with oxygen free water. With all operations carried out under nitrogen, the ether layer was separated and the product obtained and purified by vacuum fractional distillation under nitrogen in a one-piece Claisen distillation apparatus. The yield of $(C_6H_5CH_2)_3B$ (bp 159–160° (0.25 mm)) was 53%: nmr chemical shifts of neat liquid relative to internal TMS, δ 2.61 (s, CH_2), 7.2 (m,C_6H_6); principal ir bands 3.29, 3.31, 3.45, 3.55, 6.25, 6.70, 6.90, 7.88, 9.2, 9.4, 13.2, 14.1, and 19.9 μ.

Tris(*p*-fluorobenzyl)borane was prepared from p-$FC_6H_4CH_2Cl$ by the same procedure used for tribenzylborane (bp 181–183° (0.7 mm)): yield 44%; nmr chemical shifts (neat), δ 2.50 (s, CH_2), 6.8 (m, FC_6H_4); principal infrared bands 3.10, 3.25, 7.49, 6.26, 6.67, 7.86, 8.25, 8.65, 9.15, 9.80, 12.0, 13.2, 18.8, 20.5, and 25.8 μ.

Tris(*p*-methylbenzyl)boranes are prepared as above from p-$CH_3C_6H_4CH_2Br$ with a yield of 32.4% (bp 195–197° (0.15 mm)); nmr chemical shifts (neat), δ 2.60 (s, CH_2), 2.16 (s, CH_3), 6.85 (C_6H_4, m); principal infrared bands 3.17, 3.28, 3.35, 6.57, 6.90, 7.84, 9.0, 9.55, 9.75, 12.35, 17.8, 18.9, and 20.6 μ.

Tris(2,4,6-trimethylbenzyl)borane was not prepared in the usual manner due to unusually large amounts of benzyl coupling product from the reaction of 2,4,6-trimethylbenzyl chloride with magnesium. This difficulty was overcome by adding the benzyl chloride slowly to magnesium turnings in an ether solution already containing the boron trifluoride etherate under nitrogen so that the Grignard reagent was generated in the presence of the BF_3. The reaction was initiated with ethylene bromide. Work-up under nitrogen, after removal of the solvent, gave a waxy white solid which could be recrystallized from *n*-hexane to give large transparent crystals (34% yield): mp 179–180° (sealed capillary); nmr chemical shifts (CCl_4) were δ 2.10 (o-CH_3), 2.19 (p-CH_3), 2.32 (CH_2), and 6.75 (C_6H_2).

Anal. Calcd for $C_{10}H_{39}B$: C, 87.78; H, 9.58; B, 2.64. Found: C, 87.59; H, 9.75; B, 2.72.

Tris(*p*-methoxybenzyl)borane was prepared by the Grignard reaction of p-$CH_3OC_6H_4CH_2MgCl$ with boron trifluoride etherate in tetrahydrofuran (THF) under nitrogen. After the reaction was complete the reaction was hydrolyzed with NH_4Cl in deoxygenated water, and the ether layer separated and dried under argon. A large amount of coupling product $((p\text{-}CH_3OC_6H_4CH_2)_2)$ made purification difficult. After removal of the solvent, the crude product, a yellow viscous liquid, was allowed to stand for 1 week during which time p,p'-dimethoxybibenzyl separated as a sticky white solid. The remaining liquid fraction was partially distilled at 18 mm of pressure to give a fraction boiling between 65 and 71°. The major portion of the product, however, was left in the pot and redissolved in diethyl ether. Cooling of this diethyl ether solution to −30° resulted in further precipitation of bibenzyl which was again filtered off. Finally the ether was removed and the $(p\text{-}CH_3OC_6H_4CH_2)_3B$ was distilled at 0.05 mm of pressure (bp 210–212°) in an overall yield of 14%. Nmr chemical shifts in CCl_4 relative to internal tetramethylsilane were δ 2.51 (s, CH_2), 3.63 (s, CH_3O), and 6.6 (s, C_6H_4); principal infrared bands 3.33, 3.40, 3.51, 6.19, 6.31, 6.61, 6.82, 6.93, 7.89, 7.70, 7.85, 8.02, 8.5, 9.1, 9.6, 12.1, 13.1, and 19.1 μ.

Ammonia complexes of tribenzylborane and tris(tri-*p*-fluorobenzyl)borane were prepared under nitrogen by passing anhydrous ammonia gas into ether solutions of the borane, filtering off the white precipitate, washing with ether, and drying under a vacuum. Anhydrous HCl gas may be used to regenerate the borane.

Spectra. The tribenzylboranes used for ultraviolet spectra were further purified by fractional distillation in a single unit all-glass apparatus until no changes in spectral properties were observed. Spectrograde hexane previously degassed on a high-vacuum line were used to prepare solutions of the tribenzylboranes in a nitrogen-filled glovebox. The uv cells (0.1, 1.0, and 1.0 cm path lengths) were also loaded in the drybox and spectra were run on a Perkin-Elmer Model 451 spectrophotometer. Infrared spectra were recorded in 0.015-mm path-length KBr cells as neat liquids on a Perkin-Elmer Infracord, between 2.5 and 25 μ. Prior to use, the atmosphere of the box was tested by the exposure of tri-*n*-butylborane. Proton nmr spectra were obtain on a Varian Model A-60 and are reported as parts per million downfield from internal tetramethylsilane. After uv and ir spectra were obtained, the cells were briefly exposed to air which resulted in oxidation of the borane and alteration of the spectra. This provided assurance that oxidation had not previously occurred while benzylborane spectra were being recorded or in preparation of the solutions.

Semiempirical molecular orbital calculations were carried out on the Stanford University IBM 360-67 computer. The program was tested by complete CI, all β calculations on benzene, and found to give results in complete agreement with those reported by Flurry and Bell.[20]

A Charge-Transfer Model for β-Arylalkyl Carbonium Ions in Solvolysis

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Akron, Ohio 44309. Received May 26, 1971

Abstract: Solvolysis rates of β-(p-X-phenyl)alkyl tosylates, brosylates, halides, etc., are shown to be correlated by ionization potentials of XC_6H_5 from the highest filled π orbital which does not have a perpendicular nodal plane through X. This is equivalent to a correlation of solvolysis rate with para-substituted tribenzylborane CT transition energies. On this basis it is suggested that the solvolysis of β-arylalkyl derivatives with a primary carbon leaving group proceeds through a CT (π complex) transition state. A π-bridged β-arylalkyl intimate ion pair is suggested for reactions in which a secondary or possibly tertiary cation is formed. Formation of this intimate ion pair is suggested as rate limiting.

