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Kinetics and Mechanism of the Reaction of Cyclohexene with Bromine in the Presence of Pyridine: Competition between Different Electrophiles

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Abstract: The kinetics of the title reaction was investigated in 1,2-dichloroethane by the stopped-flow technique. Both free bromine and the pyridine–bromine charge-transfer complex (py·Br_2) act as electrophiles toward the double bond, a third electrophile, the tribromide ion, being formed during the course of the reaction through incorporation of pyridine to give *N*-(*trans*-2-bromocyclohexyl)pyridinium bromide, which captures bromine to yield the corresponding tribromide; this remains as the only electrophile in the later stages of the reaction when all excess bromine and py·Br_2 have been used up. The Br_3^- ion has a formation constant higher than 10^7 M^{-1} in dichloroethane. The reaction of free bromine with cyclohexene is second order in the halogen ($k = 2.39 \times 10^5$ M^{-2} s^{-1} at 25 °C); those of py·Br_2 and of the above tribromide are first order in the halogenating species (k = 12.8 and 1.2 M^{-1} s^{-1} at 25 °C). py·Br_2 produces mostly the pyridinium salt, Br_3^- *trans*-1,2-dibromocyclohexane. On the basis of the results, a mechanistic scheme is proposed, which assumes that the reaction with bromine involves a bromonium intermediate and those with py·Br_2 and with Br_3^- involve a nucleophilic attack on an alkene–bromine charge-transfer complex. The present data may explain why different product compositions have been observed in reactions of cyclohexenes and conjugated dienes involving bromine, on one hand, and py·Br_2 or Br_3^-, on the other.

The pyridine–halogen charge-transfer complexes (CTC) and the tribromides of organic bases are stable and easily handled solids that can be used with advantage in place of the corresponding free halogens, but they often yield different products. For instance, the pyridine–bromine CTC (py·Br_2) and pyridinium tribromide (pyHBr_3) react with conjugated dienes to give much higher ratios of 1,2 to 1,4 and of anti to syn dibromides than free bromine.[2] In additions to substituted cyclohexenes py·Br_2, py·BrCl, and pyHBr_3 produce larger amounts of diaxial adducts than the free halogens.[3] A similar, more pronounced trend toward diaxial products is observed in additions involving *N*-bromoamides as the sources of electrophilic halogen, and there is substantial, even if indirect, evidence pointing to an Ad-EC_2 type mechanism,[4] in which the nucleophilic step is rate determining, for the latter, and, by analogy, for the former reactions.[5] With the aim of getting an explanation for the observed, preparatively interesting differences in reactivity between free and complexed halogens, we undertook a kinetic investigation of the reactions of pyridine–halogen complexes and alkenes.

Results

The py·Br_2 CTC and cyclohexene were chosen as simple reagents, 1,2-dichloroethane was chosen as an aprotic nonnucleophilic solvent with a moderate dielectric constant (ϵ = 10.36),[6] and the reaction rates were followed in a stopped-flow apparatus at 25 °C. The reaction of cyclohexene with bromine in the absence of pyridine was first order in olefin and second order in halogen throughout the investigated range of initial bromine concentrations ((0.5–2.2) × 10^{-3} M), in agreement with eq 1 and with recent

$$-d[Br_2]/dt = k_3[Br_2]^2[\text{c-Hx}] \qquad (1)$$

$$\text{c-Hx} = \text{cyclohexene}$$

results on bromine additions to acyclic alkenes in aprotic solvents.[7] The third-order rate constants were very good within each run and fairly well reproducible from run to run; they did not exhibit the large random fluctuations[8] or dependence on bromine concentration[9] that had previously been reported for brominations in aprotic solvents (Table I).

Table I. Third-Order Rate Constants for the Reaction of Cyclohexene with Bromine in 1,2-Dichloroethane at 25 °C[a]

run	$10^3[Br_2]$, M	[c-Hx]/[Br_2]	$10^{-5}k_3$,[b] M^{-2} s^{-1}
1	0.47	30	2.20 ± 0.02
2	0.87	61	2.50 ± 0.02
3	1.10	41	2.30 ± 0.03
4	2.25	21	2.55 ± 0.01
			av 2.39 ± 0.16

[a] The disappearance of Br_2 was monitored at 402–405 nm.
[b] Errors of the individual rate constants are given as standard deviations estimated from the deviations of experimental points from the best-fit third-order straight line. The error of the average rate constant is given as standard deviation from the average.

The influence of the presence of increasing amounts of pyridine was then investigated. Figure 1 reproduces the oscilloscope tracings for a series of runs in which the initial concentrations of bromine and cyclohexene were kept constant and that of pyridine increased; recordings were made at 402–405 nm near the extinction maximum for bromine. The dashed line (time scale expanded 100-fold) corresponds to the third-order reaction with

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(1) (a) Istituto di Chimica Organica. (b) Laboratorio di Chimica Quantistica ed Energetica Molecolare.

(2) (a) V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.*, **40**, 1358 (1975); (b) G. E. Heasley, J. Mc Call Bundy, V. L. Heasley, S. Arnold, A. Gipe, D. Mc Kee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *ibid.*, **43**, 2793 (1978).

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Table II. Rate Constants for the Reaction of Cyclohexene with Bromine in the Presence of Pyridine in 1,2-Dichloroethane at 25 °C.

run	$10^3[Br_2]$, M	$[py]/[Br_2]$	$[c\text{-}Hx]/[Br_2]$	λ,[a] nm	$10^{-5}k_3$,[b] $M^{-2}\ s^{-1}$	k_2,[b] $M^{-1}\ s^{-1}$
5	2.21	0.80	21	402	2.20 ± 0.01	1.17 ± 0.01
6	1.10	0.84	41	402	2.40 ± 0.02	1.14 ± 0.01
7	2.22	2.50	22	402	2.20 ± 0.01	1.27 ± 0.02
8	2.22	4.40	22	402		1.22 ± 0.01
9	2.22	9.00	22	402		1.25 ± 0.01
10	2.22	20.40	22	402		1.27 ± 0.02
11	0.49	48.50	100	420		1.26 ± 0.01
12	4.34	57.00	36	405		1.25 ± 0.01
13	4.34	57.00	36	485		1.25 ± 0.02
						av 1.23 ± 0.05

[a] Wavelength at which the reaction was monitored. [b] 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. The errors of the average rate constants are given as standard deviations from the average.

