BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2660—2662 (1975) [Vol. 48, No. 10

Photosensitized Decomposition of Trioxalatocobaltate (III) Ion by Organic Triplet Sensitizers

Shukichi Sakuraba, Akio Kakuta, and Ryoka Matsushima

Department of Industrial Chemisty, Faculty of Engineering, Shizuoka University, Hamamatsu 432

(Received February 27, 1975)

Sensitized decomposition of the trioxalatocobaltate(III) ion was studied in deoxygenated aqueous solution at room temperature, using biacetyl as an n-π^* triplet sensitizer and 9-carboxyanthracene as a π-π^* triplet sensitizer. In the presence of one of these sensitizers the photodecomposition rate of the complex was increased, and the plot of the reciprocal of the sensitization quantum yield as a function of the concentration of the complex gave a straight line for each sensitization system. On the other hand, the complex quenched the phosphorescence without affecting the fluorescence of the sensitizers, indicating a triplet energy transfer mechanism. A photokinetic treatment of the data for both the sensitized photolysis and the quenching process gave a result in line with proposed mechanism for bimolecular triplet energy transfer.

The behavior of the photoproduced radical intermediates has extensively been studied for the photolysis of trioxalate complex ions of Co(III), Fe(III) and Mn(III),[1)] but not the nature of the primary excited states, $^*M(ox)_3^{3-}$.[2)]

Sensitization and quenching methods are useful for identifying excited states whose lifetimes are very short. Thus, triplet sensitizers have been powerful tools for determining chemically reactive excited states of transition metal complexes, *e.g.*, Co(III)[3)] and Cr(III).[4)] In the present paper we report the results on the sensitized photodecomposition of $Co(ox)_3^{3-}$, using biacetyl as an n-π^* triplet donor and 9-carboxyanthracene as a π-π^* triplet donor.

Experimental

$K_3[Co(ox)_3^{3-}]\cdot 3H_2O$ and $K_3[Cr(ox)_3^{3-}]\cdot 3H_2O$ were prepared from the corresponding chlorides and potassium oxalate,[5,6)] and were crystallized thrice. Biacetyl, 9-carboxyanthracene and organic solvents (guaranteed grade, Nakarai Chem.) were used without further purification. Water was distilled over potassium permanganate after passing through ion-exchange resins.

The light source was a 500 W high pressure mercury lamp with an attachment for obtaining a parallel light beam (Ushio Electric). Monochromatic light (366, 405 or 436 nm) was obtained by means of an interference filter or a suitable combination of glass filters. Absorption and emission measurements were carried out with a Hitachi 124-Spectrophotometer and a Hitachi 204-Fluorescence Spectrophotometer, respectively. For measurements of the emission of the sensitizers, the solutions were bubbled with purified nitrogen until there was no further increase in the phosphorescence intensity (*i.e.*, 40—60 min), and were kept air-tight with liquid paraffin and paraffin film.

Sample solutions to be photolyzed were mostly buffered at pH 3.9 with sodium acetate-acetic acid, and were irradiated at 20 °C, after deoxygenation with purified nitrogen followed by sealing. Concentrations of the Co(II) and the ox^{2-} ions formed were determined by reported methods.[7,8)] Quantum yields were measured by the usual method.[9,10)]

Results and Discussion

Direct Photolysis. Preliminary examination on the direct photolysis of $Co(ox)_3^{3-}$ under conditions similar to those of the sensitized photolysis showed that the molar ratios of Co(II) and ox^{2-} to the consumption of the complex, $-\Delta$[Co(III)], were independent of the extent of the reaction and the wavelength. The molar ratio, $[ox^{2-}]/[Co(II)]$ near 2.5, agreed with the mechanism previously proposed,[2)] though the molar ratios of Co(II) and ox^{2-} to $-\Delta$[Co(III)] were rather small. The quantum yields of the Co(III) consumption for direct photolysis, under conditions similar to those for sensitized photolysis, depended on the temperature as well as the excitation wavelength. This indicates that the charge transfer state is the reactive state (even when the ligand field state is initially reached).[1b)] The effect of the dissolved oxygen on the quantum yields was negligible for direct photolysis with light of 366 nm, while significant oxygen quenching was found for sensitized photolysis.

