

A Nitronitrosyliron Complex as a Potential Oxygen Transfer Reagent

R D ARASASINGHAM, H M N BANDARA,
B M R BANDARA & O A ILEPERUMA*

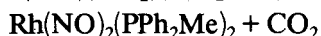
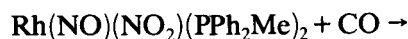
Department of Chemistry, University of Peradeniya,
Peradeniya, Sri Lanka

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The complex *cis*-Fe(NO)(NO₂)(S₂CNMe₂)₂ effects oxidation of substrates such as CO, Ph₃P and cyclohexene with concomitant reduction to Fe(NO)(S₂CNMe₂)₂.

The complex *cis*-bis(dimethyldithiocarbamato)(nitro)nitrosyliron, Fe(NO)(NO₂)(S₂CNMe₂)₂ (**1**) undergoes an intramolecular reaction whereby the coordinated nitrosyl and nitro groups interconvert through a process in which a reactive oxygen atom 'hops' back and forth between the two coordinated groups¹. The possibility that this complex would transfer the reactive oxygen atom to other species in an intermolecular process has now been investigated and this communication reports preliminary results of the reactions of this complex with CO, Ph₃P, cyclohexene and crotonaldehyde (CH₃CH=CHCHO).

The complex (**1**) was synthesized employing the literature procedure¹. When a brown solution of this complex in CHCl₃ was treated with CO gas for 1.5 hr, the solution turned green indicating the formation of Fe(NO)(S₂CNMe₂)₂. Upon removal of the solvent, the resultant solid exhibited in its IR spectrum in KBr, a band at 1690 cm⁻¹ assignable to νNO of Fe(NO)(S₂CNMe₂)₂ and a band at 1740 cm⁻¹ which was assignable to a dinitrosyl species. Although the gaseous products were not analyzed, CO was probably converted into CO₂ by the transfer of hot oxygen atom of the starting complex. The abstraction of oxygen atoms from coordinated nitro groups by CO leading to the formation of dinitrosyl species is known²:



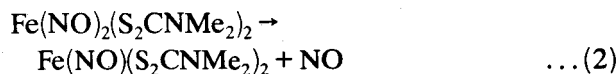
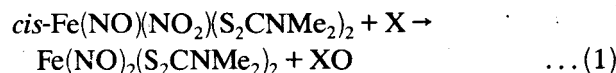
The oxidation of CO to CO₂ by nitronitrosyl complexes of iron and rhodium³ may have implications in unravelling the sequence of reactions involved in

the simultaneous oxidation-reduction between CO and NO. The latter reaction is important in the catalytic control of automobile exhaust fumes.

The brown CHCl₃ solution of **1** was treated with Ph₃P and the reaction monitored by IR spectroscopy. Gradual disappearance of the 1830 cm⁻¹ band and the appearance of bands at 1700 and 1200 cm⁻¹ indicated the consumption of starting **1** and the formation of Fe(NO)(S₂CNMe₂)₂ and Ph₃PO. Reaction mixture upon concentration gave a residue from which Ph₃PO was obtained after chromatographic fractionation. The identity of Ph₃PO was established by comparison with an authentic sample.

Similarly cyclohexene and crotonaldehyde (CH₃CH=CHCHO) were separately reacted with **1** and the reactions were monitored by IR spectroscopy. With cyclohexene as the substrate, the IR spectrum was characterised by a gradual increase in the band at 1700 cm⁻¹ due to Fe(NO)(S₂CNMe₂)₂ and the appearance of a new band at 845 cm⁻¹ which was assignable to the epoxide of cyclohexene. With CH₃CH=CHCHO, the IR bands at 1830 and 1640 cm⁻¹ due to νNO and νCO of starting **1** and the organic substrate, respectively, remained unchanged indicating that no reaction had taken place. Complex **1** did not react with crotonaldehyde presumably because of the low π-electron density at the olefinic bond.

The reaction of **1** with the substrates X (= CO, Ph₃P or cyclohexene) would lead to unstable dinitrosyl species, Fe(NO)₂(S₂CNMe₂)₂, which would decompose to the mononitrosyl species, Fe(NO)(S₂CNMe₂)₂ (see Eqs. 1 and 2). There is IR evidence for the formation of the dinitrosyl species.



References

- 1 Ileperuma O A & Feltham R D, *J Am chem Soc*, **96** (1974) 6037.
- 2 Bhaduri S, Johnson B F G, Savory C J, Segal J A & Walter R H, *Chem Commun*, (1974) 809.
- 3 Reed J & Eisenberg R, *Science*, **184** (1974) 568.