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Kinetics and Mechanism of Oxygen Atom Transfer from Nitro Compounds Mediated by Nickel(0) Complexes

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(Phosphine)nickel(0) complexes NiL_4 react readily with a variety of aliphatic and aromatic nitro compounds RNO_2 to afford the corresponding nitrosonickel(0) complexes $(RNO)NiL_2$ and the phosphine oxide in high yields. Kinetic studies show that the coordinatively unsaturated NiL_3, formed by phosphine dissociation, is involved in the rate-limiting reaction with RNO_2. The polar effects of the nitro compounds as measured by the Taft σ^* parameters for alkyl groups and the Hammett σ constants for aryl groups correlate directly with their reactivity in oxygen atom transfer. A rate-limiting transition state which is highly polar is also indicated by the linear relationship between the second-order rate constants (i.e., log k_e) and the electrochemical reduction potential E of the nitro compound with a slope of 7, closely approaching the theoretical limit predicted by Marcus' theory for outer-sphere electron transfer to afford the ion pair $[L_3Ni^I,RNO_2^-\cdot]$. Collapse of such a species to a cyclic intermediate would allow the direct elimination of phosphine oxide and concomitant formation of the nitrosonickel(0) complex.

Introduction

Nitro and nitroso groups interact with transition metals in essentially two ways: (1) as ligands directly attached to the metal in complexes such as $M(NO_2)$ and $M(NO)$[1] and (2) as organic derivatives in complexes such as $M(RNO_2)$ and $M(RNO)$.[2] In both classes of compounds, oxygen atom transfer from a nitro group to a suitable substrate results in its conversion to a nitroso functionality. For example, the facile reduction of a nitronickel(II) complex to a nitrosonickel(II) species by carbon monoxide[3] has recently been shown by ^{18}O labeling studies to involve direct transfer of oxygen:[4]

$$L_2Ni(NO_2)_2 + CO \rightarrow L_2Ni(NO_2)(NO) + CO_2$$

Moreover, the conversion of nitrobenzene to nitrosobenzene complexes with pentacarbonyliron(0)[5] and the production of *tert*-butyl isocyanate from nitrobenzene and tetrakis(*tert*-butylisocyanide)nickel(0)[6] are examples of oxygen atom transfer from organic nitro compounds.[7]

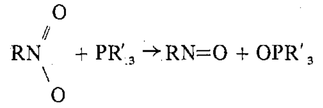
We have observed the facile reaction of (phosphine)nickel(0) complexes with a variety of aliphatic and aromatic nitro compounds to afford the corresponding nitroso complex and phosphine oxide. The clean stoichiometry of the oxygen atom transfer has allowed us to examine the mechanism of this interesting transformation, primarily by kinetic techniques. In this report, we are particularly concerned with the driving force for the rate-limiting activation process.

Results

Nitroalkanes and nitroarenes react readily with nickel(0) complexes, as indicated visually by the rapid color changes attendant upon reaction. Thus, benzene solutions which are approximately 0.05 M in the tetrakis(triethylphosphine)nickel(0) complex are purple, owing to extensive ligand dissociation to produce the three-coordinate species,[8] i.e.

$$Ni(PEt_3)_4 \overset{K_1}{\rightleftharpoons} Ni(PEt_3)_3 + PEt_3 \qquad (1)$$

absorbing at $\lambda_{max} \sim 500$ nm (ϵ 3300). Addition of 1 equiv of a colorless solution of 2-nitro-2-methylpropane causes an immediate change in color to red and a shift of λ_{max} to 479 nm. These color changes are accompanied by the disappearance of 1 equiv of 2-nitro-2-methylpropane and the concomitant formation of equimolar amounts of 2-nitroso-2-methylpropane and triethylphosphine oxide, corresponding to the net transformation



$$RN(=O)O + PR'_3 \rightarrow RN{=}O + OPR'_3$$

The material balance above thus represents, overall, an oxygen atom transfer from nitrogen to a phosphorus center.

I. Products and Stoichiometry. Oxygen transfer from nitro compounds with (phosphine)nickel(0) complexes is readily observed by the changes in the ^1H NMR and IR spectra of the solution. For example, the characteristic, single sharp resonance at δ 1.37 for the *tert*-butyl protons in the ^1H NMR spectrum of 2-nitro-2-methylpropane disappears completely upon the addition of 1 equiv of $Ni(PEt_3)_4$ and is quantitatively replaced with another sharp singlet displaced downfield to δ 1.62. The latter is associated with the 2-nitroso-2-methylpropane complex, $(t\text{-BuNO})Ni(PEt_3)_2$ (I), which can be independently synthesized from nickel(0) and 2-nitroso-2-methylpropane, i.e.

$$t\text{-BuNO} + Ni(PEt_3)_4 \rightarrow \underset{\text{I}}{(t\text{-BuNO})Ni(PEt_3)_2} + 2PEt_3 \qquad (2)$$

The 2-nitroso-2-methylpropane complex I is a dark red crystalline solid which is highly air sensitive but thermally

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(1) For reviews see: (a) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339; (b) Caulton, K. G. *Ibid.* **1975**, *14*, 317.

(2) (a) Basters, J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 50. (b) Barrow, M. J.; Mills, O. S. *J. Chem. Soc. A* **1971**, 864. (c) Mansuy, D.; Drême, M.; Chottard, J. C.; Guilhem, J. *J. Organomet. Chem.* **1978** *161*, 207. (d) Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 537. (e) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 444 and references therein. (f) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 1453. (g) Evrard, G.; Thomas, R.; Davis, B. R.; Bernal, I. *J. Organomet. Chem.* **1977**, *124*, 59. (h) Mansuy, D.; Battioni, P.; Chottard, J. C.; Lange, M. *J. Am. Chem. Soc.* **1977**, *99*, 6441. (i) Mukaida, M.; Yoneda, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1970**, *50*, 3053, (j) Waters, W. A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 732. (k) Ishigaki, A.; Oue, M.; Matsushita, Y.; Masuda, I.; Shono, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 726.

(3) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099.

(4) Doughty, D. T.; Gordon, G.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2645. See also Feltham, R. D.; Kriege, J. C. *Ibid.*, **1979**, *101*, 5064.

(5) (a) Koerner von Gustorf, E.; Henry, M. C.; Sacher, R. E.; DiPietro, C. *Z. Naturforsch., B* **1966**, *21*, 1152. (b) Barrow, M. J.; Mills, O. S. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 879. (c) Compare also: Alper, H. *Inorg. Chem.* **1972**, *11*, 976.

(6) Otsuka, S.; Aotani, Y.; Tatsuno, Y.; Yoshida, T. *Inorg. Chem.* **1976**, *15*, 656.

(7) Compare also: (a) Schorpp, K.; Beck, W. *Chem. Ber.* **1974**, *107*, 1371; (b) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501.

