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Kinetics of the Reaction of C_2Cl_3 with Cl_2

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The reaction $C_2Cl_3 + Cl_2 \rightarrow C_2Cl_4 + Cl$ has been studied using the laser photolysis/photoionization mass spectrometry technique. Rate constants were determined in time-resolved experiments as a function of temperature (299−668 K). Rate constants of the above reaction are independent of the bath gas density within the experimental range, $[\mathrm{He}] = (3-12) \times 10^{16}$ atom cm^{-3}. Within the above experimental range of temperatures, the rate constants of the above reaction can be described by the modified Arrhenius expression $k_1 = 3.79 \times 10^{-15}\ T^{0.87} \exp(-55\ \mathrm{K}/T)$ cm^3 molecule^{-1} s^{-1}.

Introduction

Reactions of chlorinated hydrocarbon radicals are important constituents of such complex processes as combustion and incineration of chlorinated hydrocarbons, industrial chlorination, and the chemistry of the Earth's atmosphere. Kinetic modeling of these processes is essential for understanding their mechanisms and for use of these mechanisms as tools of prediction and control. Success of such modeling is currently limited by the lack of fundamental information on the rates and products of a large number of elementary reactions involving chlorinated hydrocarbon radicals.[1] Reactions of the trichlorovinyl radical, C_2Cl_3, have been demonstrated to be among the most important and sensitive reactions in a number of systems of combustion and pyrolysis of chlorine-rich unsaturated chlorinated hydrocarbons.[2−4] Key reactions of C_2Cl_3 responsible for its removal are its reaction with O_2, thermal decomposition, and the reaction with molecular chlorine. The predicted concentration profiles of both the original chlorinated hydrocarbons being oxidized or pyrolyzed and chlorinated products of pyrolysis are very sensitive to the rates of these reactions.[2−4] Only the $C_2Cl_3 + O_2$ reaction has been studied experimentally before.[5] No experimental information on either the thermal decomposition of C_2Cl_3 or its reaction with Cl_2 is available in the literature.

Here we report the results of our experimental investigation of the reaction of the C_2Cl_3 radical with molecular chlorine:

$$C_2Cl_3 + Cl_2 \rightarrow C_2Cl_4 + Cl \tag{1}$$

Reaction 1 was studied in the 299−668 K temperature interval at low densities of the helium bath gas ($[\mathrm{He}] = (3-12) \times 10^{16}$ atom cm^{-3}). The experimental study is described in the next section. A discussion of the rate constant values obtained and the means of their extrapolation to temperatures outside the experimental range concludes the article.

Experimental Study and Results

Trichlorovinyl radicals were produced by the pulsed, 248-nm laser photolysis of tetrachloroethylene[5]:

$$C_2Cl_4 \xrightarrow{248\ \mathrm{nm}} Cl + C_2Cl_3$$
$$\rightarrow \text{other products} \tag{2}$$

The decay of C_2Cl_3 was subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Details of the experimental apparatus[6] and procedures[7] used have been described before and thus are only briefly reviewed here.

Pulsed unfocused 248-nm radiation (4 Hz) from a Lambda Physik EMG 201MSC excimer laser was directed along the axis of a heatable Pyrex reactor (1.05-cm i.d., coated with halocarbon wax or uncoated). Gas flowing through the tube at ≈4 m s^{-1} contained the radical precursor (≤0.01%), molecular chlorine in varying concentrations, and an inert carrier gas (He) in large excess. The flowing gas was completely replaced between laser pulses.

Gas was sampled through a hole (0.04-cm diameter) in the side of the reactor and formed into a beam by a conical skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and mass selected. C_2Cl_3 and C_2Cl_4 were ionized using the light from a hydrogen resonance lamp (10.2 eV). Temporal ion signal profiles were recorded on a multichannel scaler from a short time before each laser pulse up to 25 ms following the pulse. Typically, data from 1000 to 10 000 repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under pseudo-first-order conditions with Cl_2 in large excess over C_2Cl_3 ($[Cl_2] = 5.95 \times 10^{12} - 9.7 \times 10^{14}$ molecule cm^{-3}). The observed exponential decay of the C_2Cl_3 radical was attributed to reaction 1 and heterogeneous loss:

$$C_2Cl_3 \rightarrow \text{heterogeneous loss} \tag{3}$$

The C_2Cl_3 ion signal profiles were fit to an exponential function ($[C_2Cl_3]_t = [C_2Cl_3]_0 \exp(-k't)$, $k' = k_1[Cl_2] + k_3$) by using a nonlinear least squares procedure. In a typical experiment to determine k_1, the kinetics of the decay of C_2Cl_3 radicals was recorded as a function of concentration of molecular chlorine. Values of k_3 were determined in the absence of Cl_2. Values of k_1 were obtained from the slopes of linear plots of k' vs $[Cl_2]$. Experiments were performed to establish that the decay

