Electrophilic Bromination of Ethylene and Ethylene-d_4. A Combined Experimental and Theoretical Study

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Abstract: The deuterium kinetic isotope effect (dkie) for the electrophilic bromination of ethylene-h_4 and ethylene-d_4 in methanol and dichloroethane (DCE) at 25 °C has been determined using mass spectrometry. The dkie's are inverse, that in methanol being $k_H/k_D = 0.664 \pm 0.050$ and that in DCE being $k_H/k_D = 0.572 \pm 0.048$. A product study of the bromination of *trans*-ethylene-d_2 in dichloroethane indicates that the addition is trans. Computations of the expected equilibrium deuterium isotope effect (EIE) for the process $C_2H_4 + Br^+ \rightleftharpoons C_2H_4-Br^+$ using density functional theory indicate that the EIE is also inverse at $K_H/K_D = 0.63$. Detailed analyses of the molar partition functions and the zero-point energies for the various vibrational modes in the ground and ion states indicate that the major contributor to the EIE is the creation of a new mode in the ion, termed the CH_2-symmetric twist, that arises from the loss of the rotational freedom about the C−*C* axis in ethylene. In the absence of this new mode, the computed EIE is normal, $K_H/K_D = 1.12$. The computations also indicate that the ion state undergoes very little rehybridization of the carbons, the sum of the H−C−H and H−C−C angles at each carbon being 357.3°. A discussion is presented concerning the detailed sequence of events contributing to the reaction mechanism in both solvents and how each of these might contribute to the dkie.

Introduction

Considerable recent effort has been expended in detailed study of electrophilic bromination of congested olefins which, by virtue of their steric crowding, retard the passage of the bromonium ion intermediates to normal products of addition.[1] Particularly well-studied is the case of adamantylideneadamantane, the bromination of which was first reported by Wynberg and co-workers;[2] this olefin currently stands alone in chemistry as producing the only room-temperature stable, structurally characterized three-membered bromonium and iodonium ions.[3] Less well studied is the bromination of the simplest olefin, ethylene, which surely must form a highly unstable bromonium ion with almost no steric barrier to product formation. This olefin is technically difficult to handle because it is a gas at room temperature, so reliable kinetic data are sparse.[4] Nevertheless, because of its simplicity, high degree of symmetry, and the fact that one can substitute all four positions with deuterium, ethylene is an ideal candidate for experimental investigation of the secondary deuterium kinetic isotope effects (dkie) for various reactions which are also amenable to detailed theoretical analysis.

Secondary dkie's have been determined for a variety of electrophilic processes[5] including brominations of styrenes,[6] stilbenes,[7] 7,7′-norbornylidenenorbornane,[8] and cyclohexene.[9] In general, the observed effect for α-substitution is inverse which is commonly explained by invoking isotope-sensitive changes in the out of plane bending frequencies of the α-C−L bonds of the alkene in passing from an sp^2 ground state to an sp^3-like transition state.[10,11] Strausz and co-workers have offered another explanation for the inverse dkie observed for thiirane formation from addition of S atoms to ethylene, namely the creation of new isotopically sensitive vibrations in the transition state that were not present in the ground state.[12] In fact, recent work by Bender[13a] has shown that the inverse equilibrium isotope effect of $K_H/K_D = 0.7$ for reversible binding of C_2L_4 to (μ-η^1,η^1-C_2L_4)-

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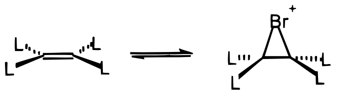
$Os_2(CO)_8$ is mostly due to a zero-point energy factor from a vibrational mode (termed a b_2-symmetry twist) for the complexed ethylene which is not present in free ethylene. Herein we report the results of an experimental study of the electrophilic addition of Br_2 to ethylene and ethylene-d_4 in methanol and dichloroethane which show that (a) there is a large inverse dkie of $k_H/k_D \sim 0.6$ for bromination in both methanol and dichloroethane and (b) the addition process in dichloroethane gives *trans*-1,2-dibromoethane. We also give a detailed theoretical analysis of the origin of the dkie based on density functional theory (DFT) computations of the equilibrium isotope effect (K_H/K_D) for the process



(1)

which is best interpreted in terms of the Strausz model.

Experimental Section

(a) Materials. Methanol (Sigma-Aldrich, 99.9% ACS HPLC grade) was purified as previously described.[14] Ethanol (Sigma-Aldrich, absolute grade) and 1,2-dichloroethane (Sigma-Aldrich, 99.8% HPLC grade) were both used without purification; however, fresh bottles of each were used and precautions were taken to minimize moisture contamination. Ethylene (Matheson of Canada Ltd., CP grade), ethylene-d_4 (Merck Sharp & Dohme), and *trans*-ethylene-d_2 (Merck Sharp & Dohme) were also used as supplied.

(b) Dkie. The secondary α-deuterium kie's were determined using a competitive technique[15] in which approximately equal amounts of ethylene and ethylene-d_4 were incompletely brominated (20−30%). The fraction of reaction, initial isotopic ratio, and final isotopic ratios were determined by gas chromatography−mass spectrometric analysis (GC−MS). In a typical experiment a stock solution was prepared by adding ethylene (1.0 mmol), ethylene-d_4 (1.0 mmol) and methane (2.5 mmol) to a specially designed vessel containing degassed purified methanol (40.0 mL) affixed to a vacuum line. The gas additions were accomplished by monitoring the pressure in a vacuum line of known volume (74.77 mL) and then freezing the sample over the solvent using liquid nitrogen.

Using a 2-mL gas-tight syringe a sample of the stock solution (1.80 mL) was withdrawn and injected into a 2-mL amber vial fitted with a Teflon-coated septum. This sample was immediately analyzed using GC−MS to determine the initial ethylene/ethylene-d_4 ratio and the ratio of methane to total ethylene. To this same vial was introduced 100 μL of a 0.11 M bromine in purified methanol solution via syringe. After mixing and allowing sufficient time for the reaction to be completed (10 min), the ethylene/ethylene-d_4 and total ethylene/methane ratios were determined by GC−MS. The analyses were performed on a Fisons Quattro mass spectrometer coupled to a Fisons GC 8000 gas chromatograph [Plot GS-Q column, Chromatographic Specialties Inc. (30 m, 0.53 mm i.d.), $T = 40$ °C, He carrier (2.0 psi)]. Each sample was subject to three or four (0.2-mL) independent analytical runs. Quantitative analysis was done by integration of the mass peaks (**15** for methane, **27** for ethylene, **30** for ethylene-d_4). Each isotope effect was confirmed by three or four independent experiments.

