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REVIEW COMMENTARY

SOLVATION, THE ELECTROPHILIC DRIVING FORCE OF IONIC BROMINATION OF ETHYLENIC COMPOUNDS. THE ADDITION-SOLVOLYSIS ANALOGY

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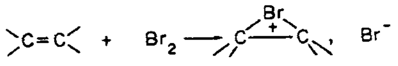
Solvation is the main driving force of electrophilic bromination since it is impossible to obtain a bromonium ion from bromine and alkene in the gas phase, whereas it is a very fast reaction in solution. The role of a protic solvent in this addition was investigated experimentally by extended Winstein–Grunwald relationships, kinetic solvent isotope effects and *R*, the rate ratios in two solvents of similar ionizing powers but different nucleophilicities. It is shown that electrostatic medium effects and electrophilic assistance to bromide ion departure are the main rate-determining factors of the reaction. These two contributions are roughly independent of the double bond substituents. Nucleophilic solvent assistance to positive charge development is also found; however, it provides only a small acceleration, the magnitude of which depends on alkene structure. This nucleophilic solvent involvement is annulled when crowded substituents inhibit approach of the solvent to the cationic part of the transition state or when positive charge is delocalized by conjugated electron-donating groups. These several solvent roles are identical in nature and in magnitude with those observed in heterolytic solvolysis. In halogenated solvents, the driving force of bromination arises from catalysis by a second bromine molecule which assists heterolysis of the bromine–bromine bond, *leading to the* bromonium–tribromide ion pair. Similar halogen catalysis occurs also in some solvolyses. Finally, return is also found in both reactions; reversible formation of bromonium ions is observed when their nucleophilic attack, the product-forming last step, is made energetically difficult either by steric inhibition or by poor nucleophilicity of the trapping nucleophiles. Similarities and differences between electrophilic bromine addition and limiting solvolysis are discussed in terms of respective intermediate stabilities and heats of formation.

INTRODUCTION

It has been intuitively accepted for a long time that electrophilic bromination of ethylenic compounds via bromonium ions is impossible, or at least extremely difficult, in the gas phase. For example, in the several studies on the reactivity and stability of bridged halonium ions in non-condensed media, bromonium ions have been prepared by heterolysis of β-bromo-substituted derivatives and not by bromine addition to a double bond.[1] The difficulty of obtaining halonium ions in the gas phase has been confirmed by recent *ab initio* calculations.[2] More than 60 kcal mol^{-1} (1 kcal = 4·184 kJ) would be necessary to form a bromonium ion from ethylene and bromine, that is, the bromination rate constant of ethylene at 25 °C in the gas phase would be as small as 10^{-32} l mol^{-1} s^{-1}! However, it is well known that alkene bromination in solution or in the condensed phase is an extremely fast reaction. For instance, the bromination rate constant of ethylene[3] in water at 25 °C is 4×10^{5} l mol^{-1} s^{-1}, which corresponds to an activation free energy of less than 10 kcal mol^{-1} and a half-life of 5 s for 5×10^{-3} M reactant concentrations. This very high rate difference between solution and the gas phase strongly underlines the fact that solvation is the main driving force of bromination.


(1)

$$R\text{—}X \longrightarrow R^{+}\ ,\ X^{-} \qquad (2)$$

At least as regards the crucial role of the solvent in promoting the reaction, there is some analogy between this electrophilic addition and limiting solvolysis. This

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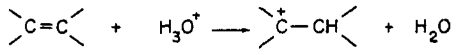

(3)

$$R{-}X \;+\; Nu^- \longrightarrow X^- \;+\; R\,Nu \qquad (4)$$

is in contrast with reactions such as olefin hydration[4] or S_N2 nucleophilic displacements,[5] the rates of which significantly decrease on going from the gas phase to solution. The first class of reactions, bromination or heterolytic solvolysis, involves neutral reagents which undergo ionization; in solution, highly charged transition states are more stabilized by solvation than ground states. In contrast, in S_N2 substitutions by anionic reagents or in olefin protonation, there are no drastic changes in the magnitude of the overall charge in the course of the reaction so that in solution the charge-delocalized transition states are less solvated than the ionic reagents. Calculations on this latter class of reactions have recently been performed to understand the role of the solvent on the free energy profiles at the microscopic level.[6] Nothing similar can be attempted at present for reactions such as bromination.

In this paper we report and discuss experimental results on solvent effects on bromination with a view to evaluating the various contributions of solvation to the reaction rates in solution.

