Notes

Nucleophilic Contribution of the Solvent in Olefin Bromination. 1. Steric Inhibition to Nucleophilic Solvation in Alkene Bromination via Bromonium Ions

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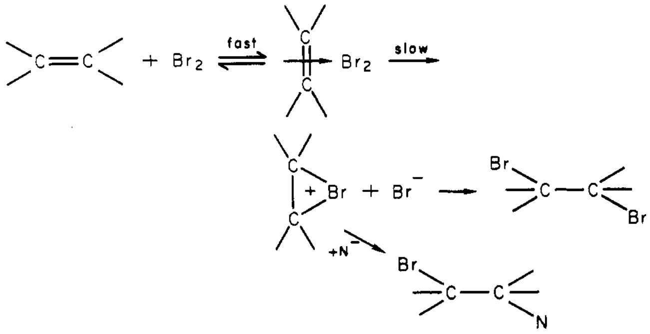
In olefin bromination via ionic intermediates, it has been established that the solvent acts by its polarity and by electrophilic assistance to the departure of the bromide ion in the rate-determining step.[1-5] The solvent behaves as a nucleophile only in the second, fast, product-forming step.



In this respect, bromination resembles closely S_N1 solvolysis. A nucleophilic role for the solvent in a mechanism analogous to the S_N1 intermediate mechanism for solvolysis has been discarded[3] in bromination on the basis of the high m values ($m = 1.16$ from $Y_{t\text{BuCl}}$ for 1-pentene) and the unsignificant l value ($l = 0.20$ for the same olefin) obtained by applying the general Winstein equation[6] to solvent effects in bromination (eq 1).

$$\log k/k_0 = mY + lN \qquad (1)$$

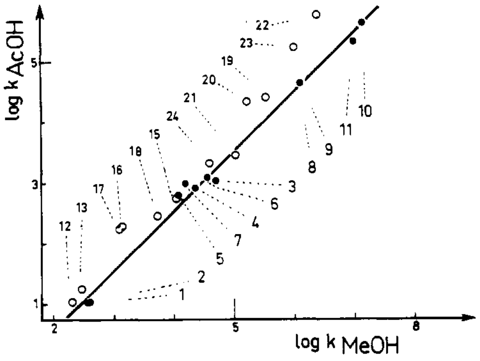


Figure 1. Comparison of polar and steric effects of alkyl groups on bromination rates of linear (●) and branched (○) alkenes in acetic acid and in methanol. Polar effects are identical in both solvents but steric effects differ. Deviations of branched alkenes are attributed to steric inhibition to nucleophilic solvation by methanol.

We present now more refined data which show that the nucleophilic role of the solvent in the ionization step of bromination via bromonium ion intermediates is not negligible. This result is deduced from a comparison of polar and steric effects of alkyl groups in methanol and in acetic acid, two solvents which differ in their ionizing power[7] (MeOH, $Y_{\text{Br}} = -1.12$; AcOH, $Y_{\text{Br}} = -2.1$) and also their nucleophilic power (MeOH, $N = 0.01$; AcOH, $N = -2.05$).

Kinetic data in methanol and in acetic acid for alkenes with linear and branched substituents are presented in Table I. When substituent effects in acetic acid are compared to the same effects in methanol (Figure 1), a very imprecise correlation is obtained: the correlation coefficient ($R = 0.983$) and standard deviation ($s = 0.20$) are poor. This is rather astonishing for several reasons: (i) the rate constants are measured by the same kinetic method with a reproducibility generally better than ±2% and at worst ±5%; (ii) there is a very close relationship between the data in methanol and in 70% aqueous methanol for the same alkenes.[9] However, if data related to linear alkenes 1 → 11 only are used in the calculation, a satisfactory linear correlation is obtained (eq 2).

$$\log k_{\text{AcOH}} = 0.99 \log k_{\text{MeOH}} - 1.41 \qquad (2)$$
$$R = 0.997 \qquad s_{\text{slope}} = 0.02$$

As shown in Figure 1, branched alkenes 12 → 24 deviate more or less systematically; moreover, the deviations are always positive; i.e., they react in acetic acid faster than expected from relationship 2. The steric deccelerating effect is less pronounced in acetic acid than in methanol whereas the polar effect is identical in these two solvents, as shown by the near unit slope of eq 2. A priori, the lessening of the steric interactions in acetic acid could result either from an earlier transition state or from a decrease of solvent–transition state interactions if some nucleophilic solvation exists in the more nucleophilic methanol.

