Reaction of Leucomalachite Green with Chloranil

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Synopsis. The reaction of Leucomalachite Green with chloranil to produce Malachite Green cations has been carried out in acetonitrile. Prior to the formation of the cations, a 1:1 CT complex is formed between the reactants. The equilibrium and the rate constants were estimated.

In preceding papers,[1,2] the proton/deuteron transfer reactions of Leucocrystal Violet (LCV) with tetracyanoethylene (TCNE) and chloranil (CA) under high pressures and in various solvents have been reported. It was concluded that both reactions probably proceed *via* an outer CT complex followed by a pair of radical ions. However, the electronic spectra assigned to the complex were observed only at low temperatures. This made the accurate estimation of thermodynamic quantities impossible.

This paper is concerned with the reaction of Leucomalachite Green (LMG) with CA. When the acetonitrile solutions of LMG and CA were mixed, a broad absorption spectrum ($\lambda_{max}\approx670$ nm) appeared at room temperatures. The color becomes deep upon cooling. Similar phenomena were observed in various solvents and LMG-TCNE system, too. Therefore, this blue-colored substance can be assigned to the CT complex formed between LMG and CA. The equilibrium constant K_1 for the formation of the complex was estimated by means of the Lang plot and checked by the Benesi-Hildebrand (B-H) plot modified as follows:

$$\frac{[\mathrm{LMG}]_0[\mathrm{CA}]_0}{A([\mathrm{LMG}]_0+[\mathrm{CA}]_0-A/\varepsilon)} = \frac{1}{([\mathrm{LMG}]_0+[\mathrm{CA}]_0-A/\varepsilon)}\cdot\frac{1}{K\varepsilon}+\frac{1}{\varepsilon}, \quad (1)$$

where A is the absorbance at 720 nm (1 cm cell), and ε is the molar extinction coefficient at this wavelength. In this study, the concentration ranges were: $[\mathrm{LMG}]_0=(2.5—12.8)\times10^{-3}$ mol dm^{-3}, $[\mathrm{CA}]_0=(7.9—10.4)\times10^{-3}$ mol dm^{-3}. The Lang and the modified B-H plots were repeated until an assumed pair of ε and K values became self-consistent. The results are given in Table 1.

The rate of reactions was followed by monitoring the absorbance at 620 nm which is assigned to Malachite Green cations (MG^+). Within the time interval of the kinetic measurement, the absorbance at 720 nm has not changed appreciably. This made the simultaneous estimations of the equilibrium and the rate constants possible. Figure 1 shows the time dependence of the absorption spectrum. The broad line at the bottom (500—900 nm) is due to the CT complex[3] (denoted as LMG→CA hereafter). It was found that the rate of appearance of MG^+ at the initial stage (conversion<0.5%) follows the overall second-order kinetics:

TABLE 1. EQUILIBRIUM CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE FORMATION OF THE CT COMPLEX IN THE LMG-CA SYSTEM

Temp	$10^{-3}K_1\varepsilon$	K_1
°C	dm^6 mol^{-2} cm^{-1}	dm^3 mol^{-1}
15	3.03±0.04	6.70±0.74
20	2.67±0.06	5.90±0.69
25	2.28±0.02	5.04±0.52
30	2.02±0.01	4.46±0.45

ε/dm^3 mol^{-1} cm^{-1}=452±43
ΔH/kJ mol^{-1}=−20.1±0.4
ΔS(298K)/J mol^{-1} K^{-1}=−51.6±2.9

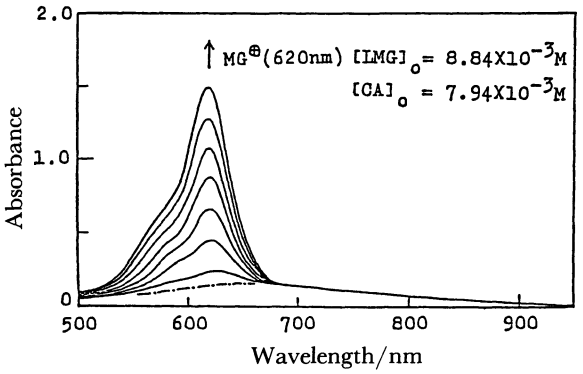

Fig. 1. Time dependence of the absorption spectrum for the reaction of LMG with CA in acetonitrile at 25 °C. Time intervals are 5 min.

$$\mathrm{d}[\mathrm{MG}^+]/\mathrm{d}t = k_{obsd}[\mathrm{LMG}]_0[\mathrm{CA}]_0 \quad (2)$$

If the proposed mechanism for the LCV-TCNE and LCV-CA systems[2] is valid for the LMG-CA system, too, the reaction route may be as follows:

$$\mathrm{LMG} + \mathrm{CA} \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} \mathrm{LMG}\longrightarrow\mathrm{CA} \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}}$$

$$(\mathrm{LMG})^{+\cdot}(\mathrm{CA})^{-\cdot} \xrightarrow[\text{slow}]{k_1} \mathrm{MG}^+ + \cdots$$

