Mode of Solvent Participation in Solvolysis Reactions at a Tertiary Carbon Atom[1]

F. G. Bordwell,* Paul F. Wiley,[2a] and Thomas G. Mecca[2b]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received March 27, 1974*

Abstract: Solvolysis of tertiary allylic bromide $p\text{-}CH_3C_6H_4SO_2CH{=}CHC(Br)Me_2$ (**3b**) was found to resemble that of *i*-PrBr rather than *t*-BuBr in: (a) rate, (b) low sensitivity to solvent ionizing power ($m = 0.56$), (c) high sensitivity to added azide ion, and (d) correlation of product distribution with mole fractions in aqueous methanol. Response of the tertiary allylic system (**3**) to three other probes [(a) β-secondary deuterium isotope effects, (b) mesylate bromide leaving group effect, and (c) a Taft correlation] was, however, similar to *t*-BuX rather than *i*-PrX. These results are interpreted as being consistent with nucleophilic attack on an intimate ion pair (S_N2^{II}-ion-pair mechanism), or an S_N2^{I} mechanism leading to the formation of an ion-pair intermediate.

In his pioneering investigations of the acetolyses of secondary arene sulfonates and related substrates Winstein accumulated convincing evidence for an ionization mechanism involving at least two kinds of ion pairs, intimate and solvent separated.[3] Supporting evidence has come from many other laboratories, particularly that of Goering,[4] and the presence of ion-pair intermediates in solvolyses has been demonstrated by at least eight separate tests.[5] It is now apparent that ionizations involving ion-pair intermediates are much more common than was formerly appreciated, not only in acetolyses but also in solvents of much greater ionizing power.

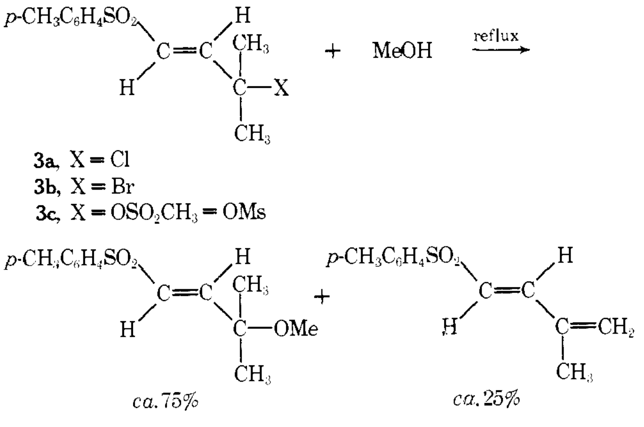
Winstein and Grunwald selected *t*-BuCl as a substrate likely to solvolyze without nucleophilic participation by the solvent, *i.e.*, exhibit limiting (Lim) behavior. This substrate was used as a reference standard to test the sensitivity (m) of a substrate to solvent ionizing power (Y).[6] A Lim solvolysis could conceivably involve ionization to free R^+, but Cocivera and Winstein found that the per cent alkene generated in the solvolysis of *t*-BuX substrates varied appreciably with the nature of X (Cl, Br, I, and SMe_2) in EtOH and HOAc and varied slightly in water.[7] It follows that ion pairs assume important roles even in Lim solvolyses. A similar conclusion can be drawn concerning hydrolyses of *t*-BuCl and related chlorides in 80% acetone in the presence of azide ion.[8] At one time the selectivity of cationoid species toward azide ion, as indicated by the $k^{N_3^-}/k^{H_2O}$ ratio, was believed to be a measure of the relative stability of the free cation, R^+, generated in these hydrolyses.[8] Ritchie has shown, however, that stable cations of three different types all exhibit the *same* sensitivity to azide ion in a given solvent (*i.e.*, the same N_+ value).[9] The N_+ value in water (>5.4) is higher than that of the most reactive chloride (Ph_3CCl) in 80% acetone. The different sensitivities displayed by *t*-BuCl, $CH_2{=}CHCMe_2Cl$, $(p\text{-}MeC_6H_4)_2CHCl$, and like chlorides in 80% acetone[8] must then be associated with ion pairing. It may be that ion pairs of a single type have different sensitivities depending on the nature of the cation, or, more likely, that different types of ion pairs (intimate, one-solvent separated, two-solvent separated, etc.[9]) differ in their sensitivities from one another and from the free cation. Indeed, Ritchie has obtained evidence for more than one type of cationoid species in the methanolysis of *p,p′*-dimethoxybenzhydryl mesitoate in the presence of varying concentrations of azide ion.[10]

