

Molecules", Prentice-Hall: Englewood Cliffs, N.J., 1939; (a) pp 411-415, (b) pp 450-453.

- (9) It is assumed that the vibrational energy  $V_B$  of  $Br_2$  follows a Boltzmann distribution and thus can be described in terms of a vibrational temperature  $T_B$ . It is further assumed that  $V_B$  is related to  $T_B$  according to the formula for a harmonic oscillator.
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- (15) It is assumed that  $E_{abs}$  in a given experiment is proportional to the IR dose delivered at time  $t$ , because in previous work  $E_{abs}/\text{dose}$  was practically constant at a given  $c$ , for a threefold variation of dose: Grunwald, E.; Olszyna, K. J.; Dever, D. F.; Knishkowsky, B. *J. Am. Chem. Soc.* **1977**, *99*, 6521-6526.

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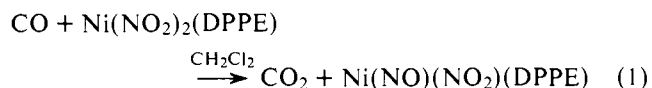
### Oxidation of CO to $CO_2$ by Ni- $NO_2$ Complexes: a Mechanistic Study<sup>1</sup>

Sir:

The oxidation of carbon monoxide by nitrite is a thermodynamically favored,<sup>2</sup> but kinetically slow,<sup>3</sup> process in the absence of transition metal complexes. However, when complexes of nickel, iron, cobalt, ruthenium, rhodium, or iridium are present, carbon monoxide reacts readily with nitrite forming carbon dioxide and the corresponding transition metal-nitrosyl complex.<sup>4</sup> The present kinetic study was undertaken to explore the specific role played by transition metal complexes in promoting the oxidation of carbon monoxide by nitrite.

The nickel complexes,  $Ni(NO_2)_2L_2$ , were selected for these investigations. In their report of the reaction between  $Ni(NO_2)_2(PEt_3)_2$  and CO, Booth and Chatt<sup>4a</sup> found that the reaction was rapid at ambient conditions and produced the reduced nickel-nitrosyl complex,  $Ni(NO)(NO_2)(PEt_3)_2$ , in good yield. However, these authors also found this  $\{NiNO\}^{10}$  product<sup>5</sup> to be air sensitive and difficult to purify. Although  $CO_2$  was presumed to be the oxidized product, it was not identified in the reaction mixtures. Consequently, several  $Ni(NO_2)_2L_2$  complexes have been prepared and their reactions with CO examined.<sup>6</sup> Among these complexes,  $Ni(NO_2)_2(DPPE)^7$  has the combination of solubility, reaction rates, and ease of product isolation most suited for the initial studies reported here.

The reaction of  $Ni(NO_2)_2(DPPE)$  with carbon monoxide in dry, oxygen-free dichloromethane produced a deep purple solution from which a dark blue microcrystalline complex,  $Ni(NO)(NO_2)(DPPE)$ , was isolated in nearly quantitative yield. The compound was characterized by elemental analysis and IR and visible-UV spectroscopy.<sup>8a</sup> The  $CO_2$  evolved in this reaction was identified by IR spectroscopy and gas chromatography and analyzed by standard vacuum line techniques.<sup>8b</sup> The stoichiometry corresponds to reaction 1:



No evidence for nickel species other than those in reaction 1 was obtained from spectroscopic examination of the reacting solutions.

The kinetic features of this reaction in  $CH_2Cl_2$  were obtained at 20 °C by following the appearance of the absorption

