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RATES AND MECHANISMS OF REACTIONS OF FLUORINE CONTAINING ROCKET PROPELLANTS

Prepared by: Thomas Houser

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Western Michigan University
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13. ABSTRACT

The rate and mechanism of pyrolysis of OF_2 has been studied using a monel, stirred-flow reactor, over the temperature range of 330 to 431°C, and a concentration range of one to ten mole % OF_2 at a total pressure of one atmosphere (helium was the inert diluent). The only observed products were oxygen and fluorine. The initial rate was found to be significantly less than first-order with respect to the reactant concentration. The true order will be less than second after the concentration of diluent has been included because of collision activation producing a rate dependence on total pressure. It was shown that the low order was not due to surface effects, thus a radical-chain mechanism was proposed to account for the observed low order. The rate of the hydrogen-oxygen difluoride reaction has been studied in the same system over the temperature range of 110-220°C, and concentration ranges of 0.5 to 2.0 mole % OF_2, 0.5 to 5.0 mole % H_2 and 0 to 5.0 mole % O_2; total pressure was one atmosphere. The products of the reaction were HF, H_2O and O_2, with about half the oxygen in the reacted OF_2 resulting in O_2. Oxygen strongly inhibits the rate, and the reaction has a substantial heterogeneous component. In order to reduce the surface effects, an aluminum reactor was used to replace the monel reactor. The rates and heterogeneous effects were significantly reduced, thus, higher temperatures, up to 260°C, were used to obtain reasonable extents of reaction. Only the inhibited reaction was examined in aluminum and for this reaction the overall order appeared to be about 1.25 and 0.25 with respect to OF_2 and H_2 respectively. It appears that the rate equation will still be very complex. A cursory examination of the hydrogen-tetrafluorohydrazine reaction indicated that to obtain a controllable, steady-state reaction, inhibition with O_2 was necessary.

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IGNITION RATES						
REACTION MECHANISMS						
FLUORINE CONTAINING OXIDIZERS						

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FOREWORD

The principal objective of this program is to obtain a better knowledge of the chemical reaction mechanisms of high energy rocket propellants containing fluorine. This final report describes research completed during the period from June 1, 1967 through August 31, 1971. The program was supported by the Air Force Office of Scientific Research, Energetics Division, United States Air Force under Grant No. AF-AFOSR-1291-67, entitled, "Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants."

During this period, contributions to the program were made by T.W. Asmus (Ph.D. Candidate), D. Humbert (technician), and T. Houser.

ABSTRACT

The rate and mechanism of pyrolysis of OF_2 has been studied using a monel, stirred-flow reactor, over the temperature range of 330 to 431°C, and a concentration range of one to ten mole % OF_2 in helium at a total pressure of one atmosphere. The only observed products were oxygen and fluorine. The reaction was found to be somewhat less than first-order with respect to the reactant concentration. It was found that the initial rate data could be represented by the following rate expression:

$$-\left[d(OF_2)/dt\right]_0 = k_2(M)(OF_2)_0 + k_{3/2}(M)(OF_2)_0^{1/2}$$

where k_2 and $k_{3/2}$ are the second-order and 3/2-order rate constants respectively and (M) is the total concentration of species in the reactor. An Arrhenius plot of the k_2 values gave the following expression:

$$k_2 = 10^{16.9 \pm .6} \exp (59,200 \pm 1,700/RT)(\text{cc/mole sec.})$$

The uncertainties in $k_{3/2}$ were too large to allow a comparable quantitative treatment. It was shown that the low order was not due to surface effects; thus, a radical-chain mechanism was proposed to account for the observed low-order.

The rate of the hydrogen-oxygen difluoride reaction has been studied in the same system using both monel and aluminum reactors over the temperature range of 110-260°C, and concentration ranges of 0.25 to 2.0 mole % OF_2, 0.5 to 5.0 mole % H_2 and 0 to 20 mole % O_2; total pressure was again one atmosphere with He as the diluent. The products of the reaction and stoichiometry are shown by the following equation:

$$2\,OF_2 + 3\,H_2 \longrightarrow 4\,HF + H_2O + 1/2\,O_2$$

Oxygen was found to strongly inhibit the rate, other products had no measurable effect on the rate. The reaction had a significant heterogeneous component in monel which was greatly reduced by the use of the aluminum reactor. The following rate law appears to fit

the data, obtained from the monel reactor:

$$-d(OF_2)/dt = k_a(OF_2) + k_b(OF_2)(H_2)^x + k_c(OF_2)(H_2)/\left[1 + b(O_2)/(OF_2)\right]$$

where x may be 1/2 or 1. The orders appear to be different than those indicated by the above equation for the fully inhibited reaction in aluminum (high concentrations of oxygen were introduced to make the third term in the rate equation negligible). The overall orders were found to be 1.25 and 0.25 with respect to OF_2 and H_2, respectively. Work is continuing to better define this rate law.

Attempts have been made to obtain rate data for the hydrogen-tetrafluorohydrazine reaction. It was found that steady-state reaction could not be achieved using only He as the diluent; the reaction did not proceed at a measurable rate at room temperature and when the reaction was initiated by heating to above 40°C, it went to completion. Thus, it appeared to be a go-no go situation, the temperature at which reaction started depended on the concentrations of reactants. By adding a large concentration (ca 50 mole %) of oxygen, a controllable rate for the inhibited reaction was obtained in the 70 to 90°C range.

CONTENTS

LIST OF FIGURES

INTRODUCTION

OBJECTIVE

The primary objective of this study is to obtain a better understanding of the chemical properties of fluorine containing rocket propellants. The compounds selected for study were OF_2 and N_2F_4 because their chemical properties have not been well established. Furthermore, they contain groups which contribute to the composition of many new high energy propellants; thus, a knowledge of their reaction mechanisms will contribute to the understanding of the chemical behavior of many new propellants. This report describes the progress made on this study during the period of 1 June 1967 to 30 September 1971, which includes the determinations of the rates of pyrolysis of OF_2 and of the OF_2-H_2 reaction, and the establishment of the conditions to be used for the study of the rate of the N_2F_4-H_2 reaction.

BACKGROUND

Although the kinetics of the thermal decomposition of OF_2 has been studied extensively, there remains considerable doubt as to the mechanism of pyrolysis. This reaction has been investigated with static[1,2] and flow[3] systems, and in shock tubes[4-7]. It has been found to be about first-order with respect to OF_2 when a large excess of inert diluent gas is present, with the pseudo first-order constant proportional to total pressure, and found to be approximately second-order when only pure OF_2 is used. The reported activation energies were in the range of 31 to 42 kcal/mole.

The main problem to be resolved is the nature of the pyrolysis mechanism of OF_2; is it chain or non-chain? There is general agreement between the previous investigators that the intial step is the FO-F bond rupture, followed by steps involving OF and F radicals. If the process is non-chain, then the activation energy for the rate of disappearance of OF_2 should correspond to the bond dissociation energy for the above rupture. Using this premise and the heat of formation of OF_2, the calculated O-F bond strength is greater than that of the FO-F bond. Thus, if the above assumption concerning the mechanism is valid, it is difficult to explain why the OF radical has not been observed directly as an intermediate.*

On the other hand, if the mechanism is a chain process, the activation energy may be less than the (FO-F) bond strength. Thus, the second F-O bond may be weaker than the first, consistent with the difficulty in observing the OF radical. In support of this possibility is the determination of the FO F bond strength from appearance potential measurements by Dibeler, et. al[8]; the value that they obtained was about 60 kcal/mole. However, it should be noted that this value probably has a large uncertainty due to the technique used. From the above discussion it can be seen that there are unanswered questions concerning the pyrolysis of OF_2, the current program is attempting to resolve some of these.

In addition to the pyrolysis of OF_2, the reactions of hydrogen with OF_2 and N_2F_4 are being studied to gain a better understanding of the chemistry of fuel-oxidizer interactions with fluorine containing compounds. No reported studies on kinetics of these reactions have been found in the literature. The H_2-OF_2 reaction has been studied in connection with a chemical laser produced by the photolysis of a mixture of the reactants[9]. In addition, the mechanism of the explosive H_2-N_2F_4 reaction has been studied[10]; the conclusions reported were based on the measured product distributions. In that reaction, N_2F_2 was postulated as a key intermediate in the mechanism, formed directly from an attack of H atoms on N_2F_4. However, because of the high degree of dissociation of N_2F_4 at the reaction conditions used, other steps may be necessary to explain the origin of the nitrogen produced.

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* Especially in the low pressure flow system of Dauerman[3], et al., since the reactor and mass spectrometer ionizing beam were very close together, thus allowing a minimum opportunity for a reactive species to disappear. In addition, in the shock tube study of Lin and Bauer[6], using mass spectrometric analysis, the calculated OF concentration is the same order of magnitude as the measured O_2 concentration over a wide range of extents of reaction; thus, it appears that it should have been possible to observe enhancement of the OF peak.

EXPERIMENTAL

APPARATUS

The rate data has been obtained using a conventional flow system equipped with a monel, stirred-flow reactor entirely housed in a 7 ft. walk-in hood (Fig. 1). However, the later experiments were conducted with an aluminum reactor of the same design.

The OF_2-He and H_2-He mixtures, stored in 5 and 10 gal. tanks respectively (not shown in Fig. 1), were introduced to the reactor (volumes were, monel, 86 ml and aluminum, 100 ml) through separate flow lines. The flow rates were regulated by pressure regulator-needle valve combinations, and measured by glass capillary flow meters (halocarbon oil was used as the manometric fluid) which had been calibrated at each concentration with a wet-test meter. The flow lines are stainless steel upstream of the reactor and monel downstream.

Each flow line has a reactor bypass so that the decrease in reactant concentrations could be measured with the greatest accuracy despite possible drifts and fluctuations in instrument sensitivity. The reactant and product concentrations were measured with a mass spectrometer (Picker Nuclear, M. S. 10), equipped with an atmospheric sampler, and connected to the flow system through a stainless steel capillary tube (ca 5 ft. long and 0.015 in. I. D.) inserted just downstream from the reactor-bypass "T" connection. Since the recorder response was obtained at a known reactant concentration for flow through the bypass, and it was found that the instrument's response was linear with concentration, the calculation of the concentration flowing from the reactor was a simple matter.

The stirred-flow reactor and furnace assembly are shown in Fig. 2. The gas stream enters the reactor through the center tube and is sprayed sideways and downward through five pin holes to give a jet-stirring effect. This design was tested several times by injecting an inert gas (e.g. nitrogen) into a helium stream and determining the non-steady-state concentration exiting from the reactor. The testing of this reactor design has been reported more