Table 1. Kinetic effects of non-protic solvents on cyclohexene bromination at 25 °C

Parameter	CCl_4	$CHCl_3$	$(CH_2Cl)_2$
ε^a	2·2	4·6	10·7
$k_{rel}{}^b$	1	$\sim 10^3$	$\sim 10^5$

[a] Dieletric constant.
[b] Relative to the imprecise rate constant ($5 \pm 3\ l\ mol^{-2}\ s^{-1}$) in CCl_4; data from Ref. 7.

MAGNITUDE AND DIVERSITY OF SOLVENT EFFECTS

According to theoretical and experimental data (see above), solvation by water would reduce the activation free energy of ethylene bromination by at least 50 kcal mol^{-1}. Moreover, not only is the solvent essential for the reaction to occur, but also bromination rates are highly sensitive to the nature of the solvent. In nonprotic solvents, the bromination rate constant of cyclohexene[7] is enhanced by a factor of 10^5 on going from carbon tetrachloride to the more polar 1,2-dichloroethane (Table 1). It is not known if this factor varies significantly with the double bond substituents. In protic solvents, bromination rates also depend strongly on the medium (Table 2). For example, the rate constant of pent-1-ene increases by a factor of 10^6 when the solvent is changed from acetic acid to the more ionizing water.[8] This rate enhancement does not vary greatly with olefin structure as long as the substituents are alkyl or unconjugated groups.[12] The fact that the kinetic solvent effects on alkene bromination are not very sensitive to the substituents is also suggested by the near-unity slopes of the several log–log correlations between the reactivities of a large variety of alkenes in methanol,[13] water,[3] aqueous methanol[14] and acetic acid.[12]

$$\log k_{H_2O} = 1{\cdot}08 \log k_{MeOH} + 4{\cdot}3 \qquad (5)$$

$$\log k_{M70} = 0{\cdot}90 \log k_{MeOH} + 2{\cdot}6 \qquad (6)$$

$$\log k_{AcOH} = 0{\cdot}99 \log k_{MeOH} - 1{\cdot}4 \qquad (7)$$

When there is resonance between the double bond and an aromatic ring, the solvent dependence of the reactivity is attenuated, as shown in the last rows in Table 2. The highest attenuation has been found in the case of aliphatic enol ethers, the rates of which hardly change from ethanol to water.[15] These attenuations

Table 2. Kinetic effects[a] of protic solvents on free bromine addition to various alkenes at 25 °C

Alkene	AcOH	MeOH	M70[b]	H_2O	$\log k_{AcOH}{}^c$
Y_{Br}	−2·10	−1·10	1·42	4·44	
n $PrCH{=}CH_2{}^d$	1	35	9×10^3	2×10^6	1·04
$Ad{=}CH_2{}^e$	1	10	3×10^4	$(1\times10^7)^h$	4·68
$PhCH_2CH{=}CH_2{}^f$	1	33	3×10^3	2×10^6	0·21
DPE[g]	1	17	1×10^3	8×10^5	3·39
4-MeO-DPE[g]	1	5·3	20	3×10^3	6·01

[a] k_{SOH}/k_{AcOH}.
[b] 30:70 (v/v) H_2O–MeOH mixture.
[c] k in $l\ mol^{-1}\ s^{-1}$.
[d] Ref. 8.
[e] Ref. 9; Ad = Adamantyl.
[f] Ref. 10.
[g] Ref. 11; DPE = 1,1-diphenylethylene.
[h] Extrapolated value.

have been attributed to weakly charged early transition states in the reaction of conjugated olefins.

In contrast, for alkene bromination the transition states are late and closely resemble the ionic intermediates[8,16] (see below) whatever the double bond substituents and whatever the alkene reactivity. In order to separate out the several solvation contributions to the bromination rates, only the solvent effects on the latter kind of olefin will be considered.

WINSTEIN–GRUNWALD RELATIONSHIPS AND HIGH SENSITIVITY TO MEDIUM ELECTROSTATIC EFFECTS

Neither Kirkwood nor E_T nor any physicochemical solvent parameter[17] alone describes the kinetic effect of protic solvents on bromination satisfactorily.[18] However, fairly linear Winstein–Grunwald relationships:

