CHEMISTRY LETTERS, pp. 1085-1088, 1975. Published by the Chemical Society of Japan

LIQUID PHASE REDUCTION OF NO TO N_2 BY USE OF TRANSITION METAL-SCHIFF'S BASE COMPLEXES

Tomoya SAKAI, Yoshitaka KURODA, Seiichi GOTO, and Yoshio YANO
Department of Chemical Reaction Engineering, Faculty
of Pharmaceutical Sciences, Nagoya City University
3-1, Tanabedori, Mizuhoku, Nagoya 467

Catalytic actions of several transition metal-Schiff's base complexes were examined on the reduction of NO to N_2 in DMF solution. By use of Co(II)(Salen) or Fe(II)(Salen) and $NaBH_4$ as a reducing reagent, thorough reduction of NO to N_2 was observed.

Some transition metal-Schiff's base complexes are known to react with NO. Salen complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) are reported to form the following products, respectively; $[MnO(Salen)]_2O_2$,[1)] Fe(Salen)NO or $[Fe(Salen)]_2O$,[2)] Co(Salen)NO,[3)] Ni(5,5'-dinitro-Salen),[4)] and Cu(5,5'-dinitro-Salen).[4)] In the cases of acacen complexes, Co(acacen) produces Co(acacen)NO,[5)] but Ni(acacen) and Cu(acacen) give oxime-type complexes.[6)] The present paper reports that Co(II)(Salen) or Fe(II)(Salen) has an ability to convert more than ten times of NO in molar ratio to the complex into N_2 by use of $NaBH_4$ as a reducing reagent in DMF solution. The following abbreviations are used. Salen = bis(salicylaldehyde)ethylenediiminato- , acacen = bis(acetylacetone)ethylenediiminato-, and DMF = N,N'-dimethylformamide.

Several transition metal-Schiff's base complexes were prepared by the literature methods; Mn(II)(Salen),[7)] Fe(II)(Salen),[7)] Co(II)(Salen),[8)] Ni(II)(Salen),[9)] Cu(II)(Salen),[9)] Co(II)(acacen),[10)] Ni(II)(acacen),[11)] and Cu(II)(acacen).[11)] The complexes were obtained in crystalline form, except in the case of Mn(II)(Salen) which was obtained in DMF dissolved form. In the cases of Co(II)(Salen) and Co(II)(acacen), the complexes were de-oxygenated at 60°C in vacuo before use. DMF, which was used as a solvent in the present experiments, was de-oxygenated by applying high vacuum at liquid nitrogen temperature. NO gas (Seitetsu Kagaku Kogyo Co.) was purified by passing through a 40% KOH and a silica gel column. N_2O gas was prepared by thermal decomposition of NH_4NO_3 at ca. 200°C, followed by purifications with a conc. H_2SO_4 solution of $FeSO_4$, a 40% KOH aq. solution and a silica gel column.

The standard procedure of the experiment was as follows. To 30 ml of anhydrous and de-oxygenated DMF in a reaction flask were added 0.1 mmoles of Co(II)(Salen) and 5 mmoles of $NaBH_4$ under an atmosphere of helium. The reaction flask was degassed again and was heated upto 80°C. A mixed gas of NO and He in a 1:1 molar ratio was introduced so that 1 mmole of NO was charged. The liquid and gas phases were stirred independently by magnetic stirrers. Progress of the reaction was monitored by gas chromatographic analysis which was carried out by use of silica gel packed column and H_2 carrier at 60°C for N_2, NO and N_2O in the gas phase.

