

Competing Mechanistic Pathways in the Bromination of 1,3-Butadiene with Molecular Bromine, Pyridine-Bromine Complex, and Tribromide Ion

Giuseppe Bellucci,* Giancarlo Berti, Roberto Bianchini, and Giovanni Ingrosso

Istituto di Chimica Organica, Facoltà di Farmacia, 56100 Pisa, Italy

Keith Yates

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada

Received October 16, 1980

The kinetics and product distribution of the reactions of 1,3-butadiene with molecular bromine, with the pyridine-bromine charge-transfer complex (PyBr₂), and with tetra-*n*-butylammonium tribromide in 1,2-dichloroethane and dichloromethane have been investigated. Whereas the reaction with Br₂ is second order in halogen, those with the other two reagents are first order in the halogenating species, and evidence is presented that both act as independent electrophiles, rather than as sources of molecular bromine. In the reaction with PyBr₂ (and to a lesser extent in that with Br₃⁻ in the presence of pyridine) substantial amounts of *N*-(4-bromo-1-buten-3-yl)pyridinium bromide are formed besides the expected 1,2- and 1,4-dibromo adducts. This is converted into the corresponding tribromide as long as free Br₂ or PyBr₂ is present in the medium. The resulting tribromide ion remains as the only brominating species during the later stages of the reaction. The change from 1,2-dichloroethane to the slightly less polar dichloromethane as solvent produces a threefold decrease in rate of reaction with Br₂ and a fourfold increase in that with Br₃⁻. Possible mechanisms for the reactions of butadiene with Br₂, PyBr₂, and Br₃⁻ are discussed in terms of the present and previous results on these reactions. These have revealed very significant differences in the ratios of 1,2- to 1,4-adducts on changing from molecular Br₂ to complexed bromine as the reagents, which are interpreted in the light of these mechanisms.

Some years ago the use of amine-bromine charge-transfer complexes of the type of pyridine perbromide (PyBr₂) in place of molecular bromine was reported by one of us to increase the ratio of diaxial to diequatorial dibromides formed from substituted cyclohexenes.^{1,2} Similar results were obtained with the PyBrCl charge-transfer complex (CTC)³ and were rationalized on the basis of an Ad_EC₂-type mechanism involving both rate and product determination during nucleophilic attack.¹⁻³ Suppression of syn addition and of hydrogen bromide elimination in favor of anti addition was also observed⁴ for 1-phenylcyclohexene with the PyBr₂ reactant. Striking differences were later reported for the reactions of conjugated dienes with molecular bromine or bromine chloride on the one hand and with amine-Br₂ or amine-BrCl complexes and Br₃⁻ or Br₂Cl⁻ salts on the other,^{5,6} the latter reagents giving much higher ratios of 1,2 to 1,4 and of anti to syn adducts than the former ones. In a recent kinetic investigation⁷ we have shown that three distinct electrophiles, molecular bromine, the PyBr₂ CTC, and the Br₃⁻ ion formed during the course of the reaction by incorporation of pyridine into the addition product, are involved in the reaction of cyclohexene with bromine in the presence of pyridine. Since these three electrophiles were found to react by different mechanisms, competition between them was assumed to determine the overall product distribution from substrates giving more than one dibromide. 1,3-Butadiene, from

which both 1,2- and the 1,4-dibromo adducts (1 and 2) can be obtained,⁸ appeared to be a very suitable substrate for a kinetic and product investigation of bromination with molecular and complexed bromine, and this was the object of the present work.



Results

The kinetics of the reaction of 1,3-butadiene with molecular bromine were followed in a stopped-flow apparatus at 410 nm near the absorption maximum of bromine in the presence of a high excess of the diene under conditions in which the 1,2- and 1,4-dibromides free from tetrabromides were formed.^{8,9} For the sake of correlation with our previous work,⁷ 1,2-dichloroethane was chosen at first as the solvent. In the concentration range investigated a clean second-order dependence on bromine (eq 1) was found, as

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

is generally observed for the bromination of simple alkenes with molecular bromine in chlorinated hydrocarbons.¹⁰ The third-order rate constants are reported in Table I.

When the bromination was carried out in the presence of an approximately twofold excess of pyridine, two consecutive reactions of rather different rates were clearly apparent from the shape of the absorbance-time curve at 410 nm (Figure 1). While the second, slower reaction exhibited a first-order dependence on both the diene and the brominating species, the faster one, analyzed on an expanded scale as described in the Experimental Section,

(1) P. L. Barili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *J. Org. Chem.*, **37**, 4353 (1972).

(2) P. L. Barili, G. Bellucci, F. Marioni, and V. Scartoni, *J. Org. Chem.*, **40**, 3331 (1975).

(3) G. Bellucci, G. Ingrosso, F. Marioni, E. Mastrorilli, and I. Morelli, *J. Org. Chem.*, **39**, 2562 (1974).

(4) P. L. Barili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *J. Org. Chem.*, **38**, 3472 (1973).

(5) V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.*, **40**, 1358 (1975).

(6) G. E. Heasley, J. McCall Bundy, V. L. Heasley, S. Arnold, A. Gipe, D. McKee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *J. Org. Chem.*, **43**, 2793 (1978).

(7) G. Bellucci, G. Berti, R. Bianchini, G. Ingrosso, and R. Ambrosetti, *J. Am. Chem. Soc.*, **102**, 7480 (1980).

(8) E. H. Farmer, C. D. Lawrence, and J. F. Thorpe, *J. Chem. Soc.*, 729 (1928).

(9) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Am. Chem. Soc.*, **81**, 5943 (1959).

(10) A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977); P. B. D. de la Mare and R. D. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 2048, 2055 (1977).

Table I. Rate Constants and Product Distributions for the Reaction of 1,3-Butadiene with Bromine in the Absence and in the Presence of Pyridine in 1,2-Dichloroethane at 25 °C

run	$10^3[\text{Br}_2]$, M	$[\text{Py}]/[\text{Br}_2]$	$[\text{But}]/$ $[\text{Br}_2]$	% free Br_2^a	λ , nm ^b	$10^{-3}k_3,^c$ M ⁻² s ⁻¹	$10^2k_2,^c$ M ⁻¹ s ⁻¹	% of 3	1/2 ratio
1	1.202		85.8	100	410	2.32 ± 0.02			
2	1.075		144.2	100	410	2.42 ± 0.02			12:88 ^d
3	1.202		42.9	100	410	2.22 ± 0.02			
4	0.538	1.37	204.7	85				10	33:67
5	0.538	2.25	288.1	77	410	2.60 ± 0.01	1.10 ± 0.01		
6	0.538	2.25	288.1	77	350		1.11 ± 0.01	15	44:56
7	0.538	11.27	288.1	39	350		1.20 ± 0.01	38	71:29
8	0.538	45.10	288.1	13	350		1.44 ± 0.01	65	88:12

^a Calculated on the basis of the reported value for the association constant of PyBr_2 ($K = 273 \text{ M}^{-1}$). ^b Wavelength at which the reaction was monitored. ^c Errors of the individual rate constants are given as standard deviations estimated from the deviations of experimental points from the best-fit third-order and second-order straight lines. ^d The same product distribution was obtained in an experiment carried out at -35°C .

