

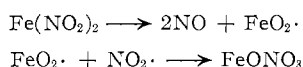
Correspondence

Transition Metal Nitrites and Nitrosyl Nitrites

Sir:

Until very recently, silver nitrite was the only known simple nitrite of any transition metal, and there has been a general belief that such compounds would have low stability. However, the recent preparation of anhydrous nickel nitrite,¹ which is stable at temperatures up to 260°, suggests that the nitrites of other transition metals may be available. This is of particular interest in view of the unexpected properties (such as volatility) observed for anhydrous transition metal nitrates,^{2,3} and the fact that the NO₂ group is usually a stronger ligand than the NO₃ group. We are therefore examining those features which might influence the stability of transition metal nitrites, and wish to report a new reaction of cobalt nitrosyl carbonyl which supports a general pattern of behavior for which limited evidence now exists. It appears that simple metal nitrites will only be stable if a higher valence state of the metal is not readily available; otherwise, ready decomposition to oxynitrites will occur to achieve the more stable valence state of the metal.

Nickel nitrite is formed by a gas phase reaction between nickel carbonyl and nitrogen dioxide, each diluted with argon. Carbonyl groups are removed and the smoke which is formed settles to a pale green deposit of pure Ni(NO₂)₂. As Ni^{II} is the stable valence state for nickel, this product has high stability. In contrast, ferrous nitrite decomposes immediately on formation. Reaction of iron carbonyl vapor with nitrogen dioxide gives a product of composition FeONO₃, containing no nitrite groups,⁴ and the reaction scheme

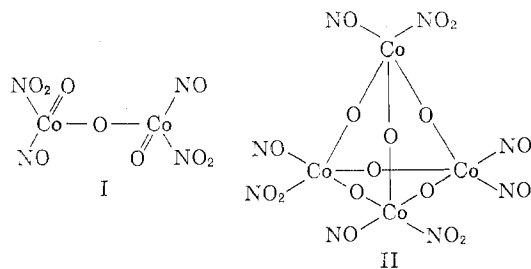


in which FeO₂· radicals combine with NO₂· radicals in the N₂O₄-NO₂ mixture, satisfactorily explains the reaction. Cobalt nitrite, Co(NO₂)₂, is produced by reaction of CO₂(CO)₃ vapor with NO₂, and is stable since the Co^{III} state is not readily available in the absence of complexing.

Using cobalt nitrosyl carbonyl under the same conditions, we have found that the metal-NO bond survives the reaction, and a pale brown compound of empirical formula CO₂(NO)₂(NO₂)₂O₃ is formed, in which cobalt is formally in the +3 oxidation state. (*Anal.* Calcd. for Co₂N₄O₉: Co, 37.1; N, 17.6. Found: C, 37.1; N, 17.3.) The infrared spectrum of the solid shows strong NO bands at 1890 and 1800 cm.⁻¹, and bands

characteristic of covalently bonded NO₂ groups. The compound dissolves in many organic solvents (C₂H₅-OAc, CH₃CN, (CH₃)₂SO, C₂H₄O₂) and in water; the ultraviolet spectrum of the aqueous solution shows an NO₂⁻ peak at 355 mμ, but no NO₃⁻ peak at 302 mμ.

In the reaction of dicobalt octacarbonyl, substitution by two NO₂ groups occurs, but in the nitrosyl complex, substitution by three NO₂ groups is required to bring the metal to the Co^{II} state, and the initial product is therefore believed to be (NO)Co^{II}(NO₂)₃. Decomposition of nitrite groups then occurs (as with Fe(NO₂)₂) to a sufficient extent to achieve oxidation to Co^{III}, yielding the structure unit Co(NO)(NO₂)O_{1.5}. The degree of polymerization has not yet been determined, since the nitrite groups, which are covalently bonded in the solid, ionize in polar solvents. Solutions are initially brown, but change slowly to pink with evolution of nitric oxide. However, only a limited number of possibilities exist for the structure. An infinite polymer would not show rapid solubility in organic solvents such as ethyl acetate. The compound is paramagnetic, with χ_g = 3.98 × 10⁻⁵ c.g.s. unit. The binuclear complex I, in which the cobalt atoms are bridged through a single oxygen atom, involves each Co^{III} atom in a four-coördinate complex, which is an unstable environment for the d⁶ state. A dimer as in I but bridged through all three oxygen atoms is possible, but in view of the manner in which cobalt atoms assume tetrahedral disposition in tetracobalt dodecacarbonyl,⁵ we prefer to regard the compound as the tetramer II.



(5) P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959).

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Xenon Hexafluoride

Sir:

The recent synthesis of xenon tetrafluoride,^{1,2} by heating xenon-fluorine mixtures at 400° in a sealed nickel tube, suggested that pressure-temperature

(1) C. C. Addison, B. F. G. Johnson, N. Logan, and A. Wojcicki, *Proc. Chem. Soc.*, 306 (1961).

(2) C. C. Addison and B. J. Hathaway, *J. Chem. Soc.*, 3099 (1958).