In a companion paper[2] we have established the presence of an intramolecular charge-transfer transition in the ultraviolet spectra of aryl-substituted tribenzylboranes such as $(C_6H_5CH_2)_3B$. If the electronic transition is written as in eq 1, then the similarity of the *excited state* of the benzylboranes to possible π-complex transition states or intermediates of β-arylalkyl tosylate, chloride, etc., solvolysis reactions is apparent. The π-complex carbonium ions **4** have been often suggested[3] as alternative intermediates or tran-

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(2) B. G. Ramsey and N. K. Das, *J. Amer. Chem. Soc.*, **94**, 4227 (1972).

(3) (a) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968); (b) M. D.

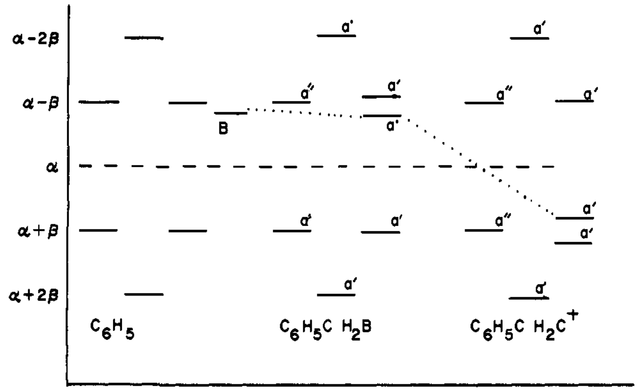
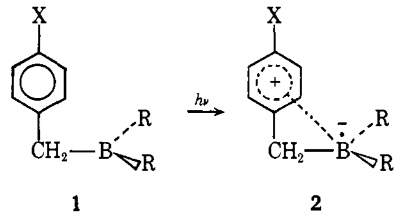
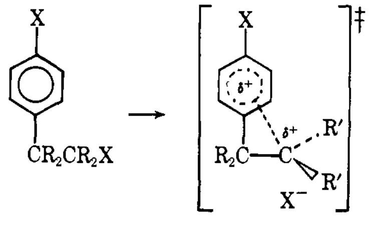


Figure 1. A qualitative simple Hückel molecular orbital diagram for C_6H_5–, $C_6H_5CH_2B$<, and $C_6H_5CH_2C$<.

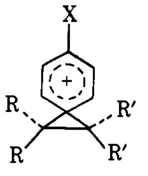


1 **2** (1)



3 **4** (2)

sition states to the widely accepted phenonium ions **5** in at least some, if not all, solvolysis reactions.



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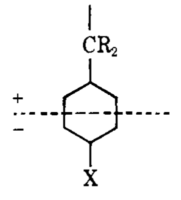
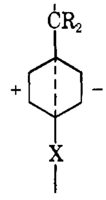
Here we suggest that the totally symmetric ($^1A'$ for C_s symmetry) charge-transfer *excited state* of a benzylborane provides an excellent and useful model for the transition state in the solvolysis reactions of a wide variety of β-arylalkyl derivatives. Our use of boranes as carbonium ion models is not new in this paper, and others have drawn similar analogies.[4] The analogy is slightly different, however, in this case, in that we *are not* comparing the ground-state properties of boranes and carbonium ions, but rather *borane excited state* energies with carbonium ion electronic ground-state energies. Before proceeding further, we will develop the rationale behind this.

Figure 1 provides a qualitative Hückel molecular orbital correlation diagram for benzene, a benzylborane, and a benzylcarbonium ion. The two highest vacant π orbitals of the benzene ring are nondegenerate. For mono- or 1,4-disubstituted benzenes the orbitals have the symmetries depicted in **6** and **7** below. Assuming the C_s geometries of **2** and **4**, the vacant 2p π orbitals of the boron or carbon will belong to the same irreducible representation of C_s point group, *i.e.*, have the same symmetry, as the benzene π orbital **6**. We have shown[2] that the boron vacant 2p orbital has no significant effect on the π-electron energies of the phenyl ring in a benzylborane. Thus, the energy of the p-$XC_6H_4CR_2$ fragment will be the same whether it is attached to $-BR_2$ or $-C(X)R_2$. The interaction of the vacant boron 2p atomic orbital with the lowest vacant $A'\pi^*$ orbital is, however, significant though small and becomes important then in determining the total energy of the CT-derived excited state. As indicated in Figure 1 the energy relationship in Hückel terms of the boron vacant 2p to the benzene π* orbitals is the mirror image of that between the carbon 2p and benzene-filled π orbitals of C_6H_5-$CR_2C^+R_2$. This would lead to an expectation of linear free-energy relationships between *excited* states of the borane and ground states of the carbonium ion **4**.

Instead of treating **4** as a π complex we may adopt an entirely equivalent valence bond nomenclature and regard **4** as an *intra*molecular charge-transfer complex in which the carbonium ion ground state ($^1A'$) is stabilized by mixing with a totally symmetric charge-transfer excited state (CT; $^1A'$) arising from promotion of an electron from the $a'\pi$ orbital **6** to the carbonium ion carbon 2p atomic orbital. From this vantage point of the ion **4**, one would argue that the ability of a para X substituent to stabilize **4** should parallel the substituent effect on the $^1A' \rightarrow {}^1A'$ benzylborane charge-transfer transition energy, but not the second CT transition energy from orbital **7** ($^1A' \rightarrow {}^1A''$). Stabilization of the $^1A'$ ground state results only from interaction with the $^1A'$ CT state.



6(a′)



7(a″)

In simple qualitative terms, the ability of X to stabilize delocalized positive charge in the CT excited state, **2**, should closely parallel its ability to do the same in a structure such as **4**, provided we recognize the molecular orbital symmetry requirements of **2** and **4**.

Ultraviolet absorption spectra for the tribenzylboranes, $(C_6H_5CH_2)_3B$, p-F-, p-CH_3-, (p-$CH_3OC_6H_4$-$CH_2)_3B$, and $[2,4,6\text{-}(CH_3)_3C_6H_4CH_2]_3B$, exhibit a medium-intensity absorption maximum which may be assigned to transitions of three nearly degenerate CT excited states which together may be reasonably described as locally excited $^1A'$ (totally symmetric) states.[2] (In fact, there is undoubtedly some small splitting between these local CT states, but this adds nothing to our discussion here.) As we had hoped on the basis of our discussion up to this point, good correlations are, in fact, observed between the reported CT transition energies of (p-$XC_6H_4CH_2)_3B$ and a variety of solvolytic reactions of

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Bentley and M. J. S. Dewar, *ibid.*, **91**, 3996 (1970), and leading references in a and b.

