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

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

the elementary rate constants related to the discrete processes:[24] addition of free bromine k, addition of bromine assisted by the bromide ion, k_{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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(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

Marie-Françoise Ruasse* and Elisabeth Lefebvre

Institut de Topologie et de Dynamique des Systèmes, Université Paris VII, associé au C.N.R.S., 1, rue Guy de la Brosse, 75005 Paris, France

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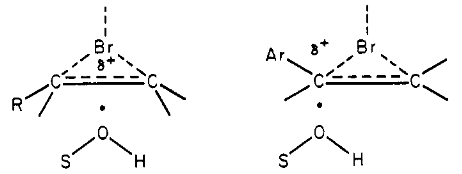
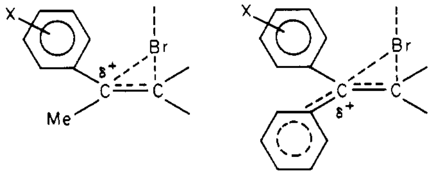
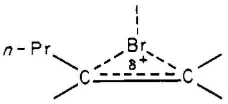
Nucleophilic solvation by hydroxylic solvents in the rate-determining step of alkene bromination has been demonstrated by comparing kinetic solvent effects on the reaction of linear and branched alkenes: steric crowding by the substituents to the double bond inhibits nucleophilic solvation.[1] The magnitude 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).

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Table I. Rate Constants[a] of Free Bromine Additions to X-Substituted 1,1-Diphenylethylenes (DPE) and α-Methylstyrenes (α-MS) in Various Hydroxylic Solvents

	X	AcOH	EtOH	aq EtOH[b]	MeOH	M85[c]	M70[c]	R^d	m_{Br}[e]
DPE	4-CF_3	6.53	1.46×10^1	4.27×10^1	3.89×10^2		5.17×10^4	6.5	0.90
	H	2.46×10^3	2.68×10^3	6.30×10^3	4.17×10^4[f]		4.34×10^6	2.6	0.83
	4-OMe	1.68×10^6	1.59×10^6	2.57×10^6	8.91×10^6[f]	3.44×10^7	1.45×10^3	1.5	0.49
α-MS	3-CF_3	3.42	5.60×10^1	1.17×10^2	9.17×10^2[g]	5.76×10^4	4.79×10^5	34	1.03
	H	4.17×10^3	9.30×10^3	2.24×10^4	1.38×10^5[g]	1.68×10^6	1.50×10^7	5.4	0.81
	4-OMe	1.10×10^7	1.20×10^7	1.86×10^7	6.60×10^7[g]	3.91×10^8		1.7	0.54

[a] In $M^{-1} s^{-1}$ at 25 °C. [b] 97.5% aqueous EtOH in volume. [c] M85: 85% aqueous MeOH; M70: 70% aqueous MeOH. [d] $R = (k_{aq\,EtOH}/k_{AcOH})_Y$. [e] m_{Br} in the Y_{Br} scale, calculated from the alcohols and their aqueous mixtures. [f] Reference 5. [g] Reference 4.

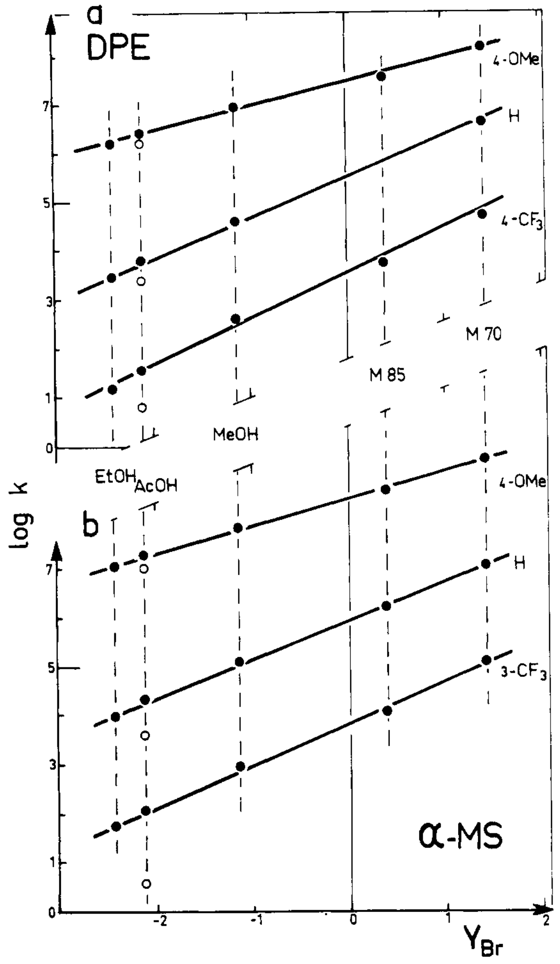


Figure 1. Solvent effects on the bromination rates of α-methylstyrenes (α-MS) and 1,1-diphenylethylenes (DPE). Alcohols and their aqueous mixtures: ●; acetic acid: ○. Acetic acid, a solvent of poor nucleophilicity, deviates systematically and the deviations increase with decreasing reactivity.

