06 M NBu_4Y in acetone and to compare the k_2^{μ} values, in the assumption that k_2^{μ} is constant within this range of ionic strength. This assumption has proved to be precisely justified in the frequent cases when it has been tested by experiment.

Experimental Section

Reagents. Commercial samples of 2,6-lutidine, *tert*-butyl bromide, methyl iodide, and *n*-butyl bromide were redistilled. Acetone was purified in the usual way.[37] Salts were purified and handled as previously described[37-39] or by methods comparable with those described below.

Kinetics and Products. Reactions were run in sealed ampoules. Acid was titrated by diluting aliquots with *ca.* 20 ml of cold dry

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(36) R. A. Sneen and F. R. Rolle, *J. Amer. Chem. Soc.*, **91**, 2140 (1969).

(37) S. Winstein, P. E. Klinedinst, and G. C. Robinson, *ibid.*, **83**, 885 (1961).

(38) M. B. Reynolds and C. H. Kraus, *ibid.*, **70**, 1709 (1948).

(39) L. G. Savedoff, *ibid.*, **88**, 664 (1966).

acetone and titrating with sodium methoxide, *p*-hydroxyazobenzene, or thymol blue being used as indicator under a nitrogen blanket. Halide ion was estimated by pouring aliquots into *ca.* 20 ml of cold carbon tetrachloride or pentane and extracting twice with cold water. The aqueous extract was then analyzed for halide ion by potentiometric titration with silver nitrate. Appropriate blank experiments established the validity of both procedures.

The reactions of *n*-butyl bromide or of methyl iodide were followed by pouring aliquots into *ca.* 20 ml of water and titrating for halide ion, potentiometrically with silver nitrate. No acid was formed and base consumed corresponded to halide ion produced. Reactions of red *p*-nitrothiophenoxide (ArS) with *tert*-butyl bromide were performed under nitrogen. The aliquots were diluted with acetone and titrated with tosylic acid in ethanol until the red color disappeared. This gave the amount of unconsumed $\mathrm{ArS^-}$. The solution was then treated with excess triethylamine and analyzed spectrophotometrically. This gave the total of ArSH and $\mathrm{ArS^-}$ present; thus the two titrations gave the $\mathrm{ArS^-}$ consumed in any SN2 process, and the proportion of substitution and elimination. Mixed halide titrations were carried out potentiometrically with silver nitrate in the presence of barium nitrate. Azide, cyanide, acetate, nitrite, and *p*-nitrophenoxide in acetone were estimated by titration with tosylic acid in ethanol using Bromphenol Blue as indicator, after previously titrating just to the thymol blue end point of the conjugate acid, with sodium methoxide as titrant. Blank experiments justified these procedures. Reactions of *p*-nitrophenoxide ion at very low concentrations were followed spectrophotometrically.

tert-Butyl chloride and 2-methylpropene were estimated by vpc on a 10% Carbowax 1500, 3-m column at 50°. Methylcyclohexane was the internal standard and detection was by a flame ionization detector.

Association Constants. These were determined conductimetrically using a Universal Bridge B221 at a frequency of 1592 Hz. The cell constants were determined with $\mathrm{Bu_4N^+Ph_4B^-}$ in 1,2-dichloroethane.[40] An oil thermostat at 25 ± 0.005° was used. Association constants were calculated from the Fuoss–Onsager–Skinner equation[41] using an IBM 360/50 computer. Manipulations with hygroscopic compounds were carried out in a drybox. A dielectric constant of 20.47 and a viscosity of 0.00304 P for acetone[38] were used in the calculations.

Tetrabutylammonium Salts. Many of the salts are extremely hygroscopic, some have a tendency to crystallize as acidic material, *e.g.*, $\mathrm{NBu_4H(OAc)_2}$, and others tend to decompose in highly concentrated syrups at elevated temperatures. A key step in their purification is filtration of benzene solutions through activity 1 basic alumina. Three procedures were used to obtain methanolic solutions of the salts.

(a) $\mathrm{NBu_4I + AgX \rightarrow NBu_4X + AgI}$, in Methanol, for X = $\mathrm{N_3}$, $\mathrm{NO_2}$, and Acetate. The use of explosive silver azide is hazardous, so preparations were always on a small scale using a slurry of moist silver azide. Supernatant liquor was tested for the absence of iodide ion with acidified silver nitrate, prior to removal of methanol.

