Absolute Rate Constants of Mo_2 ($X\ ^1\Sigma_g^+$) and Mo ($a\ ^7S_3$) with NO at Room Temperature

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The gas-phase reactivities of nitrogen monoxide for ground-state molybdenum atoms and dimers have been investigated in a mass-flow controlled cell. Transient concentration of Mo (a $^7S_3$) or Mo_2 ($X\ ^1\Sigma_g^+$, v = 0) produced by 355-nm multiphoton decomposition of $Mo(CO)_6$ was monitored by a laser-induced fluorescence. These measurements suggest the simple adduct formation such as Mo(NO) for the reaction of Mo + NO but a certain chemical bond activation of NO on Mo_2.

Over the last decade, many intensive studies on the gas-phase transition-metal chemistry have been reported mainly because it is expected to be useful for the understanding of the interaction between active sites on transition metals and small molecules based on the electronic structure theory.[1] Such a MO interaction between small molecules and transition metal centers has been gradually elucidated by the support of experimental data involving metal clusters.[2,3] Particularly in the small molecules, nitrogen monoxide has been recently revealed to play an important role in the inorganic biochemistry.[4] NO has one unpaired electron in the antibonding $2\pi^*$ orbital, making it reactive and complex in the coordination processes on transition metals.

In this study, we measured absolute reaction rate constants of molybdenum atoms and dimers with NO in the gas phase, with intention of understanding the basic interaction of NO with simple transition metal centers, free from complications due to solvent and ligands. Besides Mo atoms, an effective production of Mo_2 was observed in flash photolysis of $Mo(CO)_6$ in the gas phase.[5] A multiphoton decomposition (MPD) of $Mo(CO)_6$ seems to be convenient technique for molybdenum dimer production for kinetic studies because it gives a homogeneous distribution of Mo_2 and also the absolute pressure of reactant can be precisely controlled in a nearly static cell though the kinds of metals are limited by the volatility of their metal compounds as precursor.

Time-resolved laser-induced fluorescence (LIF) spectroscopy was used to monitor transient species, Mo (a $^7S_3$) and Mo_2 ($X\ ^1\Sigma_g^+$) produced following the intense 355-nm pulse photolysis of $Mo(CO)_6$ in the presence of NO and argon. Our time-resolved LIF apparatus was described in detail elsewhere.[6] The photolysis UV source was a pulsed Nd:YAG laser (Spectron SL803). The 355-nm laser beam was focused onto the center of a reaction cell using a quartz lens (f = 15 cm) to induce MPD of $Mo(CO)_6$. The monitoring source in LIF detection was a Nd:YAG pumped OPO laser (Spectra-Physics MOPO-730). The two laser beams were arranged to be collinear and counter-propagating. The delay time between the photolysis pulse and the probe pulse was varied by a digital delay generator (SRS DG535). The sample mixture was allowed to flow slowly through a brass cell with two suprasil windows mounted with a brewster's angle and controlled by the calibrated mass flow meters (STEC SEC-400) prior to admission to the reaction cell.

The decay rates of Mo (a $^7S_3$) and Mo_2 ($X\ ^1\Sigma_g^+$) as a function of NO pressure were measured at 6.5-Torr total pressure with balance Ar (Figure 1). The concentrations of Mo and Mo_2 were monitored at 319.40 nm ($y\ ^7P_2^o \leftarrow a\ ^7S_3$) and at 518.60 nm ($A\ ^1\Sigma_u^+$, v' = 0 $\leftarrow$ $X\ ^1\Sigma_g^+$, v'' = 0, J'' ≈ 26 and/or 28), respectively. Both decay rates increased with increasing NO pressure. The pseudo-first order decay rates were estimated by a single exponential fitting for the data in the late time region ($t \geq 10$ μs). As the formation of both species were apparently affected by the NO addition, the data in the early time region had to be excluded for the fitting. Vibrationally excited Mo_2^* ($v \geq 1$) was observed to exist even at 10 μs under 6.5-Torr Ar. However, the transient of Mo_2 ($v = 0$) was considered to be hardly affected by the quenching of these higher vibrational states because the quantity of Mo_2^* was no more than about 20 % of Mo_2 ($v = 0$) and its decay would be due to reaction with NO rather than quenching in the presence of NO. Without NO, the decay rate of Mo was observed to slightly decrease with