(3) C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 51 (1958).

(4) C. C. Addison, B. F. G. Johnson, and N. Logan, unpublished results.

(1) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(2) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

measurements might indicate the minimum temperature at which combination occurs. It also was considered that higher fluorides might be capable of existence at temperatures below 400°. Xenon-fluorine mixtures were, therefore, introduced into a 1500 cc. prefluorinated nickel vessel and the pressure-temperature dependence followed from room temperature up to 720°K. The mixtures followed ideal gas behavior up to 390°K., when a pressure decrease began to occur.

The pressure decreased rather rapidly in the temperature range 480 to 520°K. until the total decrease was about 2.5 times the pressure which would have been due to xenon alone. The temperature then was raised gradually and above 560°K. the rate of increase in pressure with temperature was abnormally large, thereby suggesting the dissociation of a molecular species. At about 710°K. the pressure *vs.* temperature curve merged into that expected for a mixture of F₂ with XeF₄. At 400° most of the xenon apparently would have been present as XeF₄.

As pressure would be expected to favor the formation of higher fluorides of xenon, three fluorine-xenon mixtures with mole-ratios varying from 4/1 to 20/1 were sealed in prefluorinated nickel tubes fitted with Hoke needle valves and brass 10/30 connections. These were heated at 500°K. for periods ranging from 1 to 10 days. Estimated pressures, in atmospheres, for runs I, II, and III were, respectively, 500, 150, and 25. They were then quenched in cold water, and the excess fluorine was removed by pumping at liquid nitrogen temperature. The tube then was warmed to room temperature and later pumped while at -78°. The gain in weight of the nickel reaction tubes permitted a calculation of the empirical formula of the xenon fluoride formed under the reaction conditions.

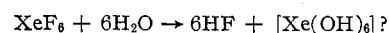
Samples from the reaction tubes were condensed in glass bulbs, under vacuum transfer conditions, forming a white solid. After these bulbs had warmed to room temperature the gas phase had a pale greenish yellow color which faded away in about 5 min. The remaining solid slowly became a liquid.

A sample was allowed to react either with water or potassium iodide solution by adding the air-free liquid to the bulb. After reaction with water the amount of xenon which could be removed by pumping was very small, but the solution had powerful oxidizing properties—much more so than hydrogen peroxide solutions of comparable strength. These solutions also failed to give the typical titanium-hydrogen peroxide test. Such solutions were analyzed for fluoride and hydrogen ions, and also for oxidizing equivalents. On the other hand, the reactions with potassium iodide liberated iodine. Gas was evolved and xenon was recovered nearly quantitatively. Some oxygen also was released in this reaction. After titration of free iodine, potassium iodate was added but no further iodine was liberated, indicating the absence of free acid. The inability to recover xenon by pumping after hydrolysis of samples suggested that the xenon was bound in solution, possibly as a xenic acid, Xe(OH)₆. This behavior is similar to

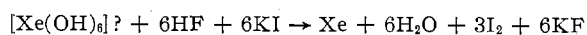
that reported for xenon tetrafluoride.^{1,2} Such an acid, if it existed, must have been very weak, because it was not neutralized when titrating the solution with 0.1 *N* sodium hydroxide to the phenolphthalein end point. A graph of pH *vs.* volume of added base failed to indicate a wave corresponding to the neutralization of an acid in the pH region 8 to 11.

In the fluoride analyses the sodium alizarin sulfonate indicator was decolorized while the solution contained oxidizing power. It was, therefore, necessary to add up to four times the normal amount of indicator solution before carrying out the titrations.

The observed behavior with water and aqueous potassium iodide solutions is consistent with the equations



(and side reactions giving HF and a small amount of oxygen).



The ratio of xenic acid to oxygen produced was variable as indicated below by the various numbers of oxidizing equivalents in solution formed per mole of XeF₆ hydrolyzed.

(a) Composition of higher xenon fluoride by synthesis. (Theoretical % F for XeF₆ = 46.5.)

Wt. of xenon taken, g.	0.409	0.455
Wt. of fluoride formed, g.	0.758	0.826
% fluorine by weight increase	46.05	45.0

(b) Xenon recovered after reaction with KI solution. (Theoretical for Xe in XeF₆ = 53.5%.)

Wt. of sample, g.	0.0607	0.2060
Wt. Xe recovered, g.	0.0327	0.1093
% Xe	53.8	53.1

(c) Analysis of higher xenon fluoride by determination of F⁻ (by thorium nitrate titration) and of H⁺; determination of oxidizing equivalents remaining after hydrolysis.

Batch of xenon fluoride	Wt. of sample, g.	% fluorine based on		Equiv. ox. agent in soln. per mole of XeF ₆ used
		F ⁻ detn.	H ⁺ detn.	
I	0.1260	44.5	47.0	5.25
	.0392	46.9	47.2	5.31
	.0525	45.4	46.3	5.78
II	.138	45.9	45.1	5.45
	.197	43.4	46.1	5.72
III	.1023	45.6	47.2	5.54

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