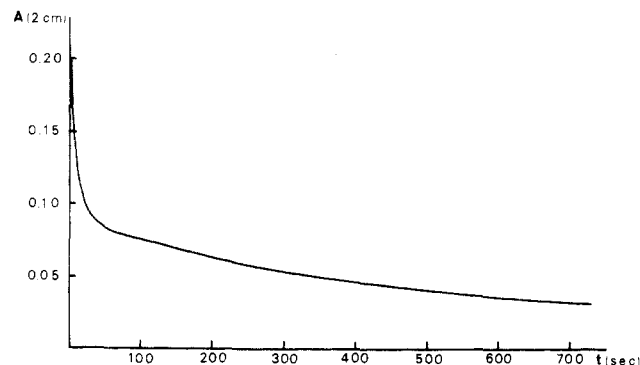


Figure 1. Absorbance (2-cm cell) at 410 nm vs. time for the reaction of $5.38 \times 10^{-4} \text{ M}$ bromine with $1.55 \times 10^{-1} \text{ M}$ 1,3-butadiene in the presence of $1.21 \times 10^{-3} \text{ M}$ pyridine in 1,2-dichloroethane at 25 °C.

showed a second-order dependence on the brominating reagent, with a third-order rate constant that was close to that measured for the reaction carried out in the absence of pyridine. This indicates that the faster process consists of the reaction of free bromine which is present in equilibrium with the pyridine–bromine CTC. On the basis of the stability constant reported for this CTC in 1,2-dichloroethane ($K = 273 \text{ M}^{-1}$),¹¹ 77% of the total amount of halogen can be evaluated to be present as free bromine at the start of the kinetic run shown in Figure 1, and this appears to be the main brominating species in the very early stages of the reaction. The third-order and second-order rate constants so obtained are listed in Table I (run 5).

The same reaction was also followed at 350 nm, where the absorption of free bromine is very low (ϵ 33) and does not interfere significantly with the pyridine–bromine charge-transfer absorption band (ϵ 660). At this wavelength the formation of an intermediate with a much higher extinction coefficient was clearly shown by the appearance of a maximum in the absorbance–time curves, whose intensity increased with increasing pyridine concentration (Figure 2). Calculations on the descending part of the curves so obtained showed a clean first-order dependence on the absorbing species and gave a value of the second-order rate constant identical with that obtained from the reaction run under identical conditions but monitored at 410 nm (runs 5 and 6 of Table I). The increase of pyridine concentration up to $2.4 \times 10^{-2} \text{ M}$ (run 8) caused, however, a small but significant increase in k_2 . Furthermore, the runs monitored at 350 nm showed a residual absorbance at the end of the reaction, indicating

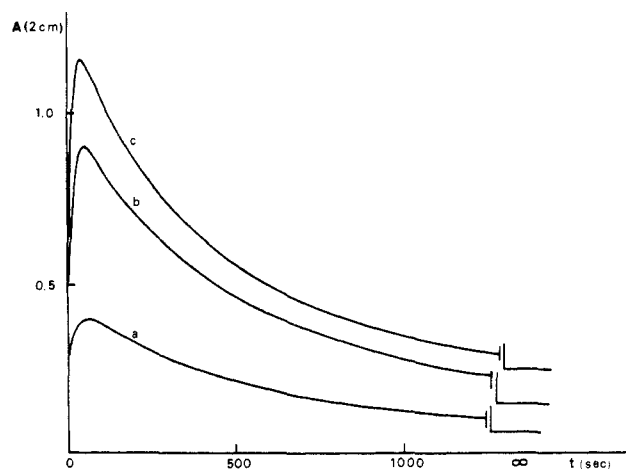


Figure 2. Absorbance (2-cm cell) at 350 nm vs. time for the reactions of $5.38 \times 10^{-4} \text{ M}$ bromine with $1.55 \times 10^{-1} \text{ M}$ 1,3-butadiene in the presence of (a) 1.21×10^{-3} , (b) 6.06×10^{-3} , and (c) $2.43 \times 10^{-2} \text{ M}$ pyridine in 1,2-dichloroethane at 25 °C.

that the 1,2- and 1,4-dibromo derivatives, which do not absorb in that region, were not the only reaction products.

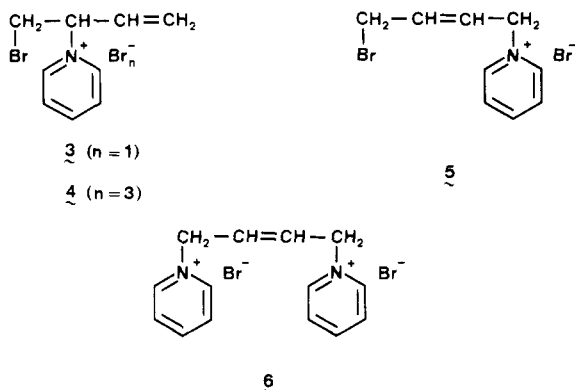
The analogy with the results previously found in the kinetic investigation of the reaction of cyclohexene with the pyridine–bromine CTC,⁷ in which *N*-(*trans*-2-bromocyclohexyl)pyridinium bromide was formed besides *trans*-1,2-dibromocyclohexane, strongly suggested that the formation of a similar product, probably a (bromoalkenyl)pyridinium bromide of type 3 or 5, arising from the addition of the pyridine–bromine CTC to one double bond of the diene, was responsible both for the final absorbance and for the shape of the absorbance–time curves obtained in the runs monitored at 350 nm. In fact, alkylpyridinium iodides and bromides in nonpolar solvents show charge-transfer absorption bands extending beyond the range of absorption of the pyridinium chromophore;^{7,12} furthermore, bromide ions have been shown to be able to abstract bromine from the pyridine– Br_2 CTC to give tribromide ions, whose formation constant in 1,2-dichloroethane is higher by several orders of magnitude than the stability constant of the pyridine–bromine CTC.⁷ Since the latter reaction is extremely fast, as long as there is free bromine or pyridine–bromine CTC available, the bromide ions once formed are immediately transformed into tribromide, with a strong hyperchromic effect accounting for the absorbance maximum observed in the curves of Figure 2. The subsequent reaction of tribromide with the diene is responsible for the descending part of the same curves,

(11) J. D'Hondt, C. Dorval, and T. Zeegers-Huyskens, *J. Chim. Phys. Phys.-Chim. Biol.*, **69**, 516 (1972).

(12) E. M. Kosower, J. A. Skorz, W. M. Schwarz, and J. W. Patton, *J. Am. Chem. Soc.*, **82**, 2188 (1960).

while the (bromoalkenyl)pyridinium bromide remaining at the end of the reaction accounts for the final absorbance.

In support of this interpretation, when butadiene was reacted with the solid pyridine-bromine CTC in 1,2-dichloroethane on a preparative scale, a crystalline precipitate was formed which analyzed correctly for pyridinium bromides 3 or 5. NMR spectra clearly indicated that it



was the 1,2-adduct 3. In the proton spectrum the signals of the aliphatic protons were very similar to the corresponding ones of 3,4-dichloro-1-butene and completely different from those of 1,4-dibromo-2-butene. The ^{13}C NMR spectrum fully confirmed this identification. The proton-decoupled spectrum showed the expected seven singlets, and in an off-resonance irradiation experiment the signal for the carbon α to the pyridinium group was converted into a doublet (secondary carbon) and that relative to the carbon α to bromine into a triplet (primary carbon).

When the stoichiometric amount of bromine was added to a solution of bromide 3 in 1,2-dichloroethane, the formation of tribromide 4 was clearly shown by a large increase of the absorbance in the UV spectrum. This absorbance was stable, indicating that the strongly deactivated double bond of the cation 4 did not react with the tribromide ion. Progressive dilution down to a concentration of 2×10^{-5} M did not cause a detectable dissociation. On the assumption that a maximum dissociation of 5% may go undetected because of the error in the spectrophotometric measurements at the lowest concentration (which is certainly an overestimate), a limiting value of $2 \times 10^7 \text{ M}^{-1}$ can be estimated for the formation constant of the tribromide ion in 4, in complete agreement with that found for *N*-(*trans*-2-bromocyclohexyl)pyridinium tribromide.⁷ Although the formation constant of the tribromide ion has been reported¹³ to depend to some extent on the counterion, in these cases the difference, if any, is certainly very small.

