nitrobenzoate was obtained by addition of the salt to a phosphate buffer (pH 7), followed by extraction with ether. Removal of the ether followed by recrystallization (ethanol–water) gave the ester: mp 68–70 °C; NMR δ 8.28 (2 H, d, $J = 9$ Hz), 8.08 (2 H, d, $J = 9$ Hz), 2.5 (1 H, br s), 1.64 (6 H, s), 1.28 (6 H, s). Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.62; H, 6.29; N, 5.08. Pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O was obtained by addition of 82% $H_2{}^{18}O$ to an acetonitrile solution of the salt. The ester analyzed as 74% ^{18}O, the difference probably arising from adventitious moisture present during the preparation. This was then added to a pH 7 buffer and the ester obtained by ether extraction as described above. *tert*-Butyl *p*-nitrobenzoate was obtained from *p*-nitrobenzoyl chloride and *tert*-butyl alcohol.

Kinetics and Spectra. A Cary 2390 spectrophotometer was used for conventional UV studies and a Durrum-Gibson spectrometer for stopped-flow studies. The 310-nm curve in Figure 2 was obtained by mixing on the stopped-flow apparatus a stock aqueous solution of pinacol mono-*p*-nitrobenzoate (2.2×10^{-4} M) with sodium hydroxide solutions of ionic strength 2.0. The absorbance reading at 50–100 ms was recorded as the "initial" absorbance. The 260-nm curve was obtained by the conventional UV with use of a 1-cm cuvette separated into two compartments but open at the top to allow mixing. A stock aqueous solution (1 mL) of pinacol mono-*p*-nitrobenzoate was placed in one side and the NaOH solution (1 mL) in the other. After temperature equilibration these were mixed. Absorbance readings commenced after about 10 s had elapsed and were continued for about 1 min. These were extrapolated to the time of mixing to give the "initial" absorbance. Hydrolysis kinetics for pinacol mono-*p*-nitrobenzoate and for *tert*-butyl *p*-nitrobenzoate were studied by using the increase (or decrease) in absorbance at 310 nm. Plots of ln ($A_t - A_\infty$) vs. time were excellently linear, with their slopes equal to the first-order rate constant. The decomposition of the hemiortho ester 2-(*p*-nitrophenyl)-2-hydroxy-1,3-dioxolane was studied as previously described for the phenyl compound,[12] by addition of a small amount of an acetonitrile solution of the dioxolan-2-ylium to aqueous acids and buffers. The change in absorbance at 290 nm was monitored. Oxygen exchange in pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O was followed as previously described.[12] In brief, the labeled ester (0.39) was added to 2 L of acid solution (0.1, 0.01, 0.001 M) and the solution thermostated at 25.0 °C. After the appropriate time, samples were withdrawn and the ester removed by extraction (no hydrolysis occurs during the time required for exchange). Four to five points were obtained for each kinetic run covering up to 2 half-lives of the exchange. Mass spectral analysis was conducted by using the ratio 269/267 corresponding to the ^{18}O and ^{16}O parent ions of the ester.

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Registry No. POH (Ar = 4-nitrophenyl), 90269-18-4; TO^- (Ar = 4-nitrophenyl), 90269-19-5; TOH (Ar = 4-nitrophenyl), 90269-20-8; 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, 16837-06-2; triphenylcarbenium tetrafluoroborate, 341-02-6; 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium tetrafluoroborate, 90365-40-5; pinacol mono-*p*-nitrobenzoate-*carbonyl*-^{18}O, 90269-21-9.

The Question of Reversible Formation of Bromonium Ions during the Course of Electrophilic Bromination of Olefins. 1. Formal Transfer of Br^+ to Scavenger Olefins from the Solvolytically Generated Bromonium Ions of Cyclohexene and Cyclopentene

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Abstract: *trans*-2-Bromo-1-[((4-bromophenyl)sulfonyl)oxy]cyclohexane and -cyclopentane (**1** and **2**), when solvolyzed at 75 °C in glacial acetic acid containing Br^- and a scavenger olefin (cyclopentene for **1** and cyclohexene for **2**) generate free molecular Br_2 as is evidenced by the formation of crossed products. **1** is more prone to yield crossed product than is **2**. In the absence of added Br^-, the amount of crossed product formed in the solvolysis is small. The results are interpreted in terms of competitive Br^- capture of the intermediate bromonium ions produced during the course of solvolysis at Br^+ and carbon, the latter event leading to trans dibromide products of the starting material, while the former event generates Br_2 and olefin. The results of these experiments, when applied to electrophilic Br_2 addition to alkenes, strongly suggest that the intermediate bromonium ions are formed reversibly. Furthermore, evidence is presented which indicates that the bromonium ion of cyclohexene reverses to a greater extent than does the bromonium ion of cyclopentene. The demonstration of such reversibility of formation of bromonium ions from simple alkenes introduces a rather severe complication into the analysis of kinetic structure–reactivity data. These observations might be invoked to explain at least part of the 6–25-fold increase in reactivity in electrophilic addition of Br_2 exhibited by cyclopentene over cyclohexene.

I. Introduction

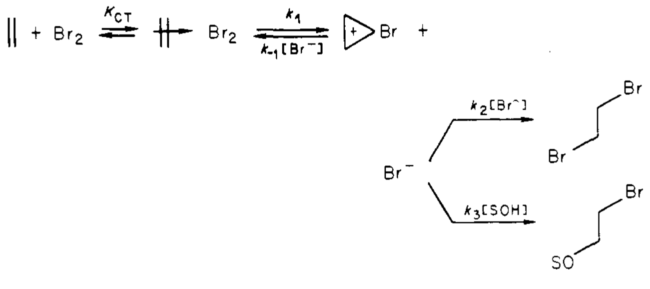
The electrophilic bromination of olefins has been extensively studied and is undoubtedly the most commonly presented example of a reaction typical of unsaturated systems.[1] Indeed every textbook of organic chemistry devotes considerable space to discussion of this ostensibly simple process.

The rates of Br_2 addition to typical olefins are described by a general equation (eq 1)[1] containing a variety of kinetic terms

$$-d[Br_2]/dt = [\text{olefin}](k_1[Br_2] + k_2[Br_2]^2 + k_{Br_3^-}[Br_2][Br^-]) \quad (1)$$

depending upon the presence of Br^- and concentration of Br_2.

