The Journal of Physical Chemistry A

VOLUME 101, NUMBER 49, DECEMBER 4, 1997

LETTERS

Inverse Kinetic Isotope Effect in the Reaction of Atomic Chlorine with C_2H_4 and C_2D_4

J. Stutz,[†] M. J. Ezell, and B. J. Finlayson-Pitts*

Department of Chemistry, University of California, Irvine, California 92697-2025

Received: September 8, 1997; In Final Form: October 6, 1997[⊗]

The kinetics of the reaction of chlorine atoms with C_2H_4 and C_2D_4 have been studied near the low-pressure limit at 1 Torr total pressure and room temperature using two independent techniques. A fast flow discharge system (FFDS) was used to follow the decay of Cl in the presence of a great excess of either C_2H_4 or C_2D_4 in He as the carrier gas. Atomic chlorine was generated from the rapid reaction $F + HCl \rightarrow Cl + HF$ and detected using resonance fluorescence at 135 nm. In relative rate (RR) studies, Cl_2 was photolyzed to generate chlorine atoms in a mixture of the two organics in N_2 or He as the bath gas, and the loss of C_2H_4 or C_2D_4 relative to CH_4 was followed using GC-FID. The rate constant for the $Cl + C_2H_4$ reaction determined using the FFDS was $(3.3 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and for the $Cl + C_2D_4$ reaction was $(10.0 \pm 1.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, a factor of 3.0 ± 0.8 times larger than that for the C_2H_4 reaction (all errors are $\pm 2\sigma$). The $Cl + C_2H_4$ rate constant determined using the RR method was $(2.9 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, based on $k_{Cl+CH_4} = (1.0 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The rate constant for $Cl + C_2D_4$ was $(7.8 \pm 1.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, a factor of 2.7 ± 0.7 times larger than that for C_2H_4, in excellent agreement with the FFDS results. This strong *inverse* kinetic isotope effect is shown to be in excellent agreement with what would be predicted from unimolecular reaction rate theory and their reverse recombination processes.

Introduction

There is a great deal of interest in the kinetics and mechanisms of chlorine atom reactions with organics, in part due to the potential for halogen atom chemistry in coastal regions and the marine boundary layer.[1−3] Thus, halogen atoms generated from the reactions of sea salt particles are expected to react rapidly with organics such as ethane, ethene, propane, propene, and isoprene, which are, for example, produced by marine phytoplankton[4,5] as well as anthropogenic activities.

The kinetics and, to a lesser extent, the mechanisms of reactions involving atomic chlorine and alkenes have been studied (for reviews, see refs 6−9). These reactions are believed to proceed primarily by chlorine atom addition to the double bond to form an excited adduct, which initially contains the reaction exothermicity. For the reaction of the smaller alkenes at room temperature, decomposition of the excited adduct competes with its stabilization at low pressures. For example, the overall rate constant for the $Cl + C_2H_4$ reaction increases by more than 3 orders of magnitude between 0.3 and 4000 Torr.[10−12] Over the same pressure range, the rate constant for the propene reaction increases by a factor of 7.[13,14] The smaller pressure dependence is due to a higher number of vibrational degrees of freedom over which the energy in the excited adduct can be distributed in the larger molecule. For the same reason, the rate constant for the isoprene reaction, C_5H_8, only increases by a factor of 1.7 from 0.16 Torr to 1 atm.[15]

For alkenes containing an allylic hydrogen, a small percentage

---

[*] To whom correspondence should be addressed: e-mail bjfinlay@uci.edu; phone (714) 824-7670; FAX (714) 824-3168.

[†] Current address: Institut für Umweltphysik, University of Heidelberg, INF366, D-69l20 Heidelberg, Germany.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

S1089-5639(97)02935-6 CCC: $14.00

of the overall reaction of alkenes with atomic chlorine proceeds via hydrogen atom abstraction at room temperature. For example, the rate constant for the reaction of chlorine atoms with fully deuterated isoprene, C_5D_8, at 298 K and 1 atm pressure is ~17% smaller than that for C_5H_8,[15] exhibiting a normal kinetic isotope effect due to zero-point energy differences. Hydrogen atom abstraction for simple alkenes such as ethene is not important at room temperature but does occur at higher temperatures.[11,16,17] The pressure dependence of the propene and isoprene reactions suggest that this process may not proceed by direct abstraction, but at least in part by rearrangement and decomposition of some initial adduct.[14,15,18]

