Rates of reaction of atomic oxygen with C2H3F, C2H3Cl, C2H3Br, 1,1-C2H2F2, and 1,2-C2H2F2

3 AUTHORS, INCLUDING:

Robert Huie
National Institute of Standards …

Rates of Reaction of Atomic Oxygen with C_2H_3F, C_2H_3Cl, C_2H_3Br, 1,1-$C_2H_2F_2$, and 1,2-$C_2H_2F_2$

ROBERT E. HUIE and JOHN T. HERRON

National Bureau of Standards, Washington, D.C. 20234

and

DOUGLAS D. DAVIS

Department of Chemistry, University of Maryland, College Park, Maryland 20740

Abstract

Rate constants for the reactions of atomic oxygen (O^3P) with C_2H_3F, C_2H_3Cl, C_2H_3Br, 1,1-$C_2H_2F_2$, and 1,2-$C_2H_2F_2$ have been measured at 307°K using a discharge-flow system coupled to a mass spectrometer. The rate constants for these reactions are (in units of 10^{11} cm³ mole⁻¹ s⁻¹) 2.63 ± 0.38, 5.22 ± 0.24, 4.90 ± 0.34, 2.19 ± 0.18, and 2.70 ± 0.34, respectively. For some of these reactions, the product carbonyl halides were identified.

1. Introduction

While the kinetics of the reaction of atomic oxygen in its ground electronic state with ethylene have been the subject of several recent investigations [1], only a limited number of relative rate constants for the reactions of atomic oxygen with halogen-substituted ethylenes have been reported [2, 3, 4]. These reactions are of interest because of the possible role of halogen-containing compounds in flame inhibition [5], as well as in understanding the effects of halogen substitution on olefin reactivity. We have therefore investigated the kinetics of the interaction of atomic oxygen with several halogen-substituted ethylenes.

2. Experimental

The details of the apparatus have been given previously [6]. Basically, it consisted of a flow reactor coupled through a pinhole orifice to a mass spectrometer. Atomic oxygen is produced by means of a microwave discharge in a dilute mixture of O_2 in argon. A stable reactant is then added to the gas stream through a movable inlet, and reactant concentrations are followed by means of the mass spectrometer.

For a simple bimolecular reaction between atomic oxygen and a second reactant,

$$O + A \rightarrow products$$

521
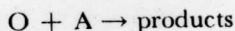
the rate of disappearance of A is given by

$$(1) \qquad\qquad -d[A]/dt = k[A][O]$$

which, upon integration and rearrangement, yields

$$(2) \qquad\qquad k = \ln([A]_0/[A]_t) \Big/ \int_0^t [O]dt$$

where $[A]_0$ and $[A]_t$ are the concentrations of A at times zero and t, respectively.

If the loss of atomic oxygen in the reaction zone is small, the integral in eq. (2) may be replaced by the average value of the atomic oxygen concentration times the reaction time. With a greater extent of reaction, the value of the integral must be determined by measuring the atom concentration at different reaction times and graphically integrating the result. The ratio $[A]_0/[A]_t$ is determined as the ratio of the ion currents in the mass spectrometer at the proper mass with the discharge off and on.

The fundamental assumptions involved in the use of eq. (1) to represent the decay of the organic reactant, and subsequently the use of eq. (2) to derive the rate constant for the reaction, is that the reactant A is lost only through reaction with atomic oxygen and is not reformed in subsequent steps. The rate expression is independent of the mode of loss of atomic oxygen. If there are secondary reactions which significantly consume the reactant A, then the apparent rate constant calculated from eq. (1) would be too high. In general, the occurrence of secondary reactions would cause a dependence of the rate constant on the relative concentrations of the reactants. Only if the rate of the secondary reaction is so rapid that it always occurred subsequent to the primary reaction within the reaction time ($\sim$20 ms) would this not be true. Under our experimental conditions, this would require that the secondary reactions proceed at collision rate, and further that the secondary reactant not react with atomic oxygen at any significant rate. It is unlikely that these two conditions would apply.

If secondary reactions are not this rapid, then a lack of dependence of the rate constant on relative concentrations is good evidence that a simple bimolecular reaction is being followed. In these experiments, rate constants were measured both with atomic oxygen in great excess and over a wide range of relative concentrations to assess the importance of secondary reactions.

In addition to the rate measurements, we have identified the product carbonyl halides formed in some of these reactions.

3. Results

Rate data are listed in Tables I through V. All runs were performed at 307°K. In Table VI, the results are summarized, along with limiting values of the rate constants for the reaction of atomic oxygen with CF_2O and CCl_2O determined in the course of this work. Also listed in Table VI are the observed products for some of these reactions.