Scheme I



Robertson and co-workers[2] first established the importance of the second-order term (k_2) at high [Br_2]. In solvents of reduced

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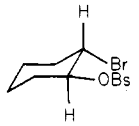
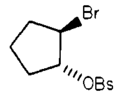
polarity such as $CHCl_3$ or chlorobenzene, the second-order term dominates.[3] However, in more polar solvents such as alcohols or acetic acid and at $[Br_2] < 10^{-3}$ M, the dominant process is first order in molecular bromine.[2d] Finally, in the presence of Br^-, an additional equilibrium ($Br_2 + Br^- \rightleftarrows Br_3^-$) is established[4] that provides a competing pathway in which Br_3^-[5] (or its kinetic equivalent[6,7]) adds to the olefin. The great bulk of kinetic study[2-6] has been undertaken under conditions where only the first and/or third terms in eq 1 are important.

For simple olefins, it is generally accepted that bromination proceeds as in Scheme I. Briefly, olefin and free Br_2 form a charge-transfer (CT) complex,[8] whose decomposition to form the cyclic bromonium ion is believed to be rate limiting.[1,2] Potentially the ion suffers three fates, two of which lead to trans addition products and a third (which is the subject of this work) that reforms the CT complex and free Br_2. Although very little is known about the existence of the reverse step,[1b] it has been considered by a few authors[9-13] to explain unusual product stereochemistry and ratios[9-10] or isomerization[11] of reisolated starting materials.[12] In an interesting example, Br_2 is regenerated from the bromonium ion of adamantylideneadamantane,[13,14] which is prevented sterically from forming 1,2-addition products. However, for simple olefins, the bromonium ion is apparently considered to be formed irreversibly[1,15] and insofar as we are aware has not been included as an important term in any detailed kinetic or structure–reactivity studies.[16] If it could be demonstrated that bromonium ions can be captured by Br^- to yield free Br_2 and the corresponding olefin, and that the extent of the capture is dependent upon the system, then existing structure–reactivity discussions would have to be reassessed.

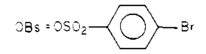
Herein we report the results of a solvolytic study of trans bromo brosylates **1** and **2** in glacial acetic acid containing Br^- and a second scavenger olefin. We believe the results clearly show that the solvolytically produced bromonium ions from **1** or **2** indeed capture Br^- to form Br_2 and furthermore do so to different extents.



1



2



II. Experimental Section

Routine NMR and IR spectra were obtained on Bruker WP-80 and Nicolet FTIR machines, respectively. Melting points were obtained using a Fisher-Johns melting point apparatus and are uncorrected.

trans-1,2-Dibromocyclohexane,[17] *trans*-2-bromocyclohexanol,[18] *trans*-1-acetoxy-2-bromocyclohexane,[18] and *trans*-1,2-dibromocyclopentane[19] were prepared and purified by literature methods. *trans*-2-Bromocyclopentanol was prepared from cyclopentene oxide[20] in 62% isolated yield by a procedure analogous to that used for *trans*-2-bromocyclohexanol,[18] bp 105–106 °C (25 torr) (lit.[21] bp 41–48 °C (1 torr)). *trans*-1-Acetoxy-2-bromocyclopentane was prepared in 84% yield according to the method used by Winstein and Buckles[18] for *trans*-1-acetoxy-2-bromocyclohexane by the reaction of *trans*-2-bromocyclopentanol with acetic anhydride: bp 102–103 °C (22 torr); ^1H NMR ($CDCl_3$) δ 1.97 (s, 3 H), 1.5–2.5 (m, 6 H), 4.25 (m, 1 H), 5.18 (m, 1 H); mass spectrum, m^+/e 166, 164, 147, 145, 85, 84, 67, 43 (base peak). *trans*-2-Bromo-1-[((4-bromophenyl)sulfonyl)oxy]cyclohexane (**1**) was prepared according to the general method of Winstein et al.[22] by the reaction of *trans*-2-bromocyclohexanol with *p*-bromobenzenesulfonyl chloride. Recrystallization of the crude product from Skelly B afforded **1** as white needles in 72% overall yield: mp 87–88 °C (lit.[22] mp 91.9–92.3 °C); ^1H NMR ($CDCl_3$) δ 1.20–2.50 (m, 8 H), 4.00 (m, 1 H), 4.60 (m, 1 H), 7.72 (m, 4 H); mass spectrum, m^+/e 400, 298, 296 (M^+), 238, 236, 221, 219, 157, 155, 81 (base peak), 80; IR (CH_2Cl_2 cast) 2930, 2850, 1580, 1470, 1450, 1390, 1370, 1190, 955, 820 cm^{-1}.

***trans*-2-Bromo-1-[((4-bromophenyl)sulfonyl)oxy]cyclopentane (2).** *trans*-2-Bromocyclopentanol (5.4 g, 0.033 mol) was reacted with *p*-bromobenzenesulfonyl chloride in pyridine according to Winstein's general procedure.[22] The crude product (9.3 g) was obtained as an oil, which solidified on standing in the refrigerator. After two recrystallizations from 30:1 pentane:CH_2Cl_2, 6.4 g (51%) of the pure brosylate **2** was obtained as small white needles: mp 49–50 °C; ^1H NMR ($CDCl_3$) δ 1.50–2.50 (m, 6 H), 4.25 (m, 1 H), 5.00 (m, 1 H), 7.70 (m, 4 H); mass spectrum, m^+/e 386, 384, 382 (M^+), 238, 236, 221, 219, 157, 155, 67 (base peak); IR (CH_2Cl_2 cast) 3080, 2960, 1580, 1470, 1435, 1370, 1190, 915, 880 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_3Br_2S$: C, 34.55; H, 3.14; S, 8.33; Br, 41.36. Found: C, 35.03; H, 3.19; S, 8.19; Br, 41.39.

Materials for Acetolysis and Bromination Experiments. Acetic acid

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(16) Dubois (ref 10a) has included a discussion of the question of reversibility in the bromination of *trans*-stilbene and concluded on the basis of his[10c] and Barteltt's[10b] previous work that it is not important for this system. There is an important mechanistic caveat to be issued with respect to reversibility since as Dubois states[10a] "For the interpretation of the structural effects, the simplified scheme" (Scheme I) "is sufficient if the rate-determining step is not reversible."

