

The Preparation and Nuclear Magnetic Resonance of Krypton Difluoride¹

F. Schreiner, J. G. Malm, and J. C. Hindman

Argonne National Laboratory, Argonne, Illinois. Received September 14, 1964

Krypton difluoride has been prepared by passing an electrical discharge through a mixture of the elements at low pressure (~ 20 mm.) and low temperature (-183°). This method has been reported previously to yield krypton tetrafluoride, a claim which could not be substantiated by the present work. The compound obtained is a white crystalline solid which sublimes at temperatures well below 0° and can be handled in dry, Pyrex glass or polychlorotrifluoroethylene containers. It is a highly reactive fluorinating agent which may be kept at Dry Ice temperature. At room temperature spontaneous decomposition occurs. Analytical data are given which establish the formula KrF_2 . Also, nuclear magnetic resonance measurements of the chemical shift for fluorine-19 of KrF_2 dissolved in anhydrous hydrofluoric acid are reported. The shielding value σ_F^2 is found to be 374×10^{-6} for a solution of 4.6 moles of KrF_2 /kg. of HF and 362×10^{-6} for a solution of 16.4 moles of KrF_2 /kg. of HF, both measured at 0° . These values agree with the value reported for a sample of krypton tetrafluoride (373×10^{-6}) which provides evidence that, in fact, the measurements were performed on krypton difluoride. Theoretical considerations treating the bonding in KrF_2 as analogous to that in XeF_2 lead to a shielding value which is in excellent agreement with the experimental one.

Introduction

The first chemical compound of krypton to be reported was krypton tetrafluoride.² It was prepared by passing an electrical discharge through a mixture of krypton and fluorine at $86^\circ K$. We have repeated this experiment and were able to produce gram amounts of a compound of krypton and fluorine. Chemical analyses and infrared spectra, however, proved that our product is the difluoride of krypton rather than the tetrafluoride.

Krypton difluoride was first produced in minute quantities by a photochemical reaction³ of fluorine with krypton embedded in an argon matrix at $20^\circ K$. Its composition was determined by studying the infrared spectrum, which shows absorption bands at 580 and 236 cm.^{-1} . Larger quantities (approximately 100 mg.) of krypton difluoride were subsequently obtained by electron-beam irradiation of a mixture of the two constituent elements at $123^\circ K$.⁴ Chemical analysis performed on the reaction product established its composition. It was also possible to obtain an infrared spectrum of the vapor in which a strong absorption band centered at 585 cm.^{-1} occurred.⁵

Nuclear magnetic resonance data for ^{19}F have been reported for a sample of krypton tetrafluoride dissolved in hydrogen fluoride.⁶ We have made similar studies of the chemical shift of the ^{19}F atom in anhydrous hydrofluoric acid solutions of krypton difluoride prepared by the electric discharge method. On the basis of these measurements we have concluded that the sample purported to be krypton tetrafluoride was probably krypton difluoride. Approximate calculations have been made to show that the observed ^{19}F shielding constant in krypton difluoride is essentially what would have been expected from the ^{19}F shielding data for the xenon difluoride, assuming the same type of bonding and taking into account the electronegativity difference between krypton and xenon.

Experimental

Materials. Fluorine of high purity ($>99.8\%$) was obtained from the General Chemical Division of the Allied Chemical Company.

Two sources of krypton were used: (1) J. T. Baker Chemical Co. According to the analysis furnished by the manufacturer, this krypton contained (in p.p.m.): N_2 , <50 ; Xe , <25 ; O_2 , <5 ; H_2 , <5 ; hydrocarbons, <15 ; and H_2O , <5 . (2) Air Reduction Co. A mass spectrometric analysis showed the following amounts of impurities (in %): N_2 , 0.9; Ar , 0.1; Xe , <0.02 ; O_2 , 0.01; H_2 , 0.05; H_2O , 0.05; and CO_2 , 0.03.

