tional level. However, this model is not consistent with the published oxygen–argon relaxation times. The "sum" rate expression, rate $= k([^{32}O_2] + [^{36}O_2])^2$, which also adequately represents the observed exchange rates, is a consequence of a two-level vibrational excitation model in which it is assumed that the rate of populating a critical vibrational level determines the rate of exchange. This model is consistent with the published oxygen–oxygen relaxation times but not with the oxygen–argon relaxation times.

The evidence for a vibrational excitation restriction in bimolecular exchange reactions is now impressive. Whereas shock tube data were instrumental in directing our attention to this mechanism, we have now independently demonstrated, on the one hand, that at room temperature vibrationally "hot" molecules produced by chemi-excitation readily exchange atoms,[35] and on the other, that when vibrationally cold molecules collide with high relative kinetic energies (in center of mass coordinates, as in molecular beams) no exchange occurs.[36]

Acknowledgments. This work was supported in part by the AFOSR, Contract No. AF49(638)-1448. Also, we wish to thank Dr. Chava Lifshitz for writing the early versions of Program SHOCK and FUNCT and Mrs. Sally Jack for subroutines LISTSQ and EQSOL used in program POLYSQ. We sincerely thank Miss Marcia Williams for supplying us with a revised card deck of the CAL Kinetics Program (compatible with the IBM 360/65) and Dr. H. Henrici for his help in running the program. H. F. Carroll wishes especially to thank Dr. Assa Lifshitz for unselfishly giving his help and advice.

Appendix

Input data and bimolecular rates constants for set A–H are given in Table VIII.

---

[35] T. Baer, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1969.

[36] S. B. Jaffee and J. B. Anderson, *J. Chem. Phys.*, **49**, 2859 (1968)

Reactions of Oxygen Fluoride in Shock Waves. I. Kinetics and Mechanism of Oxygen Fluoride Decomposition

M. C. Lin and S. H. Bauer

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received July 1, 1969*

Abstract: The thermal decomposition of F_2O was studied in a single-pulse shock tube over the temperature range 770–1390°K. For temperatures below 1000°K these results are in excellent agreement with the previous shock tube data; however, all rates obtained by conventional techniques, either in static or in flow systems, prove to be higher than those derived from the shock tube techniques. This is attributed to surface effects which cannot be avoided in conventional systems. Our present data are accounted for by the following scheme; $F_2O + Ar \rightleftharpoons F + OF + Ar$ (1, −1), $2OF \rightarrow 2F + O_2$ (2), $2F + Ar \rightleftharpoons F_2 + Ar$ (3, −3), with $k_1 = 10^{17.3\pm1.0}e^{-(42.5\pm4.1)/RT}$ cc/mole sec and $k_2 = 10^{12.10\pm0.12}$ cc/mole sec. The reverse reactions (−1) and (−3) cannot be neglected even in the early stages of reaction. The bond dissociation energy, D(FO–F), was found to be 42.7 ± 4.1 kcal/mole, on the basis of the RRKM theory. The mechanism of the F_2O_2 decomposition is also discussed.

There are still uncertainties with regard to the kinetics and mechanism of the F_2O decomposition. The products of decomposition were found to be mainly F_2 and O_2. The rates of the overall pressure changes are consistent with the following stoichiometry.[1]

$$F_2O \xrightarrow{k_{ov}} {}^1/_2O_2 + F_2$$

The activation energy for the overall process obtained by various methods, including the present study, is within the range 35 ± 5 kcal/mole.[2–5] This value was believed to be associated with the rate-controlling step

$$F_2O + M \xrightarrow{1} F + OF + M$$

Furthermore, it was postulated that the radical reactions which lead to the formation of F_2 and O_2

$$2OF \xrightarrow{2} O_2 + F_2 \text{ or } 2F$$

$$2F + M \xrightarrow{3} F_2 + M$$

take place with little or no activation energy. The presence of F atoms and of OF radicals was demonstrated in the photochemical reactions of F_2O.[6,7] It is thus reasonable to assume that the thermal decomposition of F_2O follows approximately the above scheme, including reactions 1–3.

All previous pyrolysis data were analyzed on the basis of this mechanism, with the assumption that reaction 2 was so fast that all reverse reactions were negligible, and accordingly that the observed overall rate constant, k_{ov},

---

[1] W. Koblitz and H. J. Schumacher, *Z. Phys. Chem.*, **B25**, 283 (1934).