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Table I. Product Ratios from Solvolysis of **1** in Glacial HOAc under Various Conditions[a]

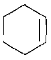
row	time, h		added[b] Br^-	product composition,[c,d] % **3**	**4**	**5**	**6**
1	23	–	–	0.4 ± 0.3	99.6 ± 0.3		
2	23	+	–	1.0 ± 0.4	97.4 ± 0.8	1.2 ± 0.1	0.4 ± 0.2
3	23	–	+	7.7 ± 0.5	92.3 ± 0.5		
4	23	+	+	2.4 ± 0.6	91.1 ± 1.0	5.2 ± 0.1	1.3 ± 0.15
5	70	–	–	<0.2	>99.8		
6	70	+	–	<0.2	98.1 ± 0.1	1.0 ± 0.1	0.8 ± 0.1
7	70	–	+	4.9 ± 0.3	95.1 ± 0.3		
8	70	+	+	3.3 ± 0.2	89.7 ± 0.3	5.6 ± 0.2	1.2 ± 0.1
9	118	–	–	<0.1	>99.9		
10	118	+	–	<0.1	97.2 ± 0.1	1.1 ± 0.1	1.6 ± 0.1
11	118	–	+	7.0 ± 0.3	93.0 ± 0.3		
12	118	+	+	6.2 ± 0.2	81.6 ± 0.4	10.9 ± 0.1	1.4 ± 0.2

[a] 2.5×10^{-4} mol of **1**, 5 mL of HOAc, 0.052 M acetic anhydride, 0.05 M KOAc, temp = 75 °C (refluxing CCl_4 vapor bath). [b] 0.3 M (when present); KBr incompletely dissolved therefore saturated solution is assumed. [c] Relative GLPC yields; **3–6** account for <90% isolated material. Averages of two or three determinations. [d] After 70 and 118 h in the presence of cyclopentene, several additional small (<10% in total) components are present. Dibromo- and bromoacetoxycyclohexane are unstable under solvolytic conditions as is evidenced by their changing proportions as a function of time. However, their decompositions are slower than that of **1**.

(Fisher) was purified according to the published procedure[23] and distilled with the middle fraction (bp 118 °C) being collected and stored in a desiccator, mp 16.6 ± 0.1 °C (lit.[23] mp 16.63 °C). KBr (Shawinigan) was used without purification. Br_2 was dried and distilled from P_2O_5 through a 20-cm Vigreux column. Cyclopentene and cyclohexene were purified as described by Hogg and Kharash.[24]

A typical acetolysis experiment was conducted as follows. Into each of four test tubes (15 × 125 mm) were placed brosylates **1** or **2** (2.5×10^{-4} mol), 5 mL of purified acetic acid, 0.025 mL of acetic anhydride (2.6×10^{-4} mol), 0.025 g (0.25×10^{-3} mol) of KOAc, and KBr (0.18 g, 1.5×10^{-3} mol) as well as 1.5×10^{-3} mol of olefin (cyclopentene in the case of **1** and cyclohexene in the case of **2**). The tubes were then sealed and immersed in the vapor of refluxing CCl_4 (75 °C). Tubes were removed at various time intervals, 2, 22, 72, and 118 h and their contents poured into 100 mL of H_2O. The aqueous solution was extracted with several portions of CH_2Cl_2 and the combined organic extracts washed with 10% Na_2CO_3 solution and then dried over anhydrous $MgSO_4$. The solvent was removed by distillation through a 60-cm Vigreux column at atmospheric pressure. The residual liquid was then immediately subjected to GLPC analysis (6 ft × 1/8 in. analytical column 10% OV-1, 80–100 mesh Chromosorb W). The GLPC analysis was carried out with a Hewlett-Packard 5830 gas chromatograph with the following conditions: flow rate 37 mL of He/min, T_1 = 110 °C for 2 min, then temperature programmed to increase by 2 °C/min. Under these conditions the retention times for *trans*-1,2-dibromocyclopentane (**5**), *trans*-1-acetoxy-2-bromocyclopentane (**6**), *trans*-1,2-dibromocyclohexane (**3**), and *trans*-1-acetoxy-2-bromocyclohexane (**4**) are 4.2, 6.5, 8.1, and 10.3 min, respectively. Although these values vary somewhat from day to day, each peak is cleanly resolved. Solvolysis control experiments for **1** and **2** were run under identical conditions but without added KBr and/or olefin. Workup and analyses in these cases were conducted as above. Control experiments to determine the efficiency of the reaction mixture extractions indicate that <2 mg of an equimolar mixture of authentic products can be removed from 25 mL of HOAc. Finally, product mixtures in representative cases were subjected to GC-mass spectral analysis, which showed that the products were identical with authentic materials.

Table II. Product Ratios from Solvolysis of **2** in Glacial HOAc under Various Conditions[a]

row	time, h		added[b] Br^-	product distribution,[c,d] % **3**	**4**	**5**	**6**
1	2	+	–			2.5 ± 0.2	97.5 ± 0.2
2	2	–	+			8.3 ± 0.1	91.7 ± 0.1
3	2	+	+	0.4 ± 0.1	0.7 ± 0.1	4.8 ± 0.1	94.0 ± 0.2
4	22	+	–			2.2 ± 0.2	97.8 ± 0.1
5	22	–	+			7.6 ± 0.3	92.4 ± 0.3
6	22	+	+	0.35 ± 0.2	0.7 ± 0.2	4.1 ± 0.2	94.7 ± 0.2
7	70	+	–	<0.1	<0.2	2.2 ± 0.1	97.5 ± 0.01
8	70	–	+			7.6 ± 0.2	92.4 ± 0.2
9	70	+	+	0.3 ± 0.1	0.4 ± 0.1	4.0 ± 0.1	95.2 ± 0.1

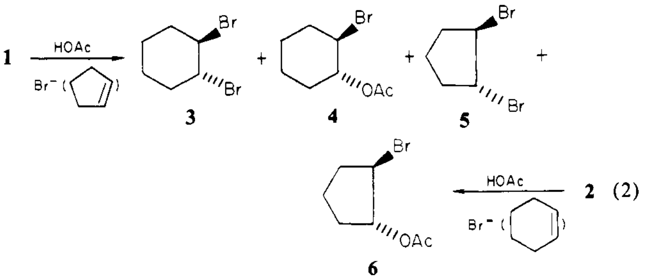
[a] Temperature 75 °C (refluxing CCl_4 vapor bath). 5.0 mL of HOAc, 0.052 M acetic anhydride, 0.05 M KOAc, 2.5×10^{-4} mol of **2**. [b] 0.3 M (when present); KBr incompletely dissolved therefore saturated solution is assumed. [c] Relative GLPC yields, products (**3–6**) account for >90% of the isolated materials. Averages of two or three determinations. [d] After 22 h, reaction mixtures darken considerably.