The anhydrous hydrogen fluoride was procured from the Harshaw Chemical Co. and was further purified by low temperature distillation. The final product had a conductivity of 3×10^{-5} (ohms cm.)⁻¹.

Preparation and Purification. Krypton difluoride was prepared in a Pyrex electrical discharge apparatus essentially identical with the reactor described for the preparation of krypton tetrafluoride² and dioxygen difluoride.^{7,8} The copper electrodes were 0.75 in. in diameter and were spaced 3 in. apart. This glass reaction vessel was part of a loop around which the gas mixture was circulated at a rate of $1300\text{ cm.}^3/\text{min.}$ by means of a modified magnetic piston pump.⁹ A schematic drawing of our apparatus showing all essential details is given in Figure 1.

Before the reaction was started, the system was pumped to a high vacuum and flamed. Thereafter, it was "seasoned" with fluorine for 12 hr., and finally evacuated again. The reactor was cooled in liquid oxygen (in some instances liquid nitrogen was used), and the mixture of krypton and fluorine was admitted at pressures ranging from 12 up to 50 mm. In some

(6) T. H. Brown and P. H. Verdier, *J. Chem. Phys.*, **40**, 2057 (1964).

(7) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

(8) A. G. Streng, A. D. Kirshenbaum, L. V. Streng, and A. V. Grosse in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 73.

(9) W. Brenschede, *Z. physik. Chem. (Leipzig)*, **A178**, 74 (1936-1937).

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) A. V. Grosse, A. D. Kirshenbaum, A. G. Streng, and L. V. Streng, *Science*, **139**, 1047 (1963).

(3) J. J. Turner and G. C. Pimentel, *ibid.*, **140**, 974 (1963).

(4) D. R. MacKenzie, *ibid.*, **141**, 1171 (1963).

(5) D. R. MacKenzie, private communication.

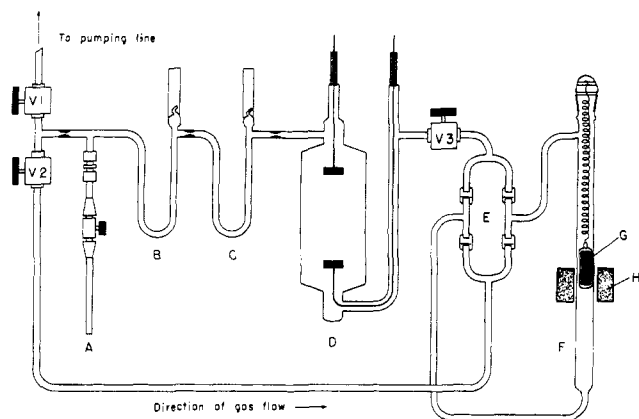


Figure 1. Diagram of apparatus used for the preparation of krypton difluoride. A: Polychlorotrifluoroethylene container for the collection and storage of the compound. Its attachment to the glass apparatus was effected by a Teflon Swagelock fitting. B and C: U-tubes of Pyrex glass with break-seals. After termination of the reaction, the compound was sublimed first into tube C and then into tube B, both of which were cooled with Dry Ice. Each U-tube was sealed off on the reactor side after the sample had been condensed into it. D: Electrical discharge reaction vessel made of Pyrex glass (diameter, 60 mm.; height of wide portion, 200 mm.). Two copper disks of 20 mm. diameter and 5 mm. thickness, spaced 75 mm. apart, served as electrodes. The leads to the electrodes were silver soldered into Kovar to glass seals. E: Valve manifold to convert push-pull operation of magnetic piston pump into unidirectional gas circulation as indicated. Each individual valve consisted of a 10-mm. glass tube ground flat at the end, protruding into a wider tube and closed with a thin square piece of glass held in place by gravity. Application of a small pressure head from below (0.1 mm.) permitted gas to flow in upward direction. Flow in downward direction is inhibited by the closure of the ground end of the glass tube by the square piece of glass. Arrangement of four valves in the way indicated in the drawing permits use of the pumping action of each half stroke of the piston. F: Magnetic piston pump after Brenschede.⁹ The pump is made from a 48-cm. long piece of precision ground Pyrex glass tubing of 0.75-in. inner diameter. G: Piston of pump suspended from stainless steel spring. The piston consists of a 50-mm. long piece of iron rod enveloped by glass. The outer diameter of the piston was ground to fit the precision ground tube of the pump with a clearance of about 0.002 in. H: Solenoid slipped over the outside of the pump. It was driven by a simple electronic multivibrator circuit supplying periodic pulses of current adjustable in frequency. In a suitable position, the solenoid actuated the up and down movement of the piston at an amplitude of 50 mm. and a frequency of two strokes per second. V1, V2, V3: Monel valves. While the reaction was going on, valve 1 was kept closed while valves 2 and 3 were open. During the purification and sublimation of the product, valves 2 and 3 were closed to separate the pump from the rest of the system, and valve 1 was open to establish a connection to the pumping line.

