Szilard-Chalmers Reaction of Trioxalatochromium Ion on Ion Exchange Resin—Static Irradiation and Its Kinetic Analysis

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The Szilard-Chalmers process can generally be divided into the following four consecutive processes.[1,2]

1) First process. This is purely a physical disruption of the bond due to the nuclear recoil. The yields in this process should be almost independent of the chemical constitution of the target material.

2) Second process. The hot atoms are thermalized in this epithermal process. In the case of a liquid phase, the hot atoms will be incorporated into some familiar stable chemical species at the end of this step.[3] Thus the yields may be more or less dependent on the chemical environment of the system.

3) Third process. During irradiation, the products of the second process undergo the radiation-induced thermal reactions. The yields are usually much influenced by various factors, such as irradiation time, chemical enviroment, and absorbed radiation dose of the system.[4]

4) Fourth process. This is the ordinary thermal annealing process. In addition, separation-induced processes may sometimes occur. The yields depend further on many factors, such as standing time and temperature[4].

It should be noted that the concomitant radiations other than the thermal neutrons in a reactor, i. e., the fast and the epithermal neutrons and the gamma rays, always produce the very same degraded species through processes similar to those mentioned above.[5] They usually decrease the separable yield through enhancement of the recombinations in the third process, and thus are the main factors complicating the true results of the recoil phenomena.

One of the authors has recently developed a flow method, using a complex-ion-loaded ion-exchanger in which an appropriate eluent continuously leaches out the recoil products from the target material immediately after their production.[6] Since this method can almost eliminate the third process, it may shed light on the immediate results at the end of the second process. Trioxalatochromium ion on an anion exchange resin is one of the most suitable samples for this purpose, considering its chemical constitution and the ionic stability in water. This paper deals with the results of the batch-wise experiments and their kinetic analysis, which have been done as an introductory approach to the flow method in this system.

Experimental

Material.—Trioxalatochromium complex ion was adsorbed on the acetate form of the anion exchange resin,[7] Dowex 1X8 (100—200 mesh), from an aqueous solution of $K_3Cr(C_2O_4)_3\cdot 3H_2O$ prepared by the usual method.[8] At about 15 hr. prior to irradiation, the resin was freed from aquated impurities with 0.01 N nitric acid and washed with water. As an irradiation sample, about 4 ml. of the resin was pipetted into a polyethylene vial with 3 ml. of the digesting solution, which was adjusted to pH 2.0 with nitric acid, pH 3.15 with acetic acid or pH 3.85 with acetic acid. The sample was stored in a frozen state until just before the irradiation.

Pile Irradiation.—Most of the samples were irradiated in a position of the reactor having minimum concomitant radiations, i. e., behind a leadblock (6.5 cm. thick) inserted in the thermal column of the TRIGA Mark II reactor, for 1.5—12 hr. at 100 kW. The thermal and the fast neutron fluxes here are about 3×10^{10} and 1×10^{8} n./cm²/sec., respectively, and the external gamma exposure rate is about 7×10^{3} r./hr. The internal radiation dose rate, i. e., the radiation energy absorbed by the sample per unit time due to the (n, γ) and the N(n, p) reactions and the collision of fast neutrons in the sample irradiated at this condition, was estimated to be about the same order of magnitude as the external exposure rate.

Some exploratory experiments were made using different positions, i. e., in the rotary specimen

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[1] A. G. Maddock and J. I. Vargas, *Trans. Faraday Soc.*, **57**, 992 (1961).

[2] K. Svoboda, IA-666-tr. (1962).

[3] G. Harbottle and N. Sutin, "Advances in Inorganic Chemistry and Radiochemistry, " Vol. I, Academic Press Inc., New York (1959).

[4] J. H. Green, G. Harbottle and A. G. Maddock, *Trans. Faraday Soc.*, **49**, 1413 (1953).

[5] R. R. Williams, *J. Phys. & Colloid Chem.*, **52**, 603 (1948).

