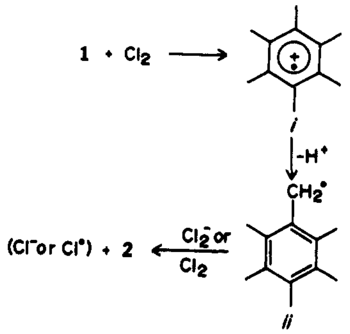
E. Baciocchi and G. Illuminati, *Prog. Phys. Org. Chem.*, **5**, 1 (1967); (c) H. Suzuki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 423 (1972).

(5) E. Baciocchi and G. Illuminati, *Tetrahedron Lett.*, 637 (1962).

(6) J. K. Kochi, *Tetrahedron Lett.*, 4305 (1974).

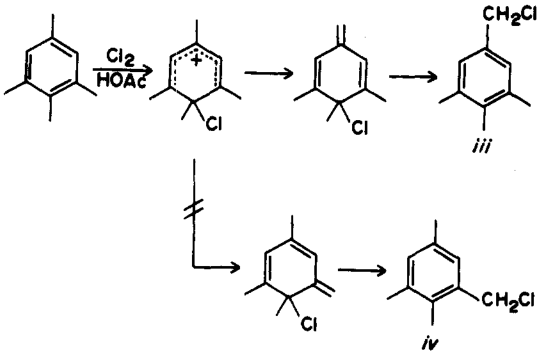
(7) (a) E. Baciocchi and G. Illuminati, *Tetrahedron Lett.*, 2265 (1975); (b) E. Baciocchi, L. Mandolini, and A. Patara, *Ibid.*, 2268 (1975).

(8) In an alternative mechanism proposed by Kochi,[6] electron transfer occurs between hexamethylbenzene and chlorine to generate radical cation i and Cl_2^-. Proton loss gives the pentamethylbenzyl radical ii which was detected by ESR.



Although this mechanism appears plausible, it does not readily explain the competitive formation of acetates and chlorides unless one adds a step in which ii is further oxidized to a pentamethylbenzyl cation (which may then react with either acetate or chloride). Additional evidence against the radical-ion mechanism is given in ref 7.

(9) In principle, proton loss could occur from either a para or an ortho substituent. However, evidence in other cases indicates that loss from a para substituent is favored. For example, analogous chlorination of isodurene gives 3,4,5-trimethylbenzyl chloride (iii) and not the 2,3,5-trimethyl isomer (iv).[7a]



(10) M. Hojo and R. Masuda, *Synth. Commun.*, **5**, 169 (1975).

(11) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142, 3432 (1939); **62**, 925 (1940).

(12) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).

(13) The chlorination was also carried out in an ESR spectrometer. No free radicals were detected (private communication from Professor Gerald Babcock, Michigan State University).

(14) H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **55**, 591 (1936).

(15) (a) B. J. Abadir, J. W. Cook, and D. J. Gibson, *J. Chem. Soc.*, 8 (1953); (b) A. Oku and Y. Yuzen, *J. Org. Chem.*, **40**, 3850 (1975).

(16) For reviews, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966); J. F. Liebman and A. Greenberg, *ibid.*, **76**, 311 (1976).

(17) V. I. Mamatyuk, A. P. Krysin, N. V. Bodoev, and V. A. Koptyug, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **23**, 2392 (1974); p 2312 in English.

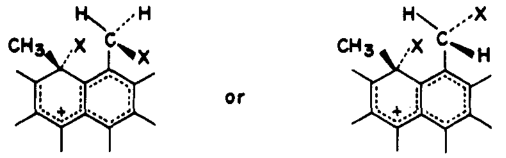
(18) The singlet at δ 4.94 sharpened when the temperature was raised to 75 °C.

(19) The ^1H NMR spectra of **4, 5, 6, 7, 12, 13,** and **14** vary with temperature; a full discussion is reserved for a separate paper.

(20) These percentages are based on isolated, pure **3, 8,** and **9**, respectively.

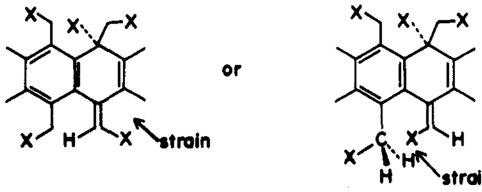
(21) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4274 (1972).

(22) For example, reasonable representations of G might be



in which the first X (in CH_2X) interacts unfavorably with either the CH_3 or X group, respectively, on the adjacent peri carbon atom. Such interactions are avoided in F.

(23) One might a priori expect proton loss to be preferred from the para position because the methylene protons of the CH_2X group should be more acidic than those of a methyl group. However, loss of a proton from the CH_2X group would give either of two products, each of which is appreciably more strained than O.



