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The Catalytic Formation of Xenon Difluoride

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It is shown that heated filaments of palladium, nickel, copper, and aluminum catalyze the combination of xenon and fluorine. The principal reaction product was identified as xenon difluoride by infrared analysis. Other metals investigated; Ti, Zr, Mo, Ta, W, Re, Ir, Fe, Cr, V, Rh, and Pt, were ineffective as catalysts. Activation energies and reaction rates are presented for palladium at 50–160°C and for nickel at 180–400°C. For both metals the reaction is shown to be zero order in xenon and fluorine pressures for partial pressures >50 torr. The catalytically active metals were shown to be coated with an ionic fluoride layer under reaction conditions and it is suggested that xenon is chemically bound to fluorine at this fluoride surface.

INTRODUCTION

The reaction of xenon with fluorine has been shown to occur at a heated nickel surface (*1*). A recently published study of the reaction (*2*) showed that in the usual preparation the reaction is mostly occurring at the fluorinated walls of the metal reaction vessel. It was also shown in (*1*) that copper and aluminum were effective catalysts and in (*2*) that fluorides of cobalt and calcium catalyzed the reaction.

The earlier experiments (*1*) were later extended to survey the catalytic activity for the xenon–fluorine reaction of a number of other metals. Of the sixteen metals studied, palladium was the most effective catalyst for the formation of xenon difluoride. In view of the revived interest in the catalytic nature of the reaction the results are presented here.

EXPERIMENTAL METHODS

Materials

Fluorine was generated by an electrolysis cell, purified by passing through sodium fluoride and cold traps, and collected in a metal cylinder. The fluorine was introduced into the apparatus through liquid nitrogen traps and stored in a glass bulb.

Xenon was obtained from 1-liter glass bulbs supplied as 99% pure, balance krypton.

Metal catalysts were in the form of wires with purities ranging from 99.5 to 99.99%. The nickel and palladium wires used in the rate studies were Johnson and Matthey spectroscopically standardized grades.

Catalytic Apparatus

The reaction vessel (Fig. 1), which was of silica, contained the catalyst filament with a graded seal to Pyrex glass for the tungsten leads. Gas pressures in the vessel were measured with an all-metal bellows manometer operated with an optical lever giving a sensitivity of approximately 0.5 torr. This gauge had a range of about 40 torr but could be reset by adjustment of the outer pressure which was measured by a mercury manometer.

The vacuum line was constructed of Monel tubing with Monel Hoke valves. This was pumped by a conventional glass line to mercury diffusion and backing pumps. The couplings of the line and vessel

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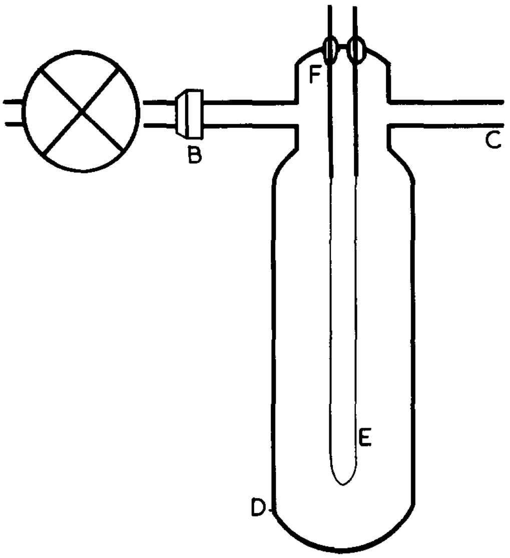


FIG. 1. Reaction vessel: A, monel valve; B, "swage-lok" joint; C, connection to bellows manometer; D, silica vessel; E, metal filament; F, Pyrex–silica seal with tungsten leads.

were "swage-lok" fittings with Teflon gaskets.

Reaction Procedure

The apparatus was prepared by prolonged pumping and heating of the vessel to remove moisture. Xenon was admitted at a measured pressure followed by fluorine. The fluorine bulb was fitted with a liquid nitrogen trap to hold any hydrogen fluoride impurity so that the maximum total reaction pressure was limited to 200 torr.

The metal filament was heated by direct current and the voltage and current measurements were used to calculate the resistance and hence the temperature of the wire. Careful calibration for each metal wire showed the procedure to be sufficiently accurate. The length of wire was sufficient to make end-cooling corrections unnecessary below about 450°C.

The silica vessel was surrounded by a dry-ice and acetone cold bath throughout the reaction. The reaction products then condensed on the wall of the vessel and the fall in reactant gas pressure could be used to monitor the reaction rate.