Figure 1. THE FLOW SYSTEM

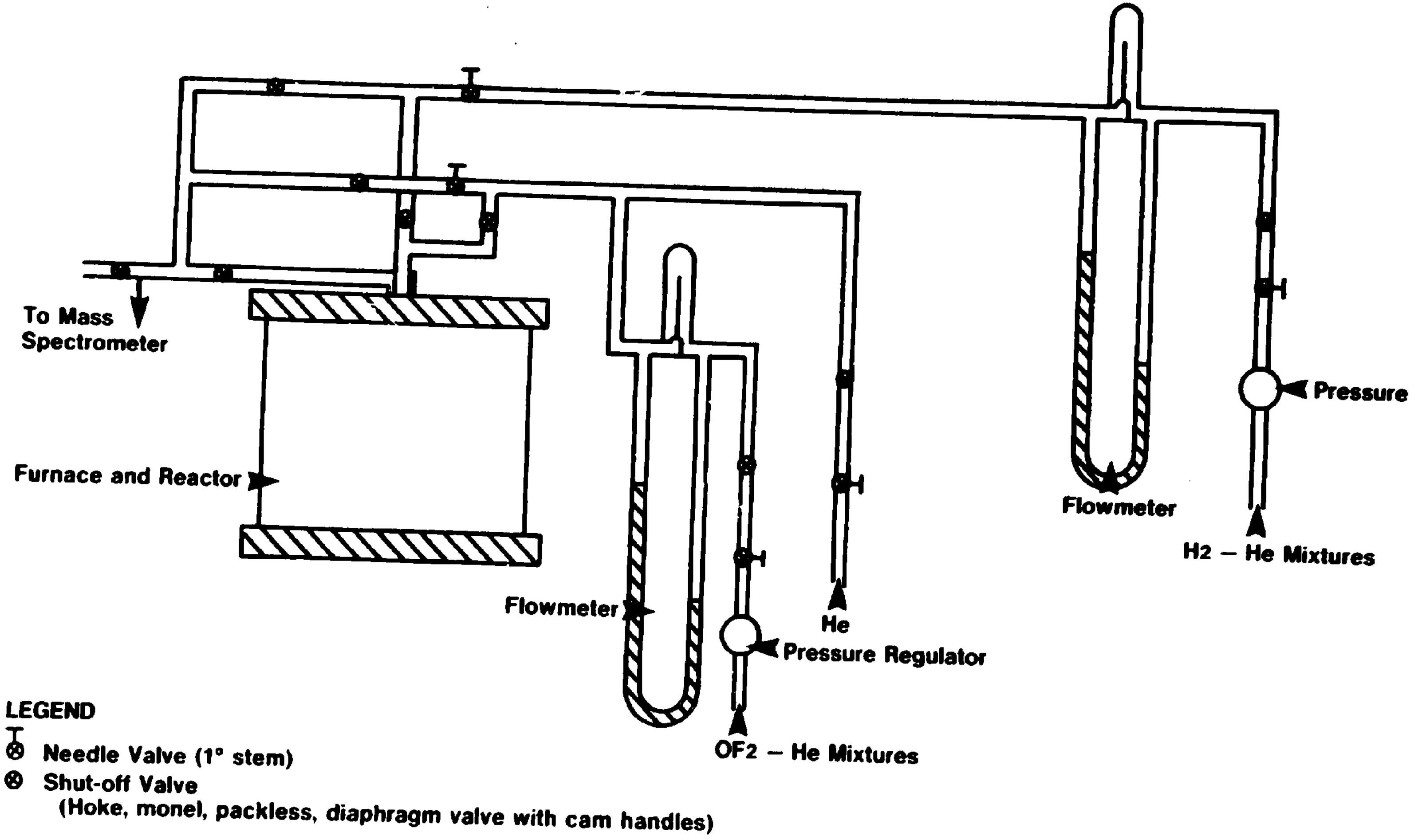
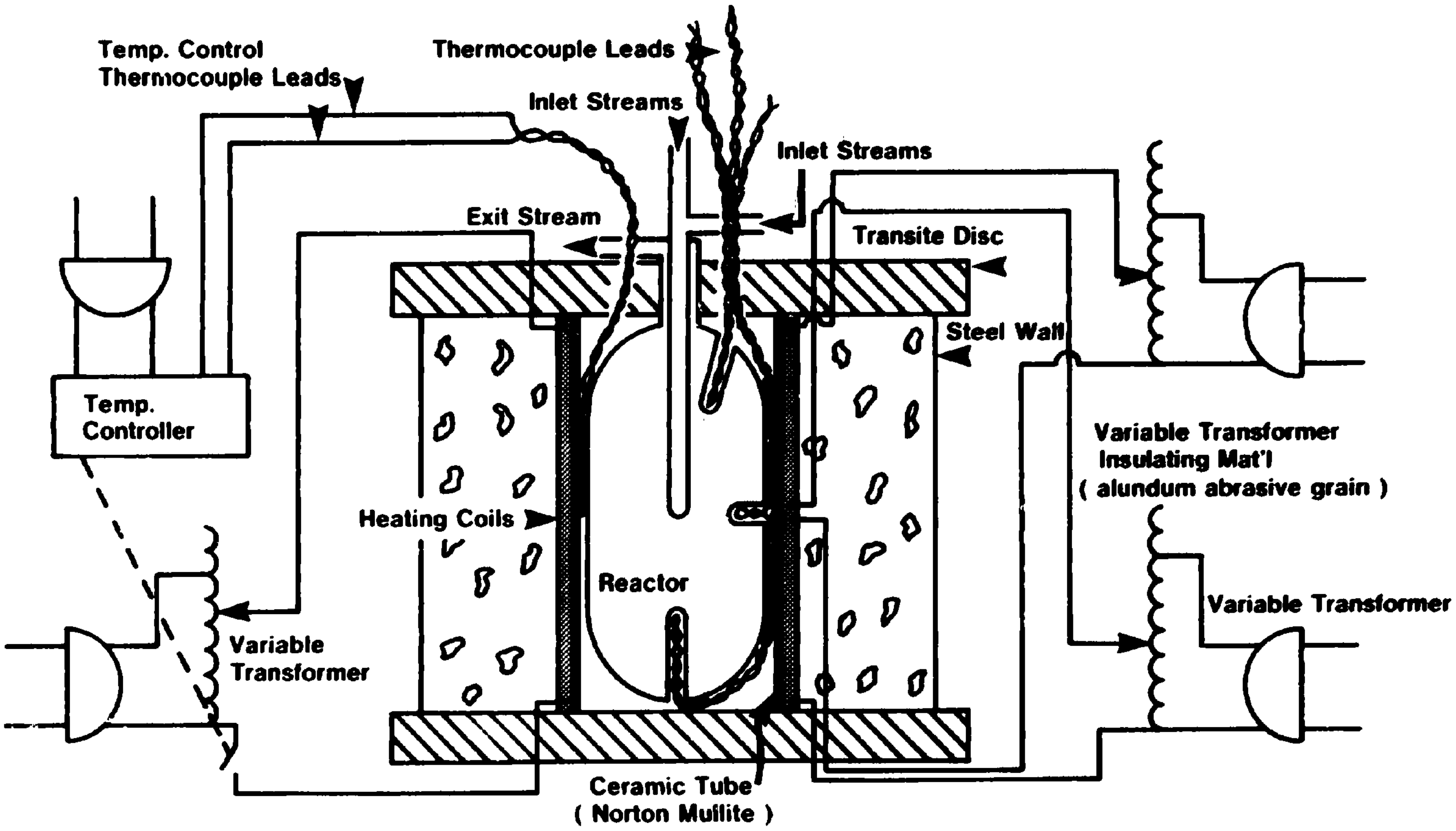


Figure 2. REACTOR AND FURNACE ASSEMBLY



quantitatively by Sullivan and Houser[11]. The reactor temperatures were measured using several standardized (NBS-Zn, Pb, Cu, Al) chromel-alumel thermocouples and a portable potentiometer (Honeywell model 2732); temperature control was maintained with a Versatronik controller (Honeywell model R7161H).

PROCEDURE

There were a few general operations which were applicable to both the pyrolysis of OF_2 and the OF_2-H_2 reaction. It was necessary to insure that the surfaces of the flow system were passivated before making rate measurements. This was done by exposing the cold surfaces (flow lines and unheated reactor) to OF_2 until a steady response by the mass spectrometer was obtained. If the ion current was constant with time and independent of the gas flow rate, it could be assumed that adsorption on these surfaces had reached steady-state and reaction with these surfaces had stopped. With regard to the heated reactor, an ion current, independent of time, indicated steady-state reaction has been reached and changes in surface area indicated the extent of the contribution of the surface to the reaction.

The tank-filling procedure for reactant mixtures was usually carried out in a stepwise fashion, diluting from 100% to 10% in one step and then further diluting to the desired concentration in the next step. In this way the uncertainties in concentration were minimized.

Because a stirred-flow reactor was used, differential rate data were obtained. The reaction rates were calculated from Eq. 1[12]

$$\text{rate} = (c_o - c)/t \qquad (1)$$

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

Oxygen Difluoride Pyrolysis. The general conditions in the pyrolysis experiments were: temperature range, 330 to 431°C; contact times of 0.5 to 20 seconds; about one atmosphere total pressure; and reactant concentrations of one to ten mole percent with helium as the diluent. The procedure was as follows: the tank, filled with the desired concentration of reactant, was attached to the flow system, and the flow rate was set at the proper value. The ion peak heights (m/e = 54) were recorded for the stream through both the bypass and reactor, and a base line determined with only He flowing. These data were used to calculate the % reaction which was used with the known initial concentration to obtain a rate.

There were some experiments which involved modifications to the procedures. Because of a concern for the possibility of the gas not heating rapidly enough during the higher flow rate experiments, the reactor entrance was provided with a preheater. Heating the entering gas to about 200°C had no effect on the apparent rate, thus, the drop in temperature at high flow rates was assumed negligible. In addition, since it was possible that the surface may influence the rate, three groups of experiments were made with an increased surface area obtained by stuffing the reactor with monel 1/4 in. rod, and wire in the form of loose spirals. The surface area was increased by factors of 1.5 and 2.5, respectively. Similarly, the effects of gaseous additives on the rate were examined by including the additives in the reactant mixtures for some experiments. The results of these experiments will be discussed later.

Finally, some experiments were conducted at reduced pressures, the results of which did not appear reasonable and thus were discarded. These results may have been poor due to a change in stirring characteristics at these low pressures.

Hydrogen-Oxygen Difluoride Reaction. The conditions for the H_2-OF_2 reaction in the monel reactor were: temperature range 110 to 220°C; contact time of 0.5 to 20 sec.; one atmosphere total pressure; and reactant concentrations of 0.5 and 1.0 mole% OF_2, 0.5 to 5.0 mole % H_2 and up to 5.0 mole % O_2, with helium as the diluent.

Only the inhibited H_2-OF_2 reaction has been studied in the aluminum reactor. Because of the reduction in surface effects on the rate, higher temperatures were necessary to achieve reasonable extents of reaction, and higher oxygen concentrations were necessary to produce maximum inhibition. These conditions were: temperature 160 to 260°C; contact times of 1.5 to 20 sec.; reactant concentrations of 0.25 to 2.0 mole % OF_2, 0.5 to 3.0 mole % H_2 and 0 to 20 mole % O_2; total pressure and diluent were the same as before.

Most of the procedures were similar to the pyrolysis reaction and those will not be described further; however, it is worthwhile to discuss some of the modifications made. It was necessary to prepare the tanks with double the concentration of reactants to be used, then set the flows at equal volume flow rates for each tank. The oxygen was added to the OF_2 tank for those experiments measuring the inhibiting effect of oxygen. Water was added to the reaction mixture by passing the H_2-He mixture through a bubble tower, and HF was added to the OF_2 tank to check the effects of these products on the rate of reaction. Aluminum wire was used to stuff the aluminum reactor for the measurement of the metal's effect on rate, the increase in surface area was again a factor of 2.5.

Most of the rate data were obtained from observing the disappearance of OF_2; however, some data were obtained by measuring the changes in hydrogen concentration, which served as a check on the stoichiometry also. In addition, the concentrations of water and oxygen produced by the reaction, were measured quantitatively by calibrating the mass spectrometer for these species. It was necessary to determine the HF concentration by wet chemical techniques, and only an approximate value was obtained because of inefficient trapping due to the reactivity of HF.

Higher concentrations of OF_2 and H_2 were tried (2 and 4 mole %, respectively) but it was not possible to maintain isothermal conditions at these concentrations in the monel reactor.

Hydrogen-Tetrafluorohydrazine Reaction. The procedures were essentially the same as those for the H_2-OF_2 reaction, but at lower reactor temperatures.

RESULTS AND DISCUSSION

REACTOR STIRRING EFFICIENCY

In order to use Eq. 1 to calculate reaction rates from the experimental observations, it is necessary to insure that efficient stirring is obtained. This can be checked by injecting a non-reactive gas (e.g. nitrogen) into a helium stream and measuring the non-steady-state concentration of this gas flowing from the reactor. The time dependence of the concentration is expressed by Eq. 2, if complete mixing is obtained[11]:

$$c = c_o\left[1 - \exp(-\tau/t)\right] \qquad (2)$$

where c = the concentration of trace gas leaving the reactor

c_o = the concentration of tracer gas entering the reactor

τ = clock time

t = contact time

Fig. 3 illustrates the stirring efficiency at high and low flow rates. At the low flow rate the stirring produces concentrations close to those predicted by Eq. 2, and at the high flow rate the calculated and experimental curves are indistinguishable. Similar results were also obtained when the reactor was stuffed with wire spirals. Thus, it can be concluded that the stirred-flow assumption is justified.

OXYGEN DIFLUORIDE PYROLYSIS

Reaction Products. The products of the thermal decomposition of OF_2 were found by mass spectrometric analysis to be O_2 and F_2, which is consistent with the products previously reported[1]. Solomon, et al.[2], reported some evidence for small amounts of O_2F_2 and the O_2F radical among the reaction products; however, no such evidence was found in this study, possibly because of the higher temperature used.