Consequently, loss of a proton from an *o*-methyl group is preferred.

(24) W. J. Humphlett and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3289 (1950).

(25) The mixture, in a separate smaller scale run, was analyzed in part by NMR and in part by conversion of **12** to **9** with silica gel chromatography.

Bromovinyl Cations in Bromination. Similarity of Solvent Effects in Limiting Solvolysis and in Bromination of Olefins and Acetylenes

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Solvent effects on styrene (S) and phenylacetylene (PA) bromination have been reinvestigated. Contrary to results by previous authors, the rate-constant ratio, $k_{C=C}/k_{C\equiv C}$, does not vary significantly when the solvent passes from acetic acid to methanol, 70 and 50% aqueous methanol and water. The correlation, $\log k_{PA} = 0.95 \log k_S - 3.26$, obtained when the solvent is varied, shows that the solvent effects on bromination via bromocarbonium ions and vinyl bromocarbonium ions are very similar. The m values for styrene and phenylacetylene are 1.20 and 1.15, respectively, at 25 °C. These results suggest that the Ad_ECl mechanism of olefin bromination is also valid in acetylene bromination. In this mechanism, the role of the solvent (electrophilic assistance to the departure of the bromide ion) is consistent with the fact that m values are high and similar for styrene and phenylacetylene bromination. The differences between the reactivity ratio $k_{C=C}/k_{C\equiv C}$ in bromination (10^3) and in hydration (1) is discussed in terms of transition-state structure and of a destabilizing influence of the C_β–Br bond which is greater in the vinyl cation than in the saturated carbonium ion.

On the basis of the similarity of solvent effects on olefin bromination and on limiting solvolysis, we suggested[1] that bromination could be a convenient reaction for studying carbonium ions because solvent nucleophilic assistance is absent in free bromine additions. In the case of vinylcarbonium ions, this proposal would be of particular interest, since

Table I. Bromination Rate Constants and Reactivity Ratios of Styrene and Phenylacetylene in Various Solvents

			k_g, $M^{-1}s^{-1}$,[a] at $[Br^-]$ =							
			0.025 M	0.05 M	0.1 M	0.2 M	0.3 M	k_{Br_2}, $M^{-1}s^{-1}$[b]	$k_{C=C}/k_{C\equiv C}$[c]	k_o/k_a[d]
(1)	H_2O	S[e]			4.70×10^6[g]	3.72×10^6[g]	2.90×10^6[g]	1.1×10^7[g,h]	0.6×10^3	0.6
		PA[e]	1.27×10^4	1.08×10^4	7.90×10^3			1.7×10^4		
(2)	AM-50[f]	S		5.90×10^5[g]	3.55×10^5[g]	2.31×10^5[g]		2.3×10^6[g]	2.9×10^3	2.3
		PA		2.75×10^2	1.90×10^2	1.25×10^2		8.0×10^2		
(3)	AM-70[f]	S		3.69×10^4	2.15×10^4	1.30×10^4		1.9×10^5	4.6×10^3	1.7×10
		PA		8.50	5.31	3.29		4.1×10		
(4)	MeOH	S		1.91×10^2[g]	1.20×10^2[g]	8.5×10[g]		1.16×10^3[g]	2.5×10^3	$>10^2$
		PA		6.10×10^{-2}	4.05×10^{-2}	2.8×10^{-2}		4.6×10^{-1}		
(5)	AcOH[i]	S			1.10×10			11.2	2.6×10^3	2.6×10^3
		PA			1.40×10^{-2}			4.3×10^{-3}		

[a] k_g, experimental rate constants at various bromide ion concentrations and at 25 °C. Errors are within 5%. [b] k_{Br_2}, rate constants for free bromine addition calculated from k_g; see Experimental Section. Errors are within 10%. [c] Rate-constant ratios from k_{Br_2}; this work. [d] Rate-constant ratios from competitive measurements, except for AcOH; ref 3. [e] S = styrene, PA = phenylacetylene. [f] 50 and 70% aqueous methanol (AM), v/v. [g] Values from ref 1. [h] This rate constant is underestimated, ref 7. [i] Direct measurements from ref 3.

these ions are more easily obtained by addition to acetylenic compounds than by solvolysis of unreactive vinylic substrates.[2] Unfortunately, previous results on acetylene bromination seem to exclude this attractive possibility: solvent effects on electrophilic brominations leading to carbonium ions have been stated to differ markedly for ethylenic and acetylenic compounds.[3] Experimentally, this statement was based on competitive measurements of the relative rates of styrene and phenylacetylene bromination. The reactivity ratio, in the range of 10^3 in acetic acid, was found to be greatly diminished by an increase in the solvent polarity, becoming less than unity in water. Since for styrene bromination the m value is near unity and therefore similar to those observed in solvolytic reactions,[1] the data of Yates et al.[3] apparently indicate that solvent effects on vinyl cations generated by bromination are much more important than those on saturated carbonium ions from bromination or from solvolysis.