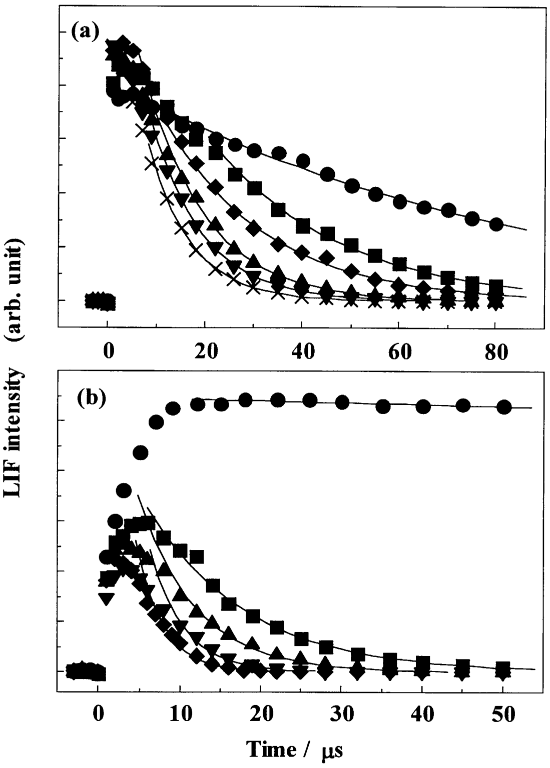

Figure 1. NO pressure dependence of transient LIF curves of Mo (a; a $^7S_3$) and Mo_2 (b; $X\ ^1\Sigma_g^+$, v = 0) following the 355-nm photolysis of $Mo(CO)_6$ (~ 10 mTorr) at 6.5 Torr of total pressure with balance Ar. In (a; Mo) NO pressures were 0 (●), 0.10 (■), 0.20 (◆), 0.30 (▲), 0.40 (▼) and 0.50 Torr (×) and in (b; Mo_2) NO pressures were 0 (●), 0.017 (■), 0.034 (◆), 0.051 (▲), and 0.11 (▼), and each solid line is a simulation curve obtained with an appropriate first-order decay rate.

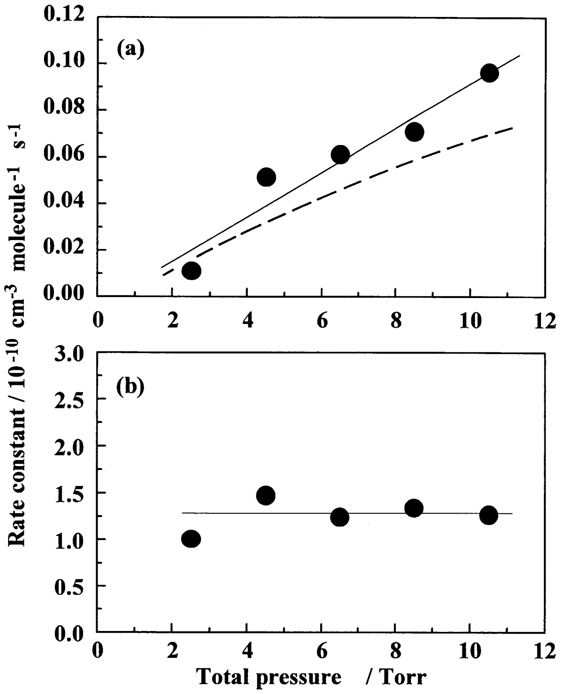

Figure 2. Total pressure dependencies of the pseudo-second-order reaction rate constants of Mo (a) and Mo_2 (b) with NO. Solid lines are smoothing lines connecting experimental data. Broken line in (a) is an empirical falloff curve previously reported by McClean et al. (see text).[10]

increasing total pressure, suggesting that the decay of Mo was not due to three-body recombination ($Mo + Mo + Ar \rightarrow Mo_2 + Ar$) but mainly due to diffusion of these species from the observation zone.[6]

The pseudo-first order decay rates of these molybdenum species were found to depend linearly on NO pressure, giving the bimolecular rate constants of $(6.1 \pm 0.5) \times 10^{-12}$ ($= k^{(2)}_{Mo}$) for reaction (1) and $(1.2 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} ($= k^{(2)}_{Mo2}$) for reaction (2) under the 6.5-Torr total pressure with balance Ar at room temperature:

$$Mo\ (a\ ^7S_3) + NO\ (+\ Ar) \rightarrow \text{product(s)} \qquad (1)$$

$$Mo_2\ (X\ ^1\Sigma_g^+, v = 0) + NO \rightarrow \text{product(s)} \qquad (2)$$

The reaction probabilities were estimated to be 0.03 for Mo and 0.4 for Mo_2 by assuming collision diameters of 3.57×10^{-8} cm,[7] 4.02×10^{-8} cm,[8] and 5.94×10^{-8} cm,[9] for NO, Mo, and Mo_2, respectively. Our value for reaction (1) is approximately agreement with the rate constant measured recently in a slowly flowing apparatus using a laser photolysis of $Mo(CO)_6$ / LIF .[10]

