OXYGENATION OF NITRIC OXIDE IN THE PRESENCE OF A NITROSYL-BRIDGED COMPLEX OF MOLYBDENUM

JAN O. DZIĘGIELEWSKI* and KRZYSZTOF FILIPEK

Department of Inorganic and Radiation Chemistry, Institute of Chemistry, Silesian University, Szkolna 9, 40006 Katowice, Poland

and

BOGUSŁAWA JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, Wrocław, Poland

(Received 15 August 1990; accepted 10 October 1990)

Abstract—The binuclear, nitrosyl-bridged complex $Cs_2[Mo_2Cl_5H(NO)_2]$ was synthesized and employed in the oxygenation of nitric oxide, with insufficient oxygen. The mechanism of the oxygenation process is discussed and the "catalytic" activity of the complex in such a process described.

The goal of our work was to synthesize a molybdenum complex with nitrosyl bridges and examine the influence of such a complex on the process of nitric oxide oxygenation when oxygen is used in an insufficient amount.

The problems of treatment and utilization of nitrogen oxides as the components of exhaust gases have been known for many years¹ and there are many catalytic and non-catalytic methods involving either reduction² or oxygenation of NO_x .³ The former reactions are much better known and applied more often, but the presence of oxygen, as an inseparable component of the gases, imposes serious difficulties on such processes.

Nitric oxide is hardly soluble in any alkaline solution, while the higher oxides of nitrogen are readily soluble.⁴ In every case nitric oxide is present in the gases since the amount of air (oxygen) is insufficient to oxygenate it. Therefore, the methods of "extra oxygenation" of oxides of nitrogen followed by the absorption of the gases in alkaline solution have been widely applied.¹

On the other hand, the reactivity of the nitrosyl complexes towards oxygen and nitric oxide has been indicated in the literature;⁵ as a rule, these reactions are redox processes.⁶ In our previous work⁷ we described the possibility of such a reaction in the

case of a molybdenum(II) complex with nitrosyl bridges and gaseous nitric oxide.

EXPERIMENTAL

The first stage of our work was to synthesize and characterize the nitrosyl molybdenum complex. The hydrido complex, Cs₃[Mo₂Cl₈H], was prepared according to the literature⁸ and the nitrosyl complex was obtained in the heterogeneous reaction with gaseous nitric oxide. Nitric oxide was formed in the reaction of NaNO₂ with FeSO₄ in H₂SO₄ solution and then purified by passing through a concentrated solution of KOH, and then over NaOH pellets. The reaction was carried out under strictly deoxygenated conditions and controlled by determination of the liberated NOCl, which was absorbed in 10% KOH, while the abstracted chlorides were determined using standard methods.⁹ The solid-state mixture (complex + CsCl) was dissolved in THF and the CsCl was filtered off and dissolved in water to determine [Cl-] ions. The organic solution was evaporated and the residue was analysed using standard methods of elemental analysis. The results based on the formula Cs₂Mo₂Cl₅HN₂O₂ were as follows: Found: Mo,27.4; Cl, 25.8; N, 4.1 (or 3.9-from TG curve). Calc. : Mo. 27.6; Cl, 25.5; N, 4.0%. The complex was formed in the following reaction:

^{*} Author to whom correspondence should be addressed.

 $Cs_3[Mo_2Cl_8H] + 4NO \longrightarrow$

$$Cs_2[Mo_2Cl_5H(NO)_2] + CsCl + 2NOCl.$$

The spectroscopic analysis of the complex was obtained with a Beckman 5240 spectrophotometer (absorption bands) and a Specord 75 IR spectrophotometer (IR measurements in KBr pellets). Magnetic susceptibility was measured using a Gouy balance and the thermogravimetric analysis was carried out with a Q-1500 D Paulik–Paulik system derivatograph.

The reactions of nitric oxide with oxygen in the presence of the complex were carried out in special tubes previously vented with argon. The mixtures of nitric oxide and oxygen (M: M = 10: 1, 20: 1,30:1) were reacted with solid $Cs_2[Mo_2Cl_5H(NO)_2]$ several times using different amounts of the complex. In every case oxygen was added as the first component. The amounts of nitrogen oxides were determined spectrophotometrically¹⁰ by dissolving in 2 M KOH and then determining as nitrites and nitrates. Since nitric oxide is almost insoluble in KOH (nevertheless the amounts of NO_2^- corresponding to nitric oxide were subtracted) the NO_2^- and NO_3^- formed are the products of the reaction of NO₂, N₂O₄ and N₂O₅ with KOH. The amounts of NO_2^- and NO_3^- could be easily converted into the quantities of the corresponding oxides. The reactions of similar compositions of the NO/O₂ mixtures were examined as references.

