Mechanistic Evaluation of the Transfer of Br⁺ from Bis(*sym*-collidine)bromonium Triflate to Acceptor Alkenes

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The kinetics of the reaction of bis(*sym*-collidine)bromonium triflate (**2**−Br⁺/OTf⁻) with adamantylideneadamantane (Ad=Ad), 4-penten-1-ol (**4**), and cyclohexene has been investigated in 1,2-dichlorethane at 25 °C under a variety of conditions. The rates of all the reactions are shown to be depressed by added collidine, indicating that the first step for all is a reversible dissociation of **2**−Br⁺/OTf⁻ into free collidine and a reactive intermediate, coll−Br⁺, which is then captured by the alkene. The product of the reaction of Ad=Ad with **2**−Br⁺/OTf⁻ is an Ad=Ad:Br⁺−coll complex, while that of reaction of **4** with **2**−Br⁺/OTf⁻ is the cyclic ether 2-bromomethyltetrahydrofuran. The reaction with cyclohexene is more complex and involves at least two reversibly formed intermediates, suggested to be coll−Br⁺ and cyclohexene:Br⁺−coll, the latter being captured by attack of triflate to give *trans*-1-bromo-2-trifluoromethanesulfonylcyclohexane. Detailed kinetic analysis shows that the reactions of collidine, Ad=Ad, cyclohexene, and 4-penten-1-ol with the reactive intermediate coll−Br⁺ are fast but not very sensitive to the nature of the nucleophile, the second-order rate constants being 3×10^6, 1.1×10^6, 1.5×10^5, and 4.5×10^4 M⁻¹ s⁻¹, respectively. ¹H NMR analysis of the reaction of *trans*-1-bromo-2(trifluoromethanesulfonyl)cyclohexane, produced in situ from cyclohexene and **2**−Br⁺/OTf⁻ in CD₂Cl₂, with tetrabutylammonium bromide or tetrabutylammonium acetate indicates a very rapid and quantitative production of *trans*-1,2-dibromocyclohexane and *trans*-1-bromo-2-acetoxycyclohexane, respectively.

Introduction

Electrophilic addition of positive halogen (X⁺/Y⁻) to alkenes is a well-understood process,[1] but it continues to be actively investigated particularly in the cases of hindered olefins[2] and those capable of undergoing halocyclizations.[3] We have extensively investigated the transfer of Br⁺ and I⁺ from the halonium ions of adamantylideneadamantane (Ad=Ad) to a variety of alkenes[3a,4] and shown that the reaction proceeds through at least two reversibly formed intermediates, as in eq 1. The most intriguing aspect of this is the fact that the actual transfer of the halogen occurs through a spiro intermediate with the donor and acceptor moieties sufficiently close that steric, and possibly stereochemical, information may be transferred from one to the other.

While the Ad=Ad system provides considerable mechanistic information about halogen transfer between alkenes, it is unlikely that it will prove generally synthetically useful as a transfer reagent because of the difficulties in making suitably modified derivatives and the inherent
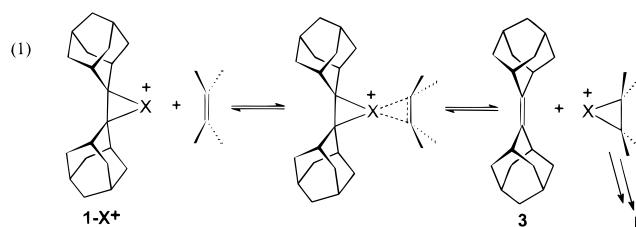
instability of the halonium ions.[4b] Another halogen transfer system that is known and readily prepared comprises the bis(*sym*-collidine)iodonium and bromonium ions, **2**.[3b,5] Bis(*sym*-collidine)halonium perchlorates were
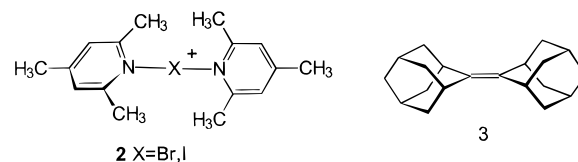
used by Lemieux and Morgan for the preparation of 2-deoxy-2-halogenoglycosides,[5b] while the iodonium ion has been used to promote the halocyclization of numerous unsaturated alcohols and carboxylic acids.[3b]

Curiously enough, despite the potential utility of this system in promoting a variety of processes, detailed mechanistic analysis of the halogen transfer has not been attempted. Some data are available concerning the kinetics of transfer of I⁺ from bis(pyridine)iodonium nitrate to olefins in 70%CHCl₃/30% pyridine.[5c] As part

(1) For reviews of the general literature, see: (a) DeLaMare, P. B. D1.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136−197. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. Transl.)* **1981,** *50,* 151. (c) Schmid, G. H.; Garrat, D. G. *The Chemistry of Double Bonded Functional Groups;* Patai, S., Ed.; Wiley: New York, 1977; Supplement A, Part 2, p 725. (d) Schmid, G. H. *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1989; Supplement A, Vol. 3, Part 1, p 699. (e) Ruasse, M.-F. *Adv. Phys. Org. Chem.* **1993,** *28,* 207.

(2) Brown, R. S. *Acc. Chem. Res.* **1997,** *30,* 131, and references therein.

