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 NO_2 group is usually a stronger ligand than the NO_3 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.

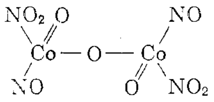
Nickel nitrite is formed by a gas phase reaction between nickel carbonyl and nitrogen dioxide, each diluted with argon. Carbonyl groups are removed and the smoke which is formed settles to a pale green deposit of pure $Ni(NO_2)_2$. As Ni^{II} is the stable valence state for nickel, this product has high stability. In contrast, ferrous nitrite decomposes immediately on formation. Reaction of iron carbonyl vapor with nitrogen dioxide gives a product of composition $FeONO_3$, containing no nitrite groups,[4] and the reaction scheme

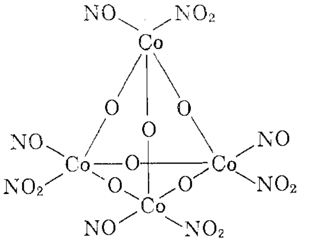
$$Fe(NO_2)_2 \longrightarrow 2NO + FeO_2\cdot$$
$$FeO_2\cdot + NO_2\cdot \longrightarrow FeONO_3$$

in which $FeO_2\cdot$ radicals combine with $NO_2\cdot$ radicals in the N_2O_4–NO_2 mixture, satisfactorily explains the reaction. Cobalt nitrite, $Co(NO_2)_2$, is produced by reaction of $CO_2(CO)_8$ vapor with NO_2, 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 $CO_2(NO)_2(NO_2)_2O_3$ is formed, in which cobalt is formally in the +3 oxidation state. (*Anal.* Calcd. for $Co_2N_4O_9$: 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 NO_2 groups. The compound dissolves in many organic solvents (C_2H_5-OAc, CH_3CN, $(CH_3)_2SO$, $C_2H_4O_2$) and in water; the ultraviolet spectrum of the aqueous solution shows an NO_2^- peak at 355 mμ, but no NO_3^- peak at 302 mμ.

In the reaction of dicobalt octacarbonyl, substitution by two NO_2 groups occurs, but in the nitrosyl complex, substitution by three NO_2 groups is required to bring the metal to the Co^{II} state, and the initial product is therefore believed to be $(NO)Co^{II}(NO_2)_3$. Decomposition of nitrite groups then occurs (as with $Fe(NO_2)_2$) to a sufficient extent to achieve oxidation to Co^{III}, yielding the structure unit $Co(NO)(NO_2)O_{1.5}$. 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 $\chi_g = 3.98 \times 10^{-5}$ 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 d^6 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.


I


II

---

[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.

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

DEPARTMENT OF CHEMISTRY, C. C. ADDISON
THE UNIVERSITY, D. SUTTON
NOTTINGHAM, ENGLAND

RECEIVED AUGUST 28, 1962

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. 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).