Reversible Formation of Bromonium Ions. Preferential Reaction of Br⁻ on the Br⁺ of the Bromonium Ion Produced from the Solvolysis of the *trans*-2-Bromotriflate of Cyclohexane in MeOH or HOAc Containing Added Bromide

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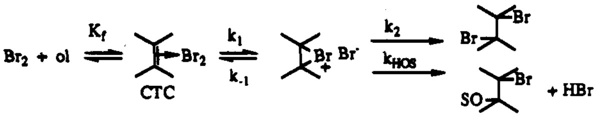
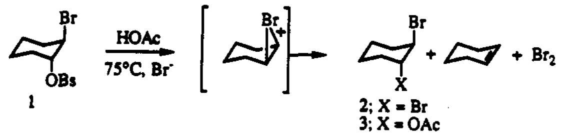
The *trans*-2-bromotriflate of cyclohexane (4) has been solvolyzed at ambient temperatures in HOAc and MeOH containing varying [Br^-] and in the presence of 0.5 M of a scavenger olefin, cyclopentene. The kinetics of solvolysis of 4 have been determined by observing the rate of change in color of an acid/base indicator that instantly responds to the production of HOTf or HBr. The kinetics show that the rate of solvolysis of 4 at constant ionic strength is independent of [Br^-]. The products of solvolysis of 4 under the various conditions have been determined by quantitative GLPC analysis. In the presence of Br^-, the products consisted of the trans 1,2-dibromides and bromosolvates of cyclohexane and cyclopentane. The cyclopentyl products are shown to be formed from the electrophilic addition of Br_2/Br_3^- to cyclopentene while *trans*-1,2-dibromocyclohexane (2) was obtained from Br^- capture of the bromonium ion of cyclohexene on carbon. The Br_2 arises from capture by Br^- of the bromonium ion on Br^+. On the basis of the ratio of the cyclopentyl products/2, Br^- capture of the solvolytically produced bromonium ion by attack on Br^+ is 4-5 times more prevalent than attack on carbon in HOAc and ~25 times more prevalent than attack on carbon in MeOH. The results have strong implications on the reversal of bromonium ions formed during the electrophilic bromination of olefins in hydroxylic solvents.

Introduction

The bromination of olefins is often considered in textbooks to be the quintessential example of the electrophilic addition reaction of the double bond.[1] The currently accepted mechanism for the process in moderate to high polarity hydroxylic solvents at low [Br_2] is given in eq 1. Recent work indicates that there are many facets of this seemingly simple reaction to be elucidated.[2-4] One area under active investigation concerns under what circumstances bromonium ion formation is reversible and whether k_{-1} in eq 1 is of comparable magnitude to the product-forming steps, k_2 and k_{HOS}. Since the first demonstration that a bromonium ion, generated from the solvolysis of the *trans*-2-bromobrosylate of cyclohexane (1), can react with external Br^- to give free Br_2 as well as cyclohexyl solvolysis products[5] (eq 2), numerous reports have appeared that indicate reversal of bromonium ions is more prevalent than was previously believed.[2a-c,3c,d,4] Detection of reversal during electrophilic Br_2 addition is made very difficult because any reformed Br_2 simply readds to the olefin. Therefore, for the most part, the studies under which such reversal can be demonstrated involve special reactants that isomerize easily (cis → trans stilbenes[4]) or ones that are sterically congested so that the product-forming steps leading away from the crowded ions are retarded.[2a-c,3b-d]



(1)



(2)

For the solvolyses and related studies,[4d,e,5] it has been contended[2d] that the evidence for reversal of noncrowded bromonium ions was obtained under "more or less drastic conditions" or in solvents such as HOAc or halogenated ones in which the fates of the bromonium ions were different from what occurs in alcohol or aqueous media in which it is suggested that there is an absence of reversal unless the olefin is highly congested.[2a] The evidence on which the latter suggestion is founded[2] derives from the consideration of extended Winstein–Grunwald relationships, solvent kinetic isotope effects, and rate ratios

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[1] (a) DeLaMare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: Netherlands, 1982; pp 136–197. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. Transl.)* 1981, *50,* 151. (c) Schmid, G. H.; Garratt, D. G. *The Chemistry of Double Bonded Functional Groups, Supplement A, Part 2,* Patai, S., Ed.; Wiley: New York, 1977; p 725.

[2] (a) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991,** *113,* 3440. (b) Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990,** *55,* 2298. (c) Ruasse, M.-F.; Motallebi, S. *J. Phys. Org. Chem.* **1991,** *4,* 527. (d) Ruasse, M.-F. *Acc. Chem. Res.* **1990,** *23,* 87.