experiments the initial F_2/Kr ratio was 2:1; in others, 1.1:1. The mixture was circulated through the loop and the discharge initiated. A current of 15 ma. was obtained with a voltage drop of 3000–4000 v., depending on the gas pressure which decreased gradually as the reaction proceeded and the reactants combined to form a compound. The mixture was replenished periodically. In a typical experiment, operating with a F_2/Kr ratio of 1.1:1 at an average pressure of 20 mm., a discharge current of 20 ma., and at liquid oxygen temperature, the rate of production of krypton difluoride was 0.25 g./hr. It should be pointed out at this time that the vapor pressure of Kr at 90°K. is 20 mm. whereas at 77°K. it is only 1.9 mm. In experiments involving liquid nitrogen as refrigerant, therefore, the partial pressure of krypton in the reaction

vessel cannot exceed 1.9 mm.; and if reactions are carried out at total pressures above 4 mm., the F_2/Kr ratio may be increased appreciably over the ratio of the initial mixture.

After terminating the reaction, any excess of unchanged gas mixture was pumped off. The liquid oxygen bath was replaced by a slush of Dry Ice and trichloroethylene (-78°) and the pumping continued for 1 hr. In this way the greater part of the more volatile by-products of the reaction, silicon tetrafluoride, and traces of dioxygen difluoride were removed. Final purification was effected by subliming the compound while pumping from the reaction vessel, which was allowed to warm up gradually to room temperature, into two U-tubes cooled in Dry Ice. The sample was eventually transferred into a glass or polychlorotrifluoroethylene (Kel-F) tube for storage. The yield of pure KrF_2 was determined by weighing and was approximately 75% based on the initial amount of krypton.

Chemical Analysis. The krypton difluoride was weighed in a tubular Kel-F container fitted with an all Kel-F valve. The container was attached to a vacuum system and Toepler pump. After pumping to a good vacuum, a solution of 1 M NaOH was admitted under vacuum onto the sample which was cooled to liquid nitrogen temperature. On warming to room temperature, the hydrolysis was observed to proceed smoothly with the evolution of gas. The amount of gas evolved was determined by collecting it in a bulb of known volume and measuring its pressure. Its composition was determined mass spectrometrically. The fluoride in solution was titrated spectrophotometrically with thorium nitrate, using sodium alizarin sulfonate as an indicator.

Results and Discussion

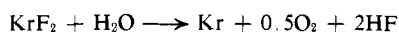
Preparation and Identification. Krypton and fluorine react readily in an electrical discharge at low temperatures and pressures. The product of this reaction in our experiments always was krypton difluoride although the conditions were as nearly as possible identical with those published for the preparation of krypton tetrafluoride.² We have found no evidence for the presence of the higher fluoride even for a large excess of fluorine over krypton. Krypton difluoride was obtained for F_2/Kr ratios ranging from 1.1:1 to 2:1 by pressure, irrespective of whether the reactor was cooled with liquid nitrogen or liquid oxygen. The actual F_2/Kr ratio in the reactor may have been as high as 20:1 in experiments conducted at a total pressure of 40 mm. and using liquid nitrogen because of the low vapor pressure of Kr, as was pointed out earlier. We find that high reaction rates are favored by the use of liquid oxygen as coolant and a low ratio of F_2 to Kr (1.1:1). Small amounts of silicon tetrafluoride and dioxygen difluoride are formed owing to an attack on the glass walls of the reactor. These impurities are not trapped at Dry Ice temperature and are therefore easy to separate from the krypton difluoride.

