per host are indicated on a difference electron density map. Position parameters have been assigned for only 30 of the solvent atoms.

The hemicarcerand is in the wrapped conformation. The distance between the planes of the four oxygen atoms of each cavitand component is about 2.4 Å. The angle between normals to these two least-squares planes is 0.6°. The four oxygen atoms are ±0.04 Å from the least-squares plane through these four atoms. The distance between the oxygen atoms within a xylyl bridge ranges from 2.76 to 2.95 Å. The approximate squares formed by the four oxygen atoms of each cavitand are twisted with respect to each other by about 21° (defined by O–square midpoint–square midpoint–O).

Supplementary Material Available: Experimental details of the crystal structure determination, including tables of atom positions and their thermal parameters and bond lengths and angles (13 pages). Ordering information is given on any current masthead page.

Electrophilic Addition of Br_2 to Olefins in the Presence of Nucleophilic Trapping Anions. Implications for the Lifetimes of Bromonium Ion Intermediates Produced from Electrophilic Bromination of Olefins in Methanol

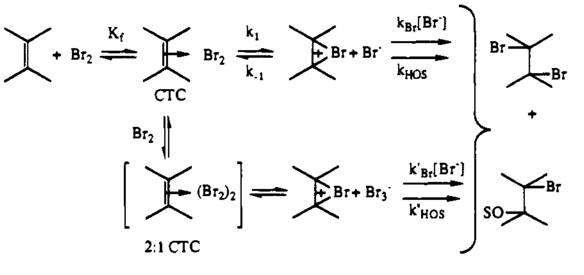
R. W. Nagorski and R. S. Brown*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received March 20, 1992*

Abstract: The product ratios for Br_2 or NBS additions to cyclopentene, cyclohexene, tetramethylethylene, and styrene in MeOH containing varying concentrations of added N_3^- or Br^- have been determined with an aim of determining the lifetimes of the bromonium ion intermediates. On the basis of the ratio of trans bromo azide to methoxy bromide products, the partitioning rate constant ratios (k_{N_3}/k_{CH_3OH}) for the four olefins are 5.9, 4.9, 9.3, and 2.7 M^{-1}, respectively. That the far better nucleophile (N_3^-) does not lead to a marked increase in product formation relative to solvent suggests that both species capture a highly reactive intermediate in a non-activation-limited process. Assuming that the N_3^- reacts with the intermediate with a diffusion-limited rate constant of 10^{10} M^{-1} s^{-1}, the respective lifetimes of the ions produced from bromination of the four olefins are 5.9×10^{-10}, 5.0×10^{-10}, 9.3×10^{-10}, and 2.7×10^{-10} s, respectively. On the basis of existing comparisons, these values indicate the following: the cyclic olefins produce ions that live about 100 times longer than a secondary carbocation; tetramethylethylene gives a bromonium ion that lives ~10 times longer than a tertiary cation; and styrene gives an ion (bromonium or β-bromo cation) that is ~40-fold longer lived than the 1-phenylethyl cation. In the case of Br_2 or NBS addition to cyclohexene in the presence of varying $[Br^-]$, the ratio of the trans dibromide to methoxy bromide product tends to zero as $[Br^-] \rightarrow 0$. This indicates that the trans dibromide cannot be formed by ion pair collapse. The solvolysis of *trans*-2-bromocyclohexyl trifluoromethanesulfonate in MeOH containing N_3^- or Br^- produces significantly less azide or bromide capture product than does electrophilic addition of Br_2 or NBS to cyclohexene under the same conditions, suggesting that the ions produced in the two cases are not identical.

Introduction

The electrophilic bromination of olefins is a well-studied reaction[1] that has recently attracted renewed interest. The generally accepted mechanism is given in eq 1. In protic solvents at low $[Br_2]$, the reaction is first order in $[Br_2]$ and proceeds via a 1:1 charge-transfer complex (CTC). At higher $[Br_2]$ or in nonprotic solvents, terms second order in $[Br_2]$ are seen and interpreted as a Br_2-assisted ionization of the 1:1 CTC (perhaps via a 2:1 CTC) to produce a bromonium ion tribromide.[2] The more recent work has centered on structural and NMR characterization of a stable bromonium ion,[3] determining the circumstances where reversible formation of the ions occurs[2,4] and determining the importance of nucleophilic solvent assistance in bromination.[4f]



(1)

In some cases, bromonium ions can be studied by NMR under stable ion conditions.[5] However, because of the general instability of three-membered bromonium ions toward nucleophilic attack, very little information exists about the characteristics of these ions in solution. One of these is the lifetime, about which virtually no data exist other than the fact that the ion must live sufficiently long to allow a translocation of Br^- from where it is formed after the ionization of the CTC to where it attacks the carbon to form

---

[1] (a) Schmid, G. H.; Garrat, D. G. *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; Suppl. A, Part 2, p 725. (b) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136–197. (c) V'yunov, K. A.; Guniak, M. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 151–163. (d) Ruasse, M. F. *Acc. Chem. Res.* **1990**, *23*, 87.

[2] Brown R. S.; Slebocka-Tilk, H.; Bennet, A. J.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310 and references therein.

[3] (a) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4505. (b) Bennet, A. J.; Brown, R. S.; McClung, R. E. D.; Aarts, G. M.; Klobukowski, M.; Santarsiero, B. D.; Bellucci, G.; Bianchini, R. *J. Am. Chem. Soc.* **1991**, *113*, 8532.

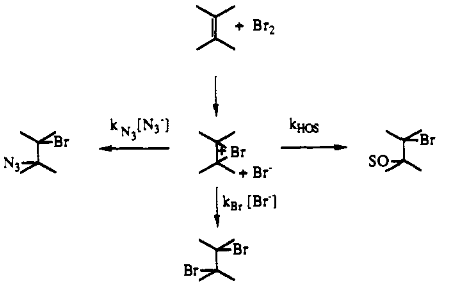
[4] (a) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. (b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988**, *110*, 546. (d) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640. (e) Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298. (f) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440.

[5] Olah, G. A. *Halonium Ions*; Wiley Interscience: New York, 1975 and references therein.

0002-7863/92/1514-7773$03.00/0

a trans dibromide product. In the case of the bromination of *cis*-stilbene in HOAc or $ClCH_2CH_2Cl$, the intermediate ions (bromonium or β-bromocarbocation) must last long enough to allow rotation about the central C–C bond and reejection of Br^+ to form isomerized starting material.[6]

We seek in this report to determine whether information about the lifetime of bromonium in solution can be probed utilizing the azide "clock" methodology developed by Jencks and co-workers.[7,8] There, partitioning of a cationic intermediate between solvent capture and capture by an added nucleophile (N_3^-) that reacts with R^+ at the diffusion limit is determined from quantitative assessment of the product ratios as a function of $[N_3^-]$. We report herein that it can be applied to the bromonium ion problem by consideration of the competing product-forming steps given in eq 2.



(2)

In what follows, we report such studies for the bromonium ions cyclohexene, cyclopentene, and tetramethylethylene, as well as that of the ion (bromonium or β-bromocarbocation) of styrene in MeOH. In addition, we provide evidence that in MeOH the collapse of intimate or solvent-separated bromonium–Br^- ion pairs to form dibromide does not represent a significant route to products. Finally, we consider the products formed from the solvolysis of the *trans*-2-bromotriflate of cyclohexane in MeOH containing Br^- and N_3^-.