[3] (a) Nagorski, R. W.; Brown, R. S. *J. Am. Chem. Soc.* **1992,** *114,* 7773. (b) Bennet, A. J.; Brown, R. S.; McClung, R. E. D.; Klobukowski, M.; Aarts, G. H. M.; Santarsiero, B. D.; Bellucci, G.; Bianchini, R. *J. Am. Chem. Soc.* **1991,** *113,* 8532. (c) Brown, R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990,** *112,* 6310. (d) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985,** *107,* 4504.

[4] (a) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991,** *113,* 8012. (b) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989,** *111,* 2640. (c) Bellucci, G.; Chiappe, C.; Marioni, F.; Marchetti, F. *J. Phys. Org. Chem.* **1991,** *4,* 387. (d) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988,** *110,* 546. (e) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987,** *109,* 515.

[5] Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984,** *106,* 4515.

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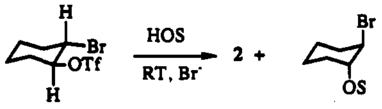
obtained in solvents of similar ionizing power but different nucleophilicities as these pertain to electrophilic Br_2 addition to olefins.

Recently, we have synthesized the *trans*-2-bromotriflate of cyclohexane (**4**) and showed that it solvolyzes rapidly at ambient temperatures in MeOH.[3a] The ease of solvolysis circumvents the requirements for the elevated temperatures (75 °C, 50–100 h) required to solvolyze the corresponding brosylate.[5] Herein we report a study of the kinetics of solvolysis of **4** at T = 25 °C in MeOH and HOAc containing varying [Br^-] at constant ionic strength. In addition, we report the products for such solvolyses conducted under the same conditions and in the presence of an acceptor olefin, cyclopentene. The results of these experiments indicate that (1) at constant ionic strength, added Br^- does not influence the kinetics of solvolysis of **4** in either medium; (2) in the presence of Br^- and cyclopentene, the products of the solvolysis of **4** consist of the dibromide and bromosolvates of cyclohexane and cyclopentane; (3) the latter products can only be formed from free Br_2 that arose from capture of the bromonium Br^+ of cyclohexene by Br^-; and (4) that far more cyclopentyl transfer products are produced from the solvolysis of **4** in MeOH (Br^-) than in HOAc (Br^-).



4; OTf = OSO_2CF_3

5

Experimental Section

(a) Materials. *trans*-1,2-Dibromocyclohexane (**2**), *trans*-2-bromocyclohexanol (**6**), *trans*-1-acetoxy-2-bromocyclohexane (**3**), *trans*-1,2-dibromocyclopentane (**7**), and *trans*-1-acetoxy-2-bromocyclopentane (**8**) were prepared by methods identified in ref 5. *trans*-1-Methoxy-2-bromocyclohexane (**9**) and *trans*-1-methoxy-2-bromocyclopentane (**10**) were prepared by procedures cited in ref 3a. All compounds were purified by spinning band distillation and had physical characteristics in agreement with those reported.

trans-2-Bromo-1-[(trifluoromethanesulfonyl)oxy]cyclohexane (**4**) was prepared from *trans*-2-bromocyclohexanol (**6**) as previously described.[3a] The product was stored as a 2.8 M solution at −78 °C in dry CH_2Cl_2. This solution is stable for several days at −78 °C, but becomes discolored when allowed to come to room temperature. The solutions can be routinely prepared in >90% purity by NMR; the major impurity is *trans*-2-bromocyclohexanol (**6**) which is either generated on workup of the reaction mixture (washing with cold 1 N HCl) or present as unreacted starting material along with a small amount (0.5–1% by GLPC) of dibromocyclohexane (**2**) that was present as an impurity in the starting bromohydrin. In either event, the presence of small amounts of **6** in the solution does not influence the solvolysis kinetics or product analyses, while the presence of small amounts of **2** in the starting material can be corrected for in the analyses of the products. LiBr and $LiClO_4$ were dried under vacuum (refluxing xylene, P_2O_5) for 24 h.

(b) Solvolysis Kinetics. The rates of solvolysis of **4** in purified[5] HOAc and purified[3c] HOMe were conducted at 25 °C, μ = 0.1 ($LiClO_4$) and μ = 0.3 ($LiClO_4$), respectively, using an indicator technique. The reaction kinetics can be observed by UV/vis spectrophotometry by monitoring the rate of change in color of an acid/base indicator that rapidly responds to the generation of triflic acid or HBr generated during the solvolysis. A typical experiment was conducted as follows.