[2] L. Dauerman, G. Salser, and Y. A. Tajima, *J. Phys. Chem.*, **71**, 3999 (1967); their *A* factor should be multiplied by 10.

[3] J. A. Blauer and W. C. Solomon, *ibid.*, **72**, 2307 (1968).

[4] W. C. Solomon, J. A. Blauer, and F. C. Jaye, *ibid.*, **72**, 2311 (1968).

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

[6] R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *ibid.*, **35**, 343 (1962); **36**, 211 (1963).

[7] I. J. Solomon, A. J. Kacmarek, and J. Raney, *J. Phys. Chem.*, **72**, 2262 (1968).

was essentially k_1, the second-order rate constant for the F_2O dissociation. Operationally, k_{ov} is defined by

$$k_{ov} \equiv \frac{1}{[M]t} \ln \frac{[F_2O]_0}{[F_2O]_t} \qquad (1a)$$

or equivalently

$$k_{ov} = \frac{1}{[M]t} \ln \frac{[F_2O]_0}{[F_2O]_0 - 2[O_2]_t} \qquad (1b)$$

where [M] is the total concentration of the reacting system. There are no published data for reaction 2. The rate constant for the analogous reaction, $2OCl \rightarrow O_2 + Cl_2$ (or 2Cl), was reported to be $\sim 10^{11}$ cc/(mole sec).[8] If one employs $k_2 = 10^{11}$ cc/(mole sec) and allows for the reverse reactions −1 and −3, one finds that the calculated yield of oxygen is considerably lower than the observed value. In this paper the importance of these reverse reactions is examined. More data were obtained (in a single-pulse shock tube study) and these underscore the conclusion that neglect of the reverse reactions was not justified.

Experimental Section

Apparatus. The experiments were carried out in a 1-in. i.d. Pyrex shock tube. Helium was used as the driver gas. The driver section was "tuned" for each temperature to produce the best pressure trace. The diaphragms were of Mylar; their thickness ranged from 0.25 to 1.0 mil. Before each shock the driver section was evacuated to $\approx 1\ \mu$ and the driven section to lower than 5×10^{-5} Torr. The leak rate was found to be significantly less than 1 μ/min. Since F_2O reacts rapidly with mercury, a calibrated Bourdon gauge was employed to measure the initial pressure, P_1.

Materials. F_2O was obtained from Allied Chemicals. It was purified by trap-to-trap distillation (at least twice) from −160 (an isopentane slush bath) to −196°. The middle two-thirds of the distillate was finally collected in a black-painted storage bulb. Kel-F grease was used for all stopcocks. F_2O is known to be one of the most toxic compounds. The glass vacuum system in which the samples were prepared was built inside a hood, and connected to a very efficient vent. The shock tube and its vacuum manifold were also vented to the outdoors. CP grade CO as obtained from Matheson was introduced into a storage bulb through two liquid nitrogen-cooled traps; no further purification was performed. Ultrapure Argon (from Matheson) was used for the carrier gas.

Analysis. The reactants and the reaction products were analyzed *via* mass spectrometry. The products of reaction were confirmed to be mainly F_2 and O_2. Only oxygen was determined quantitatively. The calibration for oxygen was done by measuring the peak height (ph) of $^{32}O_2$ relative to those of ^{36}Ar and ^{40}Ar for the different O_2–Ar mixtures of known compositions. The results of these calibrations are: $[O_2]/[Ar] = (5.556 \pm 0.036) \times 10^{-3}(^{32}O_2/^{36}Ar)_{ph}$ and $[O_2]/[Ar] = (1.673 \pm 0.010)\ (^{32}O_2/^{40}Ar)_{ph}$. The average of the two measurements was taken to be the final value for the $[O_2]/[Ar]$ ratio. The results obtained from the decomposition of F_2O are given in Table I.

