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On the Stability of Silver(I) Complexes with an Imidazole and Its Derivatives

Shigeo NAKATSUJI, Riichiro NAKAJIMA and Tadashi HARA

Department of Chemical Engineering, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto

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No report seems to have been given on the formation constant of the complexes between silver(I) ion and imidazole derivatieves except for poly-*N*-vinylimidazole[1] and *N*-methylimidazole.[2] The present paper deals with the stability of silver(I) complexes with imidazole derivatives, in which the consecutive formation constants of the silver complexes were estimated and the influences of the substituent upon the stability of the silver complexes were discussed. The molecular diagram of the imidazole derivatives was calculated and the nitrogen atom as a donor was determined. The infrared spectra of the silver complexes are also recorded and discussed.

The consecutive formation constants were estimated by applying the pH measurement and Bjerrum's methods.[3] An imidazole and its derivatives were of guaranteed-grade. The solution containing imidazole or imidazole derivatives, nitric acid and potassium nitrate (the ionic strength : 1) was titrated with a standard sodium hydroxide solution at 25°C.[4,5] The readings in the pH meter were corrected by the activity coefficients, and the dissociation constants of an imidazole and its derivatives were estimated, followed by calculation of the consecutive formation constants. From the formation curves for the imidazole derivatives, all the values of $\bar{n}$ were found to be less than 2. This is compatible with the following equilibrium.

$$\left.\begin{aligned} Ag^+ + Im &\overset{k_1}{\rightleftharpoons} AgIm^+ \\ AgIm^+ + Im &\overset{k_2}{\rightleftharpoons} AgIm_2{}^+ \end{aligned}\right) \quad (1)$$

Hence, the consecutive formation constants are given by

$$k_1 = \frac{[AgIm^+]}{[Ag^+]\cdot[Im]},\ k_2 = \frac{[AgIm_2{}^+]}{[AgIm^+]\cdot[Im]}, \quad (2)$$

where Im means imidazole or imidazole derivatives. According to Bjerrum's assumption, the values of p[Im] at $\bar{n}=1/2$ and $3/2$ on the formation curve correspond to those of $\log k_1$ and $\log k_2$. The values of $[Ag^+]$, $[AgIm^+]$ and $[AgIm_2{}^+]$ were calculated using the values of k_1 and k_2. However, Bjerrum's assumption[3] was not valid. Approximate calculation was repeated until the values of k_1 and k_2 converged. The final results are shown in Table 1 with those of pyridine derivatives. The

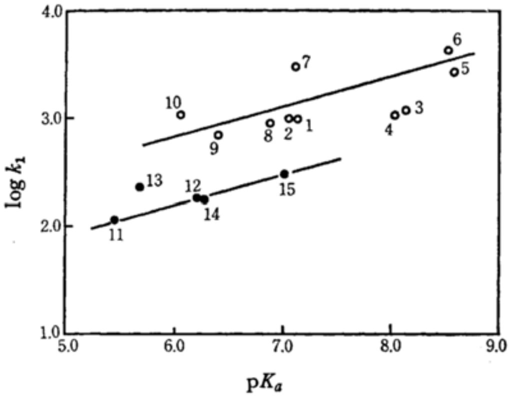

Fig. 1. Relation between pK_a and $\log k_1$. The numbers of the ligand are the same as in Table 1.

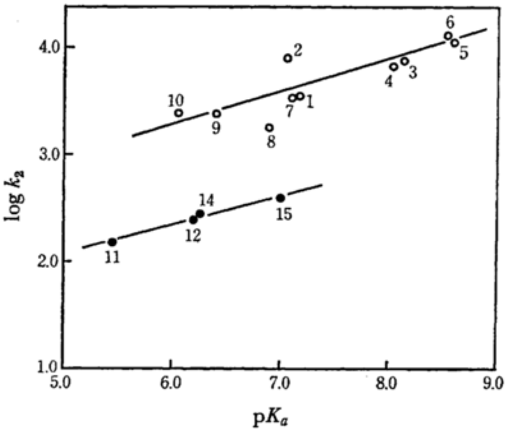

Fig. 2. Relation between pK_a and $\log k_2$. The numbers of the ligand are the same as in Table 1.