Table III. Second-Order Rate Constants for the Reaction of Cyclohexene with Bromine in the Presence of Pyridine in 1,2-Dichloroethane at 25 °C

run	$10^3[Br_2]$, M	$[py]/[Br_2]$	$[c\text{-}Hx]/[Br_2]$	$10^3[Br_2]_{free}$, M	λ,[a] nm	k_2,[b] $M^{-1}\ s^{-1}$	% of 1
14	1.10	2.4	44.4	0.68	333	1.17 ± 0.01	7
15	1.40	2.9	38.9	0.73	333	1.00 ± 0.02	10
16	1.40	3.1	17.8	0.70	333	1.10 ± 0.01	10
17	0.57	4.0	57.6	0.36	333	1.02 ± 0.03	10
18	0.58	4.0	54.5	0.37	333	1.18 ± 0.02	11
19	0.57	11.5	57.6	0.21	333	1.00 ± 0.01	22
20	0.58	12.0	54.5	0.21	333	1.13 ± 0.02	20
21	0.58	18.2	54.5	0.15	333	1.12 ± 0.01	24
22	0.57	51.6	57.6	0.064	333	1.10 ± 0.03	45
23	0.57	107.3	57.6	0.032	333	1.13 ± 0.01	52
24	0.49	10.2	100.6	0.21	350	1.11 ± 0.01	21
25	0.49	51.2	100.6	0.063	350	1.14 ± 0.01	46
26	0.49	102.4	100.6	0.034	350	1.18 ± 0.01	53
						av 1.12 ± 0.10	

[a] Wavelength at which the reaction was monitored. [b] See note *b* in Table II.

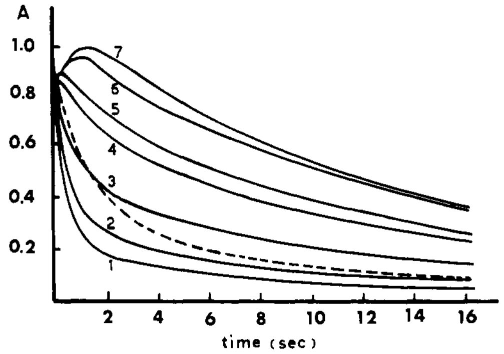

Figure 1. Plots of absorbance at 405 nm (2-cm optical path) vs. time for the reaction of 5.0×10^{-2} M cyclohexene with 2.3×10^{-3} M bromine in the presence of pyridine in 1,2-dichloroethane at 25 °C: 10^3[py] (- - -) 0 (time scale × 10^2); (1) 2.3; (2) 4.1; (3) 8.8; (4) 17.0; (5) 26.0; (6) 45.0; (7) 100.0 M.

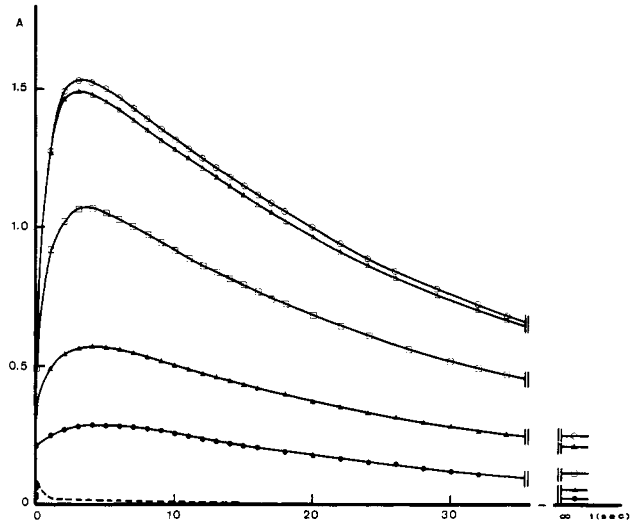

Figure 2. Plots of absorbance at 333 nm (2-cm optical path) vs. time for the reaction of 3.3×10^{-2} M cyclohexene with 5.7×10^{-4} M bromine in the presence of pyridine in 1,2-dichloroethane at 25 °C: 10^3[py] (- - -) 0; (●) 1.3; (▲) 2.3; (□) 6.6; (△) 29.4; (○) 61.0 M.

bromine in the absence of pyridine. At low pyridine/bromine ratios one can observe an initial fast reaction followed by a much slower one. With increasing pyridine/bromine ratios the shapes of the curves gradually change and a maximum indicates the formation of an intermediate. Table II summarizes the kinetic data obtained by using a wide range of reagent concentrations. An analysis of the curves recorded at the lower pyridine/bromine ratios showed that the initial fast decrease in absorbance simply corresponded to the addition of free bromine: calculations on an expansion of the rapidly descending initial part gave a third-order rate constant that was the same as that found for the reaction in the absence of pyridine (runs 5–7). Since the association constant for py·Br_2 is relatively small (K = 273 M^{-1} in dichloroethane),[10] a large amount of free bromine exists at equilibrium at the low concentrations used for the kinetic runs, when only a small excess of pyridine is present; free bromine is the main attacking species at the beginning of the reaction. When the amount of pyridine increases, that of free bromine decreases and the first part of the curves is no longer analyzable in a simple way. However the descending parts of the curves all follow pseudo-first-order kinetics with a rate constant k_2 of 1.23 $M^{-1}\ s^{-1}$ that is independent of the pyridine concentration.

The formation of an intermediate during the reaction was more evident at 333 nm (Figure 2), where the extinction coefficients of bromine and pyridine are practically zero, whereas py·Br_2 is near to one of its maxima. The reaction with free bromine is barely

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(10) J. D'Hondt, C. Dorval, and Th. Zeegers-Huyskens, *J. Chim. Phys. Phys.-Chim. Biol.*, **69**, 516 (1972).