An early transition state resembles the charge-transfer complex[5] where the olefinic carbon atoms are sp² more

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[1] F. Garnier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1968).

[2] M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 1977 (1975).

[3] M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **42**, 2689 (1977).

[4] A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **44**, 4221 (1979).

[5] This proposal assumes that solvent effects on the bromine–olefin CTC formation are negligible compared with those on the ionization step. The assumption is reasonable since charge development is considerably more important in the second than in the first step. Moreover, it is supported by the comparison of the bromination rates of α-methylstyrenes (M. F. Ruasse, A. Argile, and J. E. Dubois, *J. Am. Chem. Soc.*, **100**, 7645 (1978)) and the equilibrium constants of the acetophenone–iodine CTC formation (C. Laurence, G. Guiheneuf, and B. Wojtkowiak, *J. Am. Chem. Soc.*, **101**, 4793 (1979)): solvent and substituent effects on bromination rates are distinctly higher than those on CTC formation.

[6] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

[7] T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1982). The Y_{Br} scale proposed by these authors is more suitable than the original $Y_{t\text{-BuCl}}$ scale since the leaving group in bromination is a bromide ion and since 1-adamantylbromide solvolyses without any nucleophilic solvent assistance.

[8] F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).

[9] G. Barbier and J. E. Dubois, *J. Chim. Phys.-Phys.-Chim. Biol*, **65**, 1989 (1968).

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Table I. Bromination Rate Constants of Linear and Branched Alkenes in Methanol and in Acetic Acid. Differences in the Solvent Sensitivity of Both Sets of Alkenes Are Revealed by Δ, *R*, and *m* Values

no.	alkenes	k_{AcOH}[a]	k_{MeOH}[a]	Δ[b]	R[c]	$m_{t\text{-BuCl}}$[d]	m_{Br}[d]
1	$MeCH{=}CH_2$	11.5	4.03×10^{2}[f]	−0.10			
2	n-$PrCH{=}CH_2$	11.5[e]	3.95×10^{2}[f]	−0.09	6.0	1.16	0.96
3	$Me_2C{=}CH_2$	1.0×10^{3}	5.01×10^{4}	−0.17			
4	*cis*-$MeCH{=}CHMe$	8.10×10^{2}	2.34×10^{4}[g]	0.09			
5	*trans*-$MeCH{=}CHMe$	6.20×10^{2}	1.29×10^{4}[g]	0.14			
6	*cis*-$MeCH{=}CHEt$	1.28×10^{3}	3.47×10^{4}[g]	−0.04	4.1	1.11	0.92
7	*trans*-$MeCH{=}CHEt$	1.19×10^{3}	1.58×10^{4}[g]	0.24		1.10	0.91
8	$Me_2C{=}CHMe$	4.37×10^{4}	1.29×10^{6}[g]	0.02			
9	$Et_2C{=}CHMe$	4.16×10^{4}	1.23×10^{6}	0.02			
10	$Me_2C{=}CMe_2$	4.66×10^{5}	1.43×10^{7}	0.02	3.3	1.17	0.96
11	(Z)-$MeEtC{=}CMeEt$	2.30×10^{5}	1.00×10^{7}	−0.13			
12	t-Bu-i-$PrC{=}CH_2$	12.0	1.95×10^{2}[g]	0.22	1.4	1.31	1.08
13	t-$Bu_2C{=}CH_2$	18.2	2.82×10^{2}[g]	0.25	1.5		
14	*neo*-$Pe_2C{=}CH_2$	0.91	1.45×10[g]	0.22			
15	*cis*-$MeCH{=}CH$-t-Bu	6.75×10^{2}	1.10×10^{4}[g]	0.24	1.5	1.23	1.02
16	*trans*-$MeCH{=}CH$-t-Bu	2.01×10^{2}	1.70×10^{3}[g]	0.51	1.6		
17	*cis*-i-$PrCH{=}CH$-i-Pr	1.78×10^{2}	1.55×10^{3}[g]	0.50			
18	*trans*-i-$PrCH{=}CH$-i-Pr	2.88×10^{2}	5.25×10^{3}[g]	0.19			
19	$Me_2C{=}CH$-i-Pr	2.63×10^{4}	3.38×10^{5}	0.37	1.7		
20	$Me_2C{=}CH$-t-Bu	2.09×10^{4}	1.66×10^{5}	0.57	1.6		
21	$Me_2C{=}CH$-*neo*-Pe	2.63×10^{3}	1.05×10^{5}	−0.14	4.9		
22	$Me_2C{=}CMe$-i-Pr	4.36×10^{5}	2.40×10^{6}	0.73	1.0	1.30	1.07
23	$Me_2C{=}CMe$-*sec*-Bu	1.74×10^{5}	1.01×10^{6}	0.72			
24	$Me_2C{=}CMe$-*neo*-Pe	2.00×10^{3}	4.07×10^{4}	0.14			