[6] T. Matsuura, Proc. 5th Japan Conference on Radioisotope, 4-27 (1963): T. Matsuura, *J. Inorg. & Nucl. Chem.*, to be published.

[7] Y. Inoue, A. Kawamura, K. Wada and H. Okamura, *Japan Analyst*, 2, 121 (1953).

[8] H. S. Booth, "Inorganic Syntheses," Vol. I, 37 McGraw-Hill Book Co., Inc., New York (1939).

rack, in which the thermal and the fast neutron fluxes are about 6×10^{11} and 5×10^{10} n./sec./cm^2 respectively and the gamma exposure rate is about 1.4×10^6 r./hr., or in the thermal column without the lead shield, in which the gamma exposure rate is about 2×10^4 r./hr. However, with the samples which were irradiated in the rotary specimen rack, the yields of ^{51}Cr in the cationic species were found to be negligibly small, and even with those which had received only threefold increased gamma ray exposures by omitting the lead shield in the thermal column, the yield decreased as much as 17% on the average compared with the samples with the lead shield. In view of these results, further experiments were always carried out with the lead shield in the thermal column of the reactor.

Chemical Separation.—Although it has been reported that some part of the chromium can change its initial oxidation state by recoil[9-13] most of the chromium in this liquid system seems to maintain its lower oxidation state,[14] because the oxalate ion and the strong basic type anion exchanger form a highly reductive environment. Thus the main products from the parent complex ion were assumed to be hexaquo-, monoxalatotetraquo- and dioxalatodiaquo-chromium ions. Within 5—30 min. after the irradiation, the resin was transferred into a column (1 cm. i. d.) containing about 0.5 ml. of the acetate form of Dowex 1X8; the cationic species $[Cr(H_2O)_6{}^{3+}$ and $Cr(OX)(H_2O)_4{}^{+}]$ were firstly eluted from the resin with about 100 ml. of water, and the dioxalato species was separated from it with 300 ml. of 0.01 N nitric acid. The parent ion was finally eluted from the resin with 100 ml. of 1 N ammonium nitrate which had been adjusted to pH 1.0 with nitric acid. Though the dioxalato species was not so clearly separated from the parent one, they were distinguished by the steep change in the enrichment factors in the effluents. The cationic species were further separated by using 0.5 M perchloric acid and 6 N hydrochloric acid as eluents on a column of a cation exchange resin[15] in a few earlier runs, however this procedure was omitted in later runs and these portions were treated together as "cationic species," because the reported high rate of the equilibration reaction between them[16] was evidenced from about the same values of enrichment factors found in these fractions.

Determination of ^{51}Cr Activity and Total Chromium.—The activities of aliquots of the effluents were measured by counting the 0.32 MeV. photon emission of the ^{51}Cr with a well-type NaI(Tl) scintillation counter and a single channel analyzer. The amounts of total chromium (active and non-active chromium) were determined colorimetrically by the chromate method (using a filter of 372 mμ).[17]

Results

The Percentage Yield of ^{51}Cr. — The ^{51}Cr yields in the cationic, dioxalato and trioxalato chromium species are plotted against the irradiation time, for immersing solutions of varying pH values in Figs. 1, 2 and 3, respectively. They show that the yields of ^{51}Cr in

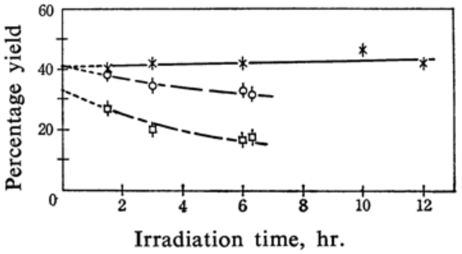

Fig. 1. Percentage yields of ^{51}Cr in the cationic species (hexaquo and monoxalatotetraquo) species against irradiation time.
—∗— pH 2.0; — —○— — pH 3.15; — -□— — pH 3.85
The lines are the calculated values.