Experimental Section

(a) General. Routine NMR and IR spectra were obtained with Bruker WP-80 NMR and Nicolet FTIR machines; 200-MHz NMR spectra were obtained with a Bruker WP-200 machine. HPLC analysis of the product mixtures was performed with a Hewlett-Packard 1081A HPLC utilizing a Waters RCM 8 × 10 radial compression module containing a Waters 10-cm C-18 μ Bondapak 8 mm × 100 mm column and Waters Differential Refractometer R401 detector. The eluent was 70:30 methanol/H_2O for all systems except tetramethylethylene where the eluent was 55:45 methanol/H_2O. GLPC analysis of the product mixtures from solvolysis experiments was done with a Hewlett-Packard 5830A gas chromatograph using a 6 ft × $^1/_8$ in. 10% DEGS on 80–100 mesh Chromosorb W column. Temperature 1 = 100 °C for 3 min, programmed at ΔT = 9 °C/min to 180 °C; He flow = 38 cc/min.

(b) Materials. *trans*-1,2-Dibromocyclohexane,[9] *trans*-1,2-dibromocyclopentane,[9] 2,3-dibromo-2,3-dimethylbutane,[10] and 1,2-dibromo-1-phenylethane[11] were prepared and purified as described. *trans*-1-Bromo-2-methoxycyclohexane[12] and *trans*-1-bromo-2-methoxycyclopentane[13] were prepared by a method outlined by Erickson and Kim[14] and purified by vacuum distillation. 2-Bromo-3-methoxy-2,3-dimethylbutane[15] was prepared analogously[14] and was purified by spinning band distillation using a water aspirator (bp 49 °C, ~20 Torr; lit.[15] bp 52 °C, 17 Torr). 2-Bromo-1-methoxy-1-phenylethane[16] was prepared[14] and purified by distillation (bp 50 °C, 0.05 Torr; lit.[16] bp 52 °C, 0.05 Torr).

All bromo azides were prepared by a general procedure described by Van Ende and Krief.[17] The crude materials were purified by column chromatography using silica gel (70–230 mesh) and an eluent of petroleum ether. The last traces of hydrocarbon solvent were removed by freeze–thaw cycles under 0.5 Torr vacuum. So prepared were *trans*-1-azido-2-bromocyclohexane,[18] *trans*-1-azido-2-bromocyclopentane [^1H NMR ($CDCl_3$, 200 MHz) δ 4.11 (m, 2 H), 2.40–1.60 (m, 6 H); FTIR (neat) 2104 cm^{-1}; exact mass calcd for $C_5H_8BrN_3$ 188.9901, found 188.9900], and 2-azido-3-bromo-2,3-dimethylbutane[19] [^1H NMR ($CDCl_3$, 200 MHz) δ 1.79 (s, 6 H), 1.49 (s, 6 H); exact mass calcd for $C_6H_{12}Br$ ($M^+ - N_3$) 165.0102, 163.0122, found 165.0102, 163.0107. Anal. Calcd for $C_6H_{12}BrN_3$: C, 34.97; H, 5.87; N, 20.39; Br, 38.77. Found: C, 34.95; H, 5.94; N, 20.31; Br, 38.70].

2-Azido-1-bromo-1-phenylethane and 1-azido-2-bromo-1-phenylethane were prepared[17] and purified by column chromatography as an inseparable 8:5 mixture (by ^1H NMR) of isomers: exact mass calcd for $C_8H_8{}^{81}BrN_3$ 226.9881, found 226.9882. Anal. Calcd for $C_8H_8BrN_3$: C, 42.50; H, 3.57; N, 18.59. Found: C, 42.64; H, 3.45; N, 18.68.

The identities of the two regioisomers were ascertained by comparison with ^1H NMR data given by Boerwinkle and Hassner.[20] 2-Azido-1-bromo-1-phenylethane: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.40 (m, 5 H), 5.00 (t, 1 H, J = 7.6 Hz), 3.88 (d, 2 H, J = 7.6 Hz). 1-Azido-2-bromo-1-phenylethane: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.40 (m, 5 H), 4.76 (t, 1 H, J = 7.6 Hz), 3.55 (d, 2 H, J = 7.6 Hz).

trans-2-Bromocyclohexyl trifluoromethanesulfonate (I) was prepared several times as needed from the corresponding *trans*-2-bromocyclohexanol[21] (1–2 g) in a solution of dry CH_2Cl_2 (10 mL) containing equimolar pyridine cooled to 0 °C in an ice bath.[22] To this was added dropwise 10–20% excess of neat trifluoromethanesulfonic anhydride at such a rate that the temperature did not exceed 5 °C. Immediately after the addition, the reaction mixture was washed with two 2-mL aliquots of ice cold 0.01 N HCl solution, and then the CH_2Cl_2 layer was dried over $MgSO_4$ in the cold, filtered through glass wool, and immediately placed in a stoppered flask in a dry ice chest. The material is stable at −78 °C for several days, but becomes discolored when kept above 0 °C for prolonged periods: ^1H NMR (CD_2Cl_2) δ 5.0–4.8 (m, 1 H), 4.2–4.0 (m, 1 H), 2.5–2.3 (m, 2 H), 2.0–1.6 (m, 4 H), 1.5–1.2 (m, 2 H).[3b] The material so-produced is ~90% pure by ^1H NMR, the remaining 10% being the 2-bromocyclohexanol that is probably formed by hydrolysis of I during the aqueous workup.

(c) Bromination. Reagent grade methanol (Mallinckrodt) was purified by distillation from CaH_2 and used within 1 day. Bromine (Fluka), cyclohexene (BDH), 2,3-dimethyl-2-butene (Aldrich), and styrene (Fischer) were used as supplied. Cyclopentene was prepared by dehydration[23] of cyclopentanol and purified by distillation (bp 44 °C, ambient pressure). NBS (MCB) was recrystallized from water.

A typical bromination was conducted under conditions where the olefin and brominating agent were maintained at as low a concentration as possible. A solution of NaN_3 (0.03–0.4 M) in MeOH (minimum volume of 70 mL) was placed in a three-necked flask equipped with a magnetic stir bar and two addition funnels. The olefin ((3.5 × 10^{-4})–(9.7 × 10^{-3}) mol) in 1.5–3.0 mL of MeOH was placed in one addition funnel, and an equimolar amount of Br_2 or NBS in a similar amount of MeOH was placed in the other. (The relative concentrations of olefin (ol) and azide were chosen such that $[N_3^-] \geq 10[\text{ol}]$, and for purposes of calculation the $[N_3^-]$ was determined at the final volume which includes all added MeOH.) The mixture was vigorously stirred, and both the olefin and Br_2 solutions were added dropwise over a period of several minutes at such a rate that the Br_2 color was discharged before the next drops were added. All reactions were conducted at ambient temperature (22 ± 2 °C). Control experiments at temperatures of 15.5 and 27.5 °C

---

(6) (a) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012. (b) Buckles, R. E.; Bader, J. M.; Thurmaier, R. J. *J. Org. Chem.* **1962**, *27*, 4523. (c) Yates, K.; McDonald, R. S. *J. Org. Chem.* **1973**, *38*, 2465.

(7) (a) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361. (b) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373. (c) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1383. (d) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1396. (e) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238. (f) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7888. (g) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.

