Kinetics and Mechanism of the Pyrolysis of Oxygen Difluoride[1]

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Abstract: Because of the considerable uncertainty about the mechanism of the pyrolysis of OF_2, despite several previous studies, the kinetics of this reaction were studied in a monel stirred-flow reactor over the temperature range of 330 to 431°. Initial reactant concentrations ranged from 1 to 10 mol % at 1 atm total pressure. The only observed products were O_2 and F_2. The reaction was found to be slightly less than first order with respect to the reactant concentrations, and the initial rate data could be represented by the rate expression $-[d(OF_2)/dt]_0 = k_2'(M)(OF_2)_0 + k_{3/2}(M)(OF_2)_0^{1/2}$, where k_2' and $k_{3/2}$ are the second- and three-halves-order rate constants, respectively, and (M) is the total concentration of helium and reactant. An Arrhenius plot of the k_2' values gave the expression $k_2' = 10^{16.9\pm0.6} \exp(-39{,}200 \pm 1{,}700/RT)$ cm^3/(mol sec). Because of the relatively small contribution of the three-halves-order term, the uncertainty in the values of $k_{3/2}$ is high, and a comparable treatment is not possible. It was shown beyond reasonable doubt that the low order did not result from surface effects. A radical chain mechanism is proposed which accounts for the observed low order.

The kinetics of the OF_2 pyrolysis have been studied in static reactors,[2,3] in shock tubes,[4-6] and in a plug-flow reactor.[7] The reaction's major products and stoichiometry are well established and are given by the following equation

$$OF_2 \longrightarrow 0.5O_2 + F_2$$

Reported values for the overall activation energy of this reaction, including that of this study, range from 30 to 40 kcal/mol,[2-6] and the following steps are considered to be major contributions to the mechanism[2-6]

$$OF_2 + M \longrightarrow F + OF + M \tag{1}$$

$$2OF \longrightarrow O_2 + 2F\ (\text{or } F_2)^2 \tag{2}$$

$$2F + M \longrightarrow F_2 + M \tag{3}$$

If these steps are the only significant contributors to the pyrolysis mechanism, then the observed activation energy is an approximation to the (FO–F) bond dissociation energy, *i.e.*, the activation energy for step 1. For those studies where large excesses of diluent were used,[3-7] the reaction kinetics were analyzed on the basis of a first-order rate law, *i.e.*, collisional activation resulted primarily from OF_2– diluent collisions. These first-order rate constants are total-pressure dependent. The reaction was observed to be close to second order when undiluted OF_2 was pyrolyzed.[2]

Despite the widespread attention which this reaction has received, there remains significant uncertainty as to the subtleties of its mechanism. The stirred-flow reactor offers the distinct advantage of permitting the direct determination of instantaneous reaction rates. This technique is useful for the elucidation of complex rate laws, because it is highly sensitive to subtle order effects which easily escape detection in systems which totally rely on the integration of assumed rate laws. In addition, the lowest temperature shock tube experiment was carried out at about 500° and the highest temperature used for a static reaction experiment was 350°. Because of this gap between the temperature regimes, it is very difficult to draw generalized conclusions regarding the reaction's mechanism by extrapolating from one regime to the other. The temperature regime of the stirred-flow reaction experiments described herein is intermediate between the two temperature extremes.

Experimental Section

Apparatus. Rate data were obtained using a conventional flow system equipped with an 86-ml monel stirred-flow reactor. The OF_2–He mixtures were stored in a 5-gal tank (OF_2 was obtained from Allied Chemical Co. and was better than 99% pure, the major impurity being O_2). The flow rates were controlled by a pressure regulator–needle valve combination and were measured with a glass capillary flowmeter (a halocarbon oil was used as the manometric fluid) which had been calibrated at each reactant concentration with a wet-test meter. Reactant and product concentrations were measured with a mass spectrometer (AEI MS-10) equipped with an atmospheric sampler connected directly to the flow system just downstream from a reactor-bypass T junction (point at which parallel lines, one from the reactor and one bypassing the reactor, join). The reactor bypass provided a means of establishing the instrument's response to known reactant concentrations following each rate measurement, thus reducing uncertainties due to instrumental fluctuations. The gaseous mixture entered the reactor through a center tube and, by virtue of a small pressure drop (2–10 Torr), jetted in all directions through five pinholes to induce stirring. The reactor's design was tested for stirring efficiency by injecting a tracer gas into a He stream and determining the non-steady-state concentration issuing from the reactor; this test has been fully described previously.[8] Calculated and experimental results were close enough at all flows used to justify the complete stirring assumption. For additional details on the apparatus, see ref 9.