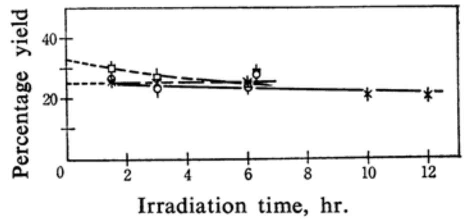

Fig. 2. Percentage yields of ^{51}Cr in dioxalato species against irradiation time.
—∗— pH 2.0; — —○— — pH 3.15; — -□— — pH 3.85
The lines are the calculated values.

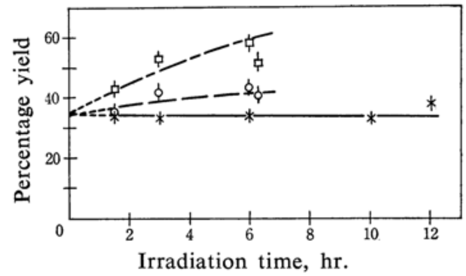

Fig. 3. Percentage yields of ^{51}Cr in trioxalato species against irradiation time.
—∗— pH 2.0; — —○— — pH 3.15; — -□— — pH 3.85
The lines are the calculated values.

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[9] G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).

[10] L. M. Fishman and G. Harbottle, ibid., **22**, 1088 (1954).

[11] N. Shibata and K. Yoshihara, This Bulletin, **32**, 422 (1959).

[12] N. Matsuura, Y. Kurimura and Y. Tsunoda., ibid., **35**, 1679 (1962).

[13] N. Saito, H. Sano and T. Tominaga, *Chem. & Ind.*, **1961**, 1796.

[14] W. H. Burgus and J. W. Kennedy, *J. Chem. Phys.*, **18**, 97 (1950).

[15] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

[16] K. V. Krishnamurty and G. M. Harris, *Chem. Revs.*, **61**, 213 (1961).

[17] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Pubs., New York (1950).

the cationic species decrease with the pH value of the digesting solution, whereas the yields of the parent species increase with it. It should be noted that while the yields of all species at pH 2.0 are almost unchanged with the irradiation time, the dependence of the yields on the irradiation time becomes noticeable as the pH value increases.

It follows from these figures, that the recombination rate is small at pH 2.0 but becomes noticeable with increasing pH value. The figures also show that the yields at zero irradiation time, i. e. the initial distribution of ^{51}Cr in each species in the epithermal process, is influenced by the pH value.

The Percentage Yield of Total Chromium and Enrichment Factor.—The yields of total chromium in the cationic, dioxalato and trioxalato species are plotted against irradiation time in Figs. 4, 5 and 6, respectively. Dividing the yields of ^{51}Cr in each species, by the yields of total chromium in the corresponding species, gives the enrichment factors shown in Fig. 7. The enrichment factors of the enriched species decrease with the irradiation time according to the general law.[18] Figure 7 also shows that the enrichment factor increased with the pH value of the digesting solution.

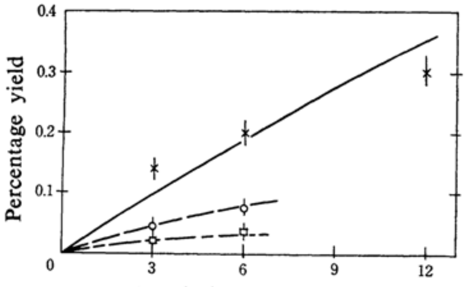

Fig. 4. Percentage yields of total chromium in the cationic species against irradiation time.
—∗— pH 2.0; ——○—— pH 3.15; ——□—— pH 3.85
The lines are the calculated values.

