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The Kinetics of the Hydrogen-Oxygen Difluoride Reaction in Monel

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The kinetics of the $\text{H}_2\text{-OF}_2$ reaction was studied in the temperature range of 110–220° at 1 atm total pressure in a Monel, stirred-flow reactor. Initial reactant concentration ranges were 0.5–2.0 mol % oxygen difluoride, 0.5–5.0 mol % hydrogen, with 0–5.0 mol % oxygen introduced as an additive; helium was used as the carrier gas. The reaction products and approximate stoichiometry are shown by the equation $2\text{OF}_2 + 3\text{H}_2 \rightarrow 4\text{HF} + \text{H}_2\text{O} + 0.5\text{O}_2$. The rate was strongly inhibited by oxygen and was unaffected by the other products. Limiting inhibition was achieved by adding a 5 mol % initial concentration of oxygen; under these conditions, the reaction was first order with respect to oxygen difluoride and had a weak hydrogen concentration dependence, *i.e.*, about 0.3 order. The reaction has a substantial heterogeneous component in a Monel reactor and increasing the reactor's surface area appeared to reduce the order with respect to hydrogen. The effect of surface area was significant only when the oxygen concentration was high. Based upon rates obtained from experimental variation of the oxygen difluoride, hydrogen, and oxygen concentrations, in addition to the previously stated observations, a rate law of the following form apparently fits the data reasonably well: $-\text{d}(\text{OF}_2)/\text{d}t = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^x + k_c(\text{OF}_2)(\text{H}_2)/[1 + b(\text{O}_2)/(\text{OF}_2)]$, where x may be $1/2$ or 1. The reaction's heterogeneous component is accounted for by the first term and the oxygen inhibition by the third term. An Arrhenius plot of the values for k_c/b yields the expression $k_c/b = 10^{11.7} \exp(-26,400/RT)$ l./mmol sec. The first two terms were too small in comparison to the third to allow quantitative evaluation of their temperature dependence.

This work is part of an effort to develop a better understanding of the chemistry of fluorine-containing oxidizers. Oxygen difluoride was selected for this study because its behavior is representative of this class of compounds and relatively little is known about the mechanisms of its reactions.

A thorough search of the literature has failed to reveal any published results in the area of the kinetics of the $\text{H}_2\text{-OF}_2$ reaction. This system, however, has been investigated in connection with a chemical laser produced by the photolysis of the mixture.² It was concluded that vibrationally excited HF is produced by the highly exothermic reaction $\text{H} + \text{OF}_2 = \text{HF} + \text{OF}$. The current investigation has measured the rate of the $\text{H}_2\text{-OF}_2$ reaction in the temperature range of 110–220°, for reaction times of 0.5–20 sec, using a Monel, stirred-flow reactor.

Experimental Section

Apparatus.—Rate data were obtained using a conventional flow system equipped with a Monel, stirred-flow reactor; this apparatus was housed in a 7-ft walk-in hood. The $\text{OF}_2\text{-He}$ and $\text{H}_2\text{-He}$ mixtures, stored in 5- and 10-gal tanks, respectively, were introduced into the reactor (volume 86 ml) through separate flow lines. The flow rates were controlled by pressure regulator-needle valve combinations and were measured with glass capillary flowmeters (a halocarbon oil was used as the manometric fluid) which had been calibrated at each concentration with a wet-test meter. The flow lines upstream from the reactor were $1/4$ in. stainless steel and those downstream were Monel. Each flow line had a reactor bypass (to establish the instrument's response to known reactant concentrations) so that decreases in reactant concentrations could be measured with the greatest accuracy, despite possible drifts and fluctuations in instrument sensitivity. Reactant and product concentrations were measured with a mass spectrometer (AEI MS-10) equipped with an atmospheric sampler and connected to the flow system through stainless steel capillary tubing (0.015-in. i.d., 5 ft long) inserted just downstream from the reactor-bypass "T" connection.