To a 1-cm quartz cuvette containing 3.0 mL of HOAc was added 10–30 μL of a 1 × 10^{-2} M stock solution of crystal violet in HOAc (final indicator concentration 3 × 10^{-5}–10^{-4} M). The cuvette was placed in the thermostated cell holder of a Cary 210 UV/vis spectrophotometer for 10 min to equilibrate at 25 °C. The reaction was initiated by injecting 3–10 μL of a 0.028 M solution of bromotriflate **4** in CH_2Cl_2 into the cuvette. The rate of diminution of the indicator peak at 630 nm was monitored, with the Abs vs time data being stored on a microcomputer system previously described.[3c] Care was taken to adjust the amount of triflate added so that the change in absorbance of the indicator peak was no more than 10–20%. In this way the response of the indicator absorbance is linear with added HOTf. The absorbance vs time data were fit to a standard exponential model using a NLLSQ fitting routine to obtain k_{obsd}, the pseudo-first-order rate constant for the production of HOTf. Excellent first-order kinetics were obeyed to at least 3 half-lives. All rate constants were determined in duplicate: the values presented in Table I are the averages. The k_{obsd} values were found to be independent of the crystal violet indicator concentration (3 × 10^{-5}–1 × 10^{-4} M), and identical values were obtained using a different indicator, malachite green.

Table I. Observed Pseudo-First-Order Rate Constants for the Solvolysis of 4 at 25 °C in HOAc (μ = 0.1 $LiClO_4$) or MeOH (μ = 0.3 $LiClO_4$) Containing Varying [Br^-][a]

[LiBr] (M)	HOAc k_{obsd}[d] (s^{-1})	MeOH k_{obsd}[d,e] (s^{-1})
0	2.11 × 10^{-3} [b]	2.14 × 10^{-2}
0	2.34 × 10^{-3} [c]	1.96 × 10^{-2}
0	2.49 × 10^{-3} [c]	
0.05	2.50 × 10^{-3} [b]	
0.05	2.48 × 10^{-3} [c]	
0.05	2.74 × 10^{-3} [c]	
0.1	2.21 × 10^{-3} [b]	
0.1	2.56 × 10^{-3} [b]	
0.1	2.33 × 10^{-3} [b]	
0.15		2.04 × 10^{-2}
0.15		1.93 × 10^{-2}
0.3		2.24 × 10^{-2}
0.3		2.23 × 10^{-2}

[a] Using 3 × 10^{-5}–1 × 10^{-4} M indicator as described in Experimental Section. [b] Malachite green indicator, by observing rate of decrease at 630 nm. [c] Crystal violet indicator, by observing rate of decrease at 630 nm. [d] Estimated error ±10% of quoted number. [e] 3 × 10^{-5}–1 × 10^{-4} thymol blue 550 nm.

A similar protocol was adopted for the solvolysis of **4** in MeOH (μ = 0.3 ($LiClO_4$)) except that the indicator chosen was thymol blue (3 × 10^{-5}–1 × 10^{-4} M) and the reaction kinetics were monitored by observing the rate of increase of the indicator band at 550 nm. Given in Table I are the solvolysis k_{obsd} values obtained in MeOH at various [Br^-].

(c) Solvolysis Products. A typical series of solvolysis experiments were conducted as follows. To five different 25-mL solutions of HOAc containing varying [Br^-] with μ = 0.1 ($LiClO_4$) were added 0.13 mL of a 2.8 M solution of bromotriflate **4** in CH_2Cl_2 (final [**4**] = 0.015 M). The mixtures were allowed to stand at room temperature for 1–2 h and then poured into 25 mL of H_2O. The resulting mixture was extracted with CH_2Cl_2 (3×), and the combined organic extracts were washed with 5% aqueous $NaHCO_3$. The CH_2Cl_2 layer was dried ($MgSO_4$) and the solvent evaporated at room temperature using a rotary evaporator. To the residue was added a few drops of CH_2Cl_2; this solution was analyzed by GLPC (6 ft × $^1/_8$-in., 10% OV/1 on 80–100-mesh Chromosorb W). The GLPC analyses were carried out in triplicate using a Hewlett-Packard 5830 gas chromatograph with the following conditions: flow rate 50 mL of He/min.; T_1 = 120 °C for 2 min then temperature programmed to increase by 5 °C/min to 150 °C. The product analyses for the solvolyses conducted in the presence of 0.5 M cyclopentene were performed in an analogous manner. Control experiments were conducted using known amounts of authentic materials subjected to the solvolysis and extraction procedures in order to establish that all materials were recovered in their proportional amounts and to establish the response factors for the GLPC analyses.