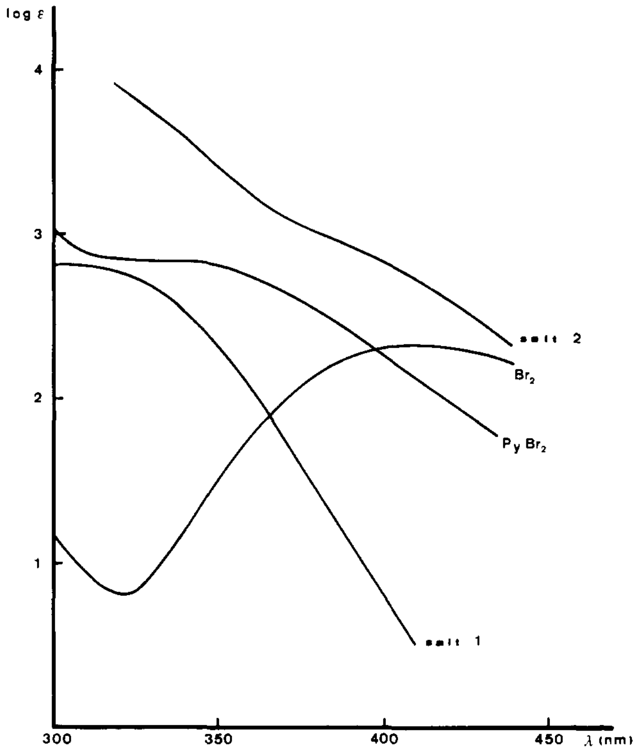
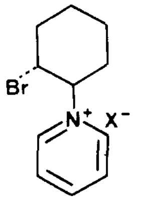


Figure 3. UV spectra of the four species involved in the bromination of cyclohexene in the presence of pyridine in 1,2-dichloroethane.

observable (dashed line) since the bromine–olefin charge-transfer complex[11] has only a very small extinction coefficient at this wavelength. The maximum in the curve can therefore be observed also at low pyridine/bromine ratios. Table III summarizes the data obtained at 333 and 350 nm. Again the descending parts of the curves correspond to pseudo-first-order kinetics that are independent of the pyridine concentrations, and the average values of k_2 differ little from those found at 402 nm.

It was also found that a UV-absorbing species, remaining at the end of the addition reactions in amounts that increased (but leveled off around 50%) with increasing pyridine concentrations, was *N*-(*trans*-2-bromocyclohexyl)pyridinium bromide (**1**).[12]

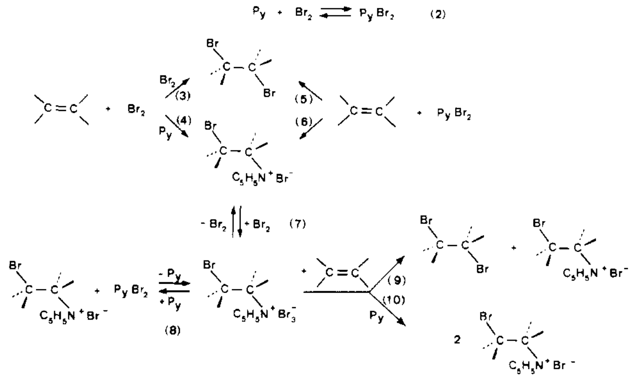


1 : X = Br

2 : X = Br_3

Although the pyridinium chromophore does not absorb above 300 nm, salt **1** has an absorption band extending up to almost 400 nm (Figure 3), which is probably due to the formation of a charge-transfer complex between Br^- and the pyridinium group, similar to those previously proposed for pyridinium iodides.[13] Salt **1** gives with bromine the corresponding tribromide salt **2** with a strong hyperchromic and bathochromic shift (Figure 3), and this explains the appearance of a maximum in the reaction curves: salt **1** is formed during the reaction of bromine or py·Br_2 with cyclohexene in the presence of pyridine and immediately captures a molecule of bromine to give salt **2**, having a much higher extinction coefficient than either bromine or py·Br_2 on the whole wavelength range above 300 nm, and this produces the reaction curves of Figure 2 that are typical of series reactions.

Scheme I



The formation constant of the Br_3^- ion is much higher in aprotic solvents than in protic ones (reported values, $K_{Br_3^-}$ = 16 M^{-1} in H_2O,[14] 177 M^{-1} in MeOH,[15] 92 M^{-1} in AcOH[16]). The reported value of $K_{Br_3^-}$ for tetrabutylammonium tribromide (TBAT) in dichloroethane is about 10^6 M^{-1}.[17] Values of the formation constant of Br_3^- can depend to some extent on the counterion.[16] Although it was not possible to determine the value of *K* for the salt **2** very accurately, it certainly is greater than 10^6, because its solutions in dichloroethane followed the Beer–Lambert law down to a concentration of 1.83×10^{-5} M. If one assumes a maximum error of 5% in the spectrophotometric measurement at the lowest concentration, which is that 5% dissociation of the salt may go undetected, this would correspond to 2×10^7 M^{-1} as the lower limit for the formation constant; the actual value should be even higher since the error in the reading may be well below 5%.

The fact that the computations on the descending parts of the reaction curves all fitted very well with pseudo-first-order kinetics, the k_2 values being independent of the concentration of pyridine, can be explained by assuming that these parts of the curves are due to the disappearance of Br_3^- after all excess free bromine and py·Br_2 have been used up in the much faster reactions with the olefin and with Br^-. The stability constant of Br_3^- being some 10^5 times higher than that of py·Br_2, the tribromide ion is practically the only electrophile present during the later stages of the reaction. The kinetic analysis of the initial part of the reactions is however much less straightforward, since three different potential electrophiles are present, Br_2, py·Br_2, and Br_3^-. Scheme I illustrates the difficulties involved in this analysis. Besides the equilibria 2, 7, and 8, one may have to cope with reactions 3, 5, and 9, producing dibromide, and reactions 4, 6, and 10, giving the salt **1**. Furthermore, the bromide arising from reactions 9 and 10 is recycled to tribromide **2** as long as there are free Br_2 and py·Br_2 available. We therefore did not try a complete and general kinetic analysis, valid for any concentration of pyridine. However, for high pyridine/Br_2 ratios, when at the start of the reaction most of the total bromine is present as py·Br_2, some simplifying assumptions can be made that allow to reproduce the kinetic behavior in a very satisfactory way. The fact that under these conditions the final amount of adduct **1** is very near to 50% can be interpreted by assuming that the reaction of py·Br_2 with the olefin gives almost entirely the salt **1** by reaction 6, whereas that of the tribromide salt **2** leads almost exclusively to the dibromide through reaction 9. If one further assumes that the conversion of Br^- into Br_3^- is much faster than reactions 6 and 9 and that reaction 6 is first order in py·Br_2 and faster than reactions 9 and 10 (so that recycling of **1** to **2** during the early stages of the reaction can be neglected),

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[12] F. N. Hayes, H. K. Suzuki, and D. E. Peterson, *J. Am. Chem. Soc.*, **73**, 4524 (1950).