$$\log(k_S/k_{S_0}) = mY \qquad (8)$$

are obtained for this reaction.[8,12,15] The first correlation was found for pent-1-ene bromination[8] in 16 solvents using the Y values defined from *tert*-butyl chloride solvolysis.[19] This one-parameter analysis was then extended to various alkenes. The best plots (Figure 1) are obtained with the Y_{Br} parameters derived from 1-bromoadamantane solvolysis,[20] a reaction which cannot involve nucleophilic solvent assistance (see below) and where the leaving group is a bromide ion, as in bromination. The m_{Br}-values for free bromine addition to alkenes are all close to unity. They vary slightly with alkene structure but not as much as when the substrate is changed from primary to secondary to tertiary in solvolysis.[21] As shown in Table 3, the bromination m values range[9,22] from 0·8 for allylbenzene (the least reactive alkene whose kinetic solvent effects have been measured) to 1·1 for methylideneadamantane, a close analogue of 1-bromoadamantane. These small variations can be attributed to a variable nucleophilic solvent assistance but neither to transition-state shifts on the reaction coordinate (see below) nor to drastic changes in the mechanism, as observed in nucleophilic substitutions.

These linear Winstein–Grunwald relationships have no physicochemical meaning *per se*; they show only that the origin and the magnitude of solvation are similar in bromination and solvolysis.

In order to understand the microscopic significance of these reactivity–solvent correlations, the multiparameter treatment of Kamlet–Taft including π^* (solvent dipolarity), α (hydrogen bond donor) and β (hydrogen bond acceptor)

$$\log(k_S/k_{S_0}) = s\pi^* + a\alpha + b\beta \qquad (9)$$

has been applied to solvent Y parameters.[24] Solvolysis of 1-X-adamantanes has been chosen to define Y_X scales because it cannot involve any nucleophilic solvent par-

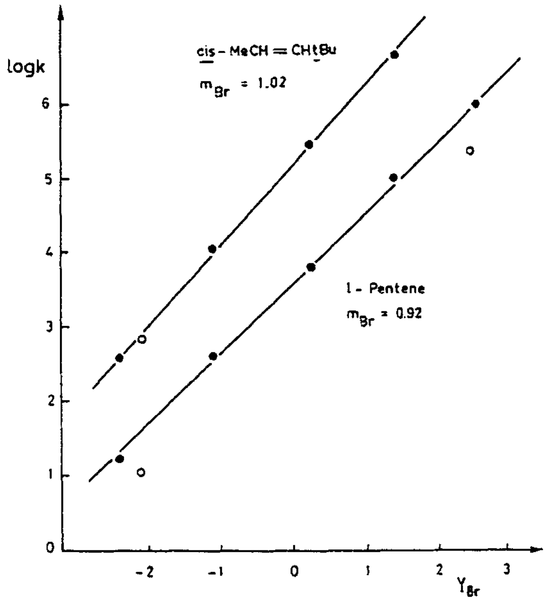


Figure 1. Typical log k_S vs Y_{Br} plots for alkene bromination. Pent-1-ene, less crowded than *cis*-methyl-*tert*-butylethylene, exhibits the smallest m value. The points corresponding to acetic acid and trifluoroethanol, two non-nucleophilic solvents, are below the regression line for aqueous solvents. In contrast, acetic acid falls on the line for *cis*-methyl-*tert*-butylethylene for which steric crowding inhibits nucleophilic assistance by alcoholic solvents. (●) Ethanol, methanol and their aqueous mixtures; (○) acetic acid and trifluoroethanol. Data from Refs. 8 and 12

Table 3. m_{Br} values[a] and KSIEs for alkene bromination in protic solvents[b]

Alkene	m_{Br}[c]	log k_{MeOH}[d]	k_{ROH}/k_{ROD}[e]
Allylbenzene	0·80[f]	1·72	1·37[f]
t-Bu-*i*-PrC=CH$_2$	1·08[g]	2·29	1·32[i]
n-PrCH=CH$_2$	0·92[g]	2·60	1·35[j]
cis-MeCH=CHEt	0·92[g]	4·54	—
Ad=CH$_2$	1·11[h]	5·62	1·35[f]
Me$_2$C=CMe$_2$	0·96[g]	7·16	—

[a] Using Y_{Br} parameters (Ref. 20).

[b] H_2O, MeOH, EtOH and their aqueous mixtures, all solvents of similar nucleophilicities.

[c] ±0·05.

[d] Standard deviation on k is ±3%, except for the very high rate constant of $Me_2C{=}CMe_2$, ±5%.

[e] ±0·08; R = Et or Me; this value does not depend on R within experimental error; $\Phi_{Br^-} = 1{\cdot}3 \pm 0{\cdot}07$ (whatever the solvent) = the maximum theoretical value of these KSIEs (see text). In acetic acid, the KSIEs are slightly smaller (about 1·25) but the Φ_{Br^-} coefficient in this solvent is not available.