Table I. Results of the Decomposition of OF_2 in a 1-in. Single-Pulse Shock Tube

Mixture[a]	P_1, Torr	P_5, Torr	T_5, °K	Dwell time, μsec	$10^3[O_2]/[Ar]$
I	19.8	2060	770	908	0.171
I	16.2	1890	810	956	0.405
I	10.6	1750	965	780	8.20
I	9.3	1930	1085	614	27.0
I	8.0	1820	1150	577	24.7
I	7.2	2190	1367	650	28.6
I	8.0	1890	1080	954	30.8
I	13.3	1950	910	984	32.0
I	11.2	2360	1103	790	16.4
I	8.5	1960	1162	635	22.4
I	11.2	2210	1065	540	14.4
II	10.4	1840	1103	588	3.89
II	8.3	1760	1205	628	4.59
II	6.9	1800	1390	586	4.42
II	8.0	1940	1335	567	4.73
II	10.1	1890	1150	535	3.72
II	8.6	1800	1220	765	4.46
II	8.9	1860	1220	860	4.14
II	9.3	1920	1208	860	5.22
II	10.0	1880	1150	824	3.94
II	8.9	2020	1280	1045	4.35
II	12.8	1910	1000	1070	2.86
II	11.4	1910	1067	660	3.37
II	10.9	1880	1085	682	5.12
II	8.8	1820	1213	645	5.68
III	18.6	1930	835	1092	0.047
III	18.1	1890	840	1027	0.041
III	16.5	1930	882	958	0.126
III	15.2	1850	898	1070	0.229
III	14.6	1890	925	993	0.200
III	16.0	1910	900	1020	0.150
III	16.0	1950	910	1024	0.175
III	13.3	1990	1020	977	1.03
III	13.3	1880	990	1000	0.824
III	12.0	1910	1055	956	1.09
III	12.0	1940	1065	930	1.07
III	12.0	1940	1065	518	0.996
III	7.1	1560	1280	610	1.17
IV	19.7	2260	823	1040	1.03
IV	18.2	2180	840	1070	1.45
IV	19.6	2210	815	1095	0.950
IV	17.4	1970	815	1040	1.00
IV	16.7	1920	823	943	1.18
IV	14.6	2060	917	1016	7.12
V	16.2	1705	835	920	0.364
V	16.2	1930	877	1012	1.33
V	14.8	1720	865	895	1.06
V	13.6	1910	960	962	4.14
V	14.5	1985	945	947	4.15

[a] The per cents of OF_2 in Ar for mixtures I to V are, respectively, 7.43, 1.17, 0.258, 5.15, and 1.94.

Calculations and Results

Evaluation of T_0 and P_5. The temperatures and pressures behind the reflected shocks were calculated according to the standard shock equations assuming no reaction either in the incident or reflected shock regimes. In this case, no corrections were made for the temperature changes during the reaction (contrast ref 9), since the heat of reaction for $F_2O \rightarrow {}^1/_2O_2 + F_2$ is only −5.9 kcal/mole.[10] Cooling corrections for both T_5 and P_5 (during the quench expansion) were made on the basis of the adiabatic expansion relation $P(t)/P_5 = [T(t)/T_5]^{\gamma/(\gamma-1)}$. The rate of pressure change after the arrival of the cooling wave was determined for each shock from the recorded pressure trace.

Evaluation of k_1 and k_2. The magnitudes of the overall second-order constant, k_{ov}, calculated according to eq 1b are shown in Figure 1, together with those obtained from the uv absorption measurements in shock tubes,[3,5] and those from mass spectrometric analyses of the reaction products in a flow tube[2] and static vessels.[4] Our results for $T_5 \leq 1000$°K are well represented by

$$k_{ov} = 10^{15.8}e^{-37{,}800/RT} \text{ cc/(mole sec)} \qquad (2)$$

The absolute values of k_{ov} given by eq 2 are in excellent agreement with the shock tube results of Troe, *et al.*,[5]

---

(8) (a) G. Porter and F. J. Wright, *Discussions Faraday Soc.*, 14, 23 (1953); (b) F. J. Lipscomb, R. G. W. Norrish, and G. Porter, *Nature* 174, 785 (1954); (c) M. A. A. Clyne and J. A. Coxon *Proc. Roy. Soc. Ser. A*, 303, 207 (1968), and other papers cited therein.

(9) M. C. Lin and S. H. Bauer, *J. Chem. Phys.*, 50, 3377 (1969).

(10) R. C. King and G. T. Armstrong, *J. Res. Nat. Bur. Stand. A*, 72, 113 (1968).

$k_{ov} = 10^{15.1}e^{-34,200/RT}$ cc/(mole sec), and those of Blauer and Solomon,[3] $k_{ov} = 10^{14.2}e^{-31,500/RT}$ cc/(mole sec). (This demonstrates again the validity of the single-pulse shock tube technique.) Our results for k_{ov} were corrected for the extent of reaction taking place during the cooling period, according to the method of Tschuikow-Roux.[11] Figure 1 exhibits another important fact; *i.e.*, all results obtained by the conventional techniques are higher than those derived from shock tube studies by a factor of 5–10. This difference is probably due to surface effects which are inherent in conventional systems. The rate constants evaluated in this investigation for $T > 1000$°K, as shown in Figure 1, tend to level off and depart significantly from the linear expression 2. This deviation at higher temperatures is readily accounted for by the proposition that the rate-controlling step of the decomposition reaction, *i.e.*, step 1, is close to equilibrium.

