

- 303 (1981).
- (3) J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).
- (4) S. Dusoleil, P. Goldfinger, A. M. Mahieu-Van Der Auwera, G. Martens and D. Van Der Auwera, *Trans. Faraday Soc.*, **57**, 2197 (1961).
- (5) P. Goldfinger, G. Huybrechts and G. Matrens, *ibid.*, **57**, 2210 (1961).
- (6) J. H. Knox, *Trans. Faraday Soc.*, **58**, 275 (1962).
- (7) P. B. Ayscough, A. J. Cocker, F. S. Dainton and S. Hirst, *Trans. Faraday Soc.*, **58**, 295 (1962).
- (8) F. S. Dainton, D. A. Lomax and M. Weston, *ibid.*, **58**, 308 (1962).
- (9) E. N. Chesnokov and V. N. Panfilov, *Dokl. Akad. Nauk, SSSR*, **261**, 925 (1981).
- (10) M. Takamizawa, H. Okamoto, M. Umemura, K. Koya and M. Aoyama, *Ger. Offen.*, **2**, 805, 824 (1078).
- (11) D. J. Schlyer, A. P. Wolf and P. P. Gaspar, *J. Phys. Chem.*, **82**, 2633 (1978).
- (12) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., P. 650-649, 1966.
- (13) H. Okabe, "Photochemistry of Small Molecules," John Wiley and Sons, Inc., p. 128, 1978.
- (14) O. Diels and W. Koil, *Ann.*, **443**, 262 (1925).
- (15) H. V. Halban and K. Siedentopf, *Z. Phys. Chem.*, **103**, 71 (1922).
- (16) F. S. Dainton and P. B. Ayscough, "Gaseous Photochlorination", in "Photochemistry and Reaction Kinetics," P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Ed., Cambridge University Press, P. 74-75, 1967.
- (17) G. M. Burnett and H. W. Melville, "Technique of Organic Chemistry," Vol. VIII, Part II, 2nd Ed., John Wiley and Sons, Inc., Chap. XX, 1967.
- (18) J. E. Huheey, "Inorganic Chemistry," 2nd Ed., Harper and Row, p. 718-719, 1978.

The Photochemistry of Co(III) Complex of Glycinemethylester

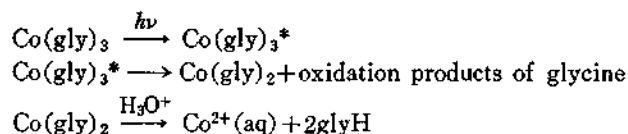
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Photochemical reactions of Co(III) complexes have often been described in terms of mechanisms involving an excited state of the metal ion which is charge transfer in character.^{1,2} Ligand field excited states play important roles in the photoreactions of transition metal complexes especially with regard to photodegradation of complexes by ligand labilization.^{3,4} Charge transfer irradiation promotes an intramolecular oxidation-reduction reaction which may be schematized as follows using the glycinate complex as an example⁵



In accordance with the intramolecular character of the photoreaction, the quantum yield was not affected by the acidity of the solution and only showed a small dependence on the glycinate and the steric arrangement of the complex.

The electronic spectra of Co(III) glycinate complexes suggest that there are significant interactions between ligand field states of the Co(III) centers. From the study of photochemical processes in Co(III) glycinate complexes, it is possible to elucidate the reactivity of different excited states

and to provide insight into nature of bonding in Co(III) methylester complexes.

In this paper we examine whether the photoreactivity is localized at the Co(III) center delocalized over the ligand-metal bonds. The photochemical behaviors of the complex will also be correlated with theoretical predictions based on the electronic absorption spectra of Co(III) glycineester complexes.

The complex, $[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$ was prepared by the published method.⁶ The crude product was recrystallized from hot water by adding sequentially methanol, absolute ethanol, and ether, and dried in vacuo over Mg $(\text{ClO}_4)_2$. The spectral properties (UV-Vis, IR, ¹H nmr) of this compound prepared were identical with those reported.

Photolysis was carried out in aqueous HClO₄ solutions (pH 1-3). Irradiations ($\lambda_{\text{irr}}=254\text{ nm}$) were utilized in an apparatus equipped with a Hanovia low-pressure mercury lamp. Light intensities were determined by ferrioxalate actinometry.⁷

The electronic structure of Co(III) glycineester complex was calculated by the CNDO/2 method with semiempirical integrals as described previously.⁸

Atomic cartesian coordinates of the molecular system

TABLE 1: Quantum Yields for the Photolysis of $[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$ at 254 nm

pH	Temp ($^{\circ}\text{C}$)	ϕ
1.0	18	0.13
1.0	25	0.16
2.0	25	0.14
3.0	25	0.11
1.0	50	0.17
1.0	75	0.20