However, it is rather difficult to understand in terms of our knowledge of the nature of the solvation of the ionic intermediates why solvent effects on bromination of olefins and acetylenes should be different. In particular, it has been shown that in bromination[4] the solvent acts through a medium effect on the stability of the intermediate and essentially by specific electrophilic solvation of the leaving bromide ion. Therefore, very large differences between the solvent effects on acetylene and olefin bromination are completely unexpected.

To reexamine the nature of the solvation in bromination, we have measured by direct kinetic methods, different from those used by the preceding authors,[3] the bromination rates of phenylacetylene in various solvents and compared them with those previously obtained for styrene.[1]

Kinetic Results

The bromination rate constants of styrene and phenylacetylene in methanol, 70 and 50% aqueous methanol and in water, were measured directly at 25 °C by following the disappearance of bromine spectroscopically[5] or electrochemically[6] under the usual conditions.[10]

Pseudo-first-order conditions, where the concentration of the unsaturated compound is in the range of 10^{-2}–10^{-3} M and is at least ten times greater than that of bromine, are used for styrene and phenylacetylene in methanol and for phenylacetylene in 70% aqueous methanol. Identical conditions cannot be applied in the other solvents because of the low solubility of the reactants in water and aqueous solvents: the solubility of styrene and phenylacetylene is less than 10^{-3} M in water. Second-order conditions, where bromine and substrate concentrations are similar (10^{-4}–10^{-6} M depending on the rate), are used for rate measurements in water and 50% aqueous methanol for both reactants and in 70% aqueous methanol for styrene. In all cases, except for styrene in water,[7] we were able to show that a change in substrate concentration does not change the rate constants, thus confirming that the reactants are completely dissolved.[8]

In the solvent systems used in this work, two brominating agents, free bromine, Br_2, and tribromide ion, Br_3^-, formed in the $Br_2 + Br^- \rightleftharpoons Br_3^-$ equilibrium, react competitively with the unsaturated substrate.[9] Thus, the experimentally measured rate constant, k_g, is composite. Owing to the complexity of the "Br_3^- mechanism",[10] the solvent effects can only be discussed in terms of the rate constant for addition of free bromine, k_{Br_2}. This rate constant is obtained[9] from the overall rate constants, k_g, measured at various bromide ion concentrations, by extrapolation to $[Br^-] = 0$ of the general equation $k_g(1 + K[Br^-]) = k_{Br_2} + Kk_{Br_3^-}[Br^-]$.

The rate constants thus obtained are given in Table I; from these values, we calculate the rate ratio of styrene and phenylacetylene, $k_{C=C}/k_{C\equiv C}$, in the various solvents. Comparison with the ratios, k_o/k_a,[11] previously obtained[3] for the same unsaturated compounds shows significant differences for water and aqueous solvents. The k_o/k_a ratios are derived from GLC and NMR measurements of the ratios of products formed in experiments where styrene and phenylacetylene react competitively with bromine. Several reasons lead us to conclude that our $k_{C=C}/k_{C\equiv C}$ values are the proper ones, rather than k_o/k_a. Firstly, it is now well established[12] that competitive kinetic experiments can lead to a compression of the reactivity span. For bromination, we showed previously[12] that these methods give reliable results in methanol only for reactant concentrations smaller than 10^{-3}–10^{-4} M. It appears that the previous authors[3] worked in the range 10^{-2}–10^{-3} M. Therefore, it is possible that the discrepancies for the polar solvents result in part from the unreliability of the competitive method. Secondly, we have observed that solubilities of styrene and phenylacetylene are less than 10^{-3} M in water. In view of the high substrate concentrations involved, it is also possible that the k_o/k_a ratios reflect the differences between the solubilities of the two substrates rather than their bromination rate constants. Consequently, it is reasonable to consider that the direct rate data $k_{C=C}/k_{C\equiv C}$ are accurate, while the k_o/k_a ratios are incorrect.

Discussion

Magnitude of Solvent Effects in Bromination of Ethylenic and Acetylenic Compounds. The $k_{C=C}/k_{C\equiv C}$ ratio, in the range of 2 × 10^3, remains constant when the solvent is changed from acetic acid to 50% aqueous methanol. The value for water is somewhat lower, probably owing to underestimation of the styrene rate constant.[7] Whatever the reason for the low ratio in water, the difference is much smaller than the variations previously[3] observed, 2.6 × 10^3 to 0.6. Results on bromination of the couple *cis*-3-hexene/3-hexyne[13] whose rate ratio, 3 × 10^5, was found to be nearly identical in acetic acid, methanol, and 50% aqueous methanol, confirm the absence of significant solvent effects on the $k_{C=C}/k_{C\equiv C}$ ratio.