[13] E. M. Kosower, J. A. Skorcz, W. M. Schwarz, and J. W. Patton, *J. Am. Chem. Soc.*, **82**, 2188 (1960).

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[15] J. E. Dubois and H. Herzog, *Bull. Soc. Chim. Fr.*, 57 (1963).

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

[17] R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 5048 (1953).

Table IV. Second-Order Rate Constants for the Reaction of Cyclohexene with Bromine at High Pyridine/Bromine Ratios in 1,2-Dichloroethane at 25 °C[a]

run	$10^4[Br_2]$, M	$[py]/[Br_2]$	$[c\text{-}Hx]/[Br_2]$	$10^4[PyBr_2]$, M	k_1,[b] $M^{-1}\ s^{-1}$	k_2,[b] $M^{-1}\ s^{-1}$	% of **1**
25	4.92	51.2	100.6	4.29	12.05 ± 0.01	1.14 ± 0.01	46
26	4.92	102.4	100.6	4.59	13.50 ± 0.02	1.18 ± 0.01	53
27	4.84	203.0	106.0			1.35 ± 0.01	57
28	5.09	301.0	101.0			1.57 ± 0.01	63
29	4.84	415.0	106.0			1.64 ± 0.02	64

[a] Reactions monitored at 350 nm. [b] See note *b* in Table II.

Table V. Second-Order Rate Constants for the Reaction of Cyclohexene with **2** and with TBAT in the Presence of Pyridine and TBAB in 1,2-Dichloroethane at 25 °C[a]

run	$10^4[\mathbf{2}]$, M	10^4[TBAT], M	$[py]/[Br_3^-]$	[TBAB]/[TBAT]	$[c\text{-}Hx]/[Br_3^-]$	k_2,[b] $M^{-1}\ s^{-1}$	% of **1**[c]
30	2.38		0		209.0	0.97 ± 0.01	0
31	2.38		102.0		213.4	1.10 ± 0.03	13
32	2.38		212.6		198.3	1.16 ± 0.02	21
33	2.38		636.5		210.0	1.38 ± 0.01	43
34		2.16	0		230.5	0.76 ± 0.01	0
35		2.16	113.4		230.5	0.82 ± 0.05	10
36		2.16	238.4		230.5	0.86 ± 0.01	15
37		2.16	1204.0		230.5	1.09 ± 0.03	55
38		2.47	0	4.7	201.6	0.60 ± 0.01	0
39		2.47	198.4	4.7	194.3	0.60 ± 0.02	0

[a] Reactions monitored at 350 nm. [b] See note *b* in Table II. [c] In runs 30–33, these values correspond to the excess of **1** with respect to the amount deriving from the reagent **2**.

the system of Scheme I could be simplified to the two series first-order reactions 11 and 12, the kinetic analysis of which can

$$c\text{-}Hx + 2py\cdot Br_2 \xrightarrow{k_1} \mathbf{2} + py \qquad (11)$$

$$c\text{-}Hx + \mathbf{2} \xrightarrow{k_2} \mathbf{1} + \text{dibromide} \qquad (12)$$

be carried out easily (see the Experimental Section for details). When the data for runs 25 and 26 (Table IV), in which the pyridine/bromine ratios were 51 and 102, were thus analyzed, it was possible to perfectly reproduce the experimental curves (Figure 4). The average values of k_1 and k_2 that give the best fitting were respectively 12.8 and 1.16 $M^{-1}\ s^{-1}$.

The above simplified treatment gives poor results when applied to reactions conducted with lower pyridine/bromine ratios, because in the presence of larger initial concentrations of free bromine the competition from the other reactions of Scheme I becomes important. It also fails with much higher concentrations of pyridine (run 27–29, Table IV); the descending parts of the curves still give good pseudo-first-order kinetics, but the values of k_2 increase with increasing pyridine concentrations. More than 50% of the salt **1** is obtained in these cases. The initial parts of the reaction curves are not reproducible by the simplified treatment, and this is at least in part due to a deviation from equilibrium 2. In fact, whereas the UV spectra of solutions in which the pyridine/bromine ratios range from 0 to 100 exhibit an isosbestic point at 398 nm, at much higher ratios the absorption curves no longer exhibit the shoulder around 350 nm shown in Figure 3 for the $py\cdot Br_2$ species and do not pass through the isosbestic point, the absorbances over the entire 300–400-nm range becoming higher than expected on the mere basis of equilibrium 2. This deviation may be due to the modification in the solvent properties by the substantial amount of pyridine and/or to the formation of other species such as $(py)_2Br^+Br_3^-$.[18]

The hypothesis that salt **2** is the actual brominating species was confirmed by reacting it with cyclohexene; clean pseudo-first-order kinetics was observed up to 90% conversion, with a k_2 that was similar to that obtained in the bromine–pyridine reactions (Table V). TBAT behaved similarly, but the rate constant was about 25% lower, thus indicating some influence of the structure of the counterion on the electrophilic properties of the tribromide ion.

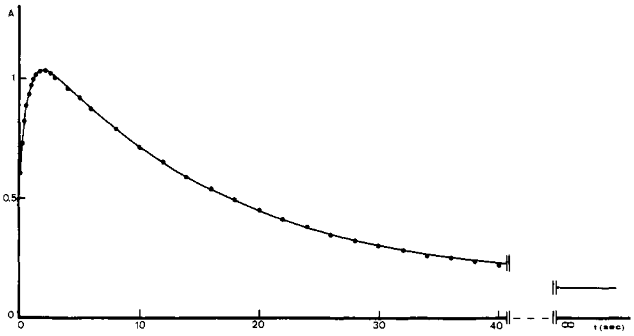

Figure 4. Experimental (–) and calculated (···) plot of absorbance at 350 nm (2-cm optical path) vs. time for the reaction of 4.92 × 10^{-4} M bromine with 4.95 × 10^{-2} M cyclohexene in the presence of 5.04 × 10^{-2} M pyridine in 1,2-dichloroethane at 25 °C (run 26 of Table III).