Biacetyl-Sensitized Photolysis. In the presence of 0.2 M biacetyl as an n-π^* sensitizer, $Co(ox)_3^{3-}$ in the concentration range 2.5×10^{-3} —1.5×10^{-4} (buffered at pH 3.9) was irradiated with a monochromatic light 366 nm at 20 °C, after deoxygenation. Under such conditions the complex absorbs the light directly up to 20% of the intensity (I_a) absorbed by the system. The number of the light quanta absorbed by the sensitizer, I_s, was estimated in proportion, *i.e.*, $I_s = I_a\varepsilon_s C_s/\sum_i \varepsilon_i C_i$. The quantum yields ($\phi$) of biacetyl-sensitized decomposition of the complex at its various concentration were determined, where photodecomposition of the complex due to its direct absorption was eliminated by calculation. The plot of $1/\phi$ as a function of 1/[Co(III)] gives a straight line with a slope, $1/K\phi_{lim}=2.1\times10^{-3}$ M and an intercept, $1/\phi_{lim}=7.6$ (Fig. 1).

9-Carboxyanthracene-Sensitized Photolysis. The quantum yields of the photosensitized decomposition of $Co(ox)_3^{3-}$ by 9-carboxyanthracene as a π-π^* sensitizer were measured at various initial concentrations of the complex in 30% aqueous acetone. The plot of $1/\phi$ as a function of 1/[Co(III)] gives a straight line with a slope, $1/K\phi_{lim}=1.28\times10^{-2}$ M, and an intercept, $1/\phi_{lim}=7.6$ (Fig. 1).

Oxygen Effect on the Sensitized Photolysis. The rate of Co(II) formation in the sensitized photolysis was depressed by the dissolved oxygen both for biacetyl- and 9-carboxyanthracene-sensitized photolyses. No significant effect was found for the rate of the direct

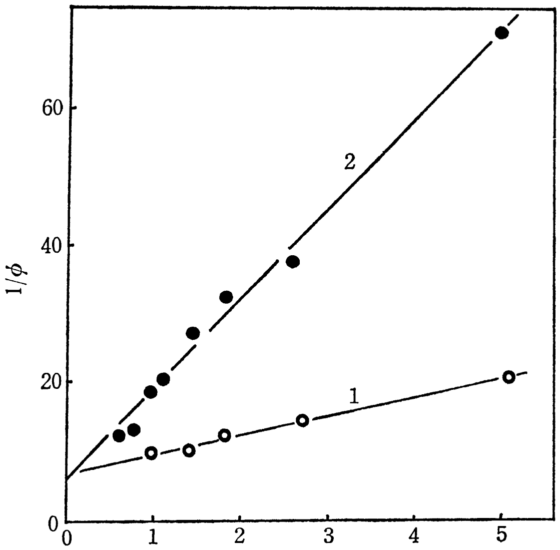

Fig. 1. Plot of $1/\phi$ *vs.* 1/[Co(III)] for organic triplet-sensitized decomposition of Co(ox)$_3^{3-}$. (1) Solvent: water (pH 3.9), sensitizer: biacetyl 0.04 M, $\lambda(h\nu)$: 366 nm. (2) Solvent: 30% aqueous acetone (pH 3.9), sensitizer: 9-carboxyanthracene 5×10^{-4} M, $\lambda(h\nu)$: 366 nm.

photodecomposition of the complex (10^{-3} M) under similar conditions. The results suggest that a bimolecular energy transfer mechanism of triplet states is involved but that the lifetime of the triplet state of the complex is too short (namely $\tau_0<10^{-9}$ s) to be significantly intercepted by the dissolved oxygen.

Quenching of the Sensitizer Emission by Complex. For clarification of the energy transfer mechanism of the sensitized reactions, quenching of the fluorescence and phosphorescence of the sensitizers by the complex were investigated. In deoxygenated aqueous solutions, Co(ox)$_3^{3-}$ quenched the phosphorescence of biacetyl without significant effect on the fluorescence. The Stern-Volmer plot is given in Fig. 2. This indicates that the n-π^* triplet state is effective in the photosensitized decomposition of the complex. Form the quenching constants and the phosphorescence lifetime of biacetyl in solution at room temperature in the absence of the quenchers, $\tau_0=2.3\times10^{-4}$ s,[11] the bimolecular quenching rate constants are estimated to be $k_5=1.7\times10^7\,\mathrm{M^{-1}\,s^{-1}}$ for Co(ox)$_3^{3-}$ and $1.0\times10^7\,\mathrm{M^{-1}\,s^{-1}}$ for Cr(ox)$_3^{3-}$.

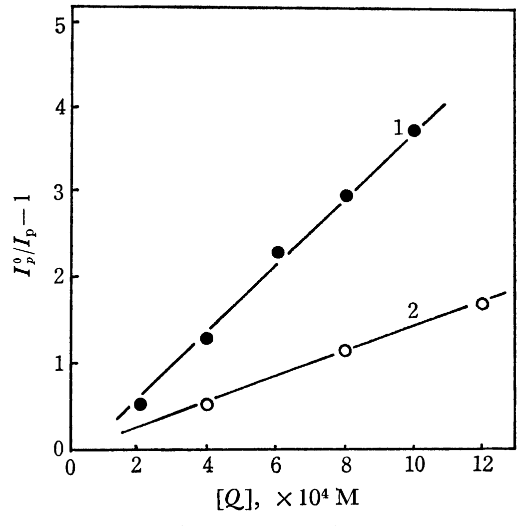

Fig. 2. Stern-Volmer plots for the quenching of biacetyl phosphosescence (512 nm peak) by (1) Co(ox)$_3^{3-}$ and (2) Cr(ox)$_3^{3-}$. Biacetyl: 0.04 M, λ(excitation): 366 nm.