Therefore, solvent effects on styrene (S) and phenylacetylene (PA) bromination are very similar. Excluding water,[7] we obtain a satisfactory linear correlation between the rate constants of the two unsaturated compounds (Figure 1).

$$\log k_{PA} = 0.95 \log k_S - 3.26 \qquad (1)$$

(correlation coefficient,[14] R = 0.9989; standard deviation, s = 0.069; Exner's test,[14] Ψ = 0.064).

The magnitude of the solvent effect on 1-pentene (1-Pe) bromination has already been measured[15] at 25 °C. Plotting $\log k_S$ or $\log k_{PA}$ against $\log k_{1\text{-Pe}}$, solvent by solvent, we obtain linear correlations with near unit slopes.

$$\log k_S = 1.08 \log k_{1\text{-Pe}} - 0.04 \qquad (2)$$

$$R = 0.996, s = 0.120, \Psi = 0.124$$

$$\log k_{PA} = 1.00 \log k_{1\text{-Pe}} - 3.30 \qquad (3)$$

$$R = 0.994, s = 0.144, \Psi = 0.140$$

Solvent effects in bromination do not depend appreciably on the nature of the unsaturated substrate.

For the bromination of 1-pentene, an m value[16] of 1.16 has been obtained[15] from 16 solvents with ionizing power Y varying from −3.5 to +3.5:

$$\log k_{1\text{-Pe}} = 1.16Y + 3.58 \qquad (4)$$

$$R = 0.972, s = 0.073, \Psi = 0.133$$

Rather than calculate m values for styrene and phenylacetylene bromination[17] from the solvents given in Table I, more reliable values[18] are obtained by combining eq 2, 3, and 4 to give m_S = 1.20 and m_{PA} = 1.15. For S_N1 solvolysis leading to saturated carbonium ions, m values at 25 °C are near 1.00. For 1-bromoadamantane,[19] a substrate in which steric constraints inhibit any nucleophilic solvent assistance, m is 1.20.

From the similarity of the solvent effects in bromination and in S_N1 solvolysis, we can deduce several important conclusions. Firstly, in free bromine additions, as in S_N1 solvolysis, the solvent does not assist nucleophilically the rate-determining step. This fact is confirmed by the absence of significant curvature in the $\log k_{1\text{-Pe}}$ vs. Y plot[15] for solvents of widely different nucleophilicities. Application of the more general relationship for solvent effects,[20] $\log k/k_0 = mY + lN$, to bromination does not change significantly the m value (1.16 ± 0.08 to 1.19 ± 0.01 for 1-pentene) and leads to a very small l value (0.19 ± 0.03). Secondly, the magnitude of the m values suggests that the charge separation in the transition states of the rate-determining step is large and, therefore, that these transition states closely resemble the intermediates; as in solvolysis, information on transition states can be extrapolated to intermediates. Finally, solvent effects on the bromination of acetylenes and olefins are similar; so are they in bromination and solvolysis. These results have interesting consequences regarding the nature of the solvation in bromination and in reactions via vinyl cations.

Solvent Effects in Reactions via Vinyl Cations. The bromination of styrenes leads to β-bromocarbonium ions (I), the charge of the intermediate being stabilized by the adjacent aromatic group rather than by the neighboring bromine atom. The unimportance of bromine bridging was established on the basis of kinetic[21] and stereochemical[22] data. It has been shown[23] in the same way that the intermediates of the bromination of ring-substituted phenylacetylenes are bromovinyl carbonium ions (II). Therefore, the m values obtained above express the magnitude of the solvent effects on reactions via analogous saturated and unsaturated carbonium ions at 25 °C.

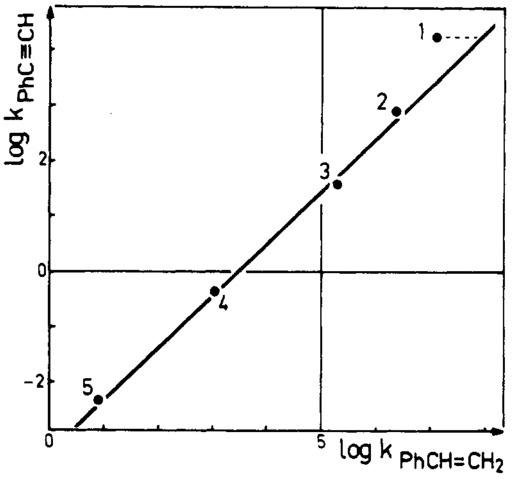
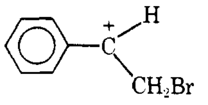


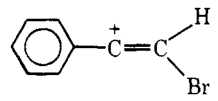
Figure 1. Similarity of the solvent effects on styrene and phenylacetylene bromination. Numbers refer to Table I.