The following general scheme is proposed, and was employed in the detailed calculations to account for the decrease in the O_2 yield at higher temperatures.

$$F_2O + M \underset{-1}{\overset{1}{\rightleftharpoons}} F + OF + M$$

$$2OF \xrightarrow{2} 2F + O_2$$

$$2F + M \underset{-3}{\overset{3}{\rightleftharpoons}} F_2 + M$$

$$OF + F_2 \underset{-4}{\overset{4}{\rightleftharpoons}} F_2O + F$$

$$OF + M \underset{-5}{\overset{5}{\rightleftharpoons}} F + O + M$$

$$O + F_2O \underset{-6}{\overset{6}{\rightleftharpoons}} 2OF$$

$$O + F_2 \underset{-7}{\overset{7}{\rightleftharpoons}} F + OF$$

Their relative importance is analyzed below. Reaction 2 probably takes place *via* the sequence

$$FO + OF \xrightarrow{2a} F\text{-}O\text{-}O^* + F \qquad \text{(fast)}$$

$$FO_2^* \xrightarrow{2b} F + O_2 \qquad \text{(very fast)}$$

The exothermicity of reaction 2a is about 30 kcal/mole. Thus FO_2 formed in (2a) is probably vibrationally excited. Since $D(F\text{–}O_2) \approx 7$ kcal/mole, FO_2^* can hardly survive longer than a few vibrations. The analogous reaction of OCl radicals is believed to take place in a similar way.[8c,12]

In the above reaction scheme none of the rate constants except (-3)[13] is known. We had to resort to the generalized Evans–Polanyi rule[14] to estimate the activation energies for the atom-transfer reactions 4, 6, and 7

$$E_i = 11.5 - 0.25q_i \tag{3a}$$

or

$$E_i = 11.5 + 0.75q_i \tag{3b}$$

where E_i and q_i are the activation energy and the absolute value of the heat of reaction, respectively, for step i. Equation 3a is applicable to exothermic reactions, whereas eq 3b applies to endothermic ones. The preexponential factors for reactions 4, 6, and 7 were taken to be 10^{11} cc/(mole sec). k_5 was estimated according to

$$k_4 \cong \lambda Z\left[\frac{D}{RT}\right]^{s-1}\frac{1}{(s-1)!}e^{-D/RT} \tag{4}$$

In the first calculation, a value of $D(O\text{–}F) \cong 45.7$ kcal/mole was employed. The collision efficiency (λ) and the effective degrees of freedom (s) were assumed to be the same as in the F_2 dissociation by Ar. The value for D is given above is the average bond dissociation energy in F_2O.[10]

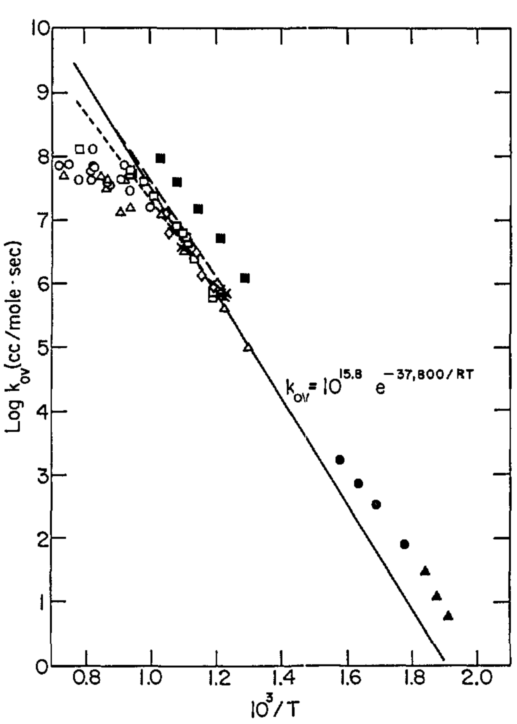

Figure 1. Log k_{ov} *vs.* $1/T$; △, mixture I; ○, mixture II; □, mixture III; ×, mixture IV; ◇, mixture V (all mixtures, this work); ●, Solomon, *et al.*; ■, Dauerman, *et al.*; ▲, Koblitz and Schumacher; – –, Troe, *et al.*; - - --, Blauer and Solomon.