In the stirred-flow reactor the gas stream enters the reactor through the center tube and is jetted sideways and downward through five pin holes by virtue of a small pressure drop (2–10 Torr) and induces stirring. The reactor's design was tested several times for stirring efficiency by injecting N_2 into a He

stream and determining the non-steady-state concentration issuing from the reactor. The calculated and experimental concentrations were close enough at all of the flow rates used, to justify the assumption of complete mixing. Sullivan and Houser³ had previously confirmed the high stirring efficiency associated with reactors of this design. The reaction temperature was measured using standardized (NBS Zn, Pb, Cu, Al) chromel-alumel thermocouples (inserted into top, middle, and bottom thermocouple wells) and a portable potentiometer (Honeywell Model 2732). Reactor temperatures were maintained with a Versatronik controller (Honeywell Model R 7161H). A more detailed description of the apparatus is given elsewhere.⁴

Procedure.—The conditions under which this reaction was studied were as follows: temperature range, 110–220°; initial reactant concentrations, 0.5 and 1.0 mol % OF_2 and 0.5–5.0 mol % H_2 and up to 5.0 mol % O_2 ;⁵ contact times, 0.5–20 sec; 1 atm total pressure; He was the diluent. Equal total reactant flows were used; thus, reactant storage tanks were prepared with double the concentrations to be introduced into the reactor. Oxygen was added to the OF_2 tank for those experiments where the inhibiting effect of O_2 was under study. Water was added to the reaction mixture by passing the He- H_2 mixture through an H_2O bath maintained at 0°, and HF was added to the OF_2 tank to investigate the effects of these products on the reaction rate.

Since relatively crude Bourdon gauges were used, the tank-filling procedure for reactant mixtures was carried out in a stepwise fashion, diluting from 100 to 10 mol % in one step and then further diluting to the desired concentration in the next step. Uncertainties in the initial concentrations were thus minimized.

Prior to beginning a series of rate measurements and starting the flow of hydrogen, it was found necessary to passivate the reactor surfaces by exposing the system to oxygen difluoride until the mass spectrometer's response to the concentrations of this reacting species reached a constant value. It was assumed that a constant ion current for oxygen difluoride as a function of time and flow rate indicated that reaction with the surfaces had stopped. Adsorption may still be occurring; however, it will have reached steady state and thus not influence the determinations.

Most of the rate data were obtained by measuring the disappearance of OF_2 ; however, some data were obtained by determining the changes in the H_2 concentrations. In addition,

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

(4) T. J. Houser, "Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants," Report 70-3010 TR, Air Force Office of Scientific Research, AFOSR, Nov 1970.

(5) Attempts were made to introduce higher reactant concentrations into the reactor, *i.e.*, 2 mol % OF_2 and 4 mol % H_2 ; however, this caused the reaction to go to completion. Observed reactor temperature rises strongly suggesting that this was a result of thermal acceleration that resulted from the reaction's exothermicity.

(1) This research represents a portion of the work presented in the Ph.D. thesis of T. W. Asmus, 1970.

(2) R. W. F. Gross, N. Cohen, and T. A. Jones, *J. Chem. Phys.*, **48**, 3821 (1968).

the concentrations of H_2O and O_2 were quantitatively determined by calibrating the mass spectrometer for these species.⁶ The HF concentration was determined by passing the gas stream through a series of bubblers filled with 0.1 M NaOH solution. The fluoride was precipitated as the lead(II) or calcium salts, dried, and weighed. Because of the possibility of the HF reacting with the glass during collection it was believed that the results from this analysis were only approximate; it was found that about 1.6 mol of HF was formed for each mole of OF_2 reacted.

In those experiments where the rate with respect to OF_2 was to be measured, the mass spectrometer's mass selector was set at the maximum ion current signal for the parent ion peak, *i.e.*, m/e 54. This is also the base peak for OF_2 and thus gave the greatest sensitivity. An ion current signal was recorded with the gaseous stream of known composition flowing through the reactor bypass. Knowledge of the ion current signal corresponding to the gaseous stream flowing through the reactor and the zero OF_2 concentration signal, *i.e.*, background, obtained by passing pure He through the system, permitted calculation of the OF_2 concentration of the stream leaving the reactor. The linearity of the ion current signal with concentration had been well established.