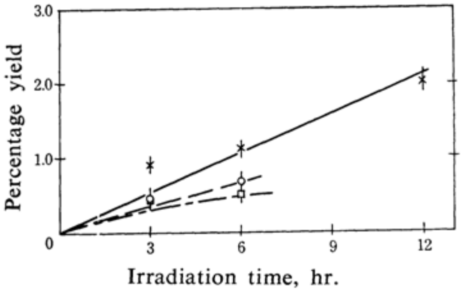

Fig. 5. Percentage yields of total chromium in dioxalato species against irradiation time.
—∗— pH 2.0; ——○—— pH 3.15; ——□—— pH 3.85
The lines are the calculated values.

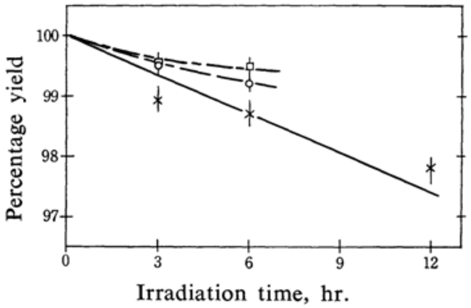

Fig. 6. Percentage yields of total chromium in trioxalato species against irradiation time.
—∗— pH 2.0; ——○—— pH 3.15; ——□—— pH 3.85
The lines are the calculated values.

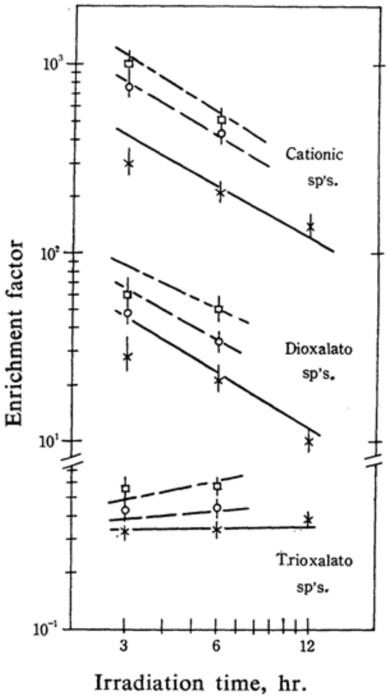

Fig. 7. Enrichment factor in each species against irradiation time.
—∗— pH 2.0; ——○—— pH 3.15; ——□—— pH 3.85
The lines are the calculated values.

Discussion

The overall reaction including the epithermal process accompanied by both recoil and gross radiolysis, and the subsequent thermal process

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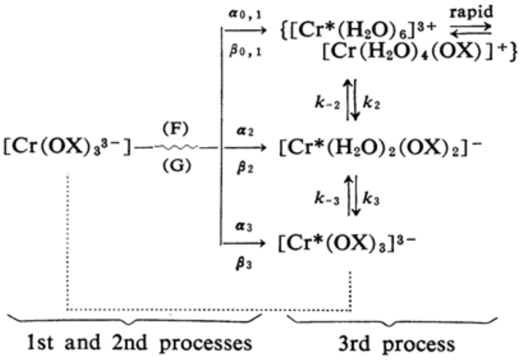
[18] G. E. Boyd, J. W. Cobble and S. Wexler, *J. Am. Chem. Soc.*, **74**, 237 (1952).

of interconversion among the main products during irradiation, can be represented by the following scheme:



Here, it should be noted that although the first and the second processes can be distinguished in the case of the labeled species, this can not be so with the total chromium species, i. e., the rate constant of the actual degradation of $Cr(OX)_3{}^{3-}$ species is expressed as $\{G(\beta_2+\beta_{0,1})+k_{-3}\}$.