[f] Ref. 10.

[g] Ref. 12.

[h] Ref. 9.

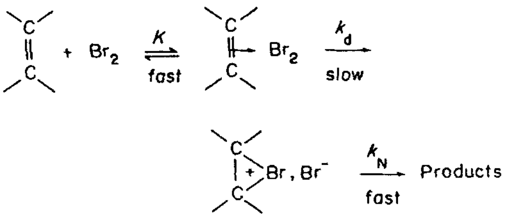
[i] Ref. 23.

[j] Ref. 16.

ticipation; in other words, the hydrogen bond acceptor ability ($b\beta$ term) cannot contribute to Y_X. In contrast, solvent hydrogen bonding to the leaving group described by the $a\alpha$ term should be significant. However, Bentley *et al.*[25] observed that the Y_X parameters do not depend on X since there are fairly linear relationships between the several Y_X scales. We are reduced, therefore, to the surprising conclusion that Y_X values, and Y_{Br} in particular, express mainly solvent dipolarity or, in other words, the solvent electrostatic effect. Nevertheless, the result of this Y analysis in terms of equation (9) is difficult to reconcile with the general agreement about the importance of leaving group–solvent interactions and electrophilic assistance in heterolytic reactions.

Since the experimental kinetic solvent effects on bromination are expressed fairly well by mY_{Br} relationships, the major role of the solvent at a microscopic level could be a medium electrostatic effect.

There is, however, a significant difference between the mechanisms of bromination and limiting solvolysis. In bromination, the ionization step is preceded by the formation of a charge-transfer complex between bromine and the alkene.[8,26,27]

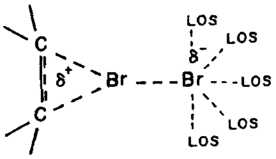


(10)

Nevertheless, it can be assumed that the electrostatic solvent effect on the pre-equilibrium, which involves neutral or slightly polarizable species, is negligible with respect to that on the rate-limiting step leading, as in solvolysis, to a highly charged transition state.[9] Therefore, the values of the m coefficients for both reactions can be directly compared. Recent data on tetraisobutylethylene bromination[28] support this assumption. For this congested alkene, the CTC formation constant increases by a factor of 1·5 on going from acetic acid to methanol whereas the bromination rate constant is multiplied by 10.

KINETIC SOLVENT ISOTOPE EFFECTS AND ELECTROPHILIC SOLVENT ASSISTANCE

The ionization process in bromination involves the formation of a bromide ion. Bromide ions are strongly solvated by protic solvents and, therefore, electrophilic assistance to the departure of the leaving bromide can be provided by the solvent. This has been shown by kinetic solvent isotope effects which have been measured for methanol,[9,16] ethanol and acetic acid[29] for several typical alkenes (Table 3). These KSIEs are very high and do not depend on alkene structure or reactivity. They are very close to their maximum possible values given by the Φ_{Br^-} coefficient corresponding to the solvent isotope effect on the stability of a fully developed bromide ion.[23] Therefore, the negative charge borne by the leaving group in bromination is close to unity; in other words, the transition states of alkene bromination are very late and closely resemble the ionic intermediates. This conclusion is also supported by the linear relationship between the bromination rate constant of pent-1-ene in several water–methanol mixtures and the transfer free energies of a bromide ion in the same solvents.[16] The slope of this relationship is 0·86, that is, the heterolytic rupture of the Br–Br bond is close to completion at the transition state.



The free energies of bromide solvation by alcohols and water[30] are in the range 56·0–61·5 kcal mol⁻¹ at 25 °C. Most of this energy contributes to the bromination rates. Consequently, electrophilic assistance by solvation of the departing bromide is important in bromination.

ROLE OF SOLVENT NUCLEOPHILICITY AND NUCLEOPHILIC SOLVENT ASSISTANCE

Nucleophilic assistance of the solvent to positive charge development at the transition state has also been found in the bromination of some alkenes.[9,12] This has been shown by a detailed study of the mY_{Br} relationships. In the log k vs Y_{Br} plots, the points corresponding to acetic acid or trifluoroethanol, two solvents whose nucleophilicities are small compared with those of water–alcohol mixtures,[31] sometimes fall[12] significantly below the regression line (Figure 1). This means that the complete Winstein–Grunwald equation[19] [equation (11)] where l represents the substrate sensitivity to the solvent nucleophilicity, N, should apply in bromination.

