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Kinetic Studies of the Polyiodide Complex Formation in the Iodine-Iodide Solutions

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Synopsis. A relaxation obviously different from that due to the triiodide complex formation was observed by the temperature-jump experiments in the iodine–iodide solution. On the basis of the dependences of the relaxation time on the concentration of iodine and iodide and on the temperature, the relaxation was assigned to the complex formation of I_6^{2-}. The rate constants of the reaction were estimated to be $2.2\times10^5\,M^{-1}$[††]$\,s^{-1}$ and $5.3\times10^5\,s^{-1}$ for forward and backward processes, respectively.

The iodine–iodide system has been subjected to extensive studies[1–4] in connection with not only the electron-transfer reaction but also the well known "blue starch–iodine" reaction. However the reactions proceeding in this system are complicated depending on the conditions of solution and their mechanisms are still obscure. In the course of our temperature-jump experiments in the cyclodextrin, iodine, and iodide system as a model system of the amylose–iodine solution, we observed a relaxation at micro second region in the iodine–iodide solution. The behavior of the relaxation phenomenon was obviously different from those reported for the hydrolysis of iodine[5] and the triiodide formation reaction.[6] This fact motivated us to clarify the origin of the observed relaxation in the iodine–iodide solution prior to the kinetic investigations on the cyclodextrin–iodide interaction.

In this paper, the observed relaxation will be discussed on the basis of the complex formation reactions proposed for the iodine-iodide system by the spectrophotometric experiments.

Experimental

The kinetic measurements were performed with a Joule heating temperature-jump apparatus equipped with a coaxial cable as a capacitor. Temperature jumps of about 2 °C was attained within 0.7 μs by matching the impedance of sample cell to that of coaxial cable. The temperature of sample solution in the cell was controlled to ±0.5 °C by circulating water from an external thermostat. In order to prevent cavitation by the intense electric current, the sample cell was maintained at constant pressure of 7 atm with nitrogen gas. The details of the apparatus has been described elsewhere.[7] To obtain a rectangular current pulse the ionic strength of solution was adjusted to be 0.023 M by an addition of KI for almost all experiments and of KCl in the case of the experiments changing the iodide concentration. The standardized thiosulfate was used for the determination of the iodine concentration. All chemicals were of reagent grade and used as be received.

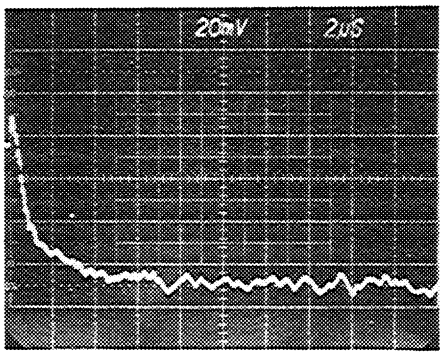

Fig. 1. Typical relaxation curve for the solution of 2.3×10^{-2}M potassium iodide and 5.0×10^{-2}M iodine at 25 °C; sweep=2 μs/division, and λ=500 nm.

Results and Discussion

A typical relaxation curve observed at 500 nm which corresponds to the absorption band of iodine is shown in Fig. 1. The relaxation curve could be analyzed as two relaxations; one has a much faster relaxation time than the resolution time (0.7 μs) of the present apparatus (fast relaxation), and the other has a relaxation time around 2 μs (slow relaxation). The directions of the both relaxation signals indicate the decrease of transmittance. Meanwhile, the relaxation curve observed at 350 nm which is absorption band of triiodide also consists of two relaxations in accordance

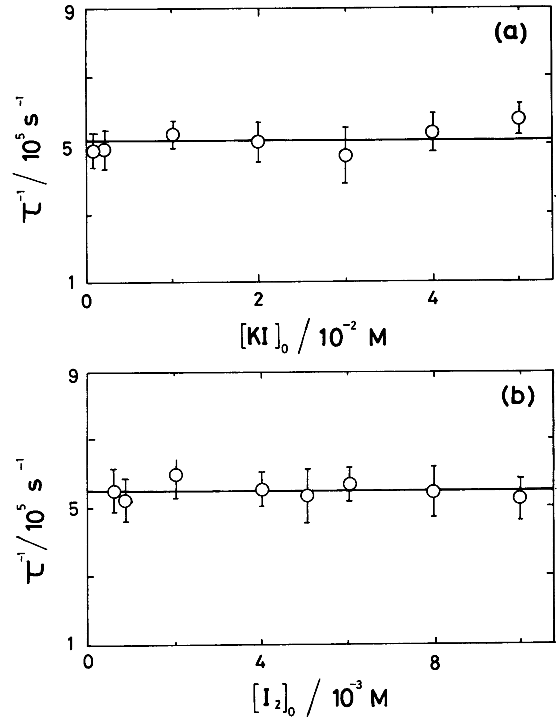

Fig. 2. Dependence of the reciprocal relaxation time on the iodide concentration at constant $[I_2]$ of 5.0×10^{-3}M (a) and on the iodine concentration at constant [KI] of 2.3×10^{-2}M (b) at 25 °C.