Further insight into the mechanism of the chlorine atom–alkene reactions can be obtained by studying the kinetics of the reaction of chlorine atoms with simple deuterated alkenes. We report here kinetics studies of the reaction of chlorine atoms with C_2H_4 and C_2D_4 at 1.0 Torr total pressure and room temperature, in which *an inverse kinetic isotope effect* is observed. Under these conditions, the rate constant for the C_2D_4 reaction is a factor of 3 *faster* than that for C_2H_4. This effect is shown to be in agreement with theories of unimolecular dissociation and their reverse recombination reactions. The mechanistic implications are discussed.

Experimental Section

Studies were carried out using two techniques: a fast flow discharge system (FFDS) and a relative rate (RR) technique. The FFDS has been described in detail elsewhere.[19] Briefly, it consists of a glass flow tube 2.54 cm in diameter and approximately 1 m in length. Chlorine atoms are formed from the fast reaction of fluorine atoms with an excess of HCl prior to entering the upstream end of the flow tube. Atomic fluorine is formed using a microwave discharge of a dilute (1%) mixture of F_2 in He. A flow of He carrier gas is added at the upstream end to bring the total pressure to 1.05 ± 0.02 Torr. The temperature in the flow tube is held constant at 20.0 ± 0.5 °C. The linear flow speed is typically 11 m s^{-1}. Chlorine atoms are detected at the downstream end of the flow tube using resonance fluorescence at 135 nm. The exciting radiation is produced using a microwave discharge of 0.6 Torr of 1% Cl_2 in He, and the fluorescence is isolated and detected using a vacuum monochromator (Minuteman 302VM) and solar blind photomultiplier (EMR 541G09-17) mounted perpendicular to the flow tube and the lamp. Ethene is added as a dilute mixture in He through a movable inlet. The position of the movable inlet was varied from the detector region to distances of ~35 cm, corresponding to reaction times up to ~30 ms.

The decay of the Cl resonance fluoresence signal was followed as a function of reaction time using varying concentrations of ethene ($(0.2-1.7) \times 10^{14}$ molecules cm^{-3}) and Cl (in the range of $10^{10}-10^{11}$ atoms cm^{-3}). The fluorescence signal was corrected for a small background due to stray light and O atoms generated as an impurity in the F_2 discharge, as well as for a 5–10% loss of Cl on the injector surface. The decay of atomic chlorine can be described by

$$\ln\frac{[\mathrm{Cl}]_t}{[\mathrm{Cl}]_0} = -(k_{\mathrm{eth}}[\mathrm{ethene}] + \Delta k_{\mathrm{w}})t = -k't \qquad \text{(I)}$$

In eq I, $[\mathrm{Cl}]_0$ and $[\mathrm{Cl}]_t$ are the chlorine atom concentrations in the absence of ethene (equivalent to a reaction time $t = 0$) and after a reaction time equal to t, respectively, k_{eth} is the rate constant for the reaction of Cl with ethene, and Δk_{w} is the change in the rate constant for the loss of Cl atoms at the walls of the flow tube upon the addition of ethene.

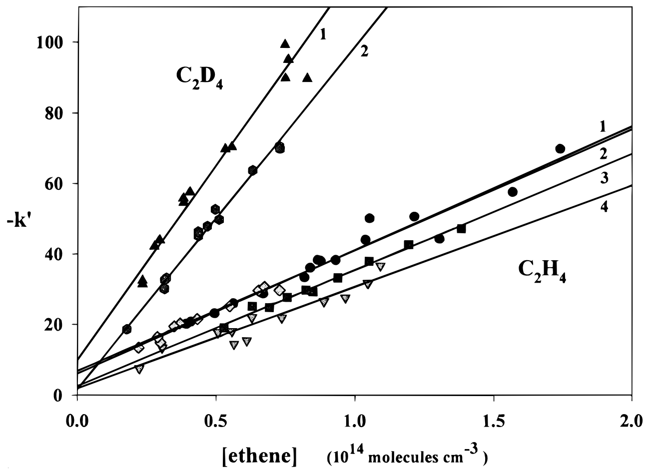

Figure 1. Pseudo-first-order rate constants for the loss of chlorine atoms on reaction with C_2H_4 and C_2D_4 in a fast flow discharge system at 1.05 Torr total pressure in He carrier gas at 20 °C. Typical error bars on each value of $(-k')$ are less than ~5%. The numbers represent different sets of experiments.