Figure 2 shows the total pressure effect on the pseudo-second order rate constants ($k^{(2)}$) for these two reactions. The linear dependence with *y*-intercept of about 0 in Figure 2(a) indicates that reaction (1) is in its third-order kinetic regime and that there is little contribution from a bimolecular dissociation channel. The slop gives the third-order rate constant of $(2.8 \pm 0.5) \times 10^{-29}$ cm^6 $molecule^{-1}$ s^{-1} for Mo + NO + Ar. The total-pressure dependence of $k^{(2)}_{Mo}$ suggests the simple adduct formation such as Mo(NO). Similar total pressure dependence of $k^{(2)}$ was observed for Mo ($a\ ^7S_3$) + NO + Ar in the higher-pressure range (Ar, 10 - 600 Torr) at 296 K.[10] Our data obtained in the lower-pressure range (Ar, 2 - 10 Torr) roughly coincide with the extrapolation curve calculated from the falloff expression proposed by McClean et al.[10] as shown in Figure 2(a). The falloff region of this reaction is also reported to be around 200 Torr at room temperature. The expectation of the simple association mechanism for this reaction is consistent with the thermo-chemical estimation, where the bond-fission reaction, $Mo + NO \rightarrow MoO + N$, is endothermic of about 33 kJ mol^{-1}.[11] On the other hand, no total pressure dependence of $k^{(2)}_{Mo2}$ in this pressure region suggests a certain chemical bond activation of NO on Mo_2. It seems possible that this Ar pressure region might be already in the high-pressure limit for dimer reaction. However, our Ar pressures were lower than the falloff pressure of atom reaction (1) by about two orders. Such a long lifetime of association species may be indicative of a transient complex formation with new chemical bond(s) other than the association bond. In the comparable Ar pressure region, Lian et al. have reported that the total pressure dependence exists for the association reaction involving Mo dimer ($Mo_2(X) + NH_3$).[12] The rate constant ($k^{(2)}_{Mo2}$) is close to the gas-kinetic collision frequency. These facts could be interpreted in terms of the indication of the bond-fission reaction with no significant energy barrier.

An experimental and theoretical examination of these reaction mechanisms (transition states and reaction products) would be required for the elucidation of the reactivities of Mo and Mo_2.

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References and Notes

1 "Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry," ed by A. Veillard, NATO ASI Series, C176, D. Reidel Publishing Company, Dordrecht (1986).

2 S. A. Mitchell, M. Blitz, Per E. M. Siegbahn, and M. Svensson, *J. Chem. Phys.*, **100**, 423 (1994).

3 J. J. Carroll, K. L. Haug, J. C. Weisshaar, M. R. A. Blomberg, Per E. M. Siegbahn, and M. Svensson, *J. Phys. Chem.*, **99**, 13955 (1995) and references therein.

4 E. Culotta and D. E. Koshland Jr., *Science*, **258**, 1862 (1992).

5 Y. E. Belyaev, A. V. Dem'yanenko, and A. A. Puretzky, in "Laser Chemistry of Organometallics," ACS Symposium Series, **530**, 220 (1993) and references therein.

6 T. Wakabayashi, Y. Ishikawa, and S. Arai, *Chem. Phys. Lett.*, **256**, 543 (1996).

7 J. T. Yardley, "Introduction to Molecular Energy Transfer," Academic Press, New York (1980).

8 J. J. Carroll, K. L. Haug, and J. C. Weisshaar, *J. Am. Chem. Soc.*, **115**, 6962 (1993).

9 $\sigma(Mo_2) \approx 4.00$ Å (≈ 2.00 Å (typical van der Waals radii of the 5th period elements) + 1.94 Å (r (Mo-Mo), J. B. Hopkins, P. R. R. Langridge-Smith, M. D. Morse, and R. E. Smalley, *J. Chem. Phys.*, **78**, 1627 (1983).).

10 R. E. McClean, M. L. Campbell, and R. H. Goodwin, *J. Phys. Chem.*, **100**, 7502 (1996).

11 JANAF Thermochemical Tables, *J. Phys. Chem. Ref. Data*, **14**, Suppl. No. 1 (1985).

12 L. Lian, S. A. Mitchell, and D. M. Rayner, *J. Phys. Chem.*, **98**, 11637 (1994).