At the end of a reaction run the filament was cooled and the total residual pressure measured at −78°C. The vessel was then cooled by liquid nitrogen and the residual fluorine was pumped away. The pressure of the remaining xenon was then measured at −78°C and the reacting ratio for xenon and fluorine was calculated.

Infrared Spectra of Reaction Products

The infrared absorption spectrum of the reaction products was measured by conducting the reaction in a special cell fitted with polythene windows. This was necessary to avoid transferring the highly reactive xenon fluorides from the usual reaction system. The cell (Fig. 2) was made of Monel with polythene sheet windows. The pressure gauge was a less sensitive but more portable Bourdon gauge and the electrical leads were brought through a glass cone cap fitted to the metal tube with Kel-F grease.

The usual reaction procedure was used with the monel tube immersed in dry ice. The products were then allowed to evaporate with the cell in the beam of the infrared spectrometer.

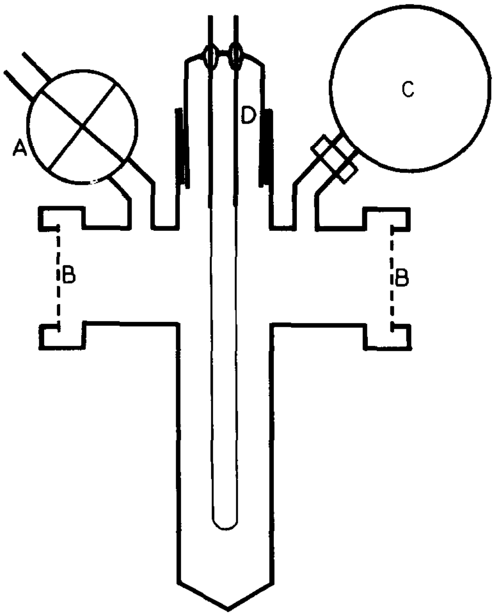


FIG. 2. Monel vessel for infrared study of reaction products: A, monel valve; B, polythene windows; C, Bourdon pressure gauge; D, glass cone filament assembly.

RESULTS

Observations of Catalytic Activity

A number of metals were investigated by the reaction procedure described above. The new wire, previously outgassed in vacuum, was exposed to a xenon–fluorine mixture at room temperature. Changes in gas pressure with time were usually noted at this or higher temperatures up to about 500°C. The composition of the remaining gas was estimated by freezing out the xenon as described above. For some metals the total drop of pressure was fully accounted for by the fluorine consumed to form the metal fluoride. In other cases a significant amount of xenon was consumed suggesting the formation of a xenon fluoride. These metals were subjected to further study using well fluorinated wires and the reaction ratio, kinetics and product identity determined.

The results of the qualitative studies on the metals are as follows: Titanium, zirconium, molybdenum, tantalum, tungsten, rhenium, and iridium were rapidly attacked by fluorine (at less than 200°C) without evidence of any reaction with xenon. Vanadium, chromium, and iron were moderately attacked by fluorine but there was no evidence of reaction with xenon at temperatures up to 350°C. Rhodium was particularly resistant to fluorine attack. There was no reaction with xenon at up to 500°C.

Platinum, as previously reported (*1*) formed a pale yellow solid when heated in the xenon–fluorine mixture. The overall reaction ratio reported, Xe:F:Pt = 2:12:1, indicates that as well as $XePtF_6$ other xenon platinum fluorides or xenon fluorides may have formed. These were not identified and no further investigations of the activity of platinum were made.

Nickel, palladium, copper, and aluminum all showed catalytic activity for the formation of xenon fluorides. The results for copper and aluminum were previously reported (*1*). The high temperatures required, 450–550°C, showed them to be less effective catalysts than nickel and unsuited to a quantitative study. The reaction range for nickel, 180–400°C, was convenient for kinetic study but palladium proved to be the most effective catalyst showing activity from about 50°C. The detailed results for these two metals are described later.

The differences in activity between the metals suggests that a specific interaction takes place on the metal which should be sensitive to the condition of the catalyst surface. Nickel wires lightly oxidized by heating in air were quite inactive for the reaction. Both palladium and nickel showed low and irreproducible rates of reaction unless the wires were carefully outgassed in vacuum. Once catalytic activity had been established, successive runs gave reproducible results.

These observations, together with the inactivity found for rhodium, are much more convincing evidence for catalysis than the "blank" previously described (*1*). In that case the whole silica vessel was hot, and no cold surface was provided for collection of the product.

Identification of Reaction Products

In the earlier report (*1*) the identity of the xenon fluoride was not established although the reaction ratio suggested that XeF_2 was the main product. The difficulty of identification arises from the extreme reactivity of the xenon fluorides towards metal and glass apparatus particularly in the presence of traces of moisture. Only small amounts of product were available from a catalytic experiment and it proved impracticable to transfer this sample to a mass spectrometer without decomposition.