$$\log k_S/k_{S_0} = mY + lN \tag{11}$$

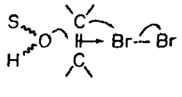
However, bromination cannot be studied in many solvents of widely variable nucleophilicity (aqueous acetone, in particular). It is not possible, therefore, to carry out a statistically significant dual-parameter analysis according to equation (11). Consequently, the magnitude of nucleophilic solvent involvement has been estimated from the deviation from the log k vs Y_{Br} correlations of the points corresponding to acetic acid and to trifluoroethanol when bromination is not too fast to

Table 4. Nucleophilic solvent assistance in alkene bromination estimated by R, the rate ratios in two solvents of different nucleophilicities but similar ionizing power

Alkene	$(k_{aqEtOH}/k_{AcOH})_Y$	$(k_{aq\,MeOH}/k_{TFE})_Y$[a]
Allylbenzene[b]	8·3	8·7
Pent-1-ene[c]	6·2	7·6
Ad=CH_2[d]	0·9	—
t-Bu-*i*-PrC=CH_2[c]	1·4	—
DPE[e]	2·6	—
4-MeO-DPE[e]	1·5	—

[a] This ratio is given only for weakly reactive alkenes because the bromination rates in trifluoroethanol (TFE) are generally too fast for kinetic measurements.
[b] Ref. 10.
[c] Ref. 12.
[d] Ref. 9.
[e] DPE = 1,1-diphenylethylene; Ref. 11.

be measured in this latter. In Table 4 these estimations are given by R, the rate ratios in two solvents of different nucleophilicities but similar ionizing power for three kinds of ethylenic compounds substituted by sterically undemanding groups, highly branched and conjugated groups. R ratios significantly greater than unity are kinetic criteria for nucleophilic involvement of the solvent in the ionization process. [A referee has suggested that R ratios higher than 1 could arise from the solvent dependence of K_{CTC}. In view of the results on tetraisobutylethylene bromination,[24] this suggestion cannot explain R values as high as 8 (Table 4). Moreover, it has been shown[32] that substituent dependence of K_{CTC} is negligible with respect to that of k. Since substituent and solvent effects are both related to charge development, both kinds of results support our assumption that kinetic data on bromination can be interpreted mainly in terms of effects on the ionization step.] As shown in Table 4, nucleophilic assistance occurs only for uncrowded alkenes; when solvent approach to the cationic part of the transition state is sterically hindered by bulky substituents or when the positive charge is delocalized by aryl groups this assistance is strongly diminished or even annulled.



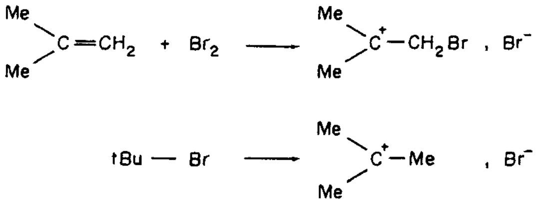
The contribution of this nucleophilic solvation of the transition states to the bromination rates is not very important since it enhances the rates by a factor smaller than 10. It is markedly less important than the contributions described above. Moreover, in contrast to medium electrostatic effects and to electrophilic assistance, nucleophilic solvation depends on alkene structure.

As in S_N2-Intermediate solvolysis,[33] when the solvent assists bromination nucleophilically, the m values (see above) are slightly smaller than those for unassisted heterolysis. This is illustrated by comparing the data for allylbenzene and methylideneadamantane. For the uncrowded alkene, the smallest m (0·8) is associated with the largest R (8·3) whereas for the adamantyl olefin m is high (1·1) and R very small (0·9). The decrease in m probably arises from the attenuation of the medium electrostatic effect whose magnitude is diminished because of transition-state charge delocalization by one or several solvent molecules.

ANALOGIES AND DIFFERENCES BETWEEN BROMINATION AND HETEROLYTIC SOLVOLYSIS

Neither electrophilic addition of bromine nor S_N1-limiting solvolysis is favoured in the gas phase. For both, solvation is the main driving force of the ionization processes forming either a more-or-less bridged bromonium ion or a carbocation. The solvent contributions to heterolysis are closely similar in nature and in magnitude; electrostatic effects and hydrogen bonding to the leaving group are equally important; small and substrate-dependent nucleophilic assistance is similarly involved.