Procedure. The conditions under which this reaction was studied were as follows: temperature range, 330–431°; initial reactant concentrations, 1.0, 3.0, and 10 mole %; contact times, 0.5 to 25 sec; one atmosphere total pressure, with He as the diluent.

Prior to initiating a series of rate measurements, it was necessary to passivate the reactor by allowing the reactant mixture to flow through it. This practice was continued until the mass spectrometer's response to the OF_2 concentrations issuing from the reactor reached steady state.

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[1] This research represents a portion of the work presented in the Ph.D. thesis of Thomas W. Asmus, 1970.

[2] W. Koblitz and H. J. Schumacher, *Z. Phys. Chem., Abt. B*, **25**, 283 (1934).

[3] W. C. Solomon, J. A. Blauer, and F. C. Jaye, *J. Phys. Chem.*, **72**, 2311 (1968).

[4] J. Troe, H. Gg. Wagner, and G. Weden, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 238 (1967).

[5] J. A. Blauer and W. C. Solomon, *J. Phys. Chem.*, **72**, 2307 (1968).

[6] M. C. Lin and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 7737 (1969).

[7] L. Dauerman, G. E. Salser, and Y. A. Yajima, *J. Phys. Chem.*, **71**, 3999 (1967).

[8] J. M. Sullivan and T. J. Houser, *Chem. Ind. (London)*, 1057 (1965).

[9] T. J. Houser, "Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants," Air Force Office of Scientific Research, AFOSR, 70-3010 TR, Nov 1970.

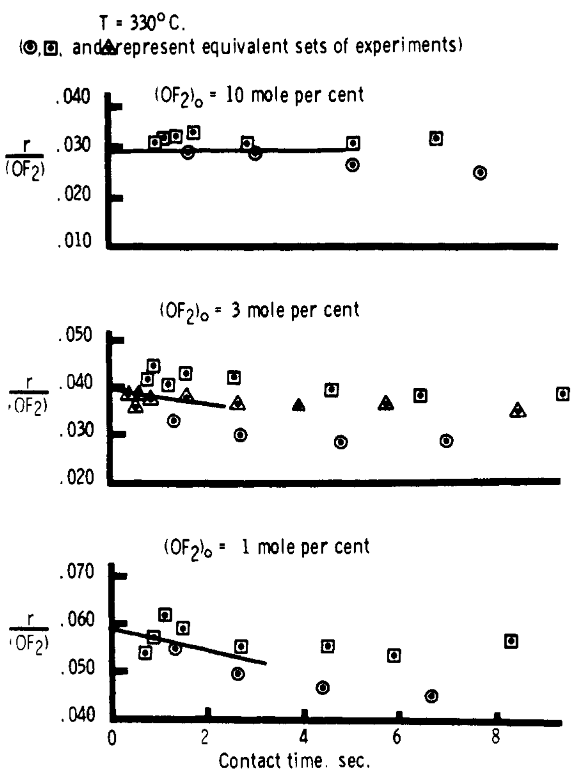

Figure 1. $r/(OF_2)$ *vs.* contact time at 330°.