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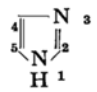
Table 1. Acid dissociation constants of imidazole and pyridine derivatives and formation constants of their silver complexes
Ionic strength; 1.0, Temp.: 25°C

No.	Ligands	pK_a	Formation constants log k_1	 log k_2	References
	Imidazole		3.11	3.73	1
1	Imidazole	7.33	3.08	3.87	
2	*N*-Methylimidazole	7.06	3.00	3.89	2
3	2-Methylimidazole	8.13	3.11	3.87	
4	2-Ethylimidazole	8.02	3.06	3.83	
5	2,4-Dimethylimidazole	8.57	3.44	4.06	
6	2-Ethyl-4-methylimidazole	8.52	3.64	4.10	
7	1-Vinyl-2-methylimidazole	7.09	3.48	3.53	
8	1-Vinyl-2-ethylimidazole	6.88	2.97	3.25	
9	1-Vinyl-2-hydroxyethylimidazole	6.39	2.86	3.38	
10	1-Vinyl-4-hydroxyethylimidazole	6.05	3.03	3.37	
11	Pyridine (μ=0.5)	5.45	2.04	2.18	6
12	α-Picoline	6.20	2.27	2.41	7
13	β-Picoline	5.68	2.35	4.35	2
14	γ-Picoline	6.26	2.24	2.46	7
15	2,4-Lutidine	6.99	2.47	2.41	7

relations between pK_a and log k_1 or log k_2 are shown in Figs. 1 and 2. These results show that the affinity of an imidazole and its derivatives to silver ion increases with an increasing affinity to hydrogen ion. The same tendency is also found in cadmium complexes,8) but not in copper complexes.9) It is characteristic that log k_1 is smaller than log k_2 in the silver complexes, while the opposite is the case in the complexes of copper, cadmium and zinc. As the formation constants of the silver complexes with 2,4-dimethyl and 2-ethyl-4-methylimidazoles are larger than those with 2-methyl and 2-ethylimidazoles, the methyl group at the 4-position makes the silver complexes very stable. This seems to come from a larger increase of electron density at the 3-position than at the 1-position since the 3-position is structurally nearer the 4-position than the 1-position. On the other hand, the vinyl group at the 1-position makes the complexes unstable. There has been conflict concerning the nitrogen atom as a donor, Edsall10) and Gold1) proposing the coordination of the pyrrole-type nitrogen atom, while Bauman2) and Li5) that of the pyridine-type one. The molecular diagram of the imidazole derivatives was calculated by the simple LCAO method11) (Table 2). The difference between our values and those obtained by Orgel12) seems to be responsible for the different selection of parameters. The fact that the nitrogen atoms at the 1- and 3-positions are assigned with the positive and negative charges supports the dissociation13–15) of hydrogen atom on the pyrrole-type nitrogen atom and the coordination with the pyridine-type nitrogen. It is understandable that the value of formation constants increases with an increasing negative charge at the 3-position. The absorption bands at 1667 ($\nu_{C=NH}$), 1440, and 1095 cm^{-1} in the infrared spectrum of the silver imidazole complexes

Table 2. Molecular diagram of imidazole derivative



Ligand	1-Position	3-Position
Imidazole	0.549	−0.277
Imidazole12)	0.41	−0.35
2-Ethylimidazole	0.421	−0.336
2,4-Dimethylimidazole	0.475	−0.392
4-Methylimidazole	0.479	−0.414
N-Methylimidazole	0.963	−0.506

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were found to shift as compared with those of imidazole alone.[16] No shift was, however, observed in the spectrum of silver complexes with vinyl derivatives. This means that the vinyl group is independent of coordination to silver ion.

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