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Production in Atmospheric-Pressure
Hydrogen-Oxygen-Fluorine Mixtures**

by

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STABILITY AND NONEXPLOSIVE HYDROGEN FLUORIDE PRODUCTION IN ATMOSPHERIC-PRESSURE HYDROGEN-OXYGEN-FLUORINE MIXTURES

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ABSTRACT

The behavior of atmospheric-pressure mixtures of H_2 , O_2 , and F_2 at ambient temperatures was studied to determine conditions under which the reagents can be combined nonexplosively. An HF probe laser monitored the formation of HF during the mixing process and for the following 30 min, under conditions where <5% of the reagents had disappeared. Hydrogen fluoride formed relatively "promptly" during mixing and at an essentially constant rate thereafter. Evidence is presented that heterogeneous reaction steps significantly influence the slow deterioration of prepared mixtures.

INTRODUCTION

Recent increased interest in the use of gaseous H_2 - F_2 mixtures in pulsed high-energy hydrogen fluoride (HF) chemical lasers has focused attention on the problem of unpredictable explosions. The problem is compounded by the pressures (≥ 1 atm at ambient temperatures) required for laser fusion applications in which short pulses are essential. Consequently, there is little use for small-scale laboratory procedures involving low temperatures^{1,2} or using extreme dilution by an inert additive, such as helium³ (both frequently with the addition of oxygen as a chemical stabilizing agent). Recent experiments with concentrated, atmospheric-pressure H_2 - O_2 - F_2 -diluent mixtures at 300 K in a small-volume (40-cm³) flash photolysis-initiated HF laser⁴ were plagued by unintended explosions and steady deterioration of the laser output with mixture storage time. These difficulties emphasize the need to characterize better the behavior of H_2 - O_2 - F_2 mixtures under the conditions of interest.

This report summarizes the results of many experiments concerned with the problems of mixture-making and short-term storage of various combinations of gaseous H_2 , O_2 , and F_2 at atmospheric pressure and near-ambient temperatures. The work was carried out in support of pulsed HF chemical laser experiments (some now complete) in which an electron beam ignited large-volume (≤ 30 -l) samples of initially stable mixtures of H_2 , O_2 , and F_2 .

The thrust of the present work has been to characterize explosive behavior with respect to H_2 - O_2 - F_2 mixture composition, density, and various construction materials. Part of this work is a continuation of compatibility studies (carried out with rods, foils, and other samples of materials) reported in Los Alamos Scientific Laboratory 1973 chemical laser internal reports. In addition, a pulsed low-energy HF probe laser was used to monitor the formation of HF in the test cells during and after successful admission of the final reagent.

EXPERIMENTAL PROCEDURE

The experimental apparatus is shown schematically in Fig. 1. Mixtures were made directly in 10-cm-long test cells of selected diameters and construction materials. Ultra-pure hydrogen and extra-dry oxygen were taken from commercial cylinders. To remove HF, Air Products F_2 was passed through an activated NaF trap before being diluted to 90% with O_2 and stored for subsequent use. The test cells, which in all cases had been prepassivated with F_2 , were filled by the successive addition of H_2 , O_2 , and the F_2/O_2 mixture at flow rates determined by preset Brooks #8744 flow controllers. When H_2 and F_2/O_2 were interchanged in the filling order the stability was reduced only in marginal cases. Pressures in the test cells were monitored with a Validyne DP7 pressure head connected to a Hewlett Packard 7128A strip chart recorder.

Preliminary experiments were carried out at ambient temperatures. However, normal day-to-day fluctuations, although having no apparent effect on mixability limits, significantly influenced HF formation rates in stable mixtures. Thereafter, a thermostat-regulated circulating air bath was used to maintain the test cells at 305 ± 1 K.

Test cells were made of Teflon (nominal 2.54-cm i.d.), 6061 aluminum (8.94-cm i.d., 630 cm³) and 304 stainless steel (1.93- and 8.94-cm i.d., 29 and 630 cm³). Sapphire windows (2.54-cm diameter and 2.0-mm thick) were axis-centered at both ends of the test cells. Explosions were audible and visible, and generally occurred during the addition of the final component. In addition, explosions were clearly indicated by rapidly decreasing pressure and by complete attenuation of the $P_1(7)$ HF line from the probe laser described below.