(b) $\mathrm{NBu_4OMe + HX \rightarrow NBu_4X + HOMe}$ in Methanol for X = Cl, Br, $\mathrm{ClO_4}$, $\mathrm{SC_6H_4NO_2}$-*p*, $\mathrm{OC_6H_4NO_2}$-*p*, $\mathrm{SC_6H_5}$, $\mathrm{OC_5H_5}$. Tetrabutylammonium iodide was recrystallized from dilute acetone to mp 145–146° and 0.135 mol was dissolved in 200 ml of methanol. Excess (0.095 mol) freshly prepared silver oxide was washed with methanol and added with stirring. Stirring was continued until the supernatant liquor gave no test for iodide with acidified silver nitrate. The solution was then filtered and neutralized with the appropriate acid in methanol.

(c) $\mathrm{NBu_4ClO_4 + KX \rightarrow NBu_4X + KClO_4}$ in Methanol for X = CN and SCN. Tetrabutylammonium perchlorate in methanol was prepared as described in b or precipitated from $\mathrm{NBu_4Br}$ + $\mathrm{NaClO_4}$ in dilute methanol, then dissolved in methanol, and stirred with an equimolar proportion of the potassium salt. The solution was filtered and concentrated on a rotary evaporator. The solution was filtered twice during the evaporation to remove traces of $\mathrm{KClO_4}$. Later recrystallizations led to a purer product.

The methanolic solutions were diluted with 100 ml of benzene and the solvents removed under reduced pressure on a rotary evaporator at temperatures below 50°. This procedure gave crystalline $\mathrm{NBu_4ClO_4}$, mp 213°, $\mathrm{NBu_4Br}$, mp 119°,[38] $\mathrm{NBu_4BF_4}$, $\mathrm{NBu_4SC_6H_5}$-$\mathrm{NO_2}$-*p*, mp 110°, and $\mathrm{NBu_4SCN}$. The salts were recrystallized from ethyl acetate, or acetone–ether mixtures at −40°, filtered, washed with dry ether, and dried at 1 mm at 100° ($\mathrm{NBu_4SC_6H_5}$-$\mathrm{NO_2}$-*p* at room temperature). The other salts gave viscous residues which were taken up in benzene and filtered through activity 1 basic alumina. The benzene was removed below 50° on a rotary evaporator. $\mathrm{NBu_4Cl}$ was recrystallized from ethyl acetate–ether, filtered under dry nitrogen, and washed thoroughly with dry ether. It was stored over $\mathrm{P_2O_5}$ and dried as a melt at 110° and 1 mm just prior to use. $\mathrm{NBu_4N_3}$ was recrystallized from benzene–pentane, and $\mathrm{NBu_4OAc}$ (mp 95–98°) from benzene–pentane–ethyl acetate in the proportion 5:4:2 at −25°. The crystalline samples of $\mathrm{NBu_4CN}$, $\mathrm{NBu_4NO_2}$, $\mathrm{NBu_4OC_6H_4NO_2}$-*p*, mp 145°, $\mathrm{NBu_4SC_6H_5}$, and $\mathrm{NBu_4OC_6H_5}$ were recrystallized from dry ether at −40° and were dried thoroughly at 1 mm.

The acetone solutions were made up by thoroughly drying the salts in a small boat in a test tube in a drying pistol at 1 mm and *ca.* 80°. The test tube was then stoppered and quickly weighed and the boat introduced into a volumetric flask containing acetone. The boat was removed and the concentration of base was checked *vs.* silver nitrate (halides, SCN) or acid (CN, $\mathrm{N_3}$, $\mathrm{NO_2}$, $\mathrm{SC_6H_4}$-$\mathrm{NO_2}$-*p*, $\mathrm{OC_6H_5NO_2}$-*p*, OAc, $\mathrm{OC_6H_5}$, $\mathrm{SC_6H_5}$) using Bromphenol Blue as indicator except for red $\mathrm{SC_6H_4NO_2}$-*p* which is its own indicator. All salts gave >95% of the expected base and were free of acid, as shown by titration with NaOMe to an immediate Thymol Blue end point. The solutions were stable under the reaction conditions, but $\mathrm{NBu_4OAc}$, $\mathrm{NBu_4CN}$, $\mathrm{NBu_4SC_6H_5}$, and $\mathrm{NBu_4}$-$\mathrm{SC_6H_4NO_2}$-*p* lost base at elevated temperatures (*ca.* 75°) in acetone over 48 hr.

