

Reactions of Nitrous Oxide with Some Transition-metal Complexes

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NITROUS OXIDE is a remarkably inert compound at room temperature and under a pressure of one atmosphere. Amongst the simpler compounds of nitrogen it is second only to N_2 itself (and possibly NF_3) in inertness. This is all the more surprising in view of its very positive free energy of formation ($\Delta G^\circ = +24.9$ kcal./mole) and potential oxidising power. If we neglect high-energy radicals and molecules formed for example by radiolysis, then the only compounds which react homogeneously with N_2O at room temperature and pressure are: metal alkyls and amides, such as $LiPh^1$ and $NaNH_2$;² HI ;³ Na_2SO_3 ;⁴ $SnCl_2$;⁴ and $Ph_3P \rightarrow CH_2$;⁵ and amongst transition-metal compounds only $TiCl_3$;⁴ and ammoniacal $CrCl_2$.⁶ $TiCl_3$ slowly reduces N_2O to NH_3 (a 0.11 M solution gave 35% reduction after 2 hr., 84% after 9 hr.), and ammoniacal $CrCl_2$ reduces N_2O to N_2 even more slowly. On the other hand, N_2O is a common product and substrate of bacterial metabolism.⁷

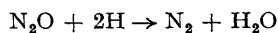
We have been interested in the possible role of transition-metal complexes in catalysing reactions of the less reactive gases, including N_2O , and now report the discovery of reactions of N_2O with several metal complexes. N_2 and N_2O (and other gases such as H_2 and NO) were analysed by mass spectrometry. It was shown that solutions of $NaBH_4$, used for reducing the metal complexes, did not by themselves react with N_2O .

(1) Dilute ($\sim 10^{-4}M$) solutions of the cobalt(I) derivative of vitamin B_{12} , prepared by controlled potential reduction⁸ in order to avoid the presence of an excess of reducing agent, reacted instantaneously with N_2O (colour change grey-green to yellow) to give the cobalt(II) complex, identified by its spectrum; the nitrogen-containing products could not be identified under these conditions. Borohydride will, however, reduce the cobalt-(III) and -(II) complexes to the cobalt(I) complex, and a cyclic reaction can therefore occur; when left overnight in

contact with a solution containing an excess of borohydride ($BH_4^-:N_2O \sim 2.5$) virtually complete reduction of N_2O to N_2 was observed. (2) Blue-green solutions of bisdimethylglyoximatocobalt(I)⁹ in 50% aqueous ethanol, prepared by mixing solutions of dimethylglyoxime and cobalt(II) acetate and then reducing with $NaBH_4$, reacted instantaneously with N_2O (colour change to brown). When an excess of borohydride was used to keep the cobalt complex reduced, N_2O was completely reduced to N_2 within 30 min. (3) *Ca.* $10^{-2}M$ solutions of $[Co^I(Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2)_2]^+ Br^-$,¹⁰ in ethanol or benzene reduced N_2O to N_2 according to the stoichiometry: $1 N_2O + 2 Co^I$. The resulting greenish complex is very air-sensitive and has not yet been identified. The rate of reaction could not be estimated from the colour change, both initial and final solutions being very strongly coloured. (4) Blue solutions of bis-(bipyridyl)cobalt(I) perchlorate¹¹ in 50% aqueous ethanol, prepared by reducing tris(bipyridyl)-cobalt(III) perchlorate with borohydride react instantaneously with N_2O (colour change to yellow); when left overnight with solutions containing an excess of borohydride, N_2O is completely reduced to N_2 . N_2O was also found to react with bis(bipyridyl)rhodium(I) chloride in 50% aqueous ethanol and with the complex(es) formed on reducing an aqueous solution of the pentacyanocobalt(II) ion with borohydride. The following showed no significant reaction with N_2O under the conditions used: $[Co^I(PhNC)_5]ClO_4$ in ethanol; $Fe(CO)_5$, $Na[Mn(CO)_5]$, and $Na_2[Cr(CO)_5]$ all in tetrahydrofuran; $[Co^0(Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2)_2]$ and $[Ir^I Cl(PPh_3)_2CO]$ both in benzene.

Nitrous oxide is clearly more reactive towards transition-metal complexes than previously suspected. Most or all of the above reactions (*ca.* neutral aqueous solutions). The four reactions, where the

main product has been identified, correspond to the simple reaction



and at least three of the complexes act as catalysts for the reduction of N_2O by borohydride.

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Reaction (1) probably occurs by a Walden-inversion type process, as this would presumably involve

Hydrogen formation could not be studied due to the large amount of H_2 carrier gas in this system.