(c) Product Study. The products for the bromination of *trans*-ethylene-d_2 in 1,2-dichloroethane were determined by ^1H and ^2H NMR analysis of the products obtained from the elimination of the bromination products. In a typical experiment 5.0 mL of a 0.1 M Br_2 in 1,2-dichloroethane solution and a stirring bar were added to a 25-mL round-bottom flask which was wrapped in foil to prevent exposure to light. The flask was attached to a vacuum line and the contents frozen using liquid nitrogen. After evacuation of the line a small amount of *trans*-ethylene-d_2 was frozen over the bromine solution. The flask was allowed to warm to room temperature and the contents stirred (15 min). If the bromine color persisted an additional amount of *trans*-ethylene-d_2 was added to the reaction vessel in a similar manner (vide supra). When no bromine color could be detected, the reaction vessel was removed from the vacuum line and the excess 1,2-dichloroethane was removed by fractional distillation (bp 83 °C at 760 mmHg, lit. 83.5 °C at 760 mmHg).[16] The remaining solution was treated with an excess of a KOH (0.063 mol) dissolved in ethanol.[17] The excess ethanol/KOH solution was used to ensure that all of the 1,2-dibromoethane and any residual 1,2-dichloroethane reacted. After sufficient time (2 h) the expected products, vinyl bromide (bp 15.8 °C)[16] and vinyl chloride (bp −13.4 °C),[16] were distilled at room temperature by flushing the flask with an argon stream and collecting the effluent in a vessel containing CD_2Cl_2 (0.5 mL) which was cooled in a dry ice/2-propanol bath. This solution was then analyzed by ^1H NMR. The products were then distilled (0 °C) into CH_2Cl_2 (0.5 mL, vide supra), and the ^2H NMR was obtained. The instrument used for the analyses of the reaction mixtures was a Bruker 400-MHz NMR.

Computational Methods

(a) Methodological Details. A computational study was undertaken to examine the equilibrium deuterium isotope effect (EIE) for the equilibrium involving the formation of the ethylene bromonium ion from ethylene plus Br^+. The isotope effects were modeled using results obtained with the density functional theory (DFT) as found in the Gaussian 94[18] program. Gradient-corrected (nonlocal) functionals are very successful in kinetic isotope effect studies,[19] and previous work with the cyclohexene system[9b] has shown that various functionals produce quite similar results. Therefore only one set of gradient-corrected functionals was used in this work: Becke's 3-parameter exchange[20] functional was combined with the Lee, Yang, and Parr[21] correlation functional, denoted as B3LYP. To minimize the computational effort, the compact effective core potentials of Stevens et al.[22] were used. The basis set for carbon was used in the original double-ζ contraction (31/31) while that for bromine was modified to give a quadruple-ζ contraction (2111/2111). A single d-type polarization function was added to carbon ($\alpha_d = 0.80$) and bromine ($\alpha_d = 0.389$). The (31) basis set from Huzinaga's (4s)[23] expansion was used for the hydrogens with a single p-type polarization function ($\alpha_p = 1.1$) added. As the present study focuses on the effect of hydrogens on the vibrational structure and on the proximity and interactions of hydrogens with the reaction site, the addition of polarization functions on hydrogens is necessary to get a better description of these atoms.

(b) System Studied. The ethylene bromonium ion is not a transition state in the bromination reaction, but rather a minimum. In solution, as expected, the transition state is calculated to be an ion pair with bromide having either C_2 or C_{2v} symmetry depending on the solvent.[24]

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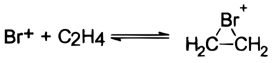
Table 1. Secondary α-Deuterium kie's for the Bromination of Ethylene in Methanol and 1,2-Dichloroethane at 25 °C

(k_H/k_D) methanol	(k_H/k_D) 1,2-dichloroethane
0.686 ± 0.052[a]	0.518 ± 0.19[a]
0.603 ± 0.053	0.635 ± 0.21
0.703 ± 0.029	0.507 ± 0.09
	0.566 ± 0.18
av 0.664 ± 0.05[b]	av 0.572 ± 0.048[b]

[a] The error calculated using eq 4. [b] The standard deviation of the mean.

In the gas phase, a transition state has been reported,[25] but at the RHF/3-21G level, its imaginary frequency does not correspond to Br^- dissociation; reoptimized at the RHF/6-311G(d) level, it is a minimum. Since the transition state in solution comprises the developing ions, the likelihood of finding a gas-phase transition state is small due to the lack of charge separation in this environment. Indeed, it is well-known that electrophilic bromination does not occur in the gas phase for this same reason.[26]

Rivail and co-workers looked at the first step of ethylene bromination in water in a recent molecular dynamics study using the novel QC/MM MD method.[24] Their results confirm that the reaction has a late transition state, with the ions already formed. According to the Hammond principle,[27] one can make the assumption that the transition state resembles the ethylene bromonium ion more than it does the ethylene and bromine reactants, as clearly shown in Figure 6 of ref 24. The structure of the ethylene bromonium ion can then be used as an adequate representation of the genuine transition state. In the present work, the calculations were done for the equilibrium isotope effect (EIE) for the equilibrium involving the formation of the reaction intermediate $[C_2H_4Br]^+$



For the equilibrium

$$X \rightleftharpoons Y$$

the EIE is calculated in the gas phase, rigid rotor, harmonic oscillator approximation according to[27]

$$K_H/K_D = \frac{Q_Y/Q_X}{Q_{Y'}/Q_{X'}} \exp[-(\delta E_0^Y - \delta E_0^X)]/RT \qquad (2)$$

where δE_0^X is the difference between the total molar vibrational zero-point energies for the light and heavy reactant compounds X and X′, δE_0^Y is the difference between the total molar vibrational zero-point energies for the light and heavy product compounds Y and Y′, and Q is the total molar partition function. The Br^+ contribution to the partition coefficient is canceled out in the term $(Q_Y/Q_X)/(Q_{Y'}/Q_{X'})$ and will not be addressed further.