Table I: Summary of rate measurements for the reaction of atomic oxygen with C_2H_3F

Reactant concentration, mol cm^{-3} × 10^{12}			$10^{12} \times \int_0^t (O)dt,$	Pressure,	Velocity,	Distance	10^{-11} k,
$(A)_o$	$(A)_t$	$(O)_{ave}$	mol cm^{-3} s	Nm^{-2}	cm s^{-1}	cm	cm^3 mol^{-1} s^{-1}
3.89	3.10	32.4		242	670	16	2.90
12.2	10.4	36.7		167	1060	16	2.91
8.39	7.14	37.6		167	1060	16	2.89
4.10	3.41	37.9		167	1060	16	3.15
7.56	5.11	153		176	1180	16	1.85*
15.7	10.3	155		176	1180	16	1.99*
3.97	2.93	46.4		312	680	16	2.74
2.74	2.00		1.17	201	1120	20	2.69
24.5	18.9		1.08	201	1120	20	2.41
51.0	39.2		.987	201	1120	20	2.64
119	96.4		.782	201	1120	20	2.75
141	116		.734	201	1120	20	2.61
348	306		.476	201	1120	20	2.66

* Atomic oxygen produced by the reaction $N + NO \rightarrow N_2 + O$

Table II: Summary of rate measurements for the reaction of atomic oxygen with C_2H_3Cl

Reactant concentration, mol cm^{-3} × 10^{12}			$10^{12} \times \int_0^t (O)dt,$	Pressure,	Velocity,	Distance	10^{-11} k,
$(A)_o$	$(A)_t$	$(O)_{ave}$	mol cm^{-3} s	Nm^{-2}	cm s^{-1}	cm	cm^3 mol^{-1} s^{-1}
.366	.139	140		176	1180	16	5.03*
1.21	.452	151		249	1310	16	5.14*
1.01	.657	53.1		206	1120	16	5.65
1.77	1.21	51.9		206	1120	16	5.11
5.58	3.93	46.0		206	1120	16	5.37
.849	.500	42.1		312	680	16	5.28
.463	.225		1.38	209	1100	20	5.23
2.11	1.16		1.16	209	1100	20	5.14
11.2	6.46		1.14	209	1100	20	4.78
57.8	40.6		.645	209	1100	20	5.44

* Atomic oxygen produced by the reaction $N + NO \rightarrow N_2 + O$

Table III: Summary of rate measurements for the reaction of atomic oxygen with C_2H_3Br

Reactant concentration, mol cm^{-3} x 10^{12}			10^{12}x$\int_0^t$(O)dt, mol cm^{-3} s	Pressure, Nm^{-2}	Velocity, cm s^{-1}	Distance cm	10^{-11} k, cm^3 mol^{-1} s^{-1}
(A)$_o$	(A)$_t$	(O)$_{ave}$					
7.35	3.91	38.4		207	1080	16	4.81
1.27	.865	27.5		242	670	16	5.39
1.13	.766	46.8		187	1080	16	5.45
2.54	1.87	44.4		187	1080	16	4.76
10.2	7.82	39.7		187	1080	16	4.53
1.42	.922	35.3		312	680	16	5.14
3.76	2.24		1.10	209	1100	20	4.73
14.1	9.22		.937	209	1100	20	4.52
25.2	17.2		.802	209	1100	20	4.76

Table IV: Summary of rate measurements for the reaction of atomic oxygen with $1,1$-$C_2H_2F_2$

Reactant concentration, mol cm^{-3} x 10^{12}		10^{12}x$\int_0^t$(O)dt, mol cm^{-3} s	Pressure, Nm^{-2}	Velocity, cm s^{-1}	Distance cm	10^{-11} k, cm^3 mol^{-1} s^{-1}
(A)$_o$	(A)$_t$					
6.04	4.68	1.20	204	1100	20	2.19
9.33	7.19	1.16	204	1100	20	2.24
6.57	5.26	.917	204	1100	20	2.32
13.2	11.1	.752	204	1100	20	2.38
4.03	3.34	.785	221	1130	20	2.41
17.5	14.8	.823	221	1130	20	1.98
21.9	18.8	.758	221	1130	20	2.07
85.5	75.6	.629	221	1130	20	1.93

Table V: Summary of rate measurements for the reaction of atomic oxygen with $1,2$-$C_2H_2F_2$

