Reactions of Some Cobalt Nitrosyl Complexes with Oxygen

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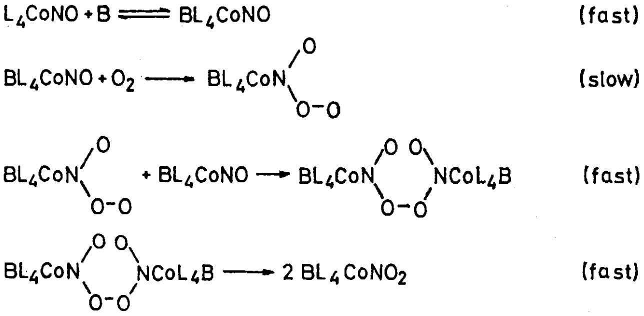
Summary Some Co(Schiff base)NO complexes, as well as $[Co(en)_2NO]^{2+}$, react with oxygen in solutions containing a base or in co-ordinating solvents to yield the corresponding nitro-complexes; kinetic studies show that the rates of reaction increase with increasing basicity of the added base.

WE are prompted to report our observations on the reaction of certain Werner-type cobalt nitrosyl complexes with oxygen because of the current interest in metal nitrosyl chemistry and because of the recent report[1] that the organometallic complex $[Os(NO)(CO)_2(PPh_3)_2]^+$ reacts with oxygen in the presence of an isocyanide to yield $[Os(NO_2)(CO)(CNR)_2(PPh_3)_2]^+$. This type of reaction was also observed[2] with $[RuO_2(NO)_2NO_3]_2O$ which, in aqueous solution, reacts with air to give $[RuO_2(NO_2)(NO_3)_2H_2O]^-$. These reactions have not been studied in detail and no information is available on the nature of these reaction processes.

We now report the well defined reactions of some cobalt nitrosyl complexes to give in high yields (>75%) the corresponding nitro-products. Kinetic studies suggest a possible mechanism for these reactions and show what factors affect the rates of reaction.

Methanol or acetone solutions of L_4CoNO in the presence of nitrogen or phosphorus bases, B, react with oxygen at room temperature to yield BL_4CoNO_2, where L_4 = the quadridentate dianions *NN'*-ethylenebis-(1-acetonylethylideneiminato); *NN'*-ethylenebis(benzoylisopropylideneiminato); and *NN'*-ethylenebis(salicylideneiminato). The reaction at room temperature of a solution of $[Co(en)_2NO](ClO_4)_2$ in MeCN with oxygen results in the precipitation of $[Co(en)_2(MeCN)NO_2](ClO_4)_2$. The isolated products were purified and found to give the expected elemental analyses for the respective nitro-derivatives.



The stoicheiometry of the reactions was established to be that represented by equation (1). Spectrophotometric

$$L_4CoNO + B + \tfrac{1}{2}O_2 \rightarrow BL_4CoNO_2 \qquad (1)$$

measurements were used to investigate the kinetics of this reaction where L_4 = *NN*′-ethylenebis-(1-acetonylethylideneiminato) and B is various different bases. The results show a first-order dependence on the concentrations of the cobalt complex and oxygen. The rate of reaction increases with increasing base concentration, but a limiting rate is reached at high base concentrations. The kinetic data obtained are consistent with the reactions in the Scheme.

Table[a]

B	[B]/M	pK_a of BH^+	$t_{\frac{1}{2}}$/s
py	0·05	5·27[b]	487
2-Me py	2·18	5·96[b]	692
4-Me py	0·05	6·00[b]	301
4-NH_2 py	0·05	9·17[b]	57
Pr^nNH_2	0·07	10·59[c]	143
Pr^i_2NH	2·74	10·91[d]	1000
Et_3N	3·43	10·75[c]	N.R.

[a] Half-lives of the reaction of $2·4 \times 10^{-4}$M L_4CoNO in acetone solution saturated with air at 1 atm and at 25°C. [b] K. Schofield, Hetero-Aromatic Nitrogen Compounds, Plenum Press, New York, 1967, p. 146. [c] C. A. Streuli, *Analyt. Chem.* 1960, **32**, 985. [d] pK_a of $Pr^n_2NH_2^+$.

The tabulated data show that, except for steric effects, the rates of reaction increase with increasing base strength of the nitrogen bases.

This result is in accord with the rate-determining step for the reaction being the electrophilic attack by oxygen on the nitrosyl nitrogen. Thus the greater the electron density on the nitrosyl nitrogen, resulting from a greater base strength of the base, then the more rapid the reaction. Preliminary observations indicate that phosphine and phosphite ligands behave similarly in that the rate of reaction increases with increasing basicity of the ligand.

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[1] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.
[2] T. Ishimyama and T. Matsumara, *Ann. Rep. Radiation Centre Osaka Prefecture*, 1970, **11**, 50 (*Chem. Abs.*, 1972, **76**, 30252v).