Reaction Order. The pyrolysis rates were measured at 5 temperatures in the range of 330 to 431°C and at initial OF_2 concentrations of 1 to 10 mole % in He. Isothermal plots of log rate versus log concentration indicated that the rates were slightly less than first-order in OF_2 at the lower temperatures, i.e. about 0.75 at 330°, and uniformly increased to first-order at the higher temperatures. Figs. 4 and 5 illustrate

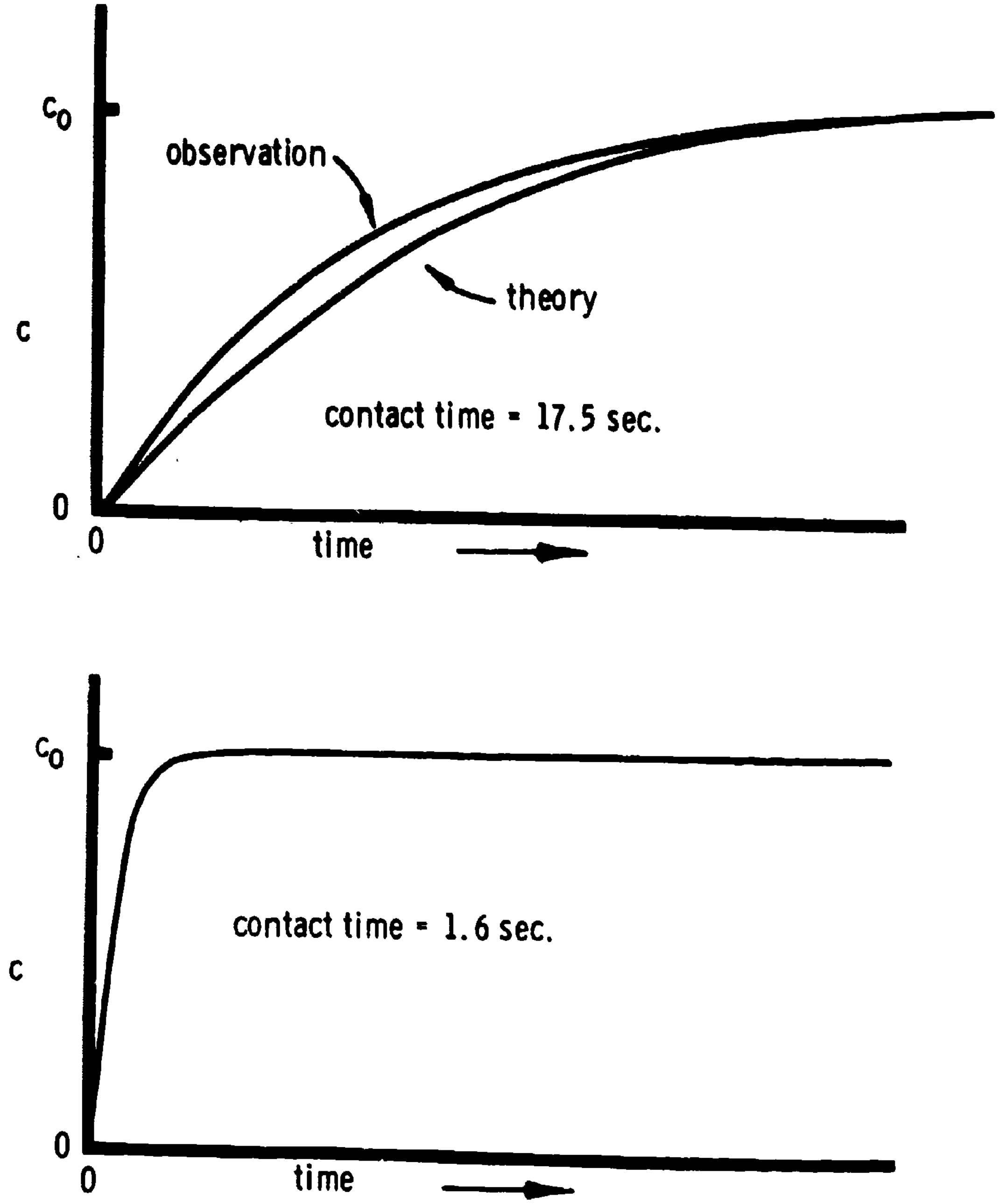


FIGURE 3 A study of stirring efficiency

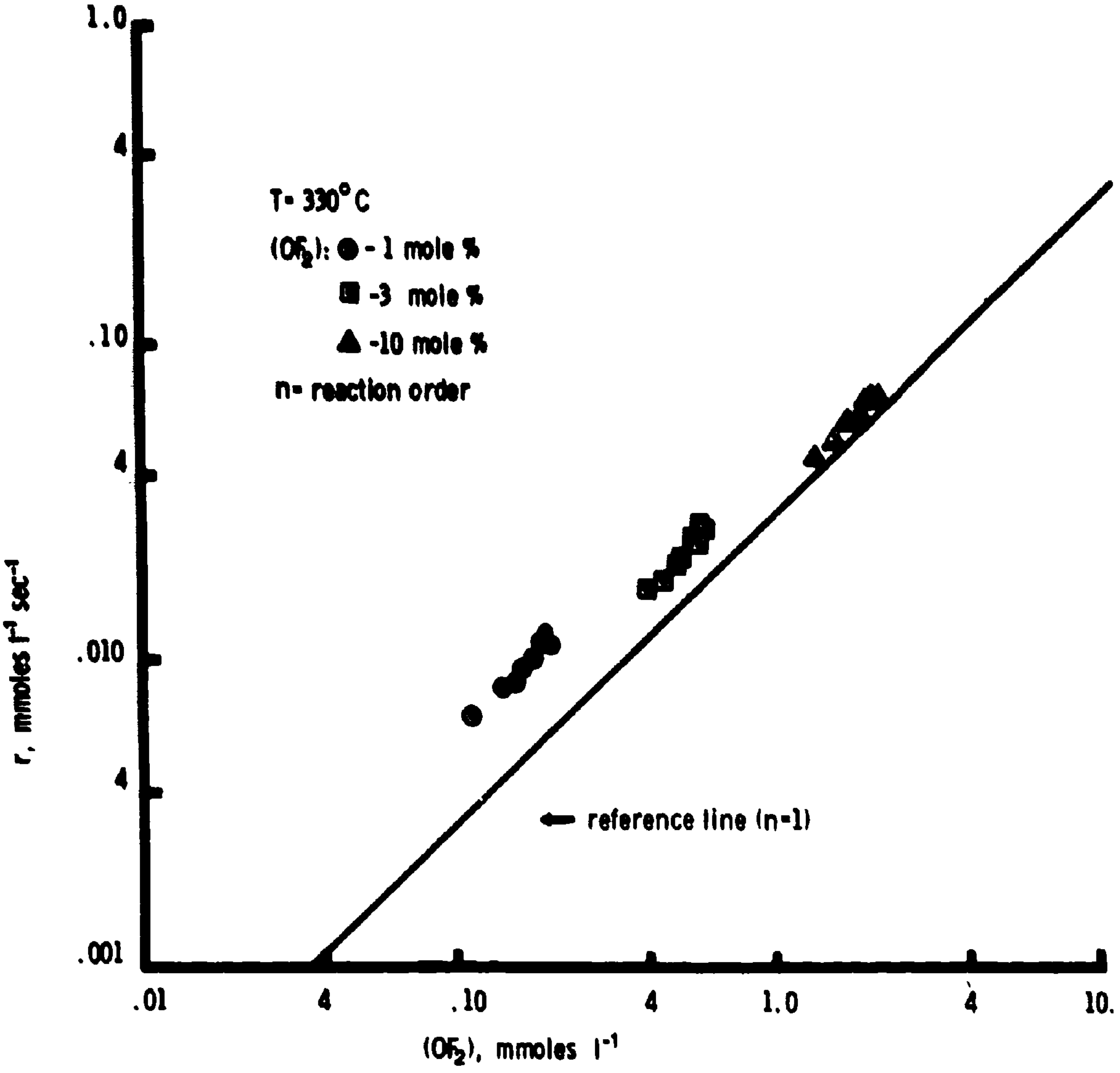


FIGURE 4 Log r versus log (OF$_2$) at 330°C.

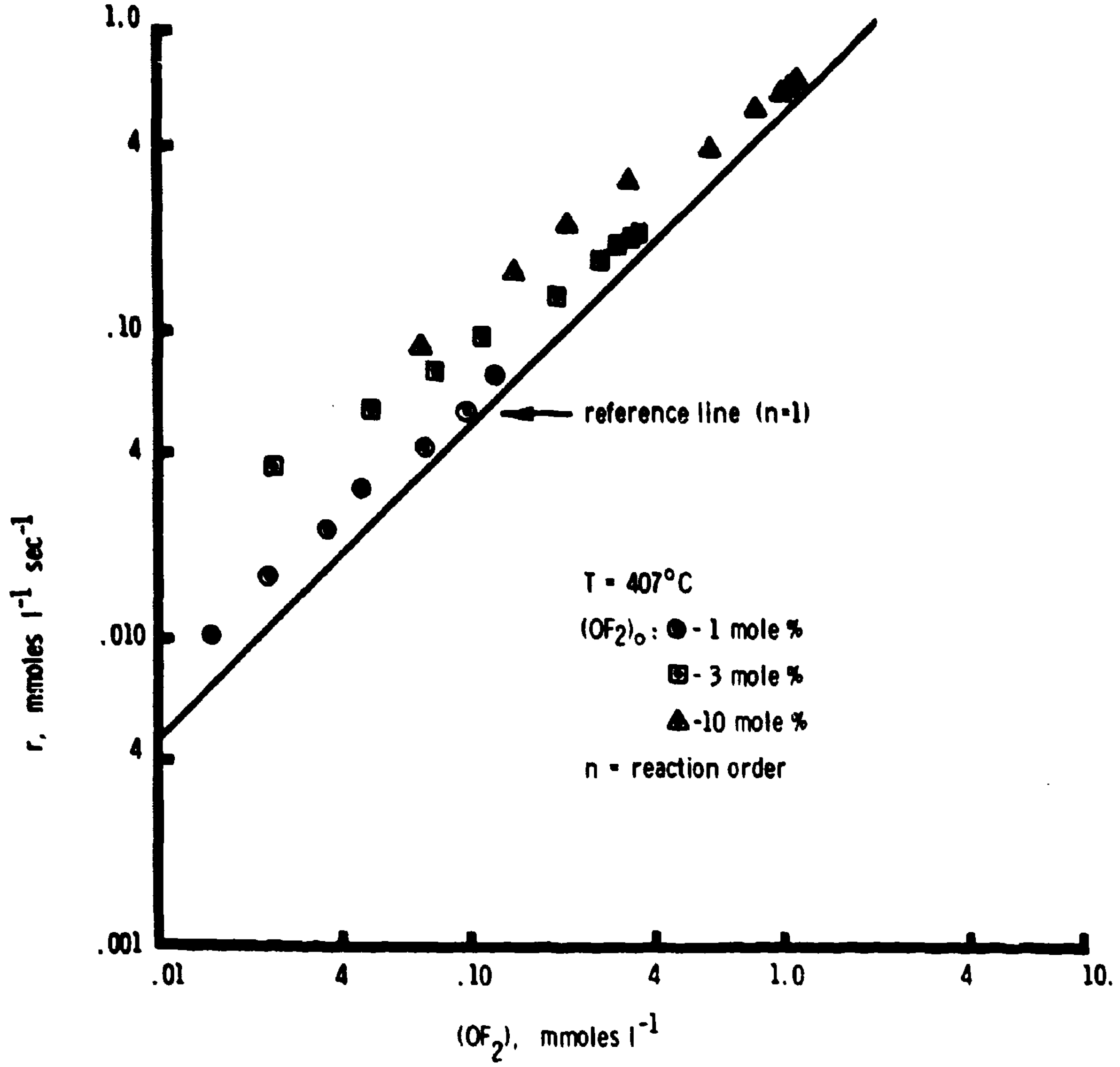


FIGURE 5 Log r versus log (OF$_2$) at 407° C.

this trend for the first set of data, showing an increase in slope with temperature for the points at low extents of reaction. The observation of low order has not been previously reported, possible because techniques that do not provide for the direct determinanion of rates are relatively insensitive to minor order variations. Schumacher and co-workers[13], however, have recently observed a similar low-order effect at low temperatures in static vessel experiments using pure OF_2. Having reproduced this crder 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, Figs. 6 and 7 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 non-zero slopes (a positive slope indicates an order of less than one); 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. Some experiments at longer contact times were left off the figures because they did not influence these extrapolations significantly.