The UV spectra of bromide 3 and of the corresponding tribromide 4 are shown in Figure 3, together with that of the pyridine-bromine CTC: they fully confirm the above interpretation of the spectral changes accompanying the reaction of butadiene with bromine in the presence of pyridine.

Besides the spectroscopic evidence of Figure 2, the following observations confirmed that salt 3 arose directly from the addition of the pyridine-bromine reagent to butadiene and not from a subsequent reaction of the unsaturated dibromo derivatives 1 or 2 with the free pyridine present in the reaction medium. When the *trans*-1,4-dibromo derivative 2 was left in contact with pyridine in 1,2-dichloroethane solution, a crystalline precipitate was

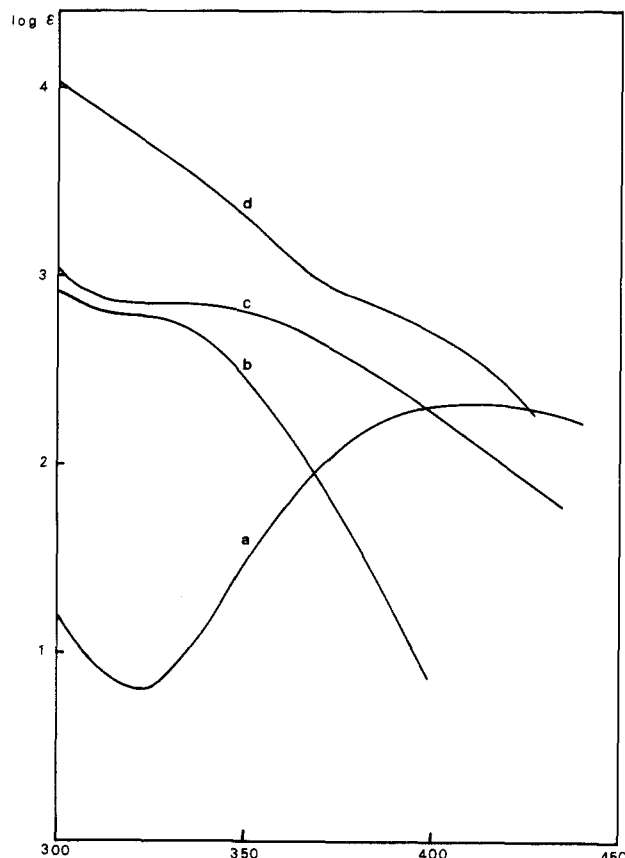


Figure 3. UV spectra of (a) Br_2 , (b) bromide 3, (c) PyBr_2 , and (d) tribromide 4 in 1,2-dichloroethane.

formed, which was identified as the *trans* dipyridinium derivative 6 by the similarity of the aliphatic proton signals in the NMR spectrum with those of the starting 1,4-dibromide. Control experiments showed, however, that under the conditions of the present kinetic investigation the rate of this reaction was so low as to exclude any competition with the bromination reaction and any significant interference with the determination of the final absorbance. The reaction of 3,4-dibromo-1-butene with pyridine was much slower, and only very small amounts of the same 1,4-dipyridinium adduct 6 separated from reaction mixtures of concentrations much higher than those used in the kinetic runs, even after very long reaction times. Presumably the inductive effect of the bromine atom at C(4) has a strong retarding effect on the breaking of the C(3)-Br bond, so that only the 1,4-dibromo derivative, slowly formed by isomerization of the 3,4-dibromo adduct, may react to give 6. Alternatively, 6 may be formed through a very slow $\text{S}_{\text{N}}1'$ reaction, giving *N*-(4-bromo-2-butenyl)pyridinium bromide, followed by a faster displacement of bromine by a second pyridine molecule.

The yields of salt 3 obtained in each run, determined spectrophotometrically, are reported in Table I, together with the ratios of the dibromo adducts formed under the conditions of the kinetic experiments (determined by GLC). The presence of increasing amounts of pyridine caused an increase both in the amount of salt 3 and in the ratio of 1,2- to 1,4-dibromo adduct. At pyridine concentrations high enough to bind most of the bromine, this ratio was exactly reversed (88:12) with respect to that formed for the bromination with molecular bromine (12:88).

A very similar picture was obtained by running the reactions of butadiene with bromine in the presence and in the absence of pyridine in dichloromethane, the solvent used by Heasley and co-workers.⁶ Bromine and pyri-

(13) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1483 (1969).

Table II. Rate Constants and Product Distributions for the Reaction of 1,3-Butadiene with Bromine in the Absence and in the Presence of Pyridine in Dichloromethane at 25 °C

run ^c	[Py]/[Br ₂]	[But]/[Br ₂]	λ, nm ^a	10 ⁻² k ₃ , ^b M ⁻² s ⁻¹	10 ² k ₂ , ^b M ⁻¹ s ⁻¹	% of 3	1/2 ratio
9		62.4	410	8.20 ± 0.01			20:80
10	1.04	62.4	410		4.68 ± 0.01	10	44:56
11	1.04	62.4	350		4.39 ± 0.01	12	44:56
12	8.34	62.4	350		4.45 ± 0.01	43	74:26

^a Wavelength at which the reaction was monitored. ^b See footnote c of Table I. ^c [Br₂] = 1.34 × 10⁻³ M in all cases.

Table III. Rate Constants and Product Distributions for the Reaction of 1,3-Butadiene with TBAT in the Absence and in the Presence of Pyridine at 25 °C^a

run	solvent	10 ⁴ [TBAT], M	[Py]/[TBAT]	[TBAB]/[TBAT]	[But]/[TBAT]	10 ³ k ₂ , M ⁻¹ s ⁻¹	% of 3	1/2 ratio
13	CH ₂ Cl ₂	2.76			301	43.70 ± 0.01		95:5
14	(CH ₂ Cl) ₂	2.43			557	8.44 ± 0.01		94:6
15	(CH ₂ Cl) ₂	2.52	30.7		536	9.33 ± 0.02	9	
16	(CH ₂ Cl) ₂	2.42	45.8		560	9.78 ± 0.01	13	
17	(CH ₂ Cl) ₂	2.43	80.5		557	10.45 ± 0.01	21	
18	(CH ₂ Cl) ₂	2.42	104.5		560	10.70 ± 0.01	24	
19	(CH ₂ Cl) ₂	2.43	126.4		557	11.30 ± 0.01	29	
20	(CH ₂ Cl) ₂	2.43	161.2		557	11.50 ± 0.01	31	
21	(CH ₂ Cl) ₂	2.62		10.0	484	6.28 ± 0.01	0	
22	(CH ₂ Cl) ₂	2.42	118.6	9.5	673	6.81 ± 0.01	16	

^a The reactions were monitored at 350 nm.

Table IV. Product Distributions from the Reactions of 1,3-Butadiene with Bromine in the Presence of Pyridine and with TBAT at 20 °C^a

run	solvent	[Br ₂], M	[TBAT], ^b M	[Py]/[Br ₂]	% free Br ₂ ^c	yield of 3, %	total yield of dibromides, %	1/2 ratio
23	(CH ₂ Cl) ₂	0.100			100		90	18:82
24	CH ₂ Cl ₂	0.102			100		93	20:80
25	(CH ₂ Cl) ₂	0.115		1.00	16	21 ^d	72	68:32
26	(CH ₂ Cl) ₂	0.094		3.25	1.7	41 ^e	43	87:13
27	CH ₂ Cl ₂	0.107		1.00	f	15 ^g	80	72:28
28	(CH ₂ Cl) ₂		0.030 ^b				95	95:5

^a The ratio of 1,3-butadiene to total bromine was always higher than 5. ^b Preformed TBAT was used. ^c See footnote a of Table I. ^d Salt 3 was isolated in a 16% yield, while a further 5% was detected spectrophotometrically in the filtered solution. ^e Salt 3 was isolated in a 35% yield, while a further 6% was detected spectrophotometrically in the filtered solution. ^f Not calculated because the exact value of the association constant of PyBr₂ in CH₂Cl₂ is not known. ^g Detected spectrophotometrically in solution.