The HF radiation for the probe laser was generated in a longitudinal 30-kV discharge through

a flowing gas mixture of $BrF_5:H_2 = 1.5$ at ~ 0.27 kPa (2 torr). Brewster-angle end windows on the Pyrex discharge cell were made of CaF_2 . The laser cavity was defined by a 300-groove/mm grating (blaze angle 22.03°) and a 10-m radius of curvature gold-coated spherical mirror containing a 2-mm axial hole for output coupling. The laser beam was split; a reference portion ($\sim 15\%$ of the total) went directly to a Jarrell Ash 82000 monochromator containing a 295-groove/mm grating blazed at $3.7 \mu m$ and coupled to a liquid nitrogen-cooled Ge:Ga detector. The other beam passed through the test cell before reaching an identical monochromator-detector combination. Detector outputs were displayed on a Tektronix 556 dual beam oscilloscope. The laser pulse rises to a maximum in $< 0.5 \mu s$ and decays to half peak intensity in $\sim 30 \mu s$.

The $P_1(7)$ HF line at 3644.26 cm^{-1} proved most suitable for use with a 10-cm absorption path length and the range of partial pressures of HF found in nonexplosive test-cell experiments. The use of two dispersing elements in each beam path assured complete isolation of the $P_1(7)$ from other HF lines at the detectors. $P_1(7)$ output energy from the laser was $< 20 \mu J$.

The optical system was aligned daily to maximize the output from each detector. The ratio of reference output to transmitted intensity with the test cell evacuated was determined twice daily. With careful alignment, scatter in this ratio from pulse to pulse could be held to less than 5%.

RESULTS

Mixture Stability Measurements

Efforts to mix hydrogen, oxygen, and fluorine, and in a few cases argon, at near-atmospheric pressures yielded reasonably reproducible boundaries in composition and density beyond which explosions always occurred. On the opposite side of such boundaries were regions with marginal stability next to a region with a wide range of conditions where, except in rare instances, the mixtures were always stable. These observations appeared to be independent of the nature of the test cell.

The results of many experiments, generally carried out with near-stoichiometric (1:1) amounts of H_2 and F_2 , are summarized in Table I. A certain minimum amount of O_2 ($\sim 5\%$) is required for stability. The addition of $\sim 25\%$ of the inert diluent, argon, appears to compensate for the absence of O_2 , although trace amounts of O_2 in the F_2 (Ref. 1) are a stabilizing factor. Section C of Table I describes the

Fig. 1.

Schematic diagram of the experimental apparatus.

TABLE I
SUMMARY OF MIXTURE STABILITY OBSERVATIONS

Partial Pressures (kPa)			Total Pressure (kPa)	H ₃ /F ₂	O ₂ (%)	Result
H ₂	O ₂	F ₂				
A. Influence of O ₂						
40.0	---	40.0	80.0	1.0	0.0	Explosion
40.0	1.33	38.7	80.0	1.0	1.7	Explosion
40.0	2.67	37.3	80.0	1.1	3.3	Marginal
40.0	4.00	36.0	80.0	1.1	5.0	Generally stable
40.0	8.00	36.0	84.0	1.1	9.5	Stable
B. Influence of argon						
40.0	4.00 ^a	40.0	84.0	1.0	0.0	Explosion
40.0	26.7 ^a	40.0	106.7	1.0	0.0	Marginal
C. Influence of Total Pressure						
40.0	4.00	36.0	80.0	1.1	5.0	Generally stable
33.3	3.33	30.0	66.6	1.1	5.0	Generally stable
26.7	2.67	24.0	53.4	1.1	5.0	Marginal
20.0	2.00	18.0	40.0	1.1	5.0	Explosion
53.3	21.3	48.0	122.6	1.1	17.4	Stable
40.0	16.0	36.0	92.0	1.1	17.4	Stable
26.7	10.7	24.0	61.4	1.1	17.4	Generally stable
20.0	8.00	18.0	46.0	1.1	17.4	Explosion
D. Influence of H ₂ /F ₂ Ratio						
64.0	5.60	14.4	84.0	4.4	7.7	Stable
40.0	8.00	36.0	84.0	1.1	9.5	Stable
16.0	10.4	57.6	84.0	0.28	12.4	Explosion
40.0	16.0	36.0	92.0	1.1	17.4	Stable
16.0	18.4	57.6	92.0	0.28	20.0	Marginal

