

Comparison of Molecular Bromine and Tribromide Ion as Brominating Reagents. 1. Kinetic Evidence for Different Mechanisms of Addition to Cyclohexene

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Received March 25, 1985

The kinetics of bromination of cyclohexene with molecular bromine and with tetrabutylammonium tribromide in a series of chlorinated hydrocarbons of dielectric constant ranging between 2.2 and 10.7 have been investigated with the stopped-flow technique. Third-order (second order in Br_2) and second-order (first order in Br_3^-) rate laws were respectively followed by the bromine and the tribromide reactions. Only in the least polar solvent, carbon tetrachloride, the reaction of molecular bromine gave erratic results even when fitted to a two-term rate equation. The rates of the bromine and of the tribromide reactions exhibited opposite temperature coefficients, negative for the former and positive for the latter. Added tetrabutylammonium bromide had only a modest negative salt effect on the rate of the Br_3^- reaction, excluding its dissociation to free Br_2 and reaction of this electrophile. The rate of the free Br_2 reaction was substantially determined by the solvent polarity. A linear plot of $\ln k_3$ against the Kirkwood function of the dielectric constant, indicating a highly polarized transition state, was obtained for reactions carried out in mixtures of 1,2-dichloroethane and chloroform. An inverted trend was observed for the rates of the tribromide reaction in the same binary mixture of solvents, but no linear plot was obtained, and the rates measured in a series of solvents correlated with the stability constants of Br_3^- and with the ability of solvents to hydrogen bond bromide ions. The reaction of tribromide, but not that of molecular bromine, was subjected to a kinetic solvent isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.175$ (0.031)) in $\text{CHCl}_3/\text{CDCl}_3$. The results are consistent with an ionic mechanism involving the rate-determining formation of a bromonium-tribromide ion pair intermediate for the free Br_2 addition. For the Br_3^- reaction they point to the formation of an olefin- Br_2 1:1 charge-transfer complex in equilibrium with the olefin and Br_3^- , followed by a rate- and product-determining nucleophilic attack by bromide on the transient complex through a transition state more charge delocalized than the initial state.

Organic tribromide salts, like pyridine hydrobromide perbromide (PHP), tetraethylammonium tribromide (TEAT), or tetrabutylammonium tribromide (TBAT), are stable, easily prepared crystalline solids, and fairly soluble in most organic solvents, which can be handled more conveniently than liquid bromine and can be used successfully for brominations. However, the two reagents give often different results in additions to the carbon-carbon double bond. For instance, the bromination of both *cis*- and *trans*-stilbenes with free Br_2 always leads to mixtures of *meso* and *d,l* dibromides in ratios depending on the solvent,¹ while PHP in acetic acid gives only the product of anti addition of bromine.² Similar differences have been reported for the bromination of β -methylstyrenes.³ The addition of free Br_2 to 1,3-butadiene in chlorinated hydrocarbons gives mostly the *trans*-1,4-dibromo adduct, but PHP and TBAT yield almost exclusively the 1,2-dibromide.^{3,4} Similar results have been obtained with other conjugated dienes, for which a change in stereochemistry in favor of anti addition was also observed with tribromide salts.³

These synthetically interesting differences in stereo- and regioselectivity of the Br_3^- and free Br_2 addition reactions clearly point to different addition mechanisms, but this question is still not settled. In order to clarify these points, we undertook a kinetic investigation of the bromination of olefins with the two above reagents in low polarity aprotic solvents, where most preparative halogenations are usually carried out. In the present paper we are reporting on the kinetics of bromination of a typical cycloalkene, cyclohexene. TBAT was used as the tribromide reagent since its very high formation constant in low polarity aprotic solvents prevents extensive dissociation to free Br_2 .^{4,5}

Table I. Second-Order Rate Constants for the Bromination of Cyclohexene with TBAT in 1,2-Dichloroethane^a

<i>t</i> , °C	<i>k</i> ₂ , M ⁻¹ s ⁻¹
9.8	0.43 (0.01)
15.0	0.51 (0.01)
20.0	0.60 (0.02)
25.0	0.72 (0.02)
30.0	0.92 (0.02)
34.8	1.06 (0.01)
41.0	1.40 (0.03)

^aRate constants are the average of at least four independent measurements carried out at 3.6×10^{-4} M TBAT and 0.1 and 0.2 M cyclohexene, monitoring at 350 nm. Errors are given as standard deviations obtained from the deviations of individual measurements from the average value.

Results

Rate Laws and Activation Parameters. The rates of bromination of cyclohexene by free Br_2 and by TBAT were first measured with a stopped-flow apparatus in 1,2-dichloroethane, the aprotic nonnucleophilic solvent of a moderate dielectric constant ($\epsilon = 10.7$)⁶ used in the previous investigation,⁵ in the presence of a large excess of olefin ([ol]).