Analogous solvolyses were conducted in MeOH containing varying [Br^-], μ = 0.3 ($LiClO_4$) both with and without added cyclopentene. In this case GLPC analyses used the same protocol and columns with the exception that T_1 = 100 °C for 6 min

Table II. Ratio of Dibromocyclohexane (2) to *trans*-1-Acetoxy-2-bromocyclohexane (3) or *trans*-1-Methoxy-2-bromocyclohexane (9) Produced from Solvolysis of 4 in HOAc (μ = 0.1 $LiClO_4$) or MeOH (μ = 0.3 $LiClO_4$) at Various [Br^-][a]

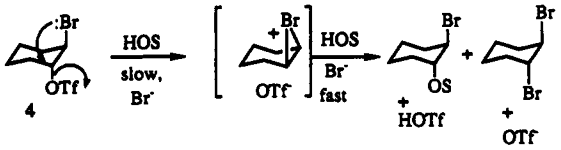
[LiBr]	HOAc,[b] 2/3	MeOH,[c] 2/9
0	0	0
0.025	0.12	
0.05	0.29	
0.075	0.51	
0.1	0.79	
0.2		0.13
0.3		0.26

[a] Ambient temperature (22–26 °C); 0.015 M 4; averages of 2–3 determinations, estimated error ±5% of quoted number. [b] Corrected for 0.4% of 2 initially present in 4. [c] Corrected for 1.2% of 2 initially present in 4.

followed by a programmed temperature increase of 5 °C/min to 150 °C. In both solvents, the anticipated products accounted for >95% of the isolated product material.

Results

(a) Solvolysis Kinetics. The kinetics of solvolysis were monitored by observing the rate of change in absorbance of a highly colored indicator that responds to the production of triflic acid that stems from the solvolysis. As shown in eq 3 each capture of the intermediate by solvent generates HOTf which can rapidly react with the indicator, while capture by Br^- generates OTf^-, with no change in the indicator color. Under the present circumstances, product analyses show that, at most, 40–50% of the product arises from Br^- capture of the intermediate(s) at the highest concentrations employed, so that solvent attack and hence the production of HOTf represents a major pathway for product formation. Thus, if the indicator responds instantly to the presence of HOTf, the rate-limiting step for the color response of the indicator will be the solvolysis rate constant for 4. Given in Table I are the observed solvolytic rate constants in HOAc and MeOH determined as a function of [Br^-]. The salient feature is that in a given solvent the rate constants are, within experimental error, independent of the presence of Br^-. This in turn indicates that Br^- does not appear in the rate-limiting step for the reaction.



(3)

(b) Solvolysis. Given in Table II are the ratios of dibromide to bromosolvate derived from the solvolysis of 4 in purified HOAc and MeOH, respectively, at ambient temperature. The general procedure involved injecting 0.13 mL of a 2.85 M solution of 4 in CH_2Cl_2 into 25 mL of purified solvent containing varying [Br^-], but at constant ionic strength (μ = 0.1 ($LiClO_4$) for HOAc; μ = 0.3 ($LiClO_4$) for MeOH). The concentrations chosen were dictated by the solubility of the salts. The mixture was allowed to stand for 1 h to ensure complete reaction, and the products were then isolated as given in the experimental section.

The *trans*-2-bromotriflate 4 was solvolyzed in a second series of experiments in the identical solvents, but this time in the presence of 0.5 M added cyclopentene. This concentration of cyclopentene is sufficient that any free Br_2 produced during the reaction will react exclusively with cyclopentene rather than with the nascent cyclohexene produced along with the Br_2. Given in Tables III and IV are the percentages of the dibromides and bromosolvates of cyclopentene and cyclohexene obtained from the solvolyses of 4 in HOAc and MeOH, respectively, containing varying [Br^-] and 0.5 M cyclopentene. Also included in Table III are the percentages of products obtained when the solvolyses are conducted in HOAc containing 0.02 M NaOAc as a buffering agent to scavenge the HOTf produced. The general feature of note is the large amount of cyclopentyl products obtained during the solvolyses of 4 in the presence of added Br^- and that added buffering NaOAc does not markedly alter the product ratios indicating that HOTf does not interfere with the chemistry. Of final note is that in all cases solvolysis products of 4 were the corresponding trans dibromides or bromosolvates; these accounted for >95% of the isolated materials. This confirms the expectation that 4 solvolyses by means of an N_DI process through the intermediacy of cyclic bromonium ions.