dine-bromine solutions in this solvent were rather unstable, but reasonably accurate kinetic measurements could be made by preparing these solutions immediately before use. Also, in dichloromethane the reaction of free bromine followed the rate law of eq 1, with a third-order rate constant (Table II, run 9) that was about one-third of that found in 1,2-dichloroethane. In the presence of pyridine, absorbance-time curves very similar to those reported in Figures 1 and 2 were observed, and good pseudo-first-order plots were obtained for the slower reaction, with second-order rate constants (Table II) four times higher than those obtained in 1,2-dichloroethane. Although salt 3 did not separate from dichloromethane, owing to its higher solubility in this solvent than in 1,2-dichloroethane, its formation was evident from the residual UV absorption at the end of the reaction. The trends in the yields of 3 and in the ratios of the dibromides obtained in dichloromethane (Table II) were very similar to those observed in 1,2-dichloroethane. The progressive change in product distribution with increasing pyridine concentration was consistent with tribromide 4 being more and more involved as the brominating reactant, since 3,4-dibromo-1-butene had been shown⁶ to be the main product of the reaction of butadiene with tribromide salts.

The fact that the pseudo-first-order reaction observed in the presence of pyridine was actually due to bromination through tribromide 4 was finally confirmed by running the reaction with a preformed tribromide, tetrabutyl-

ammonium tribromide (TBAT). Very good pseudo-first-order plots were obtained up to 90% reaction, with second-order rate constants comparable with those obtained in the pyridine-bromine reactions both in dichloromethane and in 1,2-dichloroethane. The fact that the values of *k*₂ are somewhat lower than those observed when PyBr₂ was used as brominating species is not particularly significant and may be due to the effect of the different counterion.⁷ The 1,2-dibromo adduct was by far the major product in both solvents. The influence of the presence of pyridine in the reaction with TBAT was investigated in 1,2-dichloroethane (Table III). Salt 3 was formed in the presence of the base, and an increase both in the yield of 3 and in the value of *k*₂ was observed with increasing pyridine concentration. A tenfold excess of added tetrabutylammonium bromide (TBAB) had a rather moderate retarding effect on the reaction rate of TBAT both in the absence (run 21) and in the presence (run 22) of pyridine. In the latter case TBAB also reduced, but did not completely prevent, the formation of salt 3.

The product distribution obtained on a preparative scale with molecular bromine, the pyridine-bromine reagent, and TBAT was then investigated. The results are reported in Table IV. These data show that no significant changes in the ratio of 1,2- to 1,4-dibromo adducts occurred in the reactions of molecular bromine carried out at relatively high and very low halogen concentrations in both solvents used (compare runs 23 and 24 of Table IV with run 2 of

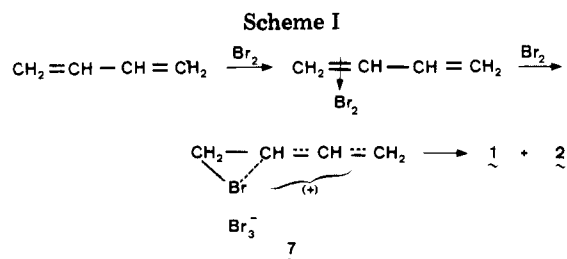
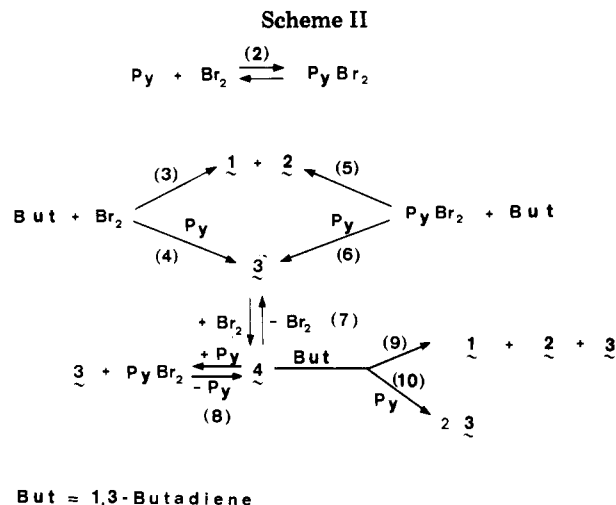


Table I and run 9 of Table II), in agreement with a previous report on the bromination of the 2,4-hexadienes in dichloromethane.⁶ In contrast, the 1/2 ratios obtained in the reactions performed with equimolecular amounts of bromine and pyridine showed a critical dependence on concentration (compare run 25 of Table IV with run 4 of Table I and run 27 of Table IV with run 10 of Table II), a 200-fold dilution of the brominating reactant causing a reversal in the ratio of dibromides obtained in 1,2-dichloroethane. Evidently, owing to the rather low value of the stability constant of PyBr_2 , dilution causes dissociation to free pyridine and bromine, and the latter becomes the main brominating species at very low concentrations. Furthermore, substantial amounts of salt 3 were obtained also in the preparative runs carried out with the pyridine-bromine reactant, especially when an excess of the amine was present (run 26 of Table IV). This probably went undetected previously⁶ because 3 is sufficiently soluble in dichloromethane (the solvent employed in the previous investigation) to prevent precipitation, and reaction mixtures were washed with aqueous HCl before product analysis. The formation of 3 accounts for the low yields of dibromo adducts obtained in the brominations performed in the presence of a large excess of amine.⁶ Finally, no concentration effect on the 1,2- to 1,4-dibromide ratio was found in the TBAT reaction (compare run 28 of Table IV with run 14 of Table III).

Discussion

Our results for the reaction of 1,3-butadiene with molecular bromine fit well into the general mechanism of bromination of alkenes in low polarity aprotic solvents,¹⁴ the second-order dependence on bromine of eq 1 indicating the intervention of a second molecule of halogen at the rate-determining transition state, which probably consists¹⁵ of a bromine-assisted heterolytic fission of the Br-Br bond in an initially formed olefin-bromine CTC to give an ion pair involving a covalent, cationic intermediate and a very stable Br_3^- ion (Scheme I). The moderate increase in rate constant on passing from dichloromethane ($\epsilon = 9.08$, $\mu = 1.55$)¹⁶ to the slightly more polar 1,2-dichloromethane ($\epsilon = 10.36$, $\mu = 2.06$)¹⁶ as solvent is consistent with the ionic nature of this process. The intermediate, which for the bromination in methanol has been viewed as an unsymmetrically bridged bromonium ion with little, if any, delocalization of the positive charge across the adjacent vinylic system,¹⁷ is likely in our solvents to be closer to a delocalized carbenium than to a bromonium ion, as shown by the prevalent nucleophilic attack of the anion of the



ion pair at the terminal vinylic carbon to give mainly the 1,4-dibromo adduct; the low solvating power favors intramolecular charge dispersion, as shown in 7.¹⁸ Both dependence and independence of the 1,4- vs. 1,2-addition of bromine to 1,3-butadiene on solvent polarity have been reported.^{8,9,19}

On the other hand, the kinetic and product data obtained in the brominations carried out in the presence of pyridine can be rationalized on the basis of the reactions of cyclohexene under the same conditions.⁷ Reactions 2, 3, 7, and 9 have been independently observed. Equilibrium 8 has not been directly investigated, but a limiting value of $K_8 > 7 \times 10^4$ can be estimated from the values of K_2 and K_7 . It is therefore strongly displaced toward the Br_3^- species in the presence of a moderate excess of pyridine. Under the latter conditions a yield of 3 higher than 50% (run 8 of Table I) suggests that reaction 10 also could be significantly involved in the reaction sequence. In fact, if 3 were formed only through the free bromine or the PyBr_2 CTC reactions (paths 4 and 6 of Scheme II) and not through the reaction of tribromide 4, a maximum 50% yield of 3 should be obtained, the remaining 50% of bromine being completely captured by 3 to give 4. The incursion of reaction 10, besides 9, is, moreover, confirmed by the significant incorporation of pyridine in the reactions of 1,3-butadiene with TBAT-pyridine, also in the presence of moderate amounts of the amine and also when a tenfold excess of TBAB over TBAT was added (Table III). On the basis of the above-mentioned limiting value of the equilibrium constant between the PyBr_2 CTC and the Br_3^- ion, the amount of PyBr_2 present at the start of runs 15 and 22 of Table III can be estimated to be less than 2% and 0.02%, respectively, and this rules out a significant competition by path 6 in the TBAT-pyridine reactions, leaving path 10 as the main or only process responsible for the observed yields of 3, at least at moderate pyridine to Br_3^- ratios.