The initial rate data are presented in Table 1; 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%

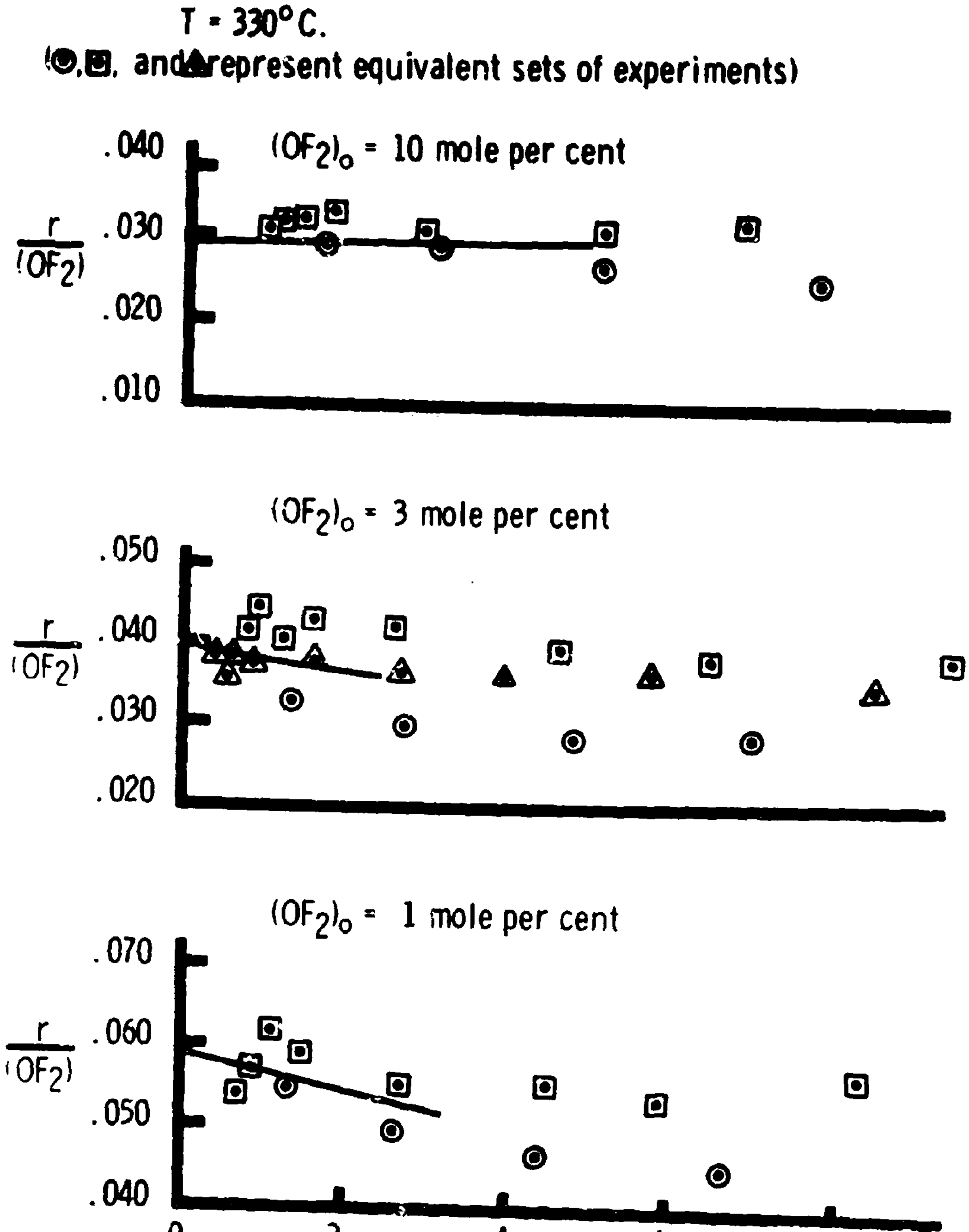


FIGURE 6 $r/(OF_2)$ versus contact time at 330° C

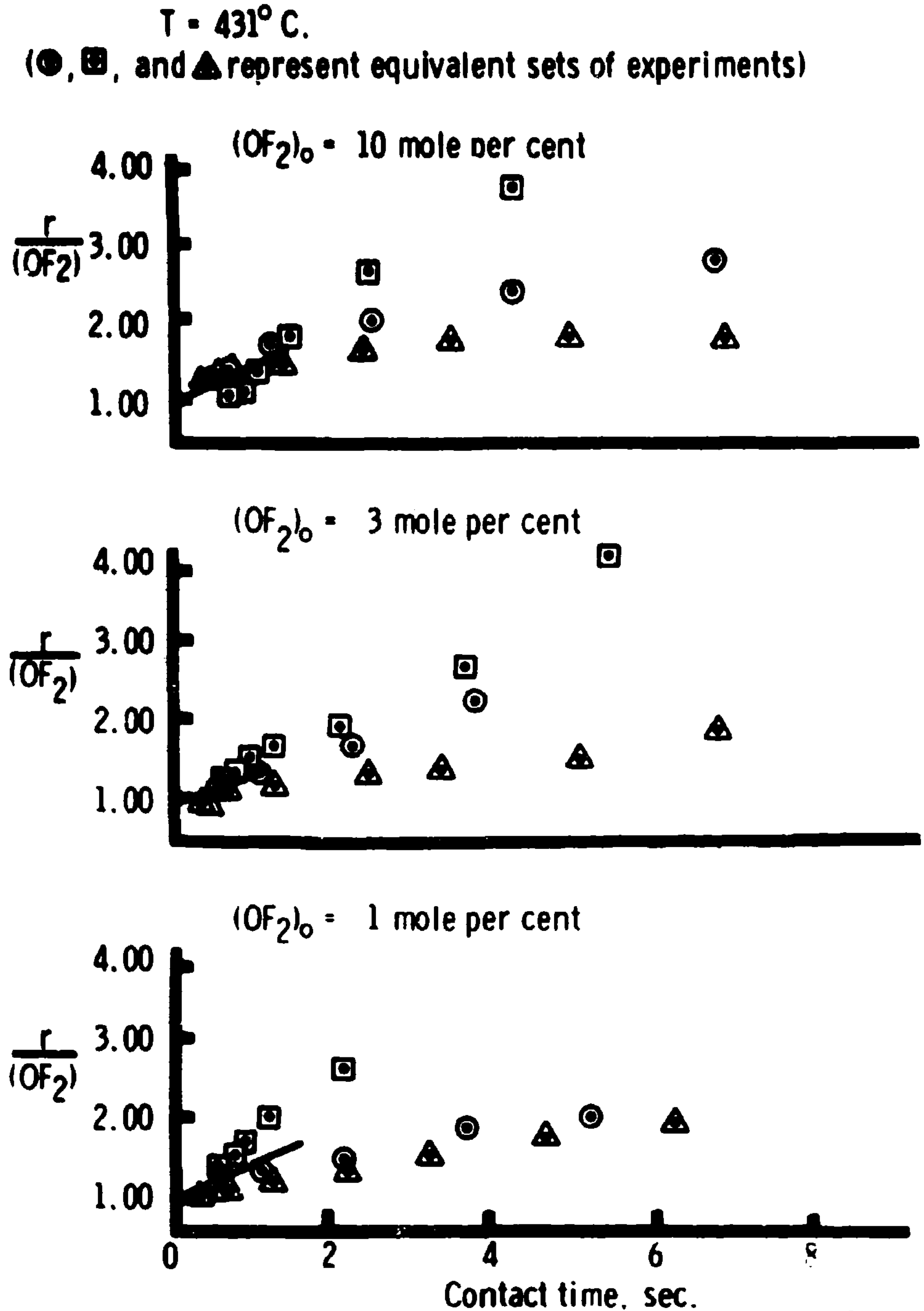


FIGURE 7 $r/(OF_2)$ versus contact time at 431° C.

Table 1

Initial Rate Data

Temperature °C	OF_2 Concentration x 10^8 mole/cc	r_0(corrected)/$(OF_2)_c$[*]
330	.197	.055 ± .001
	.591	.036 ± .003
	1.97	.024 ± .004
360	.187	.116 ± .008
	.563	.100 ± .013
	1.87	.076 ± .006
385	.181	.245 ± .013
	.543	.210 ± .023
	1.81	.180 ± .013
407	.174	.460 ± .03
	.521	.440 ± .04
	1.74	.425 ± .01
431	.168	1.01 ± .12
	.504	.85 ± .12
	1.68	.89 ± .25

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

He as the collisional activating medium[*]. The ± values are 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.

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[*] Helium is reported (Ref. 1) 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 (.90 + .10/.4 = 1.15) than if all activation came from collisions 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 mole % 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. 2), the use of which would reduce the size of the corrections discussed.

It can be seen easily 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 be due to a delay in radical intermediates reaching steady-state concentration, thus giving rise to an induction period.* In order to insure that this drop in $r/(OF_2)$ at shorter contact times was not caused by non-isothermal conditions at higher flow rates and temperatures, the gas mixture was heated to about 200°C 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 is emphasized because of its importance in the consideration of a possible mechanism to be discussed later.

Additive and Surface Effects on the Rate. Experiments (at least 12 at each temperature) were conducted whereby initial concentrations of up to 3 mole % 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 mole % F_2 and OF_2 (each) had a pyrolysis rate averaging about 15% below that of a reaction mixture 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 1/4-inch monel rods in one

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* Qualitatively similar trends were predicted for reactions involving radical intermediates[14].

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. Fig. 8 illustrates that the change in surface area of a factor of 2.5 at 385°C increased the reaction rate by only 10%. A similar set of data was obtained at 360°C also using monel spirals, however, with an average increase in the rate of only about 5%. The results at both temperatures are within the experimental reproducibility of those obtained in the empty reactor.

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, non-exponential temperature dependencies. The suggestion by Lin and Bauer[6] that the rate constants from data obtained in conventional systems are about 5 to 10 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[*]. In addition, had the low order at the lower temperatures resulted 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.

<u>Rate Law and Arrhenius Parameters.</u> To account for an observed order of less than one for a homogeneous reaction it will require that a contri-

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[*] Early work by Schumacher[1], indicated a rate constant independent of reactor materials. It is unlikely that a variety of glass and metal surfaces would have quantitatively the same effect on the rate of a heterogeneous reaction.

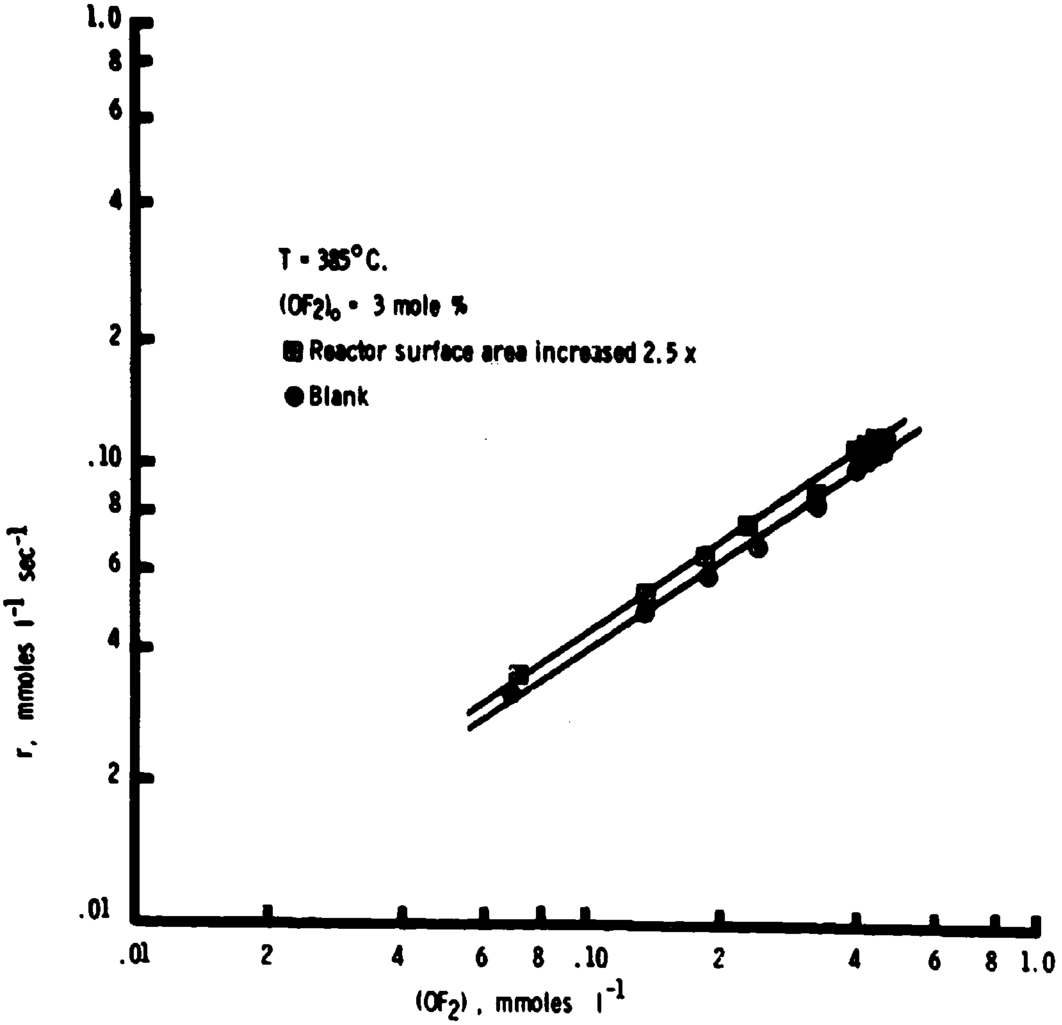

FIGURE 8 Log r versus log (OF_2) - heterogeneous effects

bution 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):

$$r_o = k_1(OF_2)_o + k_{1/2}(OF_2)_o^{1/2} \qquad (3)$$

The second term becomes less significant as the temperature increases.