Table III. Percentages of Dibromocyclohexane (2), Dibromocyclopentane (7), *trans*-1-Acetoxy-2-bromocyclohexane (3), and *trans*-1-Acetoxy-2-bromocyclopentane (8) Obtained from Solvolysis of 4 in HOAc Containing 0.5 M Cyclopentene and Varying [Br^-], μ = 0.1 ($LiClO_4$)[a,b]

[LiBr] (M)	% 7	% 8	% 2	% 3	(7 + 8)/2
0	0	0	0	100	
0.025	9.7	3.1	5.4	81.7	2.4
0.025[c]	6.9	2.3	4.5	86.3	2.0
0.05	17.4	3.7	8.4	70.5	2.5
0.05[c]	14.6	3.0	7.9	74.5	2.2
0.075	22.4	3.2	10.8	63.6	2.4
0.075[c]	21.5	2.8	11.0	64.6	2.2
0.10	26.4	2.2	12.8	58.7	2.2
0.10[c]	27.7	2.2	13.6	56.8	2.2

[a] Ambient temperature (22–26 °C); [4] = 0.015 M. [b] Averages of triplicate determinations; estimated error ±0.4%. [c] Same conditions except in presence of 0.02 M NaOAc.

Table IV. Percentages of Dibromocyclohexane (2), Dibromocyclopentane (7), *trans*-1-Methoxy-2-bromocyclohexane (9), and *trans*-1-Methoxy-2-bromocyclopentene (10) Obtained from the Solvolysis of 4 in MeOH Containing 0.5 M Cyclopentene and Varying [Br^-], μ = 0.3 ($LiClO_4$)[a,b]

[LiBr] (M)	% 7	% 10	% 2	% 9	(7 + 10)/2[c]
0.0	0	0	0	100	
0.1	3.2	9.7	1.2	84.9	10.8 ± 4.2
0.2	9.9	14.2	2.0	73.0	12.0 ± 2.5
0.3	18.9	17.1	2.5	60.5	14.4 ± 2.2

[a] Ambient temperature (22–26 °C); [4] = 0.015 M. [b] Averages of duplicate determinations; estimated error ± 0.3%. [c] Errors computed on the basis of estimated errors in percentage of 2, 7, and 10.

Discussion

As part of what is now a classic series of papers concerning neighboring group participation[6] [N_DI] Winstein and co-workers showed that three-membered cyclic bromonium ions could be formed during the solvolyses of

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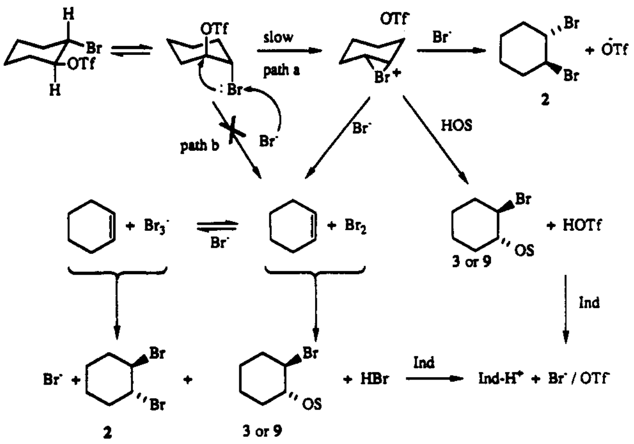
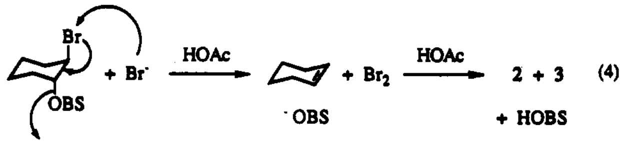
(6) (a) Winstein, S.; Buckles, R. E. *J. Am. Chem. Soc.* **1942**, *64*, 2780; (b) **1942**, *64*, 2787. (c) Winstein, S.; Lucas, H. *Ibid.* **1939**, *61*, 2845; (d) **1939**, *61*, 1576. (e) Winstein, S.; Grunwald, E. *Ibid.* **1946**, *68*, 536; (g) **1948**, *70*, 828. (h) Winstein, S.; Hanson, C.; Grunwald, E. *Ibid.* **1948**, *70*, 812. (i) Winstein, S.; Grunwald, E.; Buckles, R. E.; Hanson, C. *Ibid.* **1948**, *70*, 816.

Scheme I



trans-1-X-2-bromocyclohexanes (eq 2, X = brosylate). In a previous study,[5] we have used this solvolytic reaction to probe whether added Br^- could intercept the bromonium ion to form Br_2 and cyclohexene. The solvolyses were conducted at 75 °C for prolonged periods in HOAc containing Br^-, and any Br_2 formed was scavenged by a more reactive added olefin, cyclopentene. That *trans*-1,2-dibromocyclopentane and *trans*-1-acetoxy-2-bromocyclopentene were formed in ratios identical to what was observed from the reaction of cyclopentene + Br_2 + Br^- in HOAc at 75 °C was taken as good evidence that free Br_2 could be formed from the solvolysis reaction in the presence of added Br^-. Extending the interpretation further allowed one to suggest that since solvolytic bromonium ions generated in the presence of Br^- could form Br_2 + olefin, it was reasonable to expect that bromonium ions were formed reversibly from electrophilic addition of Br_2 to olefins.