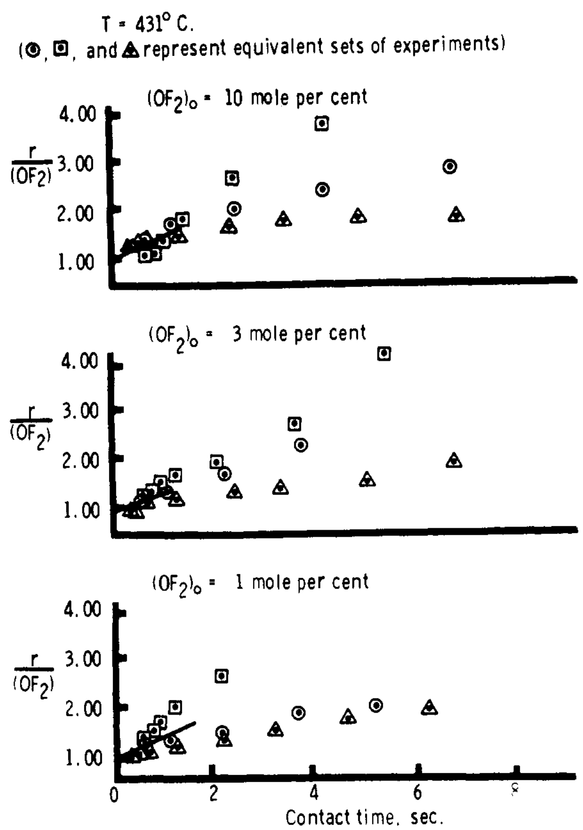

Figure 2. $r/(OF_2)$ *vs.* contact time at 431°.

All rate measurements were based on the disappearance of OF_2; the mass spectrometer's mass selector was set at the maximum ion current signal for the parent ion peak, *i.e.*, *m/e* 54. An ion current signal was recorded with the gaseous stream of known composition flowing through the reactor bypass. Determination of the ion current signals corresponding to the stream through the reactor and to zero OF_2 concentration, *i.e.*, background, obtained by passing pure He through the system, permitted calculations of the OF_2 concentration in the stream leaving the reactor. The linearity of the ion current signal with OF_2 concentration had been well established.

The stirred-flow reactor provided for the direct determination of reaction rates[10] which were calculated using the following equation

$$-dc/dt = r = (c_0 - c)/t$$

where c_0 = concentration of reactant entering reactor, c = concentration of reactant leaving reactor, and t = contact time (reactor volume/volume rate of flow).

Results and Discussion

Reaction Products. The OF_2 pyrolysis products as found mass spectrometrically in this study are O_2 and F_2, consistent with those previously reported.[2] No evidence was found for O_2F_2 or for O_2F radical which Solomon, *et al.*,[3] reported as possible minor products.

Reaction Order. The pyrolysis rates were measured at five temperatures in the range of 330–431° and at initial OF_2 concentrations of 1–10 mol % in He. Isothermal plots of log rate *vs.*. log concentration indicated that the rates were slightly less than first order in OF_2 at the lower temperatures, *i.e.*, 0.75 at 330°, and uniformly increased to first order at the higher temperatures. This observation of low order has not been previously reported, possibly because techniques that do not provide for the direct determination of rates are relatively insensitive to minor order variations. Schumacher and coworkers,[11] however, have recently observed a similar low-order effect at low temperatures in static vessel experiments. Having reproduced this order effect in two subsequent sets of experiments (consisting of about 20 runs/set at each temperature), including one set in which a smaller reactor was used to broaden the variations in stirring and surface conditions, it has been concluded that this effect is real, *i.e.*, is not apparatus induced.

The data were further analyzed by plotting rate/(OF_2) *vs.* contact time for each of the initial concentrations at each temperature. Figures 1 and 2 illustrate the data at the temperature extremes; the lines are extrapolations to give average initial ratios. This method of plotting data is a sensitive and convenient means by which minor variations from first-order dependence may be detected, since it shows the same trends as the log–log graphs more clearly, and it also allows extrapolation to initial conditions. Orders with respect to time which are not one will produce curves with nonzero slopes; orders with respect to concentration which are not one will produce variable intercepts for different initial concentrations. Extrapolation to $t = 0$ gave rise to initial rates which eliminated potential complexities resulting from product effects.

The initial rate data are presented in Table I. The averages of the intercepts [initial $r/(OF_2)$] values are listed as functions of initial OF_2 concentration and temperature; the initial rates were corrected to 100% He as the collisional activating medium.[12] The ± values are

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[10] K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, p 24.

[11] H. J. Schumacher, private communication on unpublished results, 1970.