^aPartial pressures of argon.

influence of total pressure at two fixed compositions. Clearly, an explosion boundary is being approached as the pressure is lowered, indicating the increasing influence of the well-known second explosion limit for this system.⁵ However, evidence that the true second limit has not been reached comes from later experiments in which a stable combination of 43.5% H₂-17.4% O₂-39.1% F₂ (the second mixture in Table I,C) was pumped down slowly to 6.7 kPa (59 torr) and

stored for 15 min without exploding. Evidently factors other than the total pressure play a role in the higher density experiments, e.g., proximity of the vessel walls or the dynamics of the mixing procedure, including rapid changes in the instantaneous, localized ratio of H₂/F₂.

The influence of the H₂:F₂ ratio ($0.28 \leq H_2/F_2 \leq 4.4$) is shown in Table I,D at two fixed total pressures. In both cases the percentage of O₂

required for stabilization increases with $(H_2/F_2)^{-1}$. Clearly fluorine-rich mixtures are the most difficult to make.

Several other observations are worth noting here. Compatibility of the mixtures with 1.27-cm-o.d. tubes of 347 stainless steel and 6061 aluminum was examined in several different experiments, without any detectable influence on mixture stability. For some experiments a 3.2-mm slot had been machined along the full length (~ 9 cm) of the tubes to produce rough, previously unexposed edges; in other experiments a full-length stainless steel weld was exposed to the gas mixture. Variation by a factor of about 3 in the flow rate of the final component into the test cell also had no apparent effect. The influence of pump-down time (ultimate vacuum), between successive fillings of the test cell, on the preparation and storage of one stable mixture [40.0 kPa (300 torr) H_2 -16.0 kPa (120 torr) O_2 -36.0 kPa (270 torr) F_2] was explored. No difference was found between the behavior (including that during subsequent storage described below) of mixtures prepared after pumping to ~ 13 -47 Pa (0.1-0.35 torr) and those after several hours' pumping to ~ 6 -7.8 Pa (0.5-0.6 torr).

On rare occasions the probability of an explosion occurring during preparation of the H_2 - O_2 - F_2 mixtures increased abruptly, and even large amounts of oxygen ($\sim 20\%$) did not ensure stabilization. At such times the following techniques were successfully used to bring the system back to its "normal" behavior: thorough cleaning of the cell and repassivation with F_2 ; trapping all the gases with liquid argon; and thoroughly evacuating the F_2/O_2 mix tank and preparing a fresh 90%-10% mix.

Absorption of the $P_1(7)$ HF Line

For the experiments that were free from explosions, time-resolution of the HF formation in the test cell was possible by measuring the probe laser beam's absorption at selected time intervals after the final component was added. Typically, the laser was fired and an oscillogram was taken at 3-min intervals over a 30-min period beginning 1 min (to allow for reasonably complete mixing) after filling was complete.

The ratio of incident to transmitted intensity, I_0/I , is given by

$$\frac{I_0}{I} = \left(\frac{V_1}{V_2} \right) \left(\frac{V_1}{V_2} \right)_0 \quad (1)$$

where (V_1/V_2) is the ratio of reference to transmitted beam detector outputs as determined in volts from

each oscillogram. The ratio $(V_1/V_2)_0$ for the evacuated cell was the mean value determined twice daily from a series of oscillograms. Assuming as a first approximation that the $P_1(7)$ line from the probe laser is very narrow compared with the $P_1(7)$ absorption line in the test cell (thin source line approximation, TSLA), Beer's law can be extended to describe absorption over the entire width of the source line

$$\frac{I_0}{I} = \exp(P P_{HF} \ell) \quad (2)$$

where P is the absorption coefficient at the center of the absorption line in $\text{cm}^{-1} \text{ kPa}^{-1}$, P_{HF} is the partial pressure of HF in the cell in kPa; and, in these experiments, the optical path length, ℓ , is 10.0 cm. If P is independent of P_{HF} , an approximation discussed more fully below, it follows from the TSLA that $\ln(I_0/I)$ is directly proportional to P_{HF} , and knowledge of the appropriate value of P permits evaluation of P_{HF} at all times of interest. The TSLA was used in reducing all the HF absorption data taken in this study.⁶