The emission of 9-carboxyanthracene in a deoxygenated aqueous alcohol solution at room temperature was only slightly affected by Co(ox)$_3^{3-}$, while in an aerated solution the emission was entirely unquenched. This implies that the energy transfer occurs from the triplet state (presumably π-π^*) of 9-carboxyanthracene.

Kinetic Analysis. A kinetic analysis of the energy transfer process for the photosensitized decomposition of Co(ox)$_3^{3-}$ will be given below.

Since the fluorescence of either biacetyl or 9-carboxyanthracene is not quenched by the complex, participation of the excited singlet states of the sensitizers is excluded. The excited singlet state of the complex is also excluded on the basis of the spin conservation rule for bimolecular energy transfer processes.[12] Direct chemical interactions between the complex and the excited state biacetyl, such as hydrogen abstraction or charge transfer, seem to be unimportant.[4b,c]

The following scheme can be assumed.

$$
\begin{array}{llr}
\mathrm{S} + h\nu \xrightarrow{I_s} {}^1\mathrm{S}^* \xrightarrow{\phi_{st}} {}^3\mathrm{S}^* & & (1) \\
{}^3\mathrm{S}^* \xrightarrow{k_2} & \mathrm{S} + h\nu' & (2) \\
\phantom{{}^3\mathrm{S}^*} \xrightarrow{k_3} & \mathrm{S} + \text{heat} & (3) \\
\phantom{{}^3\mathrm{S}^*} \xrightarrow{k_4,\,\mathrm{O_2}} & \mathrm{S} + {}^1\mathrm{O_2}^* \text{ (or } \mathrm{O_2}+\text{heat)} & (4) \\
{}^3\mathrm{S}^* + \mathrm{C} \xrightarrow{k_5} \mathrm{S} + {}^3\mathrm{C}^* & & (5) \\
{}^3\mathrm{C}^* \xrightarrow{k_6} & \mathrm{C} + \text{heat} & (6) \\
\phantom{{}^3\mathrm{C}^*} \xrightarrow{\phi_c} & \mathrm{Co(II)} + \text{other products} & (7)^{2)}
\end{array}
$$

Here, S and C are sensitizer and Co(ox)$_3^{3-}$, respectively. I_s is the light quanta absorbed by the sensitizer per unit time per unit volume, ϕ_{st} is the quantum yield of triplet formation from ^{1}S*, and ϕ_c is the quantum yield of Co(II) formation from ^{3}C*. Process (4) is included since a trace of the dissolved oxygen might be contained even after careful deoxygenation.

Since the lifetime of the triplet state of the complex ^{3}C* seems to be short, and the bimolecular quenching rate constant k_5 is relatively small, one may assume that the unimolecular processes (6) and (7) of the complex are fast compared to (5). The steady state assumption for ^{3}S* and ^{3}C* leads to the following equation for the quantum yield of Co(II) formation in the sensitized reaction.

$$\frac{1}{\phi} = \frac{1}{\phi_{\mathrm{lim}}}\left(1+\frac{1}{K[\mathrm{C}]}\right) \tag{8}$$

$$\phi = \phi_c + \phi_{st} \tag{9}$$

$$K = k_5\tau_0 \tag{10}$$

TABLE 1. RATE PARAMETERS FOR THE PHOTOSENSITIZED DECOMPOSITION OF $Co(ox)_3{}^{3-}$ BY BIACETYL AND 9-CARBOXYANTHRACENE.

Sensitizer	ϕ_{lim} [a)]	ϕ_{st}	ϕ_{c}	K [b)], M^{-1}	K_q, M^{-1} [c)]
Biacetyl	0.13	0.99[14)]	0.13	3.5×10^3	3.9×10^3
9-Carboxyanthracene	0.13	0.7—1[d)]	0.13—0.19[d)]	5.7×10^2	

a) From Eq. (8) and Fig. 1. b) Reciprocal of the slope of the plot of $1/\phi$ *vs.* 1/[C]. c) Quenching constant of the complex for the quenching of sensitizer phosphorscence. d) Though ϕ_{st} of 9-carboxyanthracene was not available, it is assumed to be close to unity (and hence ϕ_c to be close to 0.13), since it has been reported that the presence of the carboxyl group singificantly increases the rate of S–T intersystem crossing of aromatic hydrocarbons (*e.g.*, *J. Amer. Chem. Soc.*, **93**, 6396 (1971)).

where, $\tau_0=1/(k_2+k_3+k_4[O_2])$ is the lifetime of the triplet state of the sensitizer in the absence of the quencher (complex).