(8) (a) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53. (b) Tolman, C. A. *Ibid.* **1970**, *92*, 2953. (c) Cundy, C. S. *J. Organomet. Chem.* **1974**, *69*, 305. (d) Tolman, C. A.; Gerlach, D. H.; Jesson, J. P.; Schunn, R. A. *J. Organomet. Chem.* **1974**, *65*, C23.

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Table I. Oxygen Transfer from Nitroso- and Nitroalkanes and Nitroarenes with Tetrakis(triethylphosphine)nickel(0)[a]

N compd (1.00 mmol each)	amt of products,[b] mmol		
	PEt_3	$OPEt_3$	$(RNO)Ni(PEt_3)_2$
t-$BuNO_2$	1.0	1.0	1.0
$EtNO_2$[c]	0.98	1.0	0.84
$PhNO_2$	0.96	1.0	1.0
p-$FC_6H_4NO_2$	1.0	0.89	0.88
t-BuNO	1.9	0.04	1.0

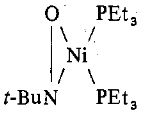
[a] In benzene solution at 22 °C containing 1.00 mmol of $Ni(PEt_3)_4$ and 1.00 mmol of n-Bu_3PO as internal standard. [b] Analysis by ^{31}P NMR spectral analysis (see Experimental Section). [c] In 50% (by volume) tetrahydrofuran for solubility.

Table II. (Triphenylphosphine)nickel(0) Reaction with 2-Nitro-2-methylpropane, 2-Nitroso-2-methylpropane and Nitroarenes[a]

N compd	amt of nitro compd,[b] mmol	amt of $Ni(PPh_3)_4$, mmol	amt of products, mmol	
			$OPPh_3$[c]	$(RNO)Ni(PPh_3)_2$[d]
t-$BuNO_2$	1.0 (0)	1.0	1.0 (0.98)[e]	1.0 (1.02)[e]
	1.0 (0)	2.0	0.98	1.0
	2.0 (1.0)[f]	1.0	0.98	1.0
p-$CH_3C_6H_4NO_2$	1.0 (0.11)	1.0	0.97	0.92
	1.0 (0.04)	2.0		0.86
	2.0 (0.85)	1.0		0.99
p-$CH_3COC_6H_4NO_2$	1.0 (0.07)	1.0		0.60
t-BuNO	2.0 (1.0)	1.0		1.0

[a] In benzene solution at 22 °C with anisole as internal standard. [b] Recovered nitro compound in parentheses. [c] Analysis by IR spectroscopy using band at 720 cm^{-1}. [d] Analysis by ^1H NMR spectroscopy. [e] Analysis by ^{31}P NMR spectroscopy. [f] After heating at 70 °C for 1 h.

stable, melting below 0 °C and decomposing at 127–133 °C. Phosphorus-31 NMR analysis indicates the presence of two nonequivalent triethylphosphine ligands. In particular, the AB quartet in the ^{31}P NMR spectrum [δ_A 20.4, δ_B 22.8 (J_{PP} = 35 Hz)] suggests a square-planar structure for I in which the 2-nitroso-2-methylpropane is bonded to nickel as a η^2 ligand, i.e.



I

similar to the nitrosoarene complexes $(ArNO)NiL_2$, where L = t-BuNC and PPh_3, examined by Otsuka and co-workers.[6] Our repeated and varied attempts to determine the structure of I directly by X-ray crystallography failed,[9] due to difficulties with its low melting point and extreme sensitivity to air (see Experimental Section).

2-Nitroso-2-methylpropane is a substitutionally labile ligand, being partially displaced from I in benzene solution by the addition of as little as 10 equiv of PEt_3, i.e.

$$(t\text{-}BuNO)Ni(PEt_3)_2 + 2PEt_3 \rightarrow t\text{-}BuNO + Ni(PEt_3)_4 \quad (3)$$

Coupled with the reverse reaction described in eq 2, the ligand-exchange equilibrium between 2-nitroso-2-methylpropane and triethylphosphine is estimated to favor I by about 3 kcal mol^{-1}. The lability of I is also shown by simply bubbling carbon monoxide through the benzene solution to afford the known bis(carbonyl) complex[10] in high yields.

$$(t\text{-}BuNO)Ni(PEt_3)_2 + 2CO \rightarrow (CO)_2Ni(PEt_3)_2 + t\text{-}BuNO \quad (4)$$

In both cases, the liberation of free 2-nitroso-2-methylpropane is readily indicated in the ^1H NMR spectrum by a singlet resonance at δ 1.27, in comparison with that of an authentic sample.

Oxygen transfer from 2-nitro-2-methylpropane occurs cleanly to triethylphosphine, and 1 equiv of triethylphosphine oxide can be detected in benzene solution by its ^{31}P NMR spectrum showing a singlet resonance at δ 42 and its IR spectrum with absorptions at 870 and 1270 cm^{-1}. Triethylphosphine oxide can be isolated in 85% yields by concentration of the reaction mixture, which upon subsequent cooling to −78 °C also deposited red crystals of I. The liberation of 1 equiv of triethylphosphine from nickel during the oxygen transfer can be detected by ^{31}P NMR spectroscopy and is represented in the overall stoichiometry in eq 5.

$$t\text{-}BuNO_2 + Ni(PEt_3)_4 \rightarrow (t\text{-}BuNO)Ni(PEt_3)_2 + OPEt_3 + PEt_3 \quad (5)$$

The reaction of nitroethane and nitrobenzene with $Ni(PEt_3)_4$ proceeds in an analogous manner, as shown in Table I.

The (triphenylphosphine)nickel(0) complex, $Ni(PPh_3)_4$, is completely dissociated in benzene solution to the three-coordinate species $Ni(PPh_3)_3$,[11] which is usually less reactive than the triethylphosphine analogue. Nonetheless, it also reacts rapidly with nitroalkanes and nitroarenes to produce 1 equiv of triphenylphosphine oxide and nitrosonickel(0) complexes II according to eq 6 where R = t-Bu, p-$CH_3C_6H_4$, and p-$CH_3COC_6H_4$, as shown in Table II.

$$RNO_2 + Ni(PPh_3)_4 \rightarrow (RNO)Ni(PPh_3)_2 + OPPh_3 + PPh_3 \quad (6)$$

The nitroso complex from 2-nitro-2-methylpropane is similar to I, but the ^{31}P NMR spectrum did not show the resolved phosphorus resonances. Some of the physical characteristics of the organic nitro complexes derived from $Ni(PEt_3)_4$ and $Ni(PPh_3)_4$ as well as those from the o-tolyl phosphite complex, $Ni[P(O\text{-}o\text{-}CH_3C_6H_4)_3]_3$, are listed in Table III.

