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LETTERS

The Kinetic Isotope Effects in the Reactions of Four Ethene Isotopologues with Chlorine and Bromine Atoms

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The kinetic isotope effects (KIEs) have been studied in the reactions of chlorine and bromine atoms with four ethene isotopologues (C_2H_4, $^{13}C_2H_4$, C_2D_4, and C_2H_3D) using FTIR spectroscopy and the relative rate technique. Halogen atoms were produced by the photolysis of Cl_2 and Br_2. For chlorine the KIEs, defined as $k_{C_2H_4}/k_{x,}$ were: 0.738 ± 0.024 (C_2D_4), 0.853 ± 0.037 (C_2H_3D), and 1.061 ± 0.023 ($^{13}C_2H_4$) and for bromine: 0.817 ± 0.016 (C_2D_4), 1.09 ± 0.13 (C_2H_3D), and 1.1172 ± 0.0053 ($^{13}C_2H_4$). Uncertainties are given as 2σ. These results are interpreted in terms of the fate of the atom−molecule adduct. The implications of the results to atmospheric chemistry are described.

Introduction

Volatile organic carbon (VOC) species in the troposphere are a significant source of ozone and aerosol haze.[1] Thus, many attempts have been made to understand their atmospheric sources (biogenic emissions and industrial activity) and removal mechanisms.[1−4] This is a complex task, and the analysis of the distributions of stable isotopes in atmospheric VOC can help by constraining the role of specific sources and sinks.[4,5] To use this approach, the isotopic signature of a given compound's sources and photochemical reaction rates must be known, in addition to the distribution of stable isotopes in atmospheric samples.[6] The present study elucidates the relative rate of reaction of isotopically substituted ethene with two atmospheric oxidants, Cl and Br.

Ethene (C_2H_4) is the simplest unsaturated hydrocarbon and contributes significantly to the total nonmethane VOC (NMVOC) emission; e.g., ethene is the third most important NMVOC precursor for ozone production in the U.K.[7] Ethene is mainly degraded by reaction with OH, O_3, and NO_3, but it also reacts with the chlorine and bromine radicals—species that can be abundant in arctic and marine environments. Concentrations for Cl and Br of 1.3×10^5 atoms/cm^3 (coastal, early sunrise)[8] and 3×10^7 atoms/cm^3 (tropospheric ozone depletion events)[9−14] can be generated due to the photolysis of gases emitted from aerosols or ice containing sea salt, resulting in a lifetime of ethene with regard to these species of about 0.8 and 0.7 days, respectively, compared to 2.7 days for standard OH concentrations (1×10^6 molecules/cm^3).

Other studies of ethene include field studies with the aim of improving the knowledge of halogen atom chemistry,[12−14] KIEs for ethene with Cl[15] and OH[16−18] and calculations of the vibrational frequencies and force fields of the ethene isotopic species based on experiment and ab initio techniques.[19−21]

The simplicity of ethene makes it ideal for fundamental studies and in this work the KIEs of four ethene isotopologues (C_2H_4, $^{13}C_2H_4$, C_2D_4, C_2H_3D) reacting with atomic chlorine and bromine have been investigated using relative rate measurements employing multipass FTIR spectroscopy.

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TABLE 1: Initial Reactant Volume Fractions (ppm) in the Four Different Experiments[a]

	Cl_2	Br_2	C_2H_4	C_2D_4	C_2H_3D	$^{13}C_2H_4$
1	10		2	2−3.5		
2	10−30		2−3		8	3
3		10	2	3		
4		30	3		8	3

[a] Three repetitions were made of experiments 1, 2, and 4 and two were made of experiment 3.