RESULTS AND DISCUSSION

Characterization of the Cs₂[Mo₂Cl₅H(NO)₂] complex

IR vibrations of the complex are presented in Table 1. The vibration at 1380 cm⁻¹ is typical for a bridging nitrosyl group.^{7,11} Dissolution of the complex in water is accompanied by the liberation of gaseous hydrogen and this fact, together with two weak intensity vibrations at 1650 and 1250 cm⁻¹, support the presence of the bridging hydrogen in the coordination sphere of the complex. The 60 cm⁻¹ shift of $v_{as}(Mo-H-Mo)$ in comparison with the initial complex¹² is due to the presence in the coordination sphere of nitric oxide, a ligand with strong π -acceptor ability. The presence of the two suggested nitrosyl groups is supported by the thermal analysis results (see Fig. 1).

Two well-distinguished slopes in the mass loss curve (TG) between 400 and 600 K could be attributed to the two different nitrosyl groups abstracted from the complex in the form of gaseous dinitrogen.¹³ These phenomena are accompanied

Table 1. IR vibrations of Cs₂[Mo₂Cl₅H(NO)₂]

Frequency (cm ⁻¹)	Assignment
1650(w)	v _{as} (Mo—H—Mo)
1380(vs)	$v(NO_b)$
1250(w)	$v_{sym}(Mo-H-Mo)$
620(m)	v(Mo—N)
550(m)	$\delta \begin{pmatrix} N \\ Mo & O & Mo \end{pmatrix}$
540(w)	δ (Mo—H—Mo)
310(w)	$v(M_0 - C^1)$
295(m)	
280(w)	$v(Mo-Cl_b)$

by two peaks in the DTG and DTA curves due to the chemical reactions taking place during heating. The absorption bands of the complexes are presented in Table 2. The decay of the band attributed to the $\delta \rightarrow \delta^*$ transition in the initial complex is due to the cleavage of the Mo—Mo multiple bond. This is a typical effect of the multiple bond complex reactions with nitric oxide.¹⁵ The complex formed is almost diamagnetic ($\mu_{eff.} = 0.3$ BM). Electrons from d_{xz} and d_{yz} orbitals could be effectively delocalized to the π^* orbitals of nitric oxide and then transferred to the lower unoccupied orbital (LUMO) of the central atom, i.e. b_2 .¹⁶ The transfer



Fig. 1. Thermal analysis curves for the decomposition of Cs₂[Mo₂Cl₅H(NO)₂] under nitrogen; heating rate 5 K min⁻¹. (1) TG—mass loss; (2) DTG—temperature derivative of the mass loss; (3) DTA—differential thermal analysis curve.

Frequency (cm ⁻¹)	З	Assignment
	Cs ₃ [Mo ₂ Cl	₈ H] ¹⁴
13,330	310	$e \rightarrow b_2$
28,570	2100	$e \rightarrow b_1$
32,790	12,500	$\pi \rightarrow \pi^*$
42,920	24,000	$e \rightarrow d_{x^2 - v^2}$
45,450	22,000	$Cl \rightarrow b_2$
	Cs ₂ [Mo ₂ Cl ₅ H	[(NO) ₂]
18,690	330	$^{2}B_{2}(\pi_{\mathrm{NO}}^{*}) \rightarrow \pi_{\mathrm{NO}}^{*}$
23,810	1700	${}^{2}A_{1} \rightarrow {}^{2}B_{2}$
42,190	12,000	$^{2}A_{1} \rightarrow \pi_{NO}^{*}$
47,600	16,500	$Cl \rightarrow {}^{2}B_{2}$

Table 2. Absorption bands and their characterization for $Cs_3[Mo_2Cl_8H]$ and $Cs_2[Mo_2Cl_5H(NO)_2]$ in 9 M HCl

mentioned is the reason for a high activation of the bridged nitrosyl group.¹⁷

Reactions with oxygen and nitric oxide mixtures

It is worthy of note that the reactions of nitric oxide with oxygen in the absence of the complex have yields of about 3% (see Fig. 2). The results of similar reactions in the presence of the complex are presented in Fig. 3.

The process is not due to adsorption since the relation between the amount of oxygenated nitric oxide and the amount of the complex is curvilinear (see Fig. 4).

Consideration of the equilibrium constants of the possible reactions during the experiment¹⁸ leads to the conclusion that the duration of the process could effect the composition of the higher nitrogen oxides formed. Since the applied method of analysis (see Experimental) enables simultaneous deter-



Fig. 2. Yields of the NO+O₂ reaction (%) vs time. [NO] = 4×10^{-3} M; [O₂] = 0.13×10^{-4} M (1), 0.2×10^{-4} M (2), 0.4×10^{-4} M (3).