Oxygen transfer from nitro compounds to phosphines as described in eq 2 takes place only in the presence of (phosphine)nickel(0). Thus, control experiments described in Table IV, using equimolar amounts of nitro compounds and free phosphines, afforded no phosphine oxides, even upon prolonged exposure. The nitro compounds were also recovered intact. Furthermore, oxygen transfer from phosphine oxide is not reversible under these conditions. For example, addition of a large excess of triphenylphosphine to a mixture of $(t\text{-}BuNO)Ni(PEt_3)_3$ and triethylphosphine oxide formed from $Ni(PEt_3)_4$ and 2-nitro-2-methylpropane afforded no triphenylphosphine oxide.

$$PPh_3 + OPEt_3 \overset{[Ni]}{\not\rightleftharpoons} OPPh_3 + PEt_3$$

Moreover the reverse combination, involving the reaction of 2-nitro-2-methylpropane and $Ni(PPh_3)_4$ followed by the addition of triethylphosphine, did not afford triethylphosphine oxide.

Oxygen transfer from 2-nitro-2-methylpropane and triethylphosphine or triphenylphosphine could not be induced by catalytic amounts of nickel(0) complexes. For example, the

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(9) (a) We with to thank Dr. J. Huffmann for extensive efforts on our behalf to mount crystals suitable for study. (b) Although we believe I to be a monomeric species as indicated, dimers and trimers of nitroso complexes are known.[2] The solubility properties of some of the other complexes encountered in this study suggest that such may be the case. Further attempts for crystallographic determinations are planned.

(10) Bigorgne, M. *J. Inorg. Nucl. Chem.* **1964**, *26*, 107.

(11) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

Table III. Physical Properties of Nitroalkane and Nitroarene Complexes of (Triethylphosphine)nickel(0) and (Triphenylphosphine)nickel(0)[a]

nitro compd	NiL_4	color	λ_{max}, nm	IR,[b] cm^{-1}	^1H NMR, δ	^{31}P NMR,[c] δ	yield,[d] %
$EtNO_2$	PEt_3	red	443	1185,1415		22	Q
i-$PrNO_2$	PEt_3	red	455			21.5	
t-$BuNO_2$	PEt_3	red	479	1343,1435	1.62 (s)	20.4,22.8	Q
$C_6H_5NO_2$	PEt_3	red		1360,1410		32	Q
p-$FC_6H_4NO_2$	PEt_3	red		1030,1415		31	90
p-$ClC_6H_4NO_2$	PEt_3	red		1037,1415		31	70
p-$CH_3C_6H_4NO_2$	PEt_3	red		1340	2.60 (s)	30	90
p-$CH_3COC_6H_4NO_2$	PEt_3	red		1356[e]	2.55 (s)	31	70
o-$CH_3C_6H_4NO_2$	PEt_3	red		1343	2.56 (s)		
CH_3NO_2	PPh_3	red		1205			
$CEtNO_2$	PPh_3	red		1200			
i-$PrNO_2$	PPh_3	red			1.48 (d, *J* = 7 Hz)		Q
t-$BuNO_2$	PPh_3	red		1343	1.52 (s)	33	Q
p-$FC_6H_4NO_2$	PPh_3	red	402	1035,1479			Q
p-$ClC_6H_4NO_2$	PPh_3	red	410	1042,1492			
t-$BuNO_2$	$P(OC_6H_4CH_3\text{-}o)_3$	orange-red	348		2.72 (s)		

[a] Measurements in benzene solutions. [b] See Experimental Section for assignments. [c] Relative to 85% H_3PO_4. [d] Based on NiL_4; Q = essentially quantitative. [e] $\nu(CO) = 1674\ cm^{-1}$.

Table IV. Nitro Compounds and Phosphines in the Absence of Nickel[a]

nitro compd (1 mmol each)	phosphine (1 mmol each)	recovery,[b] mmol
t-$BuNO_2$	Et_3P	0.95
t-$BuNO_2$	Ph_3P	1.00
p-$CH_3C_6H_4NO_2$	Ph_3P	0.98
t-BuNO	Ph_3P	1.00[c]

[a] In benzene solution at 22 °C for 3 h. [b] Analysis of unreacted nitro compound by ^1H NMR spectroscopy using toluene as internal standard. [c] Unreacted 2-nitroso-2-methylpropane.

Table V. Substituent Effects on the Rates of Formation of Nitroarene Complexes with (triethylphosphine)nickel(0) Complexes[a]

nitroarene (concn × 10^3, M)	$10^4[Ni(PEt_3)_4]$, M	k_e,[b] $M^{-1}\ s^{-1}$	$E_{1/2}$,[c] V	σ[d]
p-$CH_3OC_6H_4NO_2$ (3.0)	1.3	0.7×10^2 (1.82)	−1.25	−0.27
p-$CH_3C_6H_4NO_2$ (2.6)	1.3	3.0×10^2 (2.48)	−1.20	−0.13
$C_6H_5NO_2$ (1.2)	1.2	5.4×10^2 (2.75)	−1.14	0
$C_6H_5NO_2$ (2.5)	1.2	5.1×10^2 (2.71)		
p-$ClC_6H_4NO_2$ (2.1)	1.3	7.3×10^3 (3.86)	−1.06	0.23
p-$CH_3COC_6H_4NO_2$ (2.5)	2.5	1.9×10^4 (4.27)	−0.92	0.50

[a] In toluene solutions at 23 °C. [b] Logarithms in parentheses. [c] Reduction potentials of substituted nitrobenzenes in acetonitrile solution from ref 12. [d] From ref 13.

addition of a 10-fold excess of 2-nitro-2-methylpropane to either $Ni(PPh_3)_4$ or $Ni(PEt_3)_4$ resulted in the production of only one (*t*-BuNO)NiL_2. No additional 2-nitroso-2-methylpropane was generated when more phosphine was added. Similar results were obtained when pure (*t*-BuNO)$Ni(PEt_3)_2$ was treated with 2-nitro-2-methylpropane and triethylphosphine. These results are explained by the kinetic studies described in the next section.

II. Kinetics of Oxygen Transfer. The rates of reaction between (triethylphosphine)nickel(0) complex and 2-nitro-2-methylpropane or nitrobenzene were followed spectroscopically by monitoring the absorbance change at 500 nm for the disappearance of $Ni(PEt_3)_3$ with the aid of a Durrum-Gibson stopped flow spectrometer. The more hindered tris(tri-*o*-tolyl phosphite)nickel(0) complex reacted with 2-nitro-2-methylpropane at a slower rate which could be followed by conventional spectrophotometric techniques. Oxygen transfer in benzene solutions followed second-order kinetics, being first order in each reagent, i.e.

$$-d[NiL_3]/dt = k_e[NiL_3][RNO_2] \qquad (7)$$

For example, the second-order rate constant k_e for the reaction between 2-nitro-2-methylpropane and (triethylphosphine)nickel(0), $Ni(PEt_3)_3$, under these conditions ($k_e = 4.6 \times 10^1$ $M^{-1}\ s^{-1}$) is approximately 10^6 times faster than that ($k_e = 3 \times 10^{-5}\ M^{-1}\ s^{-1}$) for the tris(tri-*o*-tolyl phosphite)nickel(0) analogue, $Ni[(o\text{-}CH_3C_6H_4O)_3P]_3$.