As reported,⁵ the reaction of Br_2 was overall third order (second order in Br_2 , eq 1), while that of TBAT was overall second order (first order in Br_3^- , eq 2).

$$-d[\text{Br}_2]/dt = k_3[\text{Br}_2]^2[\text{ol}] \quad (1)$$

$$-d[\text{Br}_3^-]/dt = k_2[\text{Br}_3^-][\text{ol}] \quad (2)$$

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Table II. Second-Order Rate Constants for the Bromination of Cyclohexene in the Presence of TBAB in 1,2-Dichloroethane and 1,1,2,2-Tetrachloroethane at 25 °C^a

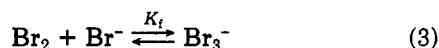
10 ⁴ [Br ₂], M	10 ⁴ [TBAB], M	k ₂ , M ⁻¹ s ⁻¹	
		1,2-dichloroethane	1,1,2,2-tetrachloroethane
3.7	3.7	0.72 (0.02)	
3.7	20.1	0.61 (0.02)	
3.7	42.6	0.58 (0.01)	
3.7	94.4	0.54 (0.02)	
3.7	197.0	0.52 (0.01)	
3.7	301.3	0.50 (0.01)	
3.7	373.3	0.48 (0.01)	
3.6	3.6		23.47 (0.20)
3.6	9.7		19.23 (0.17)
3.6	17.5		16.72 (0.15)
3.6	41.4		14.60 (0.18)
3.6	99.6		13.13 (0.15)
3.6	160.2		12.05 (0.11)
3.6	274.1		11.25 (0.15)
3.6	382.5		10.84 (0.13)

^a Rate constants were measured under pseudo-first-order conditions, monitoring at 350 nm. Errors are given as standard deviations estimated from the deviations of experimental points from the best-fit pseudo-first-order straight lines.

A negative temperature coefficient has been very recently reported⁷ for the rates of the third-order bromination of cyclohexene by free Br₂ in 1,2-dichloroethane, for which the following apparent values of the activation parameters have been evaluated: $E_a = -7.8$ (0.1) kcal mol⁻¹, $\Delta H^\ddagger = -8.4$ (0.1) kcal mol⁻¹, $\Delta S^\ddagger = -62.0$ (0.4) eu. In contrast, the second-order rate constants measured for the reaction of cyclohexene with TBAT in the 10–40 °C range showed the usual positive temperature coefficients (Table I). Fitting of these data to the Arrhenius equation gave the following values of activation parameters: $E_a = +6.6$ (0.3) kcal mol⁻¹, $\Delta H^\ddagger = +6.0$ (0.3) kcal mol⁻¹, $\Delta S^\ddagger = -40.9$ (1.1) eu. Thus, brominations by Br₂ and by Br₃⁻ both exhibit, as expected, large negative activation entropies, but the two processes are characterized by opposite apparent activation enthalpies.

Effect of Added Bromide. The influence of added bromide ions on the kinetics of bromine addition to cyclohexene was investigated by using tetrabutylammonium bromide (TBAB) in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane under pseudo-first-order conditions. The typical UV absorption of tribromide ion appeared immediately on mixing Br₂, TBAB, and the alkene in the stopped-flow apparatus, and the subsequent reactions obeyed very cleanly rate eq 2 up to over 90% consumption of the brominating reagent. Table II shows the second-order rate constants measured in the presence of increasing amounts of TBAB. Added bromide had a very modest effect on the reaction rate in both solvents, a 100-fold excess of TBAB over Br₂ producing only a 33% decrease in the rate constant in 1,2-dichloroethane and a 54% decrease in that in 1,1,2,2-tetrachloroethane.

In principle, this small deceleration could be due to the concurrence of two bromination processes, respectively by Br₃⁻ and by free Br₂ released through equilibrium (eq 3),



both first order in the brominating reagent. The formation constant of Br₃⁻ is very large in the chlorinated hydrocarbons employed as solvents (see Table V), and the very

Table III. Rate Constants for the Bromination of Cyclohexene with Br₂ (k₃) and with TBAT (k₂) in Different Solvents at 25 °C^a

solvent	ε	k ₃ , M ⁻² s ⁻¹	k ₂ , M ⁻¹ s ⁻¹
1,2-dichloroethane	10.697 ^b	2.40 × 10 ⁵ (0.11)	0.72 (0.02)
dichloromethane	8.93 ^c	1.20 × 10 ⁵ (0.08)	5.17 (0.15)
1,1,2,2-tetrachloroethane	8.20 ^c	1.60 × 10 ⁵ (0.10)	23.47 (0.20)
1,1,1-trichloroethane	7.55 ^c	3.90 × 10 ² (0.37)	2.00 × 10 ⁻² (0.10)
1-chloropentane	6.60 ^c	9.10 × 10 ² (0.30)	1.20 × 10 ⁻² (0.07)
chloroform	4.616 ^b	5.80 × 10 ³ (0.25)	13.41 (0.25)
chloroform- <i>d</i>		5.90 × 10 ³ (0.30)	11.40 (0.22)
carbon tetrachloride	2.24 ^c	8, ^d 2.4 ^e	0.102 (0.004)

^a Rate constants have been measured under pseudo-second-order and pseudo-first-order conditions, monitoring at the absorption maximum of free Br₂ and at 350 nm, respectively. Errors are given as standard deviations obtained from the deviations of individual measurements from the average values. ^b Dielectric constant measured in this work. ^c Taken from ref 6. ^d Taken from ref 10. ^e Taken from ref 12.

