BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 717—718 (1975)

Substitution Reaction of Ethylenediaminetetraacetatoaluminate(III) with Indium(III) in Aqueous Solutions

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(Received April 25, 1974)

Synopsis. The kinetics of substitution reaction between the aluminium(III) EDTA complex and the indium(III) ion has been studied in aqueous solutions of pH 2—10; the aluminium(III) complex is more labile than the gallium(III)[1)] and the indium(III)[2)] complex.

Previous kinetic studies on the isotopic exchange of ethylenediaminetetraacetatogallium(III),[1)] indium(III)[2)] and thallium(III)[3)] could not be extended to the corresponding aluminium(III) complex because of lack of suitable radioisotope. Indium(III) complex of EDTA (H_4Y) has a much greater stability constant than that of the aluminium complex $[AlY]^-$ and the following equilibrium shifts towards the right.

$$[AlY]^- + In^{3+} \rightleftarrows [InY]^- + Al^{3+} \tag{1}$$

EDTA complexes of tervalent cations have one mole of coordinated water. The formula would be more complicated than that written in terms of MY^- as done for the sake of simplicity. Determination of the rate of decrease in $[AlY]^-$ concentration is best. For measuring the rate of reaction (1) towards the right. However, $[AlY]^-$ cannot be determined quickly without separation, which takes too long as compared with the progress of the substitution reaction. Thus the concentration of free indium ions was determined by titration with EDTA. Since the liberated aluminium and excessive indium ions give a precipitate in the neutral or basic region, tartrate ions had to be added.

Reaction (1) is very fast below pH 2. The rate was determined in the pH regions 2—4, and 4—9.5 in the absence and the presence of tartrate ion, respectively. When the concentration of the indium ion ($\simeq 10^{-3}$ M) exceeds that of $[AlY]^-$ ($\simeq 10^{-4}$ M), a pseudo first-order kinetic law holds in the initial stages. The apparent first-order rate constant k_1 is a measure for the rate.

$$k_1 = (1/t) \ln (a/a-x) \tag{2}$$

The concentration of $[AlY]^-$ at time t is obtained from $(a-x)$, where x is the decrease in concentration of free indium(III) and a the initial concentration of $[AlY]^-$. The overall dependence of k_1 upon pH is shown in Fig. 1.

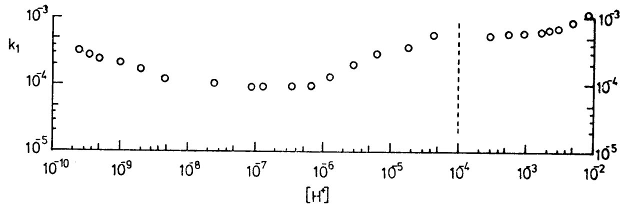

Fig. 1. pH Dependence of the rate constant k_1 in the whole pH region.
20 °C, I=0.2(KNO_3), In^{3+} 4.0×10^{-3} M, Al-EDTA 4.0×10^{-4} M; over pH 4, potassium tartrate 0.02 M, sodium barbiturate 0.002 M.

Titration of the indium ion took *ca.* 1 min., and had to be carried out at 3—10 min time intervals. The difference $(a-x)$ is relatively small as compared with a and x, and the overall error for k_1 values seems to be *ca.* ±10%. Hence only qualitative discussion was made for the initial stage of the reaction.

In Acid Region. The k_1 values increase almost linearly with increase in indium(III) ion concentration, being independent of the complex concentration at pH 2.8 (Table 1). The apparent Arrhenius activation energy is 13 kcal/mol at pH 2.8. The increase in k_1 below pH 2.5 seems to be due to acid catalysis. Dependence on indium(III) ion concentration can indicate either an electrophilic attack of indium(III) or the retardation of recombination of free acetate branch of partly dissociated $[AlY]^-$. Differentiation of the two mechanisms is difficult. However, the E_A values in acid do not differ from those in neutral or basic region. Hence the rate-determining step seems to lie in the dissociation of $[AlY]^-$, and the dependence on indium ion concentration can be reckoned as Lewis acid catalysis. Indium(III) may give an ion pair or a segment with the complex, retarding the recombination of the free end, $-CH_2COO^-$.

Table 1. Relationship between the rate constant k_1 and the concentration of uncomplexed indium(III) and Al-EDTA complex

[Al-EDTA] 10^{-4} M	$[In^{3+}]$ 10^{-3} M	k_1 (s^{-1})		
		pH 8.7	pH 7.0	pH 2.8
3.2	4.0	1.5×10^{-4}	7.5×10^{-5}	
3.6	4.0	1.2×10^{-4}	8.1×10^{-5}	5.9×10^{-4}
4.0	4.0	1.3×10^{-4}	8.1×10^{-5}	5.7×10^{-4}
4.8	4.0	1.3×10^{-4}	7.9×10^{-5}	6.1×10^{-4}
5.6	4.0	1.2×10^{-4}	8.0×10^{-5}	6.0×10^{-4}
6.4	4.0	1.0×10^{-4}	5.4×10^{-5}	4.6×10^{-4}
8.0	4.0	1.0×10^{-4}	5.2×10^{-5}	4.5×10^{-4}
4.0	2.0			2.0×10^{-4}
4.0	3.2	1.0×10^{-4}	8.2×10^{-5}	3.5×10^{-4}
4.0	4.0	1.3×10^{-4}	8.1×10^{-5}	5.7×10^{-4}
4.0	4.8			6.8×10^{-4}
4.0	6.0	1.2×10^{-4}	7.9×10^{-5}	8.4×10^{-4}
4.0	8.0	1.2×10^{-4}	8.2×10^{-5}	

20 °C, I=0.2(KNO_3); at pH 7.0 and 8.7, potassium tartrate 0.02 M, sodium barbiturate 0.002 M.