(4) (a) B. G. Ramsey, *J. Phys. Chem.*, **70**, 611 (1966); (b) H. Whitlock, *J. Amer. Chem. Soc.*, **84**, 3807 (1962); (c) A. H. Cowley and T. A. Fartsch, *ibid.*, **91**, 39 (1969).

p-$XC_6H_4C(CH_3)_2CH_2OTos$, p-$XC_6H_4CH(CH_3)CH(CH_3)O$-Brs, etc. Direct comparison between CT ($^1A'$) transition energies of tribenzylboranes and solvolysis rates, however, turns out to be limited in undesirable ways for the following reasons. First of all, because of the broad nature of the CT band envelope and its overlap with benzene ^1L_b and ^1L_a transitions, it is not possible to measure the exact position of the CT maximum in all cases with the desired precision. The second difficulty is related to the symmetries of the highest filled benzene orbitals **6** (a′) and **7** (a′′). Substituents with modest inductive effects (or resonance effects) leave the energy of the **7** (a′′) orbital unchanged; however the energy of **6** (a′) will depend on the net inductive and resonance effects of the substituent X. Where X is *net* electron releasing, for example where X is CH_3, CH_3O, F, etc., the energy of a′, orbital **6**, is greater than that of **7** (a′′). If X is net electron withdrawing, as in the cases where X is Cl, Br, CF_3, or NO_2, the energy of the a′ orbital **6** will be *lower* than **7**. The result is that for tribenzylboranes para substituted by net electron-withdrawing groups, the totally symmetric $^1A'$-derived CT transitions are shifted to the blue under the ^1B transitions and cannot be differentiated with confidence from the $^1A''$ charge-transfer transitions originating from π-orbital **7** (a′′).

There is, however, a way out of these difficulties. A good linear correlation of tribenzylborane charge-transfer transition energy with the ionization potential of the a′ (**6**) orbital has been shown[2] to exist, as required by the Mulliken expression for charge-transfer transition energies, eq 3.

$$E_{CT} = I_p - E_a - e^2/r \qquad (3)$$

Therefore, an observed linear correlation between solvolysis rates of p-$XC_6H_4CR_2CR_2Y$ and ionization potentials of p-XC_6H_5 from the a′π benzene orbital **6** *can be regarded as the equivalent of a linear relationship with tribenzylborane CT transition energies.* Turner and coworkers[5] have recently obtained, by (electron energy) photoelectron spectroscopy, adiabatic and vertical ionization potentials from *both* of the two highest filled C_6H_5X π orbitals where X is CH_3, OCH_3, Cl, and Br. The lowest ionization potentials of C_6H_5X obtained in this way are in very good agreement with those determined by other methods. It is, of course, the second lowest ionization potentials (from the π orbital **6** (a′)) for XC_6H_5 (X = Cl, Br, CF_3, NO_2) which are important to us in this context and which were previously unavailable. For chloro- and bromobenzene, the adiabatic second lowest ionization potential from the a′π orbital can be observed, but in the photoelectron spectra of $C_6H_5CF_3$ and $C_6H_5NO_2$, as a result of the very strong electron-withdrawing effect of these groups, the energy differences between orbitals **5** (a′′) and **6** (a′) are apparently less than 0.3 eV and were not resolved. The first maxima in the photoelectron spectra of $C_6H_5CF_3$ (9.90 eV) and $C_6H_5NO_2$ (10.26 eV) represent vertical ionization potentials. The average difference, however, between the vertical and adiabatic ionization potentials of C_6H_5X, where both are available, is 0.25 ± 0.05 eV. We have, therefore, adopted the values of 9.90 eV for $C_6H_5CF_3$ and 10.26 eV for $C_6H_5NO_2$ as the best available reasonable estimate of the adiabatic ionization potentials from the (a′) **6** orbitals of $C_6H_5CF_3$ and $C_6H_5NO_2$ within 0.1 eV. Values of ionization potentials used are given in Table II. It is widely known that a good linear correlation exists between σ^+ and p-XC_6H_5 ionization potentials (IP), and while as a generality this is true, it is not true in a more restricted sense. Figure 2 is a plot of the ionization potentials from Table II *vs.* σ^+. It is easily seen that if the substituents CH_3O, CH_3, F, and H are chosen to define the line for the correlation of IP with σ^+, the substituents Cl, Br, CF_3, and NO_2 deviate significantly from such a plot. Therefore, rate correlations with IP, especially where they include the halogens Cl, Br, and CF_3 and NO_2, acquire a significance beyond that of correlation with σ^+.

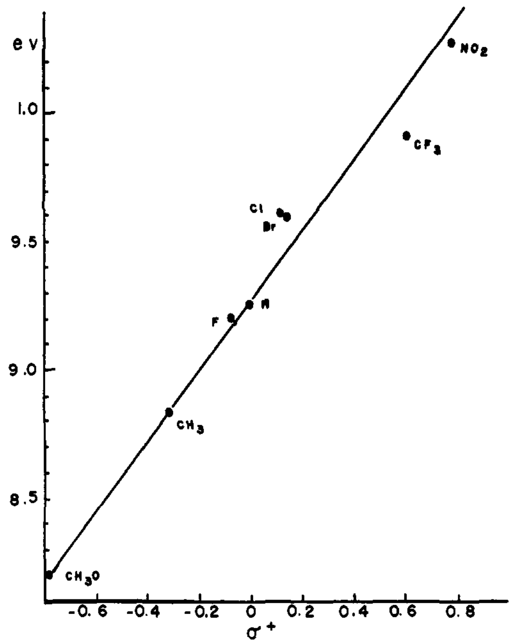

Figure 2. Ionization potentials for a′π orbital of p-XC_6H_5 (C_s symmetrical) *vs.* $\sigma_X{}^+$ parameters.

It has recently been pointed out by several research groups that the solvolysis reactions of not only primary but also secondary β-arylalkyl tosylates, brosylates, etc., may be dissected into two competing pathways, one involving neighboring aryl participation which is presumed to lead to a phenonium ion intermediate, and the second proceeding with specific solvent participation.[6] This specific solvent assistance to the ionization has generally been regarded[6e,7a] as a classical SN2 mechanism, although Brown and Kim[7b] have recently offered an alternative description. Both rates and product ratios may be accounted for without assuming *any* crossover between the solvent-assisted (SN2) pathway and the aryl-assisted path.[6] The observed titrimetric rate constants (k_t for appearance of product) in solvents such as ethanol or acetic acid are

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(5) (a) D. W. Turner, *Advan. Phys. Org. Chem.*, 4, 31 (1966); (b) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

(6) (a) M. Goodwin Jones and J. L. Coke, *J. Amer. Chem. Soc.*, **91**, 4284 (1969); (b) C. J. Lancelot and P. von R. Schleyer, *ibid.*, **91**, 4291 (1969); (c) C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, **91**, 4294 (1969); (d) C. J. Lancelot and P. von R. Schleyer, *ibid.*, **91**, 4296 (1969); (e) P. von R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4296 (1969); (f) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

(7) (a) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. von R. Schleyer, *ibid.*, 92, 5244 (1970); (b) H. C. Brown and C. J. Kim, *ibid.*, **93**, 5765 (1971).