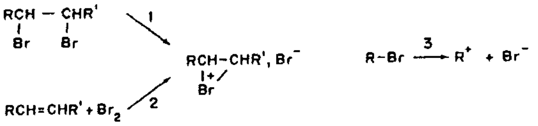
One can therefore ask why bromination is generally much faster than solvolysis. For example, the half-life of the *gem*-dimethylethylene–bromine reaction at 25 °C in methanol[12] ($k = 5{\cdot}01 \times 10^4$ l mol^{-1} s^{-1}) at 10^{-3} M reagent concentrations is as short as 20 ms, whereas that of *tert*-butyl bromide[34] (a factor of 40[20a] was taken to estimate the effect of changing the leaving group from Cl to Br) in the same solvent and at the same temperature ($k = 3{\cdot}01 \times 10^{-5}$ s^{-1}) is 6·4 h (Scheme 1).

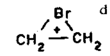
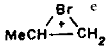
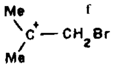
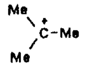


Scheme 1

Staley *et al.*[1b] measured in the gas phase the bond dissociation energies of bromides and *vic*-dibromides leading to carbocations and bromonium ions, respectively (Table 5). The formation of a carbocation by C—Br bond heterolysis is slightly more difficult, by only a few kcal mol^{-1}, than that of the corresponding bromocations. The energy required to obtain these bromocations by bromine addition to an ethylenic compound can be calculated by combining these data

Table 5. Relative ease of cation formation via electrophilic additions and heterolysis in the gas phase



Species	$\Delta H_1{}^{a,b}$	$\Delta H_2{}^{a,c}$	Species	$\Delta H_3{}^{a,b}$	$\Delta H_3 - \Delta H_2$
 [d]	165·2	136·3	$Me\overset{+}{C}H_2$	181·9	45·6
 [e]	159·6	130·4	$Me\overset{+}{C}HMe$	162·9	32·5
 [f]	146·8	115·4		148·7	33·3

[a] In kcal mol^{-1}.
[b] Data from Ref. 1b.
[c] Calculated from the heats of formation of bromine, ethylenic compounds, their dibromides and their bromonium ions; data from Refs. 1b and 35.
[d] The bridged ion is favoured over the open ion by about 8 kcal mol^{-1}; Ref. 36.
[e] Bridged and open ions have almost identical formation enthalpies; Ref. 36.
[f] Open form is more stable than bridged form by about 5 kcal mol^{-1}; Ref. 36.

with the heats of formation of bromine, of the alkene and of the corresponding dibromide (data taken from Ref. 35). The values thus obtained (second column of Table 5) are smaller than those for the heterolytic formation of the analogously substituted carbocations by about 30–40 kcal mol^{-1}. These large energy differences between bromination and heterolysis do not arise from an additional stabilization which would be provided by bromine bridging. The bromonium ion is thermodynamically favoured over the open carbocation[36] only in the case of ethylene, by about 8 kcal mol^{-1}, whereas the open bromomethyl dimethylcation is more stable than the *gem*-disubstituted bromonium ion by about 5 kcal mol^{-1}. (The stabilizing effect of a bromo substituent in the β-position with respect to a cationic centre has already been observed experimentally by comparing the relative ease of vinylcation formation by bromination or protonation[37]). Therefore, in agreement with the kinetic data, these rough calculations suggest that it is easier to obtain a cation from an electrophilic addition than from an heterolytic ionization in the gas phase.

Comparison of ΔH_2 and ΔH_3 in Table 5 tends to show that the large differences in the rates of bromination and solvolysis arise from differences in the stabilities of the species involved rather than from different solvation energies.

BROMINE-CATALYSED BROMINATION IN HALOGENATED SOLVENTS

A linear Kirkwood relationship has been found[7] for the bromination of cyclohexene at 25 °C in several 1,2-dichloroethane–chloroform mixtures, the dielectric constant of which varies by 6 units. It is concluded that electrostatic medium effects of halogenated solvents contribute significantly to the bromination rates. However, the linearity of this correlation is somewhat artificial since marked scatter is observed in the Kirkwood plot (Figure 2) when other halogenated solvents[7] are included. Therefore, another kind of solvent effect does occur, in addition to the medium electrostatic contribution.