Further insight into solvolysis mechanisms has been provided by use of adamantyl halides and tosylates as standards, wherein nucleophilic solvent participation is precluded, to define the Lim mechanism. Comparison of 1-AdBr and *t*-BuBr in a wide variety of solvents has established a linear correlation, indicating that the solvolysis of *t*-BuBr is indeed Lim in that nucleophilic solvent participation is lacking.[11a] In other words, the adamantyl systems have Grunwald–Winstein m values near that for *t*-BuCl or *t*-BuBr ($m = 1.2$ for 1-AdBr, 0.99 for 1-AdOTs),[11] which supports Winstein's view that an m value near 1.0 is good evidence for a Lim mechanism. The relatively small *t*-BuBr:*i*-PrBr solvolytic rate ratio (α-Me/α-H effect) compared to 2-Me-2-AdOTs:2-AdOTs (*ca.* 10^4 *vs.* 10^8) indicates, therefore, that *i*-PrBr must be experiencing appreciable nucleophilic solvent assistance (*ca.* 10^4).[12]

Our work has been concerned with a tertiary substrate, $ArSO_2CH{=}CHCMe_2X$, which, like 1-AdX, is of low solvolytic reactivity, but for electronic rather than steric reasons. In the previous two papers in this series[13,14] we showed that the behavior toward nucleophiles of the tertiary bromide $ArSO_2CH{=}CHC(Br)Me_2$ (**3b**) was strikingly different from that of the corresponding primary bromide, or that of ordinary primary aliphatic bromides. Instead, the reactions of **3b** with nucleophiles resembled in many respects those of *t*-BuBr. In the present paper we compare the behavior of **3b** in solvolysis reactions with that of *t*-BuBr and *i*-PrBr.

Results

The preparation of primary, secondary, and tertiary substrates, $ArSO_2CH{=}CHCH_2X$ (**1**), $ArSO_2CH{=}CHCH(X)Me$ (**2**), and $ArSO_2CH{=}CHC(X)Me_2$ (**3**) (X = Cl, Br, OSO_2CH_3) and their methanolyses has been described previously.[15]



3a, X = Cl
3b, X = Br
3c, X = OSO_2CH_3 = OMs

The hexadeuterio analog of tertiary bromide **3b** was prepared from bis(trideuteriomethylvinyl)carbinol by the method previously described for **3b**.[15] The carbinol was obtained from the reaction of vinylmagnesium bromide with

Table I. Solvolysis Data for Reactions of 3-Bromo-3-methyl-1-*p*-tolylsulfonyl-1-butene, *p*-$MeC_6H_4SO_2CH{=}CHC(Me)_2Br$, **3b** at 50°

RX	Solvent[a]	10^5k_1,[b] sec^{-1}
3b	100 MeOH	0.38
	90 MeOH	1.07
	80 MeOH	2.35
	60 MeOH	10.3
	60 MeOH	12.2[c]
	50 MeOH	26.9
	80 EtOH	0.885
	70 EtOH	1.99
	60 EtOH	8.12
$N{\equiv}CCH{=}CHC(Br)Me_2$	80 MeOH	5.9
	60 MeOH	33.4
	60 MeOH[c]	40.8
	50 MeOH	73.8
t-BuBr[d]	60 MeOH	13,700
$H_2C{=}CHC(Me_2)Br$[e]	80 EtOH	*ca.* 10^{10}

[a] Volume per cent alcohol before mixing; the balance is water. [b] Average of at least three runs with standard deviations of less than 5%, unless otherwise noted; the rate of bromide ion release was determined potentiometrically with silver nitrate. [c] $LiClO_4$ (0.3 *M*) present. [d] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79,** 1602 (1957). [e] Estimated from solvolysis data for $H_2C{=}CHC(Me_2)Cl$, assuming $k^{Br}/k^{Cl} \cong 30$.