Then the labeled and the total chromium species can be followed simultaneously by the following rate equations, the radioactive decay terms for this nuclide being neglected:

$$\left.\begin{aligned}\frac{d(X_{0,1}{}^*+X_{0,1})}{dt}&=\alpha_{0,1}FN_{cr}\\&\quad+k_{-2}(X_2{}^*+X_2)+\beta_{0,1}G(X_3{}^*+X_3)\\&\quad-k_2(X_{0,1}{}^*+X_{0,1})\\\frac{d(X_2{}^*+X_2)}{dt}&=\alpha_2FN_{cr}+k_2(X_{0,1}{}^*+X_{0,1})\\&\quad+(\beta_{0,1}G+K_{-3})(X_3{}^*+X_3)\\&\quad-(k_{-2}+k_3)(X_2{}^*+X_2)\\\frac{d(X_3{}^*+X_3)}{dt}&=\alpha_3FN_{cr}+k_3(X_2{}^*+X_2)\\&\quad-\{(\beta_{0,1}+\beta_2)G+k_{-3}\}(X_3{}^*+X_3)\end{aligned}\right\}\quad(1)$$

where

F=rate constant of formation of ^{51}Cr, $a\cdot\phi_{th}\cdot\sigma_{act}$,*

G=rate constant of initial decomposition of parent ion by radiolysis,**

α_i=initial fraction of distribution of ^{51}Cr in each species by recoil,

β_i=initial fraction of distribution of total chromium in each species by radiolysis,

k_{-i}=apparent rate constants of the aquation under irradiation condition, with respect to the complex ion,

k_i=apparent rate constants for complex formation under irradiation condition, with respect to the complex ion,

$X_i{}^*$=number of ^{51}Cr in each species,

X_i=total number of chromium atoms in each species,

N_{cr}=total number of chromium atoms in the whole system.

We obtain the equations for the active chromium by eliminating the nonactive terms in Eq. 1, and those for the total chromium by neglecting the first and the labeled terms. We assume that not only the aquation rate but also the complexing rate are first order with respect to the complex ion for each pH value as is reported in the cold condition.[19,20]

Judging from the data for the yields of ^{51}Cr and the total chromium at pH 2.0, we can assume that the complexing rates are small compared with the respective aquation rates for both the labeled and total chromium at pH 2.0. Thus by disregarding the complexing terms in Eq. 1, the following solutions are obtained for active and total chromium at pH 2.0:

$$\left.\begin{aligned}X_{0,1}{}^*&=\frac{x_{0,1}{}^*N_{cr}{}^*}{100}=(\alpha_{0,1}+\alpha_2)FN_{cr}t\\&\quad-\frac{\alpha_2FN_{cr}}{k_{-2}}\{1-\exp[-k_{-2}t]\}\\X_2{}^*&=\frac{x_2{}^*N_{cr}{}^*}{100}\\&=\frac{\alpha_2FN_{cr}}{k_{-2}}\{1-\exp[-k_{-2}t]\}\\X_3{}^*&=\frac{x_3{}^*N_{cr}{}^*}{100}=\alpha_3FN_{cr}t\end{aligned}\right\}\quad(2\text{-a})$$

$$\left.\begin{aligned}X_{0,1}&=\frac{x_{0,1}N_{cr}}{100}=\frac{\beta_{0,1}GN_{cr}}{(\beta_{0,1}+\beta_2)G+k_{-3}}\\&\quad\times\{1-\exp[-\{(\beta_{0,1}+\beta_2)G\\&\quad+k_{-3}\}t]\}\\X_2&=\frac{x_2N_{cr}}{100}=\frac{(\beta_2G+k_{-3})N_{cr}}{k_{-2}-(\beta_{0,1}+\beta_2)G+k_{-3}}\\&\quad\times\{\exp[-\{(\beta_{0,1}+\beta_2)G\\&\quad+k_{-3}\}t]-\exp[-k_{-2}t]\}\\X_3&=\frac{x_3N_{cr}}{100}\\&=N_{cr}\exp[-\{(\beta_{0,1}+\beta_2)G+k_{-3}\}t]\end{aligned}\right\}\quad(2\text{-b})$$

where $x_i{}^*$ and x_i are the percentage yields of ^{51}Cr and total chromium in the species i, respectively, and $N_{cr}{}^*$ is the number of ^{51}Cr atoms produced after t hr. of irradiation.