Fig. 3. Yields of the NO+O₂ reaction (%) vs time in the presence of Cs₂[Mo₂Cl₅H(NO)₂]. [Complex] = 0.5×10^{-4} M, [NO] = 4×10^{-3} M; [O₂] = 0.13×10^{-4} (1), 0.2×10^{-4} (2), 0.4×10^{-4} M (3).

mination of both nitrites (as the products of the NO_2+OH^- reaction) and nitrates (N_2O_4 and $N_2O_5+OH^-$ reaction), we could estimate the amounts of NO_2 and N_2O_5 gases produced. It is clear (see Fig. 5) that the longer reaction time favours the higher contents of N_2O_5 . Thus, the following reaction scheme could be proposed :

(I) coordination of oxygen into the highly activated bridging NO group:



- (II) abstraction of the very reactive NO₃ group from the coordination sphere;
- (III) reaction of NO₃ with NO supplied into the system

$$NO_3 + NO \longrightarrow 2 NO_2$$
,

with the simultaneous reconstruction of the coordination sphere of the complex;



Fig. 4. Yields of the NO+O₂ reaction (%) vs the amount of complex, t = 15 min (Concentrations of the gases as in Fig. 3.)



Fig. 5. The percentage of N_2O_5 in the gaseous products of the NO+O₂ reactions vs time. (Concentrations—as in Fig. 3.)

(IV) the slowest process,

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

The formation of the NO₃ group with the peroxo structure [reaction (I)] is a well known process,¹⁹ while the lack of nitrite or nitro complexes on the solid surface (confirmed by recording an IR spectrum after each of the experiments) suggests the homolytic liberation of the NO₃ group²⁰ [reaction (II)]. The nitric oxide supplied readily reacts with NO₃, according to the corresponding rate constant,¹⁸ while its excess reconstructs the coordination sphere of the complex [reaction (III)] and, as a consequence, the complex appears to behave as a catalyst. Kinetic factors contribute to the reaction of NO₃ with NO₂ [reaction (IV)] when sufficient time for the reaction is assured (see Fig. 5).

CONCLUSIONS

The oxygenation of nitric oxide is about 10 times more effective in the presence of the $Cs_2[Mo_2 Cl_5H(NO)_2]$ complex in a system which is deficient in oxygen, due to the reactivity of the nitrosyl bridges.

REFERENCES

1. L. H. Yaverbaun, Nitrogen Oxides Control and Removal: Recent Developments. Noyes Data Company, New York (1979).

- 2. H. Bosch and F. J. J. G. Janssen, *Catalysis Today* 1988, 2, 1.
- 3. H. T. Carlson and H. S. Rosenberg, Indian Engng Chem. Process Design Develop. 1984, 23, 808.
- 4. H. Idemura, Chem. Econ. Engng Rev. 1974, 6, 22.
- (a) S. Bhaduri, J. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal, R. Walters and C. Zuccaro, J. Chem. Soc., Dalton Trans. 1981, 234; (b) J. Backvall and A. Heumann, J. Am. Chem. Soc. 1986, 108, 7107.
- 6. J. A. McCleverty, Chem. Rev. 1979, 79, 53 and refs therein.
- 7. J. O. Dzięgielewski, K. Filipek and B. Jeżowska-Trzebiatowska, Inorg. Chim. Acta 1990, 171, 89.
- J. San Filippo Jr and H. J. Sniadoch, *Inorg. Synth.* 1979, 19, 129.
- 9. G. H. Coleman and G. A. Lillis, *Inorg. Synth.* 1939, 1, 55.
- 10. J. H. Wetters, Anal. Chem. 1970, 3, 335.
- R. C. Elder, F. A. Cotton and R. A. Schunn, J. Am. Chem. Soc. 1967, 89, 3645.
- K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley, New York (1970).
- (a) B. Mohai, K. Gyoryova and L. Bencze, J. Thermal Anal. 1979, 17, 159; (b) D. Dollimore, Differential Thermal Analysis (Edited by R. C. MacKenzie), p. 427. Academic Press, London (1970).
- 14. F. A. Cotton and R. A. Walton, *Multiple Bonds* Between Metal Atoms. Wiley, New York (1982).
- M. H. Chisholm, F. A. Cotton, M. W. Extine and R. L. Kelly, J. Am. Chem. Soc. 1978, 100, 3354.
- (a) F. Bottomley, *Inorg. Chem.* 1983, 22, 2656; (b)
 K. A. Kubat-Martin, M. E. Barr, B. Spencer and L.
 F. Dahl, *Organometallics* 1987, 6, 2570.
- (a) M. Kubota and D. A. Phillips, J. Am. Chem. Soc. 1975, 97, 5637; (b) W. J. Bykov and A. P. Svytyn, Metody razczeta parametrov aktywacji molekul, p. 129. Nauka, Novosybirsk (1988).
- F. Busi, M. D. D'Angelantonio, Q. G. Mulazzani, V. Rafaelli and O. Tubertini, *Radiat. Phys. Chem.* 1985, 25, 47.
- S. G. Clarkson and F. Basolo, *Inorg. Chem.* 1973, 12, 1528.
- B. S. Tovrog, F. Mares and S. E. Diamond, J. Am. Chem. Soc. 1980, 102, 6616.