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LETTERS

Thermal Rate Constant for Addition of Chlorine Atoms to Ethylene

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The relative reaction rate constant for removal of Cl atoms by addition to C_2H_4 in the gas phase at 4000-torr pressure has been measured at 298 K by a competitive radiochemical technique to be 2.9 ± 0.1 times faster than the abstraction of H from C_2H_6 by Cl. This removal rate corresponds to an apparent reaction rate constant of $(16.6 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, based on the measured value for reaction with C_2H_6. Correction for back-reaction of $C_2H_4Cl^*$ at 4000 torr leads to an estimated absolute reaction rate constant of $(19 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for k_1, $Cl + C_2H_4 \rightarrow C_2H_4Cl^*$ (1). The relative rates of abstraction by Cl of H from HI and PH_3 are 2.21 ± 0.10 and 4.13 ± 0.13 times faster than abstraction from C_2H_6.

Although their occurrence in the earth's atmosphere has brought interest in the absolute reaction rate for many Cl atom reactions,[1,2] no measurements have been made since the late 1960s of the rate constant for the addition of Cl to C_2H_4 as in reaction 1.[3-5] Earlier studies from this

$$Cl + C_2H_4 \rightarrow C_2H_4Cl^* \qquad (1)$$

laboratory have provided relative rate constants for the addition of chlorine atoms to various alkenes and alkynes,[6-12] and a value for k_1 is useful for conversion of these relative rate constants onto an absolute scale. In addition, the measurement of many additional Cl atom reaction rates has disclosed some inconsistencies among the absolute reaction rate constants.[1,2,13-15] Accordingly, we have carried out a series of intermolecular competitions to determine again the reaction rate constant k_1. We now report an effective value for Cl removal by C_2H_4 of $(16.6 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 4000-torr pressure of $CClF_3$. The rate constant for permanent removal of Cl by reaction 1 is pressure dependent because of the back-reaction 2, which returns thermal Cl atoms into the system

$$C_2H_4Cl^* \rightarrow C_2H_4 + Cl \qquad (2)$$

for cycling again through the available competitive path-

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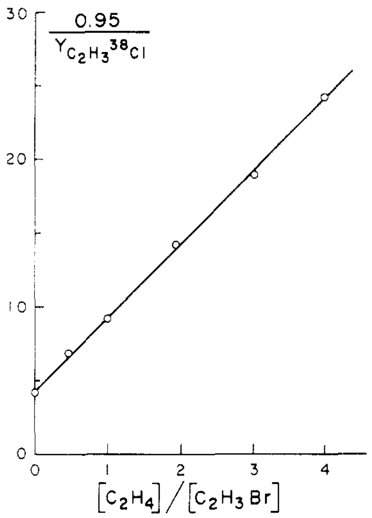

Figure 1. Reciprocal yields of $CH_2{=}CH^{38}Cl$ from competitive reactions between C_2H_4 and C_2H_3Br for ^{38}Cl atoms at 4000-torr total pressure in excess $CClF_3$.

ways. Our evaluation of the importance of k_2 from the pressure dependence of the effective removal rate leads to an estimated infinite-pressure rate constant of $k_1 = (19 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

We have utilized thermalized ^{38}Cl atoms from the neutron irradiation of $CClF_3$[6,11] for evaluation of relative reaction rate constants for C_2H_4 and C_2H_6 vs. a common competitor, $CH_2{=}CHBr$.[8] The energetic radioactive chlorine atoms formed in the $^{37}Cl(n,\gamma)^{38}Cl$ nuclear reaction are moderated to thermal energies by multiple collisions with $CClF_3$ present in great excess and then react with the competitive substrate molecules.[6,11] Vinyl bromide was chosen as the competitor standard because the reaction of ^{38}Cl with it by reaction 3 produces a good yield of

$$^{38}Cl + CH_2{=}CHBr \rightarrow CH_2{=}CH^{38}Cl + Br \qquad (3)$$

$CH_2{=}CH^{38}Cl$, which can be readily separated and assayed by radio gas chromatography.[16] The ratio of the effective rate constants for removal of ^{38}Cl by a given substrate in competition with $CH_2{=}CHBr$ is determined experimentally from the diminution in percentage yield of $CH_2{=}CH^{38}Cl$ as thermal ^{38}Cl atoms are diverted away from $CH_2{=}CHBr$ through reaction with the other substrate molecule. The reactivity of C_2H_4 vs. C_2H_6 is thus determined indirectly from their relative efficiencies in diminishing the observed yield of $CH_2{=}CH^{38}Cl$ in separate competitions with vinyl bromide. These rate constant data for C_2H_4 have then been placed on an absolute basis through the value $k_4 = (5.7 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, the consensus value from experiments by four separate research groups.[1,2]