(3) (a) Neverov, A. A.; Brown, R. S. *J. Org. Chem.* **1996,** *61,* 962 and references therein. (b) Evans, R. D.; Magee, J. W.; Schauble, J. H. *Synthesis* **1988,** 862 and references therein.

(4) (a) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994,** *116,* 2448. (b) Neverov, A. A.; Muise, T. A.; Brown, R. S. *Can. J. Chem.* **1997,** *75,* 1844.

(5) (a) Lemieux, R. U.; Morgan, A. R. *Can. J. Chem.* **1965,** *43,* 2190. (b) Diner, U. E.; Worsley, M.; Lown, J. W.*J. Chem. Soc. C.***1971,** 3131. (c) Lown, J. W.; Joshua, A. V. *Can. J. Chem.* **1977,** *55,* 122. (d) Tamaru, Y.; Kawamura, S.; Yoshida, Z. *Tetrahedron Lett.* **1985,** *26,* 2885.

of a program exploring the possibility for asymmetric transfer of halogen from derivatives of **2** where the 2- and 6-positions are substituted with chiral groups, we required a firm understanding of the various steps involved in the transfer mechanism. The following describes our findings from a study of the reaction of bis-(*sym*-collidine)bromonium triflate (**2**−Br$^+$/OTf$^-$) with various olefins including adamantylideneadamantane (Ad= Ad, **3**), cyclohexene, and 4-penten-1-ol (**4**).

Experimental Section

Materials and Methods. Dichloromethane and hexane were purified as described.[6] 1,2-Dichloroethane (Aldrich, HPLC grade) was used as supplied. Chemicals, including tetrabutylammonium bromide and tetrabutylammonium acetate, were purchased from Aldrich and used without further purification. Adamantylideneadamantane (Ad=Ad, **3**) was prepared as previously described.[7]
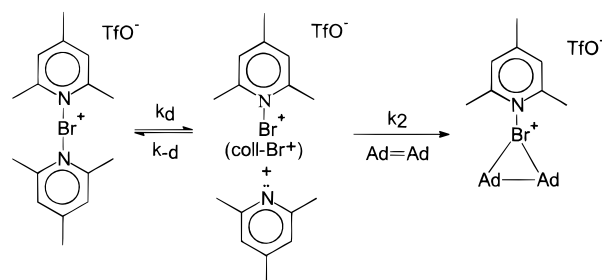
^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker WH-200 and Bruker AM-400 instruments. Spectrophotometric kinetic measurements were obtained using an OLIS modified Cary 17 UV−vis spectrophotometer or an Applied Photophysics SX-17MV stopped-flow reaction analyzer.

Bis(*sym*-collidine)bromonium Triflate (2−Br$^+$/OTf$^-$). In 20 mL of dry dichloromethane was suspended 1.41 g of silver triflate (5.48 mmol) along with 1.43 mL of 2,4,6-collidine (1.33 g, 10.97 mmol). Almost immediately all solids disappeared. A solution of 0.875 g of bromine (5.47 mmol) in 5 mL of dry dichloromethane was added to the mixture with stirring. After 10 min the solution was filtered through a Celite pad and most of the solvent removed with an Ar stream. Addition of two volumes of dry hexane under stirring resulted in formation of a white crystalline material which was filtered, washed with dry hexane, and later recrystallized from a dichloromethane/hexane system. This procedure yielded 2.32 g of a white crystalline product (90%), mp 105.5−106.5 °C; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 7.20 (s, 2H), 2.81 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (400 MHz, CD$_2$Cl$_2$) δ 155.80, 154.41, 126.13, 25.37, 21.15

Reaction of 2−Br$^+$/OTf$^-$ with Olefins. The reactions of **2**−Br$^+$/OTf$^-$ with various olefins (Ad=Ad, cyclohexene, 4-penten-1-ol, and 1-octene) have been followed using NMR and UV/vis spectrophotometry. The UV/visible spectrum of a 1 × 10^{-4} M solution of **2**−Br$^+$/OTf$^-$ in 1,2-dichloroethane has a broad absorbance with peak at 267 nm (ϵ_{267} = 11 000 M^{-1} cm^{-1}), on the side of a prominent band (ϵ_{240} = 13 500 M^{-1} cm^{-1}) approaching the solvent cutoff. In a set of experiments, the UV/vis spectrum of a 1 × 10^{-4} M sample solution of authentic Ad=Ad bromonium triflate[3a] was monitored and shows a broad featureless band from 300 to 230 nm (ϵ_{260} = 3200 M^{-1} cm^{-1}); the sample and reference solutions were treated with equimolar collidine and the UV/vis spectrum monitored again, this time showing a broad band with λ_{max} = 267.6 and 274 nm, $\epsilon_{267.6}$ = 5800 M^{-1} cm^{-1}, ϵ_{274} = 5330 M^{-1} cm^{-1}. Addition of a second aliquot of 1 × 10^{-4} M collidine to the sample and reference solutions gave no change in the appearance of the spectrum. This indicates that, at a concentration of 10^{-4} M, in the presence of collidine, the Ad=Ad bromonium ion is completely associated with a single collidine molecule.