In the previous study,[5] several experimental limitations detracted from an uncritical acceptance of the interpretation. First, the solvolysis required high temperature (75 °C) in order to proceed at a reasonable rate, and the added KBr was not completely soluble in the medium which made an accurate determination of $[Br^-]$ impossible. Second, although there was no question that free Br_2 was generated, the mechanism by which this occurred was uncertain. Even though reasonable arguments were presented to exclude the involvement of the bimolecular Br^--promoted elimination shown in eq 4, kinetic verification of this was not undertaken.



The present study of the solvolysis of the far more reactive **4** was undertaken in order to address all these concerns and to more firmly establish the utility of the solvolytic method for producing and determining the fates of bromonium ions with respect to their reaction with Br^-.

(i) Solvolysis Kinetics. Shown in Scheme I is a generalized mechanism for the solvolysis of **4** in the presence of Br^- and an indicator (Ind) such as crystal violet or thymol blue that responds rapidly to the acid produced during the reaction. In the absence of Br^-, each solvolytic event produces a bromonium ion which is captured by solvent to give **3** or **9** and 1 equiv of acid so that the rate of change in the indicator color is determined by the slow $\mathrm{N_DI}$ process labeled path a. Added Br^- can capture the bromonium ion to give dibromide directly, but also has two possibilities for producing Br_2. In the first, the rate-limiting step is still the unimolecular $\mathrm{N_DI}$ process followed by rapid Br^- capture of the bromonium ion on carbon giving dibromide **2** or on Br^+ to yield molecular Br_2. In the second (path b) Br^- is involved kinetically to facilitate the decomposition of **4** leading directly to Br_2 + olefin. In either event, the so-produced Br_2 undergoes instantaneous[7] establishment of the $Br_2 + Br \rightleftharpoons Br_3^-$ equilibrium,[8] the components of which are known to undergo rapid addition to cyclohexene to produce dibromide **2** and bromosolvates **3** and **9**. We have determined[9] that the electrophilic addition of Br_2 to cyclohexene in HOAc containing added Br^- produces dibromide (**2**)/bromoacetate (**3**) in the ratio of 27/73 ($[Br^-]$ = 0 M), 71/29 ($[Br^-]$ = 0.025 M), 82/18 ($[Br^-]$ = 0.05 M), 88/12 ($[Br^-]$ = 0.075 M), and 90/10 ($[Br^-]$ = 0.1 M). Also, we have shown[3a] that Br_2 addition to cyclohexene in MeOH containing Br^- gives dibromide (**2**)/methoxy bromide (**9**) ratios of 0.46/1.0 ($[Br^-]$ = 0.105 M) and 0.77/1.0 ($[Br^-]$ = 0.20 M). The important aspect of the above is that to the extent that anionic Br^- captures any intermediate ions to give dibromide product, acid will not be generated and the added indicator cannot respond. However, to the extent that the Br_2/Br_3^- reaction with cyclohexene gives bromoacetate **3** or methoxy bromide **9**, the indicator will respond to the kinetics of generation of HBr or HOTf.

Therefore, pathways a and b in Scheme I can be distinguished since the kinetics will be independent of $[Br^-]$ if path a is followed and exhibit a first-order dependence on $[Br^-]$ if path b is followed. The kinetic data given in Table I indicate an independence of the observed rate constant on $[Br^-]$ and therefore rule out any bimolecular reaction leading to Br_2 where Br^- is involved in the rate-limiting step.

(ii) Capture of Free Br_2/Br_3^- by Cyclopentene. Although the kinetics show no rate dependence on added $[Br^-]$, neither these data nor the information contained in Table II provide evidence for Br_2 being generated during the course of the reaction since even if this were so its ultimate fate would simply be rapid readdition to the cyclohexene along with which it was generated.

The presence of free Br_2 can be detected by its reaction with a scavenger olefin which is present during the solvolysis.[5] To this end we have employed 0.5 M cyclopentene, an olefin that reacts with Br_2/Br_3^- far more rapidly than does cyclohexene.[10] From the data given in Tables III and IV it is clear that substantial quantities of the trans dibromide and bromosolvate of cyclopentane are produced along with the cyclohexane solvolysis products. Control experiments wherein cyclopentene is subjected to reaction with Br_2 + 0.1 M Br^- in HOAc indicate that the ratio of the cyclopentyl dibromide (**7**)/bromoacetate (**8**) is 12.3 while the ratio of these products produced from

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[7] (a) Ruasse, M.-F.; Aubard, J.; Monjoint, P. *J. Chim. Phys.* **1982**, *82*, 539. (b) Ruasse, M.-F.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382.

