Bull. Chem. Soc. Jpn., **54**, 1400—1402 (1981) [Vol. 54, No. 5

Determination of Hyperoxide in Dimethyl Sulfoxide by Photometric Titration with Iodine

Katsumi Kitamura, Koichi Hasegawa, Katsura Mochizuki,
Taira Imamura,* and Masatoshi Fujimoto*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received September 26, 1980)

The concentration of hyperoxide, O_2^-, in dimethyl sulfoxide (DMSO) was determined by photometric titration with iodine. The validity of the method was confirmed on the basis of stoichiometry by use of the standardized hyperoxide solution in the reaction of the complex, MoO(tpp)NCS, with methanol, where TPP denotes $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin.

Hyperoxide solutions prepared from potassium hyperoxide solubilized in aprotic solvents by crown ether[1] have been used for the syntheses of many organic compounds[2] and for reactions of metal complexes.[3] However, for determination of hyperoxide in aprotic solvents, only two reliable methods have been reported:[4] (1) determination of the dioxygen evolved first upon mixing a hyperoxide solution with water, then by the addition of catalase to the mixed solution,[6] and (2) measurement of the absorbance at 250 nm of the solution of potassium hyperoxide solubilized by 18-crown-6 ether in DMSO.[7]

In the kinetic study of the reaction of cobalt(III) complex with hyperoxide in aprotic solvents, we proposed a simple method for the determination of hyperoxide in DMSO according to the reaction[8]

$$I_2 + 2\,O_2^- \longrightarrow 2\,I^- + 2\,O_2. \qquad (1)$$

The reaction proceeds quantitatively[7] because of a large difference in the redox potential of iodine ($E°=0.54$ V)[9] and that of hyperoxide ion ($E°=-0.5$—-0.6 V).[10] The validity of the proposed method was confirmed by applying the hyperoxide solution to the reaction between the complex, MoO(tpp)NCS, and CH_3OH in CH_2Cl_2.

Experimental

Materials. Potassium hyperoxide (KO_2, ICN Pharmaceuticals) and 18-crown-6 (Nippon Soda) were used without further purification. Potassium content in the hyperoxide specimen was determined to be 95.7% by the Kalibor-Zephiramine method.[11] The solution of hyperoxide was prepared in an argon atmosphere from potassium hyperoxide solubilized by 18-crown-6 in DMSO. About 10 h is required for the preparation of *ca.* 10^{-2} mol dm^{-3} solution.

Reagent grade iodine was purified by repeated sublimation. In order to avoid any loss of iodine in the preparation of the standard solution, the following procedure was adopted. A small amount of DMSO was taken in a well-stoppered volumetric flask, and weighed. A desired amount of iodine was carefully taken in the volumetric flask and completely dissolved. The amount of dissolved iodine was determined from the difference in weight. Then the solvent was added to a mark on the flask and mixed to prepare a standard solution. Since the absorbance at 365 nm, λ_{max} of the solution, gradually increases (*ca.* 10% for 2.0×10^{-3} mol dm^{-3} I_2 in 3 d), and decreases in the presence of 18-crown-6 (*ca.* 5% in 40 h), the standard DMSO solution of iodine should always be prepared immediately before use.

Dimethyl sulfoxide was kept with CaH_2 for several days, distilled under reduced pressure, and stored in an argon atmosphere. The water content in the purified DMSO was determined to be less than 0.03% by the Karl-Fischer method.

Dichloromethane was distilled and passed through an alumina column. The pre-purified solvent was distilled immediately before use. The complexes, MoO(tpp)NCS and MoO(tpp)Br, were synthesized.[12]

Results and Discussion

Photometric Titration with Iodine. The concentration of O_2^- in DMSO was determined as follows. A 3.00-cm^3 hyperoxide solution (2×10^{-5}—9×10^{-3} mol dm^{-3}) is taken into an optical cell in an argon atmosphere. The optical cell is sealed at once with a serum cap. A small amount of iodine solution (5×10^{-4}—1×10^{-1} mol dm^{-3}) is then injected into the optical cell with a 100 mm^3 microsyringe or a micropipet. The absorbance at 400 nm, λ_{sh} of the iodine solution, is measured and plotted against the volume of the iodine solution injected. A typical change in absorbance at 400 nm is shown in Fig. 1. The absorbance gradually decreases until the end point depicted by A in Fig. 1 is reached. After the point A, the absorbance is measured 15 min after each addition of the solution of iodine in order to complete the reaction. The concentration of hyperoxide, x, is calculated by $x=2VC/3$, where V is the volume of the iodine solution consumed and C the concentration of iodine. The 10-fold change in the concentration ratio of 18-crown-6 and weighed amount of KO_2 does not affect the