In a standard NMR experiment, 0.04−0.06 mmol of **2**−Br$^+$/OTf$^-$ was dissolved in 0.5 mL of CD$_2$Cl$_2$ and placed in an NMR tube along with an equimolar amount of the olefin. The ^{1}H NMR spectrum was recorded within 5 min. In the cases of cyclohexene and 1-octene, subsequent experiments were performed by adding a slight excess of tetrabutylammonium bromide or acetate to the above mixture and then recording the ^{1}H NMR spectra within 5 min.

(6) Perrin, D. D.; Armagero, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals,* 2nd ed.; Pergamon Press: Oxford, 1980; p 204.
(7) Flemming, M. P.; McMurry, J. E. *Org. Synth.* **1981**, *60*, 113.

Scheme 1

Kinetics. The kinetics of the reactions of bromonium bis-(*sym*-collidine)bromonium triflate with Ad=Ad, cyclohexene, and 4-penten-1-ol were monitored by observing the rate disappearance of the bromonium ion at 240 nm (the wavelength of maximum change) in 1,2-dichloroethane (DCE) at 25 °C under conditions of excess olefin, both in the presence and absence of added collidine. The concentration of **2**−Br$^+$/OTf$^-$ was 5 × 10^{-5} M. The pseudo-first- and pseudo-second-order rate constants were evaluated by nonlinear least-squares fitting of the absorbance vs time traces for disappearance of **2**−Br$^+$/OTf$^-$ to the appropriate kinetic equation. The k_{obs} values reported in the tables are the averages of four or five runs.

Results and Discussion

Adamantylideneadamantane is an ideal olefin for simplifying this investigation because the transfer of Br$^+$ to it only progresses as far as the Ad=Ad−bromonium ion.[4a] The ^{1}H and ^{13}C NMR spectra of **2**−Br$^+$/OTf$^-$ show a symmetrical system on the NMR time scale. When a NMR solution of **2**−Br$^+$/OTf$^-$ is treated with equimolar Ad=Ad and the ^{13}C NMR spectrum rerecorded, the Ad= Ad olefinic carbons at 133.61 ppm are replaced by a slightly broadened singlet at 156.38 ppm. The latter value is very close to that of the central carbons in authentic Ad=Ad−bromonium ion triflate, (156.24 ppm in dichloromethane[4a]). This observation, coupled with the UV/vis results, indicates that the product of the reaction between equimolar **2**−Br$^+$/OTf$^-$ and Ad=Ad is a an Ad=Ad−bromonium ion complex with one associated collidine.

The reaction between 5 × 10^{-5} M **2**−Br$^+$/OTf$^-$ and varying, but excess, amounts of Ad=Ad (2.5−12.2 × 10^{-4} M) leads to a decrease in optical absorbance of the solution, the final absorbance of which is independent of the [Ad=Ad]. This result also indicates that at these concentrations the reaction proceeds completely to the side of the Ad=Ad−bromonium ion which is indicated to be complexed with collidine in Scheme 1.

The reaction displays excellent pseudo-first-order kinetics under conditions of excess [Ad=Ad]. In the presence of added collidine, (0−1) × 10^{-3} M, the reaction exhibits a common species rate depression. Shown in Figure 1 is the dependence of the observed pseudo-first-order rate constants (k_{obs}) vs [collidine] at different [Ad= Ad], the k_{obs} values being given in Table 1. Given in eq 2 is the kinetic expression corresponding to the process outlined in Scheme 1 assuming a steady state in [coll− Br$^+$]. Notably, nonlinear least squares (NLLSQ) fits of the data to eq 2

$$k_{obs} = k_d k_2[\text{Ad=Ad}][\text{coll}_2-\text{Br}^+]/(k_{-d}[\text{collidine}] + k_2[\text{Ad=Ad}]) \quad (2)$$

require only an inverse first-order common species rate depression with [collidine] and not an inverse second-
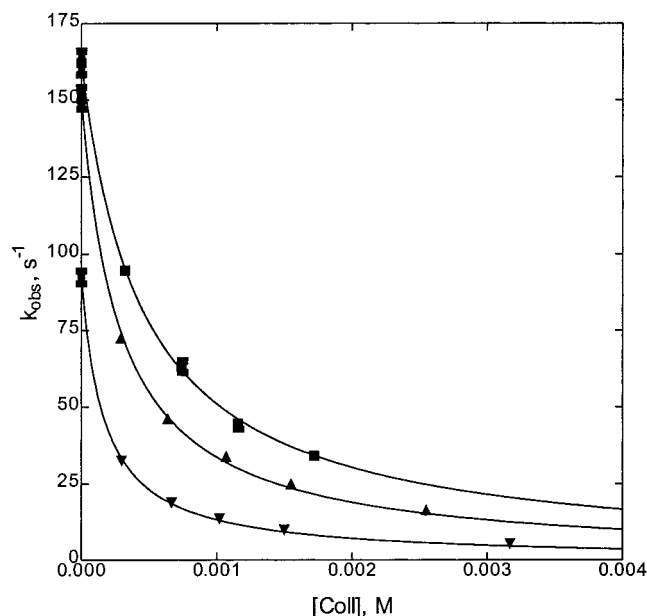
Figure 1. Plots of observed pseudo-first-order rate constants for the reaction of **2**−Br$^+$/OTf$^-$ (5×10^{-5} M) with fixed concentrations of Ad=Ad as a function of increasing [collidine] (■, 1.21×10^{-3} M; ▲, 2.5×10^{-3} M; ▼, 7.5×10^{-3} M) in 1,2-dichloroethane at 25 °C. Lines through the data are computed by NLLSQ fits to eq 2.