Table II. Rates of Solvolysis of $ArSO_2CH{=}CHCR_1R_2X$ (**1, 2,** and **3**) in 60% (v/v) Methanol–Water at 50°

RX	R_1	R_2	X	[Salt][a]	10^6k, sec^{-1}
1b	H	H	Br	0.0	3.26
2b	CH_3	H	Br	0.0	1.80
3b	CH_3	CH_3	Br	0.0	103
3b	CH_3	CH_3	Br	0.3	122
3b-d_6	CH_3	CH_3	Br	0.3	64.2
Allyl bromide				0.0	77.0

[a] $LiClO_4$ was used to maintain constant ionic strength.

Table III. Solvolyses of γ-*p*-Tolylsulfonyl-α,α-dimethylallyl Methanesulfonate (**3c**) and Its Hexadeuterated Derivative (**3c**-d_6)

RX	Solvent[a]	*T*, °C	10^3k,[b] sec^{-1}
3c	100 MeOH	0	0.162
3c	100 MeOH	25	3.52 ± 0.02
3c	100 MeOH	25	3.09[c]
3c	100 MeOH	25	3.00[d]
3c	100 MeOH	25	3.10[e]
3c	90 MeOH	25	7.97
3c	80 MeOH	25	16.9
3c	100 MeOH	50	47.9[f]
3c	80 EtOH	25	9.25
3c	aq EtOH[g]	25	1.63[g]
3c	100 AcOH	25	2.0[h]
3c-d_6	100 MeOH	25	2.01 ± 0.02
3c-d_6	80 MeOH	25	9.36

[a] Volume per cent alcohol before mixing; the balance is water. [b] Average of at least three runs with standard deviations of less than 5%, unless otherwise noted. [c] Nitrobenzene (0.4 *M*) present. [d] Piperidine (0.2 *M*) present. [e] Aniline (0.2 *M*) present. [f] Extrapolated assuming E_a = 20 kcal/mol. [g] Calculated for aqueous EtOH having $Y = -1.639$ (the value for AcOH). [h] The average of 8 runs with a standard deviation of 15%.

hexadeuterioacetone (Diaprep).

The β-methyl derivative of **3b** was obtained from 1-*p*-tolylsulfonyl-2,3-dimethyl-2-butene (from $C_7H_7SO_2Na$ and $Me_2C{=}CMeCH_2Br$ in EtOH) in the manner described earlier for the preparation of **3b**. The nmr spectrum, ir spectra, and carbon and hydrogen analysis for the resulting 1-*p*-tolylsulfonyl-3-bromo-2,3-dimethyl-1-butene, mp 74.5-75.5° (95% EtOH), were consistent with the assigned structure.[15]

Rates of solvolyses of the tertiary bromide **3b** in aqueous methanol and aqueous ethanol are summarized in Table I, together with data for the cyano analog and related tertiary bromides.

Least-squares analysis of the data in Table I gave a Grunwald-Winstein *m* value of 0.55 ± 0.02 (r = 0.9993) with log $k_0 = -4.82$ for bromide **3b** in aqueous MeOH, 0.58 ± 0.02 (r = 0.9999) with log $k_0 = -5.05$ for bromide **3b** in aqueous EtOH, and 0.69 ± 0.01 (r = 0.9999) with log $k_0 = -4.494$ for the $N{\equiv}CCH{=}CHC(Br)Me_2$ in aqueous MeOH.

The solvolysis rates in 60% MeOH of primary bromide **1b,** secondary bromide **2b,** tertiary bromide **3b,** and the hexadeuterio derivative of **3b** (**3b**-d_6) are given in Table II.

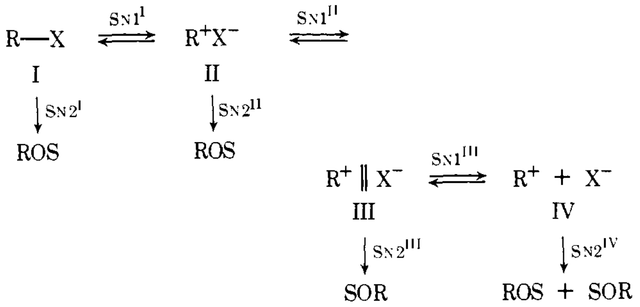
Table III summarizes rate data for the solvolysis of tertiary mesylate **3c** determined conductometrically.

The Grunwald-Winstein *m* constant for aqueous methanol determined from the data in Table III is 0.46 (± 0.01; r = 0.9998) with log $k_0 = -1.95$.