Bromination of Cyclopentene and Cyclohexene. So that the product distribution afforded by molecular Br_2 under conditions similar to those employed in the acetolysis experiments could be ascertained, both cyclohexene and cyclopentene were subjected to bromination under the following conditions. To 100 mL of purified HOAc was added 0.48 mL of acetic anhydride (1.04×10^{-3} mol) and 0.5 g of KOAc (5×10^{-3} mol). This was divided into two equal portions, which were placed into two separate flasks, each containing 1.8 g of KBr (1.5×10^{-2} mol). After it was stirred for ~30 min, 10 mL of solution was withdrawn from each flask and placed in an addition funnel along with 1 μL of Br_2 (1.8×10^{-5} mol). To the remaining 40 mL in the first flask was added 1.54 mL of cyclohexene (2×10^{-3} mol), and to the second flask also containing 40 mL of mixture was added 1.32 mL (2×10^{-3} mol) cyclopentene. The contents of each flask were heated to 75 °C and then to each was added the 10 mL of solution containing Br_2 at such a rate that the temperature remained constant (~15 min). Following the addition, the contents of each flask were worked up as in the case of the acetolysis experiments and analysed by GLPC.

A second set of brominations was conducted under the same conditions as above with the exception that KBr was omitted.

III. Results

(i) **Acetolysis of 1 and 2.** Bromo brosylates **1** and **2** were solvolyzed under a variety of conditions in glacial acetic acid, and the relative product ratios as determined by GLPC are presented in Tables I and II. Reported values are the average of two or three determinations. Under the experimental conditions, KBr when present is incompletely dissolved and the solutions are considered to be saturated. Acetic anhydride was added to the mixtures to remove traces of H_2O, which would complicate the product distributions, while KOAc was employed as a buffering agent to neutralize HOBs and HBr formed during solvolysis. Without added KOAc, the product mixtures were far more complicated by the presence of monobrominated and monoacetoxylated materials. Products **3–6**, eq 2, were identified as



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(23) "Techniques of Organic Chemistry", 2nd ed.; Weissberger, A., Prookauer, E. S., Riddick, J. A., Toops, E. E., Eds.; Wiley Interscience: New York, 1955; Vol. III, p 145.

(24) Hogg, D. R.; Kharash, N. *J. Am. Chem. Soc.* **1956**, *78*, 2728–2731.

Table III. Relative Product Ratios from the Bromination of Cyclohexene and Cyclopentene in Glacial Acetic Acid[a]

	added,[b] Br^-	product distribution,[c] %			
		3	**4**	**5**	**6**
cyclohexene	–	39.5 ± 0.5	60.5 ± 0.5		
	+	41.9 ± 1.5	58.1 ± 1.5		
cyclopentene	–			83.0 ± 0.4	17.0 ± 0.4
	+			79.2 ± 2.5	20.8 ± 2.5

[a] Conditions: 75 °C, 5×10^{-4} M Br_2, 25 mL of HOAc containing 2.6×10^{-4} mol of acetic anhydride, 1.25×10^{-3} M KOAc, 1×10^{-3} mol olefin. [b] 7.5×10^{-3} mol KBr added to above solution. [c] Averages of three determinations. Errors represent maximum deviations in the three runs.

having identical GC retention times (coinjected) and GC-ms patterns as authentic materials and in general comprise >90% of the isolated product mixture. The efficiency of the extraction procedure (see Experimental Section) is such that there is no selective extraction of any one component at the expense of the others.

For **1**, whose reported half-life is ~15 h under these reaction conditions,[22] the product mixture at times less than 22 h consisted of the anticipated products as well as a number of additional small peaks attributable to decomposition of reisolated **1** under the GLPC analysis conditions. However, this does not appear to introduce significant error in the measurements insofar as the ratios of **3**–**6** are concerned. It is also noteworthy that at times of 70 h and greater, small amounts of decomposition products are built up in the case of **1**. Among those that we have identified by GC-mass spectrometry are diacetoxycyclohexane and what appears to be the allylic acetate of cyclohexene. Production of these is a likely source of adventitious Br^- during the course of the solvolysis, which accounts for the formation of small amounts of dibromide products even when KBr is not specifically added to the solvolysis mixture (see Table I). As judged from the changing relative product ratios given in Tables I and II as a function of time, some of the products of acetolysis are slowly reacting so that we feel the "best" product ratios for the purposes of discussion will be those determined at the earliest possible time, e.g., 23 h for **1** and 2 h for **2**.

Acetolysis of **2** appears to proceed much more rapidly under these conditions[25] than does that of **1**, and after 2 h the reaction has quite cleanly generated mostly **5** and **6**. After prolonged heating at 75 °C, the reaction mixture darkens and GLPC analysis shows the buildup of some minor components (<5%) with retention times less than those of **3**–**6**. These appear (by GC-mass spectrometry) to be cyclopentene allylic acetate and bromide.

Two general features of the data in Table I and II are evident. First, in the absence of added Br^- the ratio of bromo acetate/dibromide products derived directly from **1** and **2** is >99:1 and 40:1, respectively, with the dibromide products being formed from adventitious Br^- being generated during the course of solvolysis. With added saturating KBr, these ratios drop to approximately 15:1 and 11:1, respectively, as is expected if external Br^- can successfully capture the intermediate ions formed to generate addition products.

Second, in the presence of both added Br^- and scavenger olefin, the amount of crossover product (cyclopentyl for **1** and cyclohexyl for **2**) is quite different for the two systems. Solvolysis of **1** is more prone to yield crossover product than is the solvolysis of **2**.

(ii) Bromination. So that the ratio of bromo acetate to dibromide products obtained from Br_2 addition to cyclohexene and cyclopentene could be gauged, the latter were subjected to treatment with 5×10^{-4} M Br_2 in HOAc at 75 °C under conditions as close as possible to those used for the acetolysis experiment. The concentration of Br_2 chosen for these experiments is such that the major kinetic terms are first order in $[Br_2]$ as they undoubtedly are during the acetolyses. The experiments were performed in the absence and presence of added 0.3 M KBr, and the results are given in Table III. Under the latter conditions, given the fact that K_{eq} for $Br_2 + Br^- \rightleftarrows Br_3^-$ is ~50–100 M^{-1},[4b,7a] the major species present is Br_3^-. The most striking aspect is the relative insensitivity of the bromo acetate/dibromide product ratio to the presence of added Br^-. One might have expected that if external Br^- were able to capture the intermediate bromonium ions, the proportion of dibromide products would markedly increase. However, this does not seem to be the case, since in our opinion the ratios determined in the presence and absence of added Br^- are experimentally the same.

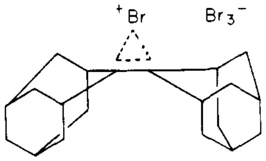
It is of note that Br_2 addition to cyclohexene affords a larger amount of bromo acetate than dibromide, in contrast to the addition of cyclopentene (Table III) and a number of other olefins.[26]

IV. Discussion

Given the complications attendant to studying electrophilic brominations of olefins in solution, it is not surprising that evidence for or against reversible formation of the bromonium ion is sparce. It has been proposed on the basis of the dependence of the global rate constant for disappearance of Br_2 as a function of $[Br^-]$ that the intermediate ion is formed irreversibly at least in the case of *trans*-stilbene.[10] However, the situation is complicated by the intervention of species generated from the additional $Br_2 + Br^- \rightleftarrows Br_3^-$ equilibrium and also by the fact that the intermediate ion produced by addition to stilbene may more closely resemble an open benzylic ion than a bromonium ion,[10a,27] particularly in polar solvents.