Plots of $r_o/(OF_2)_o$ vs $(OF_2)_o^{-1/2}$ yielded straight lines, the intercepts and slopes of which gave the pseudo first- and the pseudo 1/2-order rate constants (containing a total pressure dependence) respectively. In order to insure that a relationship of the form of Eq. 3 was reasonable in view of the scatter of the data, correlation coefficients were calculated for the five temperatures[15]. These values along with the probability that the variables $r_o/(OF_2)_o$ and $(OF_2)_o^{-1/2}$ are unrelated are given in Table 2.

Table 2

Statistical Treatment of Data

Temperature °K	Correlation Coefficient	% Probability of Unrelated Variables
603	.95	<0.1
633	.81	~ 1
658	.80	~ 1
680	.40	>20
704	.31	>20

The values obtained indicate that at the three lower temperatures Eq. 3 is a reasonable representation of the data. The pseudo first- and pseudo 1/2-order rate constants were converted to the second- and 3/2-order rate constants by dividing by total concentration (He + OF_2) and are presented in Table 3.

Table 3

Rate Constants

T °K	k_1[a] sec^{-1}	$k_2 \times 10^{-3}$ (cc/mole sec)	$k_{1/2} \times 10^5$ $(mole/cc)^{1/2}\ sec^{-1}$	$k_{3/2}$ $(cc/mole)^{1/2}\ sec^{-1}$
603	.0096 ± .001	.49	2.0	1.0
633	.060 ± .006	3.2	2.5	1.3
658	.152 ± .013	8.4	4.0	2.2
680	.41 ± .04	23.2	- b	—
704	.92 ± .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 $r/(OF_2)$ 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 $r/(OF_2)$ intercepts since it is believed that this would represent an upper limit.

An Arrenhuis treatment of the second-order rate constants gave the following results (the ± values are based on one sigma confidence level):

$$k_2 = 10^{16.9 \pm .6} \exp(-39,200 \pm 1,700/RT)(cc\ mole^{-1}\ sec^{-1})$$

This activation energy is consistent with those previously reported. It is believed that the uncertainties in the 3/2-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. 3. 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^* for reaction (kcal/mole of reactant)	
$OF_2 + M \rightarrow OF + F + M$	39	(4)
$F + OF_2 \rightarrow F_2 + OF$	1	(5)
$OF + M \rightarrow O + F + M$	53	(6)
$2\ OF + M \rightarrow O_2 + F_2 + M$	-26	(7)
$2\ O + M \rightarrow O_2 + M$	-60	(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:

$$r = 2\,k_4(M)(OF_2) + k_6(k_4/k_7)^{1/2}(M)(OF_2)^{1/2} \qquad (9)$$

The fact that Eqs. 3 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 OF_2. Schumacher[13], based on recent unpublished results, has observed orders of slightly less than two when undiluted 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 3/2. Thus, the overall order of this second term would be 2 rather than 3/2.

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* The heats of reaction were estimated using for the heats of formation for OF_2, OF, and F values of 6[16], 26[17] and 19[17] kcal/mole respectively.

Clyne and Coxon[18] 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 termolecular and may be third-order under certain conditions. At lower pressures, the bimolecular reaction could lead to Cl atom formation and would be second-order. Step 7 of the mechanism proposed in this study is consistent with these arguments. Eq. 7 has been discussed on the basis of bonding[19], and it has been concluded that it would occur with little or no activation energy, similar to the case of the OCl radical.

Reactions (10) and (11) have been used by previous investigators to

$$2\ OF \longrightarrow O_2 + 2\ F \qquad (10)$$

$$2\ F + M \longrightarrow F_2 + M \qquad (11)$$

describe the pyrolysis mechanism, and these probably contribute significantly to the reaction under the conditions in the present study*. However, these steps when combined with (4) form a first-order non-chain process, or combined with (4) and (5) form a 3/2-order chain process. In fact, all mechanisms devised using step 11 as a termination led to orders $\geqslant 1$. Thus, it can be concluded that although many steps may contribute to the overall reaction, the observed less-than-first-order kinetics strongly indicate that steps 5, 6 and 7 in the proposed mechanism must be included also. In addition, due to the complexities discussed, it would be overly simplified to consider that the experimental k_2 is equal to 2 k_4 as in Eq. 9, but instead it probably consists of a complex group of terms.

The observation that the order increases toward one at higher temperatures implies that the activation energy for the 3/2-order term in the rate law must be lower than that of the second-order term, i.e. less than 39.2 kcal mole^{-1}. Based on presently available thermochemical information on reactions in Eqs. 4, 6 and 7, i.e. unless activation energies for steps 4 and 7 are larger than expected and that for step 6 smaller, it is difficult to explain such a low overall activation energy. One possible

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* 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, these calculations are not reported.

explanation has been implied in the previous discussion, that the ΔH_f of OF is actually less than the estimated value, and the observed activation energy of k_2 is less than the FO-F bond dissociation energy because of chain propagating steps in the mechanism.

HYDROGEN-OXYGEN DIFLUORIDE REACTION

Reaction Products and Stoichiometry. The following discussion applies to experiments conducted in the monel reactor only; product studies from reactions in the aluminum reactor are yet to be completed. 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 semi-quantitatively using a wet chemical technique. These measurements of the products, plus the rates of reaction obtained from the measured disappearance of H_2 as well as OF_2, give sufficient information to establish the following stoichiometry for the reaction:

$$OF_2 + 3/2\ H_2 \rightarrow 2\ HF + 1/2\ H_2O + 1/4\ O_2$$

i.e. about one-half the oxygen from reacted OF_2 is converted to O_2 gas.

Kinetic Results Obtained in the Monel Reactor. This kinetic study was far more exploratory in nature than the study of OF_2 pyrolysis since no reported kinetic results were found in the literature. The initial experiments were carried out at 110, 130, 150, 170 and 190° C, and at concentration ratios which were thought to be approximately stoichiometric, or in some cases with large excess of H_2 to more clearly determine the OF_2 order. A list of the initial concentrations of reactants is as follows:

mole % OF_2	mole % H_2
0.5	1.0
1.0	1.0
1.0	2.0
1.0	5.0
0.5	5.0

An attempt to use higher concentrations of both reactants, i.e. 2% OF_2 and 4% H_2, resulted in thermal acceleration; thus, the reported results are based on the above concentrations only.

It was found that with approximately stoichiometric concentrations the rate of reaction dropped off very rapidly as the extent of reaction increased (all kinetic data presented in the report are based on OF_2 disappearance). The speed with which the rate decreased is indicative of strong inhibition by product(s); the other alternative explanation, approach to equilibrium, would not apply for this reaction. The decrease in the rate was too rapid to allow reliable extrapolation back to initial conditions. The three products were added to the reactant streams to determine their effect on the rate. Concentrations of 0.3 mole % H_2O and 0.8 mole % HF had no significant effect on the rate. However, the addition of 0.8 mole % O_2 at 170°C lowered the rate by a factor of about 8 at 0.5 sec. contact time and by a factor of about 1.6 at 8 sec. contact time. Thus, the apparent effect of the added O_2 becomes less as the O_2 concentration from the reaction becomes more significant.

In a preliminary examination of the effect of O_2 concentration on the rate, it was found that there was very little difference in the rates using 2% or 5% concentrations of added O_2 (the 5% rates were about 10% lower). These experiments were conducted at 190 and 220°C to get extents of reaction large enough under highly inhibited conditions so that they could be dealt with quantitatively. This indicated that with 5% O_2 added, essentially maximum inhibition had been reached, and that the rate equation must have at least two terms, one of which has an inverse dependence on (O_2). Thus, it should be possible to determine the concentration dependencies of the maximally inhibited reaction.

Fig. 9 illustrates that the OF_2 dependence of the inhibited reaction is very close to first-order at the two temperatures, i.e. the slopes of the log-log plots are about one over a wide range of OF_2 concentrations. However, the H_2 dependence of the fully inhibited rate is not as simple or as clearly defined. Table 4 shows that the (H_2) dependence of the inhibited initial rate is about 0.3 order. In addition, it was found that the rate/(OF_2) ratio for the inhibited reaction was essentially independent of extent of reaction at 190°C and showed a small (ca. 10%) increase in going from 20 to 70% reaction at 220°C, which further indicates a low order effect with respect to (H_2).

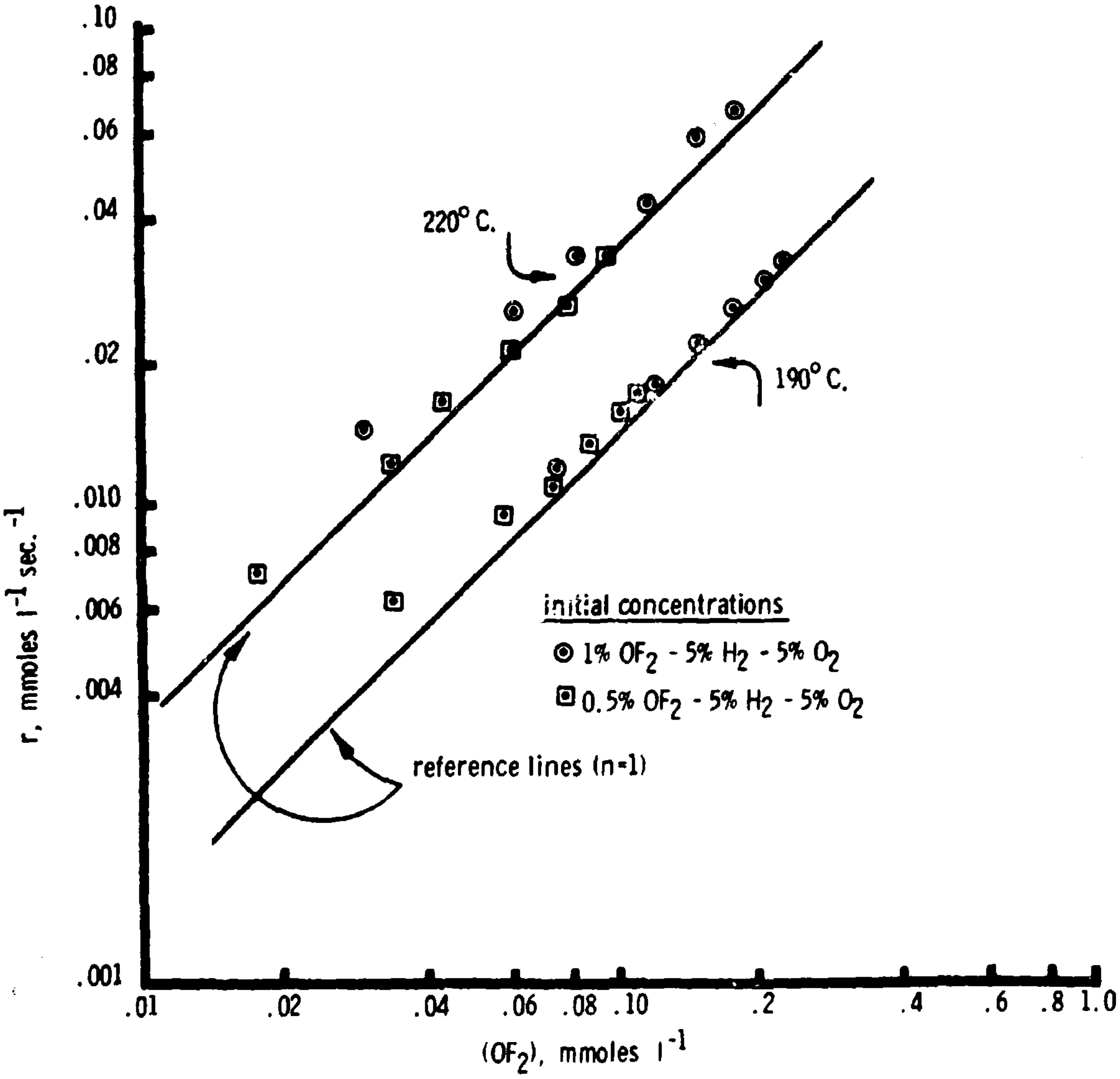

FIGURE 9 Log r versus log (OF$_2$) at 190 and 220° C. for the fully inhibited reaction

Table 4

Effect of (H_2) on Initial Rate Under Conditions of Maximum Inhibition

(Initial Concentrations: 1 Mole % OF_2, 5 Mole % O_2)

Initial rate/$(OF_2)_0$ sec^{-1}	Mole % H_2	Temperature °C	r_5/r_2
.113	2	190	1.27
.143	5	190	
.280	2	220	1.35
.380	5	220	

The surface effects on the rate were tested by stuffing the reactor with monel wire. An increase in the surface area by a factor of 2.5 produced a significant increase in the rate as shown in Fig. 10. These data were obtained at 190°C and a comparable set was obtained at 170°C giving essentially identical results, thus, were not included. It can be seen that for the inhibited reaction (solid points), the rate increased by about 50% when the higher surface was present, and again was about first-order in OF_2, independent of surface area. However, the rate of the uninhibited reaction showed negligible surface effects initially, when O_2 concentrations were low, but surface effects become significant as O_2 was produced by the reaction (open points). In addition, four sets of experiments were run similar to those listed in Table 4, but with a stuffed reactor. For these experiments, the average ratios of rates at 5% H_2 to those at 2% H_2 at comparable extents of reaction were definitely lower than those obtained from the empty reactor: $r_5/r_2 =$ 1.20 at 190°C and 1.14 at 210°C. Thus, the order with respect to (H_2) for the inhibited reaction appears to decrease with increasing surface area. It can be concluded that the term in the rate expression containing O_2 concentration appears to be dominant at low extents of reaction and is describing a homogeneous reaction; whereas, the rate of the inhibited reaction would require at least a two term expression in a monel reactor, one of which would be heterogeneous.