Scheme 2

Table 1. Pseudo-First Order Rate Constants for the Reaction of Bis(*sym*-collidine) Bromonium Triflate (2−Br$^+$/OTf$^-$) with Ad=Ad in C$_2$H$_4$Cl$_2$, T = 25 °C^a

10^4[Ad=Ad] (M)	[collidine] (M)	k_{obs} (s^{-1})
2.5	0.0	92.47 ± 1.69
2.5	0.000298	32.43 ± 0.25
2.5	0.000666	18.80 ± 0.14
2.5	0.00102	13.51 ± 0.22
2.5	0.0015	9.90 ± 0.15
2.5	0.00317	5.37 ± 0.19
7.5	0.0	150.62 ± 2.83
7.5	0.000298	72.60 ± 0.63
7.5	0.000666	46.14 ± 0.73
7.5	0.00102	33.90 ± 0.23
7.5	0.0015	24.95 ± 0.55
7.5	0.00317	16.44 ± 0.75
12.2	0.0	162.15 ± 2.41
12.2	0.000329	94.39 ± 0.83
12.2	0.000746	63.21 ± 1.51
12.2	0.00116	44.49 ± 1.40
12.2	0.00172	33.82 ± 0.97

^{a} [**2**−Br$^+$/OTf$^-$] = 5×10^{-5} M.

order dependence. This signifies that there must be one collidine associated with the reactive species up to the rate-liming step of formation of the Ad=Ad:Br$^+$−coll complex. The fits of the experimental data to eq 2 gives $k_d = 205 \pm 10$ s^{-1}, $k_2/k_{-d} = 0.38 \pm 0.03$. The value of k_d is the rate constant for dissociation of **2**−Br$^+$/OTf$^-$ and is the maximum that **2**−Br$^+$/OTf$^-$ can react with any acceptor olefin under these conditions. The ratio k_2/k_{-d} represents the partitioning of the reactive coll−Br$^+$ intermediate between olefin and collidine capture. Unfortunately, absolute values for these rate constants cannot be exactly determined from these experiments, but the reactions are anticipated to be relatively fast given that the exchange of Br$^+$ between Ad=Ad−Br$^+$ and Ad=Ad proceeds with a second-order rate constant of 2×10^7 M^{-1} s^{-1} at 25 °C.[4] Exact values for these rate constants can be evaluated from the experiments with 4-penten-1-ol given below.
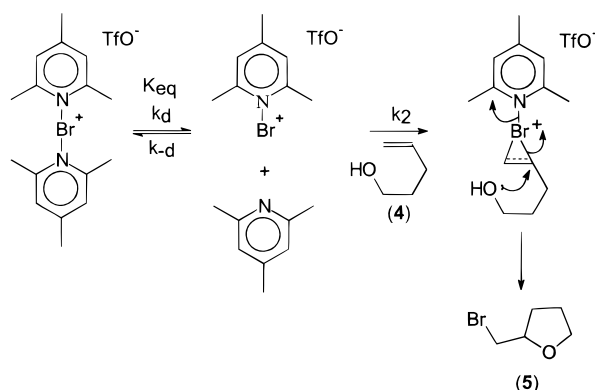
Table 2. Pseudo-First-Order Rate Constants for the Reaction of Bromonium Bis(*sym*-collidine) Bromonium Triflate (2−Br$^+$/OTf$^-$) with 4-Penten-1-ol (4) in C$_2$H$_4$Cl$_2$, T = 25 °C^a

10^4[collidine] (M)	[4-penten-1-ol] (M)	k_{obs} (s^{-1})
0.0	0.0005	37.05 ± 2.34
0.0	0.001	63.68 ± 1.84
0.0	0.0015	78.72 ± 3.17
0.0	0.002	90.89 ± 2.31
1.19	0.001	15.37 ± 0.12
2.62	0.001	8.79 ± 0.04
4.41	0.001	5.44 ± 0.03
1.22	0.0005	7.60 ± 0.19
2.69	0.0005	4.07 ± 0.02
4.61	0.0005	2.65 ± 0.01
7.25	0.0005	1.78 ± 0.01
11.41	0.0005	1.22 ± 0.01

^{a} [**2**−Br$^+$/OTf$^-$] = 5×10^{-5} M.

Reaction with 4-Penten-1-ol (4). Previous work from these[3a] and other laboratories[8] has shown that the reaction of 4-penten-1-ol with electrophilic halogen gives rise to a cyclized product, 2-bromomethyltetrahydrofuran (**5**). Br$^+$ transfer from **2**−Br$^+$/OTf$^-$ to **4** follows the mechanism[9] given in Scheme 2: given in eq 3

$$k_{obs} = k_2 K_{eq}[\mathbf{4}]/([coll] + K_{eq}) \qquad (3)$$

is the appropriate kinetic expression for the observed rate constant rate for disappearance of **2**−Br$^+$/OTf$^-$ assuming an equilibrium between it and the reactive intermediate, coll−Br$^+$, and rate-limiting formation of the coll−Br$^+$−**4** complex. NLLSQ fits of the k_{obs} values (25 °C, dichloroethane) given in Table 2 as a function of [collidine] and [4-penten-1-ol] give values for k_2 and K_{eq} of (4.5 ± 0.2) × 10^4 M^{-1} s^{-1} and (6.0 ± 0.4) × 10^{-5} M, respectively.