The infrared spectrum of the products was measured in the special cell described above. The usual reaction procedure was used for both nickel and palladium ensuring that the product examined was characteristic of the temperature, gas ratio, and nature of the catalyst. In each case the spectrum showed strong absorption peaks at 552 and 570 cm^{-1} and much weaker peaks at 586 and 594 cm^{-1}. The strong peaks correspond to the values for XeF_2 (550, 566 cm^{-1}) and the weaker peaks to XeF_4 (581, 591 cm^{-1}) (*3*).

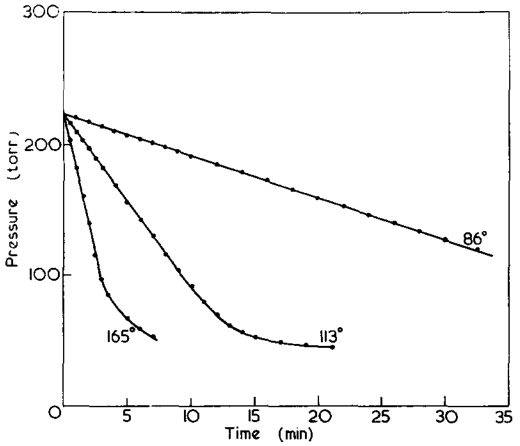


FIG. 3. Variation of reactant pressure for reaction of xenon with fluorine on palladium [temp. (°C)].

It was concluded that XeF_2 is the major reaction product with only small amounts of XeF_4. The spectrum became weaker after a time apparently due to reaction of the xenon fluorides with metal components of the vessel. Although the reaction procedure favors the collection of unstable species on the cold walls, no unexplained infrared peaks were observed in the range accessible with polythene windows.

Kinetics of Reaction on Nickel and Palladium

The reaction on nickel was studied at 180–400°C and found to be zero order in total gas pressure for initial pressures >200 torr (*1*). The reaction ratio F_2/Xe was approximately 1.2 and insensitive to initial gas ratios in the ratio 0.8:2.0. Zero-order conditions held until over half of the reactants were used, the partial pressures of xenon and fluorine then being <50 torr.

The activation energy for reaction on nickel, calculated from an Arrhenius plot (Fig. 4), was 10.4 ± 1.5 kcal mole^{-1} and the pre-exponential factor 1×10^{21} molecules sec^{-1} cm^{-2}, where the reaction area was assumed to be the apparent geometric area of the wire.

The reaction on palladium was studied in greater detail in the range 50–160°C. As for nickel, the reaction was initially of zero order (Fig. 3). The reaction ratio showed a systematic variation with initial pressures. For $F_2/Xe \leq 1$, the reaction ratio was 1.0 but for initial $F_2/Xe = 2$ the reaction ratio was 1.3. This was interpreted as due to the formation of XeF_4 as well as XeF_2. The rates plotted in Fig. 4 are calculated for the production of XeF_2 only. As shown, the initial rates are independent of the initial gas ratio within the range 0.5–2.0. The initial reaction is therefore of zero order in both xenon pressure and fluorine pressure. The activation energy for the reaction on palladium was 13.4 ± 0.7 kcal mole^{-1} and the pre-exponential factor 1.6×10^{26} molecules sec^{-1} cm^{-2}.

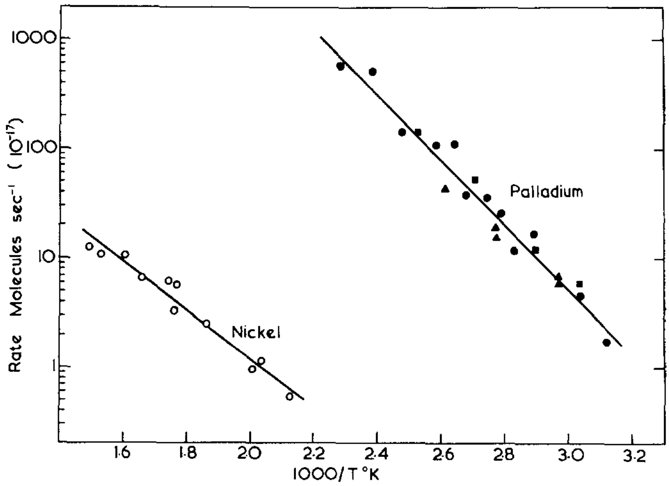


FIG. 4. Arrhenius plot for the reaction of xenon with fluorine on nickel (○); and on palladium with initial Xe/F_2 ratios of 1.0 (●); 2.0 (▲); and 0.5 (■).