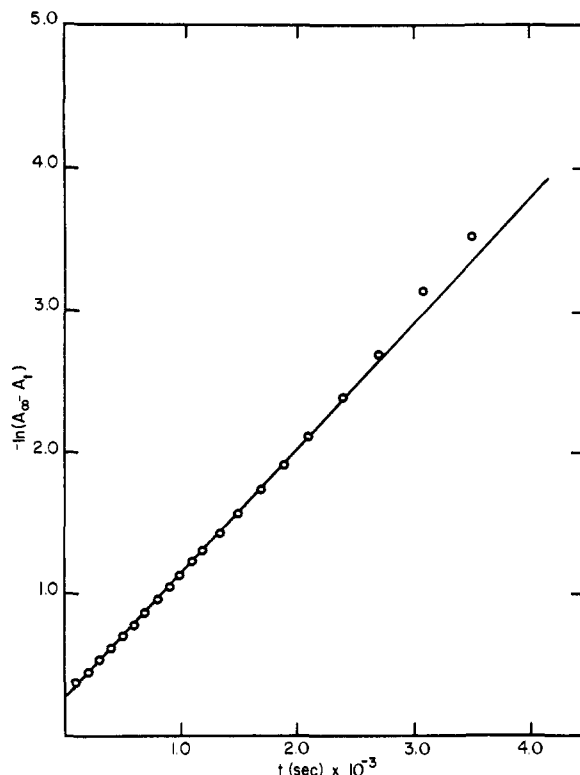


Figure 1. Plot of  $-\ln(A_\infty - A_t)$  vs.  $t$  at 570 nm for the reaction of  $Ni(NO_2)_2(DPPE)$  with CO in  $CH_2Cl_2$  at 20.0 °C.

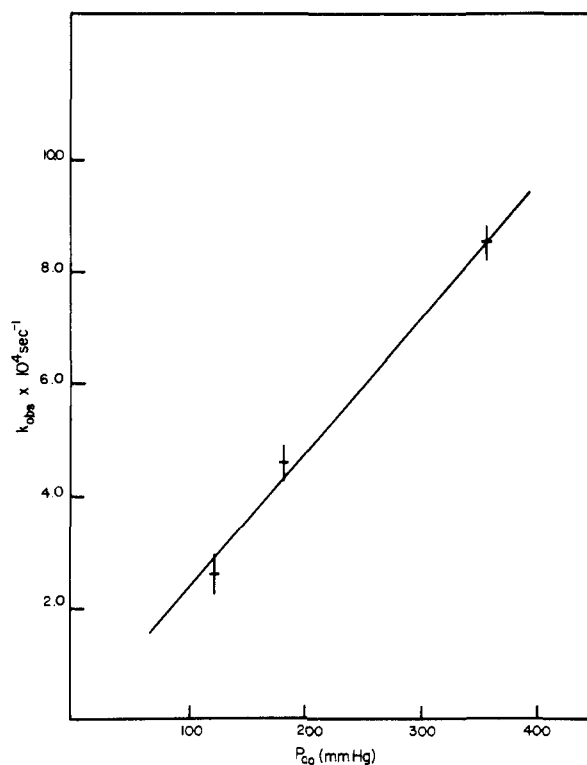
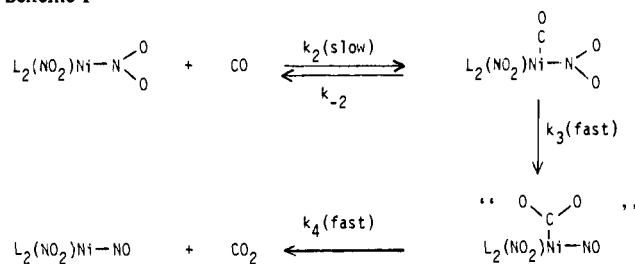


Figure 2. Dependence of  $k_{obsd}$  on  $p_{CO}$  (20.0 °C,  $CH_2Cl_2$ ) for the reaction of  $Ni(NO_2)_2(DPPE)$  with CO.

band of the  $\{NiNO\}^{10}$  product at 570 nm. The reaction rate was determined at several pressures with CO present in a three- to tenfold excess. Under these conditions, the reaction is first order in  $Ni(NO_2)_2(DPPE)$ , while  $k_{obsd}$  is linearly dependent upon  $p_{CO}$  (Figures 1 and 2). The overall reaction is second order, and there is no evidence for a first-order term in the rate law, since, within experimental error, the plot of  $k_{obsd}$  vs.  $p_{CO}$

Scheme I

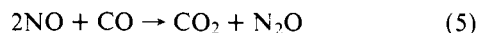


has a zero intercept (Figure 2). Addition of the free-radical inhibitor, 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide, had no effect on the rate of the reaction. Thus, the rate law,  $-d[\text{Ni}(\text{NO}_2)_2(\text{DPPE})]/dt = k_2[\text{Ni}(\text{NO}_2)_2(\text{DPPE})][\text{CO}]$ , is applicable with a value of  $2.1 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $k_2$  at 20 °C.