In the mixtures of interest here, P is a function of the initial composition and density, since pressure broadening by H_2 , O_2 , and F_2 contributes to the total absorption line profile. Eventually, with increasing extent of reaction, self-broadening by the product HF also influences P , destroying the simple relationship between $\ln(I_0/I)$ and P_{HF} described by Eq. (2). The influence of self-broadening is examined first in Fig. 2, a semilogarithmic Beer's law plot of I_0/I against optical density ($P_{HF} \ell$), incorporating a large number of calibration data obtained with pure HF in the test cell. Because HF adsorbs strongly on the vessel walls, producing a rapid initial decrease in P_{HF} , the HF pressure always was allowed to stabilize before the oscillograms were taken. The curvature, representing a nonconstant value of P , is interpreted as self-broadening in the manner described below.

The absorption coefficient at the center of a line that is both collision (pressure) and Doppler broadened is given by the equation⁷

$$\frac{P}{P'} = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{a^2 + y^2} dy \quad (3)$$

where P' is the absorption coefficient at the center of a purely Doppler broadened line, and the parameter a is proportional to the ratio of collision, b_C , to Doppler, b_D , broadened half-widths (i.e., full-width at half maximum, FWHM)

$$a = \frac{b_C}{b_D} (\ln 2)^{1/2} \quad (4)$$

Fig. 2.

Graph of $\ln(I_0/I)$ against optical density, $p_{HF} \cdot l$, for $P_1(7)$ line and pure HF at 305 K in 1.93-cm-i.d. stainless steel test cell with $l = 10.0$ cm. Dashed curve was computed for $P' = 0.68 \text{ cm}^{-1} \text{ kPa}^{-1}$ and $b_{HF} = 4.3 \times 10^{-3} \text{ cm}^{-1} \text{ kPa}^{-1}$.

Here b_C is taken as

$$b_C = \sum_i b_i p_i \quad (5)$$

where the sum is taken over all species i present in the system, and b_i and p_i are the pressure broadening coefficient and partial pressure of i , respectively. For HF at 300 K, b_D for $p_1(7)$ is computed to be 0.0101 cm^{-1} . The right-hand side of Eq. (3) has been evaluated numerically for a range of assumed values of a .

For pure HF, b_C becomes $b_{HF} p_{HF}$. If this quantity is not $\ll b_D$ it produces a nonzero value of a , and, through its influence on the right-hand side of Eq. (3), a dependence of P on p_{HF} . The actual value of P at any optical density is then determined by the two constants, P' and b_{HF} . The dashed curve in Fig. 2 was computed using the combination of these two quantities that appeared to best describe the data, $0.68 \text{ cm}^{-1} \text{ kPa}^{-1}$ ($0.090 \text{ cm}^{-1} \text{ torr}^{-1}$) and $4.3 \times 10^{-3} \text{ cm}^{-1}$

kPa^{-1} ($5.7 \times 10^{-4} \text{ cm}^{-1} \text{ torr}^{-1}$), respectively. The resulting value of P is $0.53 \text{ cm}^{-1} \text{ kPa}^{-1}$ at 0.67 kPa (5 torr) HF and $0.43 \text{ cm}^{-1} \text{ kPa}^{-1}$ at 1.3 kPa (10 torr) HF. The corresponding values of P/P' are therefore 0.78 and 0.63, respectively.

For a gaseous mixture of HF dilute in a selected broadening gas M , b_C is $b_{HF} p_{HF} + b_M p_M$, where $p_M \gg p_{HF}$. For a fixed p_{HF} , b_M can be evaluated from the measured dependence of P on p_M , because b_{HF} and P' are now known. Data obtained from the addition of large amounts of H_2 to a fixed pressure (0.78 kPa) of HF in the test cell are shown in Fig. 3. From the falloff in P/P' with increasing p_{H_2} , b_{H_2} can be evaluated. The predicted relationship for a value $b_{H_2} = 2.7 \times 10^{-4} \text{ cm}^{-1} \text{ kPa}^{-1}$ is shown as the dashed curve in Fig. 3.