Differential rate data were obtainable because a stirred-flow reactor was used.⁷ Reaction rates were calculated using

$$\frac{dc}{dt} = r = \frac{c_0 - c}{t} \quad (1)$$

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

Results and Discussion

Reaction Products and Stoichiometry.—The products of the H_2 - OF_2 reaction were found to be HF, H_2O , and O_2 . As previously discussed, H_2O and O_2 were detected and quantitatively measured mass spectrometrically. Hydrogen fluoride was confirmed and measured semiquantitatively using a wet chemical technique. Measurement of the product concentrations and the reaction rates with respect to OF_2 and H_2 enabled establishment of the reaction's stoichiometry as $2\text{OF}_2 + 3\text{H}_2 \rightarrow 4\text{HF} + \text{H}_2\text{O} + 0.5\text{O}_2$.

Reaction Kinetics.—Initial experiments were carried out at 110, 130, 150, 170, and 190° and at the following initial reactant concentrations given as mole per cent OF_2 , mole per cent H_2 : 0.5, 1.0; 1.0, 1.0; 1.0, 2.0; 1.0, 5.0; 0.5, 5.0. As discussed in the Experimental Section, attempts to use higher initial reactant concentrations, *i.e.*, 2 mol % OF_2 and 4 mol % H_2 , failed because the reaction went to completion due to thermal acceleration. Figure 1 shows a typical set of data for five temperatures and 1 mol % OF_2 and 2 mol % H_2 (these kinetic data are based on OF_2 disappearance). The rapid leveling off of the curves is indicative of inhibition by product(s). The rate changed too rapidly during early stages of the reaction to permit reliable extrapolation to time zero to obtain initial rates.

Initial concentrations of the three products were added separately to the reactant streams to determine their effect on the rate. Concentrations of 0.3 mol % H_2O and 0.8 mol % HF had no observable effect on the rate; however, 0.8 mol % O_2 at 170° lowered the rate by factors of about 8 and 1.6 at 0.5 and 8 sec con-

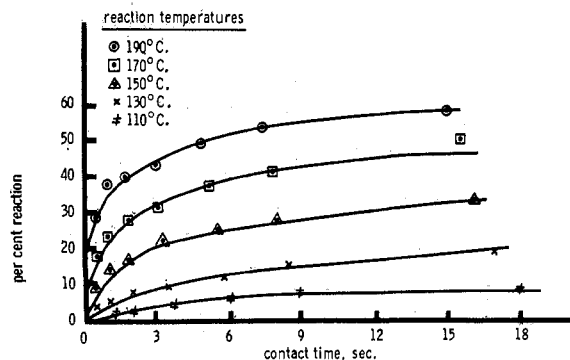


Figure 1.—Per cent reaction vs. contact time at 110, 130, 150, 170, and 190° (runs 90–123).

tact times, respectively. The effect of added O_2 proportionately decreases as the O_2 concentration, resulting from the reaction, increases. To examine further the effect of O_2 on the rate, experiments were conducted with initial O_2 concentrations of 2 and 5 mol %; it was observed that 5 mol % O_2 reduced the rate by about an additional 10% as compared to that obtained when 2 mol % O_2 was added. It was thus concluded that further increasing the O_2 concentration would have no effect on the rate and that an initial concentration of 5 mol % O_2 induced essentially maximum, or limiting, inhibition. These experiments, involving the maximally inhibited reaction, were conducted at 190 and 220° so that the extents of reaction would be high enough to be dealt with quantitatively. The above observation strongly suggested that a rate equation descriptive of this reaction must have at least two terms, only one of which must have an inverse O_2 concentration dependency.

Figure 2 illustrates that the OF_2 concentration de-

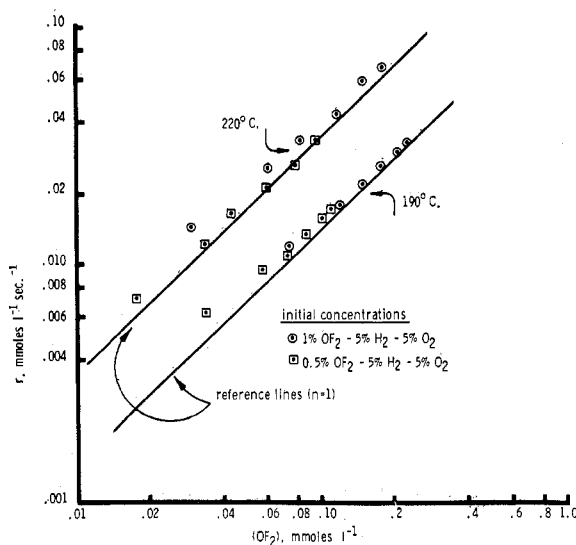


Figure 2.—Log r vs. log (OF_2) at 190 and 220° for the fully inhibited reaction.