It was concluded that this reaction is associative, which is typical for square planar complexes of nickel(II).<sup>9</sup> The proposed mechanism for this reaction, based on these results and other chemical properties of square planar  $\text{NiX}_2\text{L}_2$  complexes discussed below, is outlined in Scheme I. In this mechanism, the rate-determining step is the formation of the five-coordinate monocarbonyl complex,  $\text{Ni}(\text{NO}_2)_2(\text{CO})(\text{DPPE})$  (reaction 2), followed by the transfer of an oxygen atom to CO (reaction 3), and terminated by the loss of  $\text{CO}_2$  (reaction 4). The isolation and characterization of  $\text{NiBr}_2(\text{CO})(\text{PMe}_3)_2$  reported recently by Saint-Joly et al.<sup>10</sup> show that square planar nickel complexes of the type  $\text{NiX}_2\text{L}_2$  will indeed add one CO molecule. However, in the absence of an oxidizing  $\text{NO}_2$  ligand, no further reaction of CO takes place and the five-coordinate monocarbonyl complex can then be isolated. When the  $\text{NO}_2$  ligand is present, an intramolecular attack on the CO ligand analogous to that found for the reaction between the isoelectronic  $\text{NO}^+$  ligand and the nitro group of *cis*- $[\text{Fe}(\text{NO})(\text{NO}_2)(\text{S}_2\text{CNMe}_2)_2]$  which we reported earlier<sup>1</sup> can take place. The oxygen atom transfer from  $\text{NO}_2$  to CO would then produce an unstable intermediate or transition state similar to the C-bonded  $\text{CO}_2$  complex of Co(I), whose structure was recently reported.<sup>11</sup>

An alternative mechanism in which CO attacks the oxygen atom of the coordinated  $\text{NO}_2$  group is also consistent with the observed rate law.<sup>12</sup> However, this mechanism provides a less than satisfactory explanation of the lack of reaction between  $\text{NO}_2^-$  and CO in the absence of transition metals and of the dependence of the rate of reaction 1 on L.<sup>13</sup> In contrast, Scheme I requires the rate of formation of  $\text{Ni}(\text{NO}_2)_2(\text{CO})\text{L}_2$  to be dependent upon the electronic and steric requirements imposed by L.<sup>14</sup> Experiments in progress are designed to detect the five-coordinate intermediate required by Scheme I. It is also worth noting that these nickel complexes are potential homogeneous catalysts for the reaction between  $\text{O}_2$  and CO at subatmospheric pressure, since we have found that  $\text{O}_2$  will oxidize  $\text{Ni}(\text{NO})(\text{NO}_2)(\text{DPPE})$  to  $\text{Ni}(\text{NO}_2)_2(\text{DPPE})$ .<sup>15</sup>

Another oxidation of carbon monoxide catalyzed by transition metals (reaction 5) has been extensively studied:<sup>16</sup>



Although reaction 5 is complicated and consists of several steps, the transfer of at least one oxygen atom is required. One of the possible mechanisms proposed for this reaction involves the transfer of an oxygen atom from a coordinated nitro group as one of the key reactions.<sup>17</sup> The present study shows that the nitro group can transfer an oxygen atom directly to carbon monoxide, a step which may also play a role in the catalysis of the CO/NO reaction.

**Note Added in Proof.** A recent study using  $^{18}\text{O}$ -labeled

*trans*- $[\text{Ni}(\text{NO}_2)_2(\text{PEt}_3)_2]$  has shown that  $-\text{NO}_2$  is the oxygen source for  $\text{CO}_2$  production. The observed  $^{18}\text{O}$  enrichment of product  $\text{CO}_2$  is consistent with Scheme I, and a similar mechanism was independently proposed by Doughty et al.<sup>18</sup>