In protic media, we have shown that solvent hydrogen bonding of the leaving bromide assists bromination electrophically. In halogenated media, this solvation cannot exist but analogous assistance can be provided by bromine itself (Scheme 2). In the first solvents, bromination is first order in bromine and the counter ion of the bromonium ion is a bromide;[38] in the second, it is second order in bromine and the counter ion is a tribromide ion.[39] In the first case the bromine—bromine bond rupture is solvent assisted; in the second, it is bromine assisted. This is typically a bromine catalysis. The driving force provided by this catalysis can be important since the equilibrium constant for the formation of a tribromide ion from molecular bromine and a fully developed bromide ion:

$$Br_2 + Br^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Br_3^- \qquad (12)$$

is very high in non-protic solvents[7,40] ($k_f/k_r = K = 1{\cdot}2 \times 10^5$ and $>2 \times 10^7$ l mol^{-1} in chloroform and methylene chloride, respectively). Moreover,

k_f is almost diffusion controlled.[41] Consequently, the reaction of free bromine with a negatively charged bromine species is both thermodynamically and kinetically highly favoured in halogenated solvents.

It is noteworthy that halogen catalysis occurs also in solvolysis.[42] It has been shown that heterolyses of *tert*-amyl, *tert*-butyl and 1-adamantyl iodides in slightly ionizing aqueous ethanol are iodine catalysed. This catalysis markedly accelerates the ionization, by a factor as high as 3 × 10^4 (Table 6). It is also noticeable that it increases strongly as the solvent ionizing power decreases; the faster the uncatalysed heterolysis, the less the catalysis. This would suggest that there is competition between solvent and iodine assistance. However, bromine catalysis, which occurs in bromination, has not been detected in solvolysis (old observations of slow isomerizations of diastereoisomeric *vic*-dibromides in the presence of halogens[43] can be interpreted in terms of halogen-catalysed solvolysis). Bromine catalysis is probably less important than that of iodine since I_3^- is stabler than Br_3^- in protic solvents. In solvolysis or in bromination in protic solvents, it could be insignificant compared with solvent assistance, whereas it would dominate in halogenated solvents which are unable to assist the bromide departure.

These features of halogen catalysis underline the similarities of the several processes which promote the ionization steps of bromination and solvolysis.

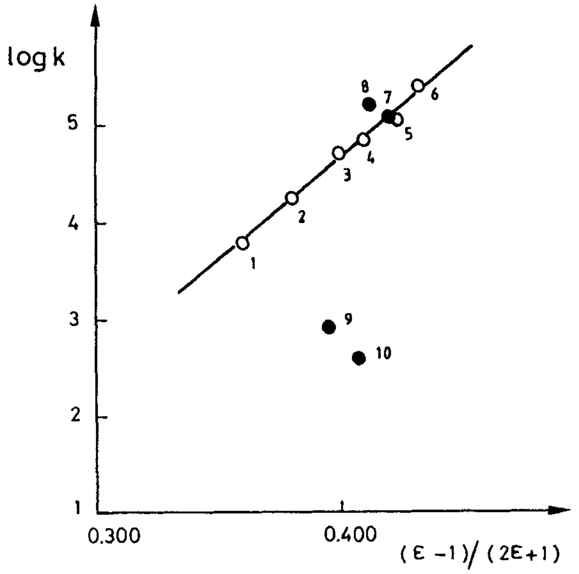
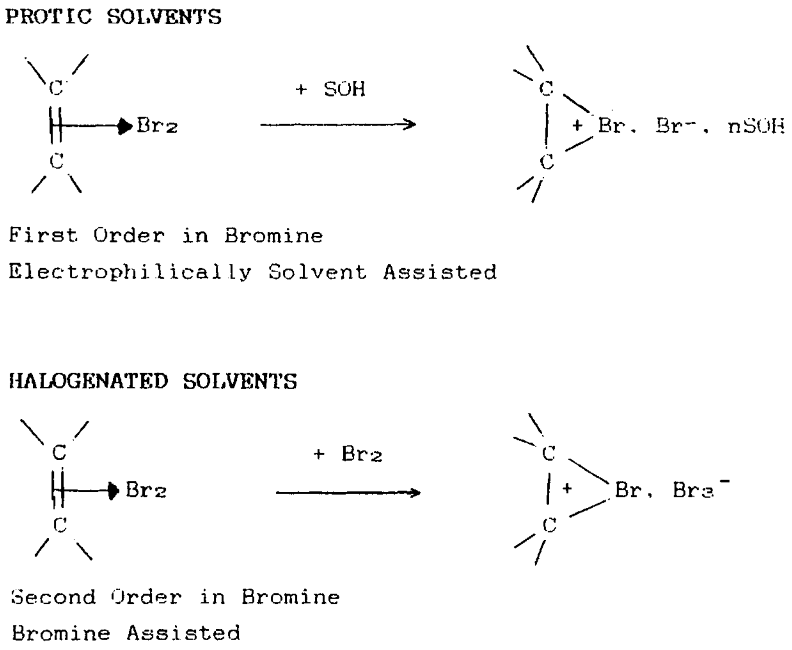


