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Kinetics of Isotopic Exchange between 8-Quinolinol-^{14}C and Tris-8-quinolinolato Complexes of Tervalent Typical Elements

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Rate of isotopic exchange between 8-quinolinol-^{14}C and the 8-quinolinolato (oxinato) complexes of aluminum, gallium and indium has been studied in chloroform. Pure yellow complexes are precipitated by adding petroleum ether to the reaction mixture. The exchange rate decreased in the sequence In > Al > Ga, and a detailed kinetic study can be substantiated only with the gallium complex below 0°C. The rate is proportional to the concentration of the complex, but is independent of that of free 8-quinolinol (quinolH) and the Arrhenius activation energy is 18 kcal per mole. The reaction is accelerated by acid and presumably by water. It appears as if one of the ligands is present as unidentate under the given condition and the break of the remaining bond would be the rate determining step. Any reagent that can retard the recombination of the free end of unidentate ligand would catalyse the exchange reaction.

Typical elements of group III in the periodic table are regarded as substitution labile.[1] One of us, however, exemplified that trisacetylacetonato- and tris-8-quinolinolatoindium exchange radioactive indium at a measureable rate in chloroform at room temperature.[2] Recently we studied the isotopic exchange kinetics of trisacetylacetonatoaluminum in tetrahydrofuran.[3] The reaction mechanism was a dissociative nature and the break of unidentate ligand seemed to be the rate determining step. The reaction was accelerated by water and some kinds of organic acids, which appear to retard the recombination of the free end of unidentate acetylacetonate. It seems thus particularly interesting to examine the rate of isotopic exchange of 8-quinolinolato complexes, having a more rigid framework structure, and oxygen and nitrogen as coordinating atoms.

The solubility of tris-8-quinolinolato complexes of aluminum, gallium, indium and thallium(III) has been extensively examined in a variety of organic solvents, and it was found that the aluminum, gallium and indium complexes are precipitated in a pure state from their chloroform solutions by adding petroleum ether. However, the same procedure was not useful for obtaining pure thallium(III) complex, and

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2) K. Saito and M. Tamura, *J. Inorg. Nucl. Chem.*, **13**, 334 (1960).

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the exchange rate was studied with only the three kinds of complex. The precipitation is not affected by excessive ligand and some kinds of organic acid including *m*-toluic.

The rate of exchange decreased in the sequence indium, aluminum and gallium and detailed kinetic studies have been made only with the gallium complex below 0°C. The influence of the concentration of the complex, the free ligand and other ingredients has been carefully examined and a probable reaction mechanism posturated.

Experimental

Materials. 8-Quinolinol-^{14}C was synthesized by Scraup's method modified to suit for small scale preparation.[4] Aniline-^{14}C (0.1 mCi, 5.3 m*l*), glycerin (17.2 m*l*), nitrobenzene (3.5 m*l*), iron(II) sulfate (heptahydrate 2.0 g) and concentrated sulfuric acid (10.0 m*l*) were boiled for about five hours, cooled to about 100°C, and steam-distilled for 30 min, to remove unchanged nitrobenzene. The residual solution was neutralized with 40% sodium hydroxide solution (*ca.* 30 m*l*) and the quinoline steam-distilled together with remaining aniline. The organic layer of the distillate was treated with concentrated sulfuric acid (3.8 m*l*), cooled to 0—5°C, treated with excessive saturated sodium nitrite solution (5.0 m*l*), warmed on a steam bath for about an hour, and steam-distilled to remove volatile materials. The product treated with 40% sodium hydroxide solution (15.0 m*l*) and steam-distilled to collect crude quinoline, which was distilled and the dry colorless distillate (*ca.* 5 m*l*) was dropped into fuming sulfuric acid (10.0 m*l*) below 90°C. The darkcolored solution was warmed at 70°C for about 40 hr in anhydrous atmosphere, cooled and poured into cold water. Precipitated colorless prisms were filtered off, washed with water, recystallized from hot water and dried (6.27 g). Sodium hydroxide (12.0 g) and water (3 m*l*) were heated at 270°C with stirring, mixed with the quinoline 8-sulfonic acid powder, kept at the temperature for 10 min and chilled. The cake was broken, dissolved in an excess of hydrochloric acid (5 N 70 m*l*), neutralized, and steam-distilled. (Yeild 2.1 g 8-quinolinol-^{14}C)

8-Quinolinolato complexes of aluminum, gallium and indium were prepared by the method ordinarily used for gravimetric analysis, from commercial 8-quinolinol and appropriate salts of the metals.