The fact that under the available experimental conditions we can analyze the respective Ad=Ad and 4-penten-1-ol data by steady state and equilibrium kinetics stems from the somewhat slower capture of coll−Br$^+$ by **4** than by Ad=Ad or collidine.[10] Taken collectively, these allow

(8) (a) Staninets, V. I.; Shilov, E. A. *Russ. Chem. Rev.* **1971**, *40*, 277. (b) Dowle, M. D.; Davies, D. I. *Chem Soc. Rev.* **1979**, 171−197. (c) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Chapter 6, Vol. 3. (d) Reitz, A. B.; Norley, S. O.; Marianoff, B. E.; Liotta, D.; Monahan, R. *J. Org. Chem.* **1987**, *52*, 4191 and references therein. (e) Cook, C. H.; Cho, Y. S.; Jew, S. s.; Jung, Y. H. *Arch. Pharmacol. Res.* **1985**, *8*, 39 and references therein.

(9) The process given in Scheme 2 does not explicitly deal with the events following rate-limiting formation of the **4**:Br$^+$−coll complex. Although the final product is the bromomethyltetrahydrofuran, we do not know whether it is produced from the corresponding bromo triflate, or by direct intramolecular capture of the bromonium ion. On the basis of our previous results, the latter seems more likely.

Scheme 3
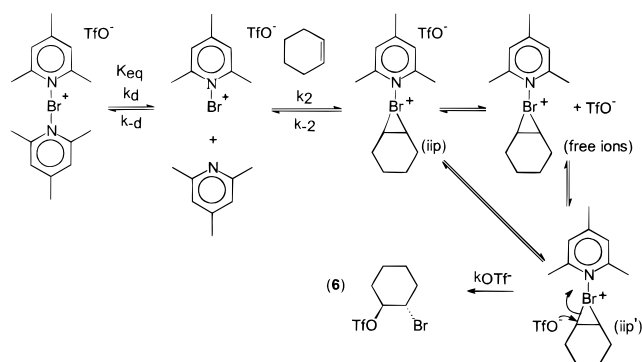
us to evaluate all the rate and equilibrium constants associated with Schemes 1 and 2.

Accordingly, the K_{eq} value computed from eq 3 should be the same as it is for the reaction with Ad=Ad, and a value for k_{-d} of 3×10^6 M^{-1} s^{-1} can be computed. From this value the k_2 rate constant for capture of coll−Br$^+$ by Ad=Ad is calculated to be 1.1×10^6 M^{-1} s^{-1}. Curiously, this rate constant is less than that for the reaction of the Ad=Ad−bromonium ion with Ad=Ad by about 10-fold, for reasons that are not clear.

Reaction with Cyclohexene. ^{1}H NMR analysis indicated that the reaction of **2**−Br$^+$/OTf$^-$ with cyclohexene in CD$_2$Cl$_2$ results in a quantitative formation of *trans*-1-bromo-2-(trifluoromethanesulfonyl)cyclohexane (**6**), an unstable material that previously could be made only with difficulty[11] or in low yield.[12] The colorless solutions are stable at room temperature for several hours but tend to darken on prolonged standing. No trace of any quaternary pyridinium product was observed, indicating that the pyridine nitrogen is significantly hindered by the presence of the 2- and 6-methyl groups of *sym*-collidine to such an extent than even triflate ion is a better nucleophile. This result is in qualitative agreement with the observations previously made by Lemieux and Morgan[5] for the reaction of bis(*sym*-collidine) halonium perchlorates and unsaturated carbohydrates. The allylic bromide 3-bromocyclohexene, possibly being formed by a base-catalyzed proton abstraction from the transient bromonium ion of cyclohexene or by collidine-promoted elimination of HOTf from of *trans*-1-bromo-2-(trifluoromethanesulfonyl)cyclohexane, was also not observed.

Kinetics of the Br$^+$ Transfer to Cyclohexene. The absorbance vs time profile for the reaction between **2**−Br$^+$/OTf$^-$ and excess cyclohexene was monitored in 1,2-dichloroethane at 25 °C in the presence of excess olefin. There are notable differences in the kinetic behavior for Br$^+$ transfer to cyclohexene relative to Ad=Ad or 4-penten-1-ol. The most striking feature is that the kinetic traces do not adhere to a first-order dependence on [**2**−Br$^+$/OTf$^-$]. It has been found that changes of [**2**−Br$^+$/OTf$^-$] vs time are better described by an equation second-order in [**2**−Br$^+$/OTf$^-$]. To explain this apparently unusual result the mechanism presented in Scheme 3 is suggested. The process consists of two reversible steps culminating in the formation of a cyclo-