Dicussion

It will be convenient to discuss the mechanistic possibilities using Scheme I, a modification of Winstein's ion-pair mechanism.[5]

Scheme I



From the evidence presented in the introduction it appears that solvolysis of *t*-BuX involves ion-pair intermediates and that the role of the solvent is to effect the separation of the R^+ and X^- ions by solvation rather than by nucleophilic attack on R^+ (Lim solvolysis). In terms of Scheme I the mechanism will be of an S_N1 type (S_N1^I, S_N1^{II}, or S_N1^{III}) rather than an S_N2 type. On the other hand, on the basis of the small α-Me/α-H effect, *i*-PrBr is assigned an S_N2-type mechanism. The latter assignments holds also for *i*-PrOTs as shown by the high $k^{i\text{-PrOTs}}/k^{2\text{-AdOTs}}$ ratios observed in nucleophilic solvents, such as aqueous ethanol.[16] In order to facilitate mechanistic assignment for solvolysis of the tertiary system *p*-$MeC_6H_4SO_2CH{=}CHC(X)Me_2$ (**3**) the data from Tables I-III have been collected in Table IV and compared with that for *i*-PrX (or MeX) and *t*-BuX.

Nucleophilic Solvent Participation. Examination of Table IV shows that in many respects tertiary bromide **3b** resembles *i*-PrBr rather than *t*-BuBr in behavior. Like *i*-PrBr, its solvolysis rate is *ca.* 4 powers of ten less than that of *t*-BuBr. The *m* values for bromide **3b** and mesylate **3c** are close to those of *i*-PrBr and *i*-PrOTs, and much smaller than that of *t*-BuCl or *t*-BuBr. Like *i*-PrX (or MeX) bromide **3b** is highly sensitive to introduction of azide ion. In fact, the rate for **3b** in MeOH is first order in azide ion. The α-Me/α-H effect for system **3** is even lower than that for simple alkyl halides. All of these data point to extensive nucleophilic solvent participation for **3.** This interpretation is supported by the observation that the product distribution for solvolysis of bromide **3b** in aqueous methanol corre-

Table IV. Behavior of Secondary and Tertiary Substrates in Solvolysis Reactions

$(\text{Ratio})_{\text{Sol}}{}^{X\,a}$	*i*-PrX or MeX	p-$C_7H_7SO_2CH{=}CHCMe_2X$	*t*-BuX
$(k_{\text{rel}}{}^{\text{Sol}})_{60\%\ \text{MeOH}}{}^{\text{Br}}$	4^{b}	(1.0)	(4.3×10^{4})
$(m)_{\text{aq alc}}{}^{\text{Br}}$	0.54^{c}	$0.56^{d,e}$	0.94–1.1
$(m)_{\text{aq MeOH}}{}^{\text{OMs}}$	0.42	0.46	
$(k^{N_3^-}/k^{\text{Sol}})_{\text{MeOH}}{}^{\text{Br}}$	$60{,}000^{f}$	6000^{g}	14.5^{h}
$(\alpha\text{-Me}/\alpha\text{-H})_{80\%\ \text{EtOH}}$		$10^{1.8}$	$10^{3.7}$
$(k_{\text{aq alc}}/k_{\text{AcOH}})_{Y}{}^{\text{OMs}}$	7.8	0.82	(1.0)
$(k^{\beta\text{-H}}/k^{\beta\text{-D}})^{i}{}_{60\%\ \text{MeOH}}{}^{\text{Br}}$	1.02^{j} 1.189^{k}	1.38 ± 0.02^{l}	1.34^{m}
$(k^{\text{OMs}}/k^{\text{Br}})_{60\%\ \text{MeOH}}$	46^{n}	12,600	$>4000^{o}$

[a] X is the leaving group, and Sol is the solvent. [b] *i*-PrBr. [c] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5937 (1957). [d] Average of values in aqueous MeOH (0.55) and aqueous EtOH (0.58). [e] For $N{\equiv}CCH{=}CHCMe_2Br$ in aqueous MeOH $m = 0.69$ (Table I). [f] MeI: R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968). [g] In 60% MeOH $k_N/k_S = 2165$. [h] In 80% acetone: R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, **88**, 2594 (1966). [i] Per CD_3 group. [j] EtBr in H_2O. [k] *i*-PrOBs in 50% EtOH. [l] For mesylate **3c** the value is 1.33 ± 0.01 in MeOH and 1.34 ± 0.01 in 80% MeOH. [m] *t*-BuCl in 50% EtOH. [n] *i*-PrX in 80% EtOH. [o] H. M. R. Hoffmann, *J. Chem. Soc.*, 6753 (1965). [p] *i*-PrOTs.