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* a=abundance of ^{50}Cr,
ϕ_{th}=thermal neutron flux,
σ_{act}=thermal neutron cross section for the reaction $^{50}Cr(n, \gamma)^{51}Cr$.

** This is not the rate constant of the apparent radiolytic decomposition but includes the immediate recombination into the parent form in the epithermal reaction, and thus is defined as pH-independent.

[19] R. E. Hamm and R. E. Davis, ibid., 75, 3085 (1953).

[20] R. E. Hamm and R. H. Perkins, ibid., 77, 2083 (1955).

At pH 3.15 and pH 3.85 it can safely be assumed that the complexing rate constants are much greater than the respective aquation ones, from the results in Figs. 1—7 and the data from the cold condition.[19-21] Thus by neglecting all the aquation terms for the ^{51}Cr and the total chromium in Eq. 1 except that for the aquation of the total parent ions, the following relationships are obtained for pH 3.15 and 3.85:

$$\left.\begin{aligned}
X_{0,1}^* &= \frac{x_{0,1}^* N_{cr}^*}{100} \\
&= \frac{\alpha_{0,1} F N_{cr}}{k_2}\{1-\exp[-k_2 t]\} \\
X_2^* &= \frac{x_2^* N_{cr}^*}{100} = \frac{(\alpha_{0,1}+\alpha_2) F N_{cr}}{k_3} \\
&\quad \times\{1-\exp[-k_3 t]\} - \frac{\alpha_{0,1} F N_{cr}}{k_3-k_2} \\
&\quad \times\{\exp[-k_2 t]-\exp[-k_3 t]\} \\
X_3^* &= \frac{x_3^* N_{cr}^*}{100} = F N_{cr} t - (X_{0,1}^* + X_2^*)
\end{aligned}\right\} \quad (3\text{-a})$$

$$\left.\begin{aligned}
X_{0,1} &= \frac{x_{0,1} N_{cr}}{100} \\
&= \frac{\beta_{0,1} G N_{cr}}{k_2}\{1-\exp[-k_2 t]\} \\
X_2 &= \frac{x_2 N_{cr}}{100} = \frac{\{(\beta_{0,1}+\beta_2)G+k_{-3}\} N_{cr}}{k_3} \\
&\quad \times\{1-\exp[-k_3 t]\} - \frac{\beta_{0,1} G N_{cr}}{k_3-k_2} \\
&\quad \times\{\exp[-k_2 t]-\exp[-k_3 t]\} \\
X_3 &= \frac{x_3 N_{cr}}{100} = N_{cr} - (X_{0,1} + X_2)
\end{aligned}\right\} \quad (3\text{-b})$$

From the experimental plots in Figs. 1—3, the initial fractions of distribution of ^{51}Cr at the end of the second process are read as $\alpha_{0,1}=0.41$, $\alpha_2=0.25$ and $\alpha_3=0.34$ for pH 2.0 and 3.15 and $\alpha_{0,1}=0.33$, $\alpha_2=0.32$ and $\alpha_3=0.35$ for pH 3.85, respectively. After these values were put into the Eqs. 2-a, 2-b, 3-a and 3-b, the other parameters $\beta_{0,1}G$, $\beta_2 G$, k_{-i} and k_i which may also be pH-dependent were estimated by trial and error method for each pH value, to give calculated yields of ^{51}Cr and total chromium which best fit the experimental ones, as is shown in Figs. 1—6. The agreement between the calculated curves and the observed plots implies that the assumptions made are reasonable. The rate constants thus determined are shown in Fig. 8.