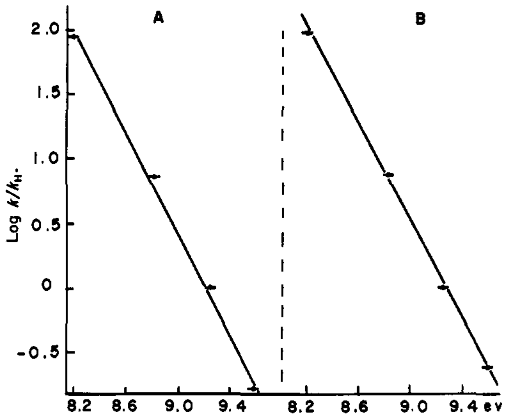

Figure 3. Log relative acetolysis rates (log k/k_H) *vs.* p-XC_6H_5 ionization potential: (a) p-$XC_6H_4CMe_2CH_2OBrs$ (X is MeO, Me, H, Br) and (b) p-$XC_6H_4CMe_2CH_2OTos$ (X is MeO, Me, H, Cl).

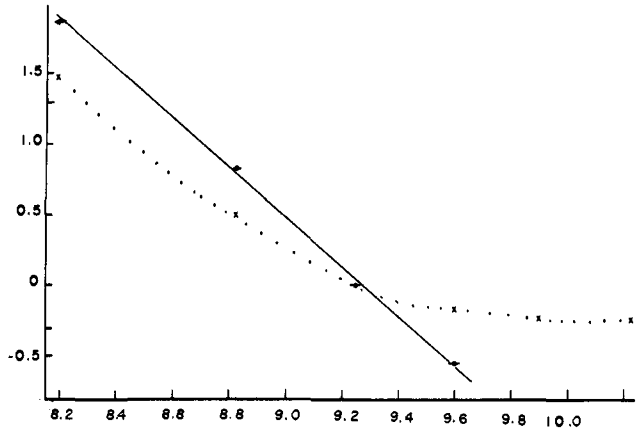

Figure 4. Log relative acetolysis rates (log k/k_H) *vs.* p-CX_6H_5 ionization potential; open circles are aryl-assisted rate for p-$XC_6H_4CH_2CH_2OTs$ (—); the × and (· · ·) represent titrimetric rates (k_t); X is CH_3O, CH_3, H, Cl, CF_3, and NO_2.

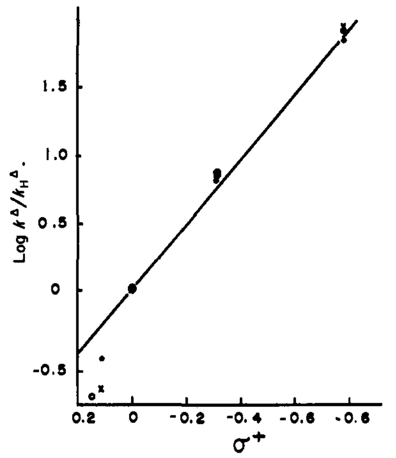

Figure 5. Log relative aryl-assisted acetolysis rate constants (log k_Δ/k_H *vs.* p-XC_6H_5 σ^+ for p-$XC_6H_4CH_2CH_2OTs$ (●), p-$XC_6H_4CMe_2CH_2OTs$ (×), and p-$XC_6H_4CMe_2CH_2OBrs$ (○). X is CH_3O, CH_3, H, and Cl or Br.

then expressed according to eq 4 where F corrects

$$k_t = Fk_\Delta + k_s \tag{4}$$

for internal return in a phenonium ion pair. An additional term, k_c, for completely unassisted solvolysis is sometimes used.

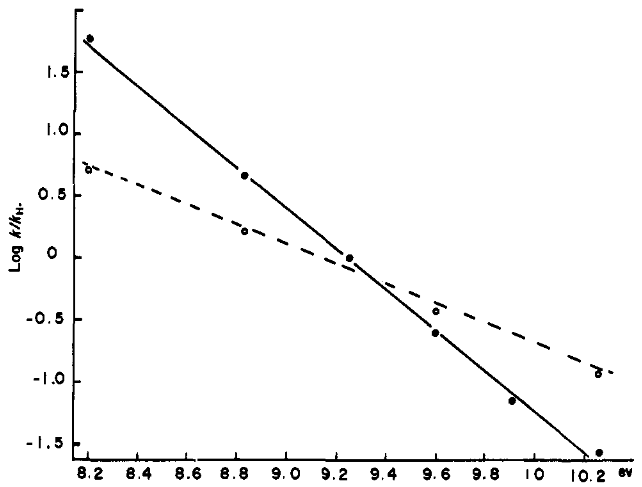

Figure 6. Log relative total acetolysis rate constants (log k/k_H) *vs.* p-XC_6H_4 ionization potentials for p-$XC_6H_4CHMeCHMeOBros$ (●) and (—), and for *trans*-p-XC_6H_4-c-C_5H_8OTs (○) and (- - -). X is MeO, Me, H, Cl, CF_3, and NO_2.

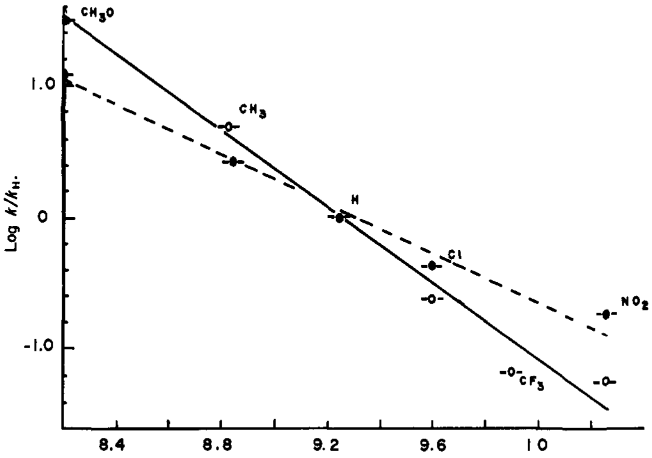

Figure 7. Log relative total solvolysis rate constants (log k/k_H) *vs.* p-XC_6H_4 ionization potential for p-$XC_6H_4CH_2CH(Me)OTs$ formolysis (—) and acetolysis (- - - -).