The results of these and similar experiments with O_2 and F_2 are summarized in Table II, which shows that HF is greater than a factor of 10 more efficient at broadening its own absorption line than is H_2 , O_2 , or F_2 . The right-hand column in Table II gives the computed FWHM for 1 atm of pure HF (b_C^{HF}) or for HF dilute in 1 atm of each M (b_C^M).

No published values of the quantities in Table II have been found for direct comparison. Herget et al.,⁸ using a more conventional line-shape measurement technique, have measured b_C^{HF} at 373 K for the lines $P_1(1-6)$ and $R_1(0-6)$. At the highest J'' their values decrease monotonically with J'' , and at $J'' = 6$ the values are 0.349 cm^{-1} for $P_1(6)$ and 0.316 cm^{-1} for

Fig. 3.

Influence of pressure broadening by hydrogen on absorption coefficient, P , at center of $P_1(7)$ absorption line. $P' = 0.68 \text{ cm}^{-1} \text{ kPa}^{-1}$. Abscissa is sum of partial pressures of HF, fixed at 0.78 kPa, and H_2 in 1.93-cm-i.d. stainless steel cell at 305 K. Dashed curve is computed for $b_{HF} = 4.3 \times 10^{-3} \text{ cm}^{-1} \text{ kPa}^{-1}$ and $b_{H_2} = 2.7 \times 10^{-4} \text{ cm}^{-1} \text{ kPa}^{-1}$.

TABLE II

COLLISION BROADENING PARAMETERS FOR HF
P₁(7) LINE^a

M	b_M^b (10 ⁻⁴ cm ⁻¹ kPa ⁻¹)	b_C^M at 1 atm (101.3 kPa) (cm ⁻¹)
HF	43.0 (57.0)	0.430
H ₂	2.7 (3.6)	0.027
O ₂	3.8 (5.1)	0.038
F ₂	1.2 (1.6)	0.012

^aThe Doppler half-width (FWHM) for HF P₁(7) line at 300 K is 0.0101 cm⁻¹.

^bValues in parentheses are b_M in units of 10⁻⁵ cm⁻¹ torr⁻¹.

R₁(6). Similarly, Smith⁹ reports ratios of b_C^M/b_C^{HF} ($M = H_2, O_2$, and F_2 , as well as many other substances) for the lines R₁(0-4) at 373 K. Smith's ratios also decrease monotonically with J'' and at $J'' = 4$ are 0.063, 0.051, and 0.071 for $M = H_2, O_2$, and F_2 , respectively, compared with the corresponding ratios computed from Table II ($J'' = 7$) of 0.063, 0.090, and 0.028. Extrapolation of Smith's results to higher J'' is complicated by differing, and variable, dependences on J'' .

In the actual H₂-O₂-F₂ mixtures for which rate measurements were made, b_C must be evaluated by summation, in Eq. (5), over the reagents and, at significant extents of reaction, over HF. In practice measurements were confined to small extents of reaction, where $p_M \sim (p_M)_0 \gg p_{HF}$, and b_C was computed by summing contributions of only H₂, O₂, and F₂ taken at their initial partial pressures. For a typical mixture, 40.0 kPa H₂-4.00 kPa O₂-36.0 kPa F₂, P becomes 0.24 cm⁻¹ kPa⁻¹ ($P/P' = 0.36$). The influence of HF on P at these large initial densities is less than for the case of pure HF (Fig. 2). This results from Eq. (3), where the dependence of P/P' on a (or b_C) decreases steadily with increasing a (or b_C), with the ratio approaching $(a\sqrt{\pi})^{-1}$, in the limit of large a . Thus, for 1.3 kPa HF in the above 80.0-kPa mixture, P is computed to be 0.19 cm⁻¹ kPa⁻¹, down 21% from the value for $p_{HF} = 0$, compared with the 37% reduction described above for 1.3 kPa of pure HF.