Experimental results are illustrated in Figures 1 - 3. Fig. 1 shows the decrease in the amount of NO in gas phase with reaction period at room temperatures for several transition metal-Schiff's base complexes as indicated in the figure. In all cases, production of N_2O was observed. Even in the case of $NaBH_4$ itself, that is, in the absence of complexes, NO was reduced to N_2O. However, in this case, no N_2 was produced even at 80°C and after 24 hours, as illustrated in Fig. 2. In the case of Co(II)(Salen) or Fe(II)(Salen) with $NaBH_4$ in DMF, small amounts of N_2 were evolved at room temperatures. Fig. 3 shows the result of the reaction by use of Co(II)(Salen), which was carried out at 80°C in order to minimize the amount of gases dissolved in the solution. In both cases, NO was finally reduced to N_2, although the nitrogen balance was as low as 70% in the case of Fe(II)(Salen). In the cases of reaction by use of Mn(II)(Salen), Ni(II)(Salen) and Co(II)(acacen), only small amounts of N_2 were evolved at room temperatures. No N_2 was evolved in the cases of Cu(II)(Salen), Ni(II)(acacen) and Cu(II)(acacen) at room temperatures. Experiments at 80°C for these complexes have not been performed yet. When N_2O was introduced, instead of NO, to the solution of Co(II)(Salen) with $NaBH_4$ in DMF, the evolution of N_2 occured in nearly stoichiometric yield to feed N_2O. On the other hand, when 5.4 mmoles of Co(Salen)NO which was prepared according to the method of literature[3)] was subjected to the reaction with 26 mmoles of $NaBH_4$ in DMF solution, N_2O was produced at first and then was converted into N_2. Moreover, Co(I)(Salen) prepared by reducing Co(II)(Salen) with $NaBH_4$ in DMF reacted with N_2O to produce N_2, in line with the result reported by Banks et al.[12)]

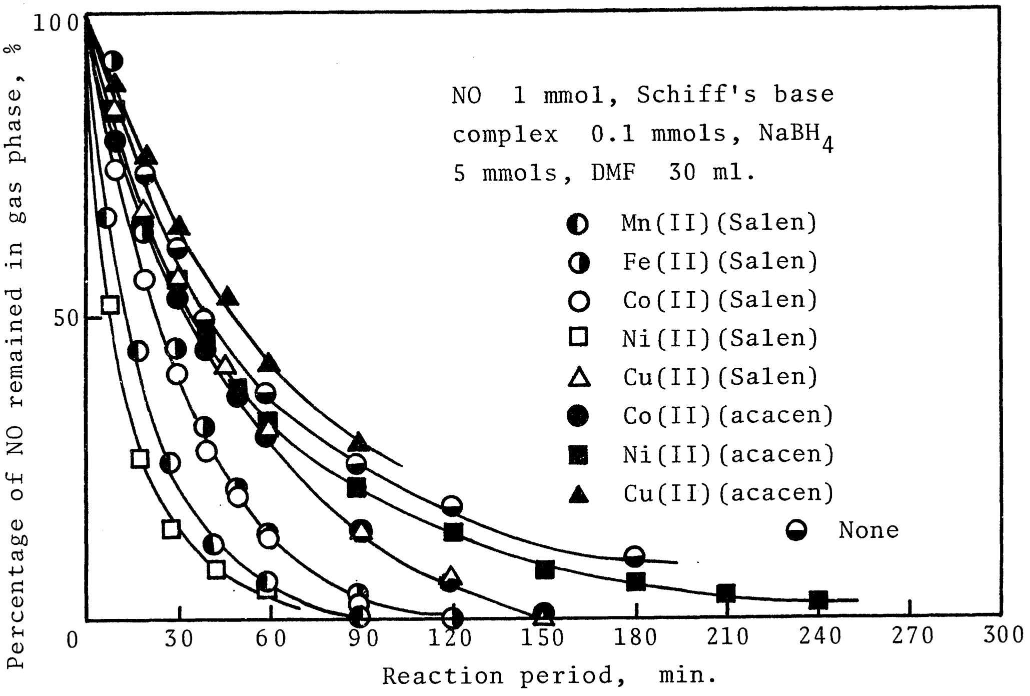


Fig. 1 Decrease in the amount of NO in gas phase at room temperatures.