If the transition state of the reaction characterized by Fk_Δ proceeds through a π-complex transition state such as **4**, then we should observe a linear correlation of log k_Δ (or Fk_Δ if F is reasonably constant) and the a′ ionization potential of C_6H_5X. We would not expect such a correlation with k_t unless k_s were negligible as is the case of neophyl ($C_6H_5CMe_2CH_2$) derivatives. As may be seen from Figure 3 there is an excellent linear correlation between log k_t (log Fk_Δ) and ionization potential for the solvolysis reactions of p-$XC_6H_4CMe_2CH_2Y$ (Y is brosylate[8] or tosylate[6a] and X is CH_3O, CH_3, H, Br, or Cl). In Figure 4 is found an equally excellent correlation with C_6H_4X ionization potentials of log Fk_Δ for acetolysis[9] of p-$XC_6H_4CH_2CH_2OTs$. As anticipated the correlation with the titrimetric rate constant for the acetolysis of p-$XC_6H_4CH_2CH_2OTs$ is poor especially if rates of p-Cl, p-NO_2, and p-CF_3 derivatives are included, Figure 4. By way of contrast, para halogen derivatives of p-$XC_6H_4CH_2CH_2OTs$ and p-$XC_6H_4CMe_2CH_2Y$ deviate significantly (0.3 of a

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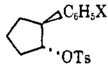
(8) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3434 (1957).

(9) J. M. Harris, F. L. Schadt, P. von R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7510 (1969).

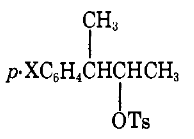
Table I[a]

No.	Reaction	k/k_H rate[b]	σ_{IP}	σ_{σ^+}[c]	C_{IP}[d]	C_{σ^+}	$-m_{IP}$	b_{IP}	ρ
1	p-$XC_6H_4CH_2OTs$[6a] + HOAc	t	0.16	0.11	0.977	0.995	1.29	12.1	−1.99
2	p-$XC_6H_4CH_2OTs$[6a] + HOAc	Δ	0.32	0.47	0.957	0.958	1.80	16.5	−2.7
3	p-$XC_6H_4CH_2CH_2OTs$[9] + HOAc	t	0.14 (0.12)	0.22	0.932 (0.984)	0.903	0.82	7.93	−1.03
4	p-$XC_6H_4CH_2CH_2OTs$[9] + HOAc	Δ	0.03	0.17	0.999	0.994	1.74	16.2	−2.2
5	p-$XC_6H_4CMe_2CH_2OTs$[6a] + HOAc	t	0.05	0.28	0.999	0.986	1.92	17.7	−2.9
6	p-$XC_6H_4CMe_2CH_2OBrs$[8] + HOAc	t	0.08	0.24	0.998	0.990	1.96	18.1	−2.8
7	p-$XC_6H_4CH(Me)CH(Me)OBrs$[7] + HOAc (75°)	t	0.04 (0.02)	0.14	0.999 (1.000)	0.988	1.64	15.2	−2.1
8	p-$XC_6H_4CH(Me)CH(Me)OBrs$[7] + HOAc (75°)	Δ	0.06	0.32	0.998	0.982	1.96	18.1	−2.9
9	p-$XC_6H_4CH(Me)CH(Me)OBrs$[e] + HOAc (25°)	t	0.03	0.19	1.000	0.988	1.82	16.8	−2.43
10	 + HOAc[10]	t	0.04 (0.06)	0.10	0.995 (0.990)	0.984	0.79	7.2	−1.05
11	p-$XC_6H_4CH_2CH(Me)OTs$[6b] + HOAc	t	0.06 (0.01)	0.15	0.991 (1.000)	0.970	0.90	8.4	−1.19
12	p-$XC_6H_4CH_2CH(Me)OTs$[6b] + HCO_2H	t	0.09 (0.07)	0.165	0.989 (0.997)	0.980	1.04	13.3	−1.84
13	p-$XC_6H_4CH_2CMe_2Cl$[11] + EtOH	t	0.05	0.14	0.971	0.950	0.55	5.0	−0.96

[a] Numbers in parentheses neglect points for CF_3 and NO_2. [b] t indicates titrimetric rate, Δ indicates aryl-assisted rate. [c] σ is standard deviation. [d] C is the correlation coefficient. [e] C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4290 (1969).

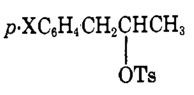
log k unit) from a correlation with the Brown σ^+ where the correlation line is defined by the substituents H, CH_3, and CH_3O (Figure 5). Thus the ionization potentials perform the significant function of placing all the substituents, CH_3O, CH_3, H, and Cl or Br, on a single line, a feat not accomplished by σ^+.

A much more surprising result appears, however, on examination of the rate constants for the solvolysis reactions of the *secondary* derivatives **8**, **9**, and **10** below.[7,6b,10] Excellent correlations of the *total* rate constants (k_t) (not just Fk_Δ) with ionization potentials of p-XC_6H_5 are found which not only include X = Cl, but also X = CF_3 and NO_2, as may be seen from Figures 6 and 7. These correlations of log k_t with IP are not only better than the correlations of log k_t with σ^+, but are also better than the correlation of log Fk_Δ with either σ^+ or IP, Table I. *We believe this result requires the conclusion that both the solvent assisted and aryl group assisted reactions proceed through the same transition state, i.e.*, have the same rate-limiting step.



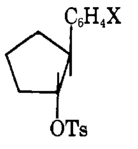
$p\text{-}XC_6H_4CH(CH_3)CH(OTs)CH_3$

8



$p\text{-}XC_6H_4CH_2CH(OTs)CH_3$

9



10

Literature results for solvolysis of tertiary derivatives are more ambiguous. In a preliminary communication[12] we pointed out that the rate constants[3a] for ethanolysis of p-$XC_6H_4CH_2CMe_2Cl$ at 50° and p-$XC_6H_4CMe_2Cl$ (where X = CH_3, H, OCH_3) are perfectly correlated by the ionization potentials of C_6H_5X. Neither σ nor σ^+ includes both CH_3O and CH_3 on the same line! Ethanolysis rate constants[11] at 40.8° of p-$XC_6H_4CH_2CMe_2Cl$ which, however, include p-F, -Cl, and -Br as substituents show only a fair correlation with ionization potential, Figure 8. The dependence of log k_t on p-XC_6H_5 ionization potential does have a correlation coefficient of 0.971 which has been regarded as good in other instances.[13] A better correlation with Hammett σ, however, is obtained: standard deviation, 0.03, correlation coefficient, 0.998.

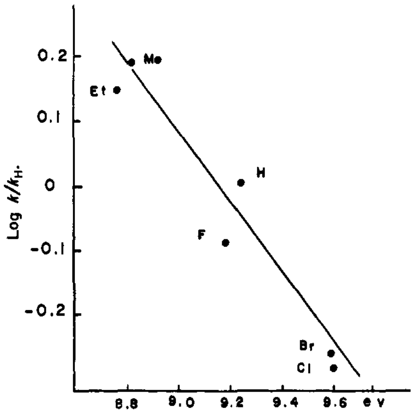


Figure 8. Log relative ethanolysis rate constants (log k/k_H) *vs.* p-XC_6H_5 ionization potential for p-$XC_6H_4CH_2CMe_2Cl$.