(8) (a) Richard, J. P.; Amyes, T. L.; Bei, L.; Stubblefield, V. *J. Am. Chem. Soc.* **1990**, *112*, 9513. (b) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 9507.

(9) Weinstock, J.; Lewis, S. N.; Bordwell, F. G. *J. Am. Chem. Soc.* **1956**, *78*, 6072.

(10) Dubois, J. E.; Chretien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506.

(11) Rolston, J.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469, 1477, 1483.

(12) Winstein, S.; Henderson, R. B. *J. Am. Chem. Soc.* **1943**, *65*, 2196.

(13) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893.

(14) Erickson, K. L.; Kim, J. L. *J. Org. Chem.* **1971**, *36*, 295.

(15) Kuivila, H. G.; Choi, Y. M. *J. Org. Chem.* **1979**, *44*, 4774.

(16) Janda, M.; Srogl, J.; Holy, P.; Nemec, M. *Z. Chem.* **1977**, *17*, 226.

(17) Van Ende, D.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 279.

(18) Maxa, E.; Zbiral, E.; Schulz, G.; Haslinger, E. *Justus Liebigs Ann. Chem.* **1975**, *9*, 1705.

(19) Lion, C.; Boukou-Poba, J.-P.; Saumtally, I. *Bull. Soc. Chim. Belg.* **1987**, *96*, 711.

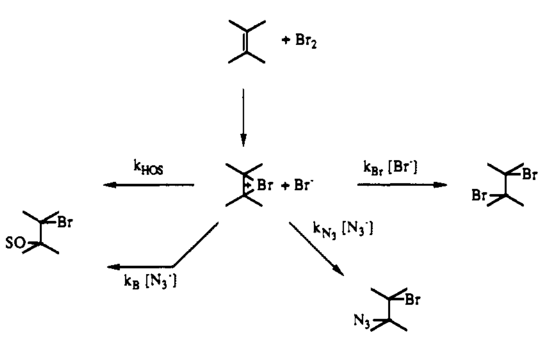
(20) Boerwinkle, F.; Hassner, A. *J. Am. Chem. Soc.* **1968**, *90*, 216.

(21) (a) Guss, C. O.; Rosenthal, R. *J. Am. Chem. Soc.* **1955**, *77*, 2549. (b) Winstein, S.; Buckles, R. E. *J. Am. Chem. Soc.* **1942**, *64*, 2780.

(22) An adaptation of the procedure of Stang, P. J.; Hancock, M.; Subramanian, L. R. *Synthesis* **1982**, *2*, 85.

(23) Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Lowe and Brydone Ltd.: London, 1956.

Scheme I[a]



[a] k_{HOS} incorporates the solvent concentration.

established that the dibromide/methoxy bromide/bromo azide product ratios for cyclohexene and styrene were invariant to these temperature changes ($[NaBr] \simeq [NaN_3] = 0.1$ M).

At the completion of the addition, the reaction mixture was poured into ~800 mL of water and then extracted with 4 × 75 mL of CH_2Cl_2. The CH_2Cl_2 solution was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The residue was diluted with a small amount of the HPLC solvent (70:30, methanol/H_2O or CH_2Cl_2) to give a final concentration of 0.01–0.7 M in total products. This sample mixture was analyzed in 5–7 separate runs by HPLC, and the values of the integrated areas were averaged for the computations.

In the case of 2,3-dimethyl-2-butene, the above extraction procedure proved to give nonreproducible results, so that an alternative workup procedure was employed. Following the bromination (as above), the reaction mixture was poured into saturated NaCl, (300–500 mL) and additional solid NaCl was added to saturate the MeOH. This mixture was extracted with hexane (5 × 50 mL), and the combined hexane extracts were dried over $CaCO_3$. The hexane was removed by distillation through a 20-cm Vigreux column, and the last traces were "chased" by codistillation with added CH_2Cl_2.

HPLC and GLPC analyses were calibrated using known amounts of the authentic materials to determine the response factors. In the case of the bromo azides of styrene, only 1-azido-2-bromo-1-phenylethane was detected during the bromination in MeOH. For each series of reactions, the extraction procedures were checked using known amounts of the authentic expected products in MeOH and subjecting this to the workup procedure. In all cases, the products were recovered in amounts that agreed with the initial ratios.

(d) Solvolysis of *trans*-2-Bromocyclohexyl Trifluoromethanesulfonate (I). The solvolysis was conducted by adding a small aliquot of the triflate in CH_2Cl_2 (1.5–2.5 mL containing (3.5×10^{-4})–(9.5×10^{-3}) mol) dropwise to 100-mL MeOH solutions containing 0–0.3 M NaN_3 or NaBr at ambient temperatures. The vigorously stirred solution was allowed to react for 10 min, after which time the products were isolated in the same fashion as in the bromination experiments. Analysis of the products for the solvolysis in the presence of N_3^- was conducted using the same HPLC protocol as in the brominations. For the solvolysis in the presence of Br^-, the analyses were conducted by GLPC.

(e) UV Studies. To ascertain the presence of new species formed from N_3^- and Br_2 or NBS, qualitative UV experiments in MeOH (purified by distillation from Br_2 as described by Dubois et al.[24]) were undertaken. With Br_2 (1.2×10^{-3} M) and NaN_3 (5.3×10^{-2} M) a very rapid formation of a new species having a λ_{max} at 312 nm was observed with subsequent decomposition ($k_{obsd} = 1.5 \times 10^{-2}$ s^{-1}) to generate a faint rose colored solution that was unreactive toward the addition of subsequently added cyclohexene. With added NBS ($(3–6) \times 10^{-3}$ M) and NaN_3 ($(3.5–5.3) \times 10^{-2}$ M) a slower buildup of the 312-nm transient was observed (approximate $k_2 = 0.1$ M^{-1} s^{-1}), followed by its decomposition ($k_{obsd} \simeq 1.5 \times 10^{-2}$ s^{-1}). The nature of the 312-nm species is unknown, but can be surmised to be BrN_3.[25]

When a MeOH solution of 3.3×10^{-3} M NBS and 0.10 M NaBr was monitored by UV-visible spectroscopy, the slow buildup (~10 min) of an absorbance at 280 nm was observed ($k_2 = 0.064$ M^{-1} s^{-1}). The resultant solution was stable for several hours. Addition of cyclohexene immediately discharged the color, suggesting that it was attributable to Br_3^-.

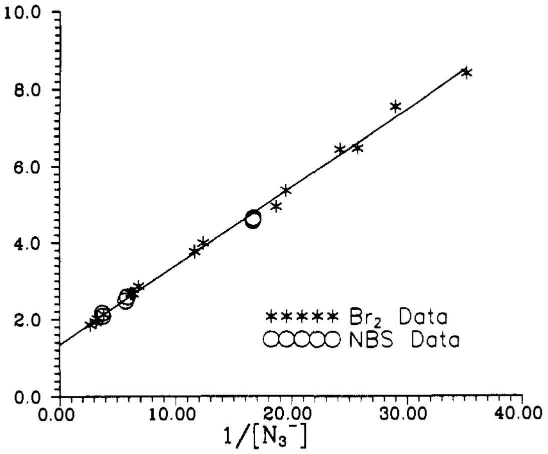


Figure 1. Plot of $1/f_{az}$ vs $1/[N_3^-]$ for the bromination of cyclohexene in MeOH, $T = 22 \pm 2$ °C. Open circles, Br_2 data; *, NBS data. Slope, 2.05×10^{-1} (0.031×10^{-1}); intercept, 1.36 (0.06).