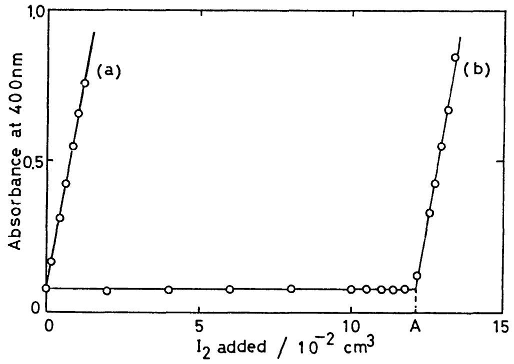

Fig. 1. Typical change in absorbance of hyperoxide solution at 400 nm by addition of an iodine solution. $[I_2]_0=3.98\times10^{-2}$ mol dm^{-3}. (a): $[O_2^-]_0=0$ and [18-crown-6]$_0=6.0\times10^{-3}$ mol dm^{-3}. (b): $[O_2^-]_0=3.12\times10^{-3}$ and [18-crown-6]$_0=6.0\times10^{-3}$ mol dm^{-3},

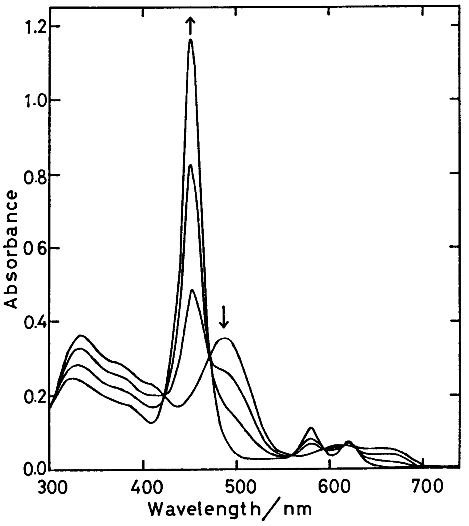

Fig. 2. Change in spectra for the reaction among MoO(tpp)NCS, CH_3OH, and O_2^- in CH_2Cl_2 containing 2%(v/v) CH_3OH, 1%(v/v) DMSO, and $[MoO(tpp)NCS]_0 = 7.54 \times 10^{-6}$ mol dm^{-3} at 25 °C.

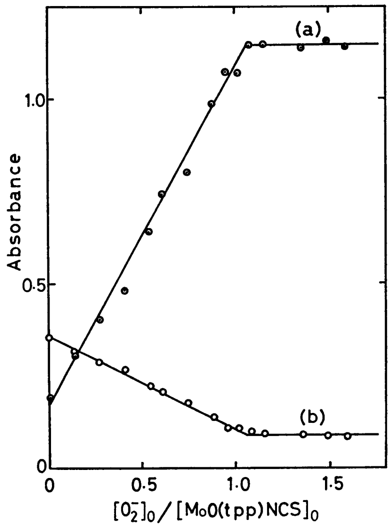

Fig. 3. Molar-ratio method for the reaction among MoO(tpp)NCS, CH_3OH, and O_2^- at 25 °C. (a): At 452 nm. (b): At 488 nm.

determination of O_2^-. Reproducibility of the data was estimated to be within ±1%.

Reaction among MoO(tpp)NCS, CH_3OH, and O_2^-. The solution of hyperoxide was applied to the reaction between the complex, MoO(tpp)NCS, and CH_3OH in order to confirm the validity of the proposed method. When the solution of hyperoxide is added to a dichloromethane solution of the complex, MoO(tpp)NCS, containing 2%(v/v) methanol, the spectrum changes with isosbestic points at 423 and 472 nm (Fig. 2).[13] The final spectrum agrees with the spectrum of the complex, $MoO(tpp)OCH_3$, synthesized from the complex, MoO(tpp)Br. The reaction should be written as follows.

$$\mathrm{Mo^{V}O(tpp)NCS + CH_3OH + O_2^-} \longrightarrow \mathrm{Mo^{V}O(tpp)OCH_3 + HO_2 + NCS^-} \qquad (2)$$

The stoichiometry of the reaction was determined to be $MoO(tpp)NCS{:}O_2^- = 1{:}1.05$ by the molar-ratio method (Fig. 3). The absorbance at 452 nm, λ_{max} of the spectrum of the complex, $MoO(tpp)OCH_3$, increased in proportion to the concentration of O_2^- with an excess of the complex, MoO(tpp)NCS, and CH_3OH. This confirms the high accuracy of the determination of O_2^- in DMSO by means of the photometric titration with iodine.

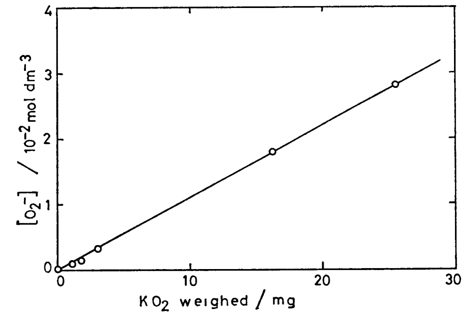

Fig. 4. Concentrations of O_2^- in DMSO *vs.* weighed amounts of KO_2. Two-fold excess of 18-crown-6 is contained over KO_2.

