1380 and 1105 cm.$^{-1}$ is consistent for a compound with one NO group and a coordinated nitrito group.[10] It is also identical with the compound obtained from the reaction of $AgNO_2$ with $NiBrNO[(C_6H_5)_3P]_2$.[8]

When nitric oxide at atmospheric pressure was treated with $Ni(CO)_3(C_6H_5)_3P$ in hexane and then extracted with methanol, the compound $Ni(OCH_3)(NO)(C_6H_5)_3P \cdot 2CH_3OH$ resulted. The compound was found to consume one equivalent of H^+ per mole of nickel, thus leading to its formulation as the monomethoxide. The air-sensitive dark purple compound is very similar to the bis(triphenylphosphine)nitrosylnickel compounds described above. Its NO absorption (1715 cm.$^{-1}$) is almost identical with that of $Ni(OH)(NO)[(C_6H_5)_3P]_2$, while all other features of the infrared spectra are due to triphenylphosphine or methanol.

Conclusions

The reaction of nitric oxide with all of the nickel(0) compounds used in these experiments leads to complexes of $(NiNO)^+$. The complexity of the system is thus due to the presence of a variety of more or less stable anions. The anions which have been identified as resulting from this reaction are $N_2O_2^{2-}$, O^{2-} (or OH^-), OCH_3^-, and NO_2^-. No evidence could be found for the presence of NO_3^-, $N_2O_3^{2-}$, CO_3^{2-}, or HCO_3^-.

The primary reaction in the absence of NO_2 is

$$4NO + 2Ni(CO)_2[(C_6H_5)_3P]_2 \longrightarrow (NiNO[(C_6H_5)_3P]_2)_2N_2O_2 + 4CO \tag{1}$$

followed by

$$(NiNO[(C_6H_5)_3P]_2)_2N_2O_2 \longrightarrow N_2O + (NiNO[(C_6H_5)_3P]_2)_2O \tag{2}$$

The oxide reacts with water (or alcohol)

$$(NiNO[(C_6H_5)_3P]_2)_2O + H_2O \longrightarrow 2Ni(OH)(NO)[(C_6H_5)_3P]_2 \tag{3}$$

In the presence of NO_2, one gets only the nitrite

$$Ni(CO)_2[(C_6H_5)_3P]_2 + 4NO \xrightarrow{NO_2} NiNO_2(NO)[(C_6H_5)_3P]_2 + N_2O \tag{4}$$

The stoichiometry of reactions 1 and 2 has been quantitatively confirmed by gas–solid chromatography of the residual gases from these reactions. Reaction 4 has been established by the isolation and analysis of nitrito bis(triphenylphosphine)nitrosylnickel.

No stable dinitrosyls were formed during these reactions as had been reported earlier,[9] although their existence as unstable intermediates is suggested both by the stoichiometry and by the isolation of an unstable nitrosyl hyponitrite from the reaction.

Acknowledgments.—The author wishes to thank Frank Kabot and Robert Reitz of the Physical Measurements group of this Institute for the chromatographic analysis of these gases, and especially Earle Hewitt for his experimental assistance.

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CONTRIBUTION FROM THE MELLON INSTITUTE,
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Metal Nitrosyls. III. The Reaction of Nitric Oxide with Nickel Carbonyl[1]

BY ROBERT D. FELTHAM AND JONATHAN T. CARRIEL

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The reaction of nitric oxide with nickel carbonyl in polar and nonpolar solvents leads to a variety of compounds derived from the species $[NiNO]^+$. When this reaction is carried out in the presence of cyclopentadiene there is almost complete conversion to nitrosylcyclopentadienylnickel.

Other workers in this field have variously described the complexes obtained from the reaction of nitric oxide with nickel carbonyl in polar solvents (particularly methanol and ethanol) as being $[NiNO]^+$ (ref. 2), $[NiNO]^{2+}$ (ref. 3), or $[NiNO]^{3+}$ (ref. 4). The two main difficulties encountered by earlier workers were (1) under their conditions a mixture of salts of $[NiNO]^+$ was obtained and (2) in the absence of stabilizing ligands these compounds slowly decompose.

The results from the reaction between nitric oxide and phosphine-substituted nickel carbonyls[5] suggest that these difficulties might be overcome by rapid reaction at superatmospheric pressure.

Experimental

Apparatus and Materials.—For the high pressure reactions a 1-l. "Magnedash" autoclave with a glass liner was used. The nickel carbonyl was used as supplied by The International Nickel Company, Inc. The nitric oxide supplied by Matheson was cooled to −78° in a Dry Ice trap to remove the traces of NO_2 which are present in the nitric oxide. All the solvents and amines used were dried over $^1/_{16}$-in. pellets of Linde Molecular Sieve No. 4A. Enjay dicyclopentadiene was cracked to the monomer at 260° and stored at −78°. The gases were analyzed by gas–solid chromatography,[6] while $Ni(CO)_4$ was analyzed by gas–liquid chromatography using a 3-m. column containing 15% P.E.G. 1500 supported on 30–60 mesh firebrick at 78° with a helium flow of 48 ml./min. All elemental analyses were done by

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[1] This research was sponsored by The International Nickel Company, Inc.