The $\mathrm{NBu_4N_3}$, $\mathrm{NBu_4ClO_4}$, $\mathrm{NBu_4SC_6H_4NO_2}$-*p*, $\mathrm{NBu_4OAc}$, and $\mathrm{NBu_4Cl}$ salts analyzed satisfactorily for C, H, and N, confirming that the ammonium cation was fully butylated. Salts were stored over phosphorus pentoxide at *ca.* 5°.

Reaction Products. Some features of reactions of *tert*-butyl bromide in acetone have been discussed by Winstein, Smith, and Darwish.[4] A solution of *tert*-butyl bromide in dry acetone at 50° develops initially a small amount (3–5%) of acid and bromide ion. This levels off and then, as a reaction with the solvent proceeds, very slowly increases again. Similar behaviour is observed in solvent nitromethane.[8] Addition of lithium perchlorate does not change this behavior, but addition of 2,6-lutidine, pyridine, or similar bases prevents the leveling off and *ca.* 96% of the theoretical acid and bromide ion is formed upon completion of reaction.[4]

A little (3 ± 1%) *tert*-butyl chloride is formed during runs with excess lithium or tetrabutylammonium chloride, whether 2,6-lutidine is present or not. 2-Methylpropene is the major product, the yield corresponding to the acid produced (90–96%).[4] Similar behaviour was observed by Cook and Parker[9] for the corresponding reactions in dimethylformamide.

Some tetrabutylammonium salts (*e.g.*, $\mathrm{NBu_4OAc}$) decompose upon prolonged heating in acetone at 75°, presumably to give tributylamine and 1-butene, or butyl derivatives. However, reaction times for all reactions of *tert*-butyl bromide with these salts were much less than the time needed for detectable decomposition of $\mathrm{NBu_4X}$. Lutidinium salts in acetone containing 2,6-lutidine do not add to 2-methylpropene at 50°.

The reactions of *tert*-butyl bromide with $\mathrm{NBu_4N_3}$ (Table I) produced only 82% acid for every mole of bromide ion, at all stages of reaction, whether 2,6-lutidine was present or not. The reactions were too fast for loss of acid due to decomposition of hydrazoic acid to be serious. The remaining 18% of the bromide ion produced is assigned to an SN2 reaction of azide ion with *tert*-butyl bromide. Azide ion has a strong tendency to utilize loose SN2 transition states,[9,22] in competition with E2C-like transition states. Rate constants for acid production were calculated on the basis of 82% theoretical acid and agreed with rate constants for bromide ion production.

Analytical Procedures. Chloride, bromide, iodide, and thiocyanate ions were estimated and identified by potentiometric titration with silver nitrate of acidified aqueous solutions which had been extracted from carbon tetrachloride to remove *tert*-butyl bromide. Azide, $\mathrm{NO_2}$, $\mathrm{CH_3CO_2}$, $\mathrm{SC_6H_4NO_2}$-*p*, $\mathrm{OC_6H_4NO_2}$-*p*, and CN were titrated, in cold acetone containing the reaction mixture, with HCl in 90% acetone–water using Bromophenol Blue as indicator. *p*-Nitrothiophenoxide was its own indicator. Acid was estimated by titration of the reaction mixture in cold acetone with sodium methoxide in methanol to the Thymol Blue, or *p*-hydroxyazobenzene end point where possible, under nitrogen.

Rate Constants. Production of both bromide ion and acid were followed. In the presence of 2,6-lutidine in acetone, the dehydrobromination, as well as the SN2 substitution, effectively consumed

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(40) J. J. Zwolenik and R. M. Fuoss, *J. Phys. Chem.*, **68,** 903 (1964).

(41) R. M. Fuoss, L. Onsager, and J. F. Skinner, *ibid.*, **69,** 2581 (1965).

1 mol of reactive base, X⁻, per mole of bromide produced. The base is lost because the unreactive heteroconjugate, lutidinium hydro X, is stable in acetone.[22-26] Thus, rates of the concurrent SN2 and E2 reactions followed a single second-order rate expression (9). This expression is useful for *recording* rates, but we do not

$$\frac{d[\mathrm{Br}^-]}{dt} = k_2(a - x)(b - x) \tag{9}$$

give it much mechanistic significance (*cf.* eq 4). The combined rate constant, k_2 in eq 9, can be split into its elimination and substitution components through the fraction of elimination $F_E = [\mathrm{H}^+]/[\mathrm{Br}^-]$, *i.e.*, $k^E = F_E k_2$. Rate expression 9 was used also for the SN2 reactions of *n*-butyl bromide (Table II).