low concentration of free bromine at equilibrium could well produce a change in kinetics from second order to first order in Br₂. Under this hypothesis, the observed rate constant should be given by eq 4,^{8,9} and a plot of $k_{2, \text{obsd}}$ (1

$$k_{2, \text{obsd}} = (k_{2, \text{Br}_2} + k_{2, \text{Br}_3^-} K_f [\text{Br}^-]) / (1 + K_f [\text{Br}^-]) \quad (4)$$

+ $K_f [\text{Br}^-]$) vs. $[\text{Br}^-]$ should yield k_{2, Br_2} and k_{2, Br_3^-} from the intercept and slope. When applied to the data of Table II, eq 4 gave the following couples of rate constants in the two solvents: $k_{2, \text{Br}_2} = 6.90 \times 10^3$ M⁻¹ s⁻¹ and $k_{2, \text{Br}_3^-} = 0.49$ M⁻¹ s⁻¹ in 1,2-dichloroethane and $k_{2, \text{Br}_2} = 2.54 \times 10^3$ M⁻¹ s⁻¹ and $k_{2, \text{Br}_3^-} = 10.70$ M⁻¹ s⁻¹ in 1,1,2,2-tetrachloroethane.

It will be easily realized that this treatment gives unacceptable results. In fact, a first-order reaction in Br₂ with the above values of k_{2, Br_2} would outweigh the second-order process in the halogen observed in the absence of TBAB, for which values of k_{3, Br_2} of 2.40×10^5 and 1.60×10^5 M⁻² s⁻¹ have been measured respectively in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane (see Table III). Very satisfactory linear pseudo-second-order plots were instead obtained for the free Br₂ reactions in both of these solvents. In particular, no contribution to the rate equation by a first-order term in bromine was observable down to 5×10^{-6} M Br₂ in 1,2-dichloroethane,⁷ indicating for the k_{2, Br_2} a limiting value of about 1 M⁻¹ s⁻¹, which is 3 orders of magnitude lower than the one obtained by eq 4.

These observations rule out the occurrence of a free Br₂ addition process in the reactions carried out in the presence of at least an equimolar amount of added TBAB (or with preformed TBAT) and reinforce the view⁵ that the small decrease in rate produced by the latter salt is due to a slight salt effect of the type reported for the reaction of Br₃⁻ with styrenes in acetic acid.⁹ For this reason the rate constants measured at TBAB to Br₂ ratios of 1–2 were taken as the true k_{2, Br_3^-} in all investigated solvents.

Solvent Effect. The influence of the solvent polarity on the rates of bromination of cyclohexene both without and with added TBAB has been investigated for a set of aprotic solvents of moderate or low dielectric constants of the type in which most preparative brominations are performed. Rate eq 2 was strictly followed by the reactions carried out in the presence of TBAB in all examined solvents. In all solvents but CCl₄, the free Br₂ reactions

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obeyed eq 1 down to the lowest attainable halogen concentration. Some small deviations from eq 1 observed in the final part of a few of the slowest kinetic runs were completely eliminated by allowing the absorbance at infinite time to be adjusted by not more than ± 0.02 AU in the fitting process.

The second-order and third-order rate constants obtained for the reactions of Br_3^- and free Br_2 in different solvents are given in Table III. Only in carbon tetrachloride, no clean second-order nor first-order dependence on free bromine was found, and erratic values of the rate constants were obtained even when the two-term eq 5 was

$$-d[\text{Br}_2]/dt = k_3[\text{Br}_2]^2[\text{ol}] + k_2[\text{Br}_2][\text{ol}] \quad (5)$$

applied. Although the reaction of cyclohexene with bromine in carbon tetrachloride has been depicted both as a simple overall third-order¹⁰ process and as a mixed second-order and third-order process,¹¹ difficulties of the presently encountered type have been most recently reported.¹² They have been attributed to the presence of small amounts of water and of HBr formed by side reactions and overcome by adding *N*-bromoamides as HBr scavengers giving reproducible reactions, second order in bromine. Values of the third-order rate constant in carbon tetrachloride taken from two different literature sources are quoted in Table III. Although quite different, they certainly give at least the right order of magnitude of k_3 .

Thus, a change from solvents of moderate polarity, like 1,2-dichloroethane, dichloromethane, and 1,1,2,2-tetrachloroethane, to the nonpolar carbon tetrachloride produces a dramatic drop of 5 orders of magnitude in the third-order rate constant for the addition of free Br_2 . Not unexpectedly, the variation with changing dielectric constant is not steady but still indicates that the bulk medium polarity has a dominant effect on the rate of this reaction, even if other more subtle factors related to the detailed structural features of solvents may not play a negligible role as well.

In contrast, a more restricted range of values ($\sim 10^3$) and no regular trend with the solvent polarity are recognizable in the second-order rate constants for the addition of Br_3^- , the lowest value being found in solvents 1-chloropentane and 1,1,1-trichloroethane, of intermediate dielectric constants, and the highest ones in solvents 1,1,2,2-tetrachloroethane, chloroform, and dichloromethane, placed on opposite extremes of the investigated range.