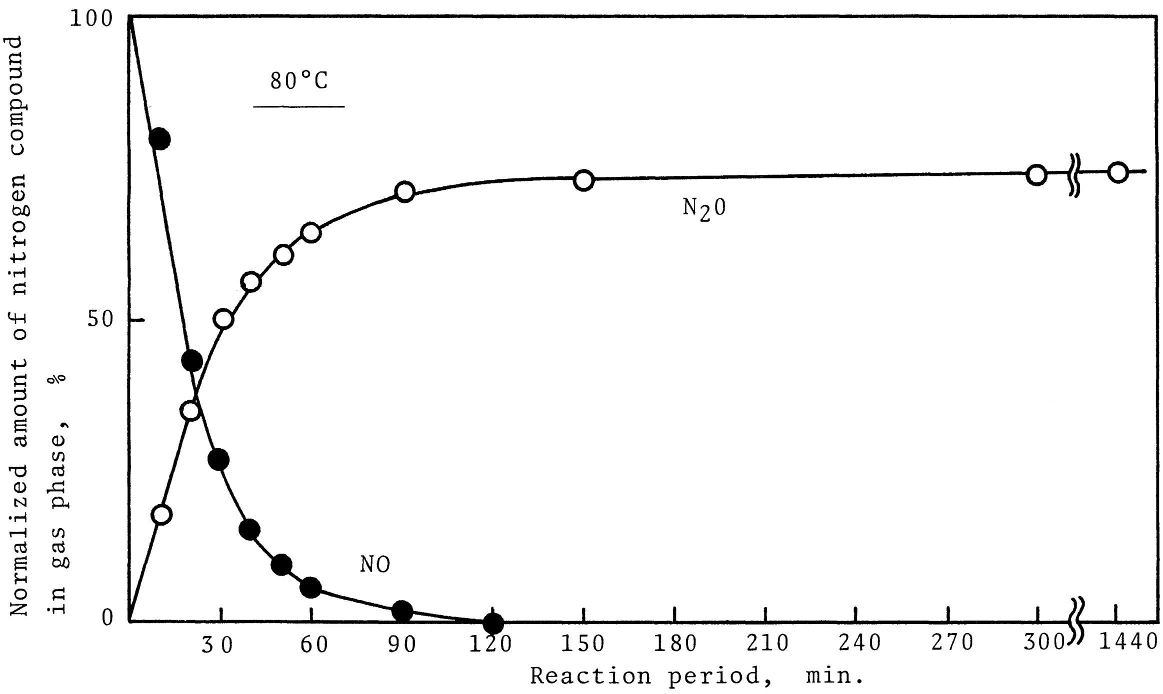


Fig. 2 Reduction of NO with $NaBH_4$ in the absence of complexes.

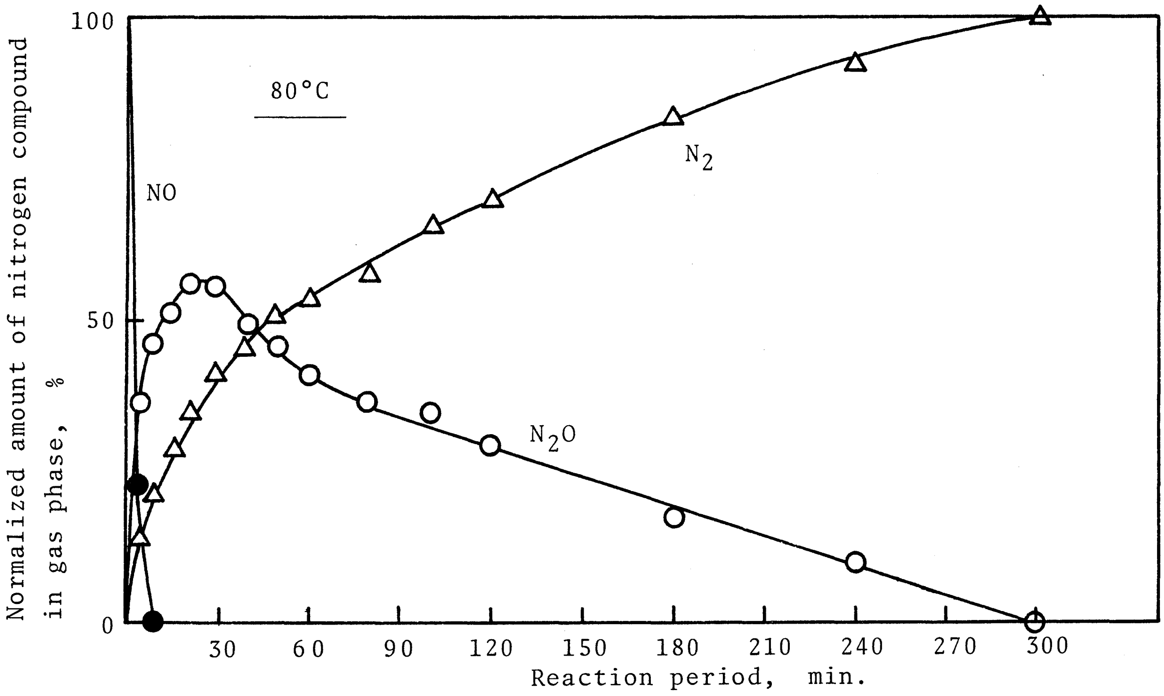
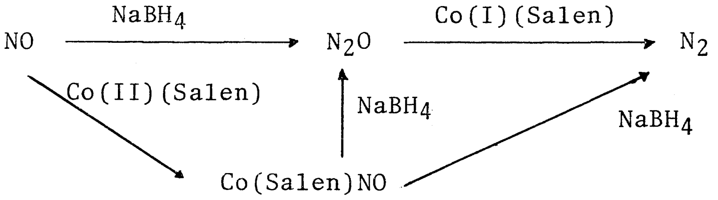