The structural effects of the nitro compound were examined in two series of compounds: (1) nitroarenes with polar para substituents and (2) nitroalkanes with varying branching at the α carbon.

A. Nitroarenes. For substituted nitrobenzenes, the rates of oxygen transfer increase in the presence of electron-withdrawing substituents, as indicated by the trend in second-order rate constants in Table V. The Hammett correlation of the rate constants for oxygen transfer induced by (triethylphosphine)nickel(0) has $\rho = +3.2$, as illustrated in Figure 1. The polarographic reduction potentials $E_{1/2}$ of the nitroarenes[12] are also included in Table V.

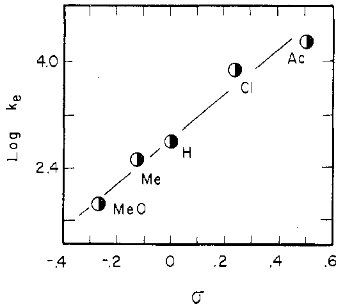

Figure 1. Hammett correlation for oxygen transfer from para-substituted nitrobenzenes induced by (triethylphosphine)nickel(0).

B. Nitroalkanes. For the aliphatic nitroalkanes, oxygen transfer is retarded by branching at the α carbon. For example, the second-order rate constant of 46 $M^{-1}\ s^{-1}$ for the reaction of 2-nitro-2-methylpropane with (triethylphosphine)nickel(0) is about one-third of that (120 $M^{-1}\ s^{-1}$) for nitromethane. This trend in reactivity of nitroalkanes parallels the Taft polar substituent constant σ* listed in Table VI.[13] Retardation of the rate by electron release from the

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(12) Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852.

Table VI. Effects of α Branching on the Reactivity of Nitroalkanes toward (Triethylphosphine)nickel(0)[a]

nitroalkane (concn × 10^3, M)	10^4[Ni-(PEt_3)$_4$], M	k_e,[b] M^{-1} s^{-1}	σ*[c]
CH_3NO_2 (2.52)	2.48	12.6 (2.10)	0
$CH_3CH_2NO_2$ (2.52)	2.48	8.9 (1.95)	−0.10
$(CH_3)_2CHNO_2$ (2.48)	2.48	6.9 (1.84)	−0.19
$(CH_3)_3CNO_2$ (2.54)	2.48	4.6 (1.66)	−0.30

[a] In toluene solutions at 23 °C. [b] Logarithms in parentheses. [c] Taft σ* values from ref 13.

Table VII. Phosphine Dependence of the Observed Second-Order Rate Constant for Oxygen Transfer from 2-Nitro-2-methylpropane with (Triethylphosphine)nickel(0) ([$(CH_3)_3CNO_2$] = 5.1×10^{-3} M; [$Ni(PEt_3)_4$] = 5.0×10^{-4} M)[a]

[added PEt_3], M	k_e,[b] M^{-1} s^{-1}	[added PEt_3], M	k_e,[b] M^{-1} s^{-1}
none	43 (2.3×10^{-2})	7.5×10^{-3}	15 (6.8×10^{-2})
2.5×10^{-3}	27 (3.7×10^{-2})	9.9×10^{-3}	13 (7.9×10^{-2})
5.0×10^{-3}	20 (4.9×10^{-2})		

[a] In toluene solution at 23 °C. [b] k_e^{-1} in parentheses.

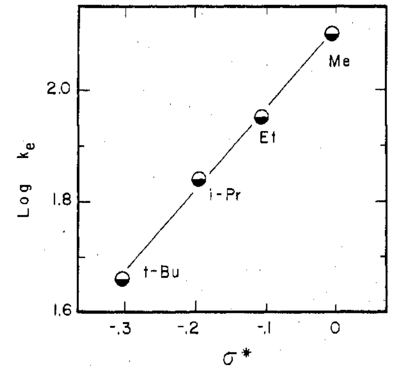

Figure 2. Reactivity of nitroalkanes in oxygen atom transfer with (triethylphosphine)nickel(0) (correlation with Taft σ* constants).

alkyl group is indicated by the positive slope of $\rho^* = 1.5$ in Figure 2, the linearity of which also suggests that steric factors do not play a decisive role in the rate-limiting transition state for reaction.

C. Phosphine Dependence. The experimental rate constant k_e in eq 7 is dependent on the presence of free phosphine, as indicated in Table VII. Quantitatively, the phosphine dependence of the second-order rate constant for oxygen transfer from 2-nitro-2-methylpropane with (triethylphosphine)nickel(0) is given by the relationship

$$1/k_e = (1/k)(1 + [PEt_3]/K) \qquad (8)$$

which is illustrated graphically in Figure 3. The phosphine-independent rate constant $k = 0.43 \times 10^2$ M^{-1} s^{-1} is obtained from the intercept and $K = 7.4 \times 10^{-3}$ M from the slope. The phosphine dependence of k_e in eq 8 is readily interpretable as the direct involvement of the coordinatively unsaturated species $Ni(PEt_3)_3$ in oxygen transfer as described further in the Discussion.

D. Solvent Dependence. The effect of solvent on the rates of oxygen transfer from nitrobenzene with (triethylphosphine)nickel(0) was examined in tetrahydrofuran, toluene, and hexane. The trend in the second-order rate constants listed in Table VIII for reactions in these solvents parallels the solvent polarity as given by empirical parameters, E_T*, which increases in the order: hexane (31 kcal mol^{-1}), toluene (34 kcal mol^{-1}), and tetrahydrofuran (37 kcal mol^{-1}).[14]

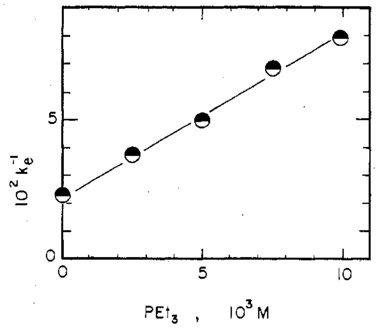

Figure 3. Phosphine dependence of the observed second-order rate constant in the reaction of 2-nitro-2-methylpropane with (triethylphosphine)nickel(0) as described by eq 8.

Table VIII. Solvent Dependence on the Rate of Formation of the Nitrobenzene Complex ([$Ni(PEt_3)_4$] = 5.0×10^{-4} M)

10^3[nitrobenzene], M	solvent	$10^{-3}k_e$, M^{-1} s^{-1}
5.1	THF	1.2
5.0	toluene	0.54
5.1	hexane	0.22

Discussion

The driving force for oxygen transfer from a nitro group to phosphine is largely derived from the formation of phosphine oxide. Indeed, oxygen transfer as described by

$$PhNO_2 + PMe_3 \rightarrow PhNO + OPMe_3$$

is exothermic by more than 40 kcal/mol.[15] The most intriguing question to evolve from such an oxygen transfer, however, is the role of nickel since no reaction occurs in its absence (Table IV). Formally, no change in the oxidation state of nickel(0) is involved, and the ligand coordination of the nitroso product to nickel(0) as either I or II provides only 3 kcal mol^{-1} of driving force.