sponds reasonably well to the mole fractions of methanol and water present. This contrasts sharply with the results with *t*-BuCl where the amount of ether formed is greatly in excess to that expected.[17] The only piece of data inconsistent with this interpretation is the smaller rate of reaction of mesylate **3c** in the more nucleophilic solvent, ethanol, than acetic acid at constant *Y*.

Evidence for Carbonium Ion Character. The β-secondary deuterium isotope effect for **3** in 60% MeOH is markedly higher than that of *i*-PrBr or *i*-PrOBs. Instead the value for bromide **3b** is close to that observed for *t*-BuCl.[18] Similar high values were also observed for mesylate **3c** in MeOH and in 80% MeOH (Table IV footnote *l*).

Changing the leaving group from bromide to mesylate for **3** caused a dramatic increase in solvolysis rate (12,600-fold). This is to be contrasted with *i*-PrX where a change from bromide to tosylate caused only a 46-fold acceleration. Large sulfonate/bromide leaving group effects have been interpreted as diagnostic of an ionic-type reaction process,[19] but steric ground-state strain also appears to be a highly important factor.[11b,20]

Further strong evidence for the importance of ionization of the C-X bond in the solvolysis of **3** is evident from the 10^{10}-fold retardation in solvolysis rate in 80% EtOH in going from $H_2C{=}CHC(Br)Me_2$ to p-$MeC_6H_4SO_2CH{=}CHC(Br)Me_2$; this corresponds to a Taft ρ^* of *ca.* −2.5, assuming $\sigma^*_{p\text{-}MeC_6H_4SO_2} = 1.4 \times 2.8$.[21] This estimate of ρ^* is, of course, very crude, since: (a) it is based on only two points, (b) the σ^* for p-$CH_3C_6H_4SO_2$ is a rough estimate, and (c) different types of intermediates are probably involved in the two solvolyses. Nevertheless, it is reassuring to note that the 3.2-fold increase in solvolysis rate for $N{\equiv}CCH{=}CHC(Br)Me_2$ *vs.* p-$MeC_6H_4SO_2CH{=}CHC(Br)Me_2$ is of the order of magnitude expected (*ca.* twofold calculated) based on $\rho^* = -2.5$. Also, introduction of a β-methyl substituent into **3b** leads to an increase in solvolysis rate (2.6-fold in 60% MeOH) as would be expected for an electron-releasing inductive effect. In any event, strong retardation of the solvolysis rate by electron-withdrawing groups is evident, as expected in an ionization mechanism. (Streitwieser obtained $\rho^* = -3.29$ for solvolysis of tertiary chlorides in 80% EtOH.[24])

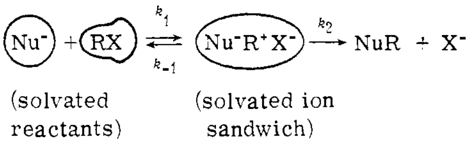
Mechanistic Assignments. In the previous paper in this series comparisons of the behavior of tertiary allylic bromide **3b** and the corresponding primary bromide in reactions with various nucleophiles revealed striking differences. It was concluded that, despite the fact that **3b** underwent kinetically second-order reactions with nucleophiles, its overall behavior toward nucleophiles was much more like that of a tertiary alkyl bromide than a primary alkyl bromide. In this paper we have compared the reactions of **3b**, *i*-PrBr, and *t*-BuBr with protic solvents. As might have been expected from its behavior toward nucleophiles, **3b** resembles *i*-PrBr much more than *t*-BuBr with respect to its susceptibility to nucleophilic solvent participation. On the other hand, it resembles *t*-BuBr more with respect to β-deuterium isotope effects, OMs/Br leaving group effects, and response to electronic substituent effects.