At present, very few data regarding solvent effects on vinyl carbonium-ion reactions are accessible, although vinyl cations and the solvolysis of vinyl derivatives have been extensively studied in recent years.[2] An m value of 0.71 at 120 °C has been reported[24] for the solvolysis of α-bromo-*p*-methoxyphenylvinyl tosylate leading to ion III analogous to ion II. Similarly, solvolysis of 1-(2,4-dimethylphenyl)vinyl tosylate leads[25] to ion IV with m = 0.65 at 25 °C. Lower values, 0.34–0.53 at 120 °C, were found for the S_N1 reactions of the trianisyl vinyl system.[26] More general studies of reactions of aliphatic vinyl triflates[27] show that only cyclic substrates solvolyze with m values (0.66–0.78 at 75 °C) approaching those of typical S_N1 reactions (m for 2-adamantyl tosylate at 75 °C is 0.78). From these results and others, it appears that m values for S_N1 solvolysis of vinyl substrates are roughly in the same range as those of saturated compounds. However, the rather special conditions required for the solvolysis of normally unreactive vinyl derivatives—high temperatures, efficient leaving groups, acceleration by crowding of the substrates[25]—make it difficult to compare saturated and unsaturated cations.



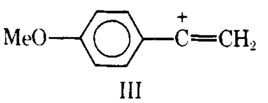
I

$m^{25°C}$ = 1.20



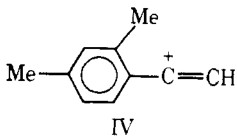
II

$m^{25°C}$ = 1.15



III

$m^{120°C}$ = 0.71



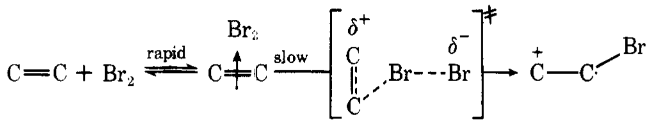
IV

$m^{25°C}$ = 0.65

Our results on bromination make such a comparison now possible: the m values for vinyl cations are similar to those for analogous saturated cations, independently of the way in which they are generated.

Solvation in Free Bromine Additions. The identity of the *m* values for styrene and phenylacetylene bromination may appear somewhat surprising. In fact, for the less reactive acetylenic substrate one would expect a more charged transition state and therefore a slightly higher *m* value than for ethylenic compounds. Structural effects are in accord with a later transition state: in acetic acid, ρ^+ for ring-substituted phenylacetylenes[23] (−5.2) is more negative than ρ^+ for styrenes[28] (−4.5). A similar constancy of solvent effects was observed for olefin bromination: styrene and stilbene, although they react with a difference of 2 log units in rates, exhibit identical *m* values, 1.20 and 1.16, respectively,[1] whereas the substituent effects ($\rho^+_{\text{stilb}} = -5.4$[29], $\rho^+_{\text{styr}} = -3.8$[30] both in methanol) indicate variations in the charge development in accord with the reactivity–selectivity principle.[31] Constancy of the solvent effect on passing from methanol in water is also observed for alkenes whose rates vary by 6 log units.[32]

In bromination, therefore, solvent and structural effects are independent. This can be understood by considering the now generally accepted[33,34] Ad$_E$Cl mechanism for molecular bromination originally proposed on the basis of solvent effects:[15] a rapid preequilibrium between olefin, bromine, and a π complex[33] precedes the rate-determining step, the dissociation of the Br–Br bond and the creation of the C–Br σ bond.[34,15] In the absence of nucleophilic solvation, the solvent can affect the rate-determining step by means of a medium effect on the magnitude of the charge separation between the cationic and anionic parts of the transition state and by electrophilic solvation of the departing bromide ion. The importance of this electrophilic solvation is revealed by the following observations:[4] high solvent isotope effect and a linear relationship between bromination rates and the free energies of solvation of the bromide ion in various solvents. Thus, in bromination the magnitude of the solvent effects depends very little, if at all, on the structure of the cationic part of the transition state. This explains why the solvent effect is independent of the bromonium or carbonium structure of the transition states[35] and also the similarity of the solvent effects on the bromination of acetylenes and olefins. This explains too why *m* values for solvolysis and bromination are so similar. The transition states of these reactions differ only with respect to the cationic part, whereas the anionic part and the charge separation are rather similar.[36]