With both of the latter reagents *trans*-1,2-dibromocyclohexane was the only addition product, and also in the presence of moderate amounts of pyridine and only at very high pyridine/tribromide ratios some of the salt **1** was formed. An increase in the value of k_2 was also observed in these cases at these very high pyridine concentrations. The presence of an excess of tetrabutylammonium bromide (TBAB) in the reactions with TBAT caused a small decrease in the reaction rate (run 38) and completely prevented the formation of the salt **1**, even when the initial ratio of pyridine to tribromide was about 200 (run 39); in this case such a high excess of the base had no influence on the reaction rate.

Discussion

The data presented in the previous section fit well into the pattern illustrated in Scheme I and provide reasonable proof that most, if not all, of the reactions included in this scheme participate to the overall course of the reaction of cyclohexene with bromine in the presence of pyridine in chloroalkane solutions. Bromide ions are formed during this reaction, acting as very efficient scavengers for free bromine and also subtracting it from $py\cdot Br_2$, since equilibrium 8 is strongly displaced in favor of the Br_3^- species, because of its very high formation constant. This species therefore becomes the only electrophile when Br_2 and $py\cdot Br_2$ are no longer present.

The hypothesis that Br_3^- may act as a primary electrophile, awkward as it may appear that an anion could play such a role, was first proposed by Bartlett and Tarbell.[19] Although kinetics

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[18] S. G. Ginn, I. Haque, and J. L. Wood, *Spectrochim. Acta, Part A*, **24A**, 1531 (1968).

cannot easily distinguish between a direct electrophilic attack by Br_3^- on the double bond and a Br^--assisted attack by Br_2, kinetic salt effects provide some evidence for the existence of both mechanisms,[20] the former one dominating for reactive and the latter one for unreactive alkenes. Further indirect proof came from the finding that supposed reactions of Br_3^- exhibited significantly lower ρ values[16] and different amounts of solvent incorporation[21] with respect to additions of Br_2. The formation of identical[22] or different intermediates[14,16,23] in the reactions of alkenes with Br_2 or Br_3^- have been alternatively formulated but with no really consistent proof in favor of either mechanism. Most of these studies were conducted in protic solvents (H_2O, MeOH, AcOH) under conditions that were not favorable for studying the behavior of the Br_3^- ion, which is highly dissociated because of its low formation constant in these solvents (4 to 5 orders of magnitude smaller than in dichloroethane), therefore requiring high concentrations of Br^- in order to reach significant concentrations, with consequent complications from salt effects. There are however some kinetic data on the reactions of TBAT with the stilbenes and with crotonic acid in $(CH_2Cl)_2$ that were found to be first order in trihalide.[8,17]

Our assumption that the reaction of cyclohexene with bromine in the presence of pyridine gives mostly, if not exclusively, the salt **1** and the reaction with Br_3^- mostly the dibromide is in accordance with the view first expressed by Kanyaev[24] for brominations of alkenes in water: that solvent incorporation to give bromohydrins takes place exclusively in the reaction with bromine and the formation of dibromides only in that with Br_3^-. It is also well-known that the incorporation of solvent in the products of bromination is depressed by an increase in bromide concentration under conditions favoring the formation of tribromide ion.[21,23]

An important point for the interpretation of our data is whether $py\cdot Br_2$ is an independent electrophile or simply serves as a source of free bromine. The data obtained at low pyridine/Br_2 ratios (runs 5–7, Table II) show that when much free bromine is present this is the main brominating agent during the early stages of the reaction. However, at higher pyridine concentrations the initial fast reaction becomes first order in the brominating species (runs 25, 26, Table IV). This does not by itself prove that a species different from Br_2 is involved in the electrophilic attack, since at the very low concentration of free halogen ($(3-6) \times 10^{-5}$ M) that is present at the start of these runs, the reaction could well become first order in Br_2, as observed in protic solvents.[25] However, the independence of k_1 of the pyridine concentration definitely points to $py\cdot Br_2$ as an independent electrophile for the following reasons. If Br_2 were the only electrophile, the rate would be expressed by eq 13. Since the reaction is followed by measuring the concentration of $py\cdot Br_2$, and the concentration of free pyridine, present in high excess with respect to bromine, remains essentially constant during the kinetic run, we convert eq 13 into eq 14. On the other hand, if $py\cdot Br_2$ were the sole brominating species, one would have the rate expression 15, equivalent to eq 16.

$$-\mathrm{d}[\mathrm{Br_2}]_\mathrm{T}/\mathrm{d}t = 2k_1'[\mathrm{Br_2}] \qquad (13)$$

$$k_1' = k_1[\text{c-Hx}]$$

$$[\mathrm{Br_2}]_\mathrm{T} = [\mathrm{Br_2}] + [\mathrm{py\cdot Br_2}] = [\mathrm{py\cdot Br_2}]\,\frac{1 + K[\mathrm{py}]}{K[\mathrm{py}]}$$

$$K = \frac{[\mathrm{py\cdot Br_2}]}{[\mathrm{py}][\mathrm{Br_2}]} = 273\ \mathrm{M^{-1}}$$

$$-\frac{1 + K[\mathrm{py}]}{K[\mathrm{py}]}\,\mathrm{d}[\mathrm{py\cdot Br_2}]/\mathrm{d}t = 2k_1'\frac{[\mathrm{py\cdot Br_2}]}{K[\mathrm{py}]}$$

$$-\mathrm{d}[\mathrm{py\cdot Br_2}]/\mathrm{d}t = \frac{2k_1'}{1 + K[\mathrm{py}]}[\mathrm{py\cdot Br_2}] = k_1'{}_\mathrm{obsd}[\mathrm{py\cdot Br_2}] \qquad (14)$$

$$k_1'{}_\mathrm{obsd} = \frac{2k_1'}{1 + K[\mathrm{py}]} \simeq \frac{2k_1'}{K[\mathrm{py}]} \text{ at high [py]}$$

$$-\mathrm{d}[\mathrm{Br_2}]_\mathrm{T}/\mathrm{d}t = 2k_1'[\mathrm{py\cdot Br_2}] \qquad (15)$$

$$-\mathrm{d}[\mathrm{PyBr_2}]/\mathrm{d}t = 2\ k_1'\frac{K[\mathrm{py}]}{1 + K[\mathrm{py}]}[\mathrm{py\cdot Br_2}] = k_1''{}_\mathrm{obsd}[\mathrm{py\cdot Br_2}] \qquad (16)$$

$$k_1''{}_\mathrm{obsd} = 2k_1'\,\frac{K[\mathrm{py}]}{1 + K[\mathrm{py}]} \simeq 2k_1' \text{ at high [py]}$$

At high pyridine concentration the observed rate constant should therefore be inversely proportional to [py] if the first hypothesis were true, but almost independent of it if the second one were true. The fact that it actually changes only little on doubling [py] (runs 25, 26, Table IV) provides strong support for a mechanism in which $py\cdot Br_2$ is a primary electrophile in competition with free bromine.