Results and Discussion

(a) Kinetic Isotope Effects (kie's). Given in Table 1 are the secondary α-deuterium kie's for the bromination of ethylene and ethylene-d_4 in methanol and 1,2-dichloroethane at 25 °C. These were determined by mass spectrometric analysis of a reaction mixture following incomplete bromination of approximately equal amounts of ethylene and ethylene-d_4 in the same reaction vessel.[15] This method requires that the ratio of ethylene and ethylene-d_4 be exactly determined before and after bromination which was accomplished by monitoring the intensities of the mass ions relative to an internal standard of CH_4 (**15** for methane, **27** for ethylene, **30** for ethylene-d_4).[28] These mass ions were chosen for analysis rather than the M^+ peaks (**16** for methane, **28** for ethylene, **32** for ethylene-d_4) for three reasons: (i) since both ethylene and ethylene-d_4 contain a mass 28 ion and these two compounds could not be separated by the gas chromatography column, it is important to choose mass ions that are exclusive to each compound, i.e., **27** for ethylene and **30** for ethylene-d_4; (ii) due to the fluctuations in O_2 and N_2 (masses 32 and 28) entering the mass spectrometer, accurate determination of the isotopic ratio of the ethylenes could only be obtained by choosing different mass ions; and (iii) the mass fragments chosen all have significant intensities (80% (**15** in methane), 65% (**27** in ethylene), 65% (**30** in ethylene-d_4)). In addition to the ethylene/ethylene-d_4 ratios, the extent of bromination is also required for this competitive technique and was determined from the ratio of total ethylene to an internal standard (methane). The kie can then be calculated using eq 3:

$$\text{kie} = \frac{k_H}{k_D} = 1 + \left(\log\left[\frac{R_f}{R_0}\right] \Big/ \log\left[(1-f)\frac{(1+R_0)}{(1+R_f)}\right]\right) \qquad (3)$$

where R_o and R_f are the ethylene/ethylene-d_4 ratios initially and after some fraction, f, of bromination, respectively. The errors for the individual kie's were calculated by propagation of error using eq 4:

$$\Delta\text{kie} = \left[\frac{\log\left(\frac{R_f}{R_0}\right)}{\log\left[(1-f)\frac{(1+R_0)}{(1+R_f)}\right]}\right] \times \left[\left(\frac{(0.434)\left[\left(\frac{\Delta R_f}{R_f}\right)^2 + \left(\frac{\Delta R_0}{R_0}\right)^2\right]^{1/2}}{\log\left(\frac{R_f}{R_0}\right)}\right)^2 + \left(\frac{(0.434)\left[\left(\frac{\Delta R_f}{R_f}\right)^2 + \left(\frac{\Delta R_0}{R_0}\right)^2 + \left(\frac{\Delta f}{f}\right)^2\right]^{1/2}}{\log\left[(1-f)\frac{(1+R_0)}{(1+R_f)}\right]}\right)^2\right] \qquad (4)$$

where ΔR_o, ΔR_f, and Δf are the standard deviations in determining R_o, R_f, and f, respectively.

There are two observations of note from the data in Table 1: (i) the α-kie's in both solvents are large and inverse and (ii) within experimental error they are of similar magnitude. Both dkie's are consistent with a rate-limiting transition state for the bromination where there is considerable rehybridization of the olefinic carbons,[10,11] but the experimental data alone do not allow one to determine the structure of the transition state. As will be shown later, there are more satisfying interpretations of the dkie's.

(b) Mechanistic Possibilities. The generalized pathways for alkene bromination are shown in Scheme 1. Across the top of the scheme is the normal mechanism proceeding via charge transfer complex (CTC) and bromonium ion intermediates. The lower half of the scheme corresponds to a preassociation mechanism occurring in the presence of a nucleophilic solvent

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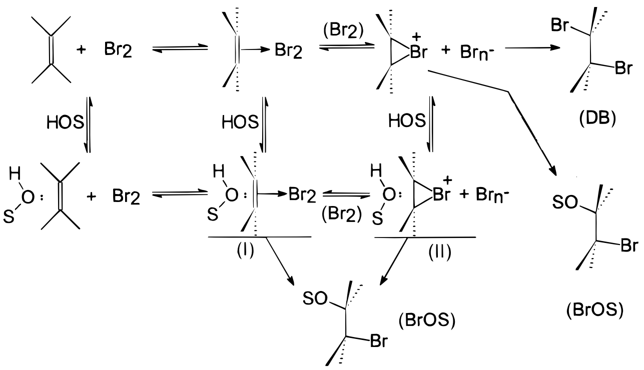
Scheme 1



which leads to bromo−solvate products and is likely followed when the bromonium ions are very unstable (vide infra).

In hydroxylic solvents such as methanol or acetic acid, electrophilic bromination of alkenes is usually second-order overall, first order in [Br_2], while in chlorinated hydrocarbon solvents such as 1,2-dichloroethane, the reaction is generally third order, second order in [Br_2].[29,30] In a nucleophilic solvent like methanol it is known that bromonium ion intermediates such as those produced from Br_2 addition to cyclohexene, cyclopentene, stryrene, or tetramethylethylene are very unstable, the lifetimes being $\sim 10^{-9}-10^{-11}$ s.[31] Due to the lack of alkyl group stabilization, the bromonium ion of ethylene must be less stable yet, so that there is a real question as to whether it can be produced as a discrete intermediate during the reaction. Ruasse et al. have commented extensively on the role of solvent nucleophilic assistance in electrophilic brominations.[32] Their recent work supports a situation where there is a preassociation mechanism[33] for the bromination of electron-deficient stilbenes in nucleophilic solvents including methanol. That mechanism is shown in Scheme 1 as the lower pathway where association of the methanol with the alkene occurs prior to the formation of the bromonium ion and would be enforced if ion pair return of the Br^- and bromonium ion is faster than diffusional separation followed by solvent capture of the free ion. Given the anticipated instability of the ethylene bromonium ion, a preassociation mechanism is likely, and if this course is followed, the rate-limiting step for the reaction could be the formation of the HOS:bromonium:Br^- complex or its breakdown to methoxy bromide product. In either event, the transition state would have to be close to the bromonium ion. If the ion is sufficiently unstable that the preassociation mechanism cannot occur, then in the limit the reaction will involve a concerted solvent attack on the CTC analogous to the S_N2 attack in nucleophilic displacement reactions.[34] In this case one anticipates small secondary dkie's.[11]

There are some experimental data that indicate that the electrophilic addition of Br_2 to ethylene proceeds much as it does with other aliphatic alkenes. On the basis of rate data for bromination of methylated ethylenes in methanol given by Dubois and Mouvier[35] and data in acetic acid and tetrachloroethylene given by Modro, Schmid, and Yates,[36] one can construct linear free energy relationships relating the log *k* and number of methyl groups attached to the double bond.[37] That ethylene lies on these lines indicates that it adheres to the same mechanism for bromination in a given solvent as do the other methylated ethylenes. This probably rules out an S_N2 displacement by methanol on the CTC but does not rule out a preassociation mechanism since that could occur to greater or lesser extents with the others as well, depending on the inherent stability of their bromonium ions.