In Table I, we have collected the results of a least-squares fit of log k_Δ and log k_t with ionization potentials of p-XC_6H_5 and σ_X^+ for the solvolysis of those β-arylalkyl primary, secondary, and tertiary derivatives available in the literature. Listed in this table are standard deviation (σ_{IP}), correlation coefficients (C_{IP}), and slopes (m) with intercepts (b) for the best least-squares fit to the equation $\log k/k^0 = mI_p + b$ for both total or titrimetric and k_Δ rates. Because the required ionization potentials for $C_6H_5CF_3$ and $C_6H_5NO_2$ are known less accurately than for other monosubstituted benzenes, we have also obtained σ_{IP} and C_{IP} neglecting these substituents. For purposes of comparison, the same least-squares treatment was applied to correlations with the Brown σ^+, for which we also list σ(standard deviation), C_{σ^+}(correlation coefficient), and ρ.

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(10) C. J. Kim and H. C. Brown, *ibid.*, **91**, 4290 (1969).

(11) A. Landis and C. A. VanderWerf, *ibid.*, **80**, 5277 (1958).

(12) B. G. Ramsey and N. K. Das, *ibid.*, **91**, 6191 (1969).

(13) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

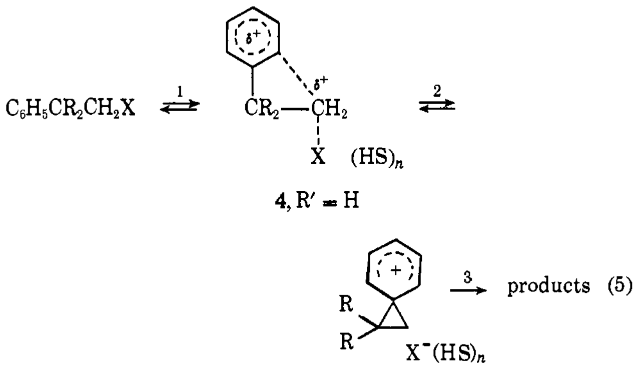
Examining the solvolysis of primary derivatives in Table I (reactions 3–6), we see that σ_{IP} is some two–five times smaller than σ_{σ^+}. Data of Jones and Coke[6a] are included (1 and 2, Table I) for completeness; however, the more extensive results on the same system of Harris, Schadt, Schleyer, and Lancelot[9] must be regarded as more complete and probably more accurate in its evaluation of Fk_Δ. Correlation coefficients for log aryl-assisted rate constants Fk_Δ with ionization potentials (4, 5, 6, Table I) are very nearly unity to three decimal places. The correlation coefficient of log Fk_Δ with σ^+ would also have to be characterized as very good; however, this hides the fact the correlation is largely the result of the excellent fit of electron-donating groups while *p*-Cl and -Br deviate significantly. For the secondary derivatives (7, 9, 10, 11, 12), the standard deviations of log k_t as a function of ionization potential range from 0.03 to 0.09 log unit ($\bar{\sigma}_{IP} = 0.06$), significantly better than the average of the standard deviations for σ^+ ($\bar{\sigma}_{\sigma^+} = 0.17$), or the standard deviation (0.32) for the correlation of log Fk_Δ (8, Table I) with σ^+. The correlation coefficients for log k_t with ionization potential in the case of secondary derivatives range from 0.989 to 1.000 and become 1.000 in reactions 7, 9, and 11 if we ignore the points for NO_2 and CF_3 on the grounds that the ionization potentials of $C_6H_5CF_3$ and $C_6H_5NO_2$ are not known with sufficient accuracy to determine the correlation coefficients to three places.

The values of $-m$ in Table I which are slopes of log k/k_H *vs.* IP, like Hammett ρ values, reflect the sensitivity of the reaction to changes in aryl substituent. These values for $-m$ in the series *p*-$XC_6H_4CH_2CH_2OTs$ (1.74), *p*-$XC_6H_4CH_2CH(CH_3)OTs$ (0.9), and *p*-$XC_6H_4C(CH_3)_2CH_2OTs$ (1.92), *p*-$XC_6H_4CH(CH_3)CH(CH_3)OBrs$ (1.64) seem more in line with our expectations than corresponding ρ values, -2.2, -1.9, -2.9, -2.9, from log Fk_Δ *vs.* σ^+ plots.

We can summarize our discussion to this point as follows. (1) Rate constants of β-arylalkyl derivative solvolysis reactions are better correlated with appropriate C_6H_5X ionization constants than with Brown σ^+ values. (2) Although for primary derivatives good correlations with ionization potential are found only for Fk_Δ (aryl-assisted rate), in the case of secondary derivatives the *total rate constants* (k_t) provide excellent correlations with C_6H_5X ionization potentials. (3) Slopes of log k/k_H *vs.* IP plots for comparable primary, secondary, and tertiary reactions seem more in keeping with expected reaction dependence on substitution than are the ρ values for the aryl-assisted rate constants log Fk_Δ for the same or similar reactions. *This is tentative.* (4) A linear correlation of β-arylalkyl derivative solvolysis log k with ionization potential is the equivalent of a correlation with benzylborane CT transition energy. We suggest that such a correlation with ionization potential reflects a π-complex (CT) intermediate or transition state of the type **4** in the rate-determining step, which is analogous to the benzylborane $^1A'$ CT excited state. A theoretical rationale is thus provided for the observed correlation with ionization potential.

We believe these observations strongly support the following mechanisms for the solvolysis reactions of β-aryl derivatives.

As suggested[6] by Winstein, Schleyer, Coke, and Jones, the reactions of primary derivatives proceed by two independent pathways, one essentially SN2 and the other aryl assisted. We would, however, modify this model with the conclusion that the *transition state of the aryl-assisted rate is best approximated by the unsymmetrical π-bridged species*, **4**, rather than a phenonium ion, **5**. It is possible also that **4** is present as an intermediate. *It might be well to remember that we expect the overall transition state for a multistep reaction to resemble the highest energy intermediate even though it may occur before the transition state.* One could envisage the aryl-assisted reaction as taking place by the mechanism of eq 5, where the highest energy transition state along the reaction coordinate lies between ions **4** and **5**, but the phenonium ion is lower in energy than π-bridged ion **4**, which is an intermediate.



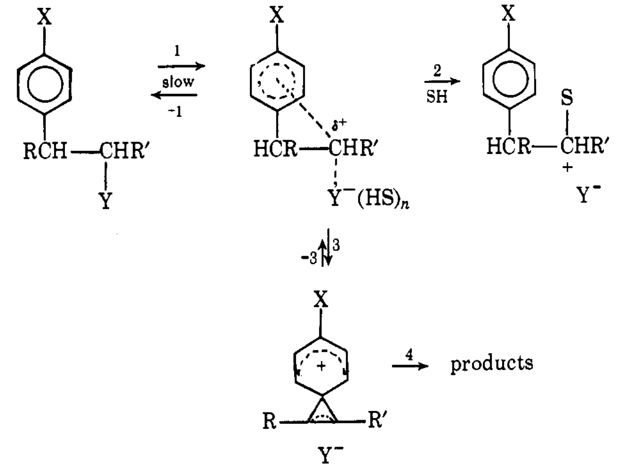
4, R′ = H

5, R = H

(5)

Solvolysis of secondary β-arylalkyl halides, we suggest, may proceed in a rate-limiting step through the initial formation of an unsymmetrical π-bridged intermediate intimate ion pair, and this ion pair subsequently partitions between phenonium ion and SN2 solvent attack on the ion pair. This reaction is outlined in Scheme I below in which the rate-determining step is 1.