From the above scheme, k_{obsd} can be expressed by

$$k_{obsd} = K_1K_2k_1 = K_1k. \quad (3)$$

The kinetic data and the activation parameters are given in Table 2. Figure 2 shows the energy profile. The numerical value in parenthesis is the one assumed for the LCV-CA system.[2]

It is interesting to compare the above results with those for the LCV-CA system. There are two notable points. The equilibrium constant K_1 for the formation of the CT complex is considered considerably

Table 2. Rate constants k_{obsd} and k defined by Eq. 3 and the activation parameters related to k

Temp	$10^4 k_{obsd}$	$10^5 k$
°C	$dm^3 mol^{-1} s^{-1}$	s^{-1}
15	0.396±0.033	0.59±0.11
20	0.654±0.005	1.11±0.15
25	1.02 ±0.02	2.02±0.25
30	1.54 ±0.03	3.45±0.48
ΔH^*(300K)/kJ mol^{-1}=83.6±0.8		
ΔS^*(300K)/J $mol^{-1} K^{-1}$=−54.7±3.0		

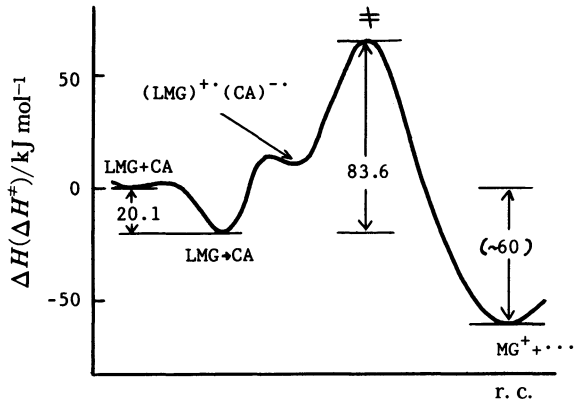

Fig. 2. Energy profile for the reaction of LMG with CA.

larger for the LMG–CA system than for the LCV–CA system, as judged from the spectral intensity observations. The second point is the k_{obsd}-value is about 10^3times smaller than that for the LCV–CA system (0.11 $dm^3 mol^{-1} s^{-1}$ at 25 °C). The ΔH^* and ΔS^* for the LCV–CA system in acetonitrile are 27.9 kJ mol^{-1} and −169 J $mol^{-1} K^{-1}$, respectively.[4] The above distinctive points are difficult to interpret in connection with the structural difference between LMG and LCV alone. We tentatively measured the ^{1}H NMR spectra and examined the chemical shift of the hydrogen being abstracted. The data are as follows: δ=2.18 in CCl_4, 2.58 in $CDCl_3$, and 3.74 in CD_3CN (s, 1H) for LMG. These values may be compared with the normal values δ=5.10—5.54 (s, 1H) for triphenylmethane, 4-diphenylmethyl-*N*,*N*-dimethylbenzenamine, and LCV, for which the solvent dependency on δ was small. The extraordinarily high-field shift and its very large solvent dependence for LMG alone in this series of compounds are very hard to interpret, and therefore require more fundamental investigations aside from this work. What we now can say is that if this high-field shift is due to the electronic effect (charge shift), it would give rise to the large K_1-value and hence the large activation energy compared with those for the LCV–CA system.

Experimental

Commercial LMG and CA were recrystallized twice from a benzene–ethanol mixture. Solvents were purified as usual manners. A Union 401 spectrophotometer was used for spectral measurements. The temperature was regulated within ±0.1 K. ^{1}H-NMR spectra were recorded on a Hitachi R-600 FT NMR spetrometer.

References

1) N. Nishimura and T. Motoyama, *Bull. Chem. Soc. Jpn.*, **57**, 1 (1984).

2) N. Nishimura and T. Motoyama, *Bull. Chem. Soc. Jpn.*, **58**, 1013 (1985).

3) There is a possibility of the existence of two kinds of CT complexes: CT_1(R′→CA, R′=phenyl) and CT_2(R→CA, R=*p*-dimethylaminophenyl). As far as the electronic spectrum was examined, no distinction was observed. If it is assumed that the equilibrium constant of CT_1 is similar to that for benzene–CA system (0.35 dm^3 mol at 25 °C[5]), K_1 in Table 1 may be regarded as the one for CT_2.

4) N. S. Isaacs, K. Javaid, and E. Rannale, *J. Chem.Soc. Perkin 2*, **1978**, 709 (data recalculated).

5) S. Fukuzumi and J. K. Kochi, *J. Org. Chem.*, **46**, 4116 (1981).