Figure 2. Kirkwood plot of cyclohexene bromination in halogenated solvents. Data from Ref. 7. 1 = $CHCl_3$; 2–5 = $CHCl_3$–DCE (dichloroethane) mixtures; 6 = $(CH_2Cl)_2$–DCE; 7 = CH_2Cl_2; 8 = $(CHCl_2)_2$; 9 = n-$BuCH_2Cl$; 10 = Cl_3CCH_3



Scheme 2

Table 6. Iodine catalytic effects k_{cat}/k_{uncat}, in alkyl iodide (RI) solvolysis[a]

	R		
Solvents[b]	*tert*-Amyl	*tert*-Butyl	1-Adamantyl
97 HFIP	—	150	—
80 E	6100	5600	3×10^4
95E	—	8500	—

[a] Ref. 42.

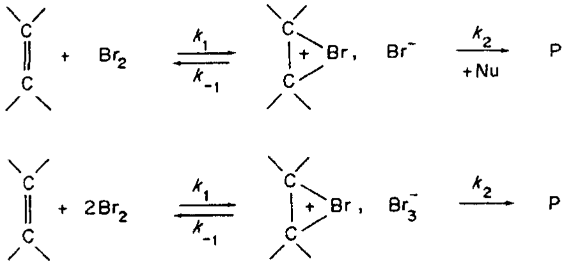
[b] 97 HFIP = 97% aqueous hexafluoroisopropanol; 80 E and 95 E = 80 and 95% aqueous ethanol, respectively.

RETURN IN BROMINATION AS IN SOLVOLYSIS

Return from the ion-pair intermediate to the neutral reagents is also an important characteristic of solvolysis,[44] which has been discussed at length[21,33,45] since the first proposal of Winstein *et al.*[46] Going further in the bromination–solvolysis analogy, it is reasonable to expect that bromonium ion formation should also be reversible. However, it is not usual to consider that return occurs in bromination; the general bromination mechanism, as taught in textbooks, does not take into account this possibility. Nevertheless, recent work suggests that bromonium ions can be formed reversibly.[27,47,48]

The first indications were given by an experiment[47] where the bromonium–bromide ion pair formed by acetolysis of β-bromocyclohexyl brosylate in the presence of bromide ions released free bromine which could be trapped by cyclopentene, an alkene more reactive than cyclohexene. Return to alkene and molecular bromine from a bromonium ion has also been shown[48] by eliminating bromine as it is formed. For instance, when hydrogen bromide is bubbled into a solution of *trans*-stilbene bromohydrin in methylene chloride, stilbene is obtained in addition to the expected stilbene dibromide.

Finally, evidence for return in the bromination of highly congested alkenes in protic solvents[22] has also been obtained from kinetic data and product analysis.[10] In these cases, the trapping of the corresponding crowded bromonium ions by nucleophiles is so hindered that the product-forming last step is of higher energy that the ionization step ($k_2 < k_{-1}$); as a consequence the ionic intermediates are formed reversibly.



This has been deduced from small kinetic solvent isotope effects associated with both small *m* and *R* values[10] (see above). The unexpectedly high kinetic isotope effect obtained by comparing the bromination rates in methanol of tetraisobutylethylene and of its analogue in which the eight allylic positions are deuteriated also strongly supports reversible formation of highly crowded bromonium ions.[28].

In short, return occurs in olefin bromination as in solvolysis. In alcoholic solvents, highly congested ions are formed reversibly, because nucleophilic attack is sterically inhibited. In halogenated solvents, it seems that return is possible even when the intermediate is not crowded. This probably arises from the fact that the product-forming step is also slow since the counter tribromide ion is not a highly nucleophilic species.

CONCLUSION

In bromination as in solvolysis, the rate-limiting ionization step is promoted by solvation. Medium electrostatic effects and electrophilic solvent or bromine assistance to the departure of the leaving counter ion contribute the most efficiently to the reaction rates. Depending on the substrates, nucleophilic solvent assistance to positive charge development is also involved. Moreover, it is noticeable that halogen catalysis and return can occur in both reactions but under different conditions.

In summary, there are numerous similarities between electrophilic bromine additions and solvolytic reactions. This may seem *a priori* surprising from a microscopic point of view, since bromination involves the transformation of a π-bond into two σ-bonds and solvolysis the cleavage of a σ-bond. However, the relevant feature is probably the fact that large charge developments occur in both reactions.

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