Scheme I



The role of the partially solvated counterion Y^- (SH) is considered to be an essential one in the intimate ion-pair mechanism of Scheme I, since recent studies on ion formation in SbF_5–SO_2 by CD_3-labeled *p*-$CH_3OC_6H_4CR_2CR_2X$ systems (X is H or CH_3) seem to indicate that "free" carbonium ions such as *p*-$CH_3OC_6H_4CH(CH_3)CHCH_3^+$ rearrange to benzylic ions much faster than they form phenonium ions or aryl-group migration products[14] The partially solvated anion in some cases also may, by rotation inside the ion pair, provide the cation center with its solvent molecule producing a product stereochemistry equivalent to that expected in a phenonium ion mechanism for ArCH$_2$C(R)HY or ArCH(R)CR$_2$Y solvolysis. This possibility does not seem to have been previously considered in the literature, where emphasis has been more on mechanisms preventing backside attack.

In Scheme I, a linear correlation of log k_t with aryl ionization potential is possible *only* if step 1 has the highest energy transition state; k_{-1} must be negligible with respect to k_2 and k_3. If the transition-state energies for either or both steps 2 and 3 were greater than that of step 1 ($k_{-1} > k_3, k_2$), each of the experimental log k_s and log Fk_Δ could exhibit linear correlations with ionization potential; however, log $(k_s + Fk_\Delta)_{\text{exp}}$ would not be a linear function of ionization potential. (A linear dependence between k_s and Fk_Δ would produce a linear correlation of k_t with ionization potential, but with an incorrect intercept.)

We cannot lose sight of the fact, however, that good correlations between product and separated experimental rate constants Fk_Δ and k_s have been obtained by evaluating k_s from $\sigma\rho$ plots in which ρ_s is defined by $k_t \simeq k_s$ for strongly electron-withdrawing substituents. It is necessary to show then that a similar resolution of k_t can be made in the case of Scheme I.

If a simple steady-state treatment, without approximations as to relative magnitudes of rate constants, is carried out, then the titrimetric rate constant is given by eq 6. The indicated substitutions of k', $Fk_\Delta{}^0$, and

$$k_t = k_1k_2\Big/\left[k_{-1} + k_2 + k_3 - \left(\frac{k_{-3}k_3}{k_4 + k_{-3}}\right)\right] + \frac{k_1k_3k_4}{(k_4 + k_{-3})\left[k_{-1} + k_2 + k_3 - \left(\frac{k_{-3}k_3}{k_4 + k_{-3}}\right)\right]} \quad (6)$$

$$k' = \frac{k_1}{(k_{-1} + k_2 + k_3) - \left(\frac{k_{-3}k_3}{k_4 + k_{-3}}\right)}$$

$$F = k_4/(k_4 + k_{-3})$$

$$k_\Delta{}^0 \equiv k_3$$

$$k_s{}^0 \equiv k_2$$

$k_s{}^0$ give eq 7. Thus, we see that k_t may be resolved into

$$k_t = k'(k_s{}^0 + Fk_\Delta{}^0) = k'k_s{}^0 + k'Fk_\Delta{}^0 \quad (7)$$

two component rate constants, one for the solvent-assisted reaction, $k'k_s{}^0$, and one for the aryl, $k'Fk_\Delta{}^0$. As required, if k_2 and $k_3 \gg k_1$, eq 6 reduces to $k_t \equiv k_1$. The fractions of product obtained from solvent- and aryl-assisted pathways are given by eq 8 and 9.

product fraction solvent assisted =

$$\frac{k'k_s{}^0}{k'(k_s{}^0 + Fk_\Delta{}^0)} = \frac{k_s{}^0}{(Fk_\Delta{}^0 + k_s{}^0)} \quad (8)$$

product fraction aryl assisted =

$$\frac{Fk'k_\Delta{}^0}{k'(k_s{}^0 + Fk_\Delta{}^0)} = \frac{Fk_\Delta{}^0}{(Fk_\Delta{}^0 + k_s{}^0)} \quad (9)$$

Obviously if $k'k_s{}^0$ could be evaluated, provided the mechanism of Scheme I were correct, a correlation between product rate constants $k'k_s{}^0$ and $Fk'k_\Delta{}^0$ could be obtained. Agreement between the specific mechanism proposed here (k_2, $k_3 > k_{-1}$) can be obtained only if $k'k_s{}^0$ is identified with k_s experimental and is therefore a linear function of σ.

After the initial submission of our manscript Professor Brown was kind enough to supply us with a copy of ref 7b prior to its publication. Brown and Kim[7b] propose a reaction scheme identical with that suggested here. They, however, correctly point out that in the complete absence of any contribution to the rate from aryl assistance ($k_3 \ll k_2$ or k_{-1}) k_t reduces to expression 10. It is then shown[7b] that satisfactory product–rate

$$k_t = \frac{k_1k_2}{k_{-1} + k_2} \quad (10)$$

correlations are possible if $k_{-1} > k_2$. The experimental k_s is assumed, therefore, to be equal to $(k_1/k_{-1})k_2$.

Brown and Kim utilize[7b] the substituents *m*-Cl, *m*-CF$_3$, *p*-CF$_3$, *p*-NO$_2$, and *m,m'*-(CF$_3$)$_2$ to define the ρ_s value for the purely solvent-assisted rate. However, for the first three of these substituents (*m*-Cl, *m*-CF$_3$, and *p*-CF$_3$) the per cent products from the aryl-assisted pathway are in the range of 6–11%. Therefore, the approximation of eq 10 may not be adequately justified for these substituents.

