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A COMPARISON OF THE RATE OF CHLORINATION AT THE METHINE IN SOME MIXED LIGAND ACETYLACETONATOCOBALT(III) COMPLEXES

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The rate of chlorination at the methine in six kinds of mixed ligand acetylacetonatocobalt(III) complexes ($(NH_3)_4$-, $(en)_2$-, α-trien-, β-trien-, fac(N)-i-DTMA-, and mer(N)-i-DTMA-complexes) have been compared in slightly acidic aqueous solution at 40°C. It has been found that the charge of the complex ions is not a dominant factor influencing the chlorination velocity.

We have found that the methine hydrogen in $[Co(acac)(en)_2]^{2+}$ and in the other mixed ligand acetylacetonatocobalt(III) complexes can be easily substituted with bromine by the action of N-bromosuccinimide.[1] We have subsequently found that the hydrogen is also substituted with chlorine and iodine by the use of N-chlorosuccinimide and N-iodosuccinimide, respectively. It is of interest to compare the rate of the halogenation, since the reactions have been considered to be electrophilic and hence the rate might be influenced by the electric charge of the substrates. This paper reports a brief comparison of the rate of the chlorination at a definite condition. The preparation and characterization of the chlorinated and the iodinated species and a more detailed results of the kinetic study will be reported shortly.

Results and Discussion. Six kinds of mixed ligand acetylacetonatocobalt(III) complexes described above were dealt with. Figure 1 shows the absorption spectra of α-$[Co(acac)(trien)](ClO_4)_2$ and its halogenated species. It may be seen that the spectra of the halogenated species are quite similar to each other. The spectral variation between an unsubstituted and its halogenated species is in a similar pattern as that in the figure.[2] Thus, the substitution can be conveniently followed by measuring the absorption curve between 280 and 360 nm. The kinetic runs were carried out in the usual manner. The reaction condition was set throughout this study at 40°C, 2×10^{-4} M $HClO_4$, 2×10^{-4} M complex ion, and 3×10^{-4} M N-halogenosuccinimide. The slightly acidic medium was used for the protection from the decomposition of the complexes, especially of the tetraammine complex. Figure 2 illustrates a spectral change of the α-trien complex. As may be seen, two isosbestic points occurred at 333 and 290 nm, which lie on the absorption curves of the pure reactant and resultant complexes. This means that no reaction but the halogenation took place at the complexes. Table 1 summarizes the fraction of the halogenated species at 40 min of the reaction.

A few can be noticed from the values in the Table:

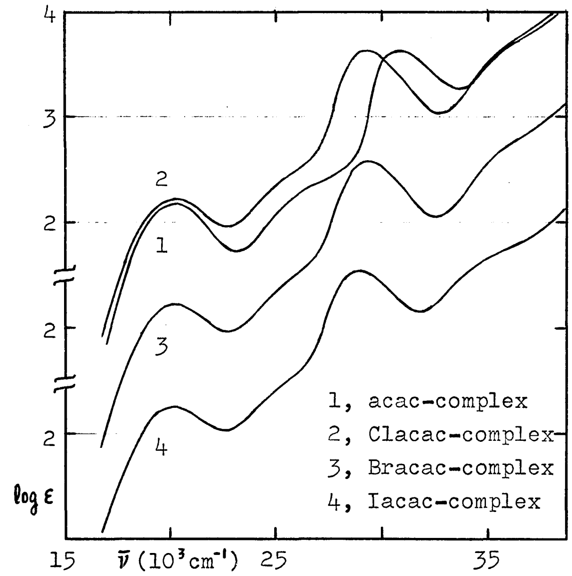

Fig. 1. Absorption spectra of α-[Co(acac)(trien)]$(ClO_4)_2$ and its halogenated complexes.

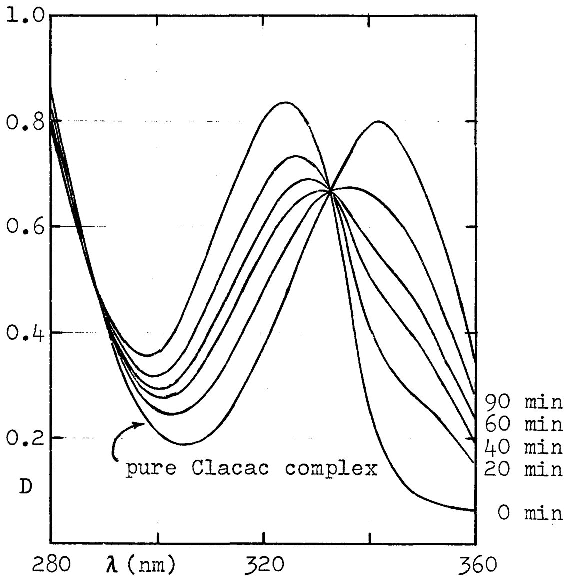

Fig. 2. Change of