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \qquad (4)$$

The yield of $CH_2{=}CH^{38}Cl$ from reaction 3 has been measured in a series of experiments with varying ratios of C_2H_4 and C_2H_3Br at 4000-torr pressure in $CClF_3$. The ratio of effective reaction rate constants can be obtained either directly from the ratio of the decrement in $CH_2{=}CH^{38}Cl$ yield to the remaining yield for a fixed competitor ratio or from the slope of the straight line in a graph of reciprocal yields, as in Figure 1.[11] This line, with allowance for the loss through energetic reactions of 5% of the total ^{38}Cl,[11,12] has a slope of 4.91 ± 0.09, representing the ratio of reactivities at 4000 torr for C_2H_4 and for $CH_2{=}CHBr$

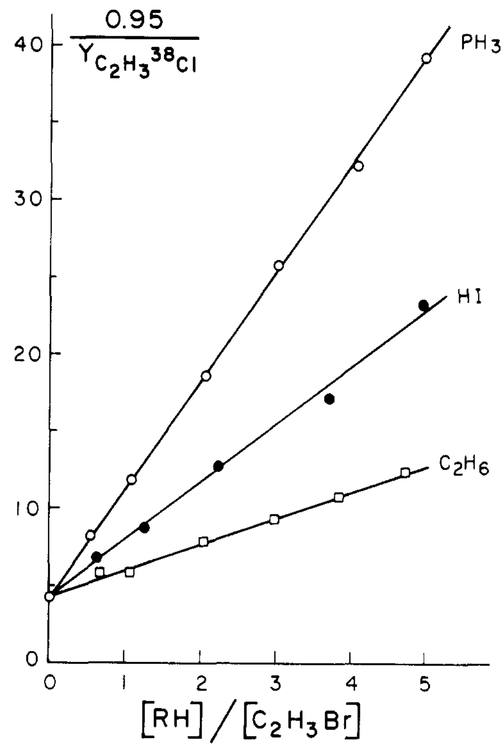

Figure 2. Reciprocal yields of $CH_2{=}CH^{38}Cl$ from competitive reactions between RH and C_2H_3Br for ^{38}Cl atoms at 4000-torr total pressure in excess $CClF_3$. RH: (○) PH_3; (●) HI; (□) C_2H_6.

leading to reaction 3. The reciprocal yields of $CH_2{=}CH^{38}Cl$ from reaction 3 in competition with hydrogen abstraction reactions for C_2H_6, PH_3, and HI are all graphed in Figure 2 vs. the respective concentration ratios. The values for the slopes in Figure 2 are 1.69 ± 0.05 for C_2H_6, 3.74 ± 0.13 for HI, and 6.98 ± 0.07 for PH_3.

The ratio of the effective rate constants for ^{38}Cl removal by C_2H_4 and C_2H_6 can be obtained from the ratios of the respective slopes, i.e., 2.91 ± 0.10 from the data given above. The corresponding absolute rate constant for removal of Cl by C_2H_4 based on the known value for k_4 is $(16.6 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 4000-torr pressure of $CClF_3$. This rate constant is more than twice as large as the existing literature value for k_1[3-5] and is only a lower limit for k_1 because the 4000-torr removal rate is somewhat less than k_1 as a consequence of the back-reaction 2.

The corresponding rate constant ratios vs. C_2H_6 are 4.13 ± 0.13 for PH_3 and 2.21 ± 0.10 for HI, and absolute reaction rate constants of $(23.5 \pm 2.5) \times 10^{-11}$ and $(12.6 \pm 1.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. This rate constant for reaction with HI is in fair agreement with the value of $(15.5 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} measured by Mei and Moore at 298 K.[13,14] The latter's experiments indicated a non-Arrhenius type of rate constant behavior vs. temperature, with a maximum in the rate constant in the temperature range from 300 to 400 K.

The ratio of total reaction rates for Cl with PH_3 vs. HI has been estimated as 1.7 ± 0.6 through observations of the summed relative intensities of infrared emission from vibrationally excited HCl ($v > 0$) product.[15] A substantial contribution to the uncertainty in the infrared measurements arises from correction from the observed 1.6 ± 0.3 ratio for the unmeasured HCl ($v = 0$) product. This rate constant ratio can also be obtained as 1.87 ± 0.10 directly from the slopes of the respective lines in Figure 2.