TABLE 2: The Atomic Net Charges on Co(III), and Glycineester

Atom	Glycine	Glycinemethyl ester	Glycineethyl ester	Glycineisopropyl ester
Co(M)	0.3075	0.3075	0.3075	0.3075
N (1)	-0.1982	-0.1974	-0.1980	-0.9177
C (2)	0.0203	0.0275	0.0276	0.0264
C (3)	0.3914	0.3892	0.3892	0.3874
O (4)	-0.3393	-0.3441	-0.3482	-0.3484
O (5)	-0.2860	-0.2251	-0.2354	-0.2498
C (6)	—	0.8855	0.1591	0.1873
C (7)	—	—	-0.0476	-0.4077
C (8)	—	—	—	0.0549

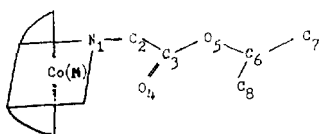


Figure 1. The unnumbering scheme of Co(III) glycineester.

were calculated with the aid of a modified version of Hildebrandt program.⁹

Irradiation of aqueous solutions of Co(III) glycinemethylester complex with light of 254 nm completely decomposes the complex, as shown by the disappearance of the characteristic visible absorption band. The values of quantum yield for the decomposition reactions are reported in Table 1.

The geometries of glycinemethylester ligand were assumed to be planar and were constructed from the probable bond angles, bond length and dihedral angles (Figure 1). Table 2 shows the electronic structure of Co(III) glycineester complexes as calculated by the CNDO/2 method.

It is seen in Table 1 that the quantum yield at 254 nm increases slightly with temperature and is practically independent of pH of the solution. It is possible that the actinic light of 254 nm is absorbed for the charge transfer from the molecular orbital mainly localized on the ligands to one of the $3d(\sigma^*)$ orbitals (E_g ; octahedral symmetry) assumed of the central metal atom.¹¹ When acid or aqueous solutions of these complexes were irradiated with 254 or 313 nm light corresponding to ligand-metal charge transfer bands, an

oxidoreductive decomposition occurs.^{5,11}

The molecular orbital calculations of the preferred conformation of the Co(III) glycineester complex in terms of the dihedral angle yield a 105.9° between $\Delta O_4C_3C_2$ and $\Delta C_3C_2N_1$. In the dihedral glycinate complexes of cobalt (III) of the octahedral ${}^1A_1-{}^1T_1$ d electron transition is broken down into components with 1A_2 and 1E symmetry in D_3 . From Table 2, we can predict that the coordination ability of glycineester is attributable to the charge transfer effect. The coordination ability of ligand as deduced by the amount of net charge transfer from the terminal nitrogen to the metal ion is in order of glycine glycineethylester glycineisopropylester and glycinemethylester. In glycinenato complex, strong charge transfer from the carboxyl oxygen and amino nitrogen to a metal orbital is expected from the values of net charge transfer (0.3393 and 0.1982, respectively). It is possible that the actinic light of 254 nm is absorbed by the charge transfer transition in their region, resulting in further charge transfer from the ligand to a metal orbital and reduction of cobalt (III) to cobalt (II).¹¹ The experimental proof that the theoretical anticipation was essentially correct lent additional credibility to the assumption that the stereochemical distribution of products is simply determined by the relative value of the relevant ligand field parameters.¹²

Acknowledgements. This investigation was supported by the Korea Science and Engineering Foundation. This research was a preliminary studies of induced electron transfer reactions.

References

- (1) V. A. Durante, P. C. Ford, *J. Amer. Chem. Soc.*, **97**, 6898 (1975).
- (2) J. Malin, D. A. Ryan, T. V. O. Halloran, *J. Amer. Chem. Soc.*, **100**, 2097 (1978).
- (3) J. A. Gelroth, J. E. Figard, J. D. Peterson, *J. Amer. Chem. Soc.*, **101**, 3649 (1979).
- (4) M. Nishizawa, P. C. Ford, *Inorg. Chem.*, **20**, 2016 (1981).
- (5) V. Balzani, V. Carassiti, L. Moggi, and N. Sabbatini, *Inorg. Chem.*, **4**, 1247 (1965).
- (6) J. H. Kim and S. C. Shim, *J. Kor. Chem. Soc.*, **24**, 356 (1980).
- (7) I. Grenthe, *Acta Chem. Scand.*, **18**, 283 (1964).
- (8) J. H. Kim, *J. Kor. Chem. Soc.*, **24**, 20 (1980).
- (9) R. L. Hildebrandt, *J. Chem. Phys.*, **51**, 1654 (1969).
- (10) H. Yamatera, *J. Inorg. Nucl. Chem.*, **5**, 50 (1960).
- (11) A. F. Vando, E. R. Kantrowitz, M. Z. Hoffman, E. Paracostantinou and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 6655 (1972).
- (12) L. G. Vanquickenborne and A. Ceulemans, *Coordination Chemistry Review*, **48**, 192 (1983).