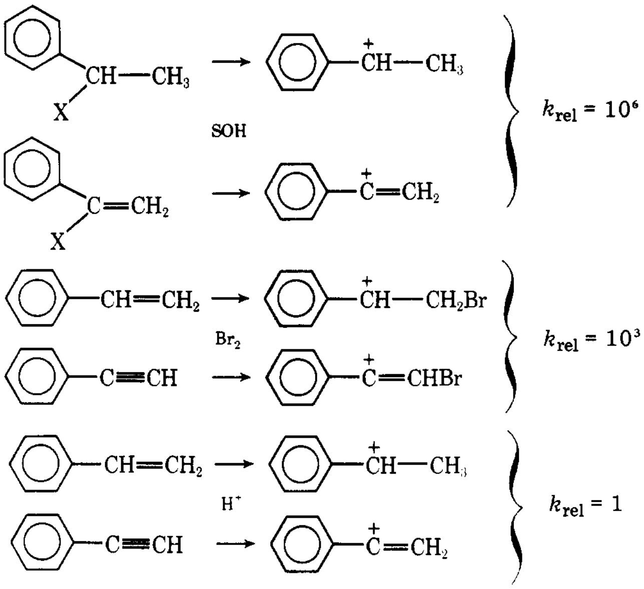


$$\mathrm{C{=}C} + \mathrm{Br_2} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{C} \overset{\mathrm{Br_2}}{\Uparrow} \mathrm{C} \xrightarrow{\text{slow}} \left[\overset{\delta^+}{\mathrm{C}} \cdots \overset{\delta^-}{\mathrm{Br{-}{-}{-}Br}} \right]^{\ddagger} \longrightarrow \overset{+}{\mathrm{C}}\mathrm{{-}C{-}Br}$$

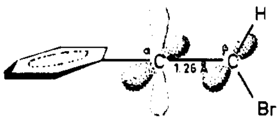
In conclusion, the solvent effects on these reactions via cationic intermediates do not give information on the structure of these intermediates; they measure only the extent to which transition states and intermediates resemble each other.

Relative Ease of Formation of Vinyl and Saturated Cations. According to previous calculations and experimental results,[25,27] the solvolytic reactivity ratio of saturated and unsaturated substrates is about 10^6. The corresponding ratio for the bromination of alkenes and alkynes via bromonium ion intermediates is slightly lower,[3,13] in the range 10^4–10^5. The present results on styrene and phenylacetylene bromination via carbonium ions lead to a ratio of about 10^3. For proton addition to the same substrates, this ratio falls to about unity.[37]

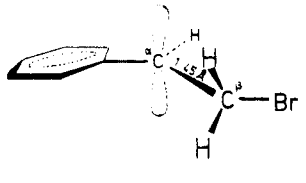
Thus, there are considerable differences in the relative ease of formation of vinyl and saturated cations, depending on their mode of generation.[38]



It is now well established[2] that relative solvolysis rates of saturated and unsaturated substrates reflect not only the differences in stabilities of the ionic intermediates but also those between the ground states, so that the reactivity ratio, 10^6, overestimates the energy differences between saturated and unsaturated cations. This explanation does not hold for the rate differences between protonation and bromination, since the ground-state energy difference is identical for both additions. The increase of 10^3 in the olefin/acetylene rate ratio on passing from protonation to bromination can only be attributed to an enhancement in the stability differences between the two types of ions by the introduction of a bromine atom in the β position.



V



VI

At present, it is considered[39] that the most probable structure for the vinyl cation is the linear[43] one, V, where the empty p orbital lies in a plane orthogonal to the ring. This is in agreement with the high sensitivity of hydration[41] and bromination[23] rates to the ring substituents; conjugation between the empty orbital and the aromatic ring is possible in such a structure. Another salient feature of V is that the σ bonds to atom C_β are of necessity coplanar with the empty p orbital; such a conformation explains why hyperconjugative stabilization of the $\mathrm{Ph{-}C^+{=}CH_2}$ cation, analogous to V, is greater than that of the saturated one.[44]

For the $k_{\mathrm{C=C}}/k_{\mathrm{C\equiv C}}$ ratio to be higher in bromination (10^3) than in hydration (1), it is necessary to assume that the replacement at C_β of a hydrogen by a bromine atom destabilizes the vinyl cation, V, more than the saturated one, VI (Figure 2). This hypothesis[47] seems to be reasonable on the following grounds. It has been shown[48] that a halogen atom in the β position relative to a cationic charge slows the rate inductively when it does not assist by a neighboring-group effect; i.e., a nonparticipating β-halogen destabilizes a carbocation. It is not surprising that this destabilization is more important in the vinyl cation than in the saturated one. Ab initio calculations[43] and experimental results[27] indicate that vinyl cations have larger β-substituent effects than saturated ones, due to the fact that sp^2–sp^2 bonds (in V) are shorter[49] than sp^2–sp^3 bonds[50] (in VI).