Commercial chloroform was shaken with concentrated sulfuric acid, then 5% sodium hydroxide solution and water, dried with phosphorus pentoxide and distilled immediately before use.

m-Toluic acid was recrystallized from water and sublimed at 105°C at 5 mmHg. Commerical anisol was shaken with sodium hydroxide solution, dried with calcium chloride, refluxed with sodium and distilled. *p*-Terphenyl was recrystallized from xylene. *p*-Di-(5-phenyl-2-oxalozyl)-benzene (POPOP) was of scintillation grade and used without further purification. Other chemicals were of all chemically pure grade.

Experimental Procedure. Weighed amounts of the complex (65 to 250 mg) and the ligand (18 to 73 mg) were dissolved in 10 m*l* portions of chloroform separately (both $\simeq 10^{-2}$ M). Other reagents such as *m*-toluic acid were previously added to the solvent whenever necessary. Both solutions were kept in a bath at −5.0 or −20°C, and mixed after their temperature reached constant. At appropriate intervals, an aliquot ($\simeq$2 m*l*) was added to chilled petroleum ether (20 m*l*) to stop the reaction. Pure 8-quinolinolato complex was separated instantaneously free from excessive ligand. The precipitate was swiftly filtered off with filter paper, washed with petroleum ether, and dried at 110°C. The time required for this separation was about 2 min. Purity of the precipitate was checked by its absorption spectrum and the chemical analysis of the metal with EDTA. Absorption spectra of the reaction mixture disclosed that no reaction other than isotopic exchange was taking place in the reaction mixtures.

Measurement of Radioactivity. One mg of the precipitate was dissolved in 15.0 m*l* anisol, and mixed with 15.0 m*l* of anisol solution containing 0.02% POPOP and 0.8% *p*-terphenyl. The counting rate was measured by the scintillation technique with a coincidence liquid scintillation counter.[3] The 8-quinolinolato complexes have yellow color and provide quite significant quenching effect. The influence was examined with standard ^{14}C-benzoic acid and the inactive 8-quinolinolato complexes, to obtain calibration curves, with which the counting rate was duly corrected. The scintillation efficiency was *e.g.* 50.0% in the presence of 1.0 mg of the gallium complex in 30 m*l* of the liquid scintillator. The counting rate at the end of isotopic exchange reaction (infinite time) was calculated from that of the 8-quinolinol-^{14}C and the used amounts of the respective complexes.

Water contents in the chloroform and the reaction mixtures were determined by Karl Fischer titration. The ultraviolet absorption spectra were measured with Hitachi EPU-3 spectrophotometer and the infrared absorption spectra with Hitachi FIS-1, and EPI-2G spectrophotometer.

Results

The experimental data were treated with McKay's equation

$$R = -2.303\frac{3ab}{3a+b}\cdot\frac{\log(1-F)}{t} \qquad (1)$$

where a and b express the concentrations of the 8-quinolinolato complex (containing 3 mol of exchangeable ligands per mole) and 8-quinolinol, respectively. F is the fraction of reaction and t the lapse of time (in minutes). The plots of $\log(1-F)$ *vs.* t were all linear to permit the treatment with Eq. (1). The approximate rates of the ligand exchange of 8-quinolonolato complexes were as follows:

Indium complex, too rapid to be measured

Aluminum complex, half period ($t_{1/2}$), 10 min at −20°C, a=0.01 M

Gallium complex, measurably slow below 0°C.