Several equations have been proposed for a quantitative approach to the solvent effects on reaction rates, using functions of the dielectric constant of the solvent considered as an isotropic continuum.¹³ The most commonly used one is perhaps eq 6,¹⁴ where k and k_0 are the rate

$$\ln k = \ln k_0 - \frac{(N_A/RT)(\epsilon - 1)/(2\epsilon + 1)(\mu_A^2/r_A^3 + \mu_B^2/r_B^3 + \mu_\ddagger^2/r_\ddagger^3)}{\quad} \quad (6)$$

constants in a medium of dielectric constant ϵ and unity, respectively, N_A is the Avogadro constant, and r_A , r_B , r_\ddagger , μ_A , μ_B , and μ_\ddagger are the radius and dipole moments of reagents and transition state, respectively. Equation 6 predicts a linear plot for $\ln k$ against the Kirkwood func-

Table IV. Rate Constants for the Bromination of Cyclohexene with Bromine (k_3) and TBAT (k_2) in Mixtures of 1,2-Dichloroethane and Chloroform at 25 °C^a

1,2-dichloroethane %	ϵ	$k_3, \text{M}^{-2} \text{s}^{-1}$	$k_2, \text{M}^{-1} \text{s}^{-1}$
100	10.697	2.40×10^5 (0.11)	0.72 (0.11)
80	9.188	1.28×10^5 (0.08)	2.40 (0.18)
60	7.921	6.99×10^4 (0.30)	4.66 (0.21)
50	7.184	5.06×10^4 (0.19)	5.80 (0.15)
40	6.677	3.55×10^4 (0.15)	7.00 (0.23)
20	5.629	1.78×10^4 (0.09)	10.05 (0.25)
10	4.976	9.50×10^3 (0.55)	11.94 (0.31)
0	4.616	5.80×10^3 (0.25)	13.41 (0.25)

^a Rate constants have been measured under pseudo-second-order conditions, at $[\text{Br}_2] = 2.6 \times 10^{-3}$ M, and pseudo-first-order conditions, at $[\text{Br}_2] = 2.3 \times 10^{-3}$ M and $[\text{Br}^-] = (3-3.5) \times 10^{-3}$ M, monitoring at 410 and 440 nm, respectively. Errors are given as standard deviations obtained from the deviations of individual measurements from the average values. ^b Dielectric constants measured in this work.

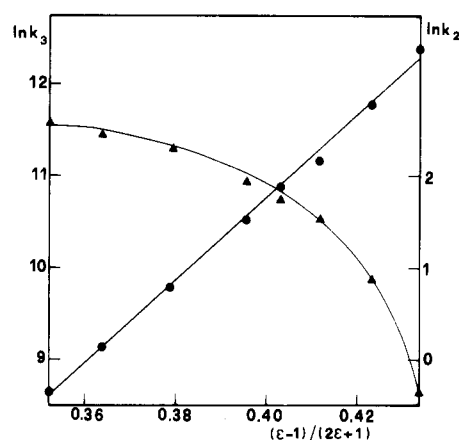


Figure 1. Plots of $\ln k$ against $(\epsilon - 1)/(2\epsilon + 1)$ for the reactions of free bromine (\bullet) and of TBAT (\blacktriangle) with cyclohexene in mixtures of 1,2-dichloroethane and chloroform at 25 °C.

tion $(\epsilon - 1)/(2\epsilon + 1)$,¹⁵ with a positive slope if the activated complex is more polar than the reactants. Poor correlations have, however, often been observed for rates obtained in various solvents, mainly because of specific solvation effects, and the required variation in ϵ is more conveniently obtained by changing the composition of binary solvent mixtures.¹³

The rate constants obtained for the addition of free Br_2 and of Br_3^- to cyclohexene in mixtures of 1,2-dichloroethane and chloroform and the relative values of the measured dielectric constants are given in Table IV. The k_3 and k_2 exhibited regular opposite trends, but the latter tended to level off with increasing chloroform content of the medium. Figure 1 shows the fittings of the rate data to the Kirkwood function. A very satisfactory linear plot was obtained for the third-order rate constants of the Br_2 reaction, with a large positive slope (45.1) indicating a markedly ionized, dipolar transition state.

The effect of solvent electrostatic interactions on the rate of addition of Br_3^- should be better described by eq 7,¹⁶ valid for reactions of an ion A with a neutral molecule B of dipole moment μ_B . This equation predicts a linear

$$\ln k = \ln k_0 + \frac{(e^2 N_A / 2RT)(1/\epsilon - 1)(1/r_A - 1/r_\ddagger) + (3e^2 N_A / 8RT)(2/\epsilon - 1)(\mu_B^2 / r_B^3 - \mu_\ddagger^2 / r_\ddagger^3)}{\quad} \quad (7)$$

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Table V. Downfield Shifts ($\Delta\delta$) of Protons of Solvents Added to a Solution of TBAB in Carbon Tetrachloride^a and Formation Constants of Tribromide Ion at 25 °C

solvent	$\Delta\delta$	$K_{\text{Br}_3^-}$, M ⁻¹
1,2-dichloroethane	0.04	$\geq 2 \times 10^7$ ^b
dichloromethane	0.06	$\geq 2 \times 10^7$ ^b
1,1,2,2-tetrachloroethane	0.20	1.9×10^5 (0.15) ^c
1,1,1-trichloroethane	0.00	$\geq 2 \times 10^7$ ^c
chloroform	0.40	1.2×10^5 ^d