We will now show that the mechanism proposed here could reasonably account for the observed[6,7] ρ_s values and product–rate correlations in the solvolysis of secondary β-arylalkyl derivatives. With very electron-withdrawing groups on the aryl ring, aryl participation should become truly negligible, in which case $k'k_s{}^0$ would in fact then be equal to $k_1 \equiv k_t$. Now then for electron-withdrawing groups *only* (*p*-NO$_2$, *p*-CF$_3$, and *p*-Cl) a fairly good straight line is obtained from a plot of ionization potential *vs.* σ, with $\rho = 1.1$. Because log k_t is a linear function of ionization potential, and ionization potential over a limited range is in turn a linear function of σ, we can calculate the expected slope of the log k_s (log k_1) line for these substituents and compare this slope with the experimental values of k_s. For cases 7, 9, 10, 11, and 12 in Table I, the experimental and calculated slopes are: (ρ_s, 1.1 m) (1.5, 1.8); (2.0, 2.0); (0.9, 0.9); (0.7, 1.0); and (0.8, 1.1). The experimental slopes, ρ_s, are therefore equal to or somewhat *less* than what we would expect from a plot of log $k'k_s{}^0$ log k_1 *vs.* σ. This is precisely the relationship between slopes we would expect if in fact k_s(exp) is to be identified with $k'k_s{}^0$, where $k'k_s$ is given by eq 11. The

$$k_s(\text{exp}) = k_1k_s{}^0\Big/\left[k_2 + k_3 - \left(\frac{k_{-3}k_3}{k_4 + k_{-3}}\right)\right] \quad (11)$$

essential point we make here is that if a plot of log $k'k_s{}^0$ *vs.* σ possesses a ρ value close to that of the ρ from a Hammett plot of $k_1 \equiv k_t$ for very strong electron-withdrawing substituents such as *p*-NO$_2$ or *m,m'*-(CF$_3$)$_2$, the deviation of the points from the line generated by the linearity of log $k'k_s{}^0$ for less deactivating substituents may not be experimentally detectable.

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(14) (a) B. C. Ramsey, J. Cook, and J. Manner, *J. Org. Chem.*, in press; (b) B. G. Ramsey and J. Cook, *Tetrahedron Lett.*, 535 (1969).

Both the mechanism proposed here and that suggested[7b] by Brown and Kim for solvolysis of β-arylalkyl derivatives introduce an intimate ion pair with π or charge-transfer delocalization of charge into the aryl ring. It seems significant and encouraging that independent considerations should arrive at the same conclusion. However, there is a basic difference between the proposed mechanisms. We suggest that the formation of the intimate ion pair **11** is the rate-determining step for both aryl- and solvent-assisted reactions. The Brown and Kim proposal involves ion **11** in a rapid prior equilibrium step before S_N2 attack on the ion by solvent. Both mechanisms share important advantages over a mechanism involving simple S$_N$2 attack on the alkyl tosylate. Acetolysis and formolysis reactions remain essentially S$_N$1 in character and the "extensive reinterpretation of acetolysis studies conducted over the past 20 years" would not be necessary as suggested[7] if the "solvent assisted" reaction proceeded by a classical S$_N$2 process. Further, a continuum of β-arylalkyl carbonium ion structures from phenonium ion to π-bridged ion becomes apparent in proceeding from primary to secondary β-arylalkyl cations, a condition which Professor Brown[3a] has said to be reasonably expected.

It is not clear from the literature whether a scheme analogous to I can be also proposed for the solvolysis reactions of tertiary derivatives. The only reaction[3a,11] we find reported in the literature with a sufficient range of substituents is the ethanolysis of p-XC$_6$H$_4$CH$_2$C(CH$_3$)$_2$Cl. In this case X varies from CH$_3$O, alkyl, and H to the halogens F, Cl, and Br. Considering only CH$_3$O, CH$_3$, and H, the correlation of log k_t with IP is excellent and the overall standard deviations σ_{IP} of 0.05 and correlation coefficient of 0.971 are at least good (see 13, Table II). If in the future solvolysis rate constants of p-XC$_6$H$_4$CR$_2$CMe$_2$Y over a greater range of substituents (*i.e.*, p-X is CF$_3$, NO$_2$), etc., and with other leaving groups in better ionizing solvents should also provide comparable or better correlations with p-C$_6$H$_5$X ionization potentials, then for the first time we would have a simple substituent constant, p-XC$_6$H$_5$ ^{1}A′ ionization potential, capable of satisfactorily correlating para X substituent effects on non-solvent-assisted β-phenylalkyl solvolysis rates over a substituent range from X = CH$_3$O to CF$_3$ and NO$_2$ and from primary to tertiary carbon sites of leaving groups.

Table II. Ionization Potentials and Hammett σ^+ Values of p-XC$_6$H$_5$

X	IP	σ^+
CH$_3$O	8.20	−0.778
CH$_3$	8.83	−0.311
F	9.195	−0.703
H	9.25	0
Br	9.59	0.150
Cl	9.60	0.114
CF$_3$	(9.9)	0.612
NO$_2$	(10.26)	0.790

What seems most compelling to us is this consistency with which the ionization potentials of the a′π orbitals of p-XC$_6$H$_5$ (and by implication benzylborane ^{1}A′ CT transition energies) correlate the available variety of solvolysis rate constants of β-arylalkyl primary, secondary, and tertiary arylsulfonates and halides.

Neither the bridged ion **4** nor the suggested possibility of preliminary intimate ion-pair formation are original here. They have been suggested by others numerous times in various guises as possibilities. We believe though that we have offered here new substantive evidence supporting the role of π-bridged or CT type β-arylalkyl cation transition states or ion-pair intermediates. These conclusions are opposed to those tentatively suggested recently by Hanstein, Berwin, and Traylor who considered a limited model based on the charge-transfer transition in TCNE complexes of diphenylmethane and triphenylmethane,[15] and emphasize the need for experiments which will clearly differentiate between π-complexed bridged ions and phenonium ion intermediates and/or transition states.

A referee of this paper has suggested that our correlations of log k should be compared with a mixed σ and σ^+ type. Probably the most rigorous dual substituent parameter treatment of substituent effects is that published recently by Ehrenson, Brownlee, and Taft.[16] Utilizing eq 12, they report a standard deviation of 0.06 for the acetolysis of 2-phenyl-2-methylpropyl brosylates (no. 6 of Table I).

$$\log k/k_0 = \sigma_I\rho_I + \sigma_R\rho_R \qquad (12)$$

In view of the fact that our *single* parameter equation obtains a standard deviation of 0.08, it would be difficult to argue that the *two*-parameter formulation provides significantly better results. We do not, however, wish to argue that two-parameter equations involving σ_I or $\sigma_R{}^+$ or σ and σ^+ will not provide useful insight into transition states. The relative values of ρ_I (−3.91) and ρ_R (−2.95) are certainly in qualitative agreement with that expected for a CT transition state such as **4**. We must, however, believe that a single-parameter relationship which may be justified by simple molecular orbital considerations is preferable to an extrathermodynamic treatment involving *two* disposable parameters. Private communication with Professor Taft indicates that satisfactory correlation of log k_t for secondary systems was not obtained with the mixed $\sigma_I\rho_I + \sigma^+{}_R{}^+$ function.

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(15) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 8929 (1970).

(16) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, "Progress in Physical Organic Chemistry," Vol. 10, Interscience Publishers, New York, N. Y. 1972.