The significant rate constants (k_1 and k_2) were evaluated by an iterative method, using an IBM 360/65 computer. The concentrations of all species, as functions of the time, were evaluated by integrating all the differential equations using a Runge–Kutta method, modified according to Treanor.[15] As stated above, since the assumption $k_1 = k_{ov}$ and $k_2 = 10^{10.9}$ cc/(mole sec) gave too low a value for the O_2 yield on the basis of the generalized mechanism, our data for $T_5 \leq 1100$°K were divided into two groups to evaluate k_1 and k_2, separately. The results obtained between 1100 and 1000°K are most suitable for determining k_2, because in this range reaction 1 is about to approach equilibrium and the observed O_2 yield is rather insensitive to the magnitude of k_1. It is, however, very sensitive to the assigned value of k_2, since the rate of O_2 production is directly proportional to this constant. Runs with $T_5 \geq 1100$°K were not used because both reactions 1 and 3 reach equilibrium within the test time.

---

(11) E. Tschuikow-Roux, *Phys. Fluids*, **8**, 821 (1965).

(12) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **27**, 1382 (1957).

(13) D. J. Seery and D. Britton, *J. Phys. Chem.*, **70**, 4074 (1966).

(14) See, for example, K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(15) C. E. Treanor, Technical Report No. AG-1729-A-4, Cornell Aeronautical Laboratory.

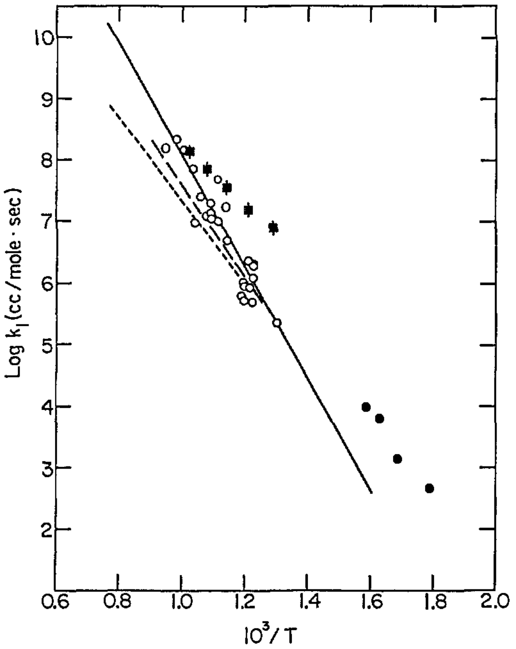

Figure 2. Log k_1 vs. $1/T$: ○, this work; ■, Dauerman, *et al.*, with estimated error range; ●, Solomon, *et al.*

The first values of k_2 were estimated by fitting the calculated O_2 yields to the experimental results. As a first approximation k_1 was assumed to be equal to k_{ov}. No temperature dependence was found for k_2 in this narrow range of temperatures. It is, however, not unreasonable to assume $E_2 = 0$, since the analogous reaction for OCl was found to take place with little or no activation energy.[8] The average value of k_2 thus obtained was then used to estimate k_1, employing data for which $T_5 \leq 1000$°K. These calculations were cycled twice. No significant changes were found in k_2 in the sequence of calculations. The final values of k_1 and k_2 are given in Table II (also Figure 2) and Table III, respectively. They are best represented by

$$k_1 = 10^{17.3\pm1.0}e^{-(42,500\pm4,100)/RT}\ \text{cc/(mole sec)} \qquad (5)$$

and

$$k_2 = 10^{12.10\pm0.12}\ \text{cc/(mole sec)} \qquad (6)$$

The limits of error cited are the standard deviations. The value of k_2 so obtained checks closely with that of $k = 10^{11.8}e^{-2,500/RT}$ obtained by Clyne and Coxon for the ClO radical reaction.[8c]

The rate constants of the remaining reactions were reevaluated after each new value of E_1 or, equivalently, D(FO–F), was obtained. The final values are given in Table IV. In Figure 2, the results of other investigations were replotted for comparison. Those of Dauerman, *et al.*,[2] and Solomon, *et al.*,[4] were recalculated on the basis of the general mechanism. It is evident that at low temperatures, the deviation due to surface effects is considerable. At higher temperatures, however, it becomes negligible, as expected.