To gain insight into the role of nickel in promoting oxygen transfer, we must resolve two important questions: (1) what is the active nickel species and (2) what is the nature of the rate-limiting activation process?

I. The Active Nickel Species. The facile dissociation of ligands from (phsophine)nickel(0) complexes[7,11] allows essentially three species to be considered for the direct reaction with nitro compounds as outlined in Scheme I (where L = PEt_3 or PPh_3).

Scheme I

$$NiL_4 \overset{K_1}{\rightleftharpoons} NiL_3 + L \qquad (9)$$

$$NiL_3 \overset{K_2}{\rightleftharpoons} NiL_2 + L \qquad (10)$$

$$NiL_4 + RNO_2 \xrightarrow{k_1} \text{products} \qquad (11)$$

$$NiL_3 + RNO_2 \xrightarrow{k_2} \text{products} \qquad (12)$$

$$NiL_2 + RNO_2 \xrightarrow{k_3} \text{products} \qquad (13)$$

The retardation of oxygen atom transfer by free phosphine is quantitatively represented by the inverse phosphine dependence of the observed second-order rate constant according to eq 8. Retardation can be attributed to the mass law effect

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(13) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 62 ff.

(14) Reichardt, C. *Angew. Chem.* **1965**, *77*, 30.

(15) Calculated from data in: Dean, J. A., Ed. "Lange's Handbook of Chemistry", XIIth ed.; McGraw-Hill: New York, 1979; pp 9–65 ff.

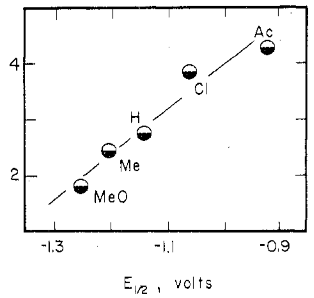


Figure 4. Correlation of the rates of oxygen transfer with (triethylphosphine)nickel(0) and the electrochemical reduction potentials of para-substituted nitrobenzenes from ref 12.

for ligand dissociation in eq 9 and 10, if either or both of the coordinatively unsaturated nickel(0) species, NiL_3 or NiL_2, are directly involved. However, K_2 is at least a factor of 10^4 less than K_1, and the simplest mechanistic formulation from Scheme I would include only eq 9 and 12, for which the overall rate expression is

$$-d[NiL_3]/dt = K_1k_2/(K_1 + [L])[NiL_3][RNO_2] \qquad (14)$$

Indeed, the phosphine dependence as shown in Figure 3 shows that the observed second-order rate constant k_e in eq 7 can be expressed as

$$k_e = K_1k_2/(K_1 + [L]) \qquad (15)$$

which is equivalent to the phenomenological expression in eq 8, with $K = K_1$ and $k = k_2$. It is noteworthy that the dissociation constant evaluated from eq 8 is $K = 7.4 \times 10^{-3}$ M, in reasonable agreement with that ($K_1 = 5.6 \times 10^{-3}$ M) measured in eq 1 directly by the spectrophotometric method. The minor discrepancy between K and K_1 arises partly from the assumption that the concentration of phosphine remains constant, particularly when low levels of (phosphine)nickel(0) complexes are employed. In either case, the results are clearly consistent with the three-coordinate NiL_3 as the prinicipal, kinetically significant species in the reaction with nitro compounds. Indeed, the inertness of the fully coordinated NiL_4 is shown by the absence of any oxygen transfer when a large excess of triethylphosphine is added to a solution of (triethylphosphine)nickel(0) prior to the addition of 2-nitro-2-methylpropane.

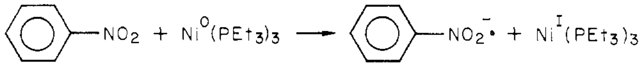
II. The Rate-Limiting Activated State in Oxygen Transfer. The question now arises as to the driving force for the activation process leading to oxygen transfer by the direct bimolecular reaction of NiL_3 with the nitro compound. There are several lines of evidence which strongly point to a considerable, if not complete development of negative charge on the nitro moiety in the rate-limiting transition state. Thus, the Hammett correlation of the second-order rate constant (i.e., log k_e) for $Ni(PEt_3)_3$ in Figure 1, which has a positive ρ value of 3.2, indicates that the process is strongly facilitated by the presence of electron-withdrawing substituents on the nitroarene. A similar conclusion derives from the correlation in Figure 2 which determines the effect of the polar properties of alkyl groups in a series of nitroalkanes. Finally, the linear correlation in Figure 4 emphasizes the similarity between the rate-limiting transition state for oxygen transfer and the driving force for the 1-equiv reduction of nitroarenes, i.e.

$$ArNO_2 + e^- \rightleftharpoons ArNO_2^-\cdot \qquad (16)$$

which is measured independently as the polarographic reduction potentials $E_{1/2}$. [Since the polarography of nitroarenes displays the characteristics of electrochemical reversibility, Maki and Geske[12] represent the values of $E_{1/2}$ as thermodynamic standard reduction potentials.] Electron accession to the nitro group is readily provided by the (phosphine)nickel(0) species which are strong 1-equiv reducing agents. For example, the oxidation of (triethylphosphine)nickel(0), i.e.

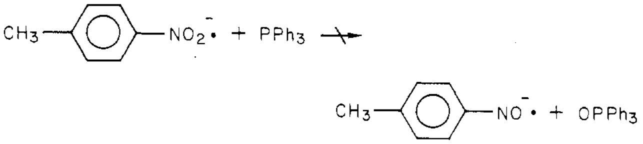
$$Ni^0(PEt_3)_3 \rightleftharpoons Ni^I(PEt_3)_3 + e^- \qquad (17)$$

occurs with $E = 1.1$ V vs. SCE, as shown by cyclic voltammetry.[16] Judging from the reduction potential of nitrobenzene ($E_{1/2} = -1.15$ V vs. SCE),[12] the overall electron-transfer reaction with (triethylphosphine)nickel(0)



(18)

is indeed thermoneutral. It is important to point out that electron transfer alone is not sufficient to promote oxygen transfer, since the nitroarene radical anion generated independently by electrochemical techniques in the presence of phosphine does not afford phosphine oxide (see Experimental Section), i.e.



III. The Mechanism of Oxygen Atom Transfer. On the basis of the kinetic evidence, the most direct formulation of the mechanism for oxygen transfer includes a prior rate-limiting electron-transfer process as shown in Scheme II.