From what has been said above one can conclude that in the system olefin/pyridine/bromine there are three species competing in the attack on the double bond: free bromine that reacts with a rate that is second order in the halogen, $py\cdot Br_2$ and the intimate ion pair **2** that undergo reactions that are first order in the halogenating species.

In order to rationalize the results obtained in the reactions of alkenes with these three brominating agents, one must consider that because of the relatively high heterolytic Br–Br dissociation energy some assistance is needed in breaking this bond, particularly in aprotic media of low solvating power. When bromine alone is available, this may be achieved by the intervention of a second molecule of bromine that provides assistance through the formation of the very stable Br_3^- ion as shown in reactions 17 of Scheme II. The initially formed CTC is thus converted into a covalent species, either an epibromonium ion or, if sufficient electron donation is available (styrenes, stilbenes), an open carbenium ion. The intermediate is then converted into the dibromide by collapse of the ion pair or into a 1-bromo-2-Y derivative if some other competing nucleophile is present in the medium. The second-order dependence of the rate on halogen and the low stereoselectivity and high solvent incorporation observed with aryl-substituted alkenes are in full agreement with this scheme involving a charged intermediate, that is by now widely accepted.[26]

When $py\cdot Br_2$ is the electrophile, the first-order dependence on this reagent implies a different mechanism, which we believe is the one sketched in reactions 18. The first step is an equilibrium between $py\cdot Br_2$ and the alkene/Br_2 complexes, which are somewhat similar CTC's. The driving force for the Br–Br bond breaking is provided by the intramolecular transfer of the pyridine from bromine to carbon in a reaction in which the positive charge being developed on nitrogen is continually compensated by the negative charge being developed on bromine; little, if any, charge develops on carbon during this process. Attack by external pyridine may compete when present in excess.

A similar situation can be visualized for the reaction with an ammonium tribromide as shown by reactions 19. In this case the transfer of the nucleophile is achieved by the ammonium/bromide ion pair that has become detached from Br_2 at the moment of the formation of the olefin/Br_2 CTC. We therefore propose that the main difference between the addition of free bromine and the reactions with $py\cdot Br_2$ or Br_3^-, at least in aprotic solvents of medium or low dielectric constant, is in the fact that in the latter reactions no epibromonium or carbenium ions are formed, the rate-determining step being one involving the alkene–bromine CTC and a nucleophile being transferred to carbon in a cage of solvent. Although no complete proof for this hypothesis can be deduced

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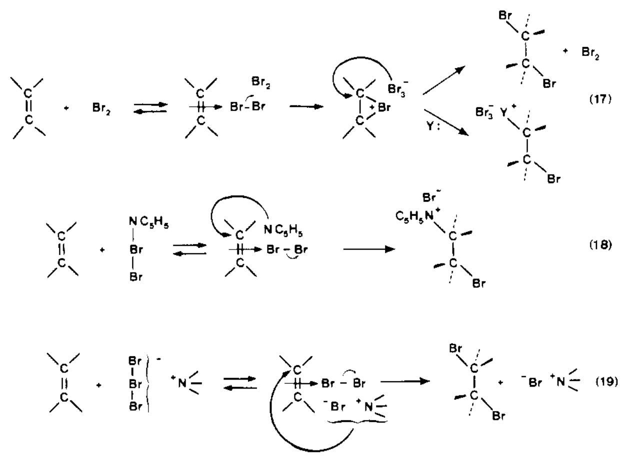
Scheme II



from the available data or easily obtained from kinetic measurements, the fact that under the conditions of the present kinetic study salt **1** is the main product of the reaction with py·Br_2 and the dibromide is the only product of the reaction with Br_3^- (except in the presence of very high excesses of pyridine) and that both reactions are first order in the brominating species, are much more antistereoselective than the corresponding additions of free bromine when arylalkenes are the substrates,[21,22,27] and give many more 1,2 adducts than molecular bromine when applied to conjugated dienes[2] can be considered as strong evidence in its favor.

Whereas these mechanistic schemes fit well with the experimental results for reactions conducted at pyridine/Br_2 ratios up to about 100, at higher pyridine concentrations some deviations are observed, and particularly an increase in the values of k_2 with increasing pyridine concentration, accompanied by some nucleophilic attack by pyridine in the reactions with Br_3^- (runs 27–29, 31–33, 35–37). It is not surprising that in the presence of such high excesses of pyridine attack by this external nucleophile (reaction 10) may become competitive with internal transfer of Br^-, even if bromide is reported to be a somewhat better nucleophile than pyridine.[28] Furthermore, although equilibrium 8 (or the analogous one with the Bu_4N^+ ion) are highly displaced to the right ($K = 3.7 \times 10^4$ if $K_{Br_3^-}$ is 10^7), at very high pyridine concentrations enough py·Br_2 is present (about 12% at the beginning of run 33, Table V) to compete with Br_3^- as the electrophilic agent, giving rise to the salt **1**. Since both reactions are first order in the brominating species, the observed rate constant is the sum of two terms, one relative to reaction 9 and the other one to reaction 6 having a higher rate and a contribution that becomes greater the higher the concentration of pyridine. In favor of this interpretation is the fact that in the presence of a fivefold excess of TBAB over TBAT only a slight decrease in rate is observed (run 38) and that under these conditions the presence of a 200-fold excess of pyridine does not affect the reaction rate nor lead to the formation of the salt **1** (run 39). The presence of an excess of bromide ion drastically reduces the amount of py·Br_2 at equilibrium; on the basis of eq 8, whereas at the start of run 36 there is about 8% py·Br_2, this should decrease to 0.1% at the start of run 39. The small decrease in rate when large amounts of Br^- are present supports the hypothesis that Br_3^- is a direct electrophile, rather than a source of molecular bromine, since in the latter case the electrophilic step would be expected to be the slow one and the common ion effect should therefore reduce the rate of addition much more than observed. A small negative salt effect on the rate of reaction of Br_3^- with styrenes in acetic acid has been observed before and tentatively attributed to a transition state being less polar than the initial state.[16]