The purified product is a white solid which sublimes readily at temperatures well below 0° . There is evidence that the compound spontaneously decomposes unless it is kept at low temperatures. For this reason,

attempts to measure its vapor pressure in quartz or Monel systems were unsuccessful, and only a crudely estimated value of 30 mm. at 0° can be given here. The compound can be stored at -78° (Dry Ice) without appreciable loss for several weeks. There is no visible attack on thoroughly dry Pyrex glass at room temperature. Equally suitable for handling and storing the krypton difluoride are containers of polychlorotrifluoroethylene (Kel-F).

For a chemical analysis, a weighed amount of 1.89 mmoles of krypton difluoride was hydrolyzed with an excess of 1 M NaOH solution. It liberated 1.83 mg.-atoms of Kr and 0.85 mmole of O₂. The total amount of F⁻ determined in the solution was 3.64 mg.-ions. In a second analysis performed on an unweighed sample, 1.30 mg.-atoms of Kr and 0.61 mmole of O₂ were collected. The total amount of F⁻ determined was 2.63 mg.-ions.

The foregoing analytical results establish the formula KrF₂. It also follows that the hydrolysis of this compound proceeds analogously to the hydrolysis of XeF₂ in basic solution according to the reaction



This same reaction occurs rapidly in acid solution, in contrast to the behavior of XeF₂ which dissolves and may persist unhydrolyzed for extended periods of time.¹⁰ It is evident that no ionic species containing Kr remains in solution after hydrolysis. This has been confirmed by separate experiments involving the radioactive isotope ⁸⁵Kr, where it has been shown that no activity nor any oxidizing power remains in solution.

Independent proof of the composition of krypton difluoride has been obtained from a study of the infrared and Raman spectra of the gaseous phase.¹¹ Two intense infrared absorption bands corresponding to fundamental vibrational frequencies have been observed at 232.6 and 588 cm.⁻¹. Only one Raman frequency at 449 cm.⁻¹ appears in the spectrum of the vapor. These data can only be interpreted in terms of a linear symmetric triatomic molecule. In addition, the absence of any extraneous bands in the region where stretching frequencies involving fluorine atoms are to be expected attested to the purity of our samples and ruled out the presence of higher fluorides of krypton other than in trace amounts.

Preliminary crystallographic studies of krypton difluoride produced by the electric discharge method are reported elsewhere.¹² These studies demonstrate the presence of only one crystalline phase, and the symmetry of this phase was found to be tetragonal.

Samples of krypton difluoride were also submitted for mass spectrometric analysis. The spectrum obtained displayed the presence of two ions, Kr⁺ and KrF⁺, only.¹³ In addition to that, samples distilled from the reactor and collected in liquid nitrogen without purification produced the same result.

Krypton difluoride reacts with antimony pentafluoride at -20° to form the compound KrF₂·2SbF₅.¹⁴ This salt is more stable and less volatile than its parent

compound, KrF₂. Here again an analogy to xenon difluoride is obvious, for it, too, forms a salt with SbF₅.¹⁵

The ¹⁹F Chemical Shift of KrF₂ in HF Solution. Krypton difluoride dissolves readily in anhydrous hydrofluoric acid to the extent of 16 moles/1000 g. of HF at room temperature. For the chemical shift measurements, two different samples of krypton difluoride were dissolved in anhydrous hydrofluoric acid. From one of these solutions, after the chemical shift measurements had been made, the hydrogen fluoride was distilled off at -78°, and the krypton difluoride was recovered with negligible loss. The identity of the residual material was established by infrared spectroscopy.