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## References and Notes

- (1) For the previous paper in this series, see O. A. Ieperuma and R. D. Feltham, *Inorg. Chem.*, **16**, 1876 (1977).
- (2) The calculated value of  $\delta H^\circ$  for the reaction of CO with  $\text{NO}_2^-$  in aqueous solution,  $2\text{CO}(\text{g}) + 2\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HCO}_3^-(\text{aq}) + \text{N}_2\text{O}(\text{g})$ , is  $-585.8 \text{ kJ}$ .
- (3) No reaction was observed between  $\text{NaNO}_2$  (0.11 M) and CO (1 atm) in water or between  $(\text{Et}_4\text{N})(\text{NO}_2)$  ( $2.2 \times 10^{-1} \text{ M}$ ) and CO (1 atm) in dichloromethane over a 2-h period. A modest search of the literature disclosed no reference to this reaction.
- (4) (a) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099; (b) K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Commun.*, 1500 (1970); (c) W. Manchot and A. Waldmuller, *Chem. Ber.*, **59**, 2363 (1926); (d) W. Hieber and J. S. Anderson, *Z. Anorg. Allgem. Chem.*, **208**, 238 (1932); (e) W. Hieber and H. Beutner, *Z. Naturforsch.*, **B**, **15**, 323 (1960); (f) W. Hieber and J. S. Anderson, *Z. Anorg. Allgem. Chem.*, **221**, 132 (1933).
- (5) The  $[\text{MNO}]^n$  notation is that of J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
- (6) The nickel compounds  $\text{Ni}(\text{NO}_2)_2\text{L}_2$  were prepared and their reactions with CO noted: L is  $1/2(\text{DPPE})$ ,  $\text{PMe}_2\text{Ph}$ , and  $1/2(\text{Ph}_2\text{PCHCHPh})_2$ . Each of the compounds has been characterized by satisfactory elemental analyses and by IR and visible-UV spectroscopy.
- (7) DPPE is 1,2-bis(diphenylphosphino)ethane.
- (8) Elemental analyses. Found (calcd) for  $\text{Ni}(\text{NO}_2)_2(\text{DPPE})$ : C, 56.71 (56.86); H, 4.24 (4.37); N, 4.88 (5.10); O, 11.41 (11.66). Found (calcd) for  $\text{Ni}(\text{NO})(\text{NO}_2)(\text{DPPE})$ : C, 58.37 (58.58); H, 4.58 (4.50); N, 5.06 (5.26); O, 9.59 (9.01). The evolved gases were collected at  $-198^\circ\text{C}$  and fractionated, and the amount of  $\text{CO}_2$  was determined by PV measurements at room temperature. The mole ratio found for  $\text{CO}_2$  and Ni was 0.94:1.00.
- (9) (a) M. Cusmano and V. Ricevuto, *J. Chem. Soc., Dalton Trans.*, 1682 (1978); (b) R. K. Murmann, *Inorg. Chem.*, **2**, 116 (1963); (c) E. J. Billo, *ibid.*, **12**, 2783 (1973); (d) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961); L. Cattalini, M. Martelli, and P. Rigo, *Inorg. Chim. Acta*, **1**, 149 (1967).
- (10) S. Saint-Joly, M. Dartiguenave, and Y. Dartiguenave, *Adv. Chem. Ser.*, **No. 173**, in press.
- (11) G. Fachinetti, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, **100**, 7405 (1978).
- (12) B. S. Tovrog, S. E. Diamond, and F. Mares, *J. Am. Chem. Soc.*, **101**, 270 (1979).
- (13) The rates of reaction of CO with the nickel complexes listed in ref 6 show considerable variation based on qualitative observations.
- (14) See, for example, C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974); Y. Nakamura, K. I. Maruya and T. Mizoroki, *J. Organomet. Chem.*, **104**, C5 (1976).
- (15) Several cycles of the reduction of  $\text{Ni}(\text{NO}_2)_2(\text{DPPE})$  in  $\text{CH}_2\text{Cl}_2$  to  $\text{Ni}(\text{NO})(\text{NO}_2)(\text{DPPE})$  followed by reoxidation to the starting material by atmospheric oxygen have been carried out. Atmospheric oxygen has also been observed to oxidize  $\text{Ni}(\text{NO})\text{Cl}(\text{DPPE})$  by R. Ugo, S. Bhaduri, B. F. G. Johnson, A. Khair, and A. Pickard, *J. Chem. Soc., Chem. Commun.*, 694 (1976).
- (16) (a) B. F. G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, 650 (1973); (b) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 3325 (1974); (c) C. D. Meyer and R. Eisenberg, *ibid.*, **98**, 1364 (1976); (d) D. E. Hendricksen and R. Eisenberg, *ibid.*, **98**, 4662 (1976); (e) D. E. Hendricksen, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **16**, 970 (1977); (f) S. Bhaduri and B. F. G. Johnson, *Trans. Met. Chem. (Weinheim, Ger.)*, **3**, 156 (1978); (g) M. Kubota, K. J. Evans, C. A. Koerntgen, and J. C. Marsters, *J. Am. Chem. Soc.*, **100**, 342 (1978); (h) R. Eisenberg and C. D. Meyer, *Acc. Chem. Resch.*, **8**, 26 (1975).
- (17) See Scheme II, ref 16h.
- (18) D. T. Doughty, G. Gordon, and R. P. Stewart, *J. Am. Chem. Soc.*, **101**, 2645 (1979).

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## Total Synthesis of *dl*-Aplysistatin

Sir:

Aplysistatin (**1**) is a brominated sesquiterpene recently extracted from the South Pacific Ocean sea hare, *Aplysia ang-*