[††] $1\,M^{-1}=1\,dm^3\,mol^{-1}$.

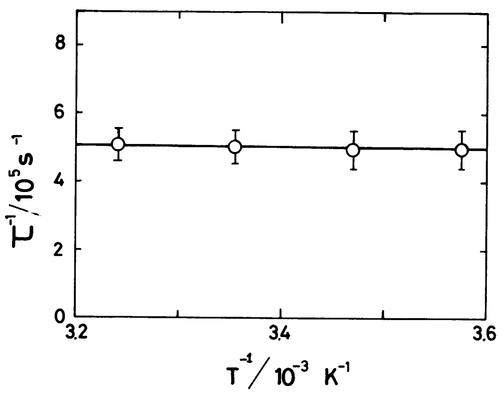

Fig. 3. Dependence of the reciprocal relaxation time on the temperature in the solution of 2.3×10^{-2}M potassium iodide and 4.0×10^{-3}M iodine.

with those observed at 500 nm; the relaxation time as well as the direction of the relaxation signal of the slow process is the same as that obtained from the experiments at 500 nm but the direction of the fast relaxation signal is opposite to that observed at 500 nm. The slow relaxation was examined quantitatively in the present study. The concentration dependence of the reciprocal relaxation time is shown in Fig. 2. The relaxation time is obviously independent of both iodine and iodide concentrations. Further, the relaxation time is insensitive to temperature as can be seen in Fig. 3.

In the system of iodine and iodide, following complex formation have been proposed from the spectrophotometric experiments.[1–6]

$$I^- + I_2 \rightleftharpoons I_3^- \tag{1}$$

$$I^- + I_3^- \rightleftharpoons I_4^{2-} \tag{2}$$

$$I_2 + I_3^- \rightleftharpoons I_5^- \tag{3}$$

$$2\,I_3^- \rightleftharpoons I_6^{2-} \tag{4}$$

Among these four reactions, the triiodide complex formation of Reaction 1 is most well known, and has been studied kinetically by several kinds of methods.[2,4,6] According to these studies, the relaxation due to this reaction is much faster than the resolution time of the present apparatus. In practice, the rapid increase of iodine and decrease of triiodie within 0.7 μs were observed at 550 and 350 nm, respectively, which indicates Reaction 1 is responsible for the fast process. Reaction 2 occurs predominantly at considerably high ionic strength of 2.0 M,[4] and then can be discared in the present system of low ionic strength (I=0.023 M). Reaction 3 is also eliminated from the possible origin of the relaxation because of the positive value of the enthalpy change reported for Reaction 3[3] ($\Delta H_3 \simeq 12$ kcal/mol) resulting in the decrease of iodine concentration with the temperature rise. Finally, Reaction 4 is remained as a plausible mechanism. The relaxation time for the Reaction 4 which is coupled with the fast reaction of triiodide complex formation, can be written as

$$\tau^{-1} = k_{-4}\left\{1+\frac{4K_1K_4(I_2+I^-)I_3^-}{1+K_1(I_2+I^-)}\right\}. \tag{5}$$

In this equation, the second term which can be calculated by using the values of K_1=732 M^{-1} [3] and K_4= 0.42 M^{-1} [1] is far smaller than unity. Thus, Eq. (5) can be transformed to

$$\tau^{-1} = k_{-4}. \tag{6}$$

Firstly, this equation implies that the relaxation time is independent of the concentration of any reaction species, satisfying the present experimental results in Fig. 2. Secondly, the insensitive temperature dependence of the relaxation time in Fig. 3 is consistent with the small and negative value of the enthalpy change ($\Delta H_4 = -0.77$ kcal/mol)[1] for Reaction 4.[8] Thirdly, the increase of both iodine and triiodide concentrations during the relaxation is also consistent with the negative value of ΔH_4. These facts finally enable us to assign the observed relaxation to Reaction 4, and an application of Eq. (6) to the present data gives the values of k_4 and k_{-4} to be $2.2\times10^5\,M^{-1}\,s^{-1}$ and $5.3\times10^5\,s^{-1}$ respectively. The obviously small value of binding rate constant k_4 compared with that of the diffusion controlled process suggests the existence of further elementary steps in Reaction 4, but the detailed discussion on the elementary process can not be advanced at the moment.

In conclusion, the relaxation phenomenon observed in the iodine–iodide solutions was assigned to the polyiodide complex formation of I_6^{2-} among the several kinds of complex formations proposed from the spectrophotometric studies. The kinetic studies of the interaction between cyclodextrin and iodide will be reported in a subsequent paper by taking into consideration the polyiodide complex formation.

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8) In the case of negative value of ΔH_4, the activation enthalpy of backward $\Delta H^{\ddagger}_{-4}$ should be greater than $|\Delta H_4|$. Accordingly, the enthalpy change ΔH_4 less than -2.0 kcal/mol gives rise to the temperature dependence of relaxation time beyond the experimental errors of about 10%.