On the other hand, it has been reported that recovered starting material from the bromination of *cis*-stilbene is substantially isomerized.[11] This has been interpreted[28] in terms of reversible formation of an intermediate ion in which rotation about the C–C central bond can occur prior to ejection of "Br^{+}". The extent to which symmetrical bromonium ions are involved is, however, unknown, and the isomerization appears to be highly dependent upon the reaction conditions.[29]

A further example in which reversible formation of a bromonium ion might be involved is that of the ion produced during the bromination of adamantylideneadamantane. The ion is suggested to have a structure resembling **7**,[13] which is apparently prevented by steric constraints from proceeding toward products. Hence when dissolved in polar solvents this ion immediately produces free Br_2 and adamantylideneadamantane. However, it has been claimed[14] that the ion **7** is really a molecular complex. The evidence on which this claim is based, in our opinion, is far from compelling.[30] In summary, it can be concluded that there is no



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(25) We estimate that **2** solvolyzes ~10-fold faster than does **1** under these conditions.

(26) Yates et al. (Yates, K.; McDonald, R. S. *J. Org. Chem.* **1973**, *38*, 2465–2478) report that for a series of simple cis and trans alkenes, >90% of the product is the trans dibromide.

(27) (a) Dubois, J.-E.; Ruasse, M.-F. *J. Org. Chem.* **1973**, *38*, 493–499; (b) *Ibid.* **1974**, *39*, 2441–2444.

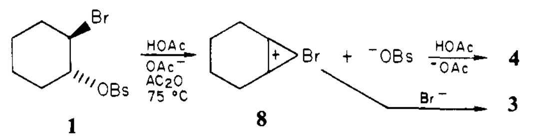
(28) Reference 1a, p 158.

(29) We have confirmed Yates' et al.[11b] kinetic parameters for the disappearance of Br_2 in bromination of both *cis*- and *trans*-stilbene in glacial acetic acid. However, at $[Br_2] = 5 \times 10^{-4}$ M (the same concentration as for the kinetic determinations), UV spectroscopic analysis of the reaction mixture without workup shows no observable conversion of *cis*- into *trans*-stilbene. Since the $[Br_2]$ used by both Buckles[11a] and Yates[11b] (in the latter case for product analysis experiments but not kinetic experiments) was substantially higher than 5×10^{-4} M, we feel that the reported isomerizations are conditional. Further experiments are under way to clarify the situation (Brown, R. S.; Slebocka-Tilk, H., unpublished results).

incontrovertible direct evidence which would suggest that a bonafide bromonium ion has available to it a reverse pathway which would regenerate olefin and molecular bromine. On the basis of indirect evidence, some authors[8,9] have invoked such reversibility to account for product stereochemistries. In other instances[1,31] such is implied without direct evidence by the presence of an arrow (sometimes dotted[1a,31a]) in the general bromination scheme.

An attractive alternative approach to the question involves determining the fate of a bromonium ion generated under solvolytic conditions. It has been elegantly demonstrated by Winstein and co-workers in what is by now a classic series of papers concerning neighboring-group participation[14,18,32] that a trans-disposed neighboring group can nucleophilically assist in ionization of an adjacent C–X bond. With neighboring Br the intermediate ion that is formed by rate-limiting assisted ionization of the C–X bond is currently accepted to be a bromonium ion which accounts for both the product stereochemistry[22] and reaction rate.[32i]

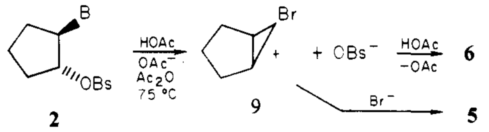
If we accept the above, then analysis of the data proceeds in a straightforward manner. Acetolysis of **1** under conditions akin to those employed by Winstein, Grunwald, and Ingraham[22] proceeds as in eq 3 to generate the cyclohexyl bromonium ion **8**,



(3)

which captures ⁻OAc (HOAc) to yield almost exclusively the trans bromo acetate **4**. However, even if Br⁻ is not added to the reaction mixture, a detectable amount of *trans*-1,2-dibromocyclohexane (**3**) is identified in the product mixture. We attribute this to the production of adventitious Br⁻ formed either by alternative pathways for decomposition of **8** (perhaps via the allylic bromide that subsequently eliminates HBr) or by further solvolysis of **3** and **4** to give the trans 1,2-diacetate of cyclohexane which we have identified by GC-mass spectrometry as a minor component present in the product mixture, particularly at longer reaction times. Nevertheless, this is a relatively minor complication since the vast majority of product is **4**.

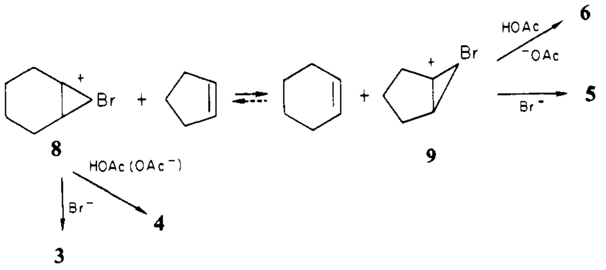
Acetolysis of **2** under the same conditions as above proceeds much more rapidly than **1** since after 2 h large amounts of products are formed. Although solvolysis of **2** has apparently not been studied in detail, it is reasonable to assume that the reaction also proceeds via an intermediate bromonium ion, **9**, as in eq 4. In support of this is the fact that the acetolysis products are exclusively trans as they are in the case of **1**. From Table II it can be seen that an appreciable amount of *trans*-1,2-dibromocyclopentane is produced even in the absence of added Br⁻, which is likely due to competing pathways occurring in the reaction mixture as discussed above for **1**.



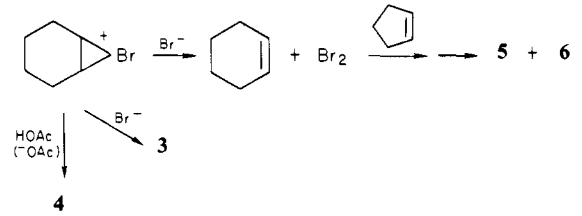
(4)

In the presence of added KBr, the acetolyses of **1** and **2** produce larger amounts of the trans dibromides (**3** in the case of **1**, Table I, rows 3, 7, 11) (**5** in the case of **2**, Table II, rows 2, 5, 8) as expected if external Br⁻ successfully captures the intermediate bromonium ions. These experiments, while providing evidence that the presence of Br⁻ influences the product distribution, do not provide information about the ability of Br⁻ to remove Br⁺ from the bromonium ion since, if this process occurs, the ultimate fate of Br_2 and olefin will be to generate dibromide and bromo acetate products.

