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REDUCTIVE DECOMPOSITION OF NITRIC OXIDE BY BIS(SALICYLALDEHYDE)ETHYLENEDIIMINO MANGANESE(II) AND FORMATION OF AN OXYGENATED MANGANESE COMPLEX

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By the reaction of Mn^{II}(Salen) [Salen: bis(salicylaldehyde)-ethylenediiminato dianion] with NO in DMSO, NO is reductively decomposed to give N_2O and N_2, and a new oxygenated manganese complex $[Mn{=}O(Salen)]_2O_2$ is formed. The complex shows IR absorption bands at 623 and 640 cm^{-1} attributed to ν_{Mn-O}, and at 884 cm^{-1} attributed to $\nu_{Mn=O}$, indicating both oxo- and μ-peroxo-bonding in the complex.

Only few examples of a metal-catalyzed decomposition reaction of NO are known up to the present. Certain transition-metal carbonyls were found to convert NO into NO_2 and N_2O.1) Recently, Rossi and Sacco reported that $Co(PPh_3)_3(NO)$ reacts with NO to give N_2O, N_2 and a nitrosylnitro-complex.2) Earnshaw et al noted that when Mn^{2+} or Fe^{2+} was reacted with $SalenH_2$ in a NO atmosphere, $[Mn^{III}(Salen)]^+$ resp. $[Fe^{III}(Salen)]_2O$ were obtained, instead of the expected nitrosyl complexes.3) Their results seem to be implying a reductive decomposition of NO.

In the present work we found out that Mn^{II}(Salen) decomposes NO to N_2O and N_2, and forms a new oxygenated manganese complex, which is tentatively formulated as $[Mn{=}O(Salen)]_2O_2$.

Reaction with NO: A reaction flask containing 50 ml of DMSO, deoxygenated

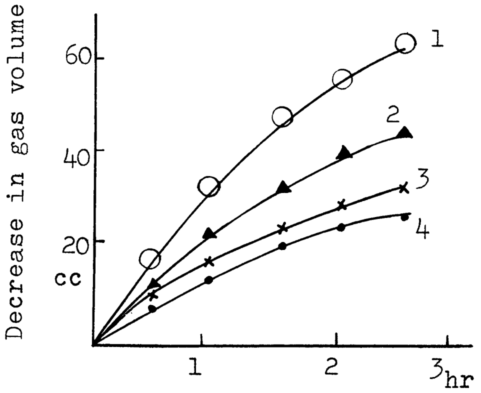

Fig. 1. Changes in gas volume.

Mn^{II}(Salen) : 1/300M; curve 1, 1/667M; curve 2, 1/1000M; curve 3, 1/2000M; curve 4, in DMSO solutions

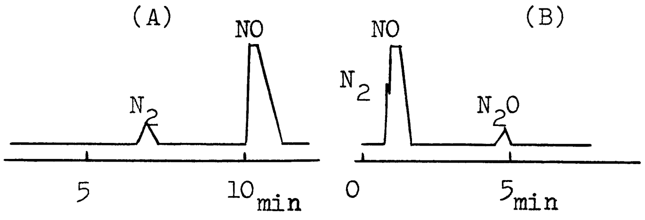

Fig. 2. Gas chromatograms.

Column ; 4mm i.d. × 3m long, Column temp ; 60°C

Column packing ; (A) Molecular sieves 5A
(B) Silicagel

Carrier gas ; (A) He, 120ml/min
(B) H_2, 60ml/min

by applying high vaccum, and equipped with a gas burette filled with liquid paraffin was filled with NO. Then, after the pressure was ajusted to 1 atm. at 25°C, Mn^{II}(Salen) was added to the solution. The changes in the gas volume are shown in Fig. 1. The result indicates that Mn^{II}(Salen) decreases the volume of the gaseous compounds by a molar ratio of 1 : 2.

Gas chromatographic analyses of the gaseous products carried out under the conditions noted in Fig. 2, indicate that N_2O and N_2 were formed during the reaction.

$[Mn{=}O(Salen)]_2O_2$: The reddish-brown compound precipitated from the reaction mixture was separated, and recrystallized from dichloromethane. Found : Mn,15.61; C,54.34; H,4.18; N,7.55%. Calcd for $MnC_{16}H_{14}N_2O_4$: Mn, 15.55; C,54.40; H,4.00; N,7.93%. The compound is paramagnetic, 2.11 B.M., and the elementary analyses agree with a formula Mn(Salen)O_2. The IR spectrum of the complex possesses almost the same pattern as that of Mn^{II}(Salen), with exception of the new bands observed at 623, 640 and 884 cm^{-1} (Fig. 3). The strong bands at 623 and 640 cm^{-1} may be ascribed to ν_{Mn-O}, and the band at 884 cm^{-1} to $\nu_{Mn=O}$.[4]

In the thermogravimetric analysis curve, the complex shows a weight loss at 190 - 220°C which corresponds to liberation of 0.5 mole O_2 per manganese atom.

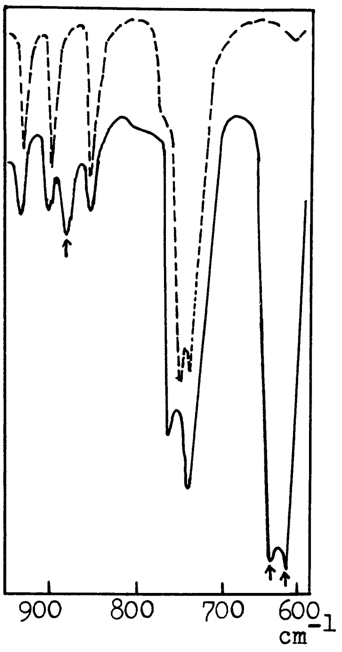

Fig. 3. IR spectra of $[Mn{=}O(Salen)]_2O_2$ (——) and Mn^{II}(Salen) (----).

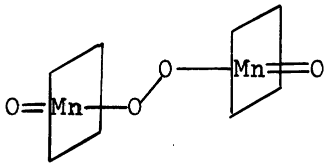

Fig. 4.

These data seem to indicate that the compound includes both oxo- and μ-peroxo-bonding. The dimeric structure shown in Fig. 4 is tentatively proposed.

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2) M. Rossi and A. Sacco, ibid., 694 (1971).
3) A. Earnshaw, E. A. King and L. F. Larkworthy, J. Chem. Soc., A, 1969, 2459; ibid., 1968, 1048.
4) T. Matsushita, T. Yarino, I. Masuda and K. Shinra, submitted for publication.

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