Reactant concentration, mol cm^{-3} x 10^{12}		10^{12} x $\int_0^t$(O)dt, mol cm^{-3} s	Pressure, Nm^{-2}	Velocity, cm s^{-1}	Distance cm	10^{-11} k, cm^3 mol^{-1} s^{-1}
(A)$_o$	(A)$_t$					
.943	.719	.957	221	1130	20	2.82
1.82	1.51	.825	221	1130	20	2.26
7.08	5.47	.813	221	1130	20	3.18
13.0	10.3	.896	221	1130	20	2.64
15.8	12.7	.836	221	1130	20	2.61

Table VI: Rate constants for the reaction of atomic oxygen with some haloethylenes at 307K.[a]

Reactant	Aldehydic Products	10^{-11} k, $cm^3 mol^{-1} s^{-1}$	$k/k(C_2H_4)$
C_2H_4	CH_2O	5.15	1.0 (b)
C_2H_3F	CHFO, CH_2O	2.63 ± 0.38	0.51
C_2H_3Cl	CH_2O	5.22 ± 0.24	1.0
C_2H_3Br		4.90 ± 0.34	0.95
$1,1-C_2H_2F_2$	CF_2O, CH_2O	2.19 ± 0.18	0.43
$1,2-C_2H_2F_2$	CHFO	2.70 ± 0.34	0.52
$1,1,2,2-C_2F_2Cl_2$	CF_2O		0.67(c)
$1,2,1,2-C_2F_2Cl_2$	CFClO		
C_2HF_3	CF_2O, CHFO		
C_2F_3Cl	CFClO (CF_2O?)		0.51(c)
C_2F_4	CF_2O		1.05(c,d)
CF_2O		< 0.2	
CCl_2O		< 0.2	

[a] This work unless otherwise noted. Error limits are one standard deviation from the mean.
[b] Ref. 1
[c] Ref. 3, 298K
[d] Ref. 4, 298K

The data of Tables I to V give kinetic results for the reactions of atomic oxygen with the halogenated ethylenes over a wide range of relative concentrations. For the reactions studied no dependence of rate constant on reactant concentration was observed. This indicated that secondary reactions resulting in the consumption of the haloethylenes were not important. For several other compounds, however, a strong dependence was found. These two cases are illustrated in Figure 1 for the reaction of atomic oxygen with $1,1-C_2F_2H_2$, which was well behaved, and C_2F_3H, which showed a strong concentration dependence. Other compounds whose rates of reaction with atomic oxygen showed this strong concentration dependence were C_2F_4, $1,1,2,2-C_2F_2Cl_2$, and C_2F_3Cl. A possible cause for the observed concentration dependence of the rate is the production of halogen atoms in secondary atomic oxygen reactions, which then react with the parent haloethylene. We have not attempted to extrapolate rate constants for these reactions.

Where comparisons can be made, the carbonyl halides observed in this work generally agree with those observed by Mitchell and Simons [7] in a study of the reactions of atomic oxygen with compounds of the type CF_2CXY, where X and Y may be either halogens or hydrogen. The major difference is that both CF_2O and CH_2O were observed as products of the $1,1-C_2F_2H_2$ reaction in this study. Mitchell and Simons saw little CF_2O from this reaction and postulated that CH_2O was formed with sufficient vibrational energy to dissociate. CH_2O, however, is
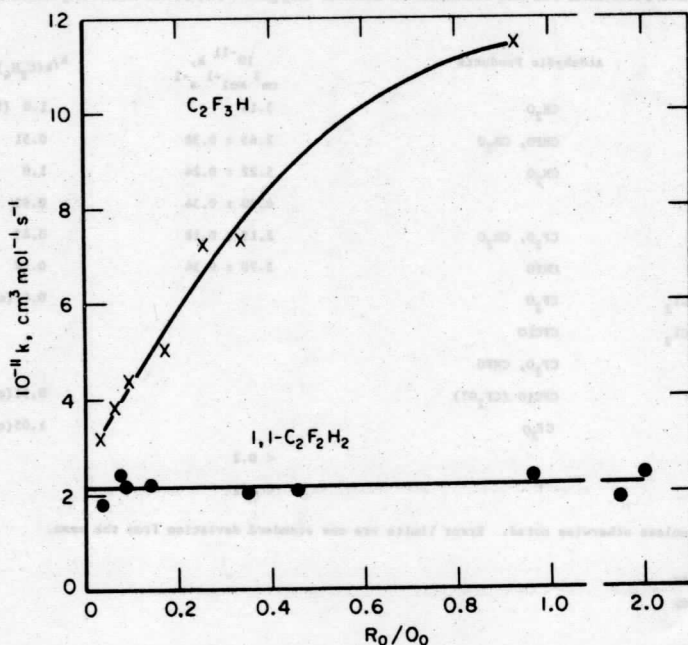
Figure 1. Rate constants for the reactions of atomic oxygen with C_2F_3H and $1,1\text{-}C_2F_2H_2$ as functions of the ratio of initial reactant concentrations.

often difficult to detect, and it is possible that the CF_2O observed in the present work could be from the reaction of CF_2 with molecular oxygen in the reaction mixture, although we think that this is improbable at the low total pressures used in our work.