The experimental techniques were the same as those used earlier for the investigation of xenon fluoride samples.¹⁶ In both samples only two resonance peaks were observed, one owing to the ¹⁹F in HF and the other owing to the ¹⁹F in the krypton difluoride, indicating the equivalence of the two fluorines in the krypton difluoride molecule. The krypton difluoride samples differed in behavior from xenon difluoride samples in that there was no evidence for exchange between the krypton difluoride fluorines and the hydrofluoric acid fluorine even at 25°.

The chemical shielding values, $\sigma_{\text{F}}^{(2)}$, relative to F₂, $\sigma_{\text{F}_2}^{(2)} = 0$, derived from these observations are given in Table I, together with the value reported earlier¹⁶ for xenon difluoride solutions in hydrofluoric acid. Also given in Table I is the shielding value reported by

Table I. Chemical Shifts and Related Quantities for ¹⁹F in XeF₂ and KrF₂ in HF^a

	Concn., moles/ 1000 g. of solvent	$\sigma_{\text{F}}^{(2)} \times 10^6$	<i>I</i>	<i>P</i> _{zz} (F)	<i>q</i> _F	<i>q</i> _R	χ_{R}
XeF ₂ (HF)	1.0	629 ^b	0.786	1.79	-0.79	1.58	2.52
KrF ₂ (HF)	4.6	374 ^c	0.468	1.47	-0.47	0.94	2.96
	...	356 ^d	0.45 ^d				
	16.4	362 ^c					
KrF ₄ (HF)	2.1	373 ^e					
	...	228 ^d	0.29 ^d				

^a $\sigma_{\text{F}_2}^{(0)} = 0$, $\sigma_{\text{HF}}^{(2)} = 627 \times 10^{-6}$. ^b From data at -19.5°
^c From data at 0° ^d Calculated, see text. ^e Reference 6, see text.

Brown and Verdier⁶ for ¹⁹F in a sample purported to be krypton tetrafluoride in hydrofluoric acid. From the data presented in the present paper, it appears probable that their sample was actually krypton difluoride.

Careful examination revealed no evidence for any hyperfine interactions between the ⁸³Kr (12% abundance, *S* = 9/2) isotope and the ¹⁹F. Failure to observe any spin coupling is consistent with the quadrupole relaxation of the ⁸³Kr in the asymmetric electric field present in the linear krypton difluoride molecule.

The Charge Distribution and Related Quantities for the KrF₂ Molecule. If we consider that the molecular structure in KrF₂ is analogous to that in the XeF_n

(15) A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 275 (1963).

(16) J. C. Hindman and A. Svirnickas, ref. 8, p. 251.

(10) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297 (1964).

(11) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, to be published.

(12) S. Siegel and E. Gebert, *J. Am. Chem. Soc.*, **86**, 3896 (1964).

(13) E. N. Sloth and M. H. Studier, *Science*, **141**, 528 (1963).

(14) H. Selig and R. D. Peacock, *J. Am. Chem. Soc.*, **86**, 3895 (1964).

compounds, corresponding essentially to binding by three-center, four-electron $p\sigma$ bonds,¹⁷⁻¹⁹ then the shielding data can be used to derive information about the charge distribution in the molecule in the same manner as has been done for the xenon compounds.^{16, 20} For this type of electron distribution, the principal contribution to the shielding arises from the paramagnetic term and depends essentially on the population in the fluorine 2p orbitals. The appropriate shielding equation²¹ can be written in terms of the gross orbital populations, $P_{x,y,z}$, on the fluorine atom as

$$\sigma_{\text{F}}^{(2)} = \sigma^{(0)} \{ (P_{xx} + P_{yy} + P_{zz}) - \frac{1}{2} (P_{xx}P_{yy} + P_{yy}P_{zz} + P_{zz}P_{xx}) \} \quad (1)$$

where

$$\sigma_{\text{F}}^{(0)} = - \left(\frac{2e^2\hbar^2}{2\Delta E m^2 c^2} \right) \left\langle \frac{1}{r^3} \right\rangle_{\text{F}} \quad (2)$$