Yields as Functions of Time. The rates of disappearance of F_2O and the formations of various species were calculated according to the proposed general reaction scheme at 770, 1020, and 1390°K, using the rate constants given in Table IV. The results are shown in Figure 3a, b, and c, respectively. In this figure, the rates of reaction 1, $v_1 = k_1[M][F_2O]$, and reaction −1, $v_{-1} = k_{-1}[M][FO][F]$, are also displayed for comparison. From the results which cover the entire temperature range used

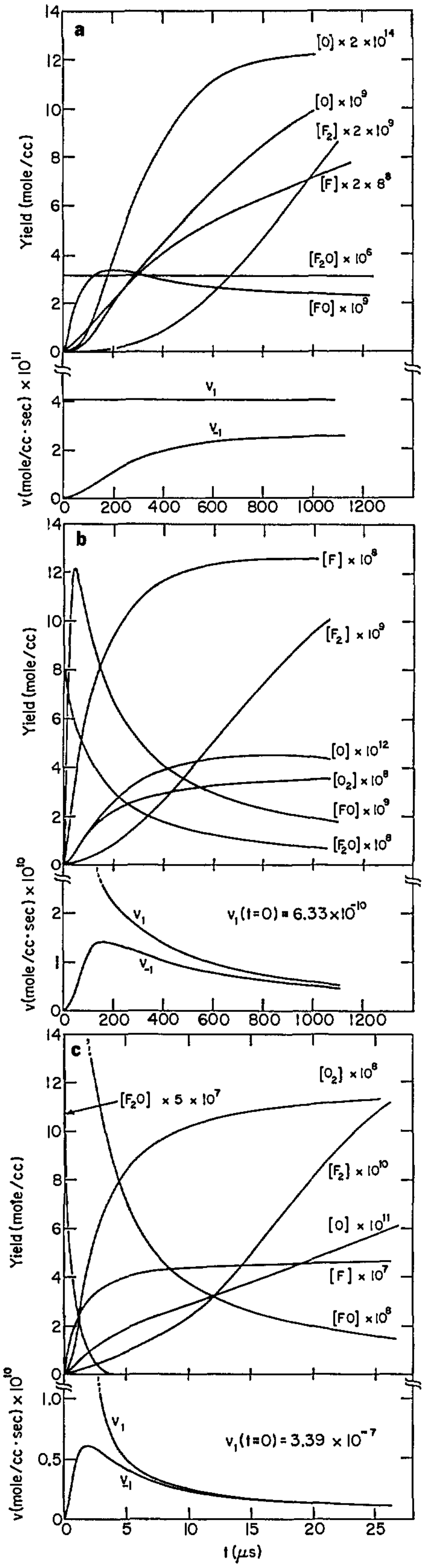

Figure 3. Typical plots of yields vs. time: (a) mixture I, T_5 = 770°K, P_5 = 2060 Torr; (b) mixture III, T_5 = 1020°K, P_5 = 1990 Torr; (c) mixture II, T_5 = 1390°K, P_5 = 1800 Torr.

Table II. Rate Constant for $OF_2 + Ar \xrightarrow{k_1} FO + F + Ar$

Mixture[a]	T_5, °K	Log k_1, cc/(mole sec)
I	770	5.35
I	810	6.35
I	818	5.70
I	910	7.30
I	965	7.85
III	835	5.98
III	840	5.81
III	882	7.26
III	898	7.72
III	900	7.00
III	910	7.05
III	925	7.10
III	990	8.15
IV	815	6.10
IV	815	6.30
IV	823	5.95
IV	823	6.40
IV	840	6.00
IV	917	7.15
V	835	5.71
V	877	6.70
V	865	6.75
V	960	6.90
V	945	7.45

[a] Same designation as in Table I.

Table III. Rate Constant for $2OF \xrightarrow{k_2} 2F + O_2$

Mixture[a]	T_5, °K	Log k_2, cc/(mole sec)
I	1080	11.77
I	1085	12.28
II	1000	11.97
II	1065	11.97
III	1065	11.90
III	1020	12.65
III	1055	12.17
	Av	12.10 ± 0.12

[a] Same designation as in Table I.