Detailed kinetic studies were substantiated only with the gallium complex. About 10% zero-time exchange was observed throughout the studies with the gallium complex. The figure is reproducible and seems to be separation induced exchange. The

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[4] G. E. McCasland, *J. Org. Chem.*, **11** 277 (1946).

time zero of each kinetic run was taken as that the first aliquot was taken from the reaction mixture, *e.g.* 5 min after the mixing of the solutions. The experimental error involved in obtaining indiviual R values was less than 9%. The temperature deviated by less than 1°C from one kinetic run to another, but remained unchanged within an error less than 0.2°C during a given run.

The dependence of R on a and b is indicated in Fig. 1 and Table 1, respectively. They show that R is proportional to a and independent of b in the examined concentration ranges. Hence, R is expressed by Eq. (2).

$$R = k[\text{complex}] = ka \tag{2}$$

The influence of water could not be examined. Saturated water concentration in chloroform at −20°C was 0.019 M. In the presence of more water, excessive water freezes on the surface of chloroform. The best dehydrated chloroform contained 0.016 M water immediately after distillation. However, even such a batch gave floating ice on the surface, whenever used as reaction medium, presumably owing to absorption of moisture from atmosphere. Thus the reaction mixture should be regarded as always saturated with water at the given temperature.

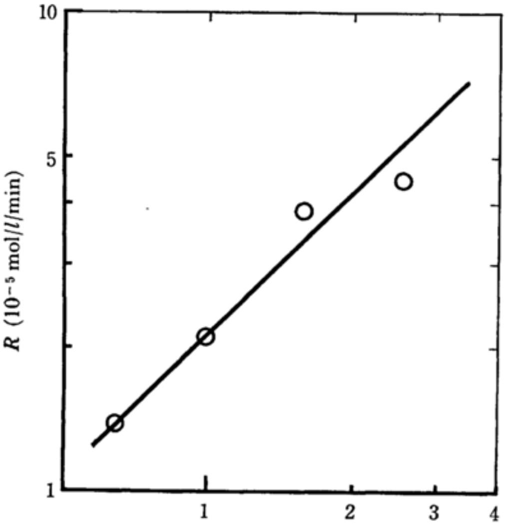

Fig. 1. Influence of the concentration of the gallium complex (a) on the exchange rate in chloroform. (−21.2°C, b=0.010 M)

TABLE 1. INFLUENCE OF THE CONCENTRATION OF FREE LIGAND (b) ON THE EXCHANGE RATE OF GALLIUM IN CHLOROFORM (a, 0.010 M)

t, °C	b, M	R,mol/ l /min
−5.0	0.010	2.1×10^{-4}
	0.030	1.8×10^{-4}
	0.040	1.9×10^{-4}
−20.2	0.010	2.4×10^{-5}
	0.016	2.6×10^{-5}
	0.025	2.6×10^{-5}

The temperature dependence of R was measured at −5.0, −10.4, −21.2°C. Arrhenius activation energy was 18.6 kcal per mole.

This reaction is catalyzed by acid, although the kinds of acid used for this examination were limited owing to the solubility. The influence of m-toluic acid upon R is shown in Fig. 2. Hence R is expressed as Eq. (3).

$$R = ka = a(k_0 + k_a[\text{acid}]) \tag{3}$$

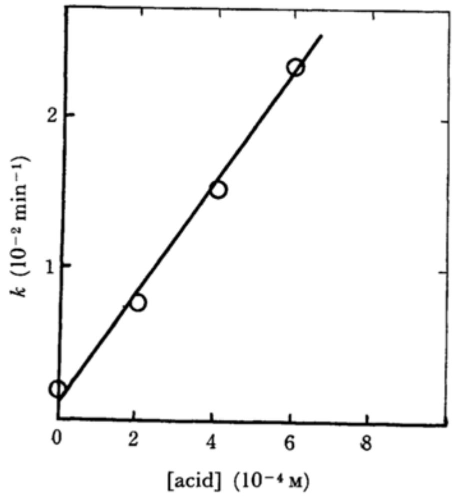

Fig. 2. Influence of the concentration of m-toluic acid on the exchange rate constant of gallium complex in chloroform. (−21.2°C, a=0.010 M)