[a] In $M^{-1}\,s^{-1}$, rate constants for free bromine addition extrapolated to $[Br^-] = 0$ from kinetic bromide ion effects; see Experimental Section. [b] $\Delta = \log k_{\mathrm{exptl}} - \log k_{\mathrm{calcd}}$ calculated by relationship 2. [c] $R = (k_{\mathrm{aq\,EtOH}}/k_{\mathrm{AcOH}})_Y$. [d] $m_{t\text{-BuCl}}$ calculated from the rate data of Table II in the Winstein–Grunwald Y scale (ref 6); m_{Br} in the Y_{Br} scale (ref 7). [e] Reference 1. [f] Reference 18. [g] Reference 19.

Table II. Solvent Effects on Bromination Rate Constants[a] of Linear and Branched Alkenes

	AcOH	EtOH	aq EtOH[b]	MeOH	M85[c]	M75[c]	M70[c]
Y_{Br}[d]	−2.10	−2.40	(−2.10)	−1.12	(0.35)	(1.10)	1.42
$Y_{t\text{-BuCl}}$[d]	−1.64	−2.03	(−1.64)	−1.09	(0.10)	(0.65)	0.96
n-Pr-$CH{=}CH_2$	11.5[e]	12.9	69.3	3.95×10^{2}[f]	1.05×10^{4}[h]	4.78×10^{4}[h]	9.85×10^{4}
cis-$MeCH{=}CHEt$	1.28×10^{3}	1.70×10^{3}	5.25×10^{3}	3.47×10^{4}[g]		3.72×10^{6}	
trans-$MeCH{=}CHEt$	1.19×10^{3}	1.09×10^{3}		1.58×10^{4}[g]		2.41×10^{6}	
$Me_2C{=}CMe_2$	4.66×10^{5}	4.47×10^{5}	1.55×10^{6}	1.43×10^{7}			
cis-$MeCH{=}CH$-t-Bu	6.75×10^{2}	3.63×10^{2}	9.55×10^{3}	1.10×10^{4}[g]	2.76×10^{5}		3.80×10^{6}
trans-$MeCH{=}CH$-t-Bu	2.01×10^{2}		3.16×10^{2}	1.70×10^{3}[g]			
cis-$EtCH{=}CH$-t-Bu	8.15×10^{2}			1.07×10^{4}[g]			5.89×10^{7}
t-Bu-i-$PrC{=}CH_2$	12.0	5.03	16.6	1.95×10^{2}[g]	5.75×10^{3}		1.13×10^{5}
$Me_2C{=}CMe$-i-Pr	4.36×10^{5}	1.58×10^{5}	4.23×10^{5}	2.40×10^{6}	5.62×10^{7}		

[a] k in $M^{-1}\,s^{-1}$ for free bromine addition, see Experimental Section. [b] 97.5% aqueous EtOH. [c] M85, M75, and M70: 85%, 75%, and 70% aqueous MeOH respectively (v/v). [d] Reference 7. [e] Reference 1. [f] Reference 18. [g] Reference 19. [h] Extrapolated from the data of ref 1.