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TABLE 1: Conditions and Results of Experiments to Determine the Rate Constants k_1 of the Reaction of C_2Cl_3 with Cl_2

T/K	[M][a]	$[C_2Cl_4]$[b]	$[Cl_2]$[c]	$[C_2Cl_3]_0$[d]	I[e]	k_3/s^{-1}	k_1[f]
299	12.0	1.2	0.67−4.97	0.04	100	23.0[g]	4.29 ± 0.79
300	11.5	4.9	0.68−4.79	0.10	33	8.8[g]	4.61 ± 0.45
323	11.7	5.3	0.06−4.03	0.11	33	9.6[g]	4.89 ± 0.42
370	12.0	143	2.41−9.73	1.0	15	34.0	5.82 ± 0.51
373	3.0	5.1	0.67−3.03	0.12	33	9.9[g]	5.95 ± 0.78
373	11.6	4.9	0.64−6.03	0.12	33	18.0[g]	5.30 ± 0.75
400	12.0	18.8	0.67−2.61	1.7	100	55.9	6.31 ± 0.87
423	12.2	5.1	0.68−3.36	0.22	34	11.6[g]	6.12 ± 0.67
425	6.0	12.9	1.74−9.14	1.3	93	37.0	6.58 ± 0.81
451	12.0	6.0	0.78−4.32	0.78	100	28.3	7.00 ± 0.55
501	12.0	4.4	0.84−6.24	0.69	100	30.3	7.16 ± 0.76
525	12.0	2.6	0.64−3.78	0.44	100	13.0	7.86 ± 0.62
550	12.0	5.0	1.10−6.03	1.0	100	31.6	8.38 ± 0.60
600	12.0	6.2	0.69−4.36	0.98	100	101.1[h]	8.9 ± 0.90
622	11.8	44.9	1.07−5.14	0.94	12	168.3[h]	9.39 ± 0.66
629	6.0	5.5	0.55−3.10	1.2	100	128.9[h]	9.06 ± 1.31
651	3.0	5.2	0.63−2.51	1.2	100	129.8[h]	10.18 ± 0.94
668	3.0	11.1	0.45−2.98	2.1	100	208.4[h]	10.21 ± 1.48

[a] Concentration of the bath gas (helium) in units of 10^{16} atom cm^{-3}. [b] In units of 10^{11} molecule cm^{-3}. [c] In units of 10^{14} molecule cm^{-3}. [d] In units of 10^{11} molecule cm^{-3}. The C_2Cl_3 concentrations were obtained by measuring the photolytic depletion of C_2Cl_4 (in the absence of Cl_2) and represent an upper limit since they were obtained assuming a 100% yield of C_2Cl_3 in the photolysis. [e] Estimated photolyzing laser intensity in mJ pulse^{-1} cm^{-2}. [f] In units of 10^{-13} cm^3 molecule^{-1} s^{-1}. Error limits represent a sum of 2σ statistical uncertainty and estimated systematic uncertainty. [g] Pyrex reactor coated with halocarbon wax was used. Uncoated Pyrex reactor was used in all other experiments. [h] These values of k_3 include a contribution from the thermal decomposition of C_2Cl_3.

constants did not depend on the initial C_2Cl_3 concentration (provided that the concentration was kept low enough to ensure that radical−radical reactions had negligible rates in comparison to the reaction with Cl_2), the concentration of the radical precursor, or the photolyzing laser intensity. Two types of reactor wall surfaces were used: an uncoated Pyrex reactor and a reactor coated with halocarbon wax. Heterogeneous wall losses on the uncoated reactor increased at temperatures below approximately 370 K; hence, a coating was used at these lower temperatures. Experiments were performed in the 370−425 K temperature range to demonstrate that the experimental rates of reaction 1 did not depend on the type of wall coating.

Rate constants of reaction 1 were determined at $T = 299-668$ K and $[He] = (3-12) \times 10^{16}$ atom cm^{-3}. The upper temperature limit of the experiments was determined by the onset of thermal decomposition of trichlorovinyl radicals. The conditions and results of these experiments are presented in Table 1. An example of a k' vs $[Cl_2]$ plot is shown in Figure 1. The intercept at $[Cl_2] = 0$ corresponds to the rate of heterogeneous decay of C_2Cl_3 radicals, k_3.

The sources of error in the measured experimental parameters were subdivided into statistical and systematic and propagated to the final values of the rate constants using different mathematical procedures for propagating systematic and statistical uncertainties.[8] The error limits of the experimentally obtained rate constant values reported in this work represent a sum of 2σ statistical uncertainty and estimated systematic uncertainty.