hexene−Br$^+$−collidine complex followed by rate-limiting capture by triflate. In the dichloroethane solvent that heavily favors ion pairing, the triflate capture process is somewhat complicated, since it requires a translocation of the ions from their initial locations (OTf$^-$ syn to the Br$^+$−coll moiety in the intimate ion pair) to the reactive form (iip′) where trans displacement on the bromonium ion can occur. In principle this translocation can be done by rotation within the ion pair complex or by a dissociation/recombination process, as indicated in Scheme 3.[13] The observed second-order dependence on **2**−Br$^+$/OTf$^-$ suggests that product formation does not occur exclusively from rotation within the intimate ion pair but must involve a significant component of ion separation/recombination followed by trans collapse of cyclohexene−Br$^+$−coll and OTf$^-$. This was tested by adding external triflate ion to the reaction mixture and observing an acceleration of the overall reaction, ultimately leading to saturation kinetics at high added [tetrabutylammonium triflate]. Under conditions where the concentration of external triflate is much higher than [**2**−Br$^+$/OTf$^-$], the former can be considered as unchanged during the course of the reaction and the kinetic behavior should change to pseudo-first-order in [**2**−Br$^+$/OTf$^-$]. Indeed, this behavior was observed when the reaction was done in the presence of excess tetrabutylammonium triflate.

Given in Table 3 are the k_{obs} values for the reaction of [**2**−Br$^+$/OTf$^-$] with 5×10^{-3} M cyclohexene under conditions of excess but varying [tetrabutylammonium triflate] and at different added [collidine]. The k_{obs} vs [OTf$^-$] data can be plotted (not shown) to yield apparent saturation curves, but the limiting values appear be faster than observed for the dissociation of coll−Br$^+$−coll in the cases of Ad=Ad and 4-penten-1-ol. This points to a possible specific salt effect on the dissociation of the latter complex. Indeed, when the [Ad=Ad]/[**2**−Br$^+$/OTf$^-$] reaction was investigated at various [tetrabutylammonium triflate], a definite increase in the k_{obs} values was observed, the data being shown in Table 4. Given that these data were obtained under a saturating [Ad=Ad], the salt effect must increase the rate constant for dissociation of **2**−Br$^+$/OTf$^-$, probably by stabilizing the coll−Br$^+$ intermediate as a contact ion pair by association with OTf$^-$.

Therefore, for the cyclohexene/**2**−Br$^+$/OTf$^-$ reaction, the k_{obs} behavior as a function of increasing [triflate ion] stems from two processes. One is a saturation phenomenon explained by a change in the rate-limiting step from triflate trapping to formation of the cyclohexene bromonium ion complex as a function of increasing [OTf$^-$]; see Scheme 3. The other process stems from the salt effect on the dissociation of **2**−Br$^+$/OTf$^-$. Although the latter is not specifically shown in Scheme 3, its presence complicates direct evaluation of the data in Table 3. To simplify the numerical evaluation, we undertook the investigation of the reaction under conditions of varying [cyclohexene] at fixed [collidine], where the added [tetrabutylammonium triflate] was sufficient (7.5×10^{-4}M) to completely trap the cyclohexene−Br$^+$−collidine complex and prevent its reversal. Under these conditions, the process in Scheme 3 yields the same steady-state kinetic expression as that for Ad=Ad and **2**−Br$^+$/OTf$^-$

(10) When the kinetic data for reaction of **4** with **2**−Br$^+$/OTf$^-$ are fit to eq 2, we noticed that the fit was not satisfactory. Treatment according to eq 3 produced satisfactory fits.

(11) Zhang, C. Y.; Slebocka-Tilk, H.; Nagorski, R. W.; Alvarado, L.; Brown, R. S. *J. Org. Chem.* **1993**, *58*, 2122.

(12) Zefirov, N. S.; Koz'min, A. S.; Sorokin, V. D.; Zdankin, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1982**, *18*, 1546.

(13) For a detailed discussion of this process in bromination, see: Slebocka-Tilk, H.; Zheng, C. Y.; Brown, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 1347. Koerner, T.; Brown, R. S.; Gainsforth, J. L.; Klobukowski, M. *J. Am. Chem. Soc.* **1998**, *120*, 5628.

Table 3. Pseudo-First-Order Rate Constants for the Reaction of Bis(*sym*-collidine) Bromonium Triflate (2−Br+/OTf−) with Cyclohexene in C$_2$H$_4$Cl$_2$, T = 25 °C[a]