Conclusions

The results presented in this paper throw some light on the previous observations[3] that different product distributions are obtained when pyridine–halogen complexes are used instead of free halogens in the additions to certain olefins. Since three distinct electrophiles, reacting with different mechanisms and possibly giving different products from appropriate olefins, are formed shortly after mixing solutions of the halogen, pyridine, and olefin, the nature and distribution of the bromination products (syn–anti adducts from conjugated substrates, diaxial–diequatorial adducts from substituted cyclohexenes, etc.) should depend on the relative rates of reaction of the different halogenating species with the specific olefin. Because equilibria of type 2, 7, and 8 of Scheme I are involved and different reaction orders are required by the different electrophiles, the competition will also depend on the values of the respective equilibrium constants and of the initial concentrations of reactants, high pyridine and low halogen concentrations favoring the reaction of the CTC to give salts of type **2** and hence halogenation through a trihalide ion.

The present data can also account, at least in part, for the literature reports on strong differences observed in the products distributions of the bromination of conjugated dienes with free bromine and with py·Br_2 or tribromide salts in dichloromethane.[2] Preliminary experiments have shown that substantial amounts of quaternary pyridinium bromides are formed in the reaction of butadiene with bromine in the presence of an excess of pyridine; they probably went undetected before because the reaction mixtures were washed with aqueous HCl before product analysis.[2] This explains both the low yields of dibromides and the similarity of the products compositions obtained under these conditions with the py·Br_2 CTC and with tribromide salts. This aspect is currently under investigation.

Experimental Section

Materials. Commercial cyclohexene was purified by fractionation shortly before the kinetic runs. Pyridine was dried by refluxing over potassium hydroxide followed by fractionation. 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 washed with concentrated sulfuric acid until the acid remained colorless and then with water, saturated aqueous sodium hydrogen carbonate, and water and fractionated through a Vigreux column collecting a fraction with bp 83.5 °C.

N-(*trans*-2-Bromocyclohexyl)pyridinium bromide (**1**) was prepared as reported[12] and crystallized from acetone–methanol: mp 180 °C (lit.[12] 170–172 °C). Tribromide **2** was obtained by adding dropwise the stoichiometric amount of neat bromine to a stirred solution of **1** in chloroform, followed by dilution with petroleum ether; the orange precipitate was crystallized from acetic acid: mp 97–99 °C. Anal. Calcd for $C_{11}H_{15}NBr_4$: C, 27.48; H, 3.14; N, 2.91; Br, 66.47. Found: C, 27.78; H, 2.93; N, 2.64; Br, 66.50.

Commercial tetra-*n*-butylammonium bromide (TBAB) was crystallized from ethyl acetate and from benzene and was transformed into the corresponding tribromide (TBAT), mp 73 °C (from acetic acid), by the reported procedure[29] (lit.[29] mp 70–72 °C).

Spectrophotometric Measurements. The UV spectra were taken from 1,2-dichloroethane solutions at 25 °C with a Zeiss PMQ II and a Perkin Elmer Model 575 spectrophotometer. The molar absorptivities of bromine were obtained from solutions whose concentrations had been determined as follows: 1 mL of the bromine solution in 1,2-dichloroethane was added to 10 mL of twice-distilled water and 1.5 mL of 1 N aqueous NaOH. The stirred mixture was treated with a few drops of 36% hydrogen peroxyde, then acidified to pH ~3 with aqueous $HClO_4$, and finally diluted with 20 mL of ethanol. A few drops of 1% ethanolic solution of diphenylcarbazone were added, and the bromide ion was titrated with 0.01 N aqueous $Hg(ClO_4)_2$[30] in comparison with a blank experiment.

The molar absorptivities of the py·Br_2 CTC were obtained from the absorbances of freshly prepared solutions containing pyridine and bromine in various ratios (up to 50), using the equilibrium concentrations of the CTC and free bromine calculated from the known value of the formation constant of py·Br_2 ($K = 273$ M^{-1} in 1,2-dichloroethane)[10] and

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[30] W. Schöniger, *Mikrochim. Acta*, 123 (1955); 869 (1956).

the absorptivities of free bromine. Pyridine did not absorb at the wavelengths used.

The limiting value of the formation constant of tribromide ion in *N*-(*trans*-2-bromocyclohexyl)pyridinium tribromide was obtained from the absorbances of solutions of decreasing concentrations prepared by dilution of a freshly prepared 3.66×10^{-4} M stock solution of **2** down to 1.83×10^{-5} M.

Solutions of bromine, of py·Br_2, and of the tribromides were stable for several hours, as shown by the constancy of their absorbances.

Kinetic Measurements. The kinetic measurements were carried out by using a Durrum stopped-flow kinetic spectrophotometer having a mixing time of about 2 ms, equipped with a 2-cm observation cell, and coupled to a Tektronix 5103 storage oscilloscope. Temperature control (±0.05 °C) was achieved by the use of a Lauda MK 70 constant-temperature circulating bath. The instrument was allowed to stabilize and the system equilibrated thermally for about 3 h before each kinetic run. The vertical (absorbance) axis of the oscilloscope was calibrated before each run; the horizontal (time) axis was also periodically calibrated. The time constant setting was always ≤0.1 of the time/division setting on the horizontal scope axis. The absorbance–time data were obtained from a photograph of the oscilloscope trace.

Bromine solutions were prepared shortly before use and the concentrations determined spectrophotometrically at 409 nm ($\epsilon = 211$) and adjusted to twice the desired initial concentration in the kinetic run. Solutions of the py·Br_2 CTC were prepared immediately before the kinetic runs by mixing bromine and pyridine solutions of the appropriate concentrations. The olefin concentration was always at least in 20-fold excess over that of initial total brominating reagents, so that the reactions of free bromine were followed under pseudo-second-order and those of py·Br_2 and tribromides under pseudo-first-order conditions.