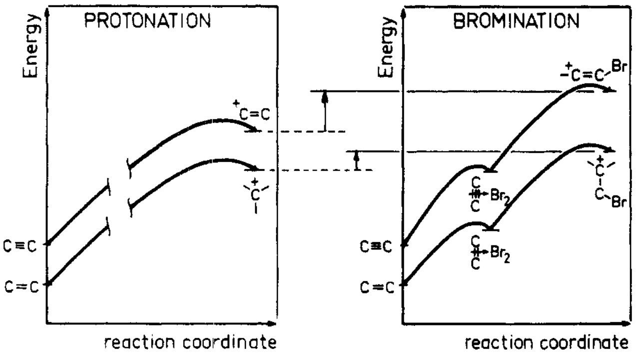


Figure 2. Schematic representation of the relative ease of formation of carbonium and vinylcarbonium ions in protonation and bromination. The β-bromine atom destabilizes the vinyl cation more importantly than the saturated one.

Experimental Section

Chemicals. Styrene and phenylacetylene were purified by preparative GLC. Methanol and water were treated as usual.[51]

Kinetic Measurements. Bromination rate constants of phenylacetylene in methanol and 70% aqueous methanol were measured by the previously described potentiometric method,[51] in pseudo-first-order conditions. The concentration of phenylacetylene was in the range 10^{-2}–10^{-3} M and that of bromine 10^{-4}–10^{-5} M.

Rate constants of styrene in 70% aqueous methanol and of phenylacetylene in 50% aqueous methanol and in water were obtained spectroscopically[5] in second-order conditions. The concentrations of unsaturated compounds were 10^{-4}–10^{-5} M; that of bromine was about twice as great.

Rate constants of styrene in water and in 50% aqueous methanol were measured by couloamperometry[51,6] at concentrations between 5×10^{-6} and 5×10^{-7} M.

Each experimental rate constant given in Table I is the average of at least four determinations wherein reactant concentrations are varied by a factor of about 10. Reproducibility between runs is within 5%.

k_{Br_2} Measurements. The overall bromination rate constants, k_g, are measured at various bromide ion concentrations. The elementary rate constants, k_{Br_2}, given in Table I, are obtained from k_g values by extrapolation to zero bromide ion concentration[9] using the equation

$$k_g(1 + K[\mathrm{Br}^-]) = k_{\mathrm{Br}_2} + Kk_{\mathrm{Br}_3^-}[\mathrm{Br}^-]$$

K, the $Br_2 + Br^- \rightleftharpoons Br_3^-$ equilibrium constant, is 177, 88, 48, and 17 in methanol, 70 and 50% aqueous methanol, and water,[52] respectively.

Solubility. Solubility of styrene and phenylacetylene measured by UV spectroscopy is 10^{-3} M in 50% aqueous methanol at 25 °C. At this concentration, a homogeneous solution (500 mL) is obtained after 15 min of vigorous stirring. Unsuccessful attempts to measure the solubilities of the unsaturated compounds in water at 25 °C were made spectroscopically

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Registry No.—I, 20500-85-0; II, 62375-55-7; phenylacetylene, 536-74-3; styrene, 100-42-5.

References and Notes

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(7) It was not possible to vary significantly the concentration of styrene in water. In this case, the rate constant is very close to the upper limit of the couloamperometric method.[6] Very low concentrations of olefin and bromine (10^{-7} M) must be used to obtain a measurable rate. Variations of the styrene concentration lead to an unsuitable amperometric response. Therefore, we cannot verify the solubility of styrene in water and the validity of the measured rate constant. For this reason, the k_{Br_2} value for styrene in water could be erroneous and somewhat underestimated, since the real styrene concentration in the homogeneous part of the reaction medium would be less than calculated from the amount of styrene present.

(8) A poor solubility of the unsaturated compounds leads generally to a characteristic variation of the apparent rate constants: the rate constant increases as the substrate concentration diminishes.

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(17) The large range of solvents used in the calculation of $m_{1\text{-Pe}}$ minimizes errors arising out of the possible inapplicability of some Y values to bromination due to various factors.[19] The indirect calculation of m_S and m_{PA} from eq 2 and 3 takes advantage of this minimization.

(18) An m value, 0.95, for styrene bromination was reported previously,[1] but the rate constant in 70% aqueous methanol was not measured at that time. The slope of the log k_S/log $k_{1\text{-Pe}}$ correlation in acetic acid, methanol, 50% aqueous methanol and water was only 0.83 ± 0.16, instead of 1.08 ± 0.05 now found from acetic acid, methanol, 70% and 50% aqueous methanol, whereas for all five solvents it is 0.96 ± 0.14. For the reasons given,[7] we reject the value for water, but this clearly does not seriously affect the m value for styrene bromination nor our conclusions (vide infra) regarding the similarity of solvent effects in bromination and in solvolysis.