In the present calculations, the value of the excitation energy, ΔE , for F is taken to be 7.9 e.v. from the spectroscopic work of Jortner, *et al.*,¹⁹ on XeF₂. It is assumed that this value is also appropriate for F in KrF₂.²² With a value of $\langle 1/r^3 \rangle_{\text{F}}$ of $44 \times 10^{24} \text{ cm.}^{-3}$ from the data of Barnes and Smith,²³ $\sigma_{\text{F}}^{(0)}$ becomes approximately -800×10^{-6} . Considering only $p\sigma$ bonds, values of the ionicity, I , the orbital population $P_{zz}(\text{F})$ and the charges on the fluorine atom, q_{F} , and on the central atom, q_{R} , were calculated from the appropriate form of eq. 1.¹⁶ The apparent electronegativity values, χ_{R} , for the central atom were obtained from these I values and the I vs. χ relations of Dailey and Townes.²⁴

The following comments can be made with respect

- (17) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).
 (18) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951); R. E. Rundle, *ibid.*, **85**, 112 (1963).
 (19) J. Jortner, E. G. Wilson, and S. A. Rice, ref. 8, p. 358 ff.
 (20) D. Ladzins, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, **39**, 1611 (1963).
 (21) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961).
 (22) J. Hinze and K. S. Pitzer, ref. 8, p. 340 ff.
 (23) R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954).
 (24) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

to the data given in Table I. First, the general consistency of the charge distribution calculated for XeF₂ from the resonance measurements and from a simple molecular orbital treatment applicable to the XeF_{*n*} compounds has already been noted.^{16, 19, 25} The actual value of I and the related $q_{\text{F,R}}$ for XeF₂ would be altered somewhat if allowance were made for the small amount of F_{2s} contribution indicated by the e.s.r. measurements of Morton and Falconer²⁶ on the XeF radical. An approximately 6% correction estimated from their data would reduce $q_{\text{F}}(\text{XeF}_2)$ to -0.73 . This contribution would be expected to be less in the KrF₂ molecule because of the greater electronegativity of the Kr. Second, the charge migration to the F atom is appreciably less in the KrF₂ molecule than in XeF₂. That this is reasonable can be shown by the following rough calculation. Assuming the bonding to be as described above, we would then expect that the amount of charge migration and the chemical shift would be proportional to the electronegativity difference between Kr and Xe. We start with $q_{\text{F}}(\text{XeF}_2)$ equal to -0.73 , corresponding to χ_{Xe} equal to 2.65. From the calculations of Noyes,²⁷ Kr is more electronegative than Xe by 0.34 unit. This would correspond to $\chi_{\text{Kr}}(\text{KrF}_2)$ equal to 2.99, which would give $q_{\text{F}}(\text{KrF}_2)$ equal to -0.445 and $\sigma_{\text{F}}^{(2)}$ equal to 356×10^{-6} , in excellent agreement with the data in Table I. Similar calculations can be made for other oxidation states by taking into account the approximately 0.1 unit increase in χ per unit increase in the formal charge on the central atom.²⁸ Such a calculation yields a shielding value for ¹⁹F in KrF₄ of 228×10^{-6} .

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- (25) See also L. L. Lohr, Jr., and W. N. Lipscomb, ref. 8, p. 347 ff.
 (26) J. R. Morton and W. E. Falconer, *J. Chem. Phys.*, **39**, 427 (1963).
 (27) R. M. Noyes, *J. Am. Chem. Soc.*, **85**, 2202 (1963).
 (28) From the observations on the xenon fluorides and the interhalogens, see ref. 16.