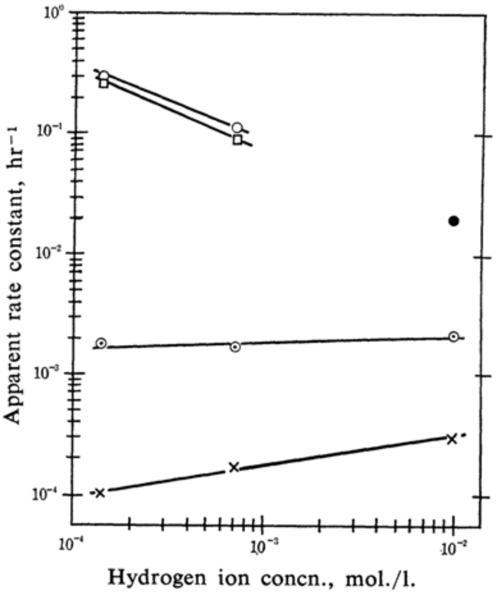

Fig. 8. The best-fit apparent rate constants against the hydrogen ion concentration.
○ k_3; □ k_2; ⊙ $(\beta_{0,1}+\beta_2)G+k_{-3}$; × $\beta_{0,1}G$; ● k_{-2}

As can be seen in Fig. 8 the gross decomposition rate constant of the parent ion under irradiation, $\{(\beta_{0,1}+\beta_2)G+k_{-3}\}$, and the rate constant of the initial direct formation of cationic species from the parent ion by radiolysis, $\beta_{0,1}G$, are only slightly dependent on the pH value, while the corresponding aquation rate constants under the cold condition have been reported to be much more dependent on the pH value.[21,22] However, the fact that the numerical values observed under irradiation condition were found to be much larger than those of the corresponding aquation rate constant of the parent ion under cold condition* may imply that the pH-independent radiation-induced term is predominant over the pH-dependent cold term even in low radiation fields as in this irradiation condition.

On the other hand, Fig. 8 shows that the apparent rate constants of the complex-forming reaction, k_i's, are nearly inversely proportional to the hydrogen ion concentration, in accord with the corresponding ones under the cold condition both in tendency and in magnitude.[19,20] This suggests that the radiation-induced term does not seriously contribute to the apparent complexing rate constant at least in the low radiation fields. However, as can be seen from the exploratory experiment, higher radiation fields may increase the recombination rate.

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[21] K. V. Krishnamurty and G. N. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

[22] N. K. Dutt and B. Sur, *Z. anorg. u. allgem. Chem.*, **293**, 195 (1957).

* These values are calculated to be 2.2×10^{-4} and 5×10^{-6} hr^{-1} for pH 2.0 and 3.85 respectively according to Krishnamurty's data.[21]

We believe that the dependence on pH value, of the initial fraction of distribution of ^{51}Cr among each species, α_i, is reasonable, because in the epithermal reaction, an immediate recombination of the degraded ion should have occured, and its extent will depend on the pH value. The lowest value of α_3 obtained, 0.34 can be referred to as the "initial retention" in this system. However, as this is the value after the completion of the epithermal reaction in this chemical environment, it seems difficult to relate it with the nuclear inefficiency of the bond rupture due to the ^{51}Cr recoil in the first process. The authors believe this value for chromium should be almost zero, as was evidenced by the reported almost zero value of retention in the $Cr(SCN)_6^{3-}$ system.[23] The same author[23] reports that the most aquated species is the most enriched one, and this is just what we found in our system, as is shown in Fig. 7.

Summary

Trioxalatochromium ion, on Dowex 1X18 immersed in a solution of pH 2.0—3.85, was irradiated batch-wise in the thermal column of a reactor for various irradiation times. With decreasing pH, the ^{51}Cr yield of the most enriched species (hexaquo- and monoxalatotetraquo-chromium ion) increased, but the enrichment factor decreased. With increasing irradiation time, while the changes in the ^{51}Cr yield of each chemical form are small at pH 2.0, the recombination reaction becomes noticeable at pH 3.15 and 3.85. These results were analyzed kinetically, and the rate constants of the aquation and the complex formation under irradiation condition as well as the initial fractions of distribution of ^{51}Cr and the total chromium among each chemical species were determined for the respective pH values.

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[23] S. Kaufman, *J. Am. Chem. Soc.*, **82**, 2963 (1960).