pendency of the maximally inhibited reaction is close to first order at the two temperatures; *i.e.*, the slopes of the log-log plots are about 1 over a wide range of OF_2 concentrations. The H_2 concentration dependency of the maximally inhibited reaction is not as clear or simple. Table I shows that the H_2 concentration depen-

(6) The determination of H_2O with a mass spectrometer is an arduous task, the results of which are subject to high uncertainties. With the mass selector "focused" on the m/e 18 peak, 20 min was required for the establishment of a steady-state ion current. Since the reaction occurred on a continuous basis, the long equilibration time posed no problem, and since the results obtained were reproducible, the mass spectrometric H_2O determination is felt to be quantitative.

(7) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, pp 21–24.

TABLE I
EFFECT OF (H₂) ON THE INITIAL RATE OF THE
FULLY INHIBITED REACTION^a

(Initial rate)/ (OF ₂), sec ⁻¹	Mol % H ₂	Temp, °C	r ₅ /r ₂
0.113	2	190	1.27
0.143	5	190	
0.280	2	220	1.35
0.380	5	220	

^a Initial concentrations: 1 mol % OF₂, 2 and 5 mol % H₂, and 5 mol % O₂.

dency of the initial rate of the maximally inhibited reaction is about 0.3 order.⁸

Possible heterogeneous effects on the reaction rate were investigated by filling the reactor with loosely wound helices of Monel wire which gave rise to a 2.5-fold increase in the reactor's surface to volume ratio. This increase in reactor surface area induced a significant increase in the rate at 190° as shown in Figure 3;

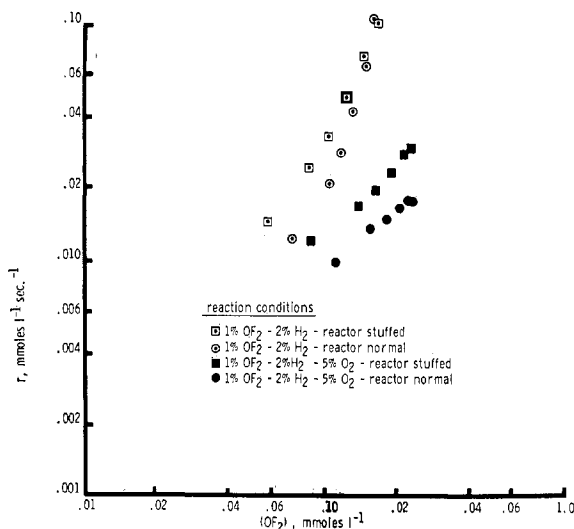


Figure 3.—Log r vs. log (OF₂) at 190° showing heterogeneous effects.

a similar set of data was obtained at 170°. It can be seen that for the maximally inhibited reaction (solid points), the rate was increased by about 50% with the presence of the higher surface area and again was close to first order in OF₂; *i.e.*, order with respect to OF₂ is independent of surface area. The rate of the uninhibited reaction showed a negligible surface effect initially, when the O₂ concentration was low; however, surface effects became significant as the O₂ concentration increased from the reaction (open points). Several experiments involving the maximally inhibited reaction were carried out in the "filled" reactor and indicated that the order with respect to H₂ was reduced when the reactor surface area was large. That is, the average ratios of (rate)/(OF₂) at 5 mol % H₂ to those at 2 mol % H₂, at comparable extents of reaction, were significantly lower than those obtained with the reactor empty ($r_5/r_2 = 1.20$ at 190° and 1.14 at 210°). Thus, that part of the rate equation which contains (O₂) is dominant at low extents of reaction and describes a homogeneous reaction; whereas, an analytical descrip-

(8) The (rate)/(OF₂) ratio was essentially independent of extent of reaction at 190 and 220° which is consistent with the low order with respect to H₂.

tion of the maximally inhibited reaction requires at least two terms when the reaction is carried out in a Monel reactor, one of which must represent a heterogeneous reaction. Based upon the (OF₂) and the (H₂) dependencies and the surface effects, the following rate equation seems to describe the data for the maximally inhibited reaction satisfactorily

$$r = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^x \quad (2)$$

where x probably is 1 or 1/2; these data are not definitive enough to establish the value of x . The first term in eq 2 describes the heterogeneous component of the reaction and, by virtue of its zero (H₂) dependency, gives rise to the low (H₂) dependency for the maximally inhibited reaction.