Experimental

The experimental setup used is as described by D'Anna et al.[22] with the exceptions that 128 co-added scans comprise each spectrum, that the resolution is 0.25 cm^{-1} (except for two runs of experiment 1 and 3, where the resolution is 0.125 cm^{-1}), and that an InSb detector was used. Briefly the system consists of a White cell with an FTIR detector. Initial reactant mixtures are described in Table 1. The halogen gases in the cell were photolyzed stepwise and spectra were recorded at each step. The temperature was that of the room (296 ± 2 K) and atmospheric pressure (970−1013 hPa) was used in the cell.

The initial gas mixtures were left unphotolyzed for half an hour, and the absorption spectrum before and after were compared, to ensure that there was no reaction without photolysis. Reference spectra of C_2H_4, C_2D_4, C_2H_3D, $^{13}C_2H_4$, CH_2O, $ClCH_2CHO$, $ClCH_2CH_2OH$, and HCl were recorded for the data analysis. Reference spectra of the bromine analogues of the chlorine species were not recorded. The gases used were: ethene (Aldrich, 99.5%), ethene-*d4* (ICN, 98 atom %), ethene-*d1* (ISOTEC, 98 atom %), ethylene-$^{13}C_2$ (ISOTEC, 99 atom %), Br_2 (Fluka p.a. > 99%), Cl_2 (AGA >99.8%), and synthetic air (AGA 4.0). All gases were used as received.

Results and Discussion

Concentrations in the gas cell were determined by spectral subtraction. The main reaction products detected were chloroactetaldehyde, 2-chloroethanol and HCl. Labile reaction products for the Br reaction include BrCHO and CHO−CHO,[23] but these were not observed in the spectra. Spectral windows of about 5 cm^{-1} centered on the Q-branches were used for the determination of isotopologue concentrations. The bands in question are those for the anti symmetric C−H (C−D) stretching vibration situated at 2989 cm^{-1} (C_2H_4), 2200 cm^{-1} (C_2D_4), 3028 cm^{-1} (C_2H_3D), and 2970 cm^{-1} ($^{13}C_2H_4$) (cf. Figure 1). These bands were chosen, as they are intense, sharp, and within the spectral window of the InSb detector.

Model. A model (available upon request) of the cell photochemistry was constructed using FACSIMILE.[24] The model contains 20 reactions, and is based on the reaction scheme for the OH- and Cl-initiated oxidation of ethene,[25] augmented by reactions accounting for the subsequent degradation of secondary reaction products.[26,27] Figure 2 shows plots of model results vs experimental concentrations of selected species. The slopes show an almost 1:1 agreement for all species except HCl. This is probably due to reactions of the Cl atom with surface-adsorbed organics not included in the model. These reactions do not affect the results of this study.

There is a possibility that OH radicals will be formed in the cell, as a consequence of the photolysis of H_2O_2 generated by the recombination of HO_2 radicals. This is not desirable, as OH also reacts with ethene and has a KIE close to one for the *4-d* isotopologue at one atmosphere pressure.[16,18] In the model, OH concentrations remain orders of magnitude lower than the concentration of Cl. In addition, the rate constant for the ethene−OH reaction is 8.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1},[16] compared to 3.2 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the Cl reaction.[15] Therefore the OH reaction is unimportant in this experiment.

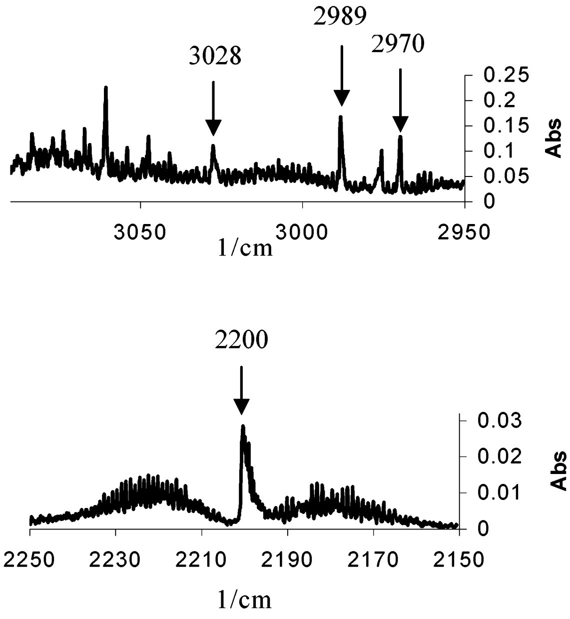

Figure 1. Bands used for analysis. 3028: C_2H_3D; 2989: C_2H_4; 2970: $^{13}C_2H_4$; 2200: C_2D_4.