[12] Helium is reported (ref 2) to be only about 40% as effective as the reactant in collisionally activating OF_2; therefore, the effective total pressure is about 15% greater for a mixture of 90% He and 10% OF_2 ($0.90 + 0.10/0.4 = 1.15$) than if all activation came from col-

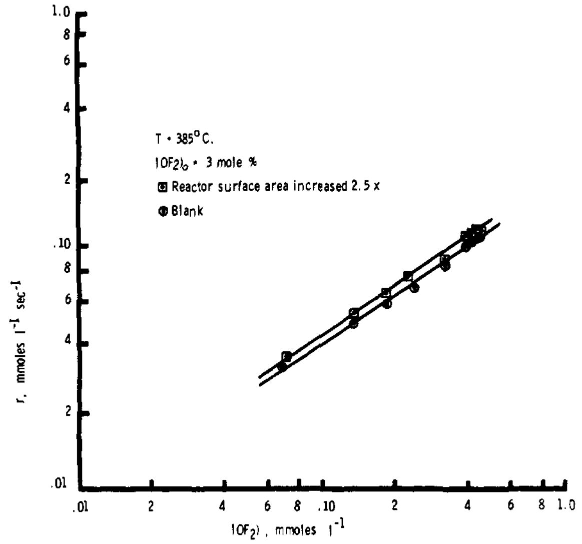

Figure 3. Log r *vs.* log (OF_2)—heterogeneous effects.

the average deviations from the mean intercept at a given temperature and concentration and are indicative of the reproducibility between sets of experiments. Most of the variation in the results can be accounted for by the uncertainties in the individual measurements, the size of which depended primarily on flow rate, extent of reaction, and concentration.

Table I. Initial Rate Data

Temp, °C	$(OF_2) \times 10^6$, mol/cm^3	$r_0(\text{corr})/(OF_2)_0{}^a$
330	0.197	0.055 ± 0.001
	0.591	0.036 ± 0.003
	1.97	0.024 ± 0.004
360	0.187	0.116 ± 0.008
	0.563	0.100 ± 0.013
	1.87	0.076 ± 0.006
385	0.181	0.245 ± 0.013
	0.543	0.210 ± 0.023
	1.81	0.180 ± 0.013
407	0.174	0.460 ± 0.03
	0.521	0.440 ± 0.04
	1.74	0.425 ± 0.01
431	0.168	1.01 ± 0.12
	0.504	0.85 ± 0.12
	1.68	0.89 ± 0.25

[a] The ± values are the average deviation from the mean intercept at each concentration.

It can be easily seen that the dependence of the apparent first-order constant on initial concentration is well outside the limits of reproducibility of the experiments at the three lower temperatures. However, the rate appears to have a first-order dependence on initial concentration at the two higher temperatures. At the same time, the order with respect to time decreases to less than one at the higher temperatures, as shown by the increasing slope in the $r/(OF_2)$ *vs.* time plots. The reasons for this observation are not clear. However, a similar observation was made in the shock tube study of Blauer and Solomon;[5] it may be caused by some autocatalysis, the source of which was not detected, or to a delay in radical intermediates reaching steady-state concentration, thus giving rise to an induction period.[13] In order to ensure that this drop in the $r/(OF_2)$ at shorter contact times was not caused by nonisothermal conditions at higher flow rates and temperatures, the gas mixture was heated to about 200° before entering the reactor in some experiments without affecting the rate significantly.

The less-than-first-order dependence of the rate at the lower temperatures and the shift in order toward one at higher temperatures are emphasized because of their importance in the consideration of a possible mechanism to be discussed later.

Additive and Surface Effects on the Rate. Experiments were conducted whereby initial concentrations of up to 3 mol % of each of the reaction products were added separately to the reaction mixture. The added O_2 had no apparent effect on the rate. However, F_2 inhibited the reaction slightly (again similar results were obtained by Blauer and Solomon[5]); *e.g.*, a reaction mixture containing 3 mol % F_2 and OF_2 had a pyrolysis rate of about 15% below that of reaction mixtures containing no initial concentration of F_2.

To investigate the possibility of the occurrence of heterogeneous reactions, several sets of experiments were conducted whereby the reactor's surface/volume ratio was significantly increased. The reactor was packed with 0.25-in. monel rods in one set of experiments and in other experiments with spirals of monel wire increasing the surface/volume ratio by factors of 1.7 and 2.5, respectively. Figure 3 illustrates that the change in surface area of a factor of 2.5 at 385° increased the reaction rate by only 10%; a similar set of data was obtained at 360° also, with, however, an average increase in the rate of only about 5%. The results at both temperatures are within the experimental reproducibility.