The latter conclusion is at variance with that inferred in the previous investigation of the bromination of cyclohexene with TBAT in the presence of pyridine,⁷ where significant incorporation of the amine occurred only at higher pyridine to tribromide ratios and was completely

(14) R. C. Fahey, *Top. Stereochem.*, **3**, 286 (1968); G. H. Schmid, and D. G. Garratt, "The Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley, New York, 1977, Chapter 9.

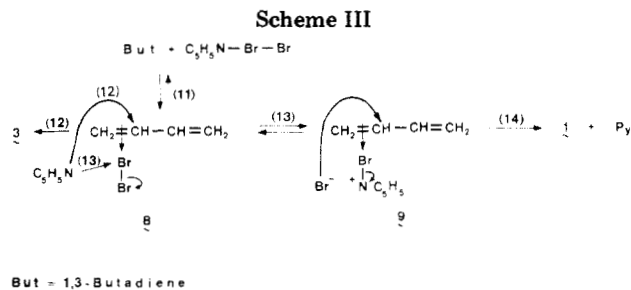
(15) K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, **38**, 2460 (1973).

(16) J. A. Riddick and E. E. Toops in "Technique of Organic Chemistry", A. Weissberger, Ed., Interscience, New York, 1955, Vol. VII, pp 192, 196.

(17) V. L. Heasley and P. H. Chamberlain, *J. Org. Chem.*, **35**, 539 (1970).

(18) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(19) A general trend toward greater 1,4-addition of bromine to 1,3-butadiene with increasing solvent polarity has been reported, although a lower 1,2 to 1,4 ratio was observed in dichloromethane than in acetonitrile (V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. Mc Connell, *J. Org. Chem.*, **37**, 2228 (1972)).

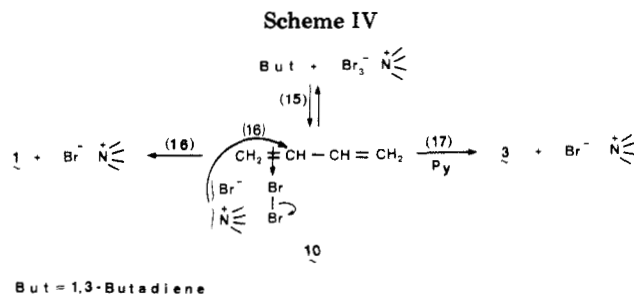


suppressed in the presence of added bromide ions. This suggested that reaction 10 was not significantly involved. The presence of the conjugated double bond appears to make 1,3-butadiene more susceptible to nucleophilic attack by the amine during the bromination reactions.

The simplification introduced in the previous study⁷ of the bromination of cyclohexene at pyridine-bromine ratios high enough to bind most of the halogen as $PyBr_2$ (which consisted of treating the complicated system of Scheme II simply as a sequence of two consecutive reactions of $PyBr_2$ and of Br_3^-) did not apply in the present case, where more reactions appeared to be involved under all conditions examined. Therefore, a complete kinetic analysis of the curves of type c in Figure 2 was not attempted, so that no direct kinetic evidence could be obtained for direct attack by the $PyBr_2$ CTC in reactions 5 and 6 of Scheme II. The intervention of the latter reaction can, however, be safely assumed by analogy with the similar reaction of cyclohexene,⁷ while the contribution of the former one is strongly suggested by the consideration of the product distributions, as discussed below.

The high ratio of 1,2- to 1,4-dibromo adducts obtained in run 8 of Table I is easily understood, since the very high yield of 3 assures that most of the dibromides originate by the reactions sequence $2 \rightarrow 6 \rightarrow 7 \rightarrow 9$ of Scheme II, that is by bromination through the tribromide ion, which has been shown to give mostly the 1,2-dibromo adduct (see run 14 of Table III), with only a very small contribution of reaction 3 due to the small amount of free bromine present initially. The distributions of the dibromides found at lower pyridine-bromine ratios, when smaller amounts of salt 3 are obtained, cannot, however, be simply rationalized on the basis of the two bromination pathways 3 and 9. In fact, the maximum yield of dibromo adducts formed through the tribromide reaction 9 cannot exceed the yield of 3 and can actually be lower if part of 3 is formed through reaction 10 when there is no more free bromine or $PyBr_2$ available to convert 3 into 4. The maximum values of the 1/2 ratio obtainable in runs 4, 6, and 7 of Table I on the simple basis of a partition between reactions 3 and 9²⁰ are therefore, respectively, 21:79, 26:74, and 62:38. All three of these ratios are significantly lower than the observed values, indicating that there must be another process, presumably reaction 5, contributing to the formation of the 1,2-dibromo adduct. Similar considerations apply to runs 10 and 11 carried out in dichloromethane.

In a previous paper we suggested⁷ that at high pyridine-bromine ratios, an equilibrium is established between the $PyBr_2$ and an olefin- Br_2 CTC. Nucleophilic attack by pyridine at carbon of the latter CTC with concerted Br-Br bond breaking gives the pyridine incorporation product. In the present case this mechanism is shown by steps 11 and 12 of Scheme III. However, the formation of a di-



bromo adduct requires preliminary breaking of the Br-Br bond in 8. In the absence of free bromine to provide electrophilic assistance, this may be achieved through nucleophilic assistance by pyridine to give a new CTC and a bromide ion as ion pair 9 (step 13). The collapse of the latter ion pair would give the dibromo adduct. The CTC character of both intermediates involved is in agreement with the exclusive formation of the 1,2-bromopyridinium adduct 3 and the prevalent formation of the 1,2-dibromo adduct 1 in the reactions of $PyBr_2$ (reactions 6 and 5 of Scheme II). If a covalent, cationic intermediate of type 7 were involved, a predominant formation of 1,4-addition products would have been expected.

The first-order dependence on tribromide and the very modest decrease in rate observed in the presence of a tenfold excess of bromide ions, when the dissociation of Br_3^- to Br_2 and Br^- is extremely depressed (compare runs 14 and 21 of Table III), are consistent with the previous proposal that Br_3^- is an independent electrophile, rather than a source of molecular bromine. Further evidence for this is provided by the opposite effect of a change in solvent on the rates of the reactions of molecular bromine and of tribromide ion: while the first one is accelerated by a factor of about 3, the latter is retarded by a factor of 4 on passing from dichloromethane to 1,2-dichloroethane. If the only function of the tribromides, as well as of $PyBr_2$, were that of limiting the concentration of free halogen, the real difference between the reaction mechanism of molecular bromine and of halogen complexes would lie in the structure of the anion of the ionic intermediates of type 7 (a tribromide ion for the first and a bromide ion for the latter, as suggested by Heasley).⁶ In this case, a change from second to first order in electrophile could occur, but the rates of the two processes involving the same cation as the intermediate formed in a rate-determining step would hardly be expected to exhibit the observed opposite trend in sensitivity to solvent changes.