At least three types of mechanisms can be visualized for the reaction of tertiary bromide **3b** with nucleophiles in protic solvents. These differ in the role assigned to the nucleophile and to the solvent. First, we can assume that a classical SN2 mechanism (SN2[I] mechanism) holds, with covalent bond making aiding bond breaking in the usual manner, but with an unusually high degree of C–Br bond breaking in the transition state. This does not account very well for the extensive evidence indicating a close similarity in the mechanisms by which **3b** and *t*-BuBr react with nucleophiles and with protic solvents. Second, we can assume that the mechanism is SN2[II].

$$\text{RBr} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^+\text{Br}^- \xrightarrow{k_2\,(\text{Nu}^-)} \text{NuR} + \text{Br}^- \quad (k_{-1} >> k_2)$$

In this mechanism the C–Br bond is broken heterolytically and reversibly in a preliminary step without participation of the nucleophile, the principal driving force being solvation of the bromide atom. The reaction is then completed by attack of the nucleophile on this intimate ion pair.[25] This mechanism does not account very well for the evidence pointing to nucleophilic solvent participation.

A third possibility is that the nucleophile participates in ion pair (SN2[I]-ion-pair mechanism or ion-sandwich mechanism).[26]



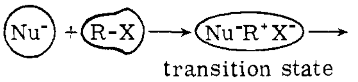
The SN2[I]-ion-pair mechanism differs from the SN2[II] mechanism in that: (a) the nucleophile is involved in ion-pair formation, and (b) k_{-1} need not be greater than k_2. It differs from the SN2[I] mechanism in that nucleophilic participation is looked on as a solvation phenomenon. In essence, reaction is initiated by entrance of RX into the solvent shell of the nucleophile. This will be accompanied by heterolytic scission of the C–Br bond, resulting in a solvated ion sandwich.[27] An important characteristic of this mechanism is that covalent bond formation between Nu^- and R occurs within the ion sandwich.[28] In our opinion it is the most attractive of the three mechanisms in that it can accommodate both varying degrees of nucleophilic participation and varying degrees of heterolytic cleavage of the C–Br bond. A detailed accounting of the manner in which the nucleophile becomes desolvated and covalently bonded to carbon and of the manner in which the bromine atom becomes solvated must await, however, further developments in our knowledge of solvation effects. It is of interest to note, however, that the response of nucleophiles toward tertiary bromide **3b** and analogous systems[29] resembles that of "free" R^+ cations (N_+ values)[9] in that azide ion is particularly reactive and PhS^- (and CH_3COS^-) is much more reactive than CH_3O^-.[29] Ritchie suggests that N_+ values represent the case of desolvation of the nucleophile by the cation in the transition state. In the present instance this would be accompanied by breaking of the C–Br bond and solvation of the resulting R^+X^- ion pair.

The same three mechanisms can, of course, apply to the solvolysis reactions of tertiary bromide **3b,** with the solvent playing the role of the nucleophile. Here the ion-pair mechanisms appear much more likely than the classical SN2$^{\mathrm{I}}$ mechanisms, and again we favor the SN2$^{\mathrm{I}}$-ion-pair mechanism.

The same three mechanisms can apply also to the reactions of tertiary bromide **3b** with nucleophiles in DMF, or in other dipolar aprotic solvents. These solvents are much poorer at solvating anions, and we can expect these reactions to involve ion-pair aggregates.

Although a relatively small amount of data is available, it is amusing to speculate on the mechanism for the reactions of the primary bromide **1b,** $ArSO_2CH{=}CHCH_2Br$, and the corresponding secondary bromide with solvents and nucleophiles. Comparison shows that the relative solvolysis rates for **1b, 2b,** and **3b** in 60% MeOH are: 2:(1.0):60, respectively. These rate differences are surprisingly small when compared to the solvolysis rates for ordinary primary, secondary, and tertiary aliphatic or allylic halides. For example, in 50% EtOH, a solvent of roughly comparable ionizing power to 60% MeOH, the relative solvolysis rates for EtBr:*i*-PrBr:*t*-BuBr are *ca.* (1.0):2.9:5 × 10^4 and for $CH_2{=}CHCH_2Cl{:}CH_2{=}CHCH(Cl)Me{:}H_2C{=}CH\text{-}C(Cl)Me_2$ they are (1.0):81:5.5 × 10^5.[30] The relative rates for **1b, 2b,** and **3b** reacting in an SN2-type reaction with LiN_3 in MeOH are 29:10:(1.0).[14] For EtX *vs.* *i*-PrX, reacting with nucleophiles in protic and dipolar aprotic solvents the average rate ratio is substantially larger than for **1b** *vs.* **2b** (about 40 compared to 2.9),[31] and the larger ratio appears to hold also for $H_2C{=}CHCH_2Cl$ *vs.* $H_2C{=}CHCH(Cl)Me$ reacting with nucleophiles.[31] There is, to our knowledge, no information available concerning the relative reactivity of simple primary and secondary alkyl halides *vs.* tertiary alkyl halides in SN2-type reactions in protic media. (In dipolar aprotic media the relative reactivity of **1b** *vs.* **3b** is *ca.* 1500, which appears to be comparable to that of EtBr *vs.* *t*-BuBr.[14]) The reason is that tertiary halides such as *t*-BuBr react with nucleophiles in protic media to give principally elimination products. (We have suggested reasons earlier as to why tertiary bromide **3b** behaves differently.[14])