Generally, rates of surface reactions are proportional to the available surface area; this reaction clearly is not. There are only two conceivable circumstances under which changes in surface area would not reflect heterogeneous reactions: (a) where chains are initiated and destroyed at equal rates at the wall, rendering the kinetics insensitive to the surface area, or (b) where the reaction rate is diffusion controlled. The first possibility appears most improbable, the second is clearly not applicable since diffusion-controlled reactions have low, nonexponential temperature dependencies. The suggestion by Lin and Bauer[6] that the rate constants from data obtained in conventional systems are about five to ten times larger than those obtained from shock tube data because of heterogeneous effects implies a reaction rate which would be significantly sensitive to surface area. This suggestion is inconsistent with the data reported herein and with other investigations for heterogeneous effects during this reaction.[2,3] In addition, had the low order at the lower temperatures re-

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lisions with He at the same total pressure. Thus the r_0 values were corrected by dividing by 1.15, 1.04, and 1.02 for the 10, 3, and 1 mol % reactant mixtures, respectively. The most significant correction comes in the case of comparing results of experiments using a diluent with those using pure OF_2. On this basis, under the same conditions, pure OF_2 should yield rates about 2.5 times higher than those reported here. It should also be noted that in another investigation the effectiveness of He relative to OF_2 is 75% (ref 3), the use of which would reduce the size of the corrections discussed.

(13) Qualitatively similar trends were predicted for reactions involving radical intermediates: T. J. Houser, *J. Chem. Phys.*, **50**, 3962 (1969).

sulted from a low-order heterogeneous reaction, then increasing the reactor's surface area would have increased the proportion of low-order reaction and would have reduced the apparent order. That this was not observed strongly implies that the observed low-order results from a homogeneous rather than a heterogeneous reaction.

Rate Law and Arrhenius Parameters. To account for an observed order of less than one for a homogeneous reaction will require that a contribution to the mechanism be made from a chain sequence of steps. An initial rate law which is consistent with that requirement and which fits the data is given by the following equation (a zero-order term was ruled out because that would require a heterogeneous reaction)

$$r_0 = k_1'(\mathrm{OF_2})_0 + k_{1/2}(\mathrm{OF_2})_0^{1/2} \qquad (4)$$

The second term becomes less significant as the temperature increases.

Plots of $r_0/(\mathrm{OF_2})_0$ *vs.* $(\mathrm{OF_2})_0^{-1/2}$ yielded straight lines, the intercepts and slopes of which gave the pseudo-first- and -one-half-order rate constants (containing a total pressure dependence), respectively. In order to ensure that a relationship of the form of eq 4 was reasonable in view of the scatter of the data, correlation coefficients were calculated for the five temperatures.[14] These values, along with the probability that the variables $r_0/(\mathrm{OF_2})_0$ and $(\mathrm{OF_2})_0^{-1/2}$ are unrelated, are given in Table II. The values obtained indicate that at the three lower temperatures eq 4 is a reasonable representation of the data. The pseudo-first- and -one-half-order rate constants were converted to the second- and three-halves-order rate constants by dividing by total concentration (He + $\mathrm{OF_2}$) and are presented in Table III.

Table II. Statistical Treatment of Data

Temp, °K	Correlation coefficient	% probability of unrelated variables
603	0.95	<0.1
633	0.81	1
658	0.80	1
680	0.40	>20
704	0.31	>20

Table III. Rate Constants

Temp, °K	k_1',[a] sec^{-1}	$k_2' \times 10^{-3}$, cm^3/(mol sec)	$k_{1/2} \times 10^5$, (mol/cm^3)$^{1/2}$/sec	$k_{3/2}$, (cm^3/mol)$^{1/2}$/sec
603	0.0096 ± 0.001	0.49	2.0	1.0
633	0.060 ± 0.006	3.2	2.5	1.3
658	0.152 ± 0.013	8.4	4.0	2.2
680	0.41 ± 0.04	23.2	*b*	
704	0.92 ± 0.15	55	*b*	

[a] It is believed that the fractional uncertainty in the rate constants would not exceed the fractional uncertainty represented by the average deviation in the $r/(\mathrm{OF_2})$ intercepts; thus, these are the ± values reported. [b] These values would be relatively too small to be significant, as shown by the correlation coefficients.