The electrophilicity of tribromide ion has been the object of a long-standing debate, mainly because of the difficulty of regarding this negatively charged ion as being able to compete favorably with molecular bromine for electrophilic attack on deactivated substrates.²¹ Direct electrophilic attack by Br_3^- and Br^- -assisted attack by Br_2 have been alternatively invoked.^{13,21-26} Although kinetics cannot distinguish between these two mechanisms, in the present case the significant incorporation of pyridine observed in the TBAT-pyridine reactions is inconsistent with the latter, since such a process alone would be expected to give

(20) Owing to the very large difference in rate between the k_3 and the k_2 processes, recycling of 3 arising from pathways 9 and 10 of Scheme II to 4 during the early stages of the reaction can be neglected.

(21) N. P. Kanyaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **29**, 825 (1959).

(22) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

(23) K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64**, 697, 704, 709 (1942).

(24) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966).

(25) J. E. Dubois, and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

(26) S. De Young, and E. Berliner, *J. Org. Chem.*, **44**, 1088 (1979).

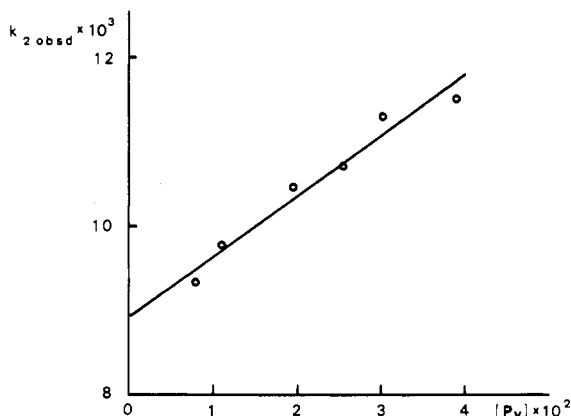


Figure 4. Plot of $k_{2,obsd}$ vs. pyridine concentration for the reaction of 1,3-butadiene with TBAT in 1,2-dichloroethane at 25 °C.

only dibromo adducts. Both the kinetic and the product data for the tribromide reactions are instead consistent with the mechanism shown in Scheme IV, in which the olefin-bromine CTC is again in equilibrium with the reactants, and the nucleophilic attack at carbon can be carried out either by the bromide of the ammonium bromide ion pair that has become detached from Br_2 at the moment of electrophilic attack or by the slightly less nucleophilic pyridine added in excess in the reaction medium.

It must be stressed that the latter mechanism requires rate- and product-determining nucleophilic steps.²⁷ Evidence in its favor is provided by the data of Table III, showing that in the reactions of 1,3-butadiene with TBAT in the presence of pyridine an increase in rate constant parallels increasing pyridine incorporation. Although only amine concentrations $\leq 4 \times 10^{-2}$ M were examined in order to avoid complications due to formation of $PyBr_2$ through equilibrium 8 of Scheme II at higher pyridine-TBAT ratios, a reasonable linear correlation (eq 20) between $k_{2,obsd}$

$$-d[Br_3^-]/dt = k_2[But][Br_3^-] + k_2'[But][Br_3^-][Py] \quad (18)$$

$$-d[Br_3^-]/dt = k_{2,obsd}[But][Br_3^-] \quad (19)$$

$$k_{2,obsd} = k_2 + k_2'[Py] \quad (20)$$

and the pyridine concentration was found (Figure 4) over the investigated range, with a slope of 7.0×10^{-2} and an intercept (8.9×10^{-3}) coincident with the rate constant measured in the absence of the amine. This indicates that the observed rate law was actually a composite of two terms (eq 18, which for $[Py] \gg [Br_3^-]$ reduces to eq 19), corresponding to the two steps 16 and 17 of Scheme IV, the second of which contains the concentration of the attacking nucleophile, as expected for a mechanism involving a rate- and product-determining nucleophilic attack. On the basis of the preequilibrium approximation for the concentration of the intermediate 10 of Scheme IV, process 16 is expected to be independent of the bromide concentration. The very modest retarding effect by a tenfold excess of added TBAB in run 21 relative to run 14 of Table III is probably due to a small negative salt effect in a process involving a transition state less polar than the initial state. A similar negative salt effect had

been previously observed for supposed reactions of Br_3^- with styrene, a process exhibiting a rather low ρ value.¹³ On the other hand, the rate of process 17 can be anticipated, on the basis of the above approximation, to be inversely dependent on bromide concentration. Both the overall rate and the amount of product 3 are therefore expected to decrease significantly when external TBAB is added to the TBAT-pyridine reactant. The comparison of the kinetic and product data obtained in runs 22 and 19 shows that both these expectations are fulfilled, giving further support for the mechanism depicted in Scheme IV. As far as the solvent effect on the reaction rate of TBAT is concerned, the distribution of negative charge between two bromine atoms on passing from the ground state 10 to the transition state, involving the synchronous formation of the Br-C(3) bond and breaking of the Br-Br bond, could account for the about fourfold decrease in rate on going from CH_2Cl_2 to the slightly more polar 1,2-dichloroethane. Thus, the basic difference between the reactions of complexed bromine, as $PyBr_2$ or Br_3^- , and that of free bromine in low-polarity aprotic solvents appears to be that, whereas the latter proceeds through a cationic intermediate formed in a rate determining electrophilic step, the former involves rate- and product-determining nucleophilic attacks on CTCs, with little charge development in the transition states. This difference explains the opposite product distributions found in the two types of reactions of 1,3-butadiene, while the substantial similarity in the reaction mechanisms of the $PyBr_2$ CTC and of the Br_3^- ion account for the preferential formation of 1,2-addition products with both these reagents.

Although the reactions carried out on a preparative scale could not be subjected to a kinetic investigation, the similarity of the product ratios obtained with molecular bromine on the one hand and with TBAT on the other, with respect to those found in the kinetic runs, confirms that one single mechanism is involved in each of these reactions at both high and low concentrations. The situation is different in the case of the $PyBr_2$ reactant, for which the higher the concentration the lower is the dissociation to free bromine and pyridine, and this affects the competition between these two electrophilic species. Furthermore, whereas a considerable excess of pyridine is needed to have most of the total bromine present as $PyBr_2$ at the low concentrations of the kinetic runs of Table I and II, which favor the formation of salt 3 at the expense of the dibromo derivatives, an equimolecular amount of the amine is sufficient at the 0.1 M concentrations used in the preparative reactions of Table IV, where the ratio of free bromine and pyridine to $PyBr_2$ is about 0.2. Under the latter conditions, direct attack by the $PyBr_2$ CTC is therefore expected to give a more important contribution to the formation of the 1,2-dibromo adduct through the mechanism shown in steps 11 and 13 of Scheme III than in the kinetic runs of Tables I and II, where bromination by free bromine or formation of salt 3 are, respectively, predominant at low or high pyridine to bromine ratios. In fact, only modest yields of 3 were found in preparative runs 25 and 27 of Table IV, while the 1,2-dibromo adduct 1 was the main product, in spite of the fact that at most one-third and one-fourth, respectively, of total dibromides could be formed by the Br_3^- reaction, and the 1,4-dibromide was the main product of the addition of free bromine. This is again strong, although indirect, evidence for dibromide formation by the $PyBr_2$ reactant, as originally proposed for the reactions of the cyclohexene derivatives.¹ The close similarity of the dibromide ratios obtained in runs 26 and 28 of Table IV is instead a consequence of the fact that

(27) According to Heasley and co-workers⁶ an Ad_2C_2 type mechanism of the type we propose for the $PyBr_2$ and Br_3^- reactions should imply, when isoprene is the substrate, a preferential attack on the less hindered 3,4-bond. The fact that this was not observed experimentally was taken as evidence against our proposal. We do not agree with this opinion, since, as pointed out by Dewar, nucleophilic attack on a π complex should be quite insensitive to steric hindrance around the double bond [M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 101, 783 (1979)].

in both cases dibromides were entirely formed by the Br_3^- reactant, preformed in run 28 and generated in situ in run 26, as shown by the similar yields of 3 and of dibromo adducts obtained in the latter.