The values of the bimolecular rate constant k_1 determined in this study are presented on an Arrhenius plot in Figure 2. The results yield the modified Arrhenius expression

$$k_1 = 3.79 \times 10^{-15}\, T^{0.87} \exp(-55\ \mathrm{K}/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} \quad \text{(I)}$$

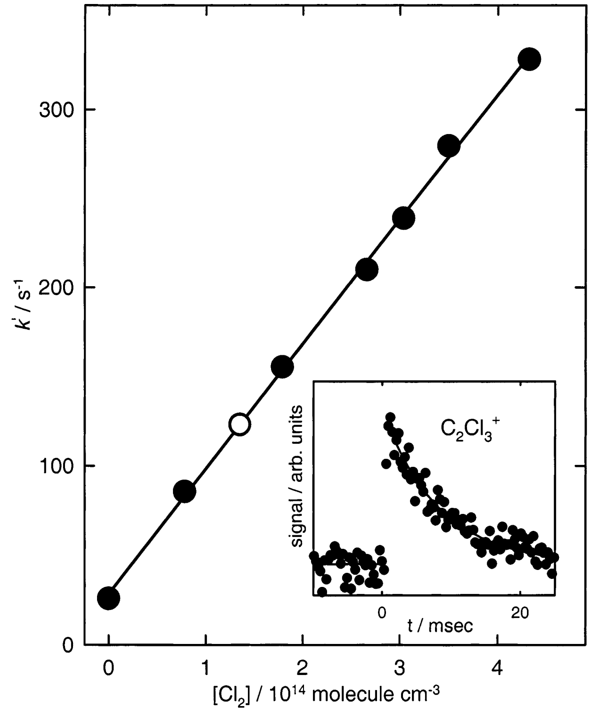

Figure 1. First-order C_2Cl_3 decay rate k' vs $[Cl_2]$. The intercept at $[Cl_2] = 0$ corresponds to the rate of heterogeneous decay of C_2Cl_3. $T = 451$ K, $[He] = 1.2 \times 10^{17}$ molecule cm^{-3}, $[C_2Cl_3]_0 \leq 7.8 \times 10^{10}$ molecule cm^{-3}, $[C_2Cl_4] = 6.0 \times 10^{11}$ molecule cm^{-3}. The inset shows the recorded C_2Cl_3 decay profile for the conditions of the open circle: $[Cl_2] = 1.35 \times 10^{14}$ molecule cm^{-3}, $k' = 123.2$ s^{-1}.

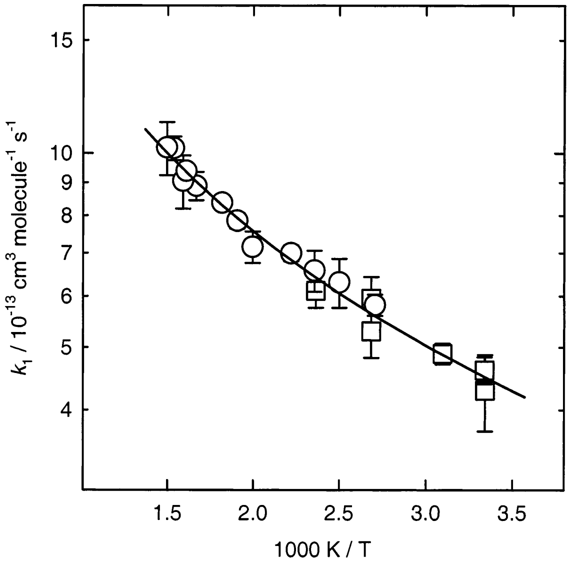

Figure 2. Temperature dependence of the rate constant of reaction 1. Symbols: experimental results. Squares represent data obtained using the reactor coated with halocarbon wax; circles: data obtained with uncoated Pyrex reactor. Error limits of individual points are 2σ statistical uncertainties. Line: Arrhenius fit (expression I).

The rate constants demonstrate no dependence on pressure within the experimental range.

Discussion

The results of the current study provide the first experimental determination of the rate constant of reaction 1. Values of k_1 were obtained in direct real-time experiments as a function of temperature. The absence of a pressure dependence is in agreement with the expected mechanism of this reaction being that of a simple abstraction.

The values of the rate constants of reaction 1 are significantly larger than previously thought: difference factors of 2−17 and 9−700 are obtained if the experimental results of the current study are compared with the expressions used in refs 2 and 3, respectively, in the temperature intervals of the current work. In these earlier modeling studies of oxidation[2] and pyrolysis[4] of C_2HCl_3 and pyrolysis of C_2Cl_4[3], in the absence of any experimental information, the rate constants of reaction 1 were estimated and thus the deviations with the results of the current experimental study are not surprising. This comparison serves to demonstrate the relevance of the new experimental information.