^a Measured at 0.24 M TBAB and 0.7 M added solvent. ^b Taken from ref 4 and 5. ^c This work. ^d Taken from: Le Goaller, R.; Handel, P.; Labbe, P.; Pierre, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1694.

dependence of $\ln k$ on the reciprocal of the dielectric constant. However, since there is, to a good approximation, a linear relationship between the Kirkwood function and $1/\epsilon$ [$(\epsilon - 1)/(2\epsilon + 1) = 1/2 - 3/4\epsilon + 3/8\epsilon^2 - 3/16\epsilon^3 + \dots$], a linear plot of $\ln k_2$ against $(\epsilon - 1)/(2\epsilon + 1)$ was expected also for the Br_3^- reaction, if specific solvation effects were absent. Therefore, while the acceleration in rate of the latter process with increasing proportion of the less polar component of the binary mixture could have been attributed to charge delocalization in the transition state relative to the initial state of the Br_3^- reaction, the curvature of the $\ln k_2$ plot shown in Figure 1 strongly suggested a specific solvation effect.

Hydrogen Bonding and Kinetic Solvent Isotope Effect. Since chloroform is known to form hydrogen bonds to halide ions,¹⁷ the accelerating effect of this and other chlorinated solvents on the rate of TBAT addition suggested a specific electrophilic solvation by hydrogen bonding to bromide ion formed in this reaction. This possibility was checked by an NMR investigation of the hydrogen-bonding abilities of solvents listed in Table III toward TBAB, as measured by the change in chemical shifts of solvent protons in the presence of this salt. Table V lists the downfield shifts observed for solvents added to a carbon tetrachloride solution of TBAB at a solvent to salt molar ratio of 3. The formation constants of Br_3^- from Br_2 and Br^- in the various solvents are also included in Table V.

As expected, chloroform underwent the highest shift, indicating the strongest hydrogen bond to bromide, followed by tetrachloroethane. Other solvents having hydrogens α to chlorine exhibited smaller shifts, pointing the weaker hydrogen bonds. Inversely, the formation constant of Br_3^- was lowest in CHCl_3 and 1,1,2,2-tetrachloroethane. Interestingly, the comparison of the kinetic data of Table III with those of Table V shows furthermore that, with the exception of 1,1,2,2-tetrachloroethane, there is a parallel trend of the TBAB-induced shifts of solvents with the rates of addition of TBAT but not with those of the third-order reaction of Br_2 . It can also be observed that the former reaction has the highest k_2 values in solvents where K_f of Br_3^- is the lowest. These facts were taken as an indication that specific electrophilic solvation of a bromide ion plays a dominant role in the Br_3^- but not in the free Br_2 reaction. In this picture the higher than expected accelerating effect of 1,1,2,2-tetrachloroethane on the TBAT reaction rate could be due to the fact that two hydrogen bonds can be formed by a molecule of this solvent.

These conclusions were further supported by an investigation of kinetic solvent isotope effect (KSIE) in the reaction of cyclohexene with free Br_2 and TBAT in CHCl_3 and CDCl_3 . As shown in Table III, no KSIE was found

for the overall third-order bromination process ($K_H/K_D = 0.983$ (0.065)) while a K_H/K_D ratio of 1.175 (0.031) was measured for the overall second-order TBAT reaction. A similar value ($K_H/K_D = 1.23$ (0.02)) had been reported for the overall second-order brominations (first order in Br_3^-) of several olefin and acetylene substrates in $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOD}$ and $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$ ^{18,19} and ascribed to hydrogen bonding to the incipient bromide ion formed during the slow unimolecular ionization of a transient substrate- Br_2 CTC.

Discussion

The Addition Mechanism of Molecular Br_2 . Most extensive kinetic investigations of olefin bromination have been carried out in hydroxylic solvents like methanol²⁰ and acetic acid^{9,18,21} at low Br_2 concentrations, under conditions in which the reaction is first order in the halogen. The ionic nature of the addition mechanism in these solvents has been established both by free energy relationships and by studies of solvent effects on rate.²² The rate-determining step is generally considered to involve an $\text{S}_{\text{N}}1$ -like unimolecular ionization of a transient 1:1 Br_2 -olefin CTC to form a bromonium (or bromocarbenium) and a bromide ion ($\text{A}_{\text{D}}\text{E}_{\text{C}}1$ mechanism). The role of hydroxylic solvents in this mechanism has been shown to consist in providing specific electrophilic solvation by hydrogen bonding to the leaving bromide ion.^{18,19}

Fewer investigations have dealt with bromination in low polarity aprotic media, where the rate can be affected considerably by trace impurities and a very careful control of the reaction conditions is needed to avoid scatter in the results. These difficulties are exemplified by the recent conflicting reports on brominations in carbon tetrachloride.^{10-12,23} The overall third-order rate law of eq 1 is usually followed in slightly polar aprotic solvents. A change in rate-determining transition-state structure from a bromonium-like σ complex toward an olefin- Br_2 π complex on changing from polar to apolar solvents like 1,1,2-trichlorotrifluoroethane (Freon 113) has been proposed.²⁴ This interpretation has since then been disproved^{25,26} in favor of the bromonium ion-like transition state involved in polar media. The ionic nature of the addition has, however, been challenged in nonpolar solvents, where a molecular mechanism involving a 2:1 Br_2 -olefin CTC has been proposed instead.¹⁰

Direct evidence for the formation of CTC's between cyclohexene and Br_2 in a solvent of moderate polarity as 1,2-dichloroethane, as well as for their involvement on the

(18) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.