DISCUSSION

Catalytic Activity

Under the conditions used in these experiments the reaction of xenon with fluorine to form xenon difluoride is catalytic. Only the metal filament was heated and the rate of reaction was a function of the temperature and composition of the filament. The different activities of palladium and nickel and the inactivity of rhodium and oxidized nickel are evidence that the reaction is dependent on the composition of the filament surface.

Examination of the metal surfaces after reaction showed them to be covered by the metal fluoride (*1*). In every case it would be expected that a bulk layer of the metal fluoride was present as the surface for reaction. For example, nickel, which is relatively resistant to fluorine attack, would have approximately 100 atom layers of fluoride formed on the surface in 10 min at 300°C (*4*). The explanation of the variations in catalytic activity requires consideration of the fluoride structures rather than those of the metals.

The most effective catalysts, palladium and nickel, form ionic difluorides with a rutile-type structure (*5*, *6*). There are no higher fluorides of nickel and PdF_3 would not be expected to form at the temperatures used here. Copper also forms a difluoride with a distorted rutile structure (*7*). Aluminum is known to form a trifluoride and a subfluoride AlF. There is some doubt concerning the structure of AlF_3 but it is known to be essentially ionic and to undergo a minor recrystallization at 454°C (*8*).

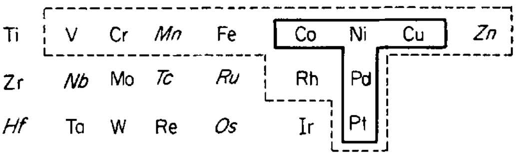
Of the metals found to be catalytically inactive, both iron and chromium can form difluorides, but at moderate temperatures the attack of fluorine on the metal would yield the trifluorides. Rhodium forms a trifluoride (and higher fluorides) but is not appreciably attacked by fluorine below 500°C. The remaining metals studied react with fluorine to form nonionic higher fluorides, e.g., MoF_6, ReF_6, TiF_4. None of these with the exception of platinum showed any reaction with xenon. The reaction on platinum apparently leads to a mixture of various xenon platinum fluorides; $XePtF_6$, Xe_2PtF_{17} and $XePtF_{11}$ (*9*).

Davis *et al.* also showed that calcium and cobalt fluorides catalyze the reaction (*2*). The CoF_3 is very difficult to prepare in a pure state and in the presence of impurities is reduced to CoF_2 on heating. The CoF_2 is an ionic fluoride with the rutile structure and CaF_2 has the fluorite structure.

It is interesting to note that of the transition metals studied, activity for the reaction is confined to a narrow group of those metals with full or nearly full *d*-orbitals (Table 1). These form ionic fluorides in which there is no overlap between the full or nearly full valence band and the empty conduction band. These fluorides are therefore insulators. However, it is suggested from the apparent ease with which the catalytic reaction occurs that a mechanism involving charge carriers is probable. These could arise either by an insulator–conductor transition as described by Mott (*10*) or by the introduction of electrons from the underlying metal. At present there is insufficient information on the electrical, optical, and magnetic properties of the transition metal fluorides to justify a quantitative treatment of these effects.

TABLE 1

PERIODIC CORRELATION OF CATALYTIC ACTIVITY[a]



Ti	V	Cr	*Mn*	Fe	Co	Ni	Cu	*Zn*
Zr	*Nb*	Mo	*Tc*	*Ru*	Rh	Pd		
Hf	Ta	W	Re	*Os*	Ir	Pt		

[a] The elements studied are not italicized; those showing catalytic activity are in the full outline; those forming stable solid fluorides at the reaction temperatures are in the broken outline.

Reaction Kinetics

The reactions on palladium and nickel were found to be zero order in xenon and fluorine pressures for partial pressures of 50–100 torr. For fluorine which is known to be strongly adsorbed this appears reasonable but the result for xenon is surprising (*2*), unless xenon also strongly adsorbed at the surface by chemical combination with fluorine. This requires further investigation (the subject of the succeeding paper).

The activation energies observed are of the same magnitude as the heat of sublimation measured for XeF_2 (12.3 kcal $mole^{-1}$) (*11*) suggesting that product desorption could be the rate-determining step. The area of the surface of the fluoride deposits is not known and the frequency factors expressed in terms of the geometric areas of the filaments may not be directly comparable.

CONCLUSION

It has been established that the combination of xenon and fluorine can be catalyzed by heated filaments of palladium, nickel, and other metals which form ionic fluorides but not by the metals which form covalent fluorides. The product of reaction for approximately equal pressures of xenon and fluorine is xenon difluoride. The kinetics of the reaction are zero order in xenon and fluorine pressure for partial pressures above ~50 torr. It is suggested that this could be due to chemical combination of xenon at the fluoride surface.

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