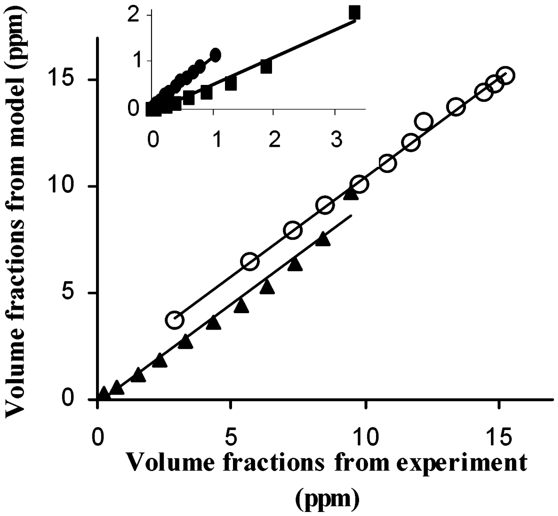

Figure 2. Linear regression of model results vs experiment. ■: HCl, ●: 2-chloroethanol, ▲: chloroacetaldehyde, ○: total ethene = the sum of ethene isotopologues in the experiment.

TABLE 2: Kinetic Isotope Effects

	$k_{C_2H_4}/k_x$[a]	N[b]	other work
Cl: C_2D_4	0.738 ± 0.024	3	0.74 ± 0.06[c]
Cl: C_2H_3D	0.853 ± 0.037	3	
Cl: $^{13}C_2H_4$	1.061 ± 0.023	3	
Br: C_2D_4	0.817 ± 0.016	2	
Br[d]: C_2H_3D	1.09 ± 0.13	3	
Br: $^{13}C_2H_4$	1.1172 ± 0.0053	3	

[a] Weighted average. Uncertainties are given as 2σ. [b] Number of experiments. [c] Stutz et al.[15] [d] The large std. dev. is due to a lack of reference spectra and a technical error in one experiment.

Results. Kinetic isotope effects were calculated using linear regression on plots of ($\ln[C_2H_4]_t/\ln[C_2H_4]_0$) against ($\ln[x]_t/\ln[x]_0$) to get ($k_{C_2H_4}/k_x$) (cf. Table 2).

As seen in Table 2, the relative rates determined from the experiments were in general reproducible, with 2σ uncertainties

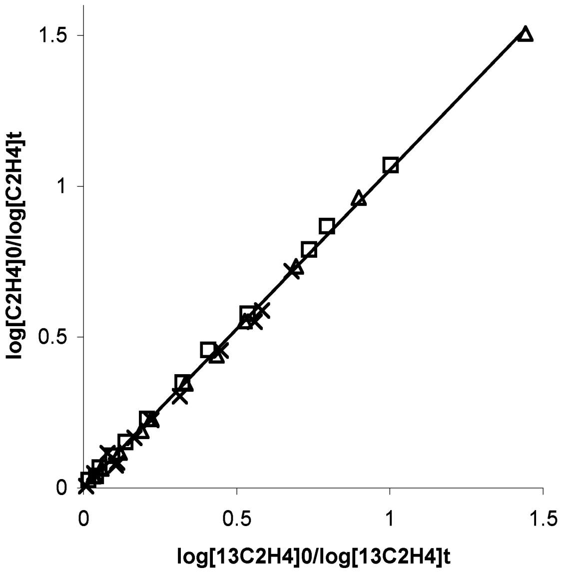

Figure 3. Data points from the three $C_2H_4/^{13}C_2H_4$ + Cl experiments.