The experimental results in Fig. 1 agree with Eq. (8), supporting the assumed scheme. From the intercept and the slope of the plot of $1/\phi$ *vs.* 1/[C], ϕ_c is derived by substituting ϕ_{lim} and ϕ_{st} into Eq. (9). These values are also given in Table 1, together with the quenching constant K_q for the quenching of the phosphorescence of biacetyl by $Co(ox)_3^{3-}$. K_q is the slope of the Stern-Volmer plot (Fig. 2) which has the following form

$$I_P^0/I_P = 1 + K_q[C] \qquad (11)$$

where I_P^0 and I_P are the phosphorescence intensities of biacetyl in the absence and presence of the complex, respectively, and

$$K_q = k_5\tau_0 \qquad (12)$$

From Eqs. (10) and (12), K and K_q (which were obtained from independent measurements) should be equal. The agreement of K with K_q in Table 1 might support the assumed scheme.

The upper limit of the sensitized photodecomposition quantum yield, ϕ_{lim}, is 0.13 which is in the range of the direct photodecomposition quantum yields at its d-d band. The rate constant k_5 is a measure of the efficiency of the triplet energy transfer from the sensitizer to the complex. Though no report was found for the lifetime of 9-carboxyanthracene, it could be assumed that the π-π^* triplet lifetime is greater than the n-π^* triplet lifetime (*e.g.*, τ_0 of anthracene in solution at 20 °C is 0.026—0.035 s,[15)] which is greater than that of biacetyl by two orders of manitude). Thus, the bimolecular rate constant k_5 for the triplet sensitized photolysis with 9-carboxyanthracene (as a π-π^* triplet sensitizer) is assumed to be smaller than that with biacetyl (as an n-π^* triplet sensitizer).

References

1) (a) C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959); (b) D. R. Eaton and S. R. Swart, *ibid.*, **72**, 400 (1968); (c) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, pp. 221—224.

2) (a) J. B. Copestake and N. Uri, *Proc. Roy. Soc.*, *Ser. A*, **228**, 252 (1955); (b) G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Amer. Chem. Soc.*, **84**, 4027 (1962).

3) (a) A. Vogler and A. W. Adamson, *ibid.*, **90**, 5943 (1968); (b) G. B. Porter, *ibid.*, **91**, 3989 (1969); (c) M. A. Scandola, F. Scandola, and V. Carassiti, *Mol. Photochem.*, **1**, 403 (1969); (d) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970); (e) M. A. Scandola and F. Scandola, *ibid.*, **94**, 1805 (1972).

4) (a) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 3017 (1968); (b) E. Zinato, P. Tulli, and P. Riccieri, *ibid.*, **75**, 3504 (1971); (c) V. Balzani, M. T. Gandolfi, and L. Moggi, *J. Amer. Chem. Soc.*, **93**, 339 (1971).

5) T. Ito, K. Inamura, H. Kobayashi, A. Nakahara, Y. Shinmura, K. Yamazaki, and S. Yamada, "Zikken Kagaku Koza," Vol. II, Maruzen, Tokyo (1956), p. 37.

6) J. C. Bailar and E. M. Jones, "Inorganic Syntheses," Vol. I, ed. by H. S. Booth McGraw-Hill, New York, N.Y. (1939), pp. 35—38.

7) (a) N. Shinotsuka and S. Kikuchi, *Nippon Kagaku Zasshi*, **87**, 97 (1966); (b) J. Aggett and A. L. Odell, *J. Chem. Soc.*, *Ser. A*, **1968**, 1415.

8) D. A. Britton and J. C. Guyon, *Anal. Chim. Acta*, **44**, 397 (1969).

9) M. Koizumi, S. Shida, S. Kato, N. Mataga, and M. Imamura, "Zikken Kagaku Koza," Vol. 6, Maruzen, Tokyo (1956), pp. 282—286.

10) (a) C. A. Parker, *Proc. Roy. Soc.*, **A220**, 104 (1953); (b) J. C. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y. (1966), pp. 738—786.

11) H. L. G. Backstorm and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

12) Ref. 10 (b), pp. 88—92.

13) (a) M. A. El-sayed, *J. Chem. Phys.*, **38**, 2834 (1963); (b) N. J. Torro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y. (1967), p. 86.

14) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

15) D. Phillips, "Photochemistry," Vol. 3, ed. by Chemical Society, Burlington House, London (1972), p. 146.