In an attempt to establish the form of the (O₂)-containing term of the rate equation, several sets of experiments were performed with initial O₂ concentrations comparable to those produced by the reaction. The initial concentrations used were 1 mol % OF₂, 2 mol % H₂, and 0–0.20 mol % O₂. It was concluded after several analytical treatments that the (O₂)-containing term in the rate law is of the form of the third term in eq 3 (total rate law). The ratio of (O₂)/(OF₂) arises

$$r = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^x + \frac{k_c(\text{OF}_2)(\text{H}_2)}{1 + b(\text{O}_2)/(\text{OF}_2)} \quad (3)$$

because of the competition which is believed to occur between O₂ and OF₂ for the H atoms (as shown in eq 6 and 7). An analytical test of the above rate law was made by plotting the data in the form of $r/(\text{OF}_2)$ vs. (OF₂)(H₂)/(O₂). Figure 4 illustrates the data ob-

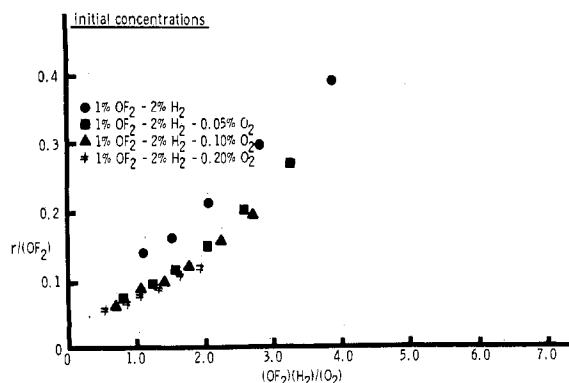
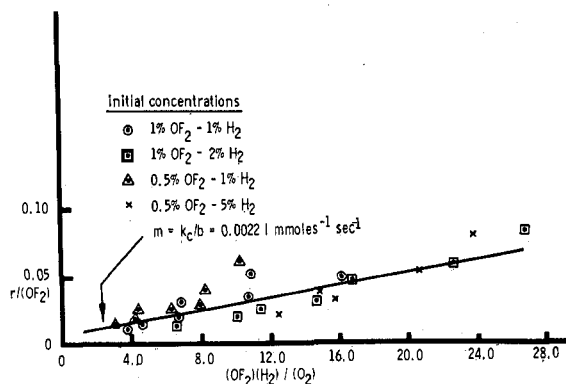
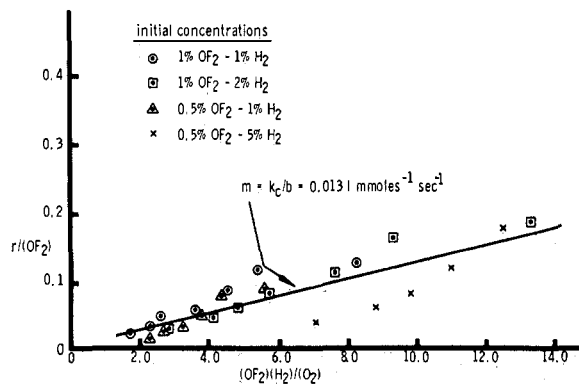
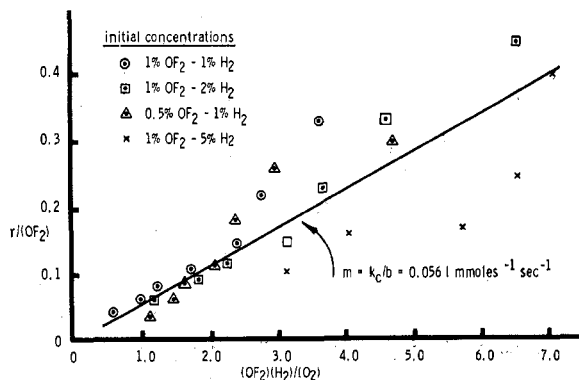