In the previous papers we have used the primary bromide **1b** and other primary bromides as models for the classical SN2 mechanism, and have shown that the reactions of these bromides often exhibit characteristics different from those of tertiary bromide **3b.** The data can therefore be rationalized by assuming a change in mechanism: a classical SN2 mechanism for **1b** and an ion-pair mechanism for **3b.** An alternative possibility is to assume that both **1b** and **3b** are reacting by ion-pair mechanisms, but that the mechanisms differ in detail. It is difficult to accept the SN2$^{\mathrm{II}}$-ion-pair mechanism for primary systems, however, since this mechanism assumes that heterolytic cleavage of the C–Br bond occurs without nucleophilic participation. On the other hand, the SN2$^{\mathrm{I}}$-ion-pair mechanism appears to be readily adaptable to the primary system since it invokes nucleophilic participation as providing part of the driving force for heterolytic cleavage of the C–Br bond. Another attractive feature of this mechanism is that it attributes the major part of the driving force for cleavage of the C–Br bond to solvation. There is some evidence to indicate that in the absence of strong solvation forces the energy released on bond making is not sufficient to cause bond breaking, since the free radical analog of substitution on carbon is unknown, although it has been sought for many years.[32] Even attempts to realize intramolecular radical-type substitution reactions on carbon have not been realized.[33] We conclude that the SN2$^{\mathrm{I}}$-ion-pair mechanism is a reasonable possibility for **1b** and **2b.** We have seen above that the behavior of **3b** and *i*-PrBr in solvolysis reactions is often similar (Table IV). The SN2$^{\mathrm{I}}$-ion-pair mechanism therefore appears applicable to *i*-PrBr and to other secondary alkyl substrates, such as cyclohexyl halides.[29] The SN2$^{\mathrm{I}}$-ion-pair mechanism differs from the classical SN2$^{\mathrm{I}}$ mechanism only in that it postulates formation of an *intermediate.* It is, of course, extremely difficult to distinguish between these two mechanisms experimentally. The pictorialization used for the SN2$^{\mathrm{I}}$-ion-pair mechanism can be used for the SN2$^{\mathrm{I}}$ mechanism by merely deleting the reverse arrow and assuming formation of a transition state (energy maximum) rather than an intermediate (energy minimum).



This representation for the classical SN2 mechanism has the advantage of including solvent as an integral part in the picture. It is vague enough to include a whole spectrum of mechanisms where the nucleophile and solvent participate to a different degree or in a different manner in C–X bond breaking. At present it is, of course, impossible to assign precise roles to the nucleophile and to the solvent with respect to C–X bond breaking. No doubt their roles change somewhat as the nature of R–X is changed. The timing of bond making and bond breaking probably also varies, depending on the nature of the nucleophile, the nature of the solvent, and the nature of RX.