than the bromonium ions where these atoms are almost sp^3. Consequently the substituent–substituent interactions should decrease as the transition state becomes earlier. To check this assumption, we measured solvent effects more extensively (Table II) for some linear and branched olefins. The m values obtained from the Y_{Br} scale[7] express the transition-state position as shown previously.[2,4,10] If the transition state is earlier for branched alkenes, we should find m values for these alkenes smaller than those for linear alkenes. The results in Table I show that this prediction is not verified; on the contrary, m values for the branched alkenes appear slightly greater than those for the linear ones. An earlier transition state is, therefore, not the reason for the positive deviations of branched olefins from relationship 2.

In the $(\log k)/Y_{\mathrm{Br}}$ plots (Figure 2) it is noticeable that the points corresponding to acetic acid are systematically below the line of the alcoholic mixtures for linear alkenes but on this line for branched alkenes. According to this picture, alcohols and acetic acid should intervene only by their ionizing power for branched alkenes whereas for linear alkenes the nucleophilicity difference between the two types of solvent has a significant influence. This result leads us to examine the second suggestion for interpreting the $(\log k)/(\log k)$ relationship 2.

The differences between branched and linear alkenes as regards relationship 2 suggest that nucleophilic solvation by methanol is important for linear but not for branched olefins. A classical method for estimating nucleophilic solvation[11] is based on the rate ratio in two solvents of similar ionizing power Y but of different nucleophilic power N. Various pairs of solvent have been proposed to carry out this measurement: aqueous ethanol/acetic acid[11a] or aqueous ethanol/trifluoroethanol,[11b] for example. The first pair is a priori less suitable than the second because more nucleophilic assistance can be conceived for acetic acid ($N = -2.04$) than for TFE ($N = -2.8$). We have, however, chosen $(k_{\mathrm{aq\,EtOH}}/k_{\mathrm{AcOH}})_Y$, denoted R, since many alkenes in Table I are too reactive for accurate measurements to be obtained in TFE: for example, a rate constant of about

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[10] Most of the solvent effect in bromination arises from the electrophilic solvent assistance to the departure of the bromide ion, as shown by the high solvent isotope effects[4] (F. Garnier, R. Donnay, and J. E. Dubois, *J. Chem. Soc. D*, 829 (1971). The solvent effect is, therefore, related to the negative charge of the transition state, i.e., to the transition-state position.

[11] (a) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, 14, 1 (1977); (b) J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.*, 102, 3829 (1980); (c) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *ibid.*, 91, 4838 (1969).

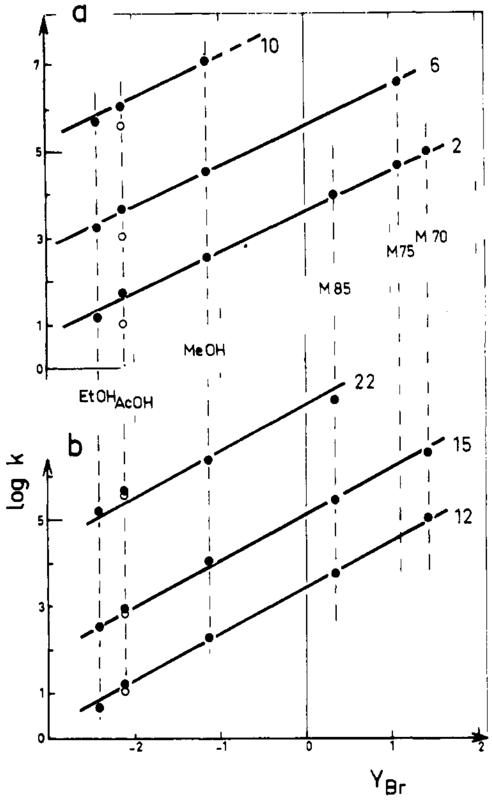
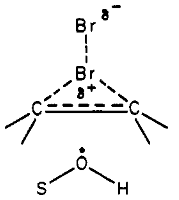
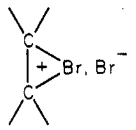


Figure 2. The (log k)/Y_{Br} plots in alkene bromination. For linear alkenes **2a**, acetic acid (○) is systematically below the line for alcohols and their aqueous mixtures (●); but, for branched alkenes **2b**, acetic acid is on the line. Nucleophilic solvation accelerates the linear alkene bromination in alcohols as compared to acetic acid.