Table IV. Summary of Rate Constants[a]

Reaction	A	E	Remarks
1	$10^{17.3\pm1.0}$	42.5 ± 4.1	This work
−1	$10^{15.6}$	0	Calcd from k_1 and $K_1 = 10^{1.7}e^{-41.7/RT}$
2	$10^{12.10\pm0.12}$	0	This work. Reverse reaction (−2) is not important
3	$10^{11.3}$	−9.9	Calcd from k_{-3} and $K_3 = 10^{-1.21}e^{37.2/RT}$
−3	$10^{12.5}$	27.3 ± 2.5	Ref 12
4	$10^{11.0}$	10.4	See text
−4	$10^{11.2}$	14.7	Calcd from k_4 and $K_4 = 0.67e^{4.3/RT}$
5	$10^{13.0}$	37.3	See text
−5	$10^{11.7}$	−10.0	Calcd from k_5 and $K_5 = 10^{1.3}e^{-47.3/RT}$
6	$10^{11.0}$	10.0	See text
−6	$10^{10.6}$	16.0	Calcd from k_6 and $K_6 = 10^{0.6}e^{6.0/RT}$
7	$10^{11.0}$	9.0	See text
−7	$10^{10.6}$	19.0	Calcd from k_7 and $K_7 = 10^{0.4}e^{10.0/RT}$

[a] Units in cc, mole, sec, and kcal/mole.

in this investigation, one may conclude that the concentration of O atoms is too low to be important even at the highest temperature (1390°K), that reaction −1 is comparable to reaction 1 even at the lowest temperature (770°K), and that step 1 soon reaches its equilibrium value at the higher temperatures. The rate of disappearance of F_2O *via* reactions other than 1 was found to be negligible at all temperatures.

There is some disagreement with regard to the effect of F_2 on the rate of F_2O decomposition. Solomon, *et al.*,[4] found an inhibition effect at 563°K, whereas Koblitz and Schumacher[1] reported an acceleration at 532°K. In order to examine the possible effect of F_2, we calculated the rates of disappearance of F_2O in the absence or presence of F_2 at both temperatures. The results are presented in Table V. In these calculations the collisional efficiency of F_2 for reactions 1 and 3 was taken to be equal to that of F_2O. In Table V the rate of formation of O_2 and the rates of reactions −1 and 4 are also listed. Reaction 4 is clearly shown to be unimportant in the absence of F_2. The addition of large amounts of F_2, however, enhances considerably both reactions −1 and 4, and retards significantly the rate of F_2O decomposition as well as the rate of O_2 formation both at 563 and 532°K. In order to enhance the rate of F_2O decomposition, the collisional efficiency of F_2 would have to be at least 1000 times greater than that of F_2O. This is rather unlikely. We therefore conclude that F_2 only inhibits the F_2O decomposition by virtue of reactions −3 and 4.

Discussion

Unimolecular Dissociation of F_2O and D(FO–F). The mechanism for the decomposition of F_2O at $T \leq 1390$°K is essentially represented by the first three steps of the generalized mechanism, and for M = Ar, k_1 is given by eq 5. The second-order rate constant for a unimolecular reaction, on the basis of the RRKM theory,[16] is related to the critical energy, E_0, by the following expression

$$k_1 = Z\frac{e^{-E_0/RT}}{Q_v}\int_0^\infty \rho(E_0 + \epsilon)e^{-\epsilon/RT}\,d\epsilon \qquad (7)$$

where Z is the collision number, Q_v the vibrational partition function, and $\rho(E_0 + \epsilon)$ the energy density in the molecule at energy $(E_0 + \epsilon)$. In the present case E_0 = D(FO–F) but its magnitude is uncertain. However, it can be obtained by interpolation of the theoretical E_1 *vs.* E_0 curve. E_1 is the activation energy for reaction 1 and is the overall temperature coefficient of eq 7. By assuming $\sigma = 4.0$ Å and $E_0 = 42.7$ kcal/mole eq 7 leads to

$$k_1(\text{calcd}) = 1.1 \times 10^{17}e^{-42,500/RT}\ \text{cc/(mole sec)} \qquad (8)$$

at 1000°K. The vibrational frequencies of F_2O were taken from the JANAF Tables.[17] This agreement is excellent, although in the present calculation of k_1 the anharmonicity and centrifugal effects were not included.

On the basis of the above result, D(FO–F) ≅ 42.7 kcal/(mole sec), and the experimental heat of formation of F_2O, $\Delta H_f{}^\circ{}_{298} = 5.86 \pm 0.38$ kcal/mole,[10] or $\Delta H_f{}^\circ{}_0 = 6.40 \pm 0.38$ kcal/mole. Also

$$\Delta H_f{}^\circ{}_0(\text{FO}) \cong 30.2 \pm 4.1\ \text{kcal/mole}$$

and

$$D(\text{FO}) \cong 48.3 \pm 4.1\ \text{kcal/mole}$$

---

(16) R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952); R. A. Marcus and O. K. Rice, *J. Phys. Chem.*, **55**, 894 (1951).