For reactions in acetone of Cl^-, OAc^-, CN^-, and $\mathrm{NO_2}^-$, if 2,6-lutidine was absent, stable homoconjugates, *e.g.*, $\mathrm{HCl_2}^-$, etc., are formed and these remove 2 mol of reactive base per mole of bromide ion produced by dehydrobromination.[4,22-26] Rate expression 10 must be used to record rates as k_2, if acid production is followed.

$$k_2 = \frac{2.303}{(b - (1 + F_E)a)} \times \Delta t \Delta \log \frac{b - [\mathrm{H}^+](1 + F_E)}{[\mathrm{H}^+]_\infty - [\mathrm{H}^+]} \tag{10}$$

In eq 10, F_E is the fraction of dehydrobromination to total bromide ion produced, b is the initial stoichiometric concentration of $\mathrm{NBu_4Cl}$, and a is the initial concentration of *tert*-butyl bromide.

The dehydrobromination in dimethylformamide by chloride ion fitted rate expression 11 when bromide ion and acid were followed.[9] Solvent DMF is more basic than acetone, so that $\mathrm{HCl_2}^-$ and lutidinium hydrochloride are less stable in DMF. Thus, reactive chloride ion is not removed by both elimination and substitution, as in acetone, but only disappears according to the fraction of substitution, represented by F_S in eq 11.

$$\frac{d[\mathrm{Br}^-]}{dt} = k_2(a - [\mathrm{Br}^-])(b - F_S[\mathrm{Br}^-]) \tag{11}$$

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The E2C Mechanism in Elimination Reactions. IV.[1] Primary Hydrogen Isotope Effects

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Abstract: Primary hydrogen isotope effects (k^H/k^D) on the rate of some halide-induced dehydrotosylations of alkyl tosylates in acetone (E2C-like reactions) are 2.3–3.2. This is considerably less than for many E2 reactions promoted by strong hydrogen bases (E2H-like reactions). The dehydrotosylation of 3-methyl-2-butyl tosylate by sodium ethoxide in ethanol gives $k^H/k^D = 2.6$ for formation of the Saytzeff olefin, 2-methyl-2-butene, but k^H/k^D is 6 for formation of the Hofmann olefin, 3-methyl-1-butene. These observations confirm the need for a spectrum of E2 transition states, positions in the spectrum depending on the nature of the base and of the substrate. The β-hydrogen isotope effect on the rate of substitution reactions accompanying E2C-like reactions is negligible, *i.e.*, $k^H/k^D = 1$, but there is a small isotope effect on the combined substitution and elimination reactions. This confirms that C_B–H bonding is different in the transition states leading to substitution and elimination products. The small kinetic isotope effects in E2C-like reactions do not distinguish between a nonlinear configuration, or an asymmetric linear configuration, of C_β, H_β, and base in the transition state but they are in accord with a paene olefin E2C-like transition state.

The hydrogen isotope effect on rates of elimination and substitution reactions enables us to focus attention on the behavior of the C_β–H bond in the respective transition states.[3-10] We will discuss the isotope effect on eliminations in terms of structures I and III, *i.e.*, the E2H–E2C spectrum of transition states. The spectrum has been described elsewhere[11-14] and will be further justified in this series of papers.

The kinetic hydrogen isotope effect for reactions proceeding through E2H-like transition states I, *i.e.*, those with a linear configuration of C_β, H, and base, B, has been observed on numerous occasions in the reactions of strong hydrogen bases, such as alkoxides, with alkyl and aralkyl halides.[5-7,10] At 25°, k^H/k^D is most often between 6 and 7,[5] but lower values are

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(1) Part III: D. A. Palmer, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2228 (1972).

(2) Deceased Nov 23, 1969.

(3) L. Melander, "Isotope Effects in Reaction Rates," Ronald Press, New York, N. Y., 1960.

(4) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1962).

(5) D. V. Banthorpe, "Elimination Reactions," Elsevier, London, England, 1963.

(6) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 228 (1962).

(7) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

(8) V. J. Shiner, *J. Amer. Chem. Soc.*, **74**, 5285 (1952).

(9) J. L. Longridge and F. A. Long, *ibid.*, **89**, 1292 (1967).

(10) K. T. Finley and W. H. Saunders, Jr., *ibid.*, **89**, 898 (1967); A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, Jr., *ibid.*, **89**, 901 (1967).

(11) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *ibid.*, **92**, 115 (1970).

(12) D. Cook, A. J. Parker, and M. Ruane, *Tetrahedron Lett.*, 5715 (1968).

(13) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *ibid.*, 2113 (1968).

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