The relative rate technique involved following the simultaneous loss of ethene and methane using gas chromatography when mixtures of these two organics were irradiated in a 6.5 L glass bulb. Cl_2 was used as the chlorine atom source, as described elsewhere.[15] The reactant concentrations were in the following ranges (in units of 10^{14} molecules cm^{-3}): C_2H_4 (1.5–5.9); C_2D_4 (1.0–2.5); CH_4 (1.4–17.9); Cl_2 (7.2–23.9) All runs were carried out at 1.05 ± 0.05 Torr total pressure at the ambient laboratory temperature, 22 ± 3 °C. N_2 was the carrier gas, except for two runs for C_2H_4 in which He was used, with no significant difference in the results. The GC (Hewlett-Packard Model 5890 Series II) was equipped with a flame ionization detector and a 30 m GS-Q column (0.32 μm i.d., J & W Scientific) operated isothermally at 60 °C. The ratio of the rate constant for the Cl + ethene reaction to that for the reference Cl + CH_4 reaction was obtained using eq II[20]

$$\ln\frac{[\mathrm{ethene}]_0}{[\mathrm{ethene}]_t} = \frac{k_{\mathrm{eth}}}{k_{\mathrm{CH_4}}}\ln\frac{[\mathrm{CH_4}]_0}{[\mathrm{CH_4}]_t} \qquad \text{(II)}$$

where initial concentrations are represented by $[\ ]_0$ and those at various reaction times, t, by $[\ ]_t$. The ratio of the concentrations was obtained using the ratio of the peak heights on the chromatograms, taking into account errors in both the ethene and methane concentrations as discussed elsewhere.[21]

The He and N_2 were both ultrahigh purity (>99.999%, Liquid Carbonic). CH_4 (Matheson Research Grade, 99.99%), C_2H_4 (Matheson Research grade, >99.98%), and C_2D_4 (>98%, Cambridge Isotope Laboratories) were used as received. GC analysis of the C_2H_4 and C_2D_4 showed methane as the only other hydrocarbon detectable by FID, at 0.6% and 0.1% levels, respectively. Since the rate constant for the Cl + CH_4 reaction[8,9] is $(1.0 \pm 0.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, CH_4 contributes <0.2% to the loss of atomic chlorine in the FFDS. Mass spectrometric analysis of the C_2D_4 showed it contained approximately 5% C_2D_3H.

Results and Discussion

Figure 1 shows the variation of $(-k')$ with the concentration of added ethene in the FFDS. The value k' varies linearly with concentration, consistent with eq I. The intercepts of runs 3 and 4 for C_2H_4 and 2 for C_2D_4 in Figure 1 are within experimental error (2σ) of zero, indicating a negligible change

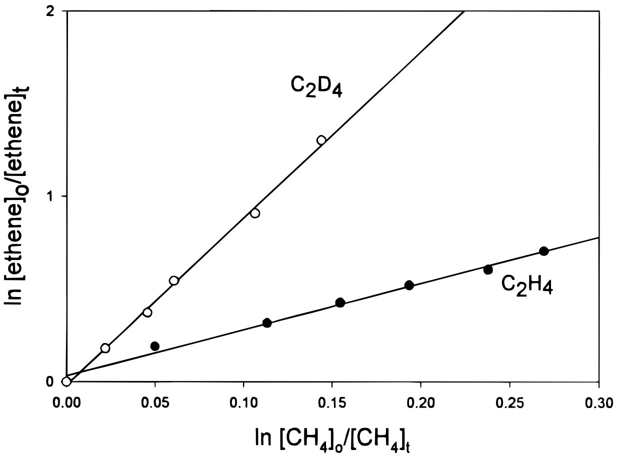

Figure 2. Typical relative rate data for the reaction of chlorine atoms with C_2H_4 and C_2D_4 at 298 K in N_2 at 1.05 Torr total pressure, using CH_4 as the reference compound.