Table II. Variation of $(k_{aq\,EtOH}/k_{AcOH})_Y$ with the Reactivity

	X	k_{AcOH}	$k_{aq\,EtOH}$[a]	R^b
DPE	4-CF_3	6.53	4.27×10	6.5
	3-Cl	4.29×10^1	2.22×10^2	5.2
	4-Cl	4.89×10^2	1.51×10^3	3.1
	H	2.46×10^3	6.30×10^3	2.6
	3-Me	5.08×10^3	1.25×10^4	2.5
	4-Me	3.55×10^4	7.08×10^4	2.0
	4-OMe	1.68×10^6	2.57×10^6	1.5
α-MS	3-CF_3	3.42	1.17×10^2	34.2
	3-Cl	2.45×10^1	5.25×10^2	21.4
	H	4.17×10^3	2.24×10^4	5.4
	3-Me	1.32×10^4	5.25×10^4	5.0
	4-OMe	1.1×10^7	1.86×10^7	1.7

[a] 97.5% aqueous EtOH. [b] $R = (k_{aq\,EtOH}/k_{AcOH})_Y$.

Table III. Dependence of the Nucleophilic Solvation on Charge Delocalization

	3-CF_3-**1**[a]	4-CF_3-**2**[b]	**3**[c]
log k_{MeOH}	2.96	2.59	2.60
R	34	6.5	6.0

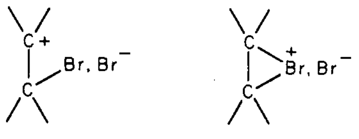
[a] 3-CF_3-α-methylstyrene. [b] 4-CF_3-diphenylethylene. [c] 1-Pentene.

Table IV. Variation of ρ with the Solvent

		AcOH[a]	aq EtOH[a]	MeOH
DPE[b]	ρ	−4.45	−3.90	−3.57[c]
	log k	3.39	3.80	4.62
α-MS[b]	ρ	−5.76	−4.60	−4.26[d]
	log k	3.62	4.35	5.14

[a] Calculated from log k/log k correlations by reference to methanol. [b] DPE: 1,1-diphenylethylenes; α-MS: α-methylstyrenes. [c] Reference 5. [d] Reference 4.

bromide-ion attack on the bromine atom of the cationic intermediate, it should be unimportant in arylolefin bromination via α-bromocarbocation where the bromine atom is uncharged.



Therefore, the different behavior of arylolefins in acetic acid and in alcohols results from differences in the solvent nucleophilicities.

The ratios, $(k_{aqEtOH}/k_{AcOH})_Y$, denoted R which express nucleophilic solvent assistance, have been measured for a large range of substituents (Table II). In both sets of olefins, this ratio decreases as the reactivity increases: the more stable the transition state, the less the demand on the solvent for charge stabilization. This effect is illustrated in Figure 2. At low reactivities nucleophilic solvation is approximately inversely proportional to reactivity; when the reactivity is increased by conjugated electron-donating substituents, R tends to 1, i.e., nucleophilic solvation tends to disappear. This trend can result from a shift in the transition-state position on the reactivity changes and from charge delocalization in the substituted aromatic ring. A shift in the transition-state position should make nucleophilic solvation reactivity dependent: the more reactive the olefin, the smaller the transition-state charge and the smaller the demand on the solvent. This Hammond effect is supported by the reactivity dependence of the m values[8] (Table I) in arylolefin bromination.[9] The effect of charge delocalization on nucleophilic solvation is also important. This can be seen by comparing, firstly, diphenylethylenes and α-methylstyrenes, and, secondly, arylolefins and alkenes. In 1,1-diarylethylenes, the charge of the transition state **2** is partly delocalized in the unsubstituted ring and nucleophilic solvation is systematically

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[8] In bromination, m values express the transition-state position (M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 1977 (1975)).

[9] In contrast with what is observed in arylolefin bromination via carbocations, in alkene bromination via bromonium ions m values and, therefore, the transition-state position do not vary with the reactivity.

