

CONTRIBUTION FROM BROOKHAVEN NATIONAL LABORATORY,
UPTON, NEW YORK

Synthesis of Noble Gas Compounds by Proton Bombardment

BY D. R. MACKENZIE AND J. FAJER

Received December 18, 1965

Ionizing radiation in the form of γ rays or electron beams has successfully been applied in this laboratory to the synthesis of xenon fluorides^{2a} and krypton difluoride.^{2b} These forms of radiation are inefficient as sources of excitation in gases. Heavy charged particle bombardment, on the other hand, results in concentrated energy deposition. We have therefore investigated the use of proton beams from a 60-in. cyclotron. Essentially all of the energy of 10-Mev protons which penetrate the container window can be absorbed in the gases being irradiated. The heavy-particle beam has the added advantage of diverging only slightly so that products diffusing to the walls of the reaction vessel are not exposed to much radiation.

In condensed-phase irradiations the impinging protons are stopped in about the first millimeter of material. We have taken advantage of this fact by bombarding thin layers of solid in contact with liquid fluorine. This results in production of high concentrations of excited and ionized species in the region of the liquid-solid interface.

Experimental Section

All irradiations were done with the 60-in. Brookhaven cyclotron, using 10-Mev protons and a beam current of $5 \mu\text{a}$ for 1 hr. For gases, the reaction vessel consisted of an 8-cm o.d. aluminum cylinder, 30 cm long, with a valve and a pressure gauge at one end and a 0.030-cm window of 1.5-cm diameter at the other. Temperatures were maintained by means of either an insulated jacket filled with coolant or copper straps in intimate contact with the vessel and immersed in coolant. For condensed phases, a cylindrical nickel cell of 2-ml volume was soldered inside a paint can so that the window (0.012 cm thick) faced out. The solid to be irradiated was frozen onto the window; the cell was filled with fluorine and held at -196° by adding liquid nitrogen to the insulated paint can. After irradiation, the fluorine was pumped off at -196° . As the reaction vessel warmed up, products were pumped and trapped into a Monel U tube attached to an infrared cell or into a quartz U tube. The infrared cell was equipped with silver chloride windows. The xenon fluorides and krypton difluoride were identified by their known spectra³ and, when required, by elemental analysis after hydrolysis. XeF_6 was prepared by thermal reaction and purified as the sodium fluoride complex.⁴

Results

Gas mixtures of xenon or krypton and fluorine readily reacted upon proton bombardment⁵ to yield xenon

and krypton difluoride. A 1-hr irradiation, at $5 \mu\text{a}$, yielded about 1 g of KrF_2 . G values for formation of the fluorides ranged from 1 to 1.5 molecules/100 ev. KrF_2 was prepared at temperatures as high as -60° although yields decreased markedly at the higher temperatures. While XeF_4 can readily be synthesized, attempts to prepare the reported⁶ KrF_4 were unsuccessful. Even at high fluorine to krypton ratios (9:1), only KrF_2 was detected. A small absorption centered at 620 cm^{-1} was observed. Whether this band was due to KrF_4 or to an impurity is uncertain. The total amount of this material was small and it could not be isolated.

In condensed phases, irradiation of XeF_2 and liquid fluorine at -196° yielded XeF_4 and XeF_6 . Attempts to prepare XeF_8 ⁷ by the analogous reaction of XeF_6 with fluorine were unsuccessful. The easy conversion of XeF_2 to XeF_4 and XeF_6 suggested a parallel attempt with KrF_2 . Again, no conclusive evidence for the formation of KrF_4 from the irradiation of KrF_2 and liquid fluorine could be obtained. During bombardment of xenon and oxygen at -196° , the window of the reaction cell blew out. When irradiation was stopped after a short period ($2 \mu\text{a}$ hr) and the gases were pumped away (25°), the hydrolyzed residue oxidized potassium iodide solutions and evolved xenon. This reaction and the explosions are presumably due to the unstable xenon trioxide.^{8a} Several other combinations of gases which would lead to compounds thought possible in the literature were attempted both in gas and condensed phases. These experiments yielded no product detectable by infrared (or the eye). The various experiments, successful or not, are summarized in Table I.