Figure 4.— $r/(\text{OF}_2)$ vs. $(\text{OF}_2)(\text{H}_2)/(\text{O}_2)$ at 170°.

tained when low concentrations of oxygen were added; Figures 5–8 are similar plots with no added oxygen. This treatment involves the assumptions that (a) $b(\text{O}_2)/(\text{OF}_2) \gg 1$ and (b) $k_a + k_b(\text{H}_2)^x$ is approximately constant under the conditions used.⁹ The slopes of the resulting lines are equal to k_c/b and are summarized in Table II. The intercepts are too small

TABLE II RATE CONSTANTS FOR THE (O ₂)-CONTAINING TERM			
Temp, °C	10 ³ k _c /b, l./mmol sec	Temp, °C	10 ³ k _c /b, l./mmol sec
130	0.22	170	5.6
150	1.3	190	17.0

(9) Scatter in the data is accentuated by the analytical treatment; *e.g.*, when the experimentally determined values of (OF₂) are too low, the rate is too high; thus, $r/(\text{OF}_2)$ values are much too high.

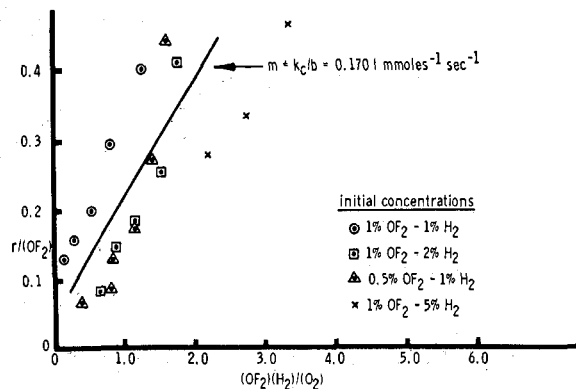

 Figure 5.— $-r/(OF_2)$ vs. $(OF_2)(H_2)/(O_2)$ at 130° .

 Figure 6.— $-r/(OF_2)$ vs. $(OF_2)(H_2)/(O_2)$ at 150° .

 Figure 7.— $-r/(OF_2)$ vs. $(OF_2)(H_2)/(O_2)$ at 170° .

to be treated quantitatively; however, Table III summarizes the composite rate terms $[k_a + k_b(H_2)^x]$ ob-

TABLE III

COMPOSITE RATE TERMS FOR THE FULLY INHIBITED REACTION

Temp, °C	(H ₂) ₀ , mol %	$k_a + k_b(H_2)^x$, sec ⁻¹	Temp, °C	(H ₂) ₀ , mol %	$k_a + k_b(H_2)^x$, sec ⁻¹
170	2	0.040	220	2	0.305
190	2	0.113	220	5	0.407
190	5	0.145			

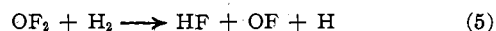

 Figure 8.— $-r/(OF_2)$ vs. $(OF_2)(H_2)/(O_2)$ at 190° .

tained at the higher temperatures for the fully inhibited reaction. An Arrhenius plot of these slopes gives eq 4 (including standard deviations resulting from slopes and intercepts). The 26.4-kcal activation

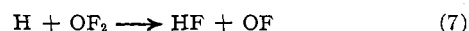
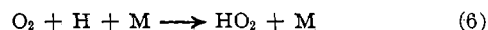
$$k_0/b = 10^{11.7 \pm 0.6} \exp((-26,400 \pm 1200)/RT) \text{ l./mmol sec} \quad (4)$$

energy is the difference between those of k_0 and b .

Reaction Mechanism.—It would be premature to attempt to propose a detailed mechanism at this point based on the present data. However, with a reasonable degree of certainty, several elementary steps can be postulated as being important in the overall mechanism. Initiation must occur by an interaction between both of the reactants since neither OF_2 nor H_2 thermally dissociates to a significant extent under the conditions of these experiments.¹⁰ A possible initiation step, which may be heterogeneous or homogeneous, is



Inhibition by O_2 probably results from the competitive reactions



The above competitive steps are analogous to those believed to occur in the H_2 - F_2 reaction mechanism.¹¹

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(11) J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **72**, 3168 (1968).