Such information is provided, however, by the experiments in which the acetolysis of **1** or **2** is conducted in the presence of a trapping olefin. In the absence of added Br⁻, acetolysis of **1** with added cyclopentene produces mostly the trans bromo acetate of cyclohexane **4** as well as detectable quantities of *trans*-1,2-dibromocyclohexane (**3**) and the crossover products **5** and **6** (Table I, rows 2, 6, 10). There are at least two possible pathways for the production of crossed product. One of these, schematically depicted in eq 5, involves direct capture of the bromonium ion of cyclohexane **8** by cyclopentene to yield **9**, which then undergoes capture by acetate and adventitious Br⁻ to give **6** and **5**, respectively. That dibromocyclohexane (**3**) is produced in this reaction (as well as in solvolysis of **1** with no added cyclopentene or Br⁻) indicates that some Br⁻ must be produced during the course of the acetolysis, which may also account for the formation of **5**. Alternatively, an additional pathway as in eq 6 could involve



(5)



(6)

capture of **8** by adventitious Br⁻ to generate cyclohexene and molecular Br_2, the latter proceeding onward to be captured by cyclopentene, which is present in great excess over nascent cyclohexene. Since the ratio of crossed products **5**/**6** is not the same as is observed in control experiments in which Br_2 is added to cyclopentene (Table III), it may be that the process depicted in eq 6 is not exclusively responsible for the formation of **5** and **6**. Admittedly, since **3**, **5**, and **6** comprise a small amount of the relative product distribution, which makes accurate assessment of their proportions difficult, the above conclusions must be considered as tenuous. This is particularly so since the product distribution changes somewhat as a function of time.

Under similar conditions (added cyclohexene, no added Br⁻) **2** solvolyses without the formation of detectable quantities of crossed product (Table II) at short reaction times.

A clearer picture can be obtained by consideration of the data obtained when **1** is solvolysed in the presence of both added Br⁻ and cyclopentene (Table I, rows 4, 8, 12). In this case, **5** and **6** comprise a greater total amount of the product mixture than does **3**. In addition, the ratio **5**:**6** is about 4.5:1 which is akin to that

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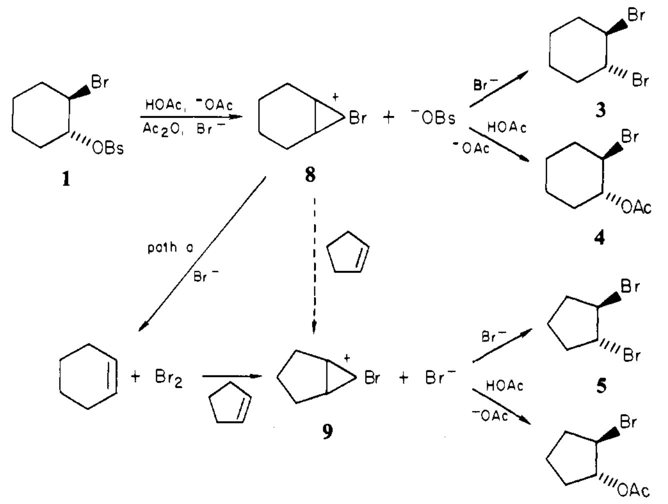
(30) This conclusion is based[14] on consideration of steric repulsion, which is claimed as being evident in a molecular model of the three-membered cyclic σ-bonded bromonium ion (even though the corresponding epoxide is known and also reported in ref 14). The complex (**7** or its equivalent) transfers Br_2 irreversibly to cyclohexene and 2,3-dimethyl-2-butene to form the corresponding dibromides and adamantylideneadamantane. Also the halogen adducts of adamantylideneadamantane on quenching with nucleophiles yield the precursor olefin rather than the 1,2-addition products. The only experimental piece of evidence bearing on the nature of **7** is ^{13}C NMR data[14] which indicate that the central C_2 and $C_{2'}$ carbons resonate downfield from those in the olefin by an amount similar to the downfield shift in the bromonium ion of tetramethylethylene. Each of the above is consistent with reversibility of the bromonium ion.

(31) (a) Balou, D.; Dubois, J.-E. *J. Chem. Res., Synop.* **1980**, 344–345; *J. Chem. Res., Miniprint* **1980**, 4449–4473. (b) Dolbier, W. R. *J. Chem. Educ.* **1969**, *46*, 342–344. (c) Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975; p 151.

(32) (a) Winstein, S.; Lucas, H. J. *J. Am. Chem. Soc.* **1939**, *61*, 2845–2848; (b) *Ibid.* **1939**, *61*, 1576–1581. (c) Winstein, S.; Buckles, R. E. *Ibid.* **1942**, *64*, 2787–2791. (d) Winstein, S. *Ibid.* **1942**, *64*, 2791–2792; (e) *Ibid.* **1942**, *64*, 2792–2795. (f) Winstein, S.; Grunwald, E. *Ibid.* **1946**, *68*, 536–537. (g) Winstein, S.; Hanson, C.; Grunwald, E. *Ibid.* **1948**, *70*, 812–816. (h) Winstein, S.; Grunwald, E.; Buckles, R. E.; Hanson, C. *Ibid.* **1948**, *70*, 816–821. (i) Winstein, S.; Grunwald, E. *Ibid.* **1948**, *70*, 828–837.

Scheme II

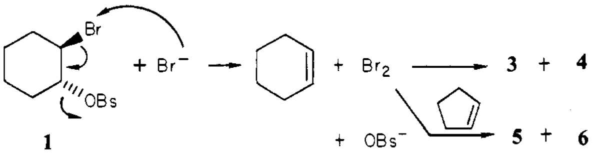


obtained from bromination of cyclopentene under similar conditions (Table III).

On the other hand, when **2** is solvolyzed in the presence of added cyclohexene and Br$^-$, crossed products **3** and **4** are produced but in amounts less than **5**. Such would indicate that the cyclopentane bromonium ion **9** is less prone to generate crossed products than is the cyclohexane ion **8**. In addition, the relative ratio of dibromocyclohexane to bromoacetoxycyclohexane (**3**/**4**) produced during the course of solvolysis of **2** is very similar to the ratio afforded when cyclohexene is brominated, Table III. We feel that this provides reasonable evidence that the major brominating species responsible for generating **3** and **4** from **2** or **5** and **6** from **1** under the above conditions arises from molecular Br_2.[33]

Given the above discussion, the best sequence of events which accommodates the data for **1** is given in Scheme II. An analogous scheme for **2** can be envisioned. However, due to the fact that lesser amounts of crossed products are obtained from **2** than from **1**, it is evident that the efficiency with which Br$^-$ removes Br$^+$ from **9** is less than is the case with **8** (indicated as path a in Scheme II).