TABLE 1: Rate Constants for the Reaction of Chlorine Atoms with C_2H_4 and C_2D_4 at 1 Torr Total Pressure and Room Temperature

reactant	kinetic technique	no. of runs	k_{eth} ($\pm 2\sigma$)[b] (10^{-13} cm^3 $molecule^{-1}$ s^{-1})	$k(Cl + C_2D_4)/k(Cl + C_2H_4)$ ($\pm 2\sigma$)
C_2H_4	FFDS[a]	4	3.3 ± 0.6	
C_2D_4	FFDS	2	10.0 ± 1.9	3.0 ± 0.8
C_2H_4	RR[a]	7	2.9 ± 0.4[c]	
C_2D_4	RR	9	7.8 ± 1.6[c]	2.7 ± 0.7

[a] FFDS = fast flow discharge system at 20 ± 0.5 °C; RR = relative rate at (22 ± 3) °C. [b] Weighted average of individual runs using $w = 1/\sigma^2$. [c] From ratio of rate constants using CH_4 as the reference compound and $k(Cl + CH_4) = (1.0 \pm 0.1) \times 10^{-13}$ cm^{-3} $molecule^{-1}$ s^{-1} from refs 8 and 9. Uncertainties include statistical uncertainties from relative rate measurements as well as 10% uncertainty in the Cl + CH_4 rate constant.[9]

in the wall loss of chlorine atoms on addition of the organic. For the other runs, the intercepts are approximately twice the 2σ errors. This is likely due to an overcorrection for the loss of Cl on the injector and does not influence the slope of the curves in Figure 1. Clearly, the reaction of C_2D_4 is much faster than that of C_2H_4.

Figure 2 shows typical relative rate data. The data are consistent with eq II, and the slopes of the plots can be used to obtain the ratio of the rate constant for the ethene reactions relative to Cl + CH_4. Again, it is clear that the C_2D_4 reaction has a significantly larger rate constant than C_2H_4.

Table 1 summarizes the kinetic data. Although FFDS studies are particularly sensitive to wall reactions and small amounts of impurities in the organics, the rate constants obtained using the RR method are in good agreement with the FFDS values and also show the factor of 3 increase for the C_2D_4 reaction compared to C_2H_4. The good agreement in the absolute values of the rate constants between the two methods is, in fact, surprising in that the FFDS studies were carried out in He and most of the RR experiments in N_2, which should be more efficient in stabilizing the excited adduct. The reasons for this are not clear.

This appears to be the first kinetics study of the Cl + C_2D_4 reaction. However, a number of measurements of the rate constant for the Cl + C_2H_4 reaction have been carried out (for reviews, see refs 6−9). Most relevant to our studies is the determination of the pressure dependence of the Cl + ethene reaction reported recently by Wallington et al.[10] and Kaiser and Wallington.[11] Our rate constant for C_2H_4 is 36% smaller than the value of $(4.7 \pm 0.6) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} calculated using their values of k_0 and k_∞ for 1 Torr.[11] It is in excellent agreement with a value of $(3.3 \pm 0.4) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} reported recently by LeBras and co-workers.[22]

In short, the reaction of Cl with C_2D_4 is a factor of 3 times faster than the reaction with C_2H_4 at 1 Torr total pressure and 20 °C, showing an *inverse* kinetic isotope effect.[23] A similar effect has been reported for the association reaction of Ni with ethene,[24] where the rate constant for the reaction of C_2D_4 at 5 Torr is a factor of 2.4 times faster than that for C_2H_4. Similarly, the ratio of the low-pressure third-order rate constants for the reaction of OH with C_2D_4 and C_2H_4 has been reported to be 3.[25]

Such increases in the low-pressure rate constant for C_2D_4 compared to C_2H_4 are in agreement with the predictions of unimolecular rate theory.[23,26−28] Thus, the mechanism of the reaction involves addition to form an excited adduct:

$$Cl + C_2H_4 \leftrightarrow (ClC_2H_4)^* \qquad (1,-1)$$

$$(ClC_2H_4)^* + M \rightarrow ClC_2H_4 + M \qquad (2)$$

At low pressures, the measured second-order rate constant approaches the value $\{k_1k_2/k_{-1}\}$, where k_1, k_2, and k_{-1} are the rate constants for reactions 1, 2, and −1 above. In the C_2D_4Cl adduct, the density of vibrational states is larger. As a result, the lifetime of $(ClC_2D_4)^*$ with respect to decomposition back to reactants, eq −1, is longer, i.e., k_{-1} is smaller than that for $(ClC_2H_4)^*$. Stabilization of the excited adduct in eq 2 becomes relatively more important, leading to an increase in the measured overall rate constant.