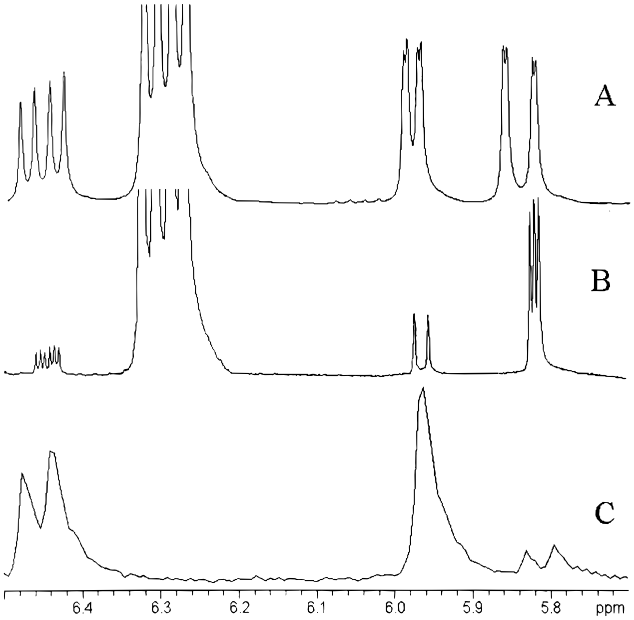


Figure 1. ^1H and ^2H spectra of the products obtained from the bromination and subsequent elimination of ethylene in DCE. (A) Bromination and elimination of ethylene. (B and C) Bromination and elimination of *trans*-ethylene-d_2.

It can safely be concluded from the bromination results in tetrachloroethylene[36] that the bromination of ethylene in the related solvent, DCE, is third-order overall, second order in [Br_2]. According to the pathway presented at the top of Scheme 1, the second Br_2 assists in the ionization of the CTC to form a bromonium ion/Br_3^- pair. Due to the instability of the ethylene bromonium ion, the contact ion pair in DCE must be short-lived so the question arises as to how the product is actually formed in this solvent. To do so, the nascent contact ion pair must translocate the Br_3^- or bromonium ion 180° from their initial positions to a configuration where displacement of the CH_2-Br^+ bond by Br^- can occur to form the dibromide product. On the basis of the rotational correlation times for molecules rotating by Brownian motion,[38] this process could take $10^{-10}-10^{-11}$ s. Even if the lifetime of the ion is comparable to, or even 100-fold shorter than, the rotational correlation, product formation could occur by leakage through this pathway and rotation would then be the rate-limiting step.

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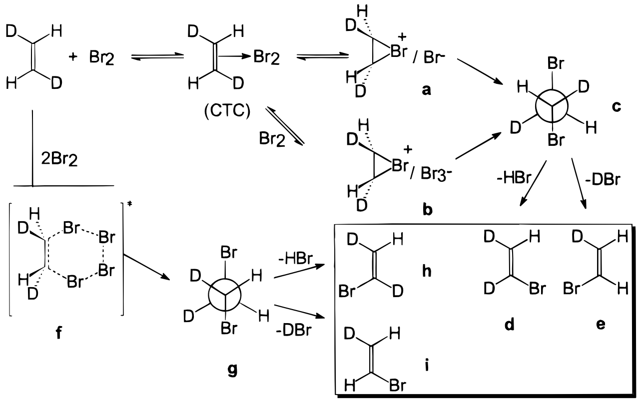
[34] It is generally considered[30] that this is an unlikely event since it has never been documented. The lack of evidence, however, is not as compelling an argument as one would like.

[35] Dubois, J. E.; Mouvier, G. *Tetrahedron Lett.***1963**, *20*, 1325.

[36] Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.

[37] The slopes and intercepts for these log *k* vs number of methyl groups are as follows: methanol, 1.64, 0.95, $r^2 = 0.9831$; acetic acid, 1.86, −0.64, $r^2 = 0.998$; tetrachloroethane, 2.19, 1.34, $r^2 = 0.987$. This form of the linear free energy relationship is equivalent to the form used by Dubois and Mouvier, who plotted log *k* vs $\sum\sigma^*$, where the latter term refers to the sum of the Taft σ^* terms for the methyl groups, regardless of their position on the double bond.

Scheme 2

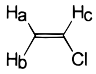
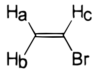
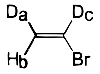
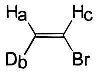


Finally, if the bromonium ion has lifetime in DCE too short to allow its existence, product formation must proceed by an alternative mechanism. A possible process could involve two Br_2 molecules and one ethylene (or the CTC and one Br_2), leading to *cis*-1,2-dibromoethane plus Br_2, by either a concerted pathway or a two-step pathway involving an open β-bromo cation. We have two pieces of data that support a bromination process in DCE that proceeds by bromonium ion/Br_3^- intermediates leading to trans dibromide products. The first is the fact that ethylene fits the linear free energy relationship described for bromination of substituted ethylenes in tetrachloroethane,[36,37] so that if these are considered to proceed via bromonium ions, then so too does ethylene. Second, we have determined that the product of the addition of Br_2 to ethylene in DCE is *trans*-1,2-dibromoethane. These experiments are described below.

(c) Product Study. Given in Figure 1 are the ^{1}H and ^{2}H NMR spectra obtained from a product study for the bromination and subsequent elimination of *trans*-ethylene-d_2 along with the ^{1}H NMR results obtained for a similar experiment using ethylene-h_4 in 1,2-dichloroethane. This study was undertaken to ascertain if the bromination of ethylene proceeded by a *trans*-addition through a bromonium ion intermediate (a or b, Scheme 2) or by some cyclic process leading to *cis*-addition (f, Scheme 2). One-to-one intermediates leading to cis addition products have been computed[39] for chlorination and bromination of ethylene and found experimentally[40] for the fluorination of olefins.

In a control experiment a small amount of ethylene was subjected to the bromination and elimination process, the results of which are presented in Figure 1A and Table 2.[41] The ^{1}H NMR indicated the only products to be vinyl chloride, which is expected because all of the DCE solvent could not be removed prior to the elimination step, and vinyl bromide, which is the expected product from the elimination of 1,2-dibromoethane, the bromination product of ethylene.