HF Formation Rates

Determining the partial pressure of HF present at any time following mixing of the three reagents is

possible with the oscillograms and synthesized absorption coefficients, P . Representative results for three selected mixtures, including one "blank" with 44.0 kPa O₂ and 36.0 kPa F₂, are shown in Fig. 4. The right-hand ordinate scale in kPa HF, for the 40.0-4.00-36.0 mixture, is approximately correct for the 40.0-12.0-36.0 mixture as well, because the effect on P of the added O₂ is small. Two features are particularly noteworthy: the significant amount of HF present 1 min after mixing ("prompt" HF) and the essentially constant rate of formation of HF over the following 30 min. The "blank" experiment, presumably influenced by desorption of HF from the test cell walls, provides an indication of the background $\Delta \ln(I_0/I)/\Delta t$ in this experiment. This background rate is always small, but variable, and no effort was made to correct the rate measurements for its contribution.

The formation of prompt HF, found to vary with mixture composition, is examined as a function of partial pressure O₂ in Fig. 5. Its magnitude varies between ~20 Pa (0.15 torr), or less, and 1.3 kPa (10 torr). Within the considerable scatter of the data, the HF magnitude shows a marked decreasing trend with increasing $(p_{O_2})_0$. Most of this prompt HF is probably formed during addition of the fuel component, F₂, and its magnitude can be used as a crude

Fig. 4.

Graphs of $\ln(I_0/I)$ for P₁(7) line and p_{HF} vs time for three experiments in the 8.94-cm-i.d. stainless steel test cell at 305 K. Time zero is point when addition of final component, F₂, is just complete. Compositions and slopes, $\Delta \ln(I_0/I)/\Delta t$ (s⁻¹) and $\Delta p_{HF}/\Delta t$ (Pa/s), for solid lines are: circles-40.0 kPa H₂-4.00 kPa O₂-36.0 kPa F₂, 4.03×10^{-3} , and 0.840; squares-40.0 kPa H₂-12.0 kPa O₂-36.0 kPa F₂, 8.83×10^{-4} , and 0.38; triangles-0 kPa H₂-44.0 kPa O₂-36.0 kPa F₂, 8.3×10^{-5} , and 0.041.

Fig. 5.

Semilogarithmic plot of partial pressure HF present 60 s after completion of F_2 addition against initial partial pressure O_2 in mixtures containing 40.0 kPa H_2 and 36.0 kPa F_2 in large stainless steel test cell (8.94-cm i.d.) at 305 K. Circles are mean values between 4 and 14 experiments, and bars indicate the computed standard deviations.

measure of how near to exploding the mixture came as it was being prepared. Large extents of reaction during mixing imply large heat release rates and temperature increases, which must be minimized by transfer to the cell walls to avoid thermal explosions.

The essentially constant (steady-state) subsequent rate of formation of HF is examined as a function of $(p_{O_2})_0$ and total density in Figs. 6 and 7, respectively. Typical rates, ~ 0.2 – 1.1 Pa/s (0.1–0.5 torr HF/min), increase with decreasing $(p_{O_2})_0$ and density (i.e., as mixture stability becomes marginal). At the smallest $(p_{O_2})_0$, $\Delta p_{HF}/\Delta t$ is nearly proportional to $(p_{O_2})_0^{-1}$, a relationship closely approximated for several other $(p_{H_2})_0$ and $(p_{F_2})_0$ combinations. In Fig. 7 $\Delta p_{HF}/\Delta t$ is nearly $\propto (p)^{-1}$ over a factor of 2 change in density.

The influence of initial H_2/F_2 ratio on $\Delta p_{HF}/\Delta t$ is shown in Table III. The reaction rate, while quite small for large excess H_2 , increases markedly as H_2/F_2 is lowered.

Fig. 6.

Steady-state rates of formation of HF, $\Delta p_{HF}/\Delta t$, as a function of initial partial pressure O_2 for mixtures 40.0 kPa H_2 and 36.0 kPa F_2 in 8.94-cm-i.d. stainless steel test cell at 305 K. Circles and bars have same meaning as in Fig. 5.

Fig. 7.