Results

In Scheme I is a simplified working model for the various fates of the ion formed at low [Br_2] in MeOH in the presence of N_3^- or Br^-. Subsequently we will show that azide performs the dual role of nucleophile and general base in delivering solvent to the ion.

The fraction of bromo azide product (f_{az}) is given as

$$f_{az} = \frac{k_{N_3}[N_3^-]}{k_{Br}[Br^-] + k_{HOS} + k_{N_3}[N_3^-] + k_B[N_3^-]} \tag{3}$$

which can be rewritten as

$$\frac{1}{f_{az}} = \frac{k_{N_3} + k_B}{k_{N_3}} + \frac{k_{Br}[Br^-] + k_{HOS}}{k_{N_3}} \frac{1}{[N_3^-]} \tag{4}$$

Shown in Figure 1 is a plot of $1/f_{az}$ vs $1/[N_3^-]$ for the bromination of cyclohexene at ambient temperature in MeOH containing varying [N_3^-]. Similar plots for cyclopentene, tetramethylethylene, and styrene (not shown) are available as supplementary material. The primary data used to construct the plots are given as Tables 1S–4S in the supplementary material. The experimental protocol was atypical of that usually adopted (see Experimental Section). This procedure was followed because we have previously shown[3b] that intermolecular transfers of Br^+ between bromonium ions and olefins have remarkably high rate constants, so that for the studies here, the [olefin] was always kept as low as possible. Also, because even so-called "innocent" anions such as triflate[26a] and perchlorate[26b] have been shown to capture bromonium ions, added electrolytes to maintain a constant ionic strength were avoided to eliminate possible complications of the product analyses. Thus, the slope of the plot in Figure 1 also incorporates effects of ionic strength changes. To simplify the analysis, only the data for the methoxy bromides (Br, OCH_3) and bromo azides (Br, N_3) were used to construct the plots.

In neither Figure 1 nor those plots for the other olefins (not shown) is the intercept unity. A unit intercept is required if only a nucleophilic role for N_3^- exists. One possible explanation for this is that N_3^- also acts as a base to assist in delivery of HOS to the ion. This sort of dual role behavior as both a nucleophile and a base has been observed before and similarly interpreted for bisulfite reactions with oxocarbonium ions produced from the acid-catalyzed cleavage of substituted acetophenone ketals.[7c] In the present case, N_3^- ion should be relatively basic since the pK_a

---

(24) Dubois, J. E.; Hegarty, A. F.; Bergmann, E. D. *J. Org. Chem.* **1972**, *37*, 2218.

(25) (a) Dehnicke, K.; Ruschke, P. *Z. Naturforsch.* **1978**, *33b*, 750. (b) Cambie, R. C.; Robertson, J. D.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1982**, *35*, 863. (c) Hassner, A. *Acc. Chem. Res.* **1971**, *4*, 9 and references therein. (d) Hassner, A.; Boerwinkle, F. P.; Levy, A. B. *J. Am. Chem. Soc.* **1970**, *92*, 4879.

(26) (a) Zefirov, N. S.; Koz'min, A. S.; Sorokin, V. D.; Zhdankin, V. V. *J. Org. Chem. USSR* (*Engl. Transl.*) **1982**, *18*, 1546. (b) Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V. *Tetrahedron* **1982**, *38*, 291 and references therein.

Table I. Partitioning Rate Constant Ratios for the Reactions of Azide and MeOH with Various Bromonium Ions Formed from Electrophilic Addition of Br^+ to Olefins in MeOH (T = 22–25 °C)[a]

olefin	k_{N_3}/k_{CH_3OH} (M^{-1})[b]	$(k_{N_3} + k_B)/k_{N_3}$	k_{N_3}/k_B
cyclohexene	4.9	1.4	2.5
cyclopentene	5.9	1.6	1.7
tetramethylethylene	9.3	2.0	1.0
styrene	2.7	1.7	1.4

[a] Errors ±5% of quoted number, except for tetramethylethylene in which errors are ±10%. [b] Calculated taking k_{CH_3OH} as a first-order rate constant.

Table II. Relative Product Ratios Observed for Bromination in Cyclohexene in MeOH (T = 22–25 °C) Using NBS or Br_2 in Presence of Added Br^- and N_3[a]

run	[NaBr] (M)	[NaN_3] (M)	brominating agent	relative product ratio[b] Br,OCH_3	Br,Br	Br,N_3
1			NBS	1.0		
2	0.075		NBS	1.0	0.33	
3	0.15		NBS	1.0	0.63	
4	0.154		NBS	1.0	0.70	
5	0.156		NBS	1.0	0.70	
6		0.06	NBS	1.0		0.28
7		0.17	NBS	1.0		0.63
8		0.27	NBS	1.0		0.86
9	0.03	0.10	NBS	1.0	0.12	0.42
10	0.10	0.10	NBS	1.0	0.36	0.40
11	0.10	0.23	NBS	1.0	0.30	0.67
12	0.15	0.10	NBS	1.0	0.58	0.37
13	0.16	0.17	NBS	1.0	0.58	0.60
14	0.05		Br_2	1.0	0.22	
15	0.105		Br_2	1.0	0.46	
16	0.11		Br_2	1.0	0.44	
17	0.15		Br_2	1.0	0.58	
18	0.18		Br_2	1.0	0.71	
19	0.20		Br_2	1.0	0.77	
20	0.035	0.10	Br_2	1.0	0.13	0.40
21	0.11	0.10	Br_2	1.0	0.41	0.33
22	0.11	0.20	Br_2	1.0	0.36	0.66
23	0.21	0.11	Br_2	1.0	0.74	0.34

[a] [NBS] = [ol] = (3×10^{-3})–(2×10^{-3}) M; NBS in 3.0 mL of MeOH was added to a solution of cyclohexene in 100 mL of MeOH containing salts. Concentration refer to final volume. [b] Relative to Br,OCH_3 product: errors ±5% of quoted number.

of HN_3 is 4.72.[27] Given in Table I are the partitioning rate constant ratios for the reaction of N_3^- and MeOH with the bromonium ions generated in MeOH. Also in the table are the intercepts of the plots of $1/f_{az}$ vs $1/[N_3^-]$, which are interpreted as $(k_{N_3} + k_B)/(k_{N_3})$, and the k_{N_3}/k_B ratio, which reflects the ratio of the nucleophilicity to basicity of N_3^- under these conditions.

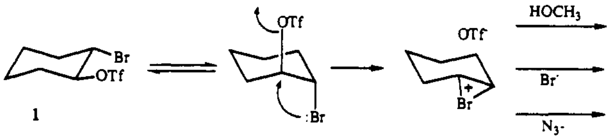
Competition experiments were undertaken to determine whether N_3^-, Br^-, and HOMe capture a common intermediate. Given in Table II are the product ratios observed for the bromination of cyclohexene in MeOH using NBS or Br_2 and varying amounts of added Br^- and N_3^-. The product ratios are controlled by the concentrations of the two added nucleophiles and less so by salt effects: no attempt was made to account for the latter. A general trend exists wherein added Br^- at constant $[N_3^-]$ leads to more dibromide, but does not markedly affect the Br,OCH_3/Br,N_3 ratios (e.g., runs 7, 13; 9, 10, 12; 20, 21, 23). Some small drop in that ratio is observed which is probably attributable to nonconstant ionic strength effects. In the cases where $[N_3^-]$ is varied at constant $[Br^-]$, the amount of Br,N_3 increases as expected, and this is coupled to an increase in the Br,OCH_3/Br,Br product ratio (runs 3–5, 12, 13; 10, 11; 15, 16, 21, 22) as would be required if N_3^- acts both as a nucleophile and as a base that assists in the delivery of $HOCH_3$ to the ion as in Scheme I.

