Catalytic Conversion of NO into N_2 and N_2O by Dinitrobis(ethylenediamine)-cobalt(III) Cation

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Summary In the presence of various amines, nitric oxide was catalytically converted into N_2 and N_2O by dinitrobis(ethylenediamine)cobalt(III) cation complex in aqueous solution.

Although the heterogeneous catalytic reduction over various noble metals and metal oxides of nitric oxide by CO, H_2, or NH_3 has been extensively studied in connection with environmental problems,[1] the corresponding reaction in homogeneous transition metal complex systems is not well known. It has been reported that certain dinitrosyl complexes catalyse the reduction of NO by carbon monoxide,[2] but this has not been achieved yet with hydrogen or ammonia.

We now report that reduction of NO takes place with amines in aqueous solutions of Co complexes; $[Co(en)_2(NO_2)_2]^+$ (en = ethylenediamine) catalyses the conversion of NO into N_2 and N_2O in aqueous solution containing ammonia or aliphatic amines ($MeNH_2$, $EtNH_2$, and Bu^nNH_2). The reaction was performed in a closed circulation system containing a vigorously stirred solution of the complex. The composition of the gas phase was analysed by g.l.c. When nitric oxide (1—10 mmol) was introduced in the gas phase with an aqueous solution (100 ml) of *cis*- or *trans*-$[Co(en)_2(NO_2)_2]X$ ($X = NO_2^-$ or NO_3^-) (1—5 mmol) containing various amines (10—100 mmol), the amount of NO decreased after several hours and approximately equal amounts of N_2 and N_2O were formed. The rate of consumption of NO obeyed the second-order rate equation $1/[NO]_t - 1/[NO]_0 = kt$ at the beginning of the reaction (Figure). N_2 and N_2O were not formed in the absence of amine or NO; NO did not react at all with primary amine in a few days at room temperature under these reaction conditions, in the absence of the complex.

The initial rate of N_2 and N_2O formation showed a first-order dependence upon the partial pressure of NO, the concentration of the complex, and the concentration of amine. The order of reactivity of the various amines was as follows: $MeNH_2 \geqslant EtNH_2 \geqslant Bu^nNH_2 > NH_3$, which corresponds qualitatively to the order of their basicities, and suggests participation of OH^- in the reaction. The reaction in fact proceeded in aqueous NaOH solution instead of amine solution, although decomposition of the complex occurred simultaneously.

A *trans* effect was observed for the NO_2^- group; the initial rate of NO consumption was 3—4 times faster with *cis*-$[Co(en)_2(NO_2)_2]^+$ than with the *trans*-isomer (Figure). However, after about one Co^{3+} catalytic cycle, the rate decreased abruptly in the case of the *cis*-isomer; for the *trans*-isomer the rate increased gradually, and at the later stage of the reaction, both *cis* and *trans*-isomers showed similar rates.

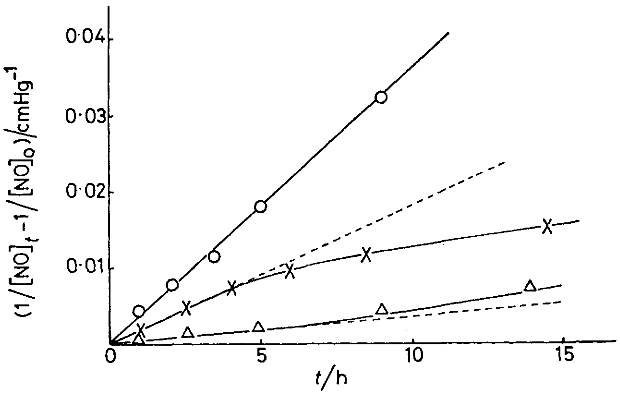

FIGURE. Plots for the second-order rate equation $1/[NO]_t - 1/[NO]_0 = kt$ for the rate of nitric oxide consumption at room temperature: ○, *cis*-$[Co(en)_2(NO_2)_2(NO_3)]$ (2·3 mmol), NH_3 (0·3 mol) in H_2O (100 ml); ×, *cis*-$[Co(en)_2(NO_2)_2(NO_3)]$ (0·55 mmol), NH_3 (0·7 mol) in H_2O (100 ml); △, *trans*-$[Co(en)_2(NO_2)_2(NO_3)]$ (0·55 mmol), NH_3 (0·7 mol) in H_2O (100 ml). Initial pressure of NO (6 mmol) = 30 cmHg in each case.

These results indicate that isomerization of the complex occurs accompanied by the reduction of NO, as was confirmed by isolation of the isomers after the reaction. However this isomerization did not take place at all in the absence of NO. Consequently, it is strongly suggested that NO reduction proceeds through an intermediate which also causes the isomerization of the complex.

A possible mechanism which would accommodate these results involves the substitution of one amino-group of en by NO and the abstraction of a nitro-group by amine to form N_2; this would be assisted by the electron-withdrawing nature of co-ordinated NO. By co-ordination of a further NO group to the vacant site, a dinitrosyl complex, a common intermediates in the reduction of NO by CO,[2] may be formed, followed by disproportionation of NO to N_2O and reformation of the original dinitro-complex. Isomerization of the complex could take place at this disproportionation step. It could be a similar process to that reported by Caulton *et al.*[3] in the disproportionation of NO by $[Co(en)_2(NO)Cl_2]$. The resulting $[Co(en)_2(NO_2)Cl_2]$ did not exhibit any activity for the present reaction, however.

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