10^{10} M^{-1} s^{-1} is expected for alkene **22** in this solvent. The results are given in Table I. The R values are near 1 for branched olefins, except for **21**, but greater than 1 for linear. This can be interpreted by assuming that nucleophilic solvation by alcohols is suppressed on going from linear to branched alkenes. This interpretation is reasonable: if nucleophilic solvation occurs during the ionization of the CTC (charge-transfer complex), the solvent molecule should approach the side of the olefin opposite to that already occupied by the bromine. For complexation with the olefin, bromine preferentially chooses the less hindered side of the alkene, and the most hindered side of the alkene is left for nucleophilic solvation. It is reasonable therefore that this solvation should be very sensitive to substituent branching. In this respect, it is interesting to note that the neopentyl group (**21**) does not seem to inhibit solvent approach as much as *tert*-butyl (**20**) or isopropyl (**19**).



Another classical interpretation of R values larger than 1 invokes ion-pair return which is possible in acetic acid but less likely in alcohols.[12] In bromination, internal return should not be sensitive to steric hindrance since it supposes the attack of the bromide ion on the bridging bromine of the bromonium ion.



We conclude, therefore, that there is a nucleophilic contribution of the solvent in the rate-determining step of alkene bromination. The transition-state stabilization provided by this solvation is always small; in no case is it as important as those observed in S_N2 solvolysis where R values go up to 70–100.[13] Our finding does not question the existence of a ionic intermediate in bromination; nucleophilic solvation in this reaction is more properly described by enclosing in the transition state a solvent molecule which would "tickle" the positive charge according to the anthropomorphic description of Jencks.[14] This picture corresponds to an enforced mechanism which can be named, by analogy with solvolysis, Ad_EC1 intermediate against the usually postulated Ad_EC1 mechanism of bromination.[1] If this parallelism between bromination and solvolysis as regards the role of the solvent is extended, an Ad_EC2 mechanism could be predicted for poorly reactive unsatured substrates. In this respect, it is interesting to note that alkyne bromination proceeds with a significant contribution of nucleophilic assistance.[4]

The existence of nucleophilic solvation in bromination has multiple consequences,[15] in particular on the interpretation of the steric effect and on the parameters of structure/solvent-reactivity relationships. The origin of the steric effect has been sought mainly in the bromine substituents interaction[16] (substitutent inhibition of bromine approach); it becomes obvious from our results that part of the steric deceleration is due to solvent–substituent interactions. On the other hand, it is well-known in solvolysis that nucleophilic solvation reduces the absolute value of the LFER coefficients such as ρ or m.[17] This decrease is generally attributed to charge delocalization by the solvent. In bromination, the m parameters also decrease ($m \simeq 0.9$ for linear and 1.1. for branched alkenes); this is not likely to be due to charge delocalization since there is no substantial bonding between the solvent and the positive charge but rather to a dependence of the nucleophilic solvation on reactivity as shown by the small R variations in the linear series. The next paper presents more significant results on this dependence.

Experimental Section

Materials. The alkenes are either commercially available (Chemical Samples) or synthetized as previously reported;[16] their purity was checked by GLC and NMR analysis. Salts (sodium or lithium bromide) are Merck products; they were dried at 120 °C overnight before use. Solvents were purified as usual;[20]

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[12] V. J. Shiner, Jr., D. A. Nolen, and K. Humski, *J. Org. Chem.*, **44**, 2108 (1979) and references there cited.

[13] J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970); J. C. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970).

[14] W. P. Jencks, *Acc. Chem. Res.*, **13**, 161 (1980); W. P. Jencks, *Chem. Soc. Rev.*, **10**, 345 (1981).