The products observed in this work for reactions of atomic oxygen with $1,1,2,2\text{-}C_2F_2Cl_2$ and C_2F_3Cl were not observed by Tyerman [3], but were observed by Mitchell and Simons [7]. In the C_2F_3Cl reaction, the CF_2O peak corresponds to a major fragment ion in the mass spectrum of the reactant, so that its indentification is less certain. CHClO, which might have been expected from the C_2H_3Cl reaction, is unstable toward dissociation [7], which is probably the case for CHBrO also.

The mechanism for the reaction of atomic oxygen with tetrafluoroethylene has been extensively studied by Heicklen and coworkers [4, 8] using the mercury-photosensitized decomposition of nitrous oxide as an oxygen atom source. From their data, they derive a mechanism for the reaction involving the production of an aldehyde and a carbene in the initial step $O + C_2F_4 \rightarrow CF_2O + CF_2$. This mechanism has been further supported by the observation of CF_2 by absorption spectroscopy after the flash photolysis of $C_2F_4\text{-}NO_2$ mixtures above 300 nm [3, 7]. Additionally, the flash photolysis studies of Mitchell and Simons support the same

type of mechanism for several other 1,1-difluoroethylenes. The present data are consistent with these observations.

Considerable experimental evidence, however, indicates that the reaction of atomic oxygen with ethylene produces a formyl and a methyl radical in the initial step [9, 10, 11]. In a discharge-flow experiment, formaldehyde is then produced by the subsequent reaction of atomic oxygen with the methyl radical. An equivalent mechanism for the reaction of atomic oxygen with haloethylenes would involve the production of the carbonyl halide from the reaction of atomic oxygen with a halomethyl radical.

The carbonyl halide products observed in the present work tend more to support the Heicklen mechanism for highly substituted haloethylenes. For example, CF_2O is produced in the reaction of atomic oxygen with $1,1,2,2-C_2F_2Cl_2$, while CFClO is produced in the reaction with $1,2,1,2-C_2F_2Cl_2$. In both cases, the halogens in the product correspond to those on one or the other carbon atom in the haloethylene. No mixing of the halogens was observed, as might be expected if a halomethyl radical were the precursor. This evidence is not conclusive, however, since the reaction of atomic oxygen with a mixed halomethyl radical might lead to only one carbonyl halide. Nor do these conclusions necessarily imply that the reactions of atomic oxygen with monosubstituted ethylenes produce an aldehyde and carbene in the initial step.

The effects of halogen substitution on reactivity are not, in general, predictable. Thus, C_2H_3F is about half as reactive as ethylene, whereas C_2F_4 is slightly more reactive. On the other hand, C_2H_3Cl or C_2H_3Br are about as reactive as ethylene, whereas some qualitative observations made during the course of this work indicate that C_2HCl_3 and C_2Cl_4 are considerably less reactive toward atomic oxygen than is ethylene.

Bibliography

[1] D. D. Davis, R. E. Huie, J. T. Herron, M. S. Kurylo, and W. Braun, *J. Chem. Phys.*, **56**, 4868 (1972).

[2] D. Saunders and J. Heicklen, *J. Phys. Chem.*, **70**, 1950 (1966).

[3] W. J. R. Tyerman, *Trans. Faraday Soc.*, **65**, 163 (1969).

[4] (a) D. Saunders and J. Heicklen, *J. Amer. Chem. Soc.*, **87**, 2088 (1965); (b) *J. Phys. Chem.*, **76**, 1950 (1966); (c) J. Heicklen and V. Knight., *ibid.*,p. 3893.

[5] E. C. Creitz, *J. Res. Nat. Bur. Stand.*, **74A**, 1326 (1969).

[6] J. T. Herron and R. E. Huie, *J. Phys. Chem.*, **73**, 1326 (1969).

[7] R. L. Mitchell and J. P. Simons, *J. Chem. Soc.*, 1005 (1968).

[8] J. Heicklen, *Advan. Photochem.*, **7**, 57 (1969).

[9] R. J. Cvetanović, *Advan. Photochem.*, **1**, 131 (1963).

[10] J. T. Herron and R. D. Penzhorn, *J. Phys. Chem.* **73**, 191 (1969).

[11] H. Niki, E. E. Daby, and B. Weinstock, Proceedings of Twelfth Symposium (International) on Combustion, Poitiers, France 1969, p. 277.