Table 2. ^{1}H and ^{2}H NMR Results Obtained for Bromination of *trans*-Ethylene-d_2 and Subsequent Elimination from the 1,2-Dibromo-1,2-dideuterioethane in 1,2-Dichloroethane along with the ^{1}H NMR for the Same Process Using Ethylene

				
H_a ppm	5.43 (5.40)[a]	5.98 (5.97)	D_a = 5.96[b]	5.96
H_b ppm	5.50 (5.48)	5.84 (5.84)	5.82	D_b = 5.81[b]
H_c ppm	6.30 (6.36)	6.45 (6.44)	D_c = 6.45[b]	6.44
J_{ac} Hz	7.0 (7.4)	7.2 (7.1)		7.2
J_{bc} Hz	14.6 (14.5)	14.8 (14.9)	J_{HD} =2.3 Hz	
			J_{DH} = 2.3 Hz[b]	

[a] The numbers in the parentheses represent the literature values for the chemical shifts and the coupling constants (see ref 41). [b] These are the chemical shifts and coupling constants from the deuterium NMR (Figure 1C).

Table 3. Geometry of Ethylene and the Ethylene Bromonium Ion

	ethylene		ethylene bromonium ion
parameter[a]	DFT[b]	exptl[c]	DFT[b]
C−C	1.364	1.339	1.472
C−H	1.107	1.087	1.104
C−Br			2.062
H−C−H	117.4	117.3	108.0
C−C−H	121.3	121.3	119.7
H−C−Br			118.5

[a] Bond lengths in Å, bond angles in deg. [b] This work. [c] Experimental r_z and θ_z from microwave studies.[44]

Two bromination products are possible from the bromination of *trans*-ethylene-d_2. The first, *meso*-1,2-dibromoethane-d_2 (**c**, Scheme 2), is a result of trans addition, (**a** or **b**, Scheme 2). Cis addition of bromine to *trans*-ethylene-d_2 through either a cyclic, concerted, or stepwise transition state (**f**, Scheme 2) forms only *d,l*-1,2-dibromoethane-d_2. Elimination of *meso*-1,2-dibromoethane-d_2 and *d,l*-1,2-dibromoethane-d_2 could result in four possible vinyl bromides, **d** or **e** and **h** or **i** (Scheme 2), respectively. It is assumed that these products are obtained from trans eliminations, which, in the absence of special effects, are greatly favored over cis eliminations in these systems.[42] The NMR results (Figure 1B) clearly indicate that the only products present are those from HBr and DBr elimination from *meso*-1,2-dibromoethane-d_2: this finding is confirmed by deuterium NMR (Figure 1C). Thus, the bromination of ethylene in DCE gives exclusive trans addition, probably via a two-step mechanism involving the bromonium ion. The relative areas of the ^{1}H and ^{2}H NMR peaks were used to obtain a primary isotope effect of 3.3 ± 0.5 for the elimination which is consistent with results found for similar processes.[43]

(d) Computations. The structural parameters for ethylene and the ethylene bromonium ion are collected in Table 3 and compared with available experimental data.[44] For ethylene, the DFT bond lengths are larger than experimental ones by about 0.02 Å, possibly due to the use of either ECPs and their associated basis sets or the B3LYP combination of functionals.

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(38) According to the following: Abragam, A. In *Principles of Nuclear Magnetism*; Clarendon Press: Oxford, U.K., 1961; p 300. The rotational correlation time for a molecule of radius a, rotating by Brownian motion in a solvent of viscosity η, is $\tau_1 = 4\pi\eta a^3/kT$, where k is Boltzmann's constant and T is the temperature in Kelvin. If the radius of the bromonium ion is 3 Å and the viscosity is that of methylene chloride (0.45×10^{-3} N m^2 s), the time for reorientation of one axis of the molecule through an angle of 1 rad (57°), or τ_1, is 38×10^{-12} s. The time for rotation by 180° would be larger.

(39) Yamabe, S.; Minato, T.; Inagaki, S. *J. Chem. Soc. Chem. Comm.* **1988**, 532.

(40) Rozen, S.; Brand, M. *J. Am. Chem. Soc.* **1986**, 51, 3607.

(41) (a) Banwell, C. N.; Sheppard, N. *Mol. Phys.* **1960**, 3, 351. (b) Bishop, E. O.; Richards, R. E. *Mol. Phys.* **1960**, 3, 114. (c) Mayo, R. E.; Goldstein, J. H. *J. Mol. Spectr.* **1964**, 14, 173. (d) Schaefer, T.; Schneider, W. G. *Can. J. Chem.* **1960**, 38, 2066. (e) Whipple, E. B.; Stewart, W. E.; Reddy, G. S.; Goldstein, J. H. *J. Chem. Phys.* **1961**, 34, 2136.

(42) (a) Skell, P. S.; Hall W. L. *J. Am. Chem. Soc.* **1963**, 85, 2851. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; pp 982−1006.

(43) Smith, P. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, Vol. 2, 1974; pp 230−269.

(44) Hirota, E.; Endo, Y.; Saito, S.; Yoshida, K.; Yamaguchi, I.; Machida, K. *J. Mol. Spectrosc.* **1981**, *89*, 223.

Table 4. Assignment of Vibrational Modes for Ethylene[a]

mode	symmetry[b]	DFT	exptl	assignment
1	b_{2u}	793	843	CH_2 sym rock
2	b_{2g}	900	959	CH_2 sym wag
3	b_{3u}	939	969	CH_2 as wag
4	a_u	1021	1044	CH_2 as twist
5	b_{3g}	1167	1245	CH_2 as rock
6	a_g	1342	1370	CH_2 sym scissors
7	b_{1u}	1413	1473	CH_2 as scissors
8	a_g	1692	1655	CC stretch
9	b_{1u}	3122	3147	CH stretch as (CH_2 sym)
10	a_g	3134	3153	CH stretch sym (CH_2 sym)
11	b_{3g}	3202	3232	CH stretch as (CH_2 as)
12	b_{2u}	3229	3234	CH stretch sym (CH_2 as)

[a] Harmonic vibrational frequencies in cm^{-1}. [b] Ethylene is located in the *yz* plane, with CC bond along the *z* axis.

The structure of the ethylene bromonium ion has not been characterized experimentally.

The harmonic vibrational modes calculated for ethylene and ethylene bromonium ion were visualized using the programs MOLDEN[45a] and MacMolPlt,[45b] and mode assignments were done for both the hydrogenated and deuterated species. Table 4 lists the assignment for ethylene comparing the unscaled calculated frequencies to experimental ones.[46] With the exception of the CC stretch, all the modes are underestimated with DFT by an average of ca. 40 cm^{-1}.