[15] Steric inhibition to solvent approach should result in smaller amounts of solvent-incorporated products for branched than for linear alkenes. This is roughly confirmed for the following alkenes: methanolic bromination of **15** gives 35% of methoxy bromide but that of **6**, 52%.

[16] M. F. Ruasse, A. Argile, E. Bienvenue-Goetz, and J. E. Dubois, *J. Org. Chem.*, **44**, 2758 (1979); D. Grosjean, G. Mouvier, and J. E. Dubois, *ibid.*, 41, 3869, 3872 (1976).

[17] D. J. McLennan and P. L. Martin, *J. Chem. Soc., Perkin Trans. 2*, 1091 (1982); S. G. Shafer and J. M. Harris, *J. Org. Chem.*, **46**, 2164 (1981); T. W. Bentley and C. T. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 557 (1978).

[18] E. Bienvenue-Goetz, J. E. Dubois, D. W. Pearson, and D. L. H. Williams, *J. Chem. Soc. B*, 1275 (1970).

methanol and ethanol were distilled over bromine and dried by distillation on magnesium; acetic acid was purified by refluxing with chromium trioxide and acetic anhydride and then distilled; water was distilled from potassium permanganate.

Kinetic Measurements. Three kinetic methods already described were used to measure the experimental rate constants: couloamperometry[20] for constants higher than 5×10^3 M^{-1} s^{-1}, potentiometry[21] and UV spectroscopy[22] for the smaller ones. Kinetic experiments were carried out in second-order conditions (first order in bromine, first order in the alkene), except for potentiometry where an excess of alkene was used (pseudo-first-order conditions). Reagent concentrations ranged from 10^{-7} to 5×10^{-4} M for bromine and from 10^{-7} to 2×10^{-2} M for the alkene, depending on the methods and the reactivities. The experimental rate constants, k_{exptl}, were obtained with a reproducibility generally better than 2%.

In all three methods, an excess of bromide ions is necessary[23] to fix equilibrium 3. The experimental rate constant combines

$$\mathrm{Br_2 + Br^- \rightleftharpoons Br_3^-} \qquad (3)$$

the elementary rate constants related to the discrete processes:[24] addition of free bromine k, addition of bromine assisted by the bromide ion, $k_{\mathrm{Br^-}}$, and that of the electrophilic tribromide ion, $k_{\mathrm{Br_3^-}}$.

k Determination. Relationship 4 expresses[24] the bromide ion effect:

$$k_{\mathrm{exptl}}(1 + K[\mathrm{Br^-}]) = k + \beta[\mathrm{Br^-}] \qquad (4)$$

Therefore, we measured k_{exptl} at several (three or four) bromide ion concentrations. According to eq 4, the plot of $k_{\mathrm{exptl}}(1 + K[\mathrm{Br^-}])$ against $[\mathrm{Br^-}]$ gave a straight line whose intercept was k.

Registry No. **1**, 115-07-1; **2**, 109-67-1; **3**, 115-11-7; **4**, 590-18-1; **5**, 624-64-6; **6**, 627-20-3; **7**, 646-04-8; **8**, 513-35-9; **9**, 816-79-5; **10**, 563-79-1; **11**, 19550-87-9; **12**, 20442-64-2; **13**, 558-37-2; **14**, 141-70-8; **15**, 762-63-0; **16**, 690-08-4; **17**, 10557-44-5; **18**, 692-70-6; **19**, 625-65-0; **20**, 107-40-4; **21**, 40467-04-7; **22**, 565-77-5; **23**, 22675-62-3; **24**, 33175-59-6.

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(19) M. de Ficquelmont-Loizos, Doctoral Thesis, CNRS AO 8355, Paris, 1976.

(20) J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964); J. E. Dubois, M. F. Ruasse, and D. Poupard, *ibid.*, **152**, 67 (1983).

(21) A. F. Hegarty, J. S. Lomas, W. V. Wright, E. D. Bergman, and J. E. Dubois, *J. Org. Chem.*, **37**, 2222 (1972).

(22) J. E. Dubois and F. Garnier, *Spectrochim. Acta, Part A*, **28A**, 2279 (1967).