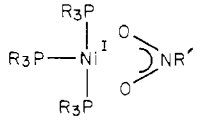
Scheme II

$$NiL_4 \underset{}{\overset{K_1}{\rightleftharpoons}} NiL_3 + L \qquad (19)$$

$$NiL_3 + RNO_2 \xrightarrow{k_2} [Ni^IL_3,RNO_2^-\cdot] \qquad (20)$$

$$[Ni^IL_3,RNO_2^-\cdot] \xrightarrow{\text{fast}} L_2Ni(ONR) + LO \qquad (21)$$

The formation of the ion pair in eq 20 is central to Scheme II. The necessity of phosphine dissociation from $Ni(PEt_3)_4$ before it reacts with the nitro compound suggests that the ion pair is intimately associated,[17] e.g.



Indeed, the absence of an ESR signal from either the paramagnetic nickel(I) or nitro anion radical (see Experimental Section) indicates that diffusive separation of the ion pair is not competitive with further reaction in eq 21.

Charge development in the rate-limiting transition state for oxygen transfer derives from (1) the strong, positive correlation of the rates (log k) with an independent measure of the energetics (E) of electron attachment to the nitro compounds and (2) the driving force for electron detachment from (phosphine)nickel(0) complexes. The high sensitivity to the polarity of the solvent in Table VIII also accords with a strongly polar transition state. It is noteworthy that the slope of 7.5 in Figure 4 is approaching the theoretical limit of 8.5 predicted by Marcus' theory,[18,19] i.e.

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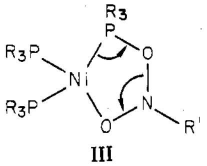
(16) Tsou, T. T.; Kochi, J. K., submitted for publication.

(17) (a) If electron transfer as described in eq 20 were a wholly outer-sphere process, it would be expected that the coordinatively saturated NiL_4 species would also react readily with nitro compounds, which it does not. (b) Nitroalkane radical anions are more susceptible to fragmentation than nitroarene radical anions [Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734]. The small amount of hydrocarbon gases observed with 2-nitro-2-methylpropane may be diagnostic of such a process. Indeed, the formation of nitroplatinum(II) adducts from such cleavages has been reported in the reactions of nitroalkanes with $Pt(PPh_3)_4$.[7a]

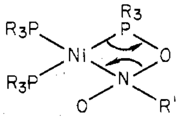
$$\log k = 8.5E° + \text{constant} \qquad (22)$$

for a complete outer-sphere process for electron transfer according to eq 20.

Whether an ion pair as in eq 20 is an *actual* intermediate or a transition state cannot be rigorously resolved, although it is abundantly clear that electron transfer from the nickel(0) to the nitro moiety must be the principal component of any activation process. In other words, the ion pair in eq 20 is a reasonable representation of the rate-limiting transition state, and neither the N–O bond breaking nor the P–O bond making are determining factors in the kinetics of the oxygen-transfer process. Since the actual transfer of oxygen from nitrogen to phosphorus occurs later along the reaction coordinate, it must be facile. Indeed, the collapse of the ion pair via a cyclic intermediate such as III or IV would provide an attractive route to the elimination of phosphine oxide and concomitant coordination of the nitroso product to nickel.[20] A similar cyclic intermediate has been proposed for oxygen transfer from nitronickel(II) complexes to carbon monoxide.[4a] Such decompositions are *formally* akin to other cyclic processes such as those suggested for olefin metathesis,[21] disiloxane disproportionation,[22] epoxidation of olefins,[23] and oxidation of molybdenum complexes.[24] The metal center plays a vital role in all of these processes even though it may not undergo an overall change in formal oxidation state.



III



IV

Experimental Section

Materials. The nickel(0) complexes of triethylphosphine $Ni(PEt_3)_4$, triphenylphosphine $Ni(PPh_3)_4$, and tri-*o*-tolyl phosphite $Ni[(o\text{-}CH_3C_6H_4O)_3P]_3$ were prepared according to the previously published procedures.[25-27] Some of the nitro compounds were commercial samples: *p*-CH_3, *p*-CH_3O, *p*-NH_2, and *p*-Cl nitrobenzenes, nitroethane, and nitro-2-propane (Matheson Coleman and Bell); *p*-nitroacetophenone (Aldrich Chemical Co.); *o*-nitrotoluene (Eastman Organic Chemical); nitromethane and nitrobenzene (Fisher Scientific Co.), repurified before use by distillation or prepared by published procedures (2-nitro-2-methylpropane[28] and *p*-fluoronitrobenzene[29]). α-Nitrocumene was a generous gift from Dr. N. Kornblum. 2-Nitroso-2-methylpropane was obtained from Aldrich Chemical Co., but nitrosobenzene and *p*-nitrosotoluene were prepared by published procedures.[30,31]

The absorption spectra of (phosphine)nickel(0) in benzene solutions were recorded on a Cary 14 spectrophotometer over a 100-fold range in concentration to check their adherence to Beer's law. The proton NMR spectra were recorded on a Varian T60 spectrometer using benzene as the internal standard. The ^{31}P NMR spectra were measured relative to 85% H_3PO_4 as an external standard on a Varian XL100 spectrometer. ESR studies were carried out on a Varian E112 spectrometer equipped with an NMR field marker and a variable temperature cell. The concentration of paramagnetic species was determined by double integration of the ESR signal relative to a standard diphenylpicrylhydrazyl calibrant. The electrochemical apparatus consisted of a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter and a voltage follower amplifier (PAR Model 178).

The nickel(0) complexes are all sensitive to oxygen, and the manipulations were carried out with Schlenk glassware either under an argon atmosphere or in vacuo. The repurified solvents[32] were redistilled from sodium benzophenone or NiL_4 under argon. The reagents were degassed by a standard freeze–pump–thaw technique prior to use.

Reaction of Nitro Compounds with (Phosphine)nickel(0) Complexes. The procedure generally consisted of adding a 10 mL solution of 0.1 M nickel(0) to a stirred solution of 0.1 M nitro compound in the absence of air. Aliquots of solution were extracted periodically with a hypodermic syringe for a spectral examination. The reaction mixture was then cooled to below −60 °C to allow precipitation of the adducts which were purified by successive recrystallizations. Some special examples for the isolation of nitrosonickel(0) adducts are described separately as follows.

A. Reaction of 2-Nitro-2-methylpropane and (Triethylphosphine)nickel(0). To a stirred solution of 1.7 g (3.2 mmol) of $Ni(PEt_3)_4$ in 5 mL of butane at −6 °C was added 0.5 mL of a 6.4 M solution of *t*-$BuNO_2$ in pentane. After 1 h of stirring, the butane was removed by slowly warming to 25 °C. To the resulting red oil was added 10 mL of butane and the red solution cooled to −20 °C which resulted in the precipitation of triethylphosphine oxide. The red liquid was carefully removed by syringe, concentrated to two-thirds its original volume, and recooled to −20 °C. Additional phosphine oxide precipitated and this procedure was repeated five times until no additional phosphine oxide separated. The remaining butane solution was cooled to −78 °C, producing red crystals of (*t*-BuNO)$Ni(PEt_3)_2$. The remaining butane was removed with a hypodermic syringe and the red crystals were dried carefully by passing dry argon over them. The red crystals melted below 0 °C.