Table III. Relative Product Ratios Observed for Solvolysis of *trans*-2-Bromocyclohexyl Trifluoromethanesulfonate in MeOH (T = 22–25 °C) Containing Added Br^- or N_3^-[a]

run	[NaBr] (M)	[NaN_3] (M)	relative product ratio[b] Br,OCH_3	Br,Br	Br,N_3
1		0.10	1.0		0.04
2		0.16	1.0		0.07
3		0.21	1.0		0.09
4		0.23	1.0		0.12
5		0.26	1.0		0.12
6		0.31	1.0		0.12
7	0.10		1.0	0.09	
8	0.15		1.0	0.13	
9	0.20		1.0	0.19	
10	0.25		1.0	0.25	
11	0.30		1.0	0.31	

[a] Concentrations of salts at the final volume. [b] Relative to Br,OCH_3 product: estimated errors ±5% of quoted numbers.

Finally, analysis of the products formed from a series of solvolysis experiments of *trans*-2-bromocyclohexyl trifluoromethanesulfonate (I, eq 5) in MeOH containing Br^- or N_3^- was undertaken in order to compare the solvolytic product ratios with those obtained from electrophilic addition of Br_2 to cyclohexene under similar conditions. The products with $HOCH_3$ and Br^- were always trans. In the case of N_3^-, although the bulk of the azide product was trans, an additional azide-containing product (by GCIR and GC mass spectral analysis) was produced that we believe arose from S_N2 displacement on the triflate to produce *cis*-1-azido-2-bromocyclohexane.[28] This material did not interfere with the analysis, which compared the ratios of the trans azide and methoxy compounds which must have arisen through a bromonium ion pathway.[4a] Given in Table III are the ratios of the trans products formed from the solvolysis. The salient feature is that, for a given concentration of N_3^- or Br^-, roughly one-fourth to one-sixth as much trans azido or bromo product is formed from solvolysis as is formed from electrophilic addition of Br_2 or NBS to cyclohexene.



(5)

Discussion

(a) Nature of the Brominating Agent. Bromination in MeOH containing added Br^- and N_3^- is a potentially complex process involving a number of competing equilibria (eq 6) that can generate different brominating species. In addition, uncertainty exists about the importance of intimate ion pairs, solvent-separated ions, and free ions in the generation of products.[1] What concerns us here is the fate of the bromonium ions after their formation and whether such ions react in ways that depend upon how they were formed. We deal first with the potential brominating species produced in situ.

$$\begin{tikzcd}
(Br^-)_x + BrN_3 \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "ol"] & N_3^- + Br_2 + (Br^-)_{x-1} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "ol"] & Br_3^- + (Br^-)_{x-2} + N_3^- \arrow[d, "ol"] \\
{} & {} & {}
\end{tikzcd} \qquad (6)$$

It is well-known that the $Br^- + Br_2 \rightleftharpoons Br_3^-$ equilibrium (K_{MeOH} = 177 M^{-1})[24,29] complicates the analysis of the kinetics of olefin bromination. The equilibrium in MeOH is established extremely rapidly ($k_f = 2.5 \times 10^9$ M^{-1} s^{-1}),[30] and in general Br_2 is a more effective brominating agent than Br_3^- ($Q = k_{Br_2}/k_{Br_3^-}$; depending on the olefin, Q commonly varies from 2 to 30).[29,31] In the present

---

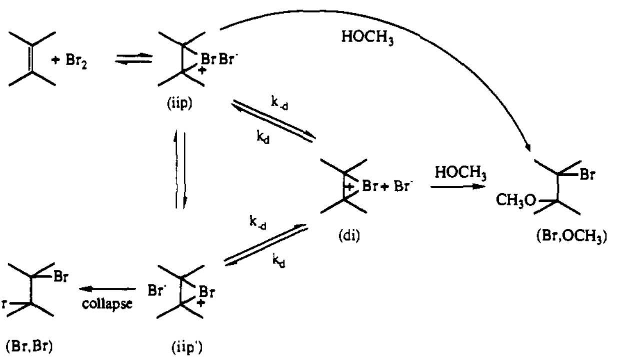
(27) *The Merck Index*, 11th ed.; Merck & Co.: Rahway, NJ, 1989; p 755.

(28) Schweng, J.; Zbiral, E. *Liebigs Ann. Chem.* **1978**, 1089.

(29) Dubois, J. E.; Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1436.

(30) (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.

Scheme II[a]



[a] iip and iip' are intimate ion pairs; di is dissociated ion.

set of experiments, the relative importance of Br_2 or Br_3^- in the addition is uncertain and changes since Br^- is continually generated because of solvent or azide capture of the intermediate bromonium ions. Nevertheless, when Br_2 was used with no added Br^-, the maximum $[Br_3^-]$ could be no more than 3×10^{-5} M while the maximum $[Br_2]$ was $\sim 1 \times 10^{-4}$ M.[32]

Control experiments establish that Br_2 in MeOH containing N_3^- and no olefin results in the formation (too rapid to be followed by conventional spectrophotometry) of a new species (λ_{max} 312 nm) which decays with a $t_{1/2}$ of $\sim$45 s. A similar transient is produced more slowly from NBS added to a solution of NaN_3 in MeOH. This is most likely BrN_3, a material originally shown by Hassner and co-workers to be capable of ionic electrophilic addition to olefins.[20,25c,d] and subsequently shown by Van Ende and Krief[17] to be generated in situ (at least as its Br^+/N_3^- constituents) by the action of NBS and NaN_3 in aqueous DME. Potentially, BrN_3 and NBS are the brominating agents in the present set of experiments. In the absence of N_3^-, NBS alone is likely the major brominating agent and not Br_2 or Br_3^-, because even when NBS and significant amounts of NaBr are used, the observed rate of formation of Br_2/Br_3^- under the present conditions appears to be too slow to account for all of the products being formed from these species.