In an attempt to clarify the order of the term in the rate expression containing the O_2 concentration, several sets of experiments at 170°C and 190°C were made with variable, low concentrations of O_2 added in about the amounts produced by the reaction. The concentrations used were 1% OF_2, 2% H_2 and 0 to .20% O_2. It was concluded after several analytical treatments of these data, that the $O(_2)$-

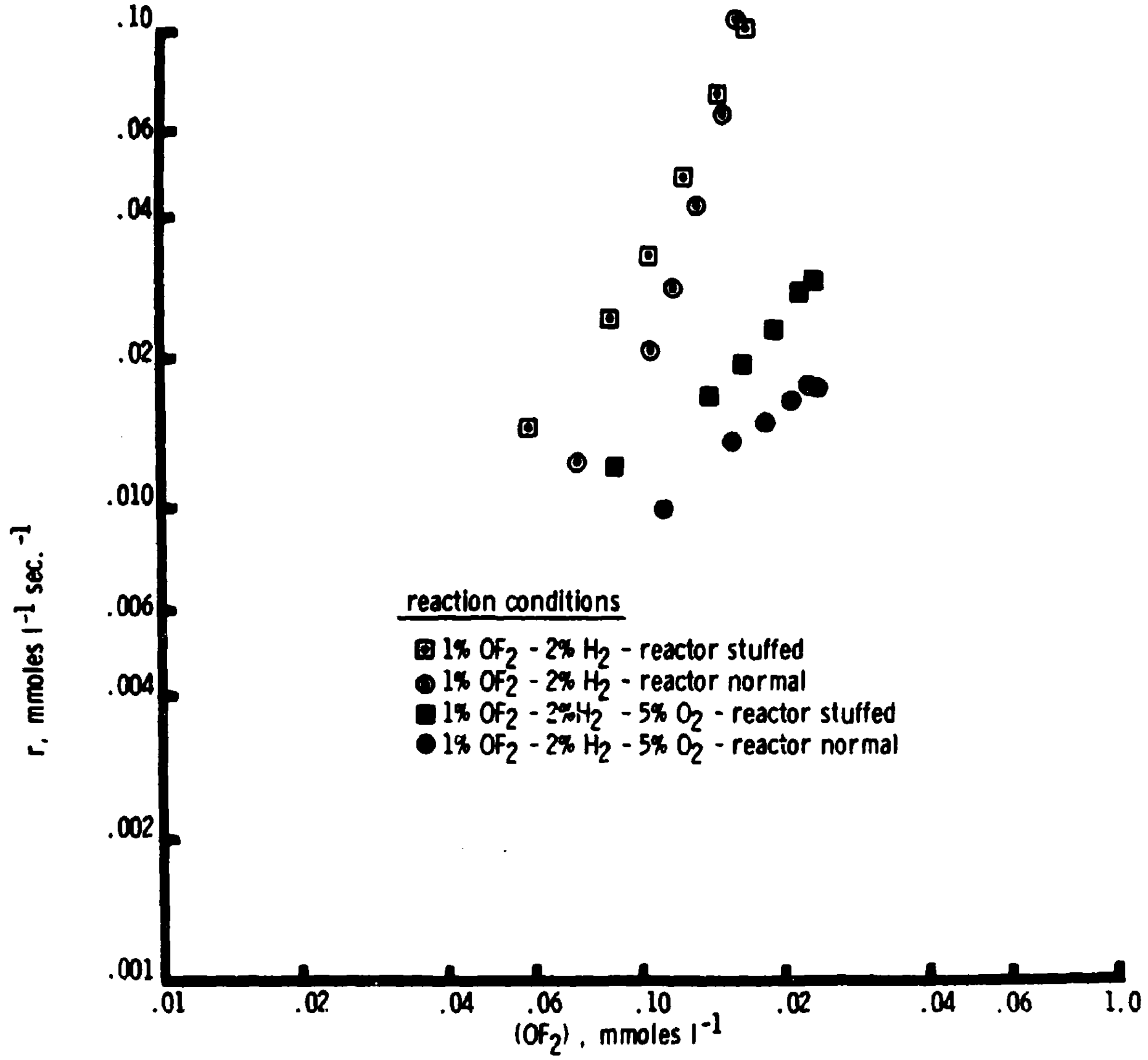

FIGURE 10 Log r versus log (OF$_2$) at 190° C, showing heterogeneous effects

containing term in the rate law that best fits the data is of the form of the third term in Eq. 12 (the total rate law)[*]:

$$r = k_a(OF_2) + k_b(OF_2)(H_2)^x + k_c(OF_2)(H_2)/[1 + b(O)_2/(OF_2)] \quad (12)$$

where x probably is 1 or 1/2; the data were not definitive enough to establish the value of x. The form of the first two terms is based on the data (orders and surface effects) obtained under conditions of maximum inhibition as discussed previously. The first term describes the heterogeneous component of the reaction and by virtue of its independence of hydrogen concentration, gives rise to the low-order with respect to H_2 for the maximally inhibited reaction.

If $b(O_2)/(OF_2)$[**] $\gg 1$ and $k_a + k_b(H)^x$ approximately constant under the conditions used, then a plot of $r/(OF_2)$ vs $(OF_2)(H_2)/(O_2)$ should be a straight line, the slope of which should be equal to k_c/b. Fig. 11 and 12 illustrate this treatment of the data obtained from experiments at 150 and 170°C and a variety of initial concentrations (no added O_2). The rate constants from the slopes are summarized in Table 5; the intercepts were generally too small to be treated quantitatively, thus, shifts due to changes in H_2 concentration had an insignificant effect on the intercepts.

Table 5

Rate Constants for the (O_2) Containing Term

T (°C)	$k_c/b \times 10^2$ (l/mmole sec.)
130	0.22
150	1.3
170	5.6
190	17.0

An Arrhenius plot of these constants gives the following equation (± values

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[*] Other analytical treatments that were tried were considerably poorer with respect to bringing the data from variable initial concentrations into alinement, with one exception. If $(H_2)^{1/2}$ was used in place of (H_2) in the third term, the resulting alinement was as good; however, the curvature was greater which made it a poorer functional fit.

[**] This ratio arises because of the competition which is believed to occur between O_2 and OF_2 for the H atoms.

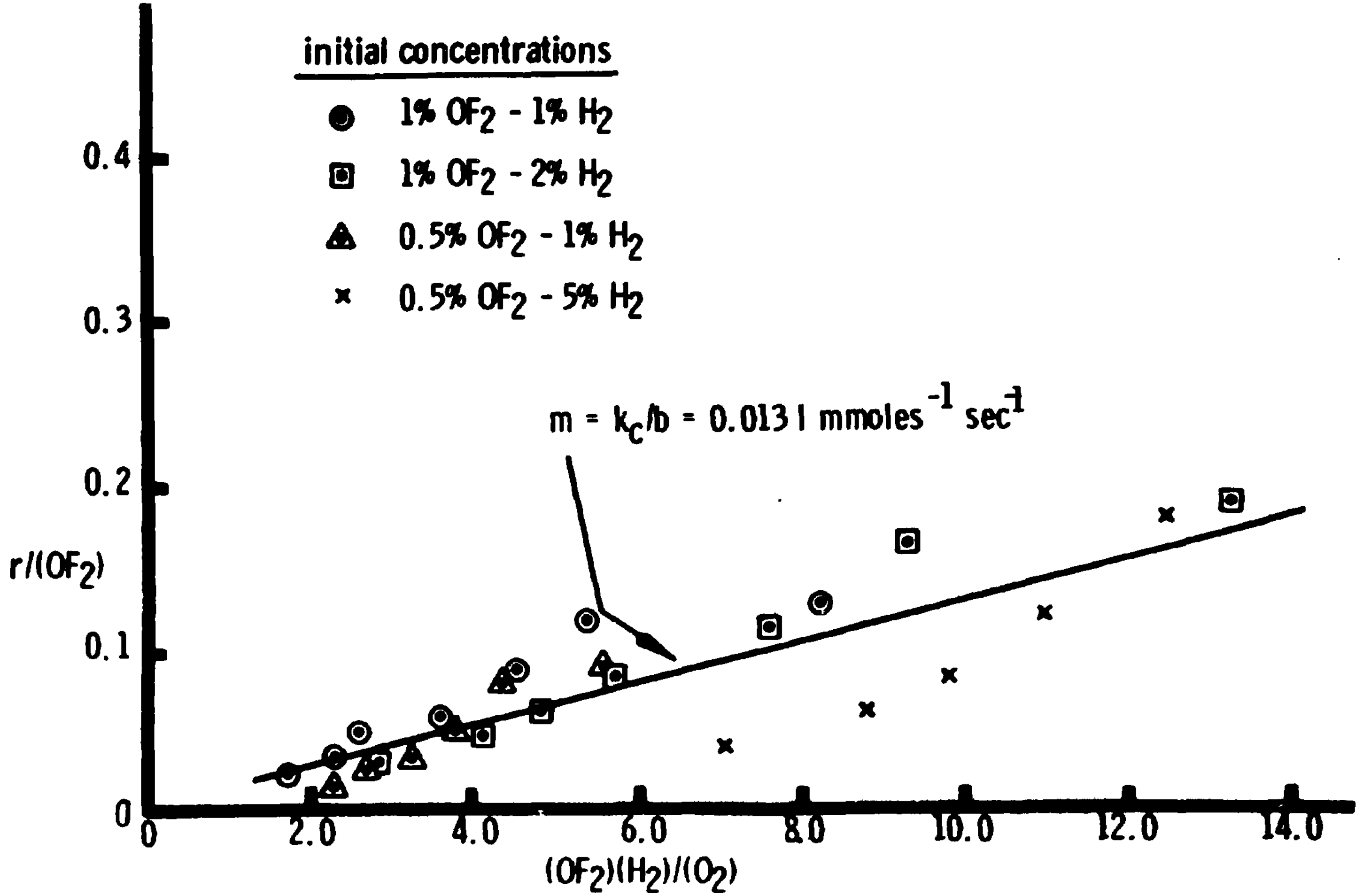

FIGURE 11 $r/(OF_2)$ versus $(OF_2)(H_2)/(O_2)$ at 150°C.