B. Reaction of Nitrobenzene with (Triphenylphosphine)nickel(0). In a typical procedure, 0.1 M $Ni(PPh_3)_4$ in benzene (10 mL) was added to a stirred solution of 0.2 M nitrobenzene in benzene (5 mL). After the solution was stirred for 1 h, the solvent was removed in vacuo, leaving a red powder which was washed several times with hot hexane (40 °C) and dried in vacuo. Similar results were obtained when either toluene or tetrahydrofuran was employed.

Special Titration of 2-Nitro-2-methylpropane and $Ni(PEt_3)_4$. Small aliquots (0.5 μL) of 2.4×10^{-2} M 2-nitro-2-methylpropane were successively added with the aid of a hypodermic syringe to a previously degassed solution of 2.75×10^{-2} M $Ni(PEt_3)_4$ contained in a cuvette equipped with a Schlenk top. With each addition, the 500-nm band of $Ni(PEt_3)_3$ with ϵ 2600 M^{-1} cm^{-1} diminished linearly, accompanied by the band of (*t*-BuNO)$Ni(PEt_3)_2$ at λ_{max} 479 nm (ϵ 650 M^{-1} cm^{-1}) with a clean isosbestic point at 430 nm.

Isolation and Characterization of Phosphine Oxide. To a solution of 0.057 g (0.55 mmol) of *t*-$BuNO_2$ in 2 mL of benzene was added a 10 mL benzene solution of 0.5 g (0.55 mmol) of $Ni(PPh_3)_4$. After solvent was removed in vacuo, 10 mL of *n*-hexane was added and the resulting heterogeneous mixture heated to 40 °C with stirring. The mixture was filtered by using a Schlenk-type apparatus to yield a red powder. This procedure was repeated several times until triphenylphosphine oxide could not be detected in the IR spectra of the red powder. The filtrates were combined, the solvent was removed, and the resulting white solid was recrystallized from absolute ethanol to yield triphenylphosphine oxide (92%): mp 152–154 °C (lit.[33] mp

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(18) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891, and earlier papers. (b) Reynolds, W. L.; Lumry, R. W. "Mechanism of Electron Transfer"; Ronald Press: New York, 1966.

(19) Compare also: (a) Ng, F. T.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 3606; (b) Cecil, R.; Fear, M. A. J.; Littler, J. S. *J. Chem. Soc. B* **1970**, 632; (c) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(20) In contrast to a wholly concerted process for oxygen atom transfer, the series of stepwise transformations in Scheme II have the advantage of clearly delineating the driving forces involved along the reaction coordinate. Even if one or more steps were concerted, the foregoing arguments and conclusions would not be fundamentally changed.

(21) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283.

(22) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362 and references therein.

(23) (a) Mimoun, H.; Machirant, M. M. P.; Sérée de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437. (b) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(24) Klingler, R. J., personal communication.

(25) Ittel, S. D. *Inorg. Synth.* **1977**, *17*, 117.

(26) Schunn, R. A. *Inorg. Synth.* **1972**, *13*, 124.

(27) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

(28) Kornblum, N.; Clutter, R. J.; Jones, W. J. *J. Am. Chem. Soc.* **1956**, *78*, 4003.

(29) Bradlow, H. L.; Vander Werf, C. A. *J. Am. Chem. Soc.* **1968**, *90*, 654.

(30) Colemann, G. H.; McColsky, C. M.; Stuart, F. A. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 668.

(31) Bamberger, E.; Rising, A. *Justus Liebigs Ann. Chem.* **1901**, *316*, 280.

(32) See: Perrin, D. D.; Amarego, W.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966.

(33) Weast, R. C., Selby, S. M., Hodgman, C. D., Eds. "Handbook of Chemistry and Physics"; 45th ed.; Chemical Rubber Co.: Cleveland, 1964; p C473.

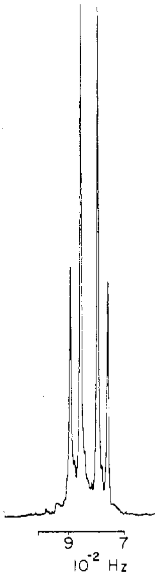

Figure 5. ^{31}P NMR spectrum of $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$ in tetrahydrofuran solution at −70 °C.

156 °C); IR (benzene) 720 cm^{-1}; ^{1}H NMR (CDCl_3) δ 7.3–7.6 (m, 15 H).

Phosphine oxide in solution could also be analyzed directly by IR spectroscopy by using the band at 720 cm^{-1}, after calibration with a series of standard solutions.

The products of the reaction of 2-nitro-2-methylpropane and $\text{Ni}(\text{PEt}_3)_4$ could be examined in situ, since the ^{31}P NMR spectra of triethylphosphine, triethylphosphine oxide, $\text{Ni}(\text{PEt}_3)_4$, and tri-*n*-butylphosphine oxide showed resolved singlet resonances at −19, 42, 22, and 39 ppm, respectively, relative to 85% H_3PO_4 (external reference). The ^{31}P NMR spectrum of $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$ consisted of a typical AB quartet [δ_A 20.4, δ_B 22.8 (J_{PP} = 35 Hz)] shown in Figure 5. The spectrum was nearly invariant between 30 and −70 °C, showing only slight broadening at the higher temperatures. [The presence of two phosphines in I is also shown in the proton NMR spectrum by integration of the *tert*-butyl and ethyl protons in a ratio of 9:30.] Quantitative analyses were carried out by integration of the resonances and comparison with calibration curves.

The assignments of the infrared bands of nitroso compounds coordinated to metals are not completely established.^{6} The absorptions included in Table III are only those not already present in the parent nitro and nitroso compounds (as well as NiL_4 and solvent) in the region of the spectrum between 1000 and 1500 cm^{-1}. The infrared spectra of free nitroso compounds have been recorded.^{34}

Kinetic Measurements. The rate of oxygen transfer was followed spectrophotometrically by following the disappearance of the absorption band of NiL_3 with the aid of a Durrum-Gibson stopped-flow spectrometer.^{16} The reactions were carried out in the presence of excess nitro compound to approximate pseudo-first-order conditions.

The techniques employed in determining the phosphine dependence of the second-order rate constant and the measurement of the equilibrium constants for the dissociation of ligands from nickel(0) species have been described.^{16} The inhibition of oxygen transfer by a large excess of phosphine was shown by adding triethylphosphine (3 M) to 5.0×10^{-2} M $\text{Ni}(\text{PEt}_3)_4$ in 10 mL benzene. The yellow solution showing no absorption at 500 nm for $\text{Ni}(\text{PEt}_3)_3$ did not react with 0.05 mmol of 2-nitro-2-methylpropane even after 1 h at 25 °C.

Reaction of $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$ with Oxygen. When air was bubbled through a red benzene solution of $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$, it rapidly turned light yellow and deposited a green amorphous precipitate (nickel hydroxide?). Roughly equimolar amounts of free 2-nitro-2-methylpropane and 2-nitroso-2-methylpropane were observed by their characteristic infrared absorptions and chemical shifts in the proton NMR spectrum of the solution.