[2] J. S. Anderson, *Z. anorg. allgem. Chem.*, **229**, 357 (1936).

[3] H. Reihlen, *ibid.*, **230**, 223 (1937).

[4] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

[5] R. D. Feltham, *Inorg. Chem.*, **3**, 119 (1964).

[6] M. Lefort and X. Tarrago, *J. Chromatog.*, **2**, 218 (1959).

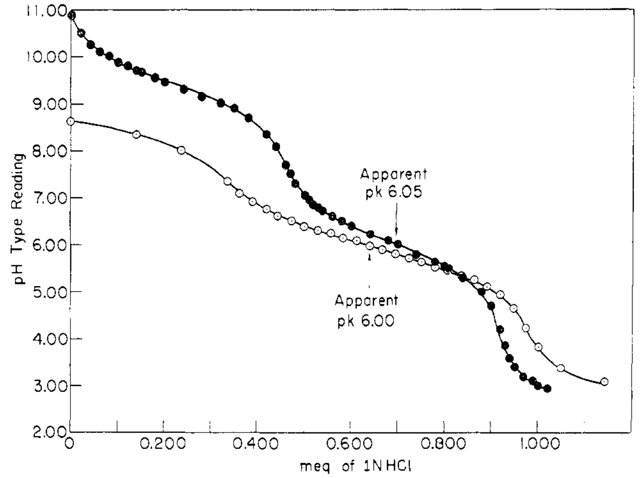

Fig. 1.—Titration of NO_2^- and $(C_2H_5)_2NH$ with aqueous 1 *N* HCl: ● represents a solution of 0.487 mmole of $(C_2H_5)_2NH$ and 0.494 mmole of KNO_2 in 60 ml. of 95% ethanol; ⊙ represents a 2.5-ml. aliquot from reaction 5 diluted with 60 ml. of 95% ethanol.

Huffman Microanalytical Laboratories, Wheatridge, Colorado.

(1) **Reaction in Cyclohexane.**—A solution of 85 mmoles (11 ml.) of $Ni(CO)_4$ in 200 ml. of dry cyclohexane was treated with 578 mmoles of NO at 23–29° for 5 min. The pressure was about 275 p.s.i.a. Gas samples were taken and analyzed. The gas analyses indicate that 4.0 moles of CO and 0.79 mole of N_2O are evolved for every 4.0 moles of NO which is used. The autoclave was purged with nitrogen and the product, consisting of a colorless solution and a blue solid, was discharged under nitrogen. Most of the solvent was removed by filtration. Since the compound decomposes if heated, it was dried at room temperature under vacuum (0.01 mm.). Unfortunately this treatment does not remove all of the hydrocarbons from the product.

A film of this solid was prepared by making a slurry in cyclohexane and dropping this slurry onto a plate of NaCl under a flow of N_2. The cyclohexane evaporated, leaving the blue product as a solid film. An infrared spectrum was taken of this film and also of Nujol and halocarbon mulls. When this film has been carefully prepared, the absorption bands due to hydroxyl groups are absent. However, a weak CH absorption band is always present at 2950 $cm.^{-1}$. There is a strong nitrosyl band at 1845 $cm.^{-1}$ and several broad bands at 1520, 1370, 1330, 1220, 1070, and 845 $cm.^{-1}$ which are typical of nitrito and bridging nitrito groups.[7]

This blue solid is extremely reactive. When treated with water in air it ignites with a yellow flame and liberates oxides of nitrogen. A nitrogen analysis of this compound was attempted by the usual Dumas method. However, this product reacts with dry CO_2 even at room temperature. In order to analyze this compound for nitrogen, a weighed sample was placed in a piece of glass tubing of small diameter, and the ends were sealed with paraffin. This could then be placed in a stream of CO_2 without decomposition. When the sample was heated, the paraffin melted and nitrogen was determined using the usual Dumas technique.

$Ni(NO_2)(NO)$: color, light blue. *Anal.* Calcd.: N, 20.8; Ni, 43.6; O, 35.6. Found: C, 4.36; H, 1.82; N, 19.6; Ni, 42.38; O, 36.9.