Experimental Section

General Methods. Melting points were determined on a Kofler block and are uncorrected. UV spectra were measured with Zeiss PMQ II and Perkin-Elmer 575 spectrophotometers. IR spectra were taken with a Perkin-Elmer 257 instrument. ^1H and ^{13}C NMR spectra were recorded on a Varian CFT 20 spectrometer in D_2O solutions with sodium 3-(trimethylsilyl)propanesulfonate as internal standard. Kinetic measurements were performed with a Durrum stopped-flow kinetics spectrophotometer equipped with a 2-cm observation cell and coupled to a Tektronix 5103 storage oscilloscope. Temperature control ($\pm 0.05^\circ\text{C}$) was achieved by the use of a Lauda MK 70 constant-temperature circulating bath. GLC analyses were carried out with a Carlo Erba Fractovap instrument equipped with a 1.5-m glass column (2.5-mm i.d.) packed with 3% neopentylglycolyl succinate on silanized Chromosorb W (80–100 mesh). MgSO_4 was always used as the drying agent. Evaporations were made in vacuo (rotating evaporator) at 15°C .

Materials. Commercial 1,3-butadiene (Fluka, >98%) was used without further purification. Pyridine was dried by being refluxed over potassium hydroxide followed by fractionation. 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 (C. Erba RPE, >99.5%) was treated before use as previously described.⁷ Dichloromethane (Hoechst, >99.5%) was refluxed over P_2O_5 and fractionated through a Vigreux column, a fraction with bp 42°C being collected and used the same day. The solid pyridine–bromine CTC was prepared as previously reported.¹ Commercial tetra-*n*-butylammonium bromide (TBAB) was recrystallized from ethyl acetate and from benzene and was transformed into the tribromide (TBAT) by the reported procedure.²⁸

Spectrophotometric Measurements. The UV spectra were taken from 1,2-dichloroethane and dichloromethane solutions at 25°C . The molar absorptivities of bromine and of the PyBr_2 CTC in 1,2-dichloroethane had been determined previously.⁷ Those of bromine in dichloromethane were obtained from solutions prepared by a 1:100 dilution with this solvent of a 1,2-dichloroethane solution of bromine of exactly known concentration.⁷ Since bromine solutions in dichloromethane, unlike 1,2-dichloroethane solutions, were rather unstable, with their absorbances tending to decrease with time, their UV spectra as well as the kinetic runs were recorded shortly after preparation.

The limiting value of the formation constant of tribromide ion in 4 was obtained as follows. Equal volumes of 4×10^{-4} M solutions of bromine and of bromide 3 in 1,2-dichloroethane were mixed and the UV spectra recorded in the 220–420-nm range [$\lambda_{\text{max}} = 272$ nm ($\epsilon_{\text{max}} 4.3 \times 10^4$)].²⁹ The solution was then progressively diluted up to 2×10^{-5} M and the spectra were recorded. In the 300–360-nm range, in which the absorbances of all solutions could be compared, the Lambert–Beer law was rigorously followed, showing that no appreciable dissociation of the tribromide ion occurred on dilution.

Kinetic Measurements. All kinetic measurements were carried out by the technique described in a previous paper.⁷ Solutions of bromine were prepared shortly before use (those in dichloromethane were obtained as described under Spectrophotometric Measurements), and the concentrations were determined spectrophotometrically at 410 nm (in 1,2-dichloroethane $\epsilon = 211$; in dichloromethane $\epsilon = 194$) and adjusted to twice the desired initial concentration for the kinetic run. Solutions of the PyBr_2 CTC were prepared immediately before the kinetic runs by mixing bromine and pyridine solutions of the appropriate concentrations. All solutions containing brominating species were protected from

external light. Solutions of 1,3-butadiene were prepared by slowly bubbling the gas through a capillary tube into a weighed amount of solvent in a volumetric flask. In order to avoid solvent evaporation during the bubbling, the solvent was kept at -30°C , and the solution was then allowed to stabilize at room temperature and was finally weighed. The diene concentration was always in a very large excess over that of initial total brominating reagents, so that the reactions of molecular Br_2 were followed under pseudo-second-order and those of Br_3^- under pseudo-first-order conditions.

The reactions of molecular bromine were monitored at its absorption maximum (410 nm) and recorded for at least 5 half-lives. A zero infinity absorbance was found in all cases. The third-order rate constants were obtained by a linear least-squares analysis of the integrated form of the third-order rate expression for the bromination under pseudo-second-order conditions.⁷ This equation was fitted very well (correlation coefficients > 0.999) from the start up to at least 80% reaction.

The reactions with bromine in the presence of pyridine were monitored at 350 nm, where the absorption of free bromine was negligibly small, by following the changes in the absorbance of PyBr_2 , tribromide 4, and bromide 3. A finite absorbance was always found at infinite time. The second-order rate constant for the disappearance of tribromide 4 formed as an intermediate (descending part of the absorbance/time curves of Figure 2) was obtained by a linear least-squares analysis of the integrated form of the second-order rate equation for the bromination under pseudo-first-order conditions.⁷ Curves of the type shown in Figure 2 fitted this equation very well after attainment of the maximum up to more than 90% reaction. The amounts of salt 3 formed in each run were determined from the absorbances at infinite time by using the molar absorptivities of 3 at 350 nm: in 1,2-dichloroethane, $\epsilon = 415$; in dichloromethane, $\epsilon = 191$.

The third-order rate constant for the fast reaction of free bromine at a low pyridine/bromine ratio (run 5 of Table I) was obtained by recording the oscilloscope trace with a 2-s/division time scale and a 0.05 absorbance units/division absorbance scale for the first 20 s. The oscilloscope trace was then rapidly photographed, the stored scope output erased, and recording continued with a 5-s/division time scale and a 0.02 absorbance units/division absorbance scale. The oscilloscope trace was photographed again at infinite time. The slope and intercept of the integrated rate equation for the bromination under pseudo-first-order conditions were calculated by a least-squares analysis of the absorbance/time data obtained with the slower time scale and amplified absorbance scale and were used to correct the absorbances of the faster reaction, obtained with the expanded time scale, for the absorbance due to tribromide 4.⁷ The corrected absorbance/time data fitted the integrated form of the third-order rate expression for the bromination under pseudo-second-order conditions (correlation coefficients > 0.999) very satisfactorily up to 20 s.

The reactions with TBAT were monitored at 350 nm. In the runs carried out in the presence of pyridine or/and TBAB, the base and/or salt were added to the solution of TBAT at concentrations twice those desired in the kinetic runs. All reactions fitted the integrated form of the second-order rate expression for the bromination under pseudo-first-order conditions very satisfactorily (correlation coefficients > 0.999) from the start up to at least 90% reaction. The amount of salt 3 obtained in each run of Table III was determined from the absorbances at infinite time.

Product Analyses. Equal volumes (10 mL) of the solutions of the diene and of the brominating reagent used in the kinetic runs were rapidly mixed at 25°C and allowed to react for a time equal to that needed to complete the reaction in the corresponding kinetic run. The reactions with bromine in the presence of pyridine were also monitored by UV in the 330–350-nm range. When the decrease in absorbance ceased, the solutions were washed with 10% aqueous HCl and water, dried (MgSO_4), and concentrated under reduced pressure at 15°C . The concentrations of salt 3 deduced from the final absorbances closely agreed with the data obtained from the corresponding kinetic runs. The reaction mixtures obtained with TBAT were washed with water, dried, and concentrated. Those obtained with molecular bromine were directly concentrated. All resulting mixtures of dibromo derivatives were then subjected to GLC analysis under conditions

(28) R. E. Buckles, A. I. Popov, W. F. Zelezny, and R. J. Smith, *J. Am. Chem. Soc.*, **73**, 4525 (1951).