The reported fractional uncertainties in the first-order rate constants are equal to the fractional uncertainties represented by the average deviations in the $r/(\mathrm{OF_2})$ intercepts, since it is believed that this would represent an upper limit.

An Arrhenius treatment of the second-order rate constants gave the following results (the ± values are based on 1σ confidence level).

$$k_2' = 10^{16.9\pm0.6} \exp(-39{,}200 \pm 1700/RT)\ \mathrm{cm^3/(mol\ sec)}$$

This activation energy is consistent with those previously reported. It is believed that the uncertainties in the three-halves-order rate constants are too large to warrant comparable quantitative treatment.

Pyrolysis Mechanism. An acceptable mechanism for this reaction must be able to account for the observed products and the initial rate law, *i.e.*, eq 4. The only conceivable way for which the less-than-first-order dependence of a homogeneous reaction can be accounted is by a chain mechanism: the following mechanism is proposed (assuming a very short chain length; ΔH,[15] kcal/mol)

$$\mathrm{OF_2 + M \longrightarrow OF + F + M} \qquad \Delta H = 39 \qquad (1)$$

$$\mathrm{F + OF_2 \longrightarrow F_2 + OF} \qquad \Delta H = 1 \qquad (5)$$

$$\mathrm{OF + M \longrightarrow O + F + M} \qquad \Delta H = 53 \qquad (6)$$

$$\mathrm{2OF + M \longrightarrow O_2 + F_2 + M} \qquad \Delta H = -26 \qquad (7)$$

$$\mathrm{2O + M \longrightarrow O_2 + M} \qquad \Delta H = -60 \qquad (8)$$

The reverse of step 5 was not included because only initial rates are being considered. Although the heats of reaction are included, there is considerable uncertainty as to the value of the heat of formation of OF; thus, the heats of reaction involving this species are also uncertain.

Steady-state treatment of this mechanism gives rise to the following rate equation

$$r = 2k_1(\mathrm{M})(\mathrm{OF_2}) + k_6(k_1/k_7)^{1/2}(\mathrm{M})(\mathrm{OF_2})^{1/2} \qquad (9)$$

The fact that eq 4 and 9 are of the same form, for constant total pressure, supports the contention that the proposed mechanism is operative and makes a significant contribution to the total reaction. This mechanism is the only one conceived which leads to orders less than one for $\mathrm{OF_2}$. Schumacher,[11] based on recent unpublished results, has observed orders of slightly less than two when undiluted $\mathrm{OF_2}$ was pyrolyzed. To render the proposed mechanism consistent with Schumacher's observation, the inclusion of M in eq 7 is necessary. Excluding M in this step increases the order with respect to M in the second term of eq 9 from one to three-halves. Thus, the overall order of this second term would be two rather than three-halves.

Clyne and Coxon[16] have discussed the OCl recombination (the analog of step 7 in the mechanism presented herein). They concluded that a reaction which leads to molecular products is possible at total pressures of above 100 Torr and that the reaction is ter-

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[14] H. D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill, New York, N. Y., 1962, pp 126–132 and 164.

[15] The heats of reaction were estimated using for the heats of formation for $\mathrm{OF_2}$, OF, and F values of 6 [R. C. King and G. T. Armstrong, *J. Res. Nat. Bur. Stand., Sect. A*, **72**, 113 (1968)], 26, and 19 [D. R. Stull, Ed., "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1965, and Addendum, 1967] kcal/mol, respectively.

[16] M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc., Ser. A*, **303**, 207 (1968).

molecular and may be third-order under certain conditions. Step 7 of the mechanism proposed in this study is consistent with these arguments. Equation 7 has been discussed on the basis of bonding,[17] and it has been concluded that it would occur with little or no activation energy, similar to the case of the OCl radical.

Reactions 2 and 3, which have been used by previous investigators to describe the pyrolysis mechanism, in all probability contribute significantly to the reaction under the conditions in the present study.[18] However, these steps, when combined with (1) form a first-order nonchain process, or combined with (1) and (5) form a three-halves-order chain process (assuming step 2 produces F atoms). In fact, all mechanisms devised using step 3 as a termination led to orders greater than or equal to one. Thus, although many steps may contribute to the overall reaction, the observed less-than-first-order kinetics strongly indicate that steps 5, 6, and 7 must also be included in the mechanism of the reaction at lower temperatures. In addition, owing to the contributions of steps other than those included in the simple mechanism, *i.e.*, steps 1, 5, 6, and 7, eq 9 is undoubtedly overly simplified and k_2' is not equal to $2k_1$ but is made up of a complex group of constants.