(b) How Is Dibromide Formed? Shown in Scheme II is a detailed pathway for Br_2 addition to olefins in CH_3OH that depicts the various fates of the ionic intermediates. Ionization of the CTC (formed in equilibrium with ol + Br_2) must generate a nascent intimate ion pair (iip) in which the Br^- and bromonium Br^+ are in close proximity. The iip has several potential fates available: (1) reversal to the CTC; (2) rapid backside capture by solvent to yield Br,OCH_3 products; (3) translocation of the Br^-/bromonium ions to form a trans-disposed intimate ion pair (iip') perhaps via the involvement of solvent-separated ions; and (4) diffusional separation of the intimate ion pairs to solvent-separated and then to free ions. At zero added $[Br^-]$, if the iip's undergo diffusional separation, the so-formed Br^- is sufficiently diluted that the major product that arises from free ions will be solvent incorporated (Br,OCH_3). This indicates that at zero added $[Br^-]$, formation of the trans dibromide product can only arise through the rapid transformation of the first-formed iip into iip' followed by collapse. Correspondingly, solvent-incorporated product can only arise from $HOCH_3$ capture of the iip or the solvent-separated/free ions. The rate constant for diffusional separation of a bromonium–bromide ion pair (k_{-d}) cannot be established with certainty, but it may be surmised from consideration of the association constants for ions in solution.[7a] In H_2O and hydroxylic solvents of high dielectric constant, the association constants for ions are small ($K_{as} = k_d/k_{-d} = \leq 1$ M^{-1}),[33a] but might be expected to increase somewhat in passing from H_2O to MeOH. Since k_d, the rate constant for formation of the ion pairs, can be assumed to be diffusion limited at (5×10^9)–(1×10^{10}) M^{-1} s^{-1} (the larger value accommodating the reduced viscosity of MeOH relative to H_2O),[33b] k_{-d} can be computed to be $\geq 10^{10}$ s^{-1}.

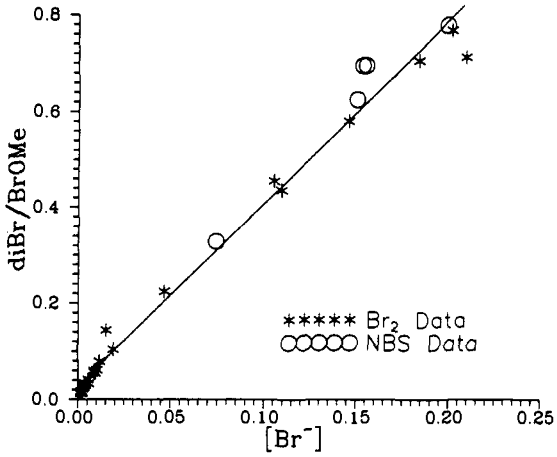


Figure 2. Plot of the ratio of dibromide/methoxy bromide products formed from the bromination of cyclohexene in MeOH, $T = 22 \pm 2$ °C, as a function of $[Br^-]$. Open circles, Br_2; *, NBS. Slope, 3.80 (0.09); intercept, 2.60×10^{-2} (0.87×10^{-2}).

Shown in Figure 2 is a plot of the dibromide/methoxy bromide ratio for the bromination of cyclohexene in MeOH as a function of added $[Br^-]$ in the absence of N_3^-. In some cases (depicted as * on the plot), NBS in the presence of added Br^- was used; otherwise Br_2 was used as the source of electrophilic bromine. Two features are apparent from the plot. First, that all data fall within respectable limits of the line suggests that all possible pathways for product formation proceed through at least one common intermediate. This is likely the free bromonium ion or a bromonium ion that is not perturbed by the presence of a counterion (nascent Br^- or succinimide). Second, the intercept of the plot tends to zero (intercept = 2.60 (0.87) $\times 10^{-2}$), indicating that significant amounts of dibromide cannot be formed in the absence of external Br^-. This in turn suggests that conversion of iip to iip' (Scheme II) followed by collapse must be slower than solvent capture of the first-formed intimate ion pair or diffusional separation followed by HOS capture of the free ion. Otherwise a non-zero intercept would be seen, the value of which would give some estimate of the relative importance of ion pair collapse vs solvent capture via the two above channels. Although we cannot rule out solvent capture of the intimate ion pair in bromination, this has recently been shown to be an unimportant pathway for product formation from the reactive carbocation produced from the S_N1 aqueous solvolysis reaction of 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl bromide.[34]

(c) Azide Capture. (i) Assumption of Diffusion-Limited Capture. The critical assumption made in using the azide capture methodology to infer the lifetimes of the bromonium ions is that N_3^- reacts with these at the diffusion limit in MeOH. Ritchie and co-workers[35] have provided seminal stopped-flow evidence concerning the relative nucleophilicities of anions with different cationic electrophiles in a variety of solvents including H_2O, MeOH, and DMSO. For the strong nucleophiles N_3^- and PhS^-, the rate constant for capture of a series of substituted aryl diazonium ions ($XC_6H_4N_2^+$) in DMSO[35a] or MeOH[35d] approached a maximal value of $\sim 10^{10}$ M^{-1} s^{-1}. This value can then be set

---

[31] (a) Dubois, J.-E.; Bienvenue-Goëtz, E. *Bull. Soc. Chim. Fr.* **1968**, 2089. (b) Dubois, J.-E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369.

[32] In a typical determination with no added Br^-, olefin and Br_2 ($\sim 10^{-3}$ mol each in 1.5 mL of MeOH) were added separately but simultaneously to 100 mL of MeOH solution containing added N_3^-. If we assume that, at the end of the reaction, all added Br_2 generates Br^- and that each drop of Br_2/MeOH is 50 μL, then toward the end of the reaction the maximum $[Br_2] = 1.0 \times 10^{-4}$ M and $[Br_3^-] \simeq 3 \times 10^{-5}$ M.

[33] (a) Davies, C. W. *Ion Association*; Butterworths: London, 1962; pp 88–101. (b) Reference 33a, pp 150–161.

[34] Richard, J. P. *J. Org. Chem.* **1992**, *57*, 625.

[35] (a) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4963. (b) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348 and references therein. (c) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1973**, *95*, 1882. (d) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 1589. (e) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

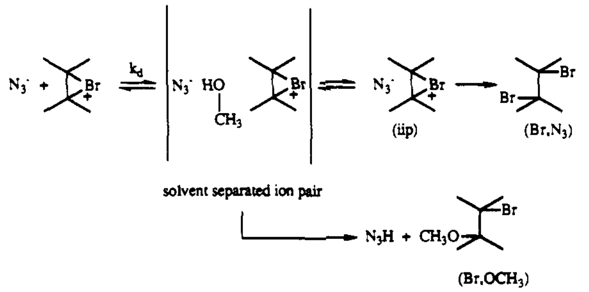
as the diffusion-limited rate constant for attack of good nucleophiles on unstable cations. Importantly, the nucleophilic selectivity of N_3^- relative to CH_3OH (defined by Ritchie[35] as $N^+ = \log k_{N_3} - \log k_{CH_3OH}$) for an activation-limited nucleophilic capture of a relatively stable cation is 8.5 (e.g., $k_{N_3}/k_{CH_3OH} = 10^{8.5}$).

On the other hand, as argued by Young and Jencks,[7e] in cases where the cations become progressively less stable, the nucleophilic selectivity between a strong nucleophile such as N_3^- or SO_3^{2-} and its host solvent is reduced. In the limit, where the cation reaches such a stability that it is just barely able to exist, the nucleophilic selectivity tends to plateau at low values between 1 and 10. For the capture of the oxocarbonium ion intermediates produced from substituted acetophenone dimethyl ketals,[7e] $k_{SO_3^{2-}}/k_{H_2O}$ ratios fell in the range $(1.3 \times 10^1)-(7 \times 10^2)$ M^{-1} and were clearly far less than expected for an activation-limited process where $k_{SO_3^{2-}}/k_{H_2O} = 10^{7.9}$.[35b,e] Variable but relatively low selectivities for k_{N_3}/k_{CH_3OH} were also observed for the capture of a series of substituted phenylethyl cations.[7a,b] The small ratios observed[7a,b,e] could be readily explained if reaction of the strong nucleophiles N_3^- or SO_3^{2-}, but not H_2O or CH_3OH, with the intermediate was diffusion limited.