| 10^4[coll] (M)	10^4[Bu$_4$N$^+$TfO$^-$] (M)	10^3[cyclohexene] (M)	k_{obs} (s^{-1})
5	0	5	24.12 ± 0.00
5	1.25	5	44.75 ± 0.14
5	2.50	5	60.75 ± 0.53
5	3.75	5	70.78 ± 0.29
5	5.00	5	76.83 ± 0.19
1.25	0	5	34.06 ± 0.26
1.25	1.25	5	101.88 ± 1.65
1.25	2.50	5	140.40 ± 1.63
1.25	3.75	5	167.26 ± 1.34
1.25	5.00	5	200.90 ± 1.36
1.25	7.50	5	216.74 ± 3.45
2.5	0	5	31.73 ± 0.13
2.5	1.25	5	74.6 ± 1.2
2.5	2.50	5	100.7 ± 0.5
2.5	3.75	5	116.2 ± 0.8
2.5	5.00	5	139.9 ± 2.2
2.5	7.50	5	158.8 ± 1.4
10.0	0	5	13.8 ± 0.0
10.0	1.25	5	27.9 ± 0.2
10.0	2.50	5	37.3 ± 0.4
10.0	3.75	5	43.8 ± 0.3
10.0	5.00	5	48.8 ± 0.5
10.0	7.50	5	55.2 ± 0.8
0	7.50	0.5	153.7 ± 3.7
0	7.50	1.0	214.3 ± 1.2
0	7.50	2.19	273.4 ± 3.6
0	7.50	3.75	317.1 ± 4
2.5	7.50	0.5	35.5 ± 0.6
2.5	7.50	1.0	63.4 ± 0.9
2.5	7.50	1.5	91.1 ± 0.4
2.5	7.50	2.0	108.3 ± 1.2
2.5	7.50	4.08	156.4 ± 1.2
7.5	7.50	0.5	13.2 ± 0.2
7.5	7.50	1.0	24.8 ± 0.3
7.5	7.50	1.5	34.9 ± 0.8
7.5	7.50	3.06	61.8 ± 1.3
7.5	7.50	6.19	99.5 ± 1.0

[a] [2−Br+/OTf−] = 5 × 10^{-5} M.

Table 4. Pseudo-First-Order Rate Constants for the Reaction of Bromonium Bis(*sym*-collidine) Triflate (2−Br+/OTf−) with Ad=Ad in the Presence of Varying Tetrabutylammonium Bromide Concentration in C$_2$H$_4$Cl$_2$, T = 25 °C[a]

[Bu$_4$N$^+$OTf$^-$] (M)	k_{obs} (s^{-1})
0	216.63 ± 5.48
0.0005	323.57 ± 9.00
0.001	382.40 ± 8.28
0.0015	410.98 ± 9.70

[a] [2−Br+/OTf−] = 5 × 10^{-5} M; [Ad=Ad] = 1.25 × 10^{-3} M.

given in eq 2. NLLSQ fits of the data in Table 3 to eq 2 give values for k_2/k_{-d} of (5.2 ± 0.8) × 10^{-2} and a conditional k_d of 378 ± 10 s^{-1} which, as stated above, incorporates the specific salt effect on the dissociation of **2**−Br+/OTf−. The computed plots are shown in Figure 3. That this treatment is essentially quantitatively correct[14] is verified by comparison of the conditional k_d with that obtained from the Ad=Ad reaction (359 s^{-1}) at the same concentration of added tetrabutylammonium triflate (7.5 × 10^{-4} M).

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(14) The dissection of the salt and saturation effect can be done in an alternative but more complex way as follows: To factor out the salt effect from the saturation effects of triflate, we computed the salt accelerating effect on k_d from the Ad=Ad data in Table 4, under the assumption that the effect is insensitive to the nature of the trapping olefin. For every concentration of triflate, the k_{obs} data in Table 3 were scaled to reflect the salt effect on k_d. These corrected values were then fit to a generic saturation equation by NLLSQ. The computed fits show clear saturation kinetics at the highest [triflate], indicating that (a) the salt effect has been removed and (b) that the saturating [triflate] is not higher that 5 × 10^{-4} M.
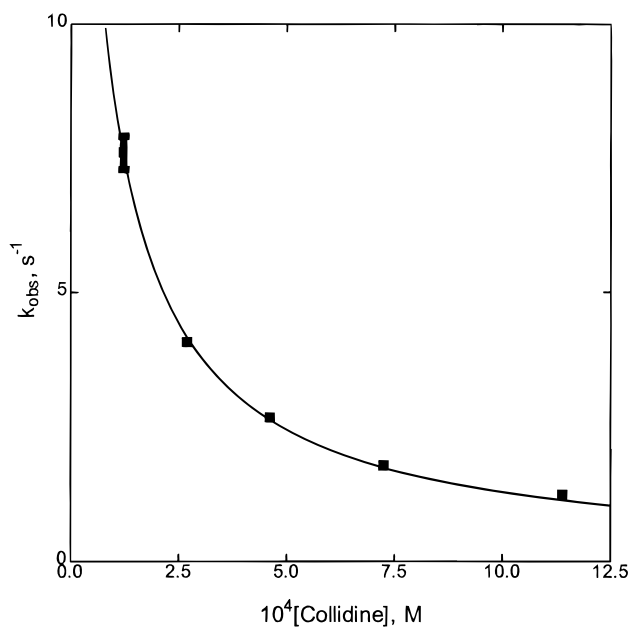
Figure 2. Plots of observed pseudo-first-order rate constants for the reaction of **2**−Br+/OTf− (5 × 10^{-5} M) with 4-penten-1-ol (5 × 10^{-3}M) as a function of [collidine] in 1,2-dichloroethane at 25 °C. Lines through the data are computed by NLLSQ fits to eq 3.
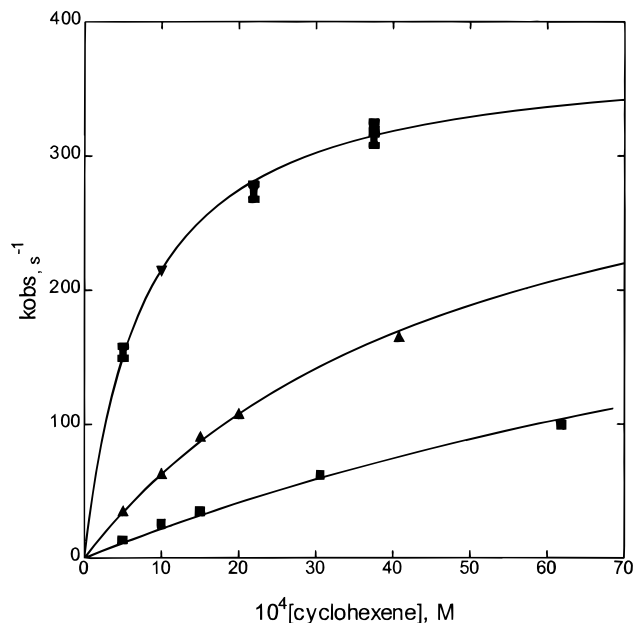
Figure 3. Plots of observed pseudo-first-order rate constants for the reaction of **2**−Br+/OTf− (5 × 10^{-5} M) with cyclohexene as a function of [cyclohexene] at different concentrations of collidine (■, 0.0 M; ▲, 2.5 × 10^{-4} M; ▼, 7.5 × 10^{-4} M) at [triflate] equal to 7.5 × 10^{-4} M in 1,2-dichloroethane at 25 °C. Lines through the data are computed by NLLSQ fits to eq 2.