Fig. 3 Reduction of NO with $NaBH_4$ in the presence of Co(II)(Salen).

By use of ascorbic acid instead of $NaBH_4$ as a reducing reagent, NO was completely reduced to N_2O in the presence of Fe(II)(Salen) or Co(II)(acacen). Ascorbic acid itself did not react with NO at 50°C during 24 hours. In this connection it is an interesting fact that Co(II)(Salen) did not behave as a reducing catalyst of NO to N_2O by use of ascorbic acid as a reducing reagent. When Na_2SO_3 was used as a reducing reagent, the reaction of NO to N_2O proceeded with or without complexes such as Co(II)(acacen), Co(II)(Salen) and Fe(II)(Salen), at nearly the same reaction rate. However, no N_2 was formed in these cases.

From the evidences obtained above, it can be said for the reaction system of NO-Co(II)(Salen)-$NaBH_4$ in DMF that 1) NO is reduced to N_2O solely by $NaBH_4$, 2) Co(Salen)NO reacts with $NaBH_4$ to produce N_2O and possibly N_2 at the same time, 3) N_2O is reduced to N_2 by Co(I)(Salen). To summarize the results mentioned above, the following scheme may be a reasonable explanation for the present reaction.



References

1) M. Tamaki, I. Masuda, and K. Shinra, Chem. Lett., 1972, 165.
2) A. Earnshaw, E.A. King, and L.F. Larkworthy, J. Chem. Soc., A, 1969, 2459.
3) A. Earnshaw, P.C. Hewlett, and L.F. Larkworthy, ibid, 1965, 4718.
4) M. Tamaki, I. Masuda, and K. Shinra, Bull. Chem. Soc. Japan, 45, 1400 (1972).
5) M. Tamaki, I. Masuda, and K. Shinra, ibid, 42, 2858 (1969).
6) I. Masuda, M. Tamaki, and K. Shinra, ibid, 42, 157 (1969).
7) A. Earnshaw, E.A. King, and L.F. Larkworthy, J. Chem. Soc., A, 1968, 1048.
8) H. Diehl and C.C. Hach, Inorg. Synth., 3, 196 (1950).
9) P. Pfeiffer, E. Breite, E. Lübbe, and T. Tsumaki, Ann., 503, 84 (1933).
10) G. Morgan and J. Smith, J. Chem. Soc., 1925, 2030.
11) P.J. MaCarthy, R.J. Hovey, K. Ueno, and A.E. Martell, J. Am. Chem. Soc., 77, 5820 (1950).
12) R.G.S. Banks, R.J. Henderson, and J.M. Pratt, Chem. Commun., 1967, 387; J. Chem. Soc., A, 1968, 2886.

(Received August 11, 1975)