ranging from 12% of the total for C_2H_3D + Br, to 0.5% for $^{13}C_2H_4$ + Br_2. The uncertainty is mainly associated with variations in the spectral fit, which may be affected by overlapping bands from other molecules. Figure 3 shows data from the three $^{13}C_2H_4/C_2H_4$ + Cl experiments. The same trends were observed in the other experiments. The C_2D_4/C_2H_4 + Cl experiment is in excellent agreement with the previous determination[15] and the other results are, to the best of our knowledge, first determinations.

For the chlorine reaction the KIE increases with deuteration. However the relative rate for C_2H_3D is not simply one-fourth that of C_2D_4. The bromine reaction displays a similar trend although the effect is not as pronounced. For ^{13}C-substitution, a small normal KIE is observed—a bit larger in the bromine-reaction than in the chlorine reaction.

Discussion. The reaction is known to proceed according to the following Lindemann-type mechanism:

$$C_2H_4 + X \rightarrow C_2H_4X^* \quad \text{forward reaction, } k_f$$

$$C_2H_4X^* \rightarrow C_2H_4 + X \quad \text{reverse reaction, } k_r$$

$$C_2H_4X^* + M \rightarrow C_2H_4X + M \quad \text{thermalization reaction, } k_t$$

$$C_2H_4X + O_2 \rightarrow CH_2XCH_2O_2 \quad \text{peroxy reaction, } k_p$$

In addition, in the case of X = Br (but not Cl), the presence of O_2 is known to accelerate the reaction, due to the addition of O_2 to the unthermalized adduct.[15,23,28]

$$C_2H_4Br^* + O_2 \rightarrow CH_2BrCH_2O_2 \qquad \text{additional peroxy reaction, } k_p'$$

Stationary points on the potential energy surface (PES) of the reaction of ethene with chlorine have been described[29,30] (see Figure 4) and can help in explaining our observations.

The ethene + halogen reactions proceed by forming an adduct which may decay to reagents,[31] be collisionally relaxed, and/or react with O_2. The direct abstraction channel is unimportant at tropospheric temperatures.[32] Since the chlorine and bromine reactions are in the falloff region at one atmosphere pressure, there is an active competition between collisional relaxation (k_t) and unimolecular decay (k_r). The effect of isotopic substitution on the rate of reaction can be understood by considering its effect on the unimolecular lifetime of the adduct. RRKM theory shows that the lifetime of the adduct ($\tau_{\text{adduct}} = 1/k_r$) is proportional to the density of states of the system (divided by the sum of states of the transition state).[33]

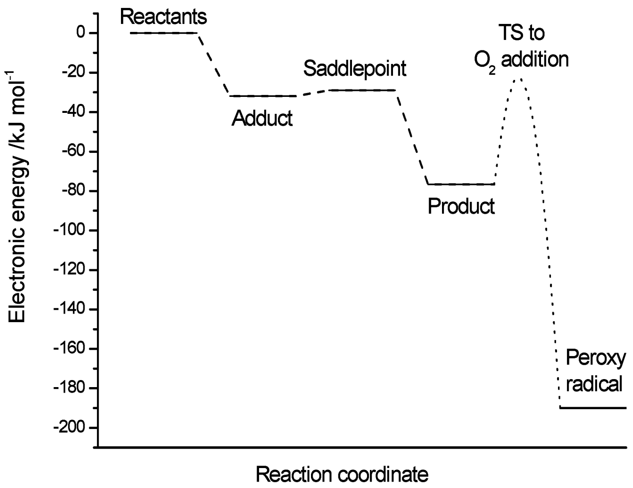

Figure 4. The potential energy surface of the ethene + Cl reaction.[29]