TABLE I

REACTIONS UPON BOMBARDMENT WITH 10-MEV PROTONS		
Reaction gas phase	Ratio noble gas:F ₂	Temp, °C
$\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2$	1:1	-78
$\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_4 + \text{XeF}_6$	1:2 to 1:10	-80
$\text{Kr} + \text{F}_2 \rightarrow \text{KrF}_2$	1:1	-140
$\text{Kr} + \text{F}_2 \rightarrow \text{KrF}_4$	1:3 to 1:9	-140 to -60
$\text{Ar} + \text{F}_2 \rightarrow$	1:1	-180
$\text{He} + \text{F}_2 \rightarrow$	1:1	-180
Condensed phase		
$\text{XeF}_2 + \text{F}_2 \rightarrow \text{XeF}_4$		
$\text{XeF}_4 + \text{F}_2 \rightarrow \text{XeF}_6$		
$\text{XeF}_6 + \text{F}_2 \rightarrow \text{XeF}_8$	$\approx 100 \text{ mg}$ of solid to	-196
$\text{KrF}_2 + \text{F}_2 \rightarrow \text{KrF}_4$	2 ml of liquid F ₂	
$\text{Ar} + \text{F}_2 \rightarrow$	(or O ₂)	
$\text{Xe} + \text{O}_2 \rightarrow \text{XeO}_3$		

We have thus successfully synthesized the noble gas fluorides characterized to date, with the exception of KrF_4 ⁶ and XeF_8 .⁷ These may conceivably decompose during the irradiations or the infrared measurements. The preparation of the two compounds, however, has

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) D. R. MacKenzie and R. H. Wiswall, Jr., *Inorg. Chem.*, **2**, 1064 (1963); (b) D. R. MacKenzie, *Science*, **141**, 1171 (1963).

(3) (a) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965); (b) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, **42**, 1229 (1965).

(4) I. Sheft, T. M. Spittler, and F. H. Martin, *Science*, **145**, 701 (1964).

(5) 40-Mev α particles were also effective.

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

(7) J. Shvniuk, B. Volavsek, J. Marsel, V. Vrscaj, A. Smalc, B. Frliec, and Z. Zemljic, *Croat. Chem. Acta*, **35**, 81 (1963).

never been reproduced by other workers.^{3a,8} In view of our results, low-temperature proton bombardment should prove generally useful as a technique for the preparation of thermally unstable compounds. Gas

(8) F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Am. Chem. Soc.*, **87**, 25 (1965).

phase irradiations should be of particular value in the synthesis of products less volatile than the reactants.

Acknowledgments.—We are indebted to Messrs. W. J. Brown, R. Smol, and particularly W. D. Riel for their assistance with the experimental work.

Correspondence

Remarks on the Electronic Spectrum of Dibenzenechromium(I) Ion

Sir:

In their discussion of the spectrum of dibenzenechromium(I) iodide, $\text{Cr}(\text{bz})_2\text{I}$, Yamada, *et al.*,^{1,2} reported four intense bands in the ultraviolet and visible spectral region in addition to other weaker bands at longer wavelengths. The spectrum of $\text{Cr}(\text{bz})_2\text{I}$ in aqueous solution is shown in Figure 1a. The band notation is that used by Yamada, *et al.*¹ On the basis of intensity, polarization, and solvent shift, the above-mentioned authors suggested that band IV is due to a $\pi\text{-}\pi^*$ transition within the benzene rings, whereas the other bands were assumed to correspond to transitions involving metal orbitals.

Berry^{3a} approached this subject in a more theoretical way. This author supported Yamada's assignment of band IV with some theoretical evidence, attributing this band to the ${}^1\text{E}_{1u} \leftarrow {}^1\text{A}_{1g} \pi\text{-}\pi^*$ benzene transition, shifted toward higher wavelengths because of the interaction between ring and chromium electrons.

Independently, Feltham⁴ reported an electronic absorption spectrum of $\text{Cr}(\text{bz})_2^+$ ion quite similar to Yamada's $\text{Cr}(\text{bz})_2\text{I}$ spectrum.