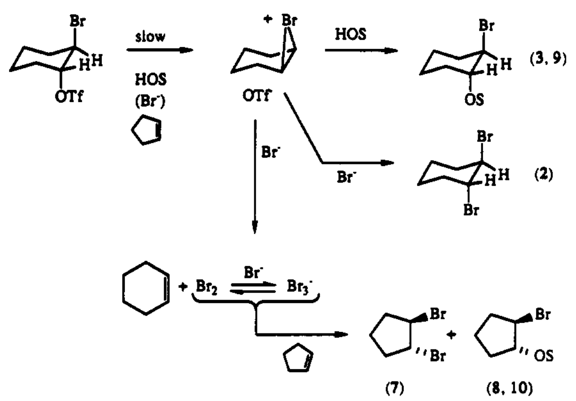
[8] Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369 and references cited therein.

[9] Slebocka-Tilk, H.; Zheng, C. Y.; Brown, R. S. *J. Am. Chem. Soc.* in press.

[10] Dubois, J. E.; Fresnet, P. *Tetrahedron Lett.* **1974**, 2195.

[11] Although cyclopentene cannot intercept the solvolytically produced bromonium ion, we have shown that transfer of Br^+ between olefins in chlorinated solvents is remarkably facile at ambient temperature; $k_{\text{transfer}} \simeq 2 \times 10^7\ M^{-1}\ s^{-1}$.[3b]

Scheme II



solvolysis of 4 in HOAc + 0.1 M Br⁻ is 12.0–12.6. Similar controls with Br_2 addition to cyclopentene in MeOH containing 0.1 and 0.3 M Br⁻ indicate respective ratios of 7/10 of 0.38 and 1.2; the ratios obtained from solvolysis of 4 under those conditions are 0.33 and 1.1. These experiments confirm that free Br_2/Br_3^- is generated by reaction of Br⁻ with the bromonium ion generated during the solvolysis of 4. The data of Tables III and IV also indicate that under these solvolysis conditions cyclopentene alone does not intercept the bromonium ion produced from 4, otherwise, at zero added [Br⁻], the bromosolvates of cyclopentene (8 and 10) would be produced.

All the above indicates that the solvolysis of 4 in the presence of Br⁻ and cyclopentene in two hydroxylic solvents, HOAc and MeOH, can be described by the process shown in Scheme II. Where comparison of the solvolyses of 4 in different solvents can be made (0.1 M added LiBr; Tables II–IV) the solvolytically produced bromonium ion leads to more cyclohexane bromosolvate in MeOH than in HOAc. This is reasonable considering MeOH is both more nucleophilic and ionizing than HOAc.[3a,9] However, to the extent that Br⁻ captures the ion, the following conclusions can be drawn. The ratios of the cyclopentyl products to dibromocyclohexane given in Tables III and IV (e.g., (7 + 8)/2 or (7 + 10)/2) provide important information concerning the ratio of Br^+/C capture of the solvolytically produced bromonium ion by Br⁻ since all free Br_2/Br_3^- is rapidly captured after its formation by added cyclopentene. The (7 + 8)/2 ratio varies from 2.0 to 2.5 while the (7 + 10)/2 ratio varies from 10.8–14.4, meaning that in both solvents there is a greater propensity of the nucleophilic Br⁻ to capture the bromonium ion on Br^+ than on either of the two carbon atoms. Moreover, the relative invariance of these ratios[12] to [Br⁻] provides valuable confirmatory evidence that these three species arise from the capture by Br⁻ of a common intermediate that we take to be the bromonium ion. If Br⁻ were involved in promoting the elimination of Br^+/OTf^- from 4, the ratio of the cyclopentyl products to 2 would increase markedly as a function of added Br⁻.

