Mechanism of the Recoil Phenomena in Hexamminecobalt(III) Chloride

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In the previous paper[1], we studied the heterogeneous extraction of recoil atoms in neutron-irradiated hexamminecobalt(III) nitrate target, and observed the anomalously high extraction yield with this compound. In the present paper, we studied the recoil effects in hexamminecobalt(III) chloride and found the following two interesting facts. 1) The recoil effects in hexamminecobalt(III) chloride involve more complicated processes than the simple replacement process. 2) A small percentage of the activity produced in the target is found in the form of chloropentamminecobalt(III) chloride as the result of recoil effect, and its radiochemical yield decreases on keeping it to stand even at room temperature; the rate determining step in this process is not diffusion, which has been usually considered to be responsible to the thermal annealing process of the recoil atom[2], but a chemical reaction.

Purified hexamminecobalt(III) chloride was subjected to neutron irradiation in the reactor, JRR-1 (neutron flux: 6×10^{11} n/cm^2/sec.) for 10 min., and was dissolved in water in about

1) N. Ikeda, K. Yoshihara and N. Mishio, *Radioisotopes*, 8, 242 (1959).

2) G. Harbottle and N. Sutin, "The Szilard-Chalmers Reaction in Solids" in "Advances in Inorganic Chemistry and Radiochemistry" Edited by H. J. Emelius and A. G. Sharpe, Academic Press, New York (1959).

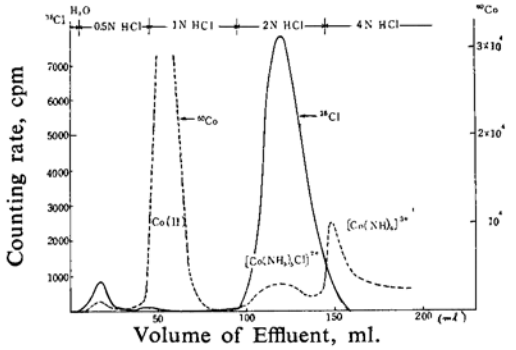

Fig. 1. Elution curve for recoil products in neutron-irradiated hexamminecobalt(III) chloride.

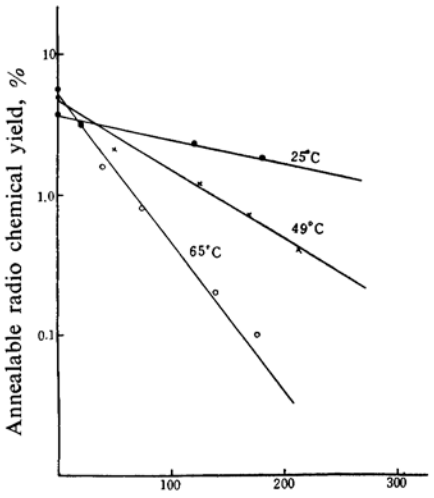

Fig. 2. Decrease of radiochemical yield of $[Co(NH_3)_5Cl^*]$ by standing irradiated hexamminecobalt(III) chloride at various temperatures.

30 min. after irradiation. The solution was passed through a cation-exchange resin column (Diaion SK #1, HR-form, 100~200 mesh, 1 cm. $\phi \times 4$ cm.). After being washed with a small quantity of water, the resin bed was eluted with hydrochloric acid of various concentrations. By the use of a pulse-height analyzoer, the γ-rays of ^{38}Cl and ^{60}Co in the eluted fractions were measured separately. The elution curve is shown in Fig. 1. The solid line shows the elution curve for ^{38}Cl activity and the dotted one shows that for ^{60}Co activity. The formation of $[Co(NH_3)_5Cl^*]^{2+}$ might be interpreted as simple replacement of NH_3 by ^{38}Cl recoil atom, but the formation of $[Co^*(NH_3)_5Cl]^{2+}$ can not be understood by this concept. Moreover, such a simple replacement can not explain the appearance of a peak at the earlier stage of the elution curve; a peak due to an unknown species containing both cobalt and chlorine atoms which might be a cobalt ammine complex, such as $[Co(NH_3)_4Cl_2]^+$.

The radiochemical yield of $[Co(NH_3)_5Cl^*]^{2+}$ was accurately measured after being separated from the luteo-salt. It was about 7% immediately after irradiation, but this value decreased on keeping the sample to stand in the solid state. At various temperatures, the relation between the standing time and the radiochemical yield of $[Co(NH_3)_5Cl^*]^{2+}$ was observed. The annealing curves for the earlier stage are shown in Fig. 2. The curves correspond to those of the first-order reaction. An apparent activation energy of 8.6 kcal. was obtained for this decreasing process of $[Co(NH_3)_5Cl^*] \cdot Cl_2$. Mori and Tsuchiya[3] studied the thermal decomposition of $[Co(NH_3)_6]Cl_3$ and reported the heat of formation $\Delta H = 9.6$ kcal./mol. and the activation energy $E_h = 18.0$ kcal./mol. for the reaction,

$$[Co(NH_3)_6]Cl_3 \rightleftarrows [Co(NH_3)_5Cl]Cl_2 + NH_3$$
(solid) (solid) (gas)

In the back-reaction, therefore, the activation energy $E_p = E_h - \Delta H = 8.4$ kcal./mol. is obtained. This value is very close to that obtained in this experiment. So that, one possible explanation of the annealing reaction observed by the present authors may be given by considering the back-reaction of the above-mentioned system provided that the quantity of ammonia is much larger compared with that of $[Co(NH_3)_5Cl]Cl_2$.

These results would lead us to the following model. In the neighborhood of the recoil atom, the chemical bonds of the molecules are broken and local fragmentation occurs. Unstable intermediate systems are formed. These are immediately rearranged into a group of several chemical species in the cooling step. However, some unbalances are still present in these systems, and slow changes occur by thermal annealing.

Details are to be reported in the full paper.

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3) M. Mori and R. Tsuchiya, This Bulletin, 32, 467 (1959).