Steady-state rate of formation of HF, $\Delta p_{HF}/\Delta t$, as a function of total pressure for mixtures containing 43.5% H_2 –17.4% O_2 –39.1% F_2 . Circles are mean values between 3 and 22 experiments, and bars indicate computed standard deviations. Aluminum test cell at 305 K.

TABLE III
INFLUENCE OF H₂/F₂ RATIO ON STEADY-STATE
HF-PRODUCTION RATE^a

Mixture Composition			Total Pressure (kPa)	H ₂ /F ₂	$\Delta p_{HF}/\Delta t$	
H ₂ (%)	O ₂ (%)	F ₂ (%)			(Pa/s)	(torr/min)
47.6	9.5	42.9	84.0	1.1	0.56	0.25
76.2	6.7	17.1	84.0	4.5	0.12	0.052
43.5	17.4	39.1	92.0	1.1	0.27	0.12
17.4	20.0	62.6	92.0	0.28	0.36	0.16

^aMeasurements in the aluminum test cell at 305 K.

Figure 8 illustrates the dependence of $\Delta p_{HF}/\Delta t$ on temperature for a limited number of experiments over the narrow range from 295-306 K. The slope of the dashed line on this Arrhenius-type graph provides a rough measure (151 kJ/mol) of the activation energy of the overall reaction.

Fig. 8.

Semilogarithmic plot of $\Delta p_{HF}/\Delta t$ against reciprocal temperature for experiments in 8.94-cm-i.d. stainless steel test cell with 40.0 kPa H₂-4.00 kPa O₂-36.0 kPa F₂ mixtures. Slope of solid line, converted into an activation energy via the Arrhenius expression, yields 151 kJ/mol (36 kcal/mol).

All of these experiments were plagued by the same irreproducibility of results apparent in Figs. 5-7. Although individual experiments like those in Fig. 4, or even a series of experiments performed on a particular day, gave no indication of misbehavior or inconsistency, comparison of rates measured over a period of time showed disturbingly large amounts of scatter. The statistical summary presented above was therefore unavoidable. Evidence that the observed rates were influenced significantly by wall reactions, and therefore by the presumably variable microscopic condition of the wall surfaces, is presented in the next section.

DISCUSSION

The detailed time history of slowly reacting H₂-O₂-F₂ mixtures under nonexplosive conditions has been the subject of several investigations.^{10,11} Additional chemical kinetic information concerning this system has been obtained from analysis of behavior near or at the second explosion limit¹² and from more traditional studies of the pertinent elementary reactions.¹³

Under concentrated, ambient temperature conditions, the chemical mechanism by which reactants are converted to products must include at least the following elementary steps.

Thermal equilibrium is assumed for all species. Reaction (a) includes contributions from both the homogeneous and heterogeneous thermal dissociation of F_2 , whereas the other reactions are treated as taking place only in the gas phase. Reaction (d) provides the inhibition path by which O_2 participates in the removal of intermediates and therefore in stabilization of these mixtures. The fate of HO_2 is not specified. Evidence¹¹ that at ambient temperatures HO_2 is removed from the system (possibly heterogeneously) without regeneration of intermediates indicates that details concerning its fate can be ignored in this discussion.

Differential equations describing the time evolution of the present system can be simplified considerably by applying the steady-state approximation to $[F]$ and $[H]$, and by employing the following reasonable assumptions. (1) $[H_2]$, $[F_2]$, and $[O_2]$ remain close to their initial values because extents of reaction are small. (2) The chain length, expressed as the ratio $k_c [F_2] / k_d [O_2] [M]$, is $\gg 1$. (3) Reaction (e) is only a minor source of HF. The expression for R_{HF} ($\equiv d [HF] / dt$) then becomes

$$R_{HF} = \frac{4 (R_a + R_e) k_c [F_2]}{k_d [O_2] [M]} \quad (6)$$

where R_a and R_e are the rates of initiation Reactions (a) and (e), respectively. The brackets in Eq. (6) represent either concentrations or partial pressures, with rate coefficients expressed in compatible units. Equation (6) predicts a constant rate of formation of HF inversely proportional to $[O_2]$. The rate's density and H_2/F_2 dependences are unknown until R_a and R_e are specified and compared.