Electron Spin Resonance Studies of Oxygen Transfer. If either 2-nitro-2-methylpropane or nitrobenzene is added to a solution of (phosphine)nickel(0) in the dark, no ESR signals were observed. However, exposure of the solution to light (even adventitious laboratory illumination) results in the development of paramagnetic species, in some cases showing well-resolved ESR spectra. For example, a solution of 2-nitro-2-methylpropane and (triphenylphosphine)nickel(0) on exposure to light afforded an anisotropic spectrum consisting of a triplet (14.8 G) of doublets (3.3 G), with *g* value of 2.001. This spectrum disappears upon exposure of the solution to oxygen, and it is replaced by the spectrum of the well-characterized di-*tert*-butyl nitroxide (a_N = 15.75 G, g = 2.0062).^{35} We tentatively suggest that irradiation of $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$ leads to a photoinduced electron-transfer process initially affording $t\text{-BuNO}^{-}\cdot$ and subsequently $t\text{-BuNHO}\cdot$ by proton transfer. The proton splitting of 3.3 G indicated above, however, is significantly smaller than those observed in similar radicals generated in other ways.^{36} The complex processes, arising from alkyl transfer ultimately leading to di-*tert*-butyl nitroxide, have been discussed.^{37} The well-resolved ESR spectrum derived from *p*-fluoronitrobenzene is reminiscent of that of the anion radical of *p*-fluoronitrosobenzene.^{38} The unusual line intensities, however, suggest a more complicated problem (possible involving the interaction with a nickel center) which must be resolved by additional studies.

Electrochemical Production of Nitroarene Anion Radical in the Presence of Phosphine. *p*-Nitrotoluene was reduced in the presence of triphenylphosphine by controlled-potential electrolysis in tetrahydrofuran solution at −1.40 V vs. SCE. After the passage of 1.08 ± 0.05 electrons/mol, *p*-nitrotoluene anion radical was produced in excellent yields, showing a stable, well-resolved ESR spectrum [a_N = 10.7, a_{2H} = 3.4, a_{2H} = 1.1, and a_{CH_3} = 4.0 G; g = 2.0045].^{39} Analysis of the solution by IR spectroscopy showed the presence of <3% triphenylphosphine oxide. No additional phosphine oxide was formed upon prolonged standing.

Acknowledgment. We wish to thank T. T. Tsou, S. Fukuzumi, and R. J. Klingler for help with the ESR and electrochemical studies, K. L. Rollick for the ^{31}P NMR spectra, and the National Science Foundation for financial support.

Registry No. $t\text{-BuNO}_2$, 594-70-7; EtNO_2, 79-24-3; PhNO_2, 98-95-3; $p\text{-FC}_6\text{H}_4\text{NO}_2$, 350-46-9; t-BuNO, 917-95-3; $p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2$, 99-99-0; $p\text{-CH}_3\text{CO}_6\text{C}_6\text{H}_4\text{NO}_2$, 100-19-6; $i\text{-PrNO}_2$, 79-46-9; $p\text{-ClC}_6\text{H}_4\text{NO}_2$, 100-00-5; $o\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2$, 88-72-2; CH_3NO_2, 75-52-5; $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NO}_2$, 100-17-4; $\text{Ni}(\text{PEt}_3)_4$, 51320-65-1; $\text{Ni}(\text{PPh}_3)_4$, 15133-82-1; $\text{Ni}(\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_3)_4$, 36841-11-9; OPEt_3, 597-50-2; $(t\text{-BuNO})\text{Ni}(\text{PEt}_3)_2$, 71928-82-0; $(\text{EtNO})\text{Ni}(\text{PEt}_3)_2$, 71928-83-1; $(\text{PhNO})\text{Ni}(\text{PEt}_3)_2$, 71928-84-2; $(p\text{-FC}_6\text{H}_4\text{NO})\text{Ni}(\text{PEt}_3)_2$, 71928-63-7; $(t\text{-BuNO})\text{Ni}(\text{PPh}_3)_2$, 71928-64-8; $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NO})\text{Ni}(\text{PPh}_3)_2$, 71928-65-9; $(p\text{-CH}_3\text{COC}_6\text{H}_4\text{NO})\text{Ni}(\text{PPh}_3)_2$, 71928-66-0; $(i\text{-PrNO})\text{Ni}(\text{PEt}_3)_2$, 71928-67-1; $(p\text{-ClC}_6\text{H}_4\text{NO})\text{Ni}(\text{PEt}_3)_2$, 71928-68-2; $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NO})\text{Ni}(\text{PEt}_3)_2$, 71928-69-3; $(p\text{-CH}_3\text{COC}_6\text{H}_4\text{NO})\text{Ni}(\text{PEt}_3)_2$, 71928-70-6; $(o\text{-CH}_3\text{C}_6\text{H}_4\text{NO})\text{Ni}(\text{PEt}_3)_2$, 71928-71-7; $(\text{CH}_3\text{NO})\text{Ni}(\text{PPh}_3)_2$, 71928-72-8; $(\text{EtNO})\text{Ni}(\text{PPh}_3)_2$, 71928-73-9; $(i\text{-PrNO})\text{Ni}(\text{PPh}_3)_2$, 71928-74-0; $(p\text{-FC}_6\text{H}_4\text{NO})\text{Ni}(\text{PPh}_3)_2$, 71928-75-1; $(p\text{-ClC}_6\text{H}_4\text{NO})\text{Ni}(\text{PPh}_3)_2$, 71928-76-2; $(t\text{-BuNO})\text{Ni}(\text{P}(\text{OC}_6\text{H}_4\text{CH}_3\text{-}o)_3)_2$, 71928-77-3; OPPh_3, 791-28-6; PEt_3, 554-70-1.

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(34) Feuer, H. "The Chemistry of the Nitroso and Nitro Groups"; Interscience: New York, 1969; Vol. 1, p 140. Nakamoto, K.; Rundle, R. E. *J. Am. Chem. Soc.* **1956**, *78*, 1113.

(35) Hoffmann, A. K.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 4675.

(36) Wajer, T. A. J. W.; Mackor, A.; DeBoer, T. J. *Tetrahedron* **1969**, *25*, 175.

(37) (a) Hoffmann, A. K.; Feldman, A. M.; Gelblum, E.; Hodgson, W. G. *J. Am. Chem. Soc.* **1964**, *86*, 639. (b) Bowman, D. F.; Brokenshire, J. L.; Gillan, T.; Ingold, K. U. *Ibid.* **1971**, *93*, 6551.

(38) The ESR spectra of nitroarene and the corresponding nitrosoarene radical anions generally show similar splitting patterns.

(39) Ayscough, P. B.; Sargent, F. P.; Wilson, R. *J. Chem. Soc. A* **1963**, 5418.