(23) Some bromination rate constants have been previously measured in acetic acid without excess added bromide ion (A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977)). This kinetic procedure is unreliable. Bromination in acetic acid liberates bromide ions which react rapidly with free bromine; therefore, tribromide ion addition competes with free bromine addition increasingly as the kinetic run proceeds. Kinetic experiments carried out in the absence of excess bromide ion give poorly reproducible (up to 20%) rate constants which are systematically higher than those obtained from bromide ion effects with a reproductibility generally better than 5%.

(24) E. Bienvenue-Goetz and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 2089 (1968); J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

Nucleophilic Contribution of the Solvent in Olefin Bromination. 2. Reactivity Dependence of the Nucleophilic Solvation in Bromination via β-Bromo Carbocations

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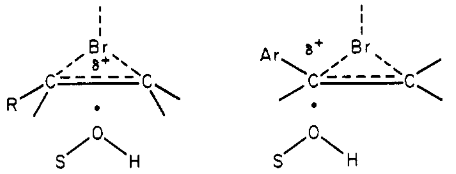
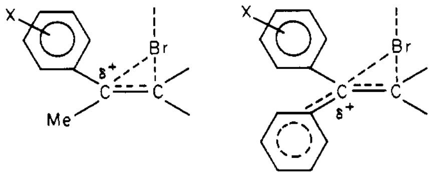
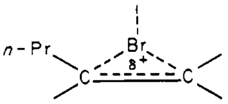
Nucleophilic solvation by hydroxylic solvents in the rate-determining step of alkene bromination has been demonstrated by comparing kinetic solvent effects on the reaction of linear and branched alkenes: steric crowding by the substituents to the double bond inhibits nucleophilic solvation.[1] The magnitude of this kind of solvation should depend on charge delocalization in the transition state: carbocation-like transition states should be solvated more strongly than bromonium-ion-like ones.[2] In this note, we present results on arylolefin bromination[3] which support this expectation.



In Table I are shown the experimental results for bromination of substituted α-methylstyrenes[4] and 1,1-diphenylethylenes.[5] These two sets of olefins react at approximately the same rate via carbonium-ion-like transition states; they differ in their abilities to stabilize the charge by resonance delocalization.





Two different types of solvent have been considered: (i) alcohols and their aqueous mixtures whose Y values[6] vary widely (−2.4 to +1.42) while the N values ($\simeq$0.0) are approximately constant;[7] (ii) acetic acid which has a Y value in the alcohol range but a very different N value[7] (−2.05). A plot of the kinetic solvent effects against Y_{Br} (Figure 1) shows that acetic acid deviates systematically from the straight line of the alcohols. Moreover, in each olefin series deviations increase as the reactivity decreases. The constantly negative values of this deviation are consistent[1] with either nucleophilic assistance by the alcohols or greater internal return in acetic acid than in alcohols.

Internal return has been ruled out in alkene bromination via bromonium ions;[1] a fortiori, since return implies

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(1) M. F. Ruasse and B. L. Zhang, *J. Org. Chem.*; preceding note in this issue.

(2) The rate-determining transition state of alkene bromination is bromonium-ion-like whatever the substituents and the reactivity: E. Bienvenue-Goëtz and J. E. Dubois, *Tetrahedron*, **34**, 2021 (1978). Olefins where a resonant substituent is conjugated with the double bond react generally via carbonium-ion-like transition states: E. Bienvenue-Goëtz and J. E. Dubois, *J. Am. Chem. Soc.*, **103**, 5388 (1981).

(3) For arylolefin bromination the transition-state structure can vary from bromonium- to carbonium-ion-like as the donor ability of the ring substituents increases (M. F. Ruasse and J. E. Dubois, *J. Org. Chem.* **37**, 1770 (1972); **38**, 493 (1973); **39**, 2441 (1974), and ref 4). It can be independent of this substituent if there is another electron-donating substituent on the double bond (M. F. Ruasse and A. Argile, *ibid.*, **48**, 202, 209 (1983).

(4) M. F. Ruasse, A. Argile, and J. E. Dubois, *J. Am. Chem. Soc.*, **100**, 7645 (1978).

(5) J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37**, 2218 (1972).

(6) T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1982).

(7) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).

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