For the analysis of the origins of the isotope effects it is convenient to factor eq 2. Setting the tunneling transmission coefficient κ equal to unity, eq 2 may be written as follows:

$$K_H/K_D = \eta(\sigma_H/\sigma_D) \tag{5}$$

where $\sigma_X = (s^R{}_X/s^P{}_X)$, X = H or D, is the ratio of symmetry numbers for products (s^P) and reactants (s^R) and η is the per-site isotope effect. Assuming the separation of rotations and vibrations, the isotope effect η may be factored as[47]

$$\eta = \eta_{trans}\eta_{rot}\eta_{vib}\zeta_{pot} \tag{6}$$

where η_X denotes the ratio of the X partition functions (X = translational, rotational, or vibrational) for light (H) and deuterated (D) products (P) and reactants (R)

$$\eta_X = (Q_X{}^{PH}/Q_X{}^{RH})/(Q_X{}^{PD}/Q_X{}^{RD}) \tag{7}$$

and ζ_{pot} represents the effect of the isotopic change on the separation of the zero-point energies:

$$\zeta_{pot} = \exp[\,-(\Delta_{ZPE}{}^{P} - \Delta_{ZPE}{}^{R})/RT] \tag{8}$$

Several deuterated ethylenes and their associated bromine adducts were studied. The contributions of various factors to the overall values of the isotope effects, calculated in the gas phase at 298.15 K and 1 atm, are shown in Table 5. The rotational contribution increases by 30% from d_1 to d_4 and, multiplied by the slowly varying translational factor, works toward a normal isotope effect. The effect of isotopic substitution on the vibrational energy levels appears in two ways: through the ratio of the vibrational partition functions in the vibrational factor η_{vib} and through the change in the zero-point energies, contained in ζ_{pot}. As Table 5 shows, η_{vib} contributes almost a unity to the overall effect making ζ_{pot} responsible for the inverse isotope effect η. The overall vibrational contribution, $\eta_{vib}\zeta_{pot}$, decreases by 50% from d_1 to d_4 and brings about a significant inverse isotope effect. Considering that no scaling of the harmonic vibrational frequencies was done, the η value for the perdeuterated system d_4, $\eta = 0.630$, is nicely bracketed by the experimentally determined values of the kinetic isotope effect $k_H/k_D = 0.664 \pm 0.05$ in methanol and 0.572 ± 0.048 in dichloroethane. As mentioned in the discussion of experimental results, changing the nucleophilicity of the solvent does not affect the kinetic isotope effect in a major way. Extending this to the gas-phase limit, the isotope effect again should not change that much either, thus leading to good agreement between the calculated and experimental values.

The ethylene−bromine system is simple enough to allow for a detailed study of the origin of the inverse isotope effects, and such a study was carried out for the d_4 system. Since the modes of all four species involved could be assigned and no vibrations were degenerate, modes could be easily correlated between the species. As Table 6 shows, deuteration of ethylene and the ethylene bromonium ion results in only minor changes of the mode ordering. (Given as Table 6S, Supporting Information, are pictorial representations of the modes corresponding to these frequencies.)

Both the η_{vib} and ζ_{vib} factors contain multiplicative contributions from each of the vibrational modes listed in Table 6; as a result, the vibrational contribution to the overall isotope effect $\zeta_{vib}\eta_{vib}$ may be easily factored into contributions corresponding to individual vibrational modes:

$$\zeta_{vib}\eta_{vib} = \Pi_{i=1,15}\eta_{vib,i}\zeta_{vib,i}$$

where the contribution of the *i*th mode to $\zeta_{vib,i}$ may be written as

$$\zeta_{vib,i} = \exp\{-[\Delta\Delta\nu_i]/2RT\} \tag{9}$$

with $\Delta\Delta\nu_i = \Delta\nu_i(R) - \Delta\nu_i(P)$ denoting the overall change in the zero-point energies (in kJ/mol) due to the mode *i* in the reactant and product. The contributions from the individual vibrational modes are collected in Table 7. The effects due to the vibrational partition function ratio are negligible (close to unity) for all modes except the new modes 13−15 created by the addition of bromine to ethylene. For a vibrational mode to contribute significantly to the total isotope effect via ζ_{vib}, the change in the harmonic frequency upon isotopic substitution in the reactant and products ought to be different: $\Delta\nu(R) \neq \Delta\nu(P)$. There are two such modes in the ethylene portion of the ethylene bromonium ion system: CH_2 symmetric scissors (mode 6) contributing to a *normal* isotope effect and the CC stretch (mode 8) contributing to the *inverse* effect. (There is a significant motion of the substituents on the carbon atoms during the CC stretch.) Despite large isotopic changes in all remaining modes (see, e.g., the CH stretches, modes 9−12), their contribution to the overall isotopic effect is negligible because $\Delta\nu(R) \approx \Delta\nu(P)$. The largest contribution from an individual mode is due to the CH_2 symmetric twist (mode 15 in Tables 6 and 7), and it adds to the magnitude of the *inverse* effect. However, Table 7 clearly shows that the CH_2 symmetric twist (mode 15), while dominant, is not the only contributor to the effect. Nevertheless, it plays a very important role: when the isotope effect is calculated in the absence of mode 15, the inverse isotope effect of $\eta = 0.630$ is replaced by a normal one of $\eta = 1.12$ (see Figure 2).

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(45) (a) Schaftenaar, G. *QCPE Bull.* **1992**, *12*, 3 (available from http://www.caos.kun.nl/~schaft/molden). (b) MacMol Plt is available from http://www.msg.ameslab.gov/GAMESS/Graphics/MacMolPlt.html.

(46) Duncan, D. L.; McKean, D. C.; Makkison, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221.

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Table 5. Contributions to Per-Site Secondary Isotope Effects[a]

system	η_{trans}	η_{rot}	$\eta_{trans}\eta_{rot}$	η_{vib}	ζ_{pot}	$\eta_{vib}\zeta_{pot}$	η
d_1 = H_2C-CDH	1.040	1.111	1.155	0.980	0.784	0.768	0.888
d_2 - trans = $DHC-CDH$	1.079	1.206	1.301	0.965	0.631	0.609	0.792
d_2 - cis = $DHC-CDH$	1.079	1.223	1.320	0.963	0.622	0.598	0.790
d_2 = D_2C-CH_2	1.079	1.232	1.329	0.962	0.617	0.594	0.789
d_3 = D_2C-CDH	1.118	1.328	1.485	0.948	0.500	0.475	0.705
d_4 = D_2C-CD_2	1.157	1.435	1.660	0.935	0.406	0.380	0.630

[a] The contributions η_{trans}, η_{rot}, η_{vib}, and η_{pot} to the per-site secondary isotope effect η are defined in eqs 5−8.