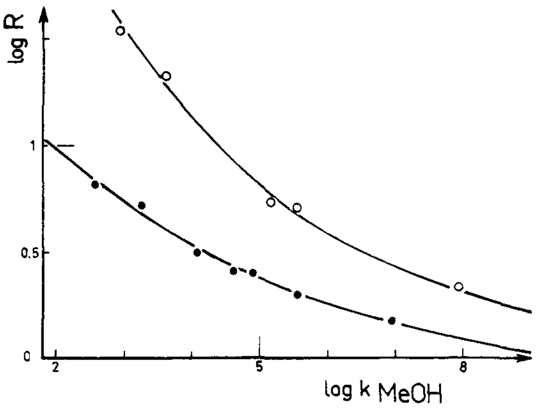

Figure 2. Nucleophilic solvation estimated by R as a function of the reactivity. (Data from Table II.)

smaller in this olefin series than in α-methylstyrenes (transition state **1**) although the two series have similar reactivities. On the other hand, R for 1-pentene, where the transition-state charge is delocalized in the bridging bromine atom **3**, is smaller than that of the α-methylstyrene of similar reactivity (Table III).[10]

The ρ values in the solvents of Table II are given in Table IV. There is a rough trend toward an inverse relationship between the reactivity and the ρ value in each olefin series. However this relationship is in no way linear as expected for a strictly unimolecular dissociation.[11] This is particularly striking for α-methylstyrene, the olefin the most sensitive to nucleophilic solvation: ρ in methanol is close to ρ in aqueous ethanol but quite different from ρ in acetic acid although the reactivity varies steadily. It appears that nucleophilic solvation causes a leveling of the ρ values for bromination in alcohilic solvents; a similar effect has been pointed out in solvolysis.[12]

It is clear that there is nucleophilic solvation in the rate-determining step of bromination. This solvent effect is minor as compared to its previously recognized effects, polarity and electrophilic assistance to the departure of the leaving bromide ion.[8] The stabilization provided by nucleophilic solvation depends on several factors: (i) the reactivity (the more reactive the olefin, the less important the stabilization; this can be due to a Hammond effect); (ii) the charge delocalization (a bridged transition state is less solvated than a carbocationic transition state and substituents able to delocalize the charge by resonance diminish strongly the magnitude of the solvent stabilization); (iii) crowding of the double bond also decreases its magnitude.[1] Intervention of nucleophilic solvation has an incidence on the LFER parameters of bromination: the p or m values for the nucleophically assisted process are smaller than those expected for a unimolecular dissociation. More work is in progress to obtain quantitative data on this last effect.

Experimental Section

Materials. The substituted 1,1-diphenylethylenes and α-methylstyrenes are synthetized and purified as already described.[4,5] Origin and treatment of solvents and salts are given in the preceding note.[1]

Kinetic Measurements and *k* Determinations. The kinetic procedures used for arylolefin bromination are those described in the preceding note.[1]

Registry No. p-$CF_3C_6H_4C(Ph){=}CH_2$, 345-88-0; $Ph_2C{=}CH_2$, 530-48-3; p-$MeOC_6H_4C(Ph){=}CH_2$, 4333-75-9; m-$CF_3C_6H_4C(Ph){=}CH_2$, 368-79-6; $PhC(CH_3){=}CH_2$, 98-83-9; p-$MeOC_6H_4C(CH_3){=}CH_2$, 1712-69-2.

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(10) In this comparison, it is assumed that there is no charge delocalization in the ring substituted by a strongly electron-attracting group such as trifluoromethyl.

(11) The ρ values are selectivity indices; there should exist an inverse linear relationship between ρ and log k if the mechanism does not change with the solvent: A. Pross, *Adv. Phys. Org. Chem.*, 14, 69 (1977); B. Giese, *Ang. Chem., Int. Ed. Engl.* 16, 125 (1977).

(12) 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).

Aliphatic Acyl Transfer in the Baker-Venkataraman Reaction

George A. Kraus,* Brian S. Fulton, and Soon Hyung Woo

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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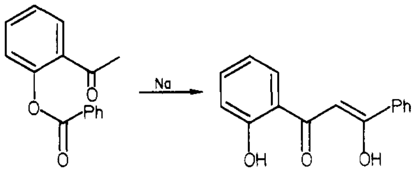
Base-mediated acylation reactions represent an important connective tool for organic chemists. Both the acetoacetic ester condensation[1] and the Claisen reaction[2] have been extensively used to produce β-keto esters and β-diketones, respectively. Harris and co-workers have elegantly demonstrated the effectiveness of the Claisen reaction through several syntheses of polyketide-derived natural products.[3] Both reactions, however, have some limitations. For example, significant problems are often encountered when esters bearing acidic hydrogen atoms are employed in the Claisen reaction. The reactions often proceed in low yield due to competing side reactions. When methods for the kinetic generation of enolate anions in aprotic media were developed,[4,5] the acylation of enolates with anhydrides or acid chlorides provided a useful route to β-dicarbonyl compounds.[6] The major side reaction, O-acylation, could be minimized either by inverse addition[7] or by the use of acyl cyanides[8] or acylimidazoles[9] instead of acid chlorides. For certain systems intramolecular acylation is possible. In the example shown in eq. 1 the Baker–Venkataraman reaction[10] is used to generate a β-diketone. This intramolecular acyl transfer reaction has become a major re-



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(8) Howard, A. S.; Meerholz, C. A.; Michael, J. P. *Tetrahedron Lett.* **1979**, 1339.

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