The reactions with bromine in the absence of pyridine were monitored by observing the decrease in absorbance of the free halogen at 402–405 nm near its absorption maximum and were recorded for at least 5 half-lives. An infinity trace was recorded after at least 10 half-lives. The third-order rate constants were obtained by a linear least-squares analysis of eq 20 where A_0, A, and A_∞ are the absorbances of bromine respectively

$$\frac{1}{A - A_\infty} = \frac{k_3[\text{c-Hx}]}{2\epsilon_{Br_2}}t + \frac{1}{A_0 - A_\infty} \qquad (20)$$

at the start, at time t, and at infinity time, [c-Hx] is the actual olefin concentration, which remained practically constant during the kinetic run, ϵ_{Br_2} is the molar absorptivity of bromine at the wavelength used for the measurements, and 2 cm is the optical path length. All reactions of free bromine fitted eq 20 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 333, 350, 402, 405, 420, and 485 nm. At the first two wavelengths only the changes in absorbances of py·Br_2, tribromide **2**, and bromide **1** were observed in practice, the molar absorptivities of free bromine being negligibly small ($\epsilon_{333} = 10$, $\epsilon_{350} = 33$) with respect to the other species involved. At higher wavelengths the absorbance changes of all three brominating species, but not of bromide **1**, were followed. The second-order rate constants for the disappearance of tribromide **2** formed as an intermediate in the py·Br_2 reactions (runs 5–26 of Tables II and III and runs 27–29 of Table IV) were obtained by a least-squares analysis of eq 21. Curves of the type shown in Figures 1 and 2 fitted eq 21 very well

$$\ln (A - A_\infty) = -k_2[\text{c-Hx}]t + \ln (A_0 - A_\infty) \qquad (21)$$

(correlation coefficients >0.999) after the maximum (or the inflection in the case of reactions at low pyridine/bromine ratios monitored above 400 nm when a maximum was not observed) up to more than 95% reaction. The amount of salt **1** formed in each run (Tables III and IV) was obtained from the absorbance at infinity time, using the molar absorptivity of **1** at the wavelength at which the reaction was monitored.

The third-order rate constants for the fast reaction of free bromine at low pyridine/bromine ratios (runs 5–7 of Table II) were obtained from a couple of consecutive runs carried out under identical conditions but recorded respectively with a 50 ms/division time scale and a 5 s/division time scale and amplified absorbance scale. The slope and intercept of eq 21 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 salt **2**. The correct absorbance–time data were then used to fit eq 20. Very good fittings (correlation coefficients >0.999) were obtained up to at least 300 msec.

The runs carried out with pyridine/bromine ratios of about 50 and 100 (runs 25 and 26 of Table IV) and monitored at 350 nm were analyzed as the series first-order reactions shown in eq 11 and 12. The differential equations are eq 22–24. Integration of eq 22–24 for the initial conditions

$$\mathrm{d}[\text{py·Br}_2]/\mathrm{d}t = -2k_1[\text{py·Br}_2][\text{c-Hx}] \qquad (22)$$

$$\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k_1\,[\text{py·Br}_2][\text{c-Hx}] - k_2\,[\mathbf{2}][\text{c-Hx}] \qquad (23)$$

$$\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_2\,[\mathbf{2}][\text{c-Hx}] \qquad (24)$$

$[\text{py·Br}_2]_0 = [\text{py·Br}_2]_{\text{eq}\,0}$, $[\mathbf{2}]_0 = 0$, and $[\mathbf{1}]_0 = 0$ gives eq 25–27, which,

$$[\text{py·Br}_2] = [\text{py·Br}_2]_{\text{eq}\,0}e^{-2k_1[\text{c-Hx}]t} \qquad (25)$$

$$[\mathbf{2}] = \frac{k_1[\text{py·Br}_2]_{\text{eq}\,0}}{k_2 - 2k_1}\left(e^{-2k_1[\text{c-Hx}]t} - e^{-k_2[\text{c-Hx}]t}\right) \qquad (26)$$

$$[\mathbf{1}] = \frac{[\text{py·Br}_2]_{\text{eq}\,0} - [\text{py·Br}_2] - 2[\mathbf{2}]}{2} = \frac{[\text{py·Br}_2]_{\text{eq}\,0}}{2}\left[1 + \frac{1}{2k_1 - k_2}\left(k_2e^{-2k_1[\text{c-Hx}]t} - 2k_1e^{-k_2[\text{c-Hx}]t}\right)\right] \qquad (27)$$

multiplied by the molar absorptivities of the respective species and summed up, because all three species contribute to the observed absorbances, give eq 28. In order to avoid errors due to small deviations in the

$$A(t) = [\text{py·Br}_2]_{\text{eq}\,0}\left\{\epsilon_{\text{py·Br}_2}e^{-2k_1[\text{c-Hx}]t} + \epsilon_2\frac{k_1}{k_2 - 2k_1}\left(e^{-2k_1[\text{c-Hx}]t} - e^{-k_2[\text{c-Hx}]t}\right) + \frac{\epsilon_1}{2}\left[1 + \frac{1}{2k_1 - k_2}\left(k_2\,e^{-2k_1[\text{c-Hx}]t} - 2k_1e^{-k_2[\text{c-Hx}]t}\right)\right]\right\} \qquad (28)$$

calibration of the monochromator of the stopped-flow spectrophotometer all molar absorptivities used for calculations were determined with this instrument at the wavelength used in the kinetic runs. The following values $\epsilon_{\text{py·Br}_2} = 660$, $\epsilon_2 = 2480$, $\epsilon_1 = 230$ were assumed as constant, exactly known quantities, together with $[\text{py·Br}_2]_{\text{eq}\,0}$ and [c-Hx]; k_1 and k_2 were instead treated as fitting parameters. The fitting of eq 28 was carried out on an IBM 370/168 computer with the use of a BASIC program, implementing a standard (normal equations) method[31] for the solution of nonlinear least-squares problems. The program was "general purpose" in the sense that only the few (typically one or two) statements defining the fitting model had to be changed in order to adapt it to different problems and has also been run on laboratory minicomputers.

The reactions with preformed *N*-(*trans*-2-bromocyclohexyl)pyridinium tribromide (**2**) and with TBAT were monitored at 350 nm under pseudo-first-order conditions. In the runs carried out in the presence of pyridine or/and TBAB, the base or/and salt was added to the solution of **2** or TBAT. Concentrations were always twice the desired values in the kinetic runs. All reactions fitted eq 21 very satisfactorily (correlation coefficients >0.999) from the start up to at least 90% reaction. The amount of adduct **1** formed in the reactions was evaluated from the absorbance at infinity time and corrected for that arising from the starting tribromide when **2** was used as the brominating reagent.

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