Table 6. Correlations of Calculated Harmonic Frequencies for C_2H_4, C_2D_4, $C_2H_4Br^+$, and $C_2D_4Br^+$ [a]

	C_2L_4			$C_2L_4Br^+$			
mode	symmetry[b]	L = H	L = D	symmetry[c]	L = H	L = D	assignment
1	b_{2u}	793	570	b_1	808	573	CH_2 sym rock
2	b_{2g}	900	743	b_2	1063	817	CH_2 sym wag
3	b_{3u}	939	711	a_1	1071	803	CH_2 as wag
4	a_u	1021	723	a_2	883	630	CH_2 as twist
5	b_{3g}	1167	950	a_2	1169	929	CH_2 as rock
6	a_g	1342	971	a_1	1481	1264	CH_2 sym scissors
7	b_{1u}	1413	1047	b_2	1414	1045	CH_2 as scissors
8	a_g	1692	1580	a_1	1176	945	CC stretch
9	b_{1u}	3122	2243	b_2	3120	2255	CH stretch as (CH_2 sym)
10	a_g	3134	2321	a_1	3120	2278	CH stretch sym (CH_2 sym)
11	b_{3g}	3202	2389	a_2	3234	2424	CH stretch as (CH_2 as)
12	b_{2u}	3229	2405	b_1	3247	2423	CH stretch sym (CH_2 as)
13				b_2	434	412	CBr stretch as
14				a_1	450	432	CBr stretch sym
15				b_1	844	619	CH_2 sym twist

[a] Harmonic vibrational frequencies in cm^{-1}. [b] Ethylene is located in the *yz* plane, with CC bond along the *z* axis. [c] In ethylene bromonium ion the CC bond is oriented along the *y* axis, while the plane of L_4 is parallel to the *xy* plane.

Table 7. Contributions of Various Modes to ζ_{pot} and η_{vib}[a]

mode[a]	$\eta_{vib,i}$	$\Delta\nu_i(R)$[b]	$\Delta\nu_i(P)$[b]	$\Delta\Delta\nu_i$[b]	$\zeta_{pot,i}$	$\eta_{vib,i}\zeta_{pot,i}$
1	1.000	223	234	11	0.973	0.973
2	1.001	157	247	90	0.805	0.806
3	1.007	229	268	39	0.909	0.915
4	0.989	299	254	−44	1.116	1.103
5	0.999	218	240	22	0.948	0.947
6	1.006	371	217	−153	1.449	1.458
7	1.000	365	369	4	0.991	0.991
8	0.993	112	230	118	0.751	0.746
9	1.000	868	865	−2	1.007	1.007
10	1.000	813	842	29	0.933	0.933
11	1.000	813	810	−2	1.008	1.008
12	1.000	824	824	0	0.999	0.999
13	0.984		22	22	0.948	0.933
14	0.988		18	18	0.958	0.947
15	0.966		225	225	0.581	0.561
total	0.935[c]			373[d]	0.406[e]	0.380[f]

[a] Assignment of modes is shown in Table 6. [b] See eq 9 for the definition of symbols. [c] $\Pi_{i=1,15}(\eta_{vib,i})$. [d] $\Pi_{i=1,15}(\Delta\Delta\nu_i)$. [e] $\Pi_{i=1,15}(\zeta_{pot,i})$. [f] $\Pi_{i=1,15}(\eta_{vib,i}\zeta_{pot,i})$.

Two models were proposed to explain the origin of the secondary α-deuterium isotope effect. The older interpretation suggested by Streitwieser et al.[10] stipulates the change of some CH vibrational modes due to rehybridization: in a reaction that involves sp^2 to sp^3 rehybridization at the α-carbons, an inverse secondary isotope effect should be observed. A more recent, alternative explanation of the secondary kinetic isotope effects was offered by Strausz et al.,[12] who attributed the effect to the creation of new, isotopically sensitive, vibration(s) in the transition state. Bender and co-workers have recently shown that, for equilibrium binding of ethylene to $Os_2(CO)_8$[13a] and equilibrium H_2/D_2 binding in a $M(\eta^2\text{-}H_2)$ complex,[13b] the zero point energy components associated with the creation of new vibrational modes in the complexes contribute most to the inverse EIE's. *In the case of bromination of ethylene, there is strong evidence in support of the model put forth by Strausz et al., namely that the inverse isotope effect arises from the creation of the CH_2 symmetric twist mode rather than it being due to a rehybridization of the carbons from sp^2 to sp^3.* It must be added here that there is little rehybridization at the carbon atoms upon the addition of bromine: the sum of the three angles C−C−H, H−C−H, and C−C−H is about 357.3°, very close to the sum of 360°, characteristic of the sp^2 hybrid.

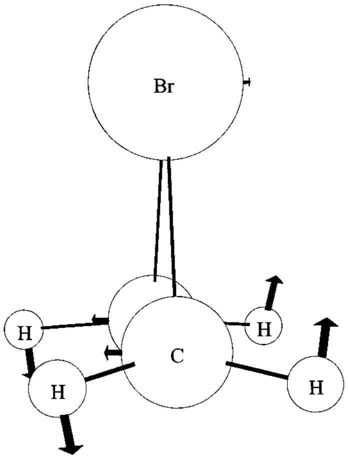


Figure 2. Displacements of atoms in mode 15 (symmetric twist of CH_2).

As a representation of the first step toward charge separation in the bromination of ethylene, the charge-transfer complex equilibrium

$$C_2H_4 + Br_2 \rightleftharpoons C_2H_4{:}Br_2$$

was studied and the isotope effects were evaluated. Table 8 compares the DFT geometry with the one calculated at the MP2 level.[48] Assignments of the vibrational modes in the CTC are listed in Table 9. The absence of imaginary frequencies

Table 8. Geometry of the CTC (bond lengths in angstroms)

bond	DFT[a]	MP2[b]
Br−Br	2.389	2.354
Br−C	2.868	3.021
C−C	1.370	1.343

[a] This work. [b] Br(16s11p5d/5s4p2d), C(10s6p1d/4s3p1d), and H(5s1p/2s1p).[48]