(29) Values of $\lambda_{\text{max}} = 273$ nm and $\epsilon_{\text{max}} = 4.0 \times 10^4$ have been reported for TBAT in 1,2-dichloroethane [R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 5048 (1953)].

avoiding isomerization: low isotherm 65 °C for 4 min; high isotherm 110 °C; temperature increment 5 °C/min; evaporator and detector 160 °C; nitrogen flow 30 mL/min. The relative retention times of 2 and 1 were 2.9:1. The dibromo derivatives were stable under the GLC conditions, and no changes in product composition were observed after repeated workup. Moreover, control experiments carried out with both dibromo derivatives 1 and 2 showed that at the highest concentration of dibromides obtained in the kinetic runs the presence of a 100-fold excess of pyridine caused only a negligible UV absorption in the 300–350-nm range within the time required to complete the kinetic runs, showing that no appreciable reaction of dibromides 1 and 2 with pyridine to give pyridinium bromides 3 or 6 occurred during these runs. No tetrabromo derivatives were formed under all bromination conditions employed. The product distributions obtained in the kinetic runs are reported in Tables I–III.

Preparative Brominations. With Molecular Bromine. Equal volumes (50 mL) of solutions of bromine and 1,3-butadiene of appropriate concentrations (Table IV) in 1,2-dichloroethane or dichloromethane were rapidly mixed at 20 °C. After 20 min, the resulting solutions were evaporated, and the residues, consisting of the dibromo derivatives 1 and 2, were weighed and subjected to GLC. The yields of dibromides and the 1/2 ratios are reported in Table IV.

With PyBr₂. (A) In 1,2-Dichloroethane. Equal volumes (50 mL) of solutions of diene and of PyBr₂ (prepared from the solid CTC and in some cases containing added pyridine) of appropriate concentrations (Table IV) were rapidly mixed and allowed to react at 20 °C. After about 10 min a white crystalline product started precipitating. Within 30 min the completely colorless solution was filtered off, and the precipitate, consisting of *N*-(4-bromo-1-buten-3-yl)pyridinium bromide (3), was collected and weighed. After crystallization from methanol–acetone, 3 had the following: mp 142–143 °C; ¹H NMR (D₂O) δ 4.12, 4.16 (2 d, *J* = 8.5 and 5.0 Hz, 2 diastereotopic H, CH₂Br), 5.51–5.82 (overlapping m, 3 H, =CH₂ and >CH–N⁺), 6.08–6.51 (m, 1 H, CH=), 8.17, 8.67, 9.00 (3 m, 5 H, C₅H₅N⁺); ¹³C NMR (D₂O) δ 34.95, 75.91, 126.47, 131.14, 133.24, 146.07, 149.64. In an off-resonance-irradiation experiment the signal at δ 34.95 became a triplet (CH₂Br) and that at 75.91 a doublet (>CH–N⁺).

Anal. Calcd for C₉H₁₁Br₂N: C, 36.89; H, 3.78; N, 4.78. Found: C, 37.00; H, 3.58; N, 4.95.

Small samples of the mother liquors were subjected to spectrophotometric measurements in the 330–360-nm range in order to calculate the amount of dissolved 3. At the same time the mother liquors were washed with 10% aqueous HCl and water, dried, and evaporated, and the residues, consisting of the dibromo

derivatives 1 and 2, were weighed and subjected to GLC. The yields of 1–3 and the 1/2 ratios are reported in Table IV.

(B) In CH₂Cl₂. The reaction was carried out at the concentrations reported in Table IV as described in section A, but no precipitation was observed within 30 min.³⁰ The concentration of the dissolved bromide 3 was then determined from the absorbances in the 320–360-nm range, the reaction mixture worked up as reported above, and the residue analyzed by GLC. The yields of 1–3 as well as the dibromide ratio are reported in Table IV.

With TBAT. Solutions of the diene and of preformed TBAT in 1,2-dichloroethane of concentrations reported in Table IV were mixed and allowed to react at 20 °C, until complete discoloration, then washed with water, dried, and evaporated. The residue was weighed and subjected to GLC. The yields of 1 and 2 and their ratio are shown in Table IV.

Reactions of Dibromides 1 and 2 with Pyridine. A. Equal volumes (15 mL) of a 0.04 M solution of the 1,4-dibromide 2 and of a 0.1 M solution of pyridine in 1,2-dichloroethane were mixed and stirred at room temperature. A white crystalline product began precipitating within 40 min. After the mixture was stirred for 24 h, the precipitate, consisting of the 1,4-dipyridinium adduct 6, was collected (0.74 g). After crystallization from methanol–acetone, the product, containing two molecules of crystallization water, had the following: mp 195–197 °C; ¹H NMR (D₂O) δ 5.38 (unresolved m, 4 H, 2 CH₂–N⁺), 6.32 (unresolved m, 2 H, 2 CH=), 8.13, 8.60, 8.90 (3 m, 10 H, 2 C₅H₅N⁺).

Anal. Calcd for C₁₄H₁₆Br₂N₂·2H₂O: C, 41.19; H, 4.95; N, 6.86. Found: C, 41.40; H, 4.77; N, 6.92.

B. When the reaction of the 1,2-dibromo adduct 1 with pyridine was carried out as described in method A, only a very small amount of 6 (~0.01 g), identified by the IR spectrum, was obtained after 3 h. A further slight precipitate of 6 (~0.01 g) was collected after 24 h, and only comparably small amounts of this salt were formed after longer reaction times.

Acknowledgment. This work was financed in part by a NATO grant and in part by a grant from the Consiglio Nazionale delle Ricerche. We thank Dr. Ferretti for the GLC analyses.

Registry No. 1, 10463-48-6; (E)-2, 821-06-7; 3, 76665-61-7; 4, 76665-64-0; (E)-6, 76665-62-8; 1,3-butadiene, 106-99-0; tetrabutylammonium tribromide, 38932-80-8; Br₂, 7726-95-6; PyBr₂, 6081-86-3.

(30) No precipitation of 3 occurred even after a long time at low temperature.

Kinetics and Mechanism of the Oxidation of Primary Alcohols by *N*-Bromoacetamide in Acid Medium

Jogeshwar Mukherjee and Kalyan K. Banerji*

Department of Chemistry, University of Jodhpur, Jodhpur-342001, India

Received November 28, 1980

The kinetics of the oxidation of ten primary alcohols by *N*-bromoacetamide (NBA) has been studied in acid medium. The main product of the oxidation is the corresponding aldehyde. The reaction is first order in alcohol, NBA, and H⁺. The oxidation of ethanol-1,1-*d*₂ indicates no primary kinetic isotope effect. A solvent isotope effect, $k(\text{D}_2\text{O})/k(\text{H}_2\text{O}) = 1.16$, was observed at 308 K. The rates were determined at four different temperatures and the activation parameters were evaluated. Addition of acetamide decreases the rate. (H₂OBr)⁺ has been postulated as the oxidizing species. A mechanism involving formation of a hypobromite ester in the rate-determining step has been proposed. The reaction constant, ρ^* , has a value of –1.53 at 303 K.

NBA has been used in preparative organic chemistry as an oxidizing and halogenating reagent.¹ There seems to be no report in the literature about its mode of oxidation. However, its analogues, *N*-bromosuccinimide (NBS) and

N-chlorosuccinimide, have received substantial attention and several studies on the mechanism of their reaction have been reported in recent years.^{2,3} The different

(1) R. Filler, *Chem. Rev.*, **63**, 21 (1963).

(2) N. Venkatasubramanian and V. Thiagarajan, *Tetrahedron Lett.* 3349 (1967); *Can. J. Chem.*, **47**, 694 (1969); *Indian J. Chem.*, **8**, 809 (1970).