The observation that the order increases toward one at higher temperatures implies that the activation energy for the three-halves-order term in the rate law must be lower than that of the second-order term, *i.e.*, less than 39.2 kcal mol^{-1}. Based on presently available thermochemical information (which has a considerable uncertainty) for the reactions in eq 1, 6, and 7, *i.e.*, unless activation energies for steps 1 and 7 are larger than expected and that for step 6 smaller, it is difficult to explain such a low overall activation energy.

In conclusion, it appears that the value for the apparent first-order rate constant for the pyrolysis of OF_2 is reasonably well established. However, it is believed that its significance in terms of elementary steps is still unresolved. The mechanism proposed in this paper is based primarily on the observed low order and does not agree with the relative importance of the steps in the mechanism proposed by Lin and Bauer.[6]

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(17) M. Green and J. W. Linnett, *J. Chem. Soc.*, 4959 (1960).

(18) A steady-state treatment of a mechanism which contains all the steps which probably contribute to the reaction yields a solution which is unmanageably complex and experimentally unverifiable. Thus, the results of these calculations are not reported.

Properties and Reactions of 1,3-Oxathiolanes. II. Kinetics, Mechanisms, and Solvent Deuterium Isotope Effects in the Hydrolytic Decomposition of 1,3-Oxathiolane, 2-Methyl-1,3-oxathiolane, and 2,2-Dimethyl-1,3-oxathiolane[1]

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Abstract: The rates of acid-catalyzed hydrolysis of 1,3-oxathiolane and its 2-methyl and 2,2-dimethyl derivatives have been measured in aqueous $HClO_4$ and $DClO_4$ solutions and in several H_2O–D_2O mixtures containing perchloric acid. The activation entropy for the hydrolysis of 2-methyl-1,3-oxathiolane in 2.025 *M* $HClO_4$ was −14.3 cal mol^{-1} deg^{-1} and that for the hydrolysis of 2,2-dimethyl-1,3-oxathiolane in 0.196 *M* $HClO_4$ +0.9 cal mol^{-1} deg^{-1}. The hydrolysis of the acetone derivative was found to be sterically hindered, as manifested by its only 57 times higher rate than that of 2-methyl-1,3-oxathiolane. The experiments in mixed water showed that the ratio of the activity coefficients of the transition state and the ground state is dependent on the deuterium atom fraction. All the data and the data for the hydrolysis in moderately concentrated perchloric acid solutions are, however, consistent with an A-1 mechanism in which the ring rupture occurs at the acetal carbon–oxygen bond.

Although the acid-catalyzed hydrolysis of acyclic and cyclic acetals has been thoroughly investigated,[2-6] very little attention has been paid to the details of the hydrolytic decomposition of cyclic acetals that contain two different heteroatoms.[7-9]

De and Fedor[7] and Fife and Jao[8] reported some results on the acid-catalyzed and mercuric-ion-catalyzed cleavage of 2-(substituted phenyl)-1,3-oxathiolanes. Moreover, Fife and Hagopian[9] also investigated the

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(1) Paper I: K. Pihlaja, *Suom. Kemistilehti, B*, **43**, 143 (1970).

(2) K. Pihlaja, *Ann. Univ. Turku., Ser. AI*, No. 114 (1967).

(3) A. Kankaanperä, *ibid.*, No. 95 (1966).

(4) (a) K. Pihlaja and K.-J. Teinonen, *Suom. Kemistilehti, B*, **43**, 206 (1970); (b) K. Pihlaja and K.-J. Teinonen, *Acta Chem. Scand.*, **25**, 323 (1971).

(5) A. Kankaanperä, *Suom. Kemistilehti, B*, 43, 133 (1970).

(6) See also citations in ref 2–5.

(7) N. C. De and L. R. Fedor, *J. Amer. Chem. Soc.*, 90, 7266 (1968).

(8) T. H. Fife and L. K. Jao, *ibid.*, **91**, 4217 (1969).

(9) T. H. Fife and L. Hagopian, *ibid.*, **90**, 1007 (1968).