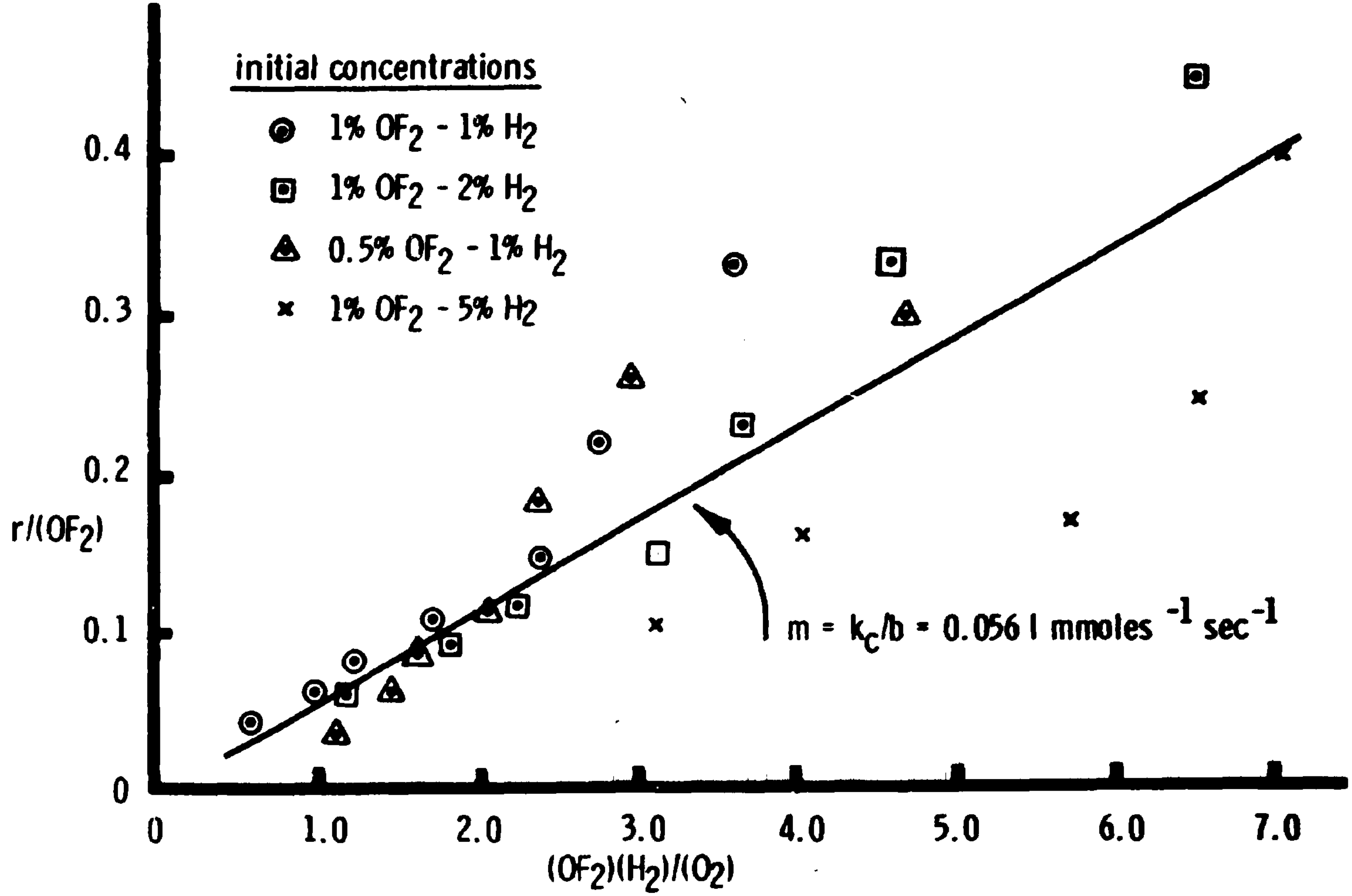

FIGURE 12 $r/(OF_2)$ versus $(OF_2)(H_2)/(O_2)$ at 170° C.

are a one σ confidence level):

$$k_c/b = 10^{11.7 \pm .8} \exp. (26,400 \pm 1,200/RT)(1/\text{mmole sec.})$$

The 26.4 kcal activation energy is the difference between those of k_c and b.

Kinetic Results Obtained in the Aluminum Reactor. Only the rate of the inhibited reaction has been examined to date, since under these conditions a larger heterogeneous effect was exhibited in the monel reactor. During the preliminary experiments and the examination of the surface effects it was noted that the rates were much lower than those obtained in monel (concurrently the surface effects were significantly reduced). Thus, it was necessary to use higher temperatures, 160-260°C, than those used previously. The same stoichiometry was assumed for the reaction in aluminum as in monel, i.e. $(H_2)/(OF_2) = 1.5$.

Table 6 illustrates these observations, listing average rate/(OF_2) ratios for each series of experiments in both reactors under about the same conditions. It can be readily seen that the rates for the inhibited reaction in aluminum are about a factor of 3 lower than those in monel under about the same conditions. In addition, increasing the surface area by a factor of about 2.5 increased the rate by only about an average of 20% as compared to about 50% in monel.

Table 6

Comparison of Data from Both Reactors and Heterogeneous Effects[a]

Monel			Aluminum		
Av $r/(OF_2)$ sec^{-1}	Temperature °C	Reactor Condition[b]	Av $r/(OF_2)$ sec^{-1}	Temperature °C	Reactor Condition[b]
.056	170	P	.085	220	E
.040	170	E	.116	220	P
.127	190	P	.227	240	E
.081	190	E	.222	240	P
.33	220	E	.048	200	E
			.094	220	E
			.192	240	E

[a] The concentrations of reactants were (in mole %) 1.0 - OF_2, 1.5 (Al) or 2.0 (Monel) - H_2 and 5 - O_2.

[b] E = empty, P = packed with spirals to increase surface area.

Because of the lower rates, it was believed that the O_2 possibly was not as effective in producing maximum inhibition. Thus, rates were measured using 5, 10 and 20 mole % O_2. There appeared to be no significant differences in the results using the higher two concentrations, therefore, 10% O_2 was used in all subsequent experiments.

Most of the kinetic experiments to determine the reaction order were run at 200 and 220°C, since reasonable extents of reaction were obtained over a wide range of initial concentrations. An examination of the data indicated an order of slightly greater than one with respect to OF_2 and a very low order with respect to H_2. Preliminary treatment of the data, i.e. dividing average $r/(OF_2)$ values by the initial concentration of reactants each to the 1/4 power, indicated that approximate orders of 1.25 and 0.25 for OF_2 and H_2 respectively appeared reasonable. The data at 220°C obtained from intial OF_2-H_2 concentrations of 1 - 1.5, 0.5 - 0.75, 0.5 - 1.5 and 0.25 - 1.5 mole % appeared to fit a rate equation of the form:

$$r = k_1(OF_2) + k_2(OF_2)^{3/2}(H_2)^{1/2}$$

Using the variables $r/(OF_2)$ and $(OF_2)^{1/2}(H_2)^{1/2}$ a correlation coefficient, slope and intercept were calculated:

cor. coef. = .81 (21 points) $k_1 = .0315$ $k_2 = .250$

The high correlation coefficient indicates a better than 99.9% probability of a functional relationship between the variables, and since the data at 200°C gave comparable results, it appears that this may be a fruitful approach, and attempts will be made to expand the concentration range at several temperatures.

Reaction Mechanism. It would be premature to attempt to present a detailed mechanism based on the present data. However, with a reasonable degree of certainty a few elementary reactions can be postulated as participating in the overall mechanism. Initiation must occur by an interaction between both reactants, since OF_2 and H_2 do not significantly dissociate under the conditions used. A possible initiation step is as follows:

$$OF_2 + H_2 \longrightarrow HF + OF + H$$

In addition, the inhibition by O_2 is probably due to the following competitive reactions, which are analogous to those believed to occur in the H_2-F_2 reaction mechanism:[20]

$$M + O_2 + H \longrightarrow HO_2 + M$$

$$H + OF_2 \longrightarrow HF + OF$$

It is apparent that much more work is necessary before a study of the kinetics of the OF_2-H_2 reaction would be considered reasonably complete.

HYDROGEN-TETRAFLUOROHYDRAZINE REACTION

The study by Kuhn and Wellman[10] of the explosive reaction between H_2 and N_2F_4 showed that the stoichiometry was simplest with $(H_2)/(N_2F_4) = 2$; with this ratio the only products formed were N_2 and HF. As the relative amount of H_2 went down, F_2 and NF_3 became significant products. Therefore, it appears that the intial work should involve hydrogen rich reactant ratios.

With only H_2 and N_2F_4 in He it was not possible to get a controlled reaction. Using concentrations of N_2F_4 down to about .25 mole % and H_2 as low as .5% a non-steady-state behavior was obtained. It was found that at temperatures low enough (e.g. 40°C), no reaction would occur. As the temperature was raised, reaction would occur in an oscillatory manner, i.e. the reaction would start to go to completion, then stop while the concentration of N_2F_4 was built up on the reactor, then go to completion again after reaching a particular value, followed by a repeat of the cycle; thus, never reaching a steady-state. In addition, these oscillations in concentration were accompanied by pressure pulses and audible pops. The temperature at which these oscillation started depended on the concentration of reactants and was about 70°C for the lowest concentrations used.

However, if O_2 was added as an inhibitor, a controllable, steady-state reaction could be obtained. With the above reactant concentrations and about 50% O_2, about 20% and 50% reaction were obtained at 76 and 90°C respectively. This will be the starting point for the rate studies.

DEVIATIONS FROM STEADY-STATE

Prior to obtaining the experimental data already discussed, some thought was given to the problem of deviations from steady-state as applied to the concentrations of intermediates formed in complex reactions. Specifically, the problem of interest was the forms of the experimental rate expressions for reactions involving radical intermediates as the temperatures increased sufficiently to invalidate the steady-state assumption. The mechanisms treated were Rice-Herzfeld chain reaction and consecutive-parallel, non-chain reaction, i.e. a radical produced in step one attacks the reactant molecule in step two. The results of this effort were published in the Journal of Chemical Physics and are included in the Appendix.

It is of interest to note that although direct quantitative application of the methods developed in this paper do not appear possible in the case of OF_2 pyrolysis, due to complexities of the reaction, the observed rise in $r/(OF_2)$ as a function of time at the higher temperatures is qualitatively similar to that predicted for deviations from steady-state in the case of a consecutive-parallel mechanism.

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APPENDIX

RATE EQUATIONS FOR REACTIONS AT HIGH TEMPERATURES INVOLVING RADICAL INTERMEDIATES: CONSECUTIVE-PARALLEL AND RICE-HERZFELD MECHANISMS

I

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Rate Equations for Reactions at High Temperatures Involving Radical Intermediates: Consecutive-Parallel and Rice–Herzfeld Mechanisms

T. J. HOUSER

Chemistry Department, Western Michigan University, Kalamazoo, Michigan 49001

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For complex reactions which produce, in the initial step, radical intermediates that attack the reactant in a subsequent step, the form of the rate equation will change as the reaction temperature increases. This is caused by a change in the relative rates of the individual steps in the mechanism due to differences in activation energies. A method has been developed for calculating the form of the rate equation at these higher temperatures for two mechanisms: a consecutive-parallel nonchain process and the Rice–Herzfeld chain reaction. The method is based on the elimination of time as the independent variable from the rate equations. It was calculated, for the consecutive-parallel mechanism, that the rate is a complex increasing function of the extent of reaction at temperatures high enough so that the steady-state assumption was not valid, i.e., the rate of the radical attack step was too slow compared to rate of radical production. Using this approach it was shown that significant deviations from steady state would be found in the case of methane pyrolysis at about 2200°K for concentrations below 10^{-6} mole/cm^3. It was found for the Rice–Herzfeld mechanism that a shift from three-halves to first-order kinetics occurs as the temperature increases, although the concentrations of radicals in the transition temperature range would still be low enough not to invalidate the steady-state assumption. For acetaldehyde and dimethyl ether pyrolyses, these shifts would occur at about 1100° and 900°K, respectively.

For most reactions involving radical intermediates, treatments of kinetic data involve the use of the steady-state assumption for the concentrations of the radicals, which is usually valid because of low radical concentrations. However, with the increasing interest in fast reactions at high temperatures, it is essential to have a means available for the calculation of deviation from steady-state behavior and/or to be able to predict the form of the rate equation for the disappearance of the reactant as the reaction temperature increases. The objective of this study is to extend the methods developed by Benson[1] in order to calculate the changes in the form of the rate equation with increasing radical concentration for two mechanisms: consecutive-parallel nonchain and Rice–Herzfeld[2] chain reactions. This will provide a simpler method for calculating the temperature at which deviations from steady state will occur than the procedures developed by Giddings and Shin[3] for the consecutive-parallel mechanism.

The consecutive-parallel mechanism can be expressed by the equations

$$A \rightarrow B + X, \tag{1}$$

$$A + B \rightarrow C + Y, \tag{2}$$

where A is the reactant, B the radical intermediate, C the stable product, and X and Y may be other products, or radicals which lead to products, but do not react with A or produce species which react with A. At steady state, the rate of Step (1) equals that of Step (2), or two molecules of A disappear for each occurrence of Step (1).

The kinetic equations for A and B in this mechanism are

$$dA/dt = -k_1A - k_2AB, \tag{3}$$

$$dB/dt = k_1A - k_2AB. \tag{4}$$

These equations cannot be solved explicitly except by approximate methods. But the concentration of B as a function of the concentration of A can be obtained by the elimination of the time variable, by dividing Eq. (4) by Eq. (3) to yield Eq. (5).[1b]

$$dB/dA = (B - K)/(B + K), \tag{5}$$

where $K = k_1/k_2$. This can be integrated directly to yield, with some rearrangement ($B = 0$ when $A = A_0$),

$$B/K + 2\ln(1 - B/K) = (-A_0/K)(1 - A/A_0). \tag{6}$$

A table of values, or family of curves, of B/K [relative rates of Steps (1) and (2)] vs extent of reaction $(1 - A/A_0)$ for different values of A_0/K can be constructed, as illustrated by Table I.