For the bromonium ions generated in this study, the data presented in Table I suggest relatively low nucleophilic selectivities ($k_{N_3^-}/k_{CH_3OH} = 2.7-9.3$ M^{-1}). These values are clearly smaller than the $10^{8.5}$ expected for an activation-limited process[35] and can be taken as evidence that whatever intermediate is being attacked is a highly unstable species and that N_3^- reacts with the intermediates in a diffusion-limited process. This would be consistent with the expected behavior of a reactive bromonium ion, but not a neutral CTC.

(ii) Do Br^-, N_3^-, and CH_3OH Capture a Common Intermediate? It is important to distinguish N_3^- capture of a free bromonium ion from a process where N_3^-, olefin, and brominating agent appear in a rate-limiting step. Normally this is done for solvolysis reactions by determining an insensitivity of the reaction rate to increasing $[N_3^-]$ along with an increasing amount of azide capture product (in a post-rate-limiting step). For bromination in MeOH, we were unable to perform kinetic measurements since (a) the reactions are too fast for our existing equipment and (b) added N_3^- introduces the possibility of a new competitive brominating agent (BrN_3, eq 6) that can complicate the UV-vis spectrophotometry. Therefore we have employed a competition method[4c,8] wherein the products of bromination of cyclohexene in MeOH containing N_3^- were monitored as a function of $[Br^-]$. If a third nucleophile (Br^-) competes with MeOH and N_3^- for a common intermediate, then the $Br,OCH_3/Br,N_3$ ratio should be unchanged as a function of $[Br^-]$. Within acceptable experimental variance, the data in Table II show the expected trend and suggest that all species capture a common intermediate, which we take to be the bromonium ion. Note that this protocol does not specify what the intermediate is, but only that all three species are involved in its capture. While it may be argued that this common intermediate is really the CTC, arguments presented above concerning the relatively low capture ratios (k_{N_3}/k_{CH_3OH}) tend to suggest the capture arises not from any activation-limited process, but from attack on a highly unstable intermediate such as the bromonium ion.

The Table II data also provide evidence consistent with our explanation of the non-unity intercepts of Figure 1 and those plots for the other olefins, which suggests that the role of N_3^- is not simply that of a trapping nucleophile. At a given $[Br^-]$, added azide increases the $Br,OCH_3/Br,Br$ ratio as well as producing Br,N_3 product. This can be explained, as in Scheme I, by a process wherein N_3^- additionally acts as a base in assisting the delivery of solvent to the bromonium ion. The process is visualized in eq 7 where diffusion of N_3^- from the bulk solvent to the back side of the bromonium ion must first proceed through a solvent-separated ion pair in which the relatively basic[27] N_3^- could assist in the delivery of solvent in competition with intimate ion pair formation followed by collapse. The k_{N_3}/k_B ratio for these azide-dependent processes in the case of cyclohexene is 1.4 (Table I). Using that value and the slopes of the lines of the plots of the dibromide/methoxy bromide or bromo azide/methoxy bromide ratios vs $[Br^-]$ or $[N_3^-]$ (Table II, runs 1–7, plots not shown) allows one to determine the partitioning of the bromonium ion between N_3^- and Br^- nucleophilic capture. The value, $k_{Br^-}/k_{N_3^-} = 4.15/(3.4 \times 1.4) = 0.87$, indicates a relative insensitivity of the capture to the two anionic nucleophiles, as would be expected for a bromonium ion having little or no activation barrier toward attack.



(7)

(iii) The Question of N_3^-, Br^- and Solvent Assistance in Electrophilic Bromination. Ruasse and co-workers[36] have reported studies of the differential effects of solvents on the kinetics of bromination of linear and branched alkenes. These were interpreted[36] in terms of a significant but small nucleophilic assistance by solvent in promoting bromination. Additionally, it has long been noted from kinetic studies that Br_3^- or its kinetic equivalent, $Br^- + Br_2$, can contribute to the bromination of olefins.[4f,11,29–31,37] While an exact interpretation of the Br_3^- mechanism is not presently at hand, reasonable (but not entirely satisfying[11,37]) possibilities are a Br^--assisted ionization of the CTC, external Br^- capture of a reversibly formed bromonium–bromide ion pair, or true electrophilic addition of Br_3^- to the olefin to form a bromonium ion plus two associated Br^- ions.

It has been pointed out that there is no nucleophilic assistance by solvent for the S_N1 ionization of 1-(4-methoxyphenyl)ethyl chloride in 50% $MeOH/H_2O$ or the corresponding pentafluorobenzoate in 50% TFE/H_2O.[4c,38] This was based on the observed rate constants for the S_N1 reactions, which were shown to be independent of $[N_3^-]$. In our case, due to the experimental limitations listed above, the rate constants for bromination in the presence of added nucleophile were not determined, and we rely heavily on the trapping ratios to provide information about nucleophilic capture of the intermediates. The N_3^-/CH_3OH trapping ratios provided in Table I indicate that, despite its much greater nucleophilicity in an activation-limited process,[35] N_3^- is unable to generate the large amount of bromo azide product that would be anticipated if N_3^- assisted significantly in the ionization of the CTC. We conclude, following Jencks and Richard,[4c,38] that if there is little or no assistance by a strong nucleophile, then substantial assistance by the weakly nucleophilic solvent is not expected.[39,40] Similarly, if assistance to ionization occurs in bromination, then a strong dependence on the nature of the departing anion should be observed.[7a] Correspondingly, the absence of an effect of structure or charge of the leaving group on the partitioning of an intermediate suggests that it is a species whose reactivity is independent of the counterion, perhaps behaving as a free ion.[39] With respect to bromination of the olefins here, in MeOH containing N_3^- it is particularly important that the ratio of azide to methoxy capture is independent of whether Br_2 or NBS was used as the brominating agent. This fact and the plot in Figure 2 showing that the $Br,Br/Br,OCH_3$ ratio for bromination of cyclohexene in the presence of Br^- is independent of whether the source of electrophilic Br is Br_2 or NBS argue strongly for the capture of a free intermediate with either leaving group and

---

(36) (a) Ruasse, M.-F.; Zhang, B. L. *J. Org. Chem.* **1984**, *49*, 3207. (b) Ruasse, M.-F.; Montallebi, S. *Bull. Soc. Chim. Fr.* **1988**, 349.

(37) (a) DeYoung, S.; Berliner, E. *J. Org. Chem.* **1979**, *44*, 1088. (b) Atkinson, J. R.; Bell, R. P. *J. Chem. Soc.* **1963**, 3260.

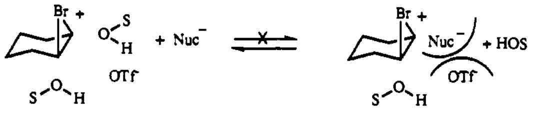
(38) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4691.

(39) McLennan, D. J.; Martin, P. L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1099.

(40) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821.

against significant nucleophilic involvement of N_3^-,Br^- or solvent in assisting the bromination.