(2) **Reaction of $Ni(NO_2)(NO)$ with Triphenylphosphine.**—A small amount of $Ni(NO_2)(NO)$ was dissolved in ethanol and treated with a solution of triphenylphosphine in ethyl acetate. After three recrystallizations from ethyl acetate the product was found to be identical with $NiNO_2NO[(C_6H_5)_3P]_2$.[8]

$Ni(NO_2)(NO)[(C_6H_5)_3P]_2$: color, blue; m.p. 206–210. *Anal.* Calcd.: C, 65.5; H, 4.59; N, 4.25; Ni, 8.91; O, 8.28; P, 9.40. Found: C, 65.2; H, 4.68; N, 4.13; Ni, 9.4; O, 7.52; P, 9.3.

(3) **Reaction in Ethanol.**—A solution of 11 ml. of $Ni(CO)_4$ (85 mmoles) in dry ethanol was treated with 436 mmoles of NO at 230 p.s.i.a. for 7 min., while the temperature rose from 24 to 39°. At the end of this time the gas was sampled. It was found that 3.9 moles of CO and 1.38 moles of N_2O were evolved for every 4.0 moles of NO that reacted. Ten ml. of this solution was treated with triphenylphosphine, which gave a mixture of $Ni[CO]_2[(C_6H_5)_3P]_2$ and $Ni(NO_2)(NO)[(C_6H_5)_3P]_2$ as identified by their infrared spectra. Nickel analysis of an aliquot of the solution showed that 3.97 moles of NO had reacted for every mole of $Ni(CO)_4$ that reacted. A nitrogen analysis of an aliquot of the solution showed there to be at least 1.6 g.-atoms of nitrogen per mole of nickel reacted. Unfortunately this nitrogen analysis was not done immediately and there was some decomposition.

(4) **Reaction in Cyclohexane in the Presence of Amine and Cyclopentadiene.**—A solution consisting of 11 ml. of $Ni(CO)_4$ (85 mmoles), 20 ml. of diethylamine (215 mmoles), 20 ml. of cyclopentadiene (250 mmoles), and 200 ml. of cyclohexane was treated with 560 mmoles of NO at 260 p.s.i.a. for 3.5 min. The temperature rose from 20 to 57°. A gas sample was taken and it was found that 3.94 moles of CO and 1.05 moles of N_2O were evolved for every 4.0 moles of NO that reacted. The system was purged with N_2 and the solution filtered. The resultant red solution was analyzed and found to contain 37.0 mmoles of $NiNOC_5H_5$ (44% yield based on $Ni(CO)_4$). This compound was identified by distillation and its infrared spectrum.[9]

(5) **Reaction in Ethanol in the Presence of Amine and Cyclopentadiene.**—A solution of 11 ml. of $Ni(CO)_4$ (85 mmoles), 10 ml. of diethylamine (97.4 mmoles), and 15 ml. of cyclopentadiene (193 mmoles) in 200 ml. of absolute ethanol dried over molecular sieve were treated with 386 mmoles of NO at about 180 p.s.i.a. The initial temperature was 27°, rising to a maximum temperature of 42.5°. After 20 min. a gas sample was taken and it was found that 3.8 moles of CO and 1.1 moles of N_2O were evolved for every 4.0 moles of NO that reacted. The solution was purged with N_2 and filtered. Analysis of the liquid product by gas–liquid chromatography showed 10 mmoles of $Ni(CO)_4$ and 26 mmoles of diethylamine were left unreacted while 69 mmoles (92% based on the $Ni(CO)_4$ that reacted) of $NiNOC_5H_5$ were produced.

Results and Discussion

The results of all the above reactions between NO and $Ni(CO)_4$ are summarized as shown in eq. 1.

$$Ni(CO)_4 + 4NO \longrightarrow NiNO_2NO + 4CO + N_2O \quad (1)$$

The results of the gas analysis agree closely with this stoichiometry in every case. The reaction of $NiNO_2NO$ in alcohol with cyclopentadiene and diethylamine should then be

$$NiNO_2NO + (C_2H_5)_2NH + C_5H_6 \longrightarrow NiNOC_5H_5 + (C_2H_5)_2NH_2NO_2 \quad (2)$$

leading to an over-all reaction

$$Ni(CO)_4 + 4NO + (C_2H_5)_2NH + C_5H_6 \longrightarrow NiNOC_5H_5 + N_2O + 4CO + (C_2H_5)_2NH_2NO_2 \quad (3)$$

The ethanol reaction was found to consume 81.4 mmoles of diethylamine (*vs.* 75 mmoles of $Ni(CO)_4$ reacted). The resultant solution was also titrated with 1 *N* HCl. A typical titration is shown in Fig. 1 along with the titration of a solution of a mixture of KNO_2 and diethylamine. These solutions containing $(C_2H_5)_2NH_2NO_2$ are unstable so that the titrations are somewhat unreliable. However, good qualitative

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[7] J. Chatt, *et al.*, *J. Chem. Soc.*, 4073 (1959).

[8] R. D. Feltham, *Inorg. Chem.*, **3**, 116 (1964).