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References and Notes

(1) For a preliminary account of part of this work, see F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94,** 2119 (1972).
(2) (a) Visiting Scholar from the Upjohn Co., Kalamazoo, Mich., 1970–1971; (b) National Institutes of Health Predoctoral Fellow, 1968–1971.
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A Study of the Formation and Reactions of Alkane Molecular Ions and Alkyl Cations with Tri-*n*-butylborane by Ion Cyclotron Resonance[1]

Daniel J. Pasto

Contribution from the Departments of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Stanford University, Stanford, California 94305. *Received July 30, 1973*

Abstract: In contract to the conventional mass spectrum of tri-*n*-butylborane (**1**) which is dominated by boron-containing cationic species, the icr spectrum of **1** shows the formation of only low molecular weight ions ($<$ *m/e* 59), including ethane, propane, and butane molecular ions, with essentially no boron-containing species (<5%). This is discussed in terms of a lesser stability of boron-containing cations relative to only C,H-containing cations. A number of reversible reactions of alkane molecular ions and/or alkyl cations with **1** have been characterized by double resonance techniques.

Mass spectral fragmentation patterns and the study of ion–molecule reactions can provide substantial information concerning structures, stabilities, and reactions of ions. The formation of new and unusual ions and the characterization of their reactions is of great current interest. In a study of the mass spectral behavior of trialkylboranes, a number of unique characteristics have been noted.[2] The mass spectra of trialkylboranes is dominated by boron-containing ions of which $C_nH_{2n+2}B^+$ is the dominant series with $C_2H_6B^+$ being, in general, the most abundant ion in the spectra. A second unique feature of the mass spectral behavior of trialkylboranes is the formation of appreciable quantities of alkane molecular ions containing up to twice the number of carbon atoms contained in a single alkyl group attached to the boron. The formation of alkane molecular ions is not observed in the mass spectra of hydrocarbons, except for the parent ion, and hydrocarbon derivatives. The formation of the $C_nH_{2n+2}B^+$ and alkane molecular ions must involve rearrangement processes,[2] and thus the structures of the ions cannot be assigned with certainty. In an attempt to derive information concerning the possible structures of the boron-containing ions and to investigate the gas-phase reactions of these species, a study of the ion cyclotron resonance behavior of tri-*n*-butylborane was undertaken.

Results and Discussion

The icr spectrum of **1** displays only peaks from *m/e* 15 to 59 (Figure 1). A detailed comparison of expanded peak shapes (Figure 2) and relative intensities over a 2×10^{-8} to 1×10^{-4} Torr pressure range indicates that boron-containing ions are present only at *m/e* 40 and 41 ($C_2H_6{}^{10}B$ and $C_2H_6{}^{11}B$) and in very low abundance (<5 and <1% of the total ion current at 2×10^{-8} and 4×10^{-7} Torr, respectively). These features of the icr spectrum are in distinct contrast to the conventional mass spectrum of **1** which contains a large number of C,H- ($C_5 \rightarrow C_8$) and boron-containing peaks above *m/e* 59, and in which boron-containing cationic species are dominant (>60% of the total ion current). The very significant lack of boron-containing cationic species in the icr spectrum of **1** must be due to a lesser stability of the boron-containing cationic species relative to only C,H-containing cationic species, an important conclusion inferred from the observed electron distributions between the products of the fragmentations of the boron-containing ions in the mass spectrometer.[2] The considerably longer residence time and the occurrence of bimolecular ion–molecule reactions in the icr cell provide for a closer approach to the equilibrium distribution of cationic charge between only C,H- and boron-containing ions.[3]

A second characteristic feature of the icr spectrum of **1** is the presence of appreciable quantities of alkane molecular ions ($C_1 \rightarrow C_4$). The intensities of the *m/e* 16, 30, 44, and 58 peaks are far too great to be due to ^{13}C-containing alkyl cations and, thus, must represent alkane molecular ions. Furthermore, some of the reactions of the *m/e* 16, 30, 44, and 58 species, characterized by double resonance techniques,[4] are different from those characterized for the alkyl cations of *m/e* 15, 29, 43, and 57.

The icr spectrum of **1** also contains an unusual peak at *m/e* 59 corresponding to $C_4H_{11}{}^+$. The assignment of this peak as representing $C_4H_{11}{}^+$ is based on the relative intensities of the *m/e* 58 and 59 species. The *m/e* 59 peak is too intense to arise solely from $C_3{}^{13}CH_{10}{}^+$ and, thus, must represent mostly $C_4H_{11}{}^+$ (~77%). Further evidence in support of this assignment is based on observed differences in the reactions of the *m/e* 58 and 59 species (*vide infra*). The intensities of the weak peaks at *m/e* 31 and 45 are consistent

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* Address correspondence to the University of Notre Dame.