Finally, the above data allow us to determine the rate constant for attack of cyclohexene on coll−Br+ assuming that the salt effect of added tetrabutylammonium triflate does not appreciably affect the k_{-d} and k_2 terms. Given a k_{-d} of 3 × 10^6 M^{-1} s^{-1}, the cyclohexene capture rate constant is 1.5 × 10^5 M^{-1} s^{-1}. Thus the relative reactivities toward coll−Br+ of collidine, Ad=Ad, cyclohexene, and 4-penten-1-ol are 66, 24, 3, and 1, showing an attenuated sensitivity to the nature of the olefinic nucleophile. This can be contrasted to the situation for

transfer of Br^+ from the Ad=Ad bromonium ion to Ad=Ad, cyclohexene, and 4-penten-1-ol, the respective values being 2×10^7, 1.1, and 3.4 $M^{-1} s^{-1}$.[3] The difference can readily be explained by the fact that the transfer from coll$-Br^+$ to the alkene is largely exothermic, having an early TS with little charge development on the alkene, while the transfer from Ad=Ad$-Br^+$ to the alkenes is thermoneutral (in the case of Ad=Ad) or largely endothermic and in the latter case must proceed through a late transition state with a large degree of charge on the alkene.

Reaction of Bromo Triflates with Nucleophiles. Preliminary experiments indicate that bromo triflates prepared from transfer of Br^+/OTf^- from **2**$-Br^+/OTf^-$ to acceptor alkenes can be used for convenient preparation of *trans*-1-bromo-2-X substituted alkanes, where X = nucleophile. For example, *trans*-1-bromo-2-(trifluormethanesulfonyl)cyclohexane was prepared in situ as above by reacting equimolar cyclohexene and **2**$-Br^+/OTf^-$ in CD_2Cl_2. After 5 min the ^1H NMR showed no trace of starting materials, the cyclohexene vinyl protons being replaced by signals at δ 4.95 and 4.10 attributable to C*H*OTf and C*H*Br, respectively.[11] The mixture was then treated with a CD_2Cl_2 solution containing a roughly 50% excess of tetrabutylammonium bromide or acetate and the ^1H NMR recorded again after 5 min. No trace of the bromo triflate could be observed, the only products being *trans*-1,2-dibromocyclohexane (C*H*Br, δ 4.40) or *trans*-1-bromo-2-acetoxycyclohexane (C*H*Br δ 4.85, C*H*OAc δ 4.99).[11]

A similar reaction was performed treating 1-octene with equimolar **2**$-Br^+/OTf^-$ in CD_2Cl_2. Immediately after the addition, the ^1H NMR was recorded and indicated the presence of 85% of 1-bromo-2-trifluormethanesulfonyloctane (C*H*OTf δ 5.06, C*H*$_2$Br δ 3.67, 3.61) and 15% of the isomeric 2-bromo-1-trifluoromethanesulfonyloctane (C*H*$_2$OTf δ 4.71, 4.65, C*H*Br δ 4.18). Treatment of this solution with a CD_2Cl_2 solution of tetrabutylammonium bromide gave, after 5 min, only 1,2-dibromooctane (C*H*Br δ 4.21, C*H*$_2$Br δ 3.85, 3.68).

Previous work[11] has shown that the solvolysis of 1-bromo-2-trifluormethanesulfonylcyclohexane in methanol and acetic acid proceeds via a N_DI-assisted formation of the corresponding cyclohexenyl bromonium ion that subsequently yeilds the *trans*-bromo solvate product. For the latter studies the half-time of the solvolysis is about 30 s in methanol and 300 s in acetic acid, which is comparable to or slower than the reactions described here. From the present studies in CD_2Cl_2, the fact that the products are trans rules out an S_N2 displacement of the OTf and indicates that the in situ prepared bromo triflates are reactive in chlorinated hydrocarbons as sources of bromonium ions. Further work is underway to investigate the scope and limitations of this surprisingly facile reaction.