The effect of deuteration on the low-pressure rate constants for Cl + C_2D_4 and Cl + C_2H_4 can be estimated if the energy in the excited adduct is known. The heat of formation of the radical adduct $ClCH_2CH_2$ has been reported in various studies[29−31] to be 22.8 ± 2, 21.8 ± 1, and 26.2 kcal mol^{-1}, respectively. The first two are in reasonable agreement with a value of 19.3 kcal mol^{-1} estimated using group additivity methods.[32] Taking $\Delta H_f^\circ(ClCH_2CH_2) = 21.8$ kcal mol^{-1},[30] and $\Delta H_f^\circ(Cl) = 28.9$ and $\Delta H_f^\circ(C_2H_4) = 12.45$ kcal mol^{-1} for the reactants,[9] the net energy residing in the adduct is 19.6 kcal mol^{-1}.

The mechanism of unimolecular thermal dissociations is similar to eq 1, −1 and 2 above, except that the excited adduct is formed by collisions with other gases rather than by the chemical reaction 1. The kinetics of such reactions have been treated in detail elsewhere.[23,26−28,32,33] For example, using the formulation of Troe and co-workers,[26−28] the ratio of the limiting low-pressure rate constants for thermal unimolecular reactions is given by eq III:

$$\frac{k_0(C_2D_4)}{k_0(C_2H_4)} = \frac{\left[\frac{\rho_{vib}(E_0)}{Q_{vib}}\right]_{C_2D_4}}{\left[\frac{\rho_{vib}(E_0)}{Q_{vib}}\right]_{C_2H_4}} \cdot \frac{[F_E F_{ROT} F_{ROT-INT}]_{C_2D_4}}{[F_E F_{ROT} F_{ROT-INT}]_{C_2H_4}} \qquad (III)$$

In eq III, $\rho_{vib}(E_0)$ is the harmonic oscillator density of states at the threshold energy for dissociation ($E_0 = 19.6$ kcal mol^{-1}), Q_{vib} is the vibrational partition function, F_E reflects the energy dependence of the density of states, F_{ROT} reflects the rotational state dependence of the threshold energy and vibrational density of states, and $F_{ROT-INT}$ is a correction for internal rotations in the molecule. The density of states for each adduct was calculated using the Whitten−Rabinovitch approximation.[23,34] Vibrational frequencies[35] for C_2H_4Cl were taken as 3394, 3272, 3264, 3191, 1557, 1529, 1338, 1315, 1127,1118, 803, 714, 620, 317, and 218 cm^{-1} and those for C_2D_4Cl as 2531, 2372, 2427, 2319, 1261, 1130, 1031, 1016, 937, 844, 586, 679, 535, 272, and 157 cm^{-1}. The factors F_E, F_{ROT} and $F_{ROT-INT}$ were calculated as suggested by Troe.[26-28] This approach gives $k_0(C_2D_4)/k_0(C_2H_4) = 3.2$. This ratio reflects the slower decomposition of the excited (C_2D_4Cl) adduct due to the increased density of states and is also the ratio predicted for $k_{Cl+C_2D_4}/k_{Cl+C_2H_4}$. This value is in excellent agreement with the experimentally determined ratio of rate constants.