The larger experimental values of the rate constant and the corresponding lower activation energy may have implications for the role of the $C_2Cl_3 + Cl_2$ reaction in the combustion of chlorinated hydrocarbons. In particular, this reaction may result in formation of tetrachloroethylene in the relatively cool post-flame zone where Cl_2 can be present in substantial concentrations.[9]

An attempt at using transition state theory to extrapolate the experimental data to temperatures outside the experimental range was performed. The properties (rotational constants and vibrational frequencies) of the C_2Cl_3 radical and the initial approximation to the properties of the transition state of reaction 1 were obtained in ab initio calculations performed at the UMP2/6-311G(d) level. (Reference 10 can be consulted for the description of the method.) IRC (intrinsic reaction path)[11] calculations were performed in mass weighted internal coordinates[12] to ensure that the transition state structure found in geometry optimization corresponds to reaction 1. The Gaussian 98[13] program was used in the calculations. Experimental properties[14] of Cl_2 were used. The energy barrier of reaction 1 and the three lowest vibrational frequencies of the transition state (replaced with one triple-degenerate frequency in the fitting procedure) were adjusted to achieve agreement of the calculated $k_1(T)$ dependence with the experimental data. The resultant optimized energy of the transition state was found to be 4.15 kJ mol^{-1} below the energy of the reactants. The temperature dependence of the rate constant is positive despite the negative barrier because of the increase with temperature of the ratio of the partition functions of the transition state and the reactants. This strong temperature dependence of the partition functions ratio is due to the presence in the transition state of three low-frequency vibrational modes (27, 50, and 62 cm^{-1} obtained in ab initio calculations), which are in the classical limit at all experimental temperatures.

A transition state with energy below the energy of reactants is not physically unrealistic. For example, formation of an intermediate complex followed by a transition state, the energy of which is below the energy of the reactants, has been suggested earlier by Russell and co-workers in order to explain the negative temperature dependences of the rate constants of the reactions of HBr with CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9 radicals.[15−17] Their hypothesis was later corroborated by quantum chemical calculations and RRKM analysis carried out by Chen and co-workers for the H-atom abstraction from the hydrogen halides by methyl and ethyl radicals.[18−20] However, such a structure of the potential energy surface (loosely bound intermediate → low energy barrier) has negative implications for the use of transition state theory. Extensive information on the properties of the intermediate and the part of the potential energy surface responsible for its formation is needed for meaningful modeling. Such information is not currently available. Although properties of an oversimplified model with a single transition state created in the modeling attempt of the current work can be fitted to approximately reproduce the $k_1(T)$ dependence, the resultant curvature of the Arrhenius plot does not match the experimental results (see Supporting Information). Such a model cannot be used for extrapolation of the experimental temperature dependence of the rate constant. Therefore, no alternative to the use of the modified Arrhenius expression I can be suggested at this time.

Detailed information on the properties of the transition state and the C_2Cl_3 molecule obtained in ab initio calculations, those of the transition state theory model, and the resultant temperature dependence of k_1 are provided in the Supporting Information.

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Supporting Information Available: Includes the results of the quantum chemical and rate constant calculations (Table 1S) and plot of the calculated and the experimental $k_1(T)$ dependences (2 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tsang, W. *Combust. Sci. Technol.* **1990**, *74*, 99.

(2) Chang, W. D.; Senkan, S. M. *Environ. Sci. Technol.* **1989**, *23*, 3, 442.

(3) Taylor, P. H.; Tirey, D. A.; Dellinger, B. *Combust. Flame* **1996**, *104*, 260.

(4) Taylor, P. H.; Tirey, D. A.; Rubey, W. A.; Dellinger, B. *Combust. Sci. Technol.* **1994**, *101*, 75.

(5) Russell, J. J.; Seetula, J. A.; Gutman, D.; Senkan, S. M. *J. Phys. Chem.* **1989**, *93*, 1934.

(6) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342.

(7) Knyazev, V. D.; Bencsura, A.; Stoliarov, S. I.; Slagle, I. R. *J. Phys. Chem.* **1996**, *100*, 11346.

(8) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(9) Procaccini, C.; Bozzelli, J. W.; Longwell, J. P.; Smith, K. A.; Sarofim, A. F. *Environ. Sci. Technol.* **2000**, *34*, 4565.

(10) Foresman, J. B.; Frisch, A. E. *Exploring Chemistry With Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(11) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(12) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, 1.

(15) Russell, J. J.; Seetula, J. A.; Senkan, S. M.; Gutman, D. *Int. J. Chem. Kinet.* **1988**, *20*, 759.

(16) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.

(17) Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084.

(18) Chen, Y.; Tschuikov-Roux, E. *J. Phys. Chem.* **1993**, *97*, 3742.

(19) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.* **1991**, *95*, 9900.

(20) Chen, Y.; Tschuikow-Roux, E.; Rauk, A. *J. Phys. Chem.* **1991**, *95*, 9832.