To estimate the magnitude of R_{HF} , consider first the case where $R_a \gg R_e$ and Reaction (a) is the homogeneous decomposition of F_2 ($R_a = k_a [F_2] [M]$).

$$R_{HF} = \frac{4 k_a k_c [F_2]^2}{k_d [O_2]} \quad (7)$$

k_a (300 K) is obtained from the product of the equilibrium constant K_a and the recently measured value¹⁴ of k_{-a} for F-atom recombination. k_c and k_d are reasonably well known at ambient temperatures.¹³ The resulting value of R_{HF} from Eq. (7), 1.1×10^{-9} Pa/s (5×10^{-10} torr/min), computed for a 40.0-4.00-36.0 mixture, is so low as to confirm that the homogeneous decomposition of F_2 is an unimportant source of atoms in the present experiments.

Considering the case where $R_e \gg R_a$,

$$R_{HF} = \frac{4 k_c k_e [H_2] [F_2]^2}{k_d [O_2] [M]} \quad (8)$$

With k_e taken as $10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ times the fraction of H_2 molecules in the $v = 1$ state¹² (2×10^{-5}), R_{HF} becomes 0.13 Pa/s (0.06 torr/min), a value within an order of magnitude of the experimental measurements. (Compare the 40.0-4.00-36.0 mixture in Fig. 6.) The difference could be accounted for by uncertainties in the rate coefficients. However, Eq. (8) has the wrong dependence on total density, thereby leading to the conclusion that Reaction (e) cannot account for the experimental observations.

The mechanism described by Reactions (a)-(e) predicts a minimum rate of formation of HF in the sense that steps involving chain continuation, via subsequent HO_2 reactions,¹¹ and chain branching, via supraprecipitation populations of vibrationally excited HF or H_2 ,^{12,15} have been omitted. Inclusion of such additional reactions will bring predicted rates into better agreement with experimental ones. However, no obvious combination of these additional steps will account for the observed behavior with respect to total density, H_2/F_2 ratio, and O_2 partial pressure.

In addition, the experimental results apparently were influenced by heterogeneous (wall) reactions, providing yet another means of enhancing the overall rate above the one predicted by homogeneous Reactions (a)-(e). The unusually large day-to-day scatter in steady-state HF formation rates is believed to be an indication of this influence. The importance of wall reactions is further evidenced by examining the influence of test cell diameter and wall material on the reaction rate. The mean rates observed in two 304 stainless steel cells at 297 K for a 40.0-4.00-36.0 mixture were 1.93 cm-0.69 Pa HF/s and 8.94 cm-0.24 Pa HF/s. The larger rate corresponds to the smaller diameter (larger surface/volume ratio) vessel. At 305 K mean rates measured for 40.0-8.00-36.0, 40.0-16.0-36.0, and 40.0-24.0-36.0 mixtures in the 8.94-cm-i.d. vessels were 0.71, 0.40, and 0.42 Pa HF/s for the 304 stainless steel and 0.56, 0.27, and 0.20 Pa HF/s for the aluminum.

This dependence of rate on the nature of the vessel wall material was most apparent in a series of experiments in the aluminum cell. On two occasions, following several low-density (~ 46.7 -kPa) explosions, the rate dropped by a factor of ~ 10 from the "normal" behavior described above. Normal rates could be restored by removing the white deposit found on and imbedded somewhat below the inside wall surface, or by deliberately utilizing ~ 80.0 -kPa marginal mixtures to generate a series of higher density explosions upon filling. The presence or absence of this deposit appeared to have no effect on the location of explosion boundaries. No evidence was found

of similar deposits in the stainless steel cells, and no abrupt changes in rate were ever observed in these vessels.

The conclusion from these results, is that wall reactions played a significant role in the generation, and perhaps the removal, of intermediates in the present experiments. Rapid heterogeneous dissociation of F_2 in Reaction (a) was probably a major contributor to this process. When applied to the larger vessels of interest in e-beam experiments, these observations suggest slower mixture deterioration and, perhaps, a somewhat greater range of conditions for which H_2 , O_2 , and F_2 can be reproducibly mixed without unintended explosions.

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