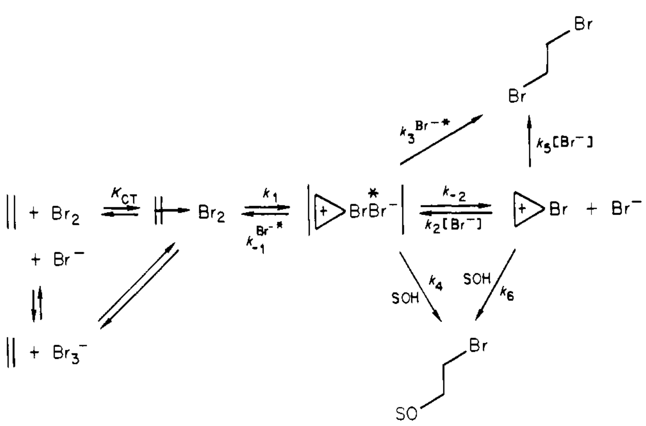
Having presented Scheme II, it is well to consider a possible complication that could be envisioned as a route to the production of Br_2 from **1** or **2**. It is possible that added Br$^-$ might partake in a bimolecular attack on **1** as in eq 7, but we feel this is not a



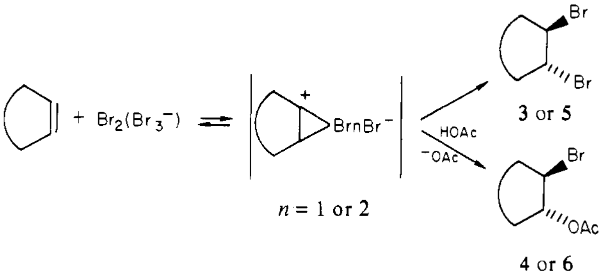
(7)

dominant pathway for decomposition on the basis of the following evidence. First, such would imply that Br$^-$ is able to accelerate the decomposition of **1**, which would be reflected in an increased rate of formation of products. However, after 2 h, acetolysis of **1** both in the presence and absence of Br$^-$ produces no qualitative difference in the extent of product formation.[34] Furthermore it can be calculated[35] that the second-order rate constant for Br$^-$ attack on **1** is in the order of 1×10^{-3} M^{-1} h^{-1} yielding a half-time for the process in eq 7 of >2000 h or about 100 times longer than for the unassisted solvolysis. A similar argument can be made for **2** based on data in ref 19.

Scheme III



A Unified Picture of Bromination at Low [Br_2]. Consideration of the data presented in Table III for bromination of cyclopentene and cyclohexene with 5×10^{-4} M Br_2 shows clearly that the ratios of dibromide to bromo acetate products are relatively insensitive to the presence of added Br$^-$. One might have expected that if added Br$^-$ were able to compete effectively for the intermediate bromonium ions produced during the course of the reaction, the proportion of dibromide adducts would increase substantially over the case where [Br$^-$] → 0. Furthermore, when **1** and **2** are solvolyzed in the presence of added Br$^-$, the corresponding bromo acetates comprise >90% of the product mixture. However, addition of Br_2 (Br_3^-) to cyclohexene produces about ~60% of the bromo acetate, while with cyclopentene the bromo acetate forms ~20% of the product mixture. That the product ratios in solvolysis of **1** or **2** differ substantially from those derived from bromination of the olefins suggests that the intermediate bromonium ions formed in the two processes differ. The most likely explanation, as in eq 8, requires that the bromonium ions formed during the course of addition of Br_2 (Br_3^-) to the olefins are associated with Br$^-$ as an intimate ion pair,[1c,4b] which then suffers rapid collapse to form the dibromides or capture by surrounding HOAc (OAc$^-$) to yield the bromo acetates. We believe the fact that added Br$^-$



(8)

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[33] Given the fact that K_{eq} for $Br_2 + Br^- \rightleftarrows Br_3^-$ in glacial acetic acid is between 50 and 100 M^{-1} [4a,7a] once Br_2 is introduced into a solution containing 0.3 M Br$^-$ and equilibrium attained, >94% of the Br_2 is converted into Br_3^-. On the basis of our experiments, we cannot determine which of Br_3^- or Br_2 is the brominating agent. However, the conclusions we have drawn concerning product ratios and the formation of Br_2 during the course of the solvolysis do not require consideration of this point. Since KBr is incompletely dissolved in the medium, the values are upper limits.

[34] Given a $t_{1/2}$ of ~15 h for **1** under these conditions[22] roughly 10% of the starting material would have reacted to afford **3** and **4** if the reaction were not catalyzed. Qualitatively, the amount of **3** and **4** produced in the competition reactions is the same, although we recognize that some differences are likely due to medium and ionic strength differences.

[35] Winstein[32e] has reported that KI reacts with *trans*-dibromocyclohexane in MeOH at 75 °C with a second-order rate constant of 0.02 M^{-1} h^{-1}. Given that Br$^-$ is generally about 50-fold less nucleophilic than is I$^-$ in S_N2 reactions ($n_{CH_3I}Br^- = 5.79$; $n_{CH_3I}I^- = 7.85$),[36] the corresponding second-order rate constant for Br$^-$ attack on dibromocyclohexane is estimated to be ~4×10^{-4} M^{-1} h^{-1}. Of course the leaving group in the case of **1** is not Br$^-$ but OBs$^-$; however, in S_N2 reactions (to which we consider the displacement in eq 6 to be formally equivalent) aryl sulfonates have similar (or only slightly greater)[37] leaving abilities to Br$^-$. In internally assisted displacements with neighboring Br, the relative rates of OBs$^-$ to Br$^-$ solvolysis is 2.5,[32i] and if the factor of 2.5 is used to compensate for the increased leaving-group ability of OBs$^-$ over Br$^-$, the second-order ratio constant should be approximately 1×10^{-3} M^{-1} h^{-1}. Hence, under the solvolytic conditions employed here (0.3 M Br$^-$), $t_{1/2}$ for the process in eq 6 can be calculated to be roughly 2300 h. Admittedly, the solvent system here is HOAc rather than MeOH, but the trend should be the same.

[36] Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319–326.

[37] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 340–342.

does not increase significantly the yield of dibromide products attests to the inability of external Br^- to compete under these conditions with ion pair collapse. Whether the course of the reaction proceeds via initial formation of a Br_2 (Br_3^-)-olefin π-complex as has been suggested by several authors[8] does not alter the outcome once the bromonium ion is generated.