The rate constant for reaction 3 against the C_2H_6 standard is considerably smaller than the recently measured[17] value of $k_3 = (14 \pm 3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

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TABLE I: Rate Constants for Various Reactions of Atomic Chlorine

molecule	measured slope vs. C_2H_3Br	rel reaction rate constant	ref	absolute reaction rate constant, 10^{-11} cm^3 molecule^{-1} s^{-1}
		$Cl + RH \rightarrow HCl + R$		
C_2H_6	1.69 ± 0.05	(1.0)	this work	(5.7 ± 0.6)
HI	3.74 ± 0.13	2.21 ± 0.10	this work	12.6 ± 1.4
PH_3	6.98 ± 0.07	4.13 ± 0.13	this work	23.5 ± 2.5
$(CH_3)_4Pb$		(4.3/2.5) vs. k_1	9	33 ± 4
		$Cl + C_xH_y \rightarrow C_xH_yCl^*$		
C_2H_4	4.91 ± 0.09	3.3 ± 0.3[a]	this work	19 ± 2
		1.7 ± 0.1 vs. k_{HI}	6	21 ± 3
C_2H_2		0.8 ± 0.1 vs. k_1	9	15 ± 2
		1.2 ± 0.1 vs. k_{HI}	7	15 ± 2
$CH_3CH{=}CH_2$		1.6 ± 0.1 vs. k_{HI}	10	20 ± 3
$CH_3C{\equiv}CH$		1.9 ± 0.2 vs. k_{HI}	11	24 ± 4
		$Cl + R_4M \rightarrow RCl + R_3M$		
$(CH_3)_4Pb$		$(2.5 \pm 0.2)^{-1}$ vs. k_1	9	8 ± 1

[a] Relative reaction rate constant of 2.91 ± 0.10 at 4000 torr used as comparison standard.

However, those experiments were carried out at pressures of 2 torr and less, while the yield from reaction 3 represents only about one-fourth of the available ^{38}Cl in reactions with $CH_2{=}CHBr$ at 4000 torr.[18]

The removal rates of Cl by both C_2H_4 and C_2H_3Br are pressure dependent, but the latter is not of concern here because it is used throughout only as a comparison standard. An earlier study by Lee and Rowland has established the slopes of reciprocal yield curves in HI/C_2H_4 competitions at pressures of 640, 1050, and 4100 torr in $CClF_3$.[6] The average energy loss in collisions of $C_2H_4{}^{38}Cl^*$ with $CClF_3$ has not been established, and relatively weak collisions were observed in similar experiments for $C_2H_4{}^{18}F^*$ with CF_4.[19] We have fitted the earlier $C_2H_4{}^{38}Cl^*$ data with several assumed energy-loss models ranging from strong, single deexcitation collisions to as little as 3 kcal/mol average energy loss and have found that the infinite-pressure removal rate of Cl by C_2H_4 is 1.15 ± 0.05 times the value found for 4000 torr over this range of assumed energy losses. Accordingly, our estimated value for k_1 is $(1.15 \pm 0.05)(16.6 \pm 1.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which we summarize as $k_1 = (19 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

All of these relative data are summarized in Table I and then converted to an absolute basis through comparison with k_4. Other chlorine atom reaction rate constants which have been placed previously on an absolute basis by us[9] through normalization to the value for k_1 are reevaluated here and included in Table I. Experiments with alkenes and alkynes[11] have provided a set of rate constants relative to one another which can also be placed on an absolute scale with knowledge of k_1, as given in Table I.

Finally, although there is a major revision in the best estimate of the reaction rate constant for Cl atom addition to C_2H_4, the experimental disagreement between our results and the previous work with ethylene is substantially smaller than the change in the absolute reaction rate constant for k_1. The actual measurements of Franklin et al. were carried out in a complicated system but eventually involved a competition between C_2H_6 and C_2H_4, with an observation of $k_4/k_1 = 0.38$.[4] Our measured experimental ratio for k_4/k_1 at 4000 torr is 0.34, and our ratio corrected to infinite pressure for full stabilization of all $C_2H_4Cl^*$ radicals is 0.30. The earlier ratio already contained a correction for complete radical stabilization, so the discrepancy between the two competitive experiments is only of the order of 30%. There has, however, been a substantial revision during the past decade in the preferred value for k_4.[1,2]

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