(17) "JANAF Thermochemical Tables," D. R. Stull, Ed., the Dow Chemical Co., Midland, Mich., 1965.

Table V. Effect of F_2 on OF_2 Decomposition[a]

T_5, °K	P_{F_2}, Torr	P_{OF_2}, Torr	$-v_{OF_2}$	v_{O_2}	v_{-1}	v_4
563	0	100	1.6×10^{-16}	1.3×10^{-16}	3.0×10^{-18}	3.6×10^{-24}
	1560	100	5.7×10^{-19}	2.9×10^{-18}	3.4×10^{-14}	1.3×10^{-15}
532	0	100	2.0×10^{-17}	2.1×10^{-17}	5.3×10^{-19}	1.6×10^{-24}
	1560	100	4.9×10^{-20}	2.6×10^{-20}	4.7×10^{-15}	2.4×10^{-16}

[a] All rates are in units of mole/(cc sec); v_M denotes either d[M]/dt or the rate of the Mth reaction, at t = 0.02 sec.

This value for D(FO–F) is substantially higher than that derived by Troe, *et al.*,[5] D(FO–F) = 37 ± 1 kcal/mole, on the basis of their value $E_1 = 34.2$ kcal/mole. Their low value for the bond dissociation energy is inconsistent with the relatively higher stability of F_2O relative to F_2. One should expect $D(\text{FO–F}) > D(\text{F–F})$.

Mechanism of F_2O_2 Decomposition. The thermal decomposition of F_2O_2 has been studied by Schumacher and Frisch.[18] At −80 to 0° the products are similar to those for the F_2O decomposition, mainly O_2 and F_2. The activation energy for the decomposition in its first-order region was found to be ≈17 kcal/mole. This low activation energy could be accounted for as follows.

$$F_2O_2 + M \xrightarrow{8} F + FO_2 + M$$

$$FO_2 + M \xrightarrow{9} F + O_2 + M$$

$$F + F_2O_2 \xrightarrow{10} F_2 + FO_2$$

$$F + F + M \xrightarrow{3} F_2 + M$$

The steady-state treatment of this scheme, with the assumption that the reaction chain is long, leads to

$$-\frac{d[F_2O_2]}{dt} \cong k_{10}\left[\frac{k_8}{k_3}\right]^{1/2}[F_2O_2]^{3/2} \qquad (9)$$

Overall first-order kinetics can be reached experimentally when reaction 8 becomes first order. Since reaction 3 is third order under ordinary conditions, in the case of pure F_2O_2, eq 9 reduces to

$$-\frac{d[F_2O_2]}{dt} \cong k_{10}\left[\frac{k_8^{\infty}}{k_3^{0}}\right]^{1/2}[F_2O_2] \qquad (10)$$

where $k_3^0 = k_3[M] = k_3/[F_2O_2]$. An alternative initiation step has been suggested by Benson.[19]

$$F_2O_2 + M \xrightarrow{11} 2FO + M$$

This reaction appears less likely on the energetic grounds. E_{11} was estimated to be as high as 70 kcal/mole. The overall activation energy according to eq 10 is

$$E_{ov} \cong E_{10} + {}^1/_2E_8 - {}^1/_2E_3 \qquad (11)$$

On the basis of the Evans–Polanyi rule cited previously, and the heats of formation of F_2O_2 and FO_2 recommended by Benson,[19] $E_{10} \approx 8$ and $E_8 \approx 24 \pm 10$ kcal/mole. E_3 is not known in the low-temperature range (−80 ∼ 0°) but probably it is slightly negative. Thus we have $E_{ov} \approx 20 \pm 5$ kcal/mole, which agrees with the experimental value of 17 kcal/mole. When one considers reaction 11 rather than 8, one concludes that $E_{ov} \approx 43$ kcal/mole.

In summary, it appears that the mechanisms for the decompositions of F_2O and F_2O_2 are somewhat more complicated than had been previously assumed. The observed overall second-order and first-order rate constants for the decomposition of F_2O and F_2O_2, respectively, should not be taken as those of the initiation reactions.

Acknowledgments. This work was supported by the Office of Naval Research, under Contract No. N0014-67-A-0077-0006.

---

(18) H. J. Schumacher and F. Frisch, *Z. Phys. Chem.*, **24**, 332 (1934).

(19) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968.