Table 9. Assignment of Modes for the CTC[a]

mode	symmetry[b]	DFT[c]	assignment
1	b_1	74	Br−Br−C_2H_4 def. (front to back)
2	b_2	74	Br−Br−C_2H_4 def. (right to left)
3	a_1	112	Br_2−C_2H_4 stretch
4	b_2	155	C_2H_4 twist of Br−C as stretch
5	a_1	262	Br−Br stretch
6	b_1	293	CH_2 sym twist
7	b_1	800	CH_2 sym rock
8	b_2	928	CH_2 as wag
9	a_1	972	CH_2 sym wag
10	a_2	1005	CH_2 as twist
11	a_2	1180	CH_2 as rock
12	a_1	1336	CH_2 sym scissors
13	b_2	1420	CH_2 as scissors
14	a_1	1649	CC stretch
15	b_2	3132	CH stretch sym (CH_2 as)
16	a_1	3141	CH stretch sym (CH_2 sym)
17	a_2	3219	CH stretch as (CH_2 as)
18	b_1	3245	CH stretch as (CH_2 sym)

[a] Harmonic vibrational frequencies in cm^{-1}. [b] CTC was assumed to have C_{2v} symmetry, with Br_2 was aligned along the z axis and CC bond parallel to the y axis. [c] This work.

indicates that the CTC is a minimum on the potential energy surface. A substantial inverse isotope effect of $\eta = 0.89$ is found; however, it is small when compared with the effect found in the bromonium ion. In contrast to the ethylene bromonium ion, there is no single mode responsible for the isotopic effect in the charge-transfer complex.

Conclusions and Mechanistic Implications

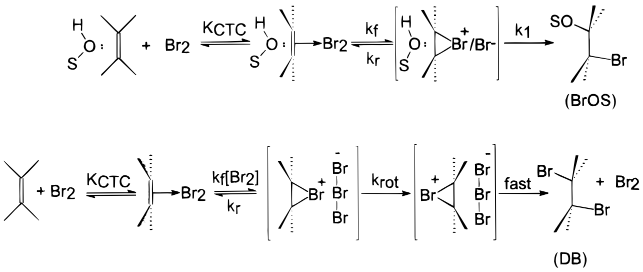
From the product study of the bromination of ethylene, the reaction proceeds exclusively by a two-step trans addition process. Kinetic measurements using the method of incomplete bromination indicate that the dkie's in both methanol and dichloroethane are large ($k_H/k_D = 0.61$) and inverse, and the experimental values are in remarkably good agreement with what is computed for the equilibrium EIE for $Br^+ + CH_2{=}CH_2 \rightleftharpoons$ bromonium ion by the methods described above.

Given the experimental and computed dkie's, kinetic data, the anticipated instability of the ethylene bromonium ion, and due consideration of the constraints placed upon the ion lifetime and the time required for ion reorganization to produce products, the most likely mechanism(s) for bromination of ethylene are given in Scheme 3. In methanol, the presently available evidence supports a process involving a preassociation mechanism leading through a CTC which evolves to a reversibly formed bromonium ion with an associated solvent. A generalized kinetic expression based in Scheme 3 and assuming a steady state in the bromonium ion can be given as

$$\frac{d[BrOS]}{dt} = \frac{k_1 k_f K_{CTC}[Br_2][olefin]}{k_r + k_1} \tag{10}$$

In one limit, where reversal of the ion to the CTC is more prominent than solvent capture, k_f/k_r becomes a true equilibrium constant, K_{eq}, so the expression reduces to

Scheme 3



$$\frac{d[BrOS]}{dt} = k_1 K_{eq} K_{CTC}[Br_2][olefin] \tag{11}$$

In this case, the α-dkie comprises the kinetic and equilibrium terms, k_1, K_{CTC}, and K_{eq}. Since the transition state for the solvent capture is very early, and since the contribution of the CTC to the α-dkie is small (vide supra), the largest contributor to the dkie is K_{eq}.

In another limit where each time the bromonium ion is formed it proceeds to products, the expression reduces to

$$\frac{d[BrOS]}{dt} = k_f K_{CTC}[Br_2][olefin] \tag{12}$$

and the dkie must arise largely from the k_f term. Note here that since this transition state will be relatively late it will strongly resemble the bromonium ion with its associated equilibrium isotope effect.

In DCE, the mechanism for bromination of ethylene (Scheme 3) proceeds through a CTC that evolves to an ion pair complex with the assistance of a second Br_2. In this case, product formation can only occur if the ions rotate to bring the CH_2−Br^+ moiety into a configuration where it can be displaced by Br_3^-. This step, with its associated rotational rate constant, k_{rot}, from the calculations presented above[38] is surprisingly slow and could limit the rate of the reaction. A set of kinetic expressions for the formation of dibromide that strongly resemble those above describing the situation in methanol can be written. Assuming a steady state in the nascent bromonium ion complex, we can write

$$\frac{d[DB]}{dt} = \frac{k_{rot} k_f [Br_2] K_{CTC}[Br_2][olefin]}{k_{rot} + k_r} \tag{13}$$

In the limit where the ion rotation is slow relative to the reversal to reform the CTC, the expression reduces to

$$\frac{d[DB]}{dt} = k_{rot} K_{eq} K_{CTC}[Br_2]^2[olefin] \tag{14}$$

Once again, the α-dkie comprises two equilibrium terms and one kinetic term, but the isotopic sensitivity of the rotational term must be nil and, for reasons presented above, that associated with K_{CTC} is small. This leaves the primary contributor to the dkie as being the equilibrium isotope effect associated with bromonium ion formation.

In another limit, if the rate-limiting step is really bromonium ion formation and rotation followed by ion pair collapse to form product is fast, then eq 13 reduces to

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(48) Assfeld, X.; Garapon, J.; Rinaldi, D.; Ruiz-López, M. F.; Rivail, J.-L. *THEOCHEM* **1996**, *371*, 107.

$$\frac{\mathrm{d[DB]}}{\mathrm{d}t} = k_\mathrm{f}K_\mathrm{CTC}[\mathrm{Br_2}]^2[\mathrm{olefin}] \qquad (15)$$

and the dkie resides primarily in the k_f term. As was the case for bromination in methanol, this transition state must be late, resembling the bromonium ion, so the dkie can be well approximated by the equilibrium isotope effect.

Finally, we conclude that DFT calculations of the EIE for the equilibrium $\mathrm{Br^+ + C_2H_4 \rightleftharpoons [C_2H_4Br]^+}$ confirm the validity of Strausz's model[12] where the creation of a new isotopically sensitive mode is responsible for the dkie. The ethylene system is small enough to allow for unambiguous identification of vibrational modes in all the species involved leading to the identification of a single mode—CH_2 symmetric twist—that is undoubtedly responsible for the inverse EIE.[13]

The good agreement between the experimental and calculated isotope effects indicates that DFT is a useful tool for studying the nature of secondary isotope effects which cannot be resolved experimentally.

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Supporting Information Available: Table 6S, Assignment of Modes and Frequency Comparison for the Ethylene Bromonium Ion (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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