(iv) The Location of the Counterion Influences the Bromonium Ion Partitioning. All of the above suggests that, in the electrophilic bromination of cyclohexene, N_3^-, Br^-, and solvent capture a highly reactive bromonium ion whose reactivity and partitioning to trans products are insensitive to how the ion was formed. This might imply that the ion is completely free from its associated counterion, but does not necessarily exclude capture of a solvent-separated ion pair. In the latter case, the associated counteranion is sufficiently far away from the attacking (trans) nucleophile that mutual interaction is minimal. However, we can provide evidence indicating that solvolytically produced bromonium ions may react in ways that are influenced by the nature and location of their counterions. In an effort to determine whether the ions produced from electrophilic bromination and neighboring group assisted solvolysis are equivalent, we have determined the products of solvolysis in the *trans*-2-bromo triflate of cyclohexane (I) in MeOH containing varying N_3^- and Br^-. The assisted solvolysis (eq 5) should generate a bromonium ion/triflate ion pair, whose subsequent nucleophilic capture reactions will generate *trans*-2-bromocyclohexyl adducts. The corresponding product ratios are given in Table III: the main finding is that there is less attack of the anionic nucleophiles N_3^- or Br^-, and more attack of solvent in the case of the solvolysis, than is observed during electrophilic bromination of cyclohexene under comparable conditions. This finding requires that one or both of the two intermediate bromonium ions retains knowledge of its counterion, which in turn affects the partitioning. The most sensitive ion in this respect would be the one formed from solvolysis since the nascent OTf^- occupies the same region of space that the attacking nucleophile must in order to form trans addition products. The observations can be readily explained if the departing OTf^-, when as a solvent-separated ion pair (II), preferentially delivers MeOH and, by charge repulsion, discriminates against anionic nucleophiles as in **III**. This sort of favored delivery of solvent molecules that are H-bonded to a departing anion has been invoked several times to explain the retained configuration of products arising from S_N1 solvolyses.[41] Also of note in such S_N1 solvolyses is that N_3^- capture proceeds with excess inversion of configuration, probably due to charge repulsion between the anionic nucleophile and leaving group.[41]



II
solvent separated
ip

III

(d) Implications for the Lifetimes of Bromonium Ions in MeOH. Use of the k_{N_3}/k_s partitioning constants given in Table I and the diffusion-limited rate constant of 1×10^{10} M^{-1} s^{-1} determined by Ritchie and co-workers[35] for N_3^- attack on cations in MeOH allows computation of lifetimes of 5.0×10^{-10}, 5.9×10^{-10}, 9.3×10^{-10}, and 2.7×10^{-10} s, respectively, for the ions produced from electrophilic bromination of cyclohexene, cyclopentene, tetramethylethylene, and styrene. The ions produced from the cyclic olefins are undoubtedly of the bromonium type since only trans addition products are observed. These ions last longer by ca. 100-fold than what would be expected for a secondary carbocation: e.g., isopropyl, the lifetime of which is estimated to be 5×10^{-12} s by extrapolation of a σ-constant correlation[42] for cation hydration. The ion formed from bromination of tetramethylethylene is probably also of the bromonium ion type, but no stereochemical data are available from the present study to determine whether the additions are trans. For a simple tertiary carbocation in H_2O, the lifetime is estimated[42] to be $\sim 10^{-10}$ s, which implies that such an ion is just barely stable enough to be a solvationally equilibrated reaction intermediate in dilute aqueous solution. That the lifetime of the ion produced by Br^+ addition to tetramethylethylene is $\sim 10^{-9}$ s in MeOH suggests some extra stability and the involvement of a bridged bromonium ion.

The situation with respect to styrene is less clear, and the extent of bromine bridging in the ion has been the subject of much debate.[1d,11,43-45] The ρ^+ value determined for Br_2 addition to substituted styrenes in MeOH (−4.3[43]) suggests considerable development of positive charge on the benzylic carbon in the rate-limiting step. With strong electron donors some evidence for deviations from a linear free energy plot was observed and interpreted as a change in the extent of bridging in the transition state.[43-45] Styrene, by implication, apparently produces an ion having some unspecified, but definite bridging. That bridging imparts kinetic stability to the ion as judged by its longer lifetime (2.7×10^{-10} s) relative to the unsubstituted 1-phenylethyl cation (1×10^{-11} s).[7a]

As a final consideration, it seems surprising that the tetrasubstituted bromonium ion of tetramethylethylene has only a factor of 2 longer lifetime than cyclohexene or cyclopentene. On the basis of the compared lifetimes for isopropyl/*tert*-butyl cations[42] or $HC^+(OR)_2/CH_3C^+(OR)_2$ cations,[46] substitution of CH_3 for H on a cationic site leads to a 20–1000-fold increase in lifetime, with the lower value pertaining to inherently shorter lived cations.[42] It is well-known that increased substitution on the double bond leads to marked increases in the rate of bromination. For the compounds studied here, the reported k_{Br_2} values in MeOH are as follows: styrene,[43] 1.5×10^3; cyclohexene,[47] 1.14×10^4; cyclopentene,[47] 6.25×10^4; tetramethylethylene,[36a] 1.4×10^7 M^{-1} s^{-1}. The increase in rate stems from substituent-induced positive charge stabilization of the transition state leading to the bromonium ion and implies that considerable charge is developed on the olefinic carbons. Recent theoretical analyses[48-50] have indicated that the bromine atom in the ethylene bromonium ion is nearly neutral, and almost all of the positive charge is born by the carbons. However, these charges refer to isolated gas-phase species, and solvent interactions could markedly affect the charge distributions. Nevertheless, how these charges relate to the ion lifetimes in solution is difficult to assess, particularly since for the symmetrically bridged ions the charge is distributed equally over two carbons and the property of lifetime is a kinetic one that is determined by transition-state energies associated with solvent attack. The evidence presently available accumulated from the N_3^- trapping experiments described above suggests that these ion lifetimes are rather insensitive to substituent effects in the narrow range of olefins investigated.

Acknowledgment. The authors gratefully acknowledge the continued financial support of the Natural Sciences and Engineering Research Council of Canada and the University of Alberta. They also are grateful to the referees of an earlier version of this manuscript for their constructive comments.

Supplementary Material Available: Tables of HPLC-determined product ratios as a function of [added nucleophiles] for cyclohexene, cyclopentene, tetramethylethylene, and styrene and plots of $1/f$ vs $1/[N_3^-]$ (10 pages). Ordering information is given on any current masthead page.

---

(41) Goering, H. C.; Hopf, H. *J. Am. Chem. Soc.* **1971**, *93*, 1224 and references therein.

(42) (a) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Powell, M. F.; Szilagyi, S. *J. Org. Chem.* **1984**, *49*, 5218. (b) Chiang, Y.; Kresge, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 6363.

(43) Ruasse, M.-F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645.

(44) Dubois, J.-E.; Schwarcz, A. *Tetrahedron Lett.* **1964**, 2167.

(45) Dubois, J.-E.; Ruasse, M.-F.; Argile, A. *Tetrahedron Lett.* **1978**, 177.

(46) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 4967.

(47) Dubois, J.-E.; Fresnet, P. *Tetrahedron Lett.* **1974**, 2195.

(48) Cioslowski, J.; Hamilton, T.; Scuseria, G.; Hess, B. A.; Hu, J.; Schaad, L. J.; Dupuis, M. *J. Am. Chem. Soc.* **1990**, *112*, 4183.

(49) Hamilton, T. P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1990**, *112*, 8260.

(50) Galland, B.; Elveth, E. M.; Ruasse, M.-F. *J. Chem. Soc., Chem. Commun.* **1990**, 898.