Conclusions and Relevance to Electrophilic Addition of Br_2 to Olefins. In earlier studies, we have determined the dibromide/bromosolvate product ratio for electrophilic addition of Br_2 to cyclohexene in the presence of added Br⁻ in both HOAc[9] and MeOH.[3a] In both solvents, there is more dibromide formed from the electrophilic addition reaction than from the solvolysis of 4. For example, in HOAc at the highest [Br⁻] employed (0.1 M), the ratio of 2/3 found for solvolysis of 4 is 44/56 (Table III), while from the electrophilic addition of Br_2/Br_3^-, the ratio is 90/10.[9] In the case of MeOH, at 0.3 M added Br⁻, the solvolysis of 4 gives a ratio of 2/9 of 20/80, while electrophilic addition of Br_2/Br_3^- gives a ratio of 77/100.[3a] These findings indicate that the Br_2/Br_3^- addition pathways and the solvolysis pathway(s) do not proceed through fully equivalent intermediates even though the bulk of the data indicates the intermediacy of a bromonium ion in both situations. For the electrophilic addition and solvolysis processes in MeOH, the ionic intermediates are short lived,[5] and the nucleophilic capture of the bromonium ion by solvent or Br⁻ is perturbed by the presence of the counterion generated along with the bromonium ion. The most sensitive ion in this respect would be the solvolytically generated one since the departing OTf⁻ and incoming Br⁻ or HOS must occupy the same region of space. It is reasonable to expect that the anionic OTf⁻ will electrostatically repel the incoming Br⁻ but at the same time direct, by H-bonding, the delivery of solvent to form the trans bromosolvate product in preference to the trans dibromide. A similar rationale explains the reduced dibromide 2/bromoacetate 3 ratio seen for solvolysis of 4 in HOAc relative to Br_2 addition to cyclohexene, although the latter situation is complicated by a prominent Br_3^- reaction at high [Br⁻] that leads directly to trans dibromide.[3a,9]

The above solvolysis experiments unequivocally establish that free Br_2 is formed from the solvolysis of 4 in hydroxylic solvents containing Br⁻ and the scavenger olefin, cyclopentene. That the solvolysis kinetics in each solvent are independent of [Br⁻] indicates that this anion cannot be involved in a rate-limiting step leading to Br_2 + cyclohexene. The kinetic and product data indicate that Br⁻ captures the bromonium ion of cyclohexene in a post-rate-limiting step: capture on carbon gives *trans*-1,2-dibromocyclohexane (2) while capture on Br^+ gives Br_2 that immediately reacts with the scavenger olefin to give the trans dibromide and bromosolvates of cyclopentene. That the ratio of the sum of the cyclopentyl products to 2 is >1 indicates that there is a preferential capture of the bromonium ion on Br^+. Statistically correcting for the two carbon atoms of the cyclic bromonium ion leads to the inescapable conclusion that Br⁻ preferentially captures Br^+ by a factor of 4–5 in HOAc, and by a factor of ~25 in MeOH. Even if there is some small perturbation of the preference of Br⁻ capture of the bromonium ion Br^+, or carbons by the OTf⁻ counterion, the solvolysis results indicate that an external Br⁻ can capture an unhindered "normal" bromonium ion in hydroxylic solvents to form olefin and Br_2. Since these solvolysis results depend on the ability of *external* Br⁻ to capture the bromonium ion, it is clear that at zero added Br⁻, such capture reactions cannot occur.

Whether reversal in electrophilic Br_2 addition to alkenes occurs when there is no external Br⁻ depends upon the partitioning of the first formed Br⁻/bromonium ion pairs between dissociation (to infinitely dilute the nascent Br⁻) or internal return. We have shown recently[9] that at zero added Br⁻ in HOAc, electrophilic bromination of cyclohexene generates 27% of the trans bromide, this arising from ion pair collapse. However, in MeOH at zero added Br⁻, no dibromide is formed, meaning that pair dissociation

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(12) That the ratio of (7 + 10)/(2) varies from 10.8 to 14.4, we believe, is due to the relatively small amount of dibromocyclohexane 2 produced (0–2.5%, Table VI). Given the experimental uncertainty of ±0.4% on these small numbers, the ratios reported are experimentally the same.

and/or capture by MeOH exceeds ion pair collapse to form the dibromide.[3a] Of course, Br^- attack on Br^+ cannot be probed in these experiments, but it can be reasonably argued on the basis of the solvolysis results that it should occur roughly at the same, or slightly greater rate than Br^- capture at carbon.

Coupling of the above solvolysis and electrophilic bromination results leads to the conclusions that for the latter process involving normal, noncongested olefins (1) reversal in the absence of added Br^- most likely occurs by collapse of the ion pairs to reform Br_2 in competition with dibromide formation in HOAc, but this is probably not an important process in MeOH, and (2) in the presence of added external Br^-, an important channel for reaction of the bromonium ion in both HOAc and MeOH is capture by Br^- to form both the dibromide, and free Br_2, the latter being the preferential process. These experiments indicate that during the course of electrophilic Br_2 additions to an olefin in HOAc, or MeOH containing external Br^-, reversal of ion formation, even in the case of normal olefins, is an important process.

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