Discussion

The mechanism would be of dissociative nature, because the exchange rate is independent of concentration of the free ligand. Since simultaneous break of two bonds, Ga–O and Ga–N, is not probable, we have to consider either that one of the ligands is present as unidentate and break of the remaining bond would be the rate-determining step, or that the break of one of the metal ligand bonds is the rate determining step and the liberation of unidentate ligand quite fast. In a kinetic study of isotopic exchange of trisacetylacetonato aluminum complex in THF, which gives similar kinetic formula, the two possible mechanisms were discriminated by examining the influence of water content upon the exchange rate.[3] In the present case, such a discrimination cannot be expected because we could not change the water content in chloroform. Hence Eq. (3) is only an apparent formula at a given concentration of water, in that the participation of water is not taken into consideration.

Nevertheless, the catalytic action of m-toluic acid could provide useful information. The proton could

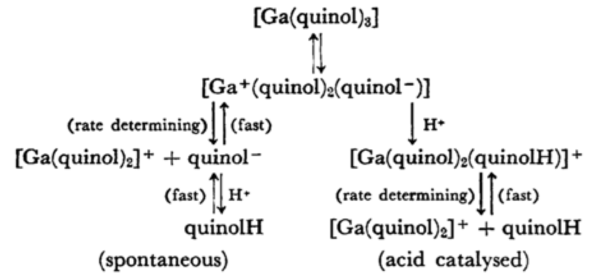

Fig. 3. Apparent mechanism of isotopic exchange for the gallium complex.

be transferred either to the free end of the unidentate ligand or to the coordinated oxygen. (Transfer to the negatively charged oxygen would be more feasible than to the nitrogen.) It remains again uncertain whether the proton is carried by the acid itself or by the hydronium ion, because the influence of water content upon the rate was neither known in the presence of acid. However, the proton would be more readily transferred to the negatively charged free end of unidentate ligand from the carrier, rather than the carrier reaches the co-ordinated oxygen atom making its way through the ligand sphere entangled with the bidentate chelates. Hence the plausible reaction mechanism would be postulated as seen in Fig. 3.

Eigen measured the exchange rate of coordinated water of various metal ions and found that the rate increases with increase in radii of ions with a given charge.[1] Hence the order of increasing reactivity among tervalent typical ions was aluminum, gallium, indium and thallium. The energy of hydration of the aquo complexes decreases in the same sequence and Eigen's order of reactivity is in accord with this order.

Our results are not consistent with his. The reason should be sought for in some factors characteristic of tris-8-quinolinolato complexes. If all the three complexes underwent isotopic exchange through similar dissociation mechanisms as exemplified by the gallium complex, their reactivity would be reflected, at least partly, in the stability of the tris complexes.

No reliable data are, however, available concerning the stability of tris-8-quinolinolato complexes of these metals. They form molecular lattice crystals and the solubility product[5] cannot be a good measure of stability. The shift of characteristic bands of the ligand in ultraviolet region due to complex formation was claimed to provide useful information concerning the stability of complexes with similar skeletal structure and symmetry.[6] Such a correlation cannot be always substantial, as exemplified by the comparison between the stability constants[7] and the absorption peaks of trisacetylacetonato complexes of these metals. The infrared absorption spectra in the region from 200 to 5000 cm^{-1} are too complicated for unambiguous band assignments to be made, and there is no concrete evidence that the force constant of metal-ligand bonds is simply interrelated with stability or lability of the complex.

Pritchard and Skinner compiled the electronegativity data of elements measured by various methods, and gave most probable values.[8] Since then, Allred and Rowchow[9] gave slightly different values obtained by electrostatic calculation, and Laubengayer *et al.*[10] compared the values for aluminum and gallium from proton magnetic resonance .data. All these estimations are consistent with one another in that the values for aluminum and indium are almost equal and that for gallium is significantly greater. Although the value for indium could become greater in some kinds of compound,[11] gallium seems always more electronegative than aluminum. If the reactivity of these complexes were governed by both the stability related to the electronegativity and the general reactivity represented in Eigen's experiment, the order of reactivity of tris-8-quinolinolato complexes, *i.e.* gallium$<$aluminum$<$indium, would not be very unreasonable.

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