(19) A somewhat higher value ($k_H/k_D = 1.40$ (0.2)) has been reported by Dubois for the bromination of 1-pentene in $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}$: Garnier, F.; Donnay, R.; Dubois, J. E. *J. Chem. Soc. D* **1971**, 829.

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(25) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 1977.

(26) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.

(17) Ahmed, W. *J. Chem. Educ.* **1979**, *56*, 795. Green, R. D.; Martin, J. S. *J. Am. Chem. Soc.* **1968**, *90*, 3659.

reaction pathway for ionic bromination, has been very recently reported by our group.⁷ This has provided conclusive support to the mechanistic rationalization²¹ of the overall third-order rate law of eq 1 shown in Scheme I, where the rate-limiting step consists of the ionization of a 2:1 Br₂-olefin CTC and the second Br₂ molecule takes the place of a protic solvent in aiding bromine-bromine bond breaking by forming a charge-dispersed tribromide ion.⁷ In such a process an overall apparent negative activation energy is the consequence of exothermic pre-equilibrium steps having an enthalpy higher, in absolute value, than the activation energy of the rate-determining stage.

The implication of CTC's in the bromination process raises the question of how much solvent and substituent effects on the rate are due to a shift in the pre-equilibrium steps of Scheme I.²⁷ As for the solvent, it has been shown⁷ that the formation constant of the 1:1 Br₂-cyclohexene CTC is very similar in 1,2-dichloroethane and in carbon tetrachloride, indicating that the dielectric constant of the medium has no influence on the stability of this and, by analogy, probably also of the 2:1 complex. Therefore the decrease in k_3 for the Br₂ addition with decreasing solvent polarity reported in Table III should mainly reflect an increasing difficulty in the ionization step of the mechanism shown in Scheme I. In particular, the excellent linear dependence of $\ln k_3$ on the Kirkwood function of the dielectric constant in mixtures of 1,2-dichloroethane and chloroform conclusively shows that the same polar mechanism operates also in such a poorly polar solvent as the latter. Furthermore, the absence of specific solvation effects by hydrogen bonding to the anionic part of the transition state, demonstrated by the above linear correlation, by the lack of any correlation between k_3 and the hydrogen-bonding abilities of solvents, and by the absence of a KSIE in the Br₂ reaction carried out in CHCl₃/CDCl₃, is consistent with the formation of a tribromide ion in the slow step. In fact, although the possibility of hydrogen bonding to tribromide ion could not be checked by NMR, owing to the low solubility of TBAT in CCl₄, this large ion is stabilized by internal charge delocalization and is expected to require much less electrophilic solvation by hydrogen bonding than bromide ion. A much reduced electrophilic solvation of Br₃⁻, as compared to a strong solvation of Br⁻, is also consistent with the trend in the formation constants observed in aprotic and in protic solvents for equilibrium in eq 3: K_f is a maximum in solvents of low or no hydrogen-bonding ability, where Br⁻ cannot be stabilized, lower in hydrogen-bonding low-polarity solvents like chloroform or 1,1,2,2-tetrachloroethane, and a minimum in protic solvents like methanol ($K_f = 177 \text{ M}^{-1}$),²⁸ acetic acid (92 M^{-1}),⁹ and water (16 M^{-1}),²⁹ where Br⁻ is highly solvated.

The Addition Mechanism of Tribromide Ion. A kinetic term proportional to the concentration of both Br₂ and Br⁻ has been generally recognized in reactions carried out in the presence of added bromide salts, but its mechanistic meaning has not been univocally explained.^{30,31} Different but kinetically indistinguishable processes have been proposed.^{4,5,32} They involve rate-determining attack

by bromine and bromide on the double bond, either synchronous or after preassociation in an olefin-Br₂ CTC, direct electrophilic attack by tribromide on reactive olefins, and nucleophilic attack by tribromide on electron-poor substrates. Most of these data have been obtained in protic solvents, where Br₃⁻ is highly dissociated to Br₂ and Br⁻ and multiple reaction pathways are probably available.

One hypothesis advanced to rationalize the change in bromination products of conjugated dienes observed when a tribromide salt or an amine-Br₂ CTC in chlorinated hydrocarbons is used as the brominating reagent simply considers Br₃⁻ as an unreactive species, having the only role of reducing the actual concentration of free Br₂. This would impose a change from second order (or higher) to first order in the halogen and therefore from a bromonium-tribromide (or -polyhalide) to a bromonium-bromide intermediate. The role of hydrogen bonding in the TBAT reactions, indicated by the increase of k_2 with increasing hydrogen-bonding ability of solvents and by the KSIE found in CHCl₃/CDCl₃, could at first sight appear to be consistent with the above interpretation, since similar effects are found in overall second-order brominations by free Br₂ in protic solvents. However, the results of the investigation of the effect of added bromide ion on the rates of the TBAT addition definitely rule out any intervention by a reaction of a free Br₂ and show that TBAT is actually the only brominating species under the conditions of this investigation.