While studying the photochemistry of some metal sandwich compounds, we examined the photochemical decomposition of $\text{Cr}(\text{bz})_2\text{I}$ in aqueous solution. The spectral changes during irradiation suggested that band IV was not concerned with the $\text{Cr}(\text{bz})_2^+$ ion. In fact it can easily be shown that *band IV corresponds to the well-known absorption band of the I^- ion*⁵ (Figure 1b). As a matter of fact, the spectrum of $\text{Cr}(\text{bz})_2\text{OH}$ ⁶ does not exhibit such a band (Figure 1c). *This spectrum must be considered the real spectrum of $\text{Cr}(\text{bz})_2^+$ cation.*⁷

In order to verify the assignment of $\text{Cr}(\text{bz})_2\text{I}$ band IV to the I^- ion, we have compared the spectra of I^- ion in water and in ethanol. The maxima were found at 225

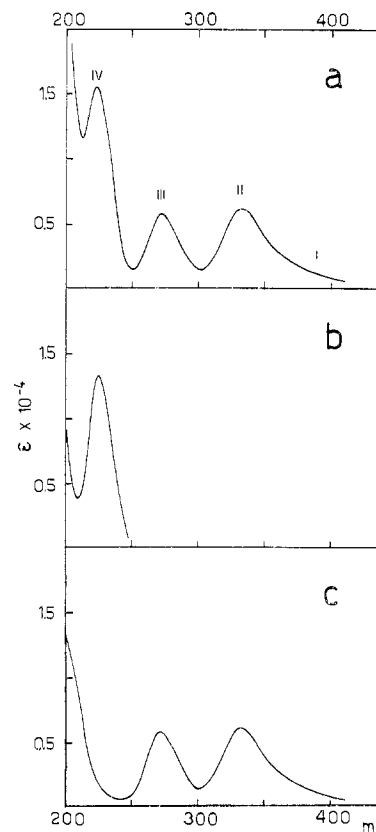


Figure 1.—(a) Spectrum of $\text{Cr}(\text{bz})_2\text{I}$. (b) Spectrum of I^- ion. (c) Spectrum of $\text{Cr}(\text{bz})_2\text{OH}$.

and 221 $\text{m}\mu$, respectively, showing a red shift as observed by Yamada, *et al.*,¹ in the case of $\text{Cr}(\text{bz})_2\text{I}$ band IV.

All the spectra of chromium-arene compounds agree with the above-stated considerations. In fact, all the cationic species (whose spectra were evidently recorded as iodide salts) show a band at about 225 $\text{m}\mu$,⁴ whereas the neutral complexes obviously do not exhibit such a band.^{3b,4} It can also be noted that the band below 200 $\text{m}\mu$ reported by Feltham⁴ as a band of chromium-arene cations very likely corresponds to the iodide absorption band at $\sim 195 \text{m}\mu$.⁵

It must be noted that the erroneous assignment of band IV to a $\pi\text{-}\pi^*$ benzene transition has been taken as proof of considerable localization of π electrons in benzene rings.^{1,3a} Actually, the fact that benzene bands are not substantially shifted toward higher

(1) S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 647 (1957).

(2) S. Yamada, H. Yamazaki, H. Nishikawa, and R. Tsuchida, *ibid.*, **33**, 481 (1960).

(3) (a) R. S. Berry, *J. Chem. Phys.*, **35**, 29 (1961); (b) R. S. Berry, *ibid.*, **35**, 2025 (1961).

(4) R. D. Feltham, *J. Inorg. Nucl. Chem.*, **16**, 197 (1961).

(5) (a) J. Franck and G. Scheiber, *Z. Physik. Chem.*, **A139**, 22 (1928); (b) L. E. Orgel, *Quart. Rev. (London)*, **8**, 422 (1954).

(6) This compound was obtained from $\text{Cr}(\text{bz})_2\text{I}$ by precipitating I^- with fresh Ag_2O .

(7) The absorbance of OH^- ion is negligible at wavelengths higher than 210 $\text{m}\mu$.^{3b}