[9] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

agreement was found between the amount of $Ni(CO)_4$ that reacted and the NO_2^- formed. The presence of NO_2^- was also confirmed by the isolation of $NiNO_2NO[(C_6H_5)_3P]_2$ from the reaction of triphenylphosphine with these blue materials. Some material is always formed (5–10%) which is unreactive with cyclopentadiene. Its composition could not be determined but seemed to consist of Ni(II), NO_2^-, OH^-, and $N_2O_2^{2-}$.

The results of an experiment which was identical with (5) above are shown in Fig. 2. These results were obtained by taking several small samples of the gas in the autoclave during the course of the reaction. It was difficult to get many gas samples when only a little of the nickel carbonyl had reacted since 50% reacted within 1 min. Considering the analytical difficulties, these results closely correspond to eq. 1.

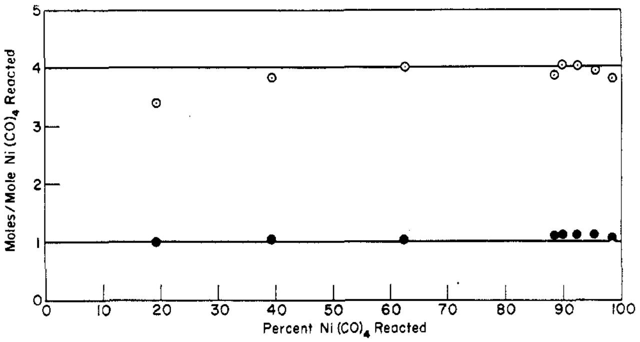

Fig. 2.—Experimental points and calculated values for the reaction of NO with $Ni(CO)_4$: —•— represents the theoretical values according to eq. 1 or eq. 3; ○ represents the experimental results for NO; ● represents the experimental results for N_2O.

The results obtained in cyclohexane and ethanol show that the solvent plays no role in the reaction (eq. 1). The only difference in the products obtained in cyclohexane and ethanol is due to solvation. In ethanol, the product is solvated and soluble but the product is not solvated or soluble in cyclohexane. The compound which is obtained from cyclohexane analyzed reasonably well for $Ni(NO_2)(NO)$ and its infrared spectrum shows that it is definitely a nitrosyl. Due to its reactivity the compound was not further characterized. It undoubtedly has a structure more complex than the simple monomer. Its nitrosyl frequency at 1845 cm.$^{-1}$ along with its composition suggest that it is similar to the nitrosyl nickel halides $(NiBrNO)_x$ described by Jahn and Hieber.[10] It has been reported[8] that solutions of this compound in alcohol are unstable. However, our experience has shown that when oxygen and/or water are absolutely excluded these blue solutions can be kept for months without change, but when exposed to traces of water or oxygen they decompose rapidly.

Conclusions

When nickel carbonyl is treated with nitric oxide at superatmospheric pressure the compound $Ni(NO_2)(NO)$ is almost exclusively obtained. This is a mononitrosyl similar to those previously obtained from the reaction between nitric oxide and dicarbonylbis(triphenylphosphine)nickel.[5] Thus the only nitrosyl nickel complexes which result from the reactions between Ni(0) complexes and nitric oxide are of the type $[NiNO]^+$.

Acknowledgment.—The authors thank Earle Hewitt for his experimental assistance and the Physical Measurements group of this Institute for the chromatographic analyses.

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[10] A. Jahn and W. Hieber, *Z. anorg. allgem. Chem.*, **301**, 301 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Metal Derivatives of Arylazopyrazolone Compounds. VI. Molarity Quotients of Azo Derivatives of 1-Phenyl-3-methyl-5-thiopyrazolone

BY FRED A. SNAVELY, WALTER S. TRAHANOVSKY,[1] AND FRED H. SUYDAM

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The relative formation constants of the metal derivatives of some azo derivatives of 1-phenyl-3-methyl-5-thiopyrazolone have been measured in 75 vol. % dioxane. The decreasing order of stability (K_1) for the bivalent derivatives of 1-phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone is Cu > Ni > Cd > Co > Zn, which compares with Cu > Ni > Co > Zn for the analogous derivative of 5-pyrazolone. The azothiopyrazolones show a stronger affinity for metal ions than their oxygen analogs. Infrared and chemical data favor a thiopyrazolone structure for the azo derivatives analogous to the azopyrazolone structure for the 5-pyrazolone series. The C=S peak for the chelating agents is assigned from 1240 to 1200 cm.$^{-1}$. Metal derivatives were prepared and characterized.

Introduction

This report is a continuation of our study on the relative bonding of oxygen, sulfur, and nitrogen to metal ions. Recently we reported data[2,3] on the relative coordination affinities of oxygen-, sulfur-, and nitrogen-containing chelating agents in which methoxy,

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[2] F. A. Snavely and G. C. Craver, *Inorg. Chem.*, **1**, 890 (1962).

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