All experimental facts concerning the TBAT reaction can be accommodated by the mechanism shown in Scheme II. This mechanism involves as the first step an equilibrium between two complexes of bromine, i.e., Br₃⁻ and a 1:1 olefin-Br₂ CTC. The equilibrium constant is given by the ratio of the formation constants of these two species: $K = K_{\text{ol-Br}_2}/K_{\text{Br}_3^-}$. This step is followed by a rate-determining nucleophilic attack by the bromide of the ammonium bromide ion pair that has become detached from Br₂ at the moment of the formation of the olefin-Br₂ CTC or that is present as added salt, while a Br-Br bond is being broken and a new bromide ion formed. The expected rate law is given by eq 8, which, introducing the constant K for

$$-d[\text{Br}_3^-]/dt = k_2'[\text{ol-Br}_2][\text{Br}^-] \quad (8)$$

$$-d[\text{Br}_3^-]/dt = k_2 K [\text{Br}_3^-][\text{ol}] \quad (9)$$

the equilibrium step, becomes eq 9, equivalent to the observed rate law of eq 2. The accelerating effect of increasing concentrations of Br⁻ on the rate of nucleophilic attack is balanced by a reduction in the concentration of the olefin-Br₂ CTC, and the bromination rate is not affected by added bromide salts, except for a small negative salt effect on a transition state more charge delocalized than the initial state.

The latter feature of the transition state is also in agreement with the decrease in reaction rate observed in mixtures of 1,2-dichloroethane and chloroform with increasing proportion of the first, more polar component.

The positive value of the activation energy measured for the Br₃⁻ reaction, at variance with the negative one found for the third-order addition of molecular Br₂, is consistent with this picture. In fact, of the two 1:1 complexes of Br₂ involved in the equilibrium step of Scheme II, Br₃⁻ and the olefin-Br₂ CTC, the former is enormously more stable

(27) See, for instance, footnote 19 in: Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* 1984, 106, 3230.

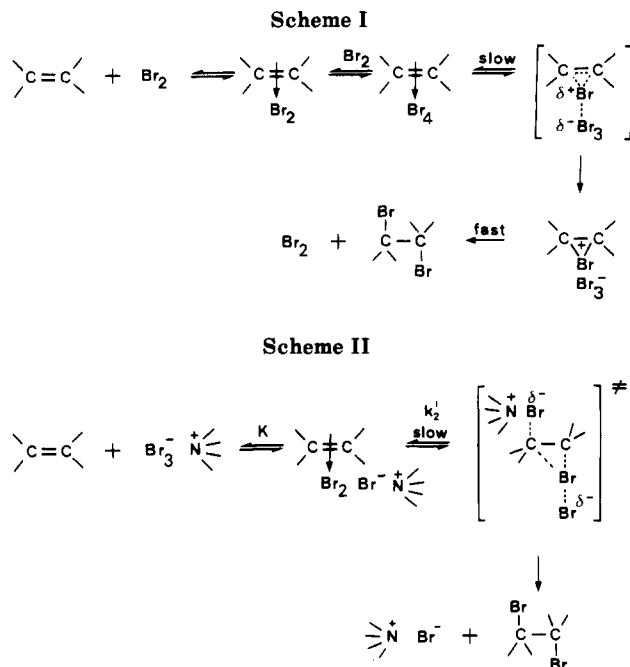
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than the latter. Since this difference must be essentially due to the enthalpy content, this step is expected to be endothermic ($\Delta H > 0$) and give a positive contribution to the overall activation energy, which therefore can only be positive, in contrast with the bromination by free Br_2 , where exothermic equilibrium steps determine a negative value of the apparent E_a .⁷

A rationalization of the accelerating effect of hydrogen-bonding solvents, as well as of the KSIE, on the rate of the Br_3^- reaction is complicated by the fact that electrophilic solvation may be involved both in the equilibrium and in the rate-determining step of Scheme II.

For the above discussed reasons, electrophilic solvation of Br_3^- is expected to be relatively unimportant, while the Br^- ion formed in the equilibrium step should be hydrogen bonded to the solvent. This would reduce its nucleophilicity and produce a decrease in k_2' in the best hydrogen-bonding solvents.³³ On the other hand, hydrogen bonding to the leaving bromide ion formed by breaking of the $\text{Br}-\text{Br}$ bond of the olefin- Br_2 CTC, as found in the first-order brominations in Br_2 carried out in hydroxylic solvents, may well balance the above retarding effect and also overvalance it, if this solvation were more important than the desolvation of the attacking bromide ion. A more effective electrophilic solvation of the leaving group relative to the attacking bromide could be due, for instance, to the proximity of the ammonium cation to the latter but not to the former anion. Furthermore, hydrogen-bonding solvents are expected to increase the value of K for the equilibrium step of Scheme II, since $K_{\text{Br}_3^-}$ is reduced and $K_{\text{ol-Br}_2}$ is scarcely affected, thus contributing to the observed increase in the overall reaction rate.