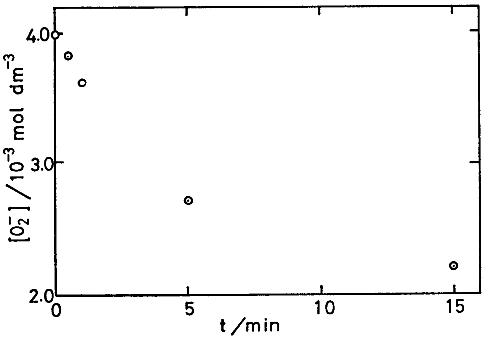

Fig. 5. Decomposition of hyperoxide solution in a flask placed in the ultrasonic cleaner (Bransonic, B-220, 45 kHz, 100 W).

Stability of O_2^- in DMSO. The concentration of hyperoxide in a stock solution was *ca.* 70% of that calculated from the weighed amount of KO_2, showing the decomposition of *ca.* 30% of O_2^- during the course of preparation of the solution (Fig. 4). The concentration gradually decreased *ca.* 2% a day.

When 1 volume of a 3.51×10^{-3} mol dm^{-3} hyperoxide solution was accurately diluted to 10 volumes with DMSO, a 3.19×10^{-4} mol dm^{-3} solution was obtained, which indicates partial decomposition of O_2^- by the addition of DMSO. Thus a hyperoxide solution should be standardized immediately before use.

A decrease in the concentration of O_2^- in DMSO was also observed when the solution was treated in an ultrasonic cleaner (Fig. 5).

References

1) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975); R. A. Johnson and E. G. Nidy, *J. Org. Chem.*, **40**, 1680 (1975).

2) E. Lee-Ruff, *Chem. Soc. Rev.*, **6**, 195 (1977); C. I. Chern, R. DiCosimo, R. D. Jenus, and J. S. Filippo, Jr., *J. Am. Chem. Soc.*, **100**, 7317 (1978); R. A. Johnson, E. G,

Nidy, and N. V. Merritt, *ibid.*, **100**, 7960 (1978).

3) J. A. Fee and J. S. Valentine, "Superoxide and Superoxide Dismutase," ed by A. M. Michelson, J. M. McCord, and I. Fridovich, Academic Press, New York, N. Y. (1977); J. S. Valentine and A. E. Quinn, *Inorg. Chem.*, **15**, 1997 (1976); J. S. Valentine, Y. Tatsuno, and M. Nappa, *J. Am. Chem. Soc.*, **99**, 3522 (1977); J. Stein, J. P. Fackler, Jr., G. J. McClume, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, **18**, 3511 (1979); M. Nappa, J. S. Valentine, A. R. Miksztal, H. J. Schugar, S. S. Isied, *J. Am. Chem. Soc.*, **101**, 7744 (1979); R. F. Pasternack and B. Halliwell., *ibid.*, **101**, 1026 (1979).

4) Nitrotetrazolium Blue (NBT) was used to assay O_2^- in DMSO solutions of tetramethylammonium hyperoxide.[5] The spectra of the products in the reaction of NBT with O_2^- in DMSO change with the concentrations of O_2^-; with increase in the concentration of O_2^-, the absorption peak at 680 nm shifted to 725 nm. Beer's law does not hold at 680 nm.

5) C. S. Foote, F. C. Shook, and R. A. Abakerli, *J. Am. Chem. Soc.*, **102**, 2503 (1980).

6) J. A. Fee and P. G. Hildenbrand, *FEBS Lett.*, **39**, 79 (1974).

7) S. Kim, R. DiCosimo, and J. S. Filippo, Jr., *Anal. Chem.*, **51**, 679 (1979).

8) K. Mochizuki, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **53**, 1757 (1980).

9) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1952).

10) D. T. Sawyer and J. L. Roberts, Jr., *J. Electroanal. Chem.*, **12**, 90 (1966); M. E. Reover and B. S. White, *Electrochim. Acta*, **11**, 1061 (1966); D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965); E. L. Johnson, K. H. Pool, and R. E. Hamm, *ibid.*, **38**, 183 (1966); J. Chevelet, F. Rovelle, L. Gierst, and J. P. Lambert, *J. Electroanal. Chem.*, **39**, 201 (1972).

11) E. M. Epps and J. C. Burden, *Anal. Chem.*, **30**, 1882 (1958); K. Ueno, M. Saito, and K. Tamaoku, *Bunseki Kagaku*, **18**, 81 (1969).

12) T. Imamura, M. Terui, Y. Takahashi, T. Numatatsu, and M. Fujimoto, *Chem. Lett.*, **1980**, 89; T. Imamura, T. Numatatsu, M. Terui, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **54**, 170 (1981).

13) When methanol is absent in the reaction system, the complex, MoO(tpp)NCS, is reduced by O_2^- to form the complex, $Mo^{IV}O(tpp)$.