In Neutral and Basic Region. Tartrate ion does not affect titration. k_1 is independent of the free indium(III) ion concentration, but increases linearly

Table 2. Influence of ionic strength(KNO_3) and potassium tartrate upon the rate constant k_1

KNO_3 (M)	Potassium tartrate (M)	k_1 (s^{-1})		
		pH 8.7	pH 7.0	pH 2.8
0.05	0.02	1.3×10^{-4}	7.5×10^{-5}	6.1×10^{-4}
0.4	0.02	1.4×10^{-4}	8.1×10^{-5}	5.5×10^{-4}
0.2	0.01	1.2×10^{-4}	7.0×10^{-5}	
0.2	0.016	1.4×10^{-4}	8.2×10^{-5}	
0.2	0.03	1.8×10^{-4}	1.5×10^{-4}	
0.2	0.04	2.2×10^{-4}	2.0×10^{-4}	

20 °C, In^{3+} 4.0×10^{-3} M, Al-EDTA 4.0×10^{-4} M; at pH 7.0 and 8.7, sodium barbiturate 0.002 M.

with increase in tartrate ion concentration (Table 2). E_A depends on the tartrate ion concentration; 16 and 13 kcal per mole in the presence of 0.02 M tartrate ion for 4.0×10^{-4} M complex, at pH 7.0 and 8.7, respectively. The buffering agent, barbiturate, does not affect the rate; neither does the ionic strength. k_1 decreases slightly with increase in the complex concentration.

The complex has a coordinated water which dissociates with a $pK\simeq10^{-6}$ and can be replaced by other ligands including tartrate.[4] Substitution of tartrate for the ligand water seems to facilitate the bond break of $[AlY]^-$. With increase in complex concentration, coordinated tartrate may act as a bridging ligand to give a binuclear complex such as $[YAl\cdot tart\cdot AlY]^{4-}$, which may dissociate with slightly greater difficulty than the uninuclear species.

Comparison with Related Reactions. It is remarkable that the dissociation reaction of $[AlY]^-$ is faster than that of the corresponding gallium(III) and indium(III) complex (*e.g.* R/a values are 1.7×10^{-5}, 4.3×10^{-5}, 3.7×10^{-5} and 4.0×10^{-5} s^{-1} for $[GaY]^-$ at pH 1.0 and 8.6 and $[InY]^-$ at pH 1.36 and 10.98, respectively.[1,2]). The lability of $[AlY]^-$ seems to be reflected in the smaller E_A values given above. (The E_A values for the isotopic exchange between MY^- and M^{3+} (M=Ga, In) are 15 to 18, and 25 kcal/mol, M in acid and basic regions respectively.[1,2]) Aluminium(III) is generally understood to be more inert than gallium(III) and indium(III) towards substitution reactions, on the basis of kinetic studies of solvent exchange in water and dimethylformamide,[5] intermolecular ligand isotopic exchange[6] and intramolecular site-exchange of β-diketonato complexes involving one bond break.[7] The present study does not allow more precise discussion because of experimental difficulty. The results, however, suggest remarkable influence of the ligand on the lability, especially of the coordinating atoms in such a multidentate ligand. Figure 1 shows a similar pattern to that of the isotopic exchange of $[GaY]^-$ and $[InY]^-$, although the details are different. Such must be the common pattern for substitution reactions of EDTA complexes of tervalent typical metal ions.

Experimental

Procedure. Aqueous solution (10^{-3} M, 50 ml) of indium(III) nitrate of a given pH containing potassium nitrate (and tartrate whenever necessary) was mixed with the complex[4] solution (10^{-4} M, 50 ml) of the same pH. Ten milliliter portions were withdrawn at appropriate time intervals, diluted with 20 ml of water (and 1 ml of 0.02 M potassium tartrate solution, when the reaction mixture does not contain tartrate ion), and titrated with 0.01 N disodium salt of EDTA with 0.1% xylenol orange solution (1 or 2 drops) as indicator, the pH being adjusted to 4—5 with an acetate buffer. The acid concentration below pH 4 was adjusted with nitric acid.

The free aluminium(III) ion liberated by reaction (1) did not interfere with the titration of free indium(III) in the presence of tartrate ion. Reaction (1) proceeds very slowly at pH 4—5 under the given conditions.

The author wishes to thank Professor Kazuo Saito, Tohoku University, for valuable discussions and suggestions, and Dr. Kazuko Ogino, Tohoku University, for numerical calculations.

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