It can finally be pointed out that a mechanism of the type shown in Scheme II, in which rate- and product-determining transition states are coincident and no ionic intermediates are involved, can account for the suppression of syn addition to conjugated olefins and of 1,4 addition to dienes.²⁻⁴

This mechanism also rationalizes differences in diaxial to diequatorial dibromide ratios observed for substituted cyclohexenes using molecular Br_2 and tribromide salts.

The latter finding will be the object of a forthcoming publication.

Experimental Section

Materials. Cyclohexene (EGA, >99%) was refluxed over LAH and fractionally distilled on a Vigreux column immediately before each set of kinetic experiments. The best quality commercial bromine (C. Erba RPE, >99.5%) was kept in 1-mL sealed vials which were opened immediately before use. 1,2-Dichloroethane, dichloromethane, chloroform, and 1,1,1-trichloroethane were purified and dried with the previously reported method.^{4,5} 1,1,1-Trichloroethane was finally distilled from P_2O_5 . Chloroform-*d* (Prolabo, >99.8% *d*), 1-chloropentane, and carbon tetrachloride were simply refluxed over P_2O_5 and distilled. 1,1,2,2-Tetrachloroethane was washed with concentrated H_2SO_4 until the acid wash remained colorless. The solvent was then washed with water until neutral, dried over K_2CO_3 , then distilled under reduced pressure, and immediately used. Tetrabutylammonium tribromide (TBAT) was prepared from tetrabutylammonium bromide (TBAB) and bromine as previously reported.⁵

Analytical Procedures. Bromine concentrations were determined from the UV spectra taken on a Pye Unicam SP8-400 UV-vis spectrophotometer equipped with a thermostated cell holder, by using the previously determined value of the molar absorptivity for 1,2-dichloroethane⁵ and dichloromethane.⁴ In the other solvents the molar absorptivities, evaluated from solutions prepared by 1:100 dilution of a 1,2-dichloroethane solution of bromine of an exactly known concentration with each solvent, were the following: 1,1,1-trichloroethane, $\epsilon = 186 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 415 \text{ nm}$); 1-chloropentane, $\epsilon = 205 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 412 \text{ nm}$); 1,1,2,2-tetrachloroethane, $\epsilon = 221 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 410 \text{ nm}$); chloroform, $\epsilon = 197 \text{ M}^{-1}$ ($\lambda_{\text{max}} = 412 \text{ nm}$).

The limiting value of the formation constant of tribromide ion of TBAT in 1,1,1-trichloroethane was obtained⁵ from the absorbances of solutions of decreasing concentrations prepared by dilution of a freshly prepared $3 \times 10^{-4} \text{ M}$ stock solution of TBAT down to $1.5 \times 10^{-5} \text{ M}$. The value of $K_{\text{Br}_3^-}$ in 1,1,2,2-tetrachloroethane was calculated from the absorbances, measured at 273, 300, 350, 370, and 410 nm, of eight solutions of $2.8 \times 10^{-4} \text{ M}$ Br_2 and $(2.2-4.8) \times 10^{-4} \text{ M}$ TBAB. The 40 data were fitted with a nonlinear least-squares program that also gave the estimate of the standard deviation of $K_{\text{Br}_3^-}$.

Dielectric constants of the 1,2-dichloroethane-chloroform mixtures reported in Table IV were determined with an rf vector impedance meter Hewlett-Packard Model 4815 A, working at 1.59 MHz with a 90° phase at 25 °C.

NMR spectra were registered from a EM 360 A Varian spectrometer.

Kinetic Measurements. The kinetic measurements were performed with a Durrum Model D-110 stopped-flow apparatus equipped with a 2-cm observation cell and coupled to a Tektronix 5103 storage oscilloscope and a data acquisition system built around a 12-bit A/D converter interfaced to a Commodore 4032 personal computer, as previously reported.^{5,7} Temperature control ($\pm 0.05 \text{ }^\circ\text{C}$) was achieved with a Lauda MK 70 constant-temperature circulating bath. The reactions of free Br_2 in the different solvents were monitored at the respective absorption maxima. Those of Br_3^- were monitored at 350 or 440 nm. Freshly prepared reagents solutions were always used. Bromine solutions were periodically checked spectrophotometrically during the measurements and discarded when their absorbances at the absorption maximum started decreasing. The instrument was allowed to stabilize and the system equilibrated thermally before each kinetic measurement. A few preliminary runs were monitored on the oscilloscope, and only when they were found to be exactly reproducible, the data were acquired and logged on disk for subsequent processing, which was performed with the same microcomputer used for the acquisition.

Acknowledgment. This work was supported by a grant from the Consiglio Nazionale delle Ricerche and from the Ministero della Pubblica Istruzione. We thank Prof. D. Senatra and Dr. C. Gambi (Dipartimento di Fisica, Università di Firenze) for the measurement of the dielectric constants.

Registry No. D_2 , 7782-39-0; cyclohexene, 110-83-8.