The rate of decomposition of A as expressed by Eq. (3) can be rewritten

$$-dA/dt = \text{rate} = k_1A(1 + B/K). \tag{7}$$

Thus, the experimental values, rate/A, at different extents of reaction are proportional to the values of $(1 + B/K)$; the proportionality constant is k_1. The shape of the experimental rate/A vs extent of reaction curve will indicate the value of A_0/K applicable to the data, which in turn will provide B/K values at different extents of reaction. Values of k_1 and k_2 can be calculated from Eq. (7) and the definition of K. If A_0/K is large

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[1] (a) S. W. Benson, J. Chem. Phys. **20**, 1605 (1952); (b) *The Foundations of Chemical Kinetics* (McGraw-Hill Book Co., New York, 1960), Sec. III.7.

[2] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

[3] (a) J. C. Giddings and H. K. Shin, J. Chem. Phys. **36**, 640 (1962); (b) J. Phys. Chem. **65**, 1164 (1961); (c) Trans. Faraday Soc. **57**, 468 (1961).

enough, ≈100, then steady state applies (i.e. $B/K=1$) and rate/A $=2k_1$ for all extents of reaction. The extent of deviation from steady state is given by the value of $(1-B/K)$; the larger this value, the farther the reaction is from steady-state conditions. Thus, it appears that for A_0/K values above 30, the steady-state approximation applies for most of the reaction, and for values below 30, deviations from steady state will become serious.

If equations are available for k_1 and k_2, then a simple calculation can be made to predict the temperature at which deviation from steady state would occur. The pyrolysis of methane has been studied extensively at high temperatures using the shock tube[4–7] and serves as an example of the above reaction scheme. From the literature a reasonable mechanism for the pyrolysis appears to be

$$CH_4 \rightarrow CH_3 + H, \qquad (8)$$

$$H + CH_4 \rightarrow CH_3 + H_2, \qquad (9)$$

$$2CH_3 \rightarrow C_2H_6. \qquad (10)$$

Alternates for Steps (9) and (10) are possible, but if it is assumed that the rates of Steps (9) and (10) are approximately equal to their alternate counterparts,[4] then the mechanism fits the model being discussed. The values for the rate constants are given by Eqs. (11)[4] and (12)[8]:

$$k_8 = 10^{14.8}\exp(-103\,000/RT)\,(\mathrm{sec}^{-1}), \qquad (11)$$

$$k_9 = 10^{13}\exp(-12\,000/RT)\,(\mathrm{cm}^3/\mathrm{mole\cdot sec}). \qquad (12)$$

The initial concentrations of methane in the shock-tube studies were in the range of 3×10^{-7}–4×10^{-6} mole/cm³. The calculated values of A_0/K at 2200°K based on the above information ranged from 6–80, depending on A_0. This shows that at the lower concentration, deviations from steady-state kinetics would be expected for the decomposition of methane at 2200°K. Since most of the results reported in the literature are for temperatures below 2000°K, the steady-state assumption appears valid.

It was found that $A_0/K=20$ at 2400°K, if the calculation was carried out using the same parameters as Giddings and Shin[1b] (the main difference is that they assume $A_0=10^{-6}$ mole/cm³). This indicates that deviations from steady state would become significant under these conditions, which is in good agreement with the previous work. It should be noted that if the rate-constant frequency factor is of the form $A/T^{1/2}$, that the rate constant for Step (2) will not increase as rapidly as predicted by the Arrhenius equation. Thus, deviation from steady state would occur at a slightly lower temperature than predicted from the above calculation.

The more complicated case of two radicals produced in the first step which both can attack the reactant is handled in essentially the same manner. This initiation will lead to two parallel abstraction steps [Step (2)] which will have equal rates at the lower temperatures (i.e., at steady state). As the reaction temperature increases, the slower Step (2) (i.e., that with the lower activation energy) would be the first to cause deviation to occur, and this could be detected in a shift in the relative amounts of products. For example, the steps in the mechanism of the pyrolysis of chloromethane which involve the reactant are[9]

$$CH_3Cl \rightarrow CH_3 + Cl, \qquad (13)$$

$$CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl, \qquad (14)$$

$$Cl + CH_3Cl \rightarrow HCl + CH_2Cl. \qquad (14')$$

Thus, one mole of methane is produced for three moles of reactant consumed at steady-state conditions. If Step (14) was slower than (14′) at higher temperatures, then this ratio should drop to less than 1:3, and the analysis can be made as before. Calculations based on available data for Reactions (13)[9] and (14)[10] show that deviation from steady-state kinetics would be expected at about 1500°K, i.e., $A_0/K=8$ for $A_0=4\times10^{-7}$ mole/cm³, $k_{13}=50$, $k_{14}=10^{9.0}$ (sec⁻¹ and cm³/mole·sec, respectively).

It should be noted that implicit in the above development is the assumption that Reaction (1) (initiation) is in the first-order region and k_1 is the limiting value at infinite pressure. However, reactants with few atoms in a molecule, such as the examples given probably are in

TABLE I. Concentration[a] of intermediate in consecutive-parallel reaction.

A_0/K	Extent of reaction 0.1	0.2	0.3	0.5
100	0.99	1.00	1.00	1.00
30	0.85	0.97	0.99	1.00
10	0.53	0.74	0.85	0.95
3	0.23	0.39	0.51	0.66
1	0.09	0.17	0.24	0.35

[a] Values given as $B/K=Bk_2/k_1$, or relative speeds of Steps (1) and (2). Some values were obtained from Ref. 1(b).

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[4] H. B. Palmer and T. J. Hirt, J. Phys. Chem. 67, 709 (1963).

[5] G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. 63, 1736 (1959).

[6] V. Kevorkian, C. E. Heath, and M. Boudart, J. Phys. Chem. 64, 964 (1960).

[7] G. I. Kozlov and V. G. Knorre, Combust. Flame 6, 256 (1962).

[8] J. C. Polanyi, J. Chem. Phys. 23, 1505 (1955).

[9] (a) A. E. Shilov and R. D. Sabirova, Russ. J. Phys. Chem (English Transl.) 33, 1365 (1959). (b) K. A. Holbrook, Trans. Faraday Soc. 57, 2151 (1961).

[10] F. A. Raal and E. W. R. Steacie, J. Chem. Phys. 19, 329 (1951).

TABLE II. Concentration of intermediate[a] and relative rates for Rice–Herzfeld mechanisms.

T°K	K_1	β[b] mole/cm^3	(β/K_1)[c]
		Acetaldehyde[d]	
1000	1.7×10^{-12}	2.6×10^{-11}	15
1200	3.3×10^{-10}	5.7×10^{-10}	1.7
		Dimethyl ether[e]	
800	1.2×10^{-14}	1.8×10^{-13}	15
1300	4×10^{-6}	2.9×10^{-9}	7.2×10^{-4}

[a] Initial concentration of reactants $A_0=10^{-6}$ mole/cm^3.
[b] Steady-state concentration of β.
[c] Relative rates of Steps (16) and (17).
[d] Data from Ref. 3(a).
[e] Data from S. W. Benson, Ref. 1(b), p. 391.

the second-order or transition region for unimolecular decompositions. Therefore, in order for the calculations outlined to be valid, it would be necessary to keep the total pressure constant (assuming a sufficient concentration of inert diluent so that activation is mainly by diluent). Under these conditions the rate equation has the form[11]

$$\text{rate}=(k_ak_rM\text{A})/(k_{-a}M+k_r)+k_2\text{BA}, \tag{15}$$

where k_a and k_{-a} are the rate constants for activation and deactivation by collision, respectively, k_r is the specific rate for the decomposition of activated reactant, and M is the concentration of inert diluent. It would be difficult to interpret data with this form of the rate equation, i.e., in the transition region. However, for the decompositions of large molecules at reasonable pressures, $k_1=k_ak_r/k_{-a}$, and for small molecules at pressures sufficiently low to reduce the rate equation to the second-order region, $k_1=k_aM$; thus, these are the desired conditions for the experiments. For the latter case, the treatment of the data can be carried out as outlined previously with the total pressure effect showing up in $\text{A}_0/K=\text{A}_0k_2/k_aM$.

In dealing with the more complicated case of a radical-chain process, such as a Rice–Herzfeld mechanism, steady state may not be the important consideration. For a Rice–Herzfeld mechanism with β–β or μ–μ terminations, the nomenclature is that of Laidler,[12] the steady-state concentrations of β and μ are not constant but are functions of the reactant concentration (unlike the previous mechanism treated, in which the steady-state concentration of $B=K$). The problem becomes the need for a description of the dependence of the radical concentration on reactant concentration as the radical concentration increases (and the rate of the initiation step becomes competitive with that of the propagation steps) since this will determine the order of the rate equation.

The mechanism used for the model is the Rice–Herzfeld mechanism in its simplest form

$$\text{A}\rightarrow\beta+\text{X}, \tag{16}$$

$$\beta+\text{A}\rightarrow\mu+\text{P}_1, \tag{17}$$

$$\mu\rightarrow\beta+\text{P}_2, \tag{18}$$

$$2\beta\rightarrow\text{P}_3, \tag{19}$$

where β and μ are the radicals involved in the bimolecular and monomolecular propagation steps respectively; P_1, P_2, and P_3 are products; and X may be a product or radical which does not contribute to propagation. The β–β termination is favored, because the β radical concentration increases more rapidly as temperature increases than does that of the μ radical.

The rate equations for the propagating radicals and reactant are

$$-d\text{A}/dt=k_{16}\text{A}+k_{17}\beta\text{A}, \tag{20}$$

$$d\beta/dt=k_{16}\text{A}-k_{17}\beta\text{A}+k_{18}\mu-2K_{19}\beta^2, \tag{21}$$

$$d\mu/dt=k_{17}\beta\text{A}-k_{18}\mu. \tag{22}$$

Again, the direct solution of these equations is not possible. However, if steady state is assumed for μ,[13] then elimination of the time variable from Eqs. (20) and (21) yields the concentration dependence of β on A

$$d\beta/d\text{A}=\frac{(K_2\beta^2/\text{A})-K_1}{K_1+\beta}, \tag{23}$$

where $K_1=k_{16}/k_{17}$, $K_2=k_{19}/k_{17}$, and $\beta=0$ at $\text{A}=\text{A}_0$. It was found (through a Runge–Kutta numerical solution) that the concentration of β was about equal to that found by the steady-state treatment for temperatures at which the rates of Reactions (16) and (17) become competitive. Thus, the order of reaction will shift although the concentrations of radicals are small enough to allow the steady-state treatment to be a valid approximation.

Usually, in the steady-state treatment of the Rice–Herzfeld mechanism, the rate of disappearance of reactant is taken as $k_{17}\beta\text{A}$ since it is considered to be much larger than $k_{16}\text{A}$, which justifies dropping the latter term (considering the rate of formation of a product has the same result). Table II lists the relative

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[11] F. A. Lindemann, Trans. Faraday Soc. 17, 598 (1922).

[12] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill Book Co., New York, 1965), p. 390.

[13] The justification for this assumption is based on the following considerations. The steady-state concentration of $\mu=k_{17}\beta\text{A}/k_{18}$. It can be assumed that at lower temperatures, the steady-state approximation is reasonable for both radicals. As the temperature increases k_{18} will probably rise at a more rapid rate than k_{17} since the latter usually has the smaller activation energy. Therefore, the ratio of rate constants will decrease with temperature; hence the concentration of μ does not increase as rapidly as that of β.

IV

rates of Steps (16) and (17) as β/K_1 for the pyrolyses of acetaldehyde and dimethyl ether at several temperatures. If this ratio is sufficiently large, i.e., >10, the reaction order for the disappearance of reactant will be determined by Step (17). For smaller values of β/K_1, the reaction will be a transition region [or determined by Step (16) if the ratio is small enough].

Since β (steady state) is proportional to $A^{1/2}$, the rate equation would have the form

$$\text{rate} = k_{16}A + k_{17}'A^{1/2}, \tag{24}$$

where $k_{17}' = k_{17}(k_{16}/k_{18})^{1/2}$. It can be concluded, from the β/K_1 values in Table II, that a shift in order from three-halves toward one could be expected for the pyrolysis of acetaldehyde and dimethyl ether in the temperature region of about 1100° and 900°K, respectively, although the steady-state assumption may be valid at these conditions. The application of Eq. (24) to rate data in the transition region from which k_{16} could be calculated explicitly would be straightforward.

The Rice–Herzfeld mechanism has been presented in its simplest form; side reactions and shifts in mechanism may also complicate the interpretation of data. In addition, the problems of collision activation for the unimolecular steps in the mechanism for the pyrolysis of smaller molecules and collision deactivation for termination (third body) must be considered, as discussed in the previous section. The effects discussed in this presentation should be considered in addition to these other complications.

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