The presence of substantial amounts of crossed product in the case of acetolysis of **1** and lesser amounts in the case of **2** is, in our opinion, valid evidence for the differential ability of external Br^- to capture Br^+ from the solvolytically produced brominium ions (**8** and **9**). If we are allowed to use the ratio of the total amount of crossed products to dibrominated product of the precursor (**5** + **6**)/**3** in the case of **1** and (**3** + **4**)/**5** in the case of **2**) as a crude measure of the ability of external Br^- to capture the bromonium ion at C or Br^+, then it is evident that the reversal capture of ion **8** proceeds at least 11 times more efficiently than in the case of **9**.

These data cannot be related in a straightforward way to the relative extents of reversibility of the intimate ions formed during the course of molecular bromination of the olefins, since the former sequence requires that *external* Br^- capture Br^+. However, we see no compelling reasons that the intimate ion pair formed during bromination would not suffer such reversibility, since in this case diffusion of external Br^- to the bromonium ion is not required to regenerate Br_2 and olefin.

Given the above two sets of observations, a unified picture of bromination emerges which is akin to that reported in a recent review.[1b] This is presented in Scheme III in which $^*Br^-$ indicates the intimately associated bromide. On the basis of our results, we have no additional information concerning the effects of the $Br^- + Br_2 \rightleftarrows Br_3^-$ equilibrium on the initial stages of the reaction. However, we believe our demonstration of reverse capture of solvolytically generated bromonium ions to form Br_2 provides convincing evidence that such a process should be considered for a bromonium ion generated during the course of electrophilic addition of Br_2 to alkenes.

Unless specifically accounted for, the presence of reversibility during the course of bromination introduces a rather severe complication into kinetic studies.[16] From a steady-state approximation for the kinetic sequence given in Scheme I, eq 9 can

$$\frac{-\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = k_1K_{\mathrm{CT}}[\|][\mathrm{Br_2}]\left(\frac{k_2[\mathrm{Br^-}] + k_3[\mathrm{SOH}]}{(k_{-1} + k_2)[\mathrm{Br^-}] + k_3[\mathrm{SOH}]}\right) \tag{9}$$

be derived.[38] In this scheme it is implied that the intermediate bromonium ion can be captured by external Br^-; however, the general form of eq 9 is similar even if the dominant pathways involve collapse of the intimate ion pair to give products or regenerated starting materials.[38] The important aspect for our purposes is that the *observed* rate constant for disappearance of $[Br_2]$ is only equivalent to k_1K_{CT} in one extreme where $k_{-1}[Br^-] \rightarrow 0$ (i.e., reversibility is unimportant). In the other limit where $k_{-1}[Br^-] >> k_2[Br^-] + k_3[SOH]$, which is perhaps the situation for severely hindered cases such as **7**, reversibility is so dominant that Br_2 never disappears. Indeed, reversibility retards the observed rate of disappearance of Br_2 over what it would be in the absence of such. For the great bulk of olefins the true situation lies somewhere in between the two limits, but there is no guarantee that the extent of reversibility is the same for different olefins.

Consider the cases of cyclopentene and cyclohexene. It is generally observed that the k_{obsd} for bromination of the former in hydroxylic solvents is between 6- and 25-fold faster than that for the latter,[39] depending upon the conditions. We have presented evidence that the solvolytic bromonium ion **9** of cyclopentene is ~10–11 times less prone to reverse back to Br_2 and olefin than is the bromonium ion **8** of cyclohexene. While we recognize that a variety of explanations relating to structural factors might be invoked, it seems quite likely that differing extents of reversibility in ion formation might also contribute to the differences in reactivity.

V. Summary

(1) Solvolytically produced bromonium ions of cyclohexene and cyclopentene can be captured by Br^- to generate Br_2 and olefin. Furthermore, the extent to which Br_2 is generated in this fashion differs for the two systems with the cyclohexene ion being 10–11 times more efficient than the cyclopentene ion.

(2) These observations provide strong evidence that the bromonium ion generated during the course of electrophilic bromination of simple olefins is formed reversibly. Most likely the extent of such reversibility varies for different olefins.

(3) Such reversibility causes the rate of disappearance of Br_2 to be slower than in the absence of such. Unless specifically accounted for, reversibility complicates the analysis of structure reactivity data.

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Registry No. 1, 41914-96-9; **2**, 90530-61-3; **3**, 7429-37-0; **4**, 5837-71-8; **5**, 10230-26-9; **6**, 53093-42-8; KBr, 7758-02-3; Br^-, 24959-67-9; Br_2, 7726-95-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; *trans*-2-bromocyclohexanol, 2425-33-4; cyclopentene oxide, 285-67-6; *trans*-2-bromocyclopentanol, 20377-79-1.

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[38] It can be shown, by a steady-state treatment of Scheme III, that even if the mechanism involves a complex combination of reversibly formed intimate and open ion pairs, the rate equation for disappearance of $[Br_2]$ is that given below, which is kinetically equivalent to eq 9.

$$\frac{-\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = k_1K_{\mathrm{CT}}[\|][\mathrm{Br_2}]\left(\frac{CB - k_2k_{-2}[\mathrm{Br^-}]}{AB - k_2k_{-2}[\mathrm{Br^-}]}\right)$$

where

$$A = k_{-1}^{\mathrm{Br}^{-*}} + k_{-2} + k_3^{\mathrm{Br}^{-*}} + k_4[\mathrm{SOH}]$$

$$B = k_2[\mathrm{Br^-}] + k_5[\mathrm{Br^-}] + k_6[\mathrm{SOH}]$$

$$C = k_{-2} + k_3^{\mathrm{Br}^{-*}} + k_4[\mathrm{SOH}]$$

[39] (a) Dubois, J. E.; Fresnet, P. *Tetrahedron Lett.* **1974**, 2195–2198. (b) We have determined that at 25 °C in HOAc, 5×10^{-4} M Br_2, in the absence of Br^-, the second-order rate constants for bromination of cyclopentene and cyclohexene are $(8.9 \pm 0.4) \times 10^3\ M^{-1}\ s^{-1}$ and $(3.88 \pm 0.08) \times 10^2\ M^{-1}\ s^{-1}$, respectively (Brown, R. S.; Slebocka-Tilk, H., unpublished results). (c) Robertson et al.[2b] have reported that in glacial HOAc at 25 °C (no added Br^-) the relative rates of cyclopentene and cyclohexene are 4:3. However, given the limitations of the kinetic method these authors were forced to use, we feel our numbers[38b] are more likely to be correct.