Calculations at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory of the energetics and vibrational frequencies of the 8 adducts addressed in this study have recently been completed.[29] The electronic energy of the minimum-energy symmetrical adduct is −29.5 kJ/mol for Br and −31.9 kJ/mol for Cl. The density of states can be calculated using either the classical expression or the semiclassical Marcus−Rice method[33] at a total system energy of the electronic energy of the adduct plus a thermal energy of *kT*. Using either method, it is found that the ratio of the density of states of $C_2H_4Cl/C_2D_4Cl/C_2H_3DCl/^{13}C_2H_4Cl$ is 1:43.1:2.54:1.14, and that the ratio of the density of states of $C_2H_4Br/C_2D_4Br/C_2H_3DBr/^{13}C_2H_4Br$ is 1:44.2:2.56:1.15. This series lies behind the gross ordering of the isotope effects shown in Table 2.

However, other factors also influence the relative rates in Table 2. The rate of X + $^{13}C_2H_4$ is an exception to the trend implied by RRKM theory. Because of its geometry, the ^{13}C species shows the smallest shift in density of states of the species listed. There is not terribly much vibrational energy present in the adduct. The change in electronic energy will give the Cl adduct 31.9 kJ/mol = 2670 cm^{-1} (plus a thermal energy *k*T of ca. 210 cm^{-1}) to distribute among 15 vibrational normal modes with frequencies extending from 240 to 3322 cm^{-1}. In this energy region it is unlikely that the vibrational energy levels will be evenly spaced, and the rate of the reaction will be influenced by the chance proximity of the available energy levels to the system energy.

One of the unique features of the reactions under consideration is the possibility for the $C_2H_4Br^*$ adduct to react with O_2, a possibility not available to the Cl adduct.[15,23,28] A barrier is expected for this reaction (k_p'), and the barrier will be lower for the Br adduct due to its greater polarizability. This type of potential energy surface typically gives rise to a normal kinetic isotope effect—an isotopically heavy system with a lower zero-point energy will experience a higher barrier and slower reaction rate. This mechanism could explain the quantitatively smaller relative rates observed in the case of Br reactions, relative to the analogous Cl reactions.

Finally, it is important to note the role of collisional quenching in producing the observed results. For the OH + C_2H_4 reaction at one atmosphere pressure, C_2H_4 reacts at the same rate as

C_2D_4, presumably because the reaction takes place in the high-pressure regime.[16,18] It is reasonable to assume that the relative rate of C_2H_3D is also one (note, however, that $k_{C_2H_4}/k_{^{13}C^{12}CH_4} = 1.0176$).[17] Stutz et al.[15] observed that the relative rate of C_2H_4/C_2D_4 reacting with Cl decreases from 0.74 to 0.35 as the pressure decreased from 1 atm to 1 Torr, illustrating how collisions (k_t) reduce the effect of the unimolecular lifetime (k_r) in determining the relative rate. Since the Br + C_2H_4 reaction probably is closer to the high-pressure limit than the Cl + C_2H_4 reaction, one would expect the relative rates to be closer to unity for the set of Br reactions. Table 2 confirms that this is the case.

It should also be noted that the rate of collisional relaxation is dependent on the density of states of the adduct. Isotopically heavy systems will have a faster overall reaction rate since they are more quickly thermalized.

Application. The results presented here will hopefully prove helpful in the understanding of KIEs for more complex unsaturated VOCs, such as isoprene. The results for C_2H_3D can be useful in the tracing of ethene sources and sinks and in the study of halogen atom concentrations. Since the KIE of C_2H_3D is different for OH, Cl, and Br, it should, for instance, be possible to use it as further proof to the claim that the concentration of bromine atoms is indeed 3 orders of magnitude higher than that of chlorine.[9−14]

It is important to note that the experimental technique produces a relative rate of reaction with an error of a few percent. The error of absolute rates derived from these relative rates will be much higher (typically 10 to 20%), but it is the relative rate that would be put to use in interpreting atmospheric data.

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