The inverse isotope effect is pronounced in the low-pressure limit, which is the case for the ethene reaction at 1 Torr. At the high-pressure limit, stabilization of the adduct predominates and this effect should not be observed. For higher alkenes with allylic hydrogens where abstraction can occur, the opposite effect, i.e., smaller rate constants for the deuterated species, is expected due to zero-point energy changes. This has indeed been observed for the case of the isoprene reaction.[15]

Conclusions

The reaction of chlorine atoms with ethene is in the low-pressure limit at 1 Torr total pressure and room temperature. The rate constant for Cl + C_2D_4 under these conditions determined using two independent approaches, fast flow discharge and relative rate methods, is a factor of 3 times larger than that for the C_2H_4 reaction. This inverse kinetic isotope effect is caused by the increased lifetime of the deuterated excited adduct with respect to dissociation back to reactants due to the increased density of states and is in excellent agreement with the predictions of unimolecular rate theory.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. ATM-9302475) and the Department of Energy (Grant No. DE-FG03-94ER61899) for support of this work. We also thank M. McGrath for providing the vibrational frequencies, Ms. Noyan Aynechi for experimental assistance, J. Greaves for mass spectral analysis and S. W. Benson, M. Wolfsberg, F. P. Tully, R. Atkinson, F. S. Rowland, and K. Oum for helpful discussions.

References and Notes

(1) Finlayson-Pitts, B. J. *Res. Chem. Intermed.* **1993**, *19*, 235.

(2) Keene, W. C. Inorganic Cl Cycling in the Marine Boundary Layer: A Review. In *Naturally Produced Organohalogens*; Grimvall, A., de Leer, E. W. B., Eds.; Kluwer Academic Publishers: Dordrecht, 1995; pp 363−373.

(3) Keene, W. C.; Jacob, D. J.; Fan, S. *Atmos. Environ.* **1996**, *30*, i.

(4) McKay, W. A.; Turner, M. F.; Jones, B. M. R.; Halliwell, C. M. *Atmos. Environ.* **1996**, *30*, 2583.

(5) Moore, R. M.; Oram, D. E.; Penkett, S. A. *Geophys. Res. Lett.* **1994**, *21*, 2507.

(6) NIST Standard Reference Database 17, NIST Chemical Kinetics Database Version 6.01.

(7) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data*, **1997,** *26*, 521.

(8) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(9) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation No. 12. JPL Publication No. 97-15; JPL: Pasadena, CA, 1997.

(10) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marston, G. *J. Phys. Chem.* **1990**, *94*, 3644.

(11) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 4111.

(12) Iyer, R.; Rogers, P. J.; Rowland, F. S. *J. Phys. Chem.* **1983**, *87*, 3799.

(13) Lee, F. S. C.; Rowland, F. S. *J. Phys. Chem.* **1977**, *81*, 1222.

(14) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 9788.

(15) Ragains, M.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **1997**, *101*, 1509.

(16) Pilgrim, J. S.; Taatjes, C. A. *J. Phys. Chem. A* **1997**, *101*, 4172.

(17) Benson, S. W. Personal communication.

(18) Pilgrim, J. S.; Taatjes, C. A. *J. Phys. Chem. A* **1997**, *101*, 5776.

(19) Beichert, P.; Wingen, L.; Lee, J.; Vogt, R.; Ezell, M. J.; Ragains, M.; Neavyn, R.; Finlayson-Pitts, *J. Phys. Chem.* **1995**, *99*, 13156.

(20) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley: New York, 1986.

(21) Brauers, T.; Finlayson-Pitts, B. J. *Int. J. Chem. Kinet.* **1997**, *29*, 665.

(22) LeBras, G. ARCTOC Final Report; Platt, U., Lehrer, E., Eds.; University of Heidelberg: Heidelberg, July, 1997.

(23) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

(24) Mitchell, S. A. *Int. J. Chem. Kinet.* **1994**, *26*, 97.

(25) Tully, F. P. Unpublished data as reviewed by: Atkinson, R. Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds. *J. Phys. Chem. Ref. Data* **1989**, Monograph No. 1, 101.

(26) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4745.

(27) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4758.

(28) Troe, J. *J. Phys. Chem.* **1979**, *83*, 114.

(29) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.

(30) Miyokawa, K.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990**, *94*, 715.

(31) Sekušak, S.; Güsten, H.; Sabljić, A. *J. Chem. Phys.* **1995**, *102*, 7504.

(32) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(33) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, 1990.

(34) Whitten, G. Z.; Rabinovitch, B. S. *J. Chem. Phys.* **1963**, *38*, 2466.

(35) McGrath, M. Personal communication, unscaled MP2/6-31G(d,p) frequencies.