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(36) For this reason, we compared the solvent effects on bromination with those

on solvolysis of bromides where the leaving group is also a bromide ion. In solvolysis, a change in the leaving group leads to significant variation in the *m* value. For example, $m_{1\text{-AdOTs}} = 0.97$ (D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92**, 7300 (1970)), whereas $m_{1\text{-AdBr}} = 1.20$ at 25 °C.[19]

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Neutral Solvolysis of Covalent Arylsulfonylmethyl Perchlorates. The Kinetic Basicity of Water and Some Aliphatic Alcohols

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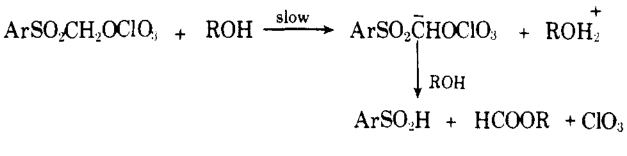
Rates and activation parameters for rate-determining deprotonation of two covalent arylsulfonylmethyl perchlorates (**1**, **2**) in water and a series of aliphatic alcohols have been determined to assess the *kinetic* basicity of these solvents. Second-order rate constants for solvent-induced deprotonation do not decrease upon decreasing solvent polarity but follow the sequence CF_3CH_2OH(TFE) < H_2O < MeOH < EtOH < *n*-PentOH < *t*-BuOH. Except for TFE, the $\Delta H^{\ddagger}$ values for solvolysis of **1** are linearly related to the gas-phase proton affinities of these solvents. The $\Delta S_2^{\ddagger}$ values parallel the cohesive energy densities of the solvents. The kinetic data are rationalized in terms of a "proton-binding" and a "solvent-ordering" process. Several factors which affect the kinetic basicity of water and organic solvents are discussed.

Recent comparisons of the gas-phase proton affinities (PA) of organic solvents with the corresponding Brönsted basicities have dramatically illustrated the crucial role of solvation effects in determining the solution basicities.[1-3] For oxygen bases such as water, alcohols, and ethers it was shown that hydrogen bonding interactions are of paramount importance in stabilizing protonated onium ions in the condensed phase.[4] These results have served as an explanation for the discrepancy between the low PA of water (165 kcal mol^{-1}) relative to that of alcohols and ethers (ca. 180–200 kcal mol^{-1}) and the relatively high equilibrium basicity of water in aqueous solutions as judged from proton exchange equilibria between water and alcohols in alcohol–water mixtures.[5] In addition, it has been shown that proton exchange of carboxylic acids is faster in water than in alcohols.[6]

For some years we have been especially interested in the kinetic basicity of solvent molecules. In this context, we now report rate constants and activation parameters for the general-base-catalyzed solvolysis of two covalent arylsulfonylmethyl perchlorates (**1**, **2**) in water and in a series of aliphatic alcohols. In the absence of other effective Brönsted bases, the solvolysis process has been shown to involve irreversible proton transfer from the substrate to the solvent[7] (primary kinetic deuterium isotope effect k_H/k_D ca. 6) and offers a quantitative but specific probe for the kinetic basicity of the solvent. Previously, the reaction has been used as a model to assess the kinetic basicities of water,[8] aqueous solvent mixtures,[9] dipolar aprotic solvents,[10] and some Brönsted bases in the presence of surfactant micelles.[11]



$$\begin{array}{l} ArSO_2CH_2OClO_3 + ROH \xrightarrow{\text{slow}} ArSO_2\bar{C}HOClO_3 + RO\overset{+}{H}_2 \\ \qquad\qquad\qquad\qquad\qquad \downarrow ROH \\ \qquad\qquad\qquad\qquad ArSO_2H + HCOOR + ClO_3^- \end{array}$$

1, Ar = *p*-$NO_2C_6H_4$
2, Ar = *p*-$CH_3C_6H_4$
R = H, alkyl

Results and Discussion

Table I reports pseudo-first-order rate constants (k_{obsd}), activation parameters, and deuterium isotope effects for the solvolysis of **1** and **2** in water and in a series of aliphatic alcohols. All rate constants pertain to rate-determining deprotonation of the substrate by solvent molecules as indicated by the large values of the primary kinetic deuterium isotope effects (k_H/k_D) and by the observation that small amounts of acid do not influence the rates (see Experimental Section). The data summarized in Table I show that, except for 2,2,2-trifluoroethanol (TFE), water and the alcohols exhibit comparable kinetic basicities. However, direct comparison of k_{obsd} values for solvents acting as Brönsted bases is misleading because of the differences in solvent concentrations in the pure solvents. If *n* represents the number of solvent molecules which are tightly bound in the transition state for the deprotonation of **1** and **2**, k_{obsd} will be represented by $k_{n+1}[\text{solvent}]^n$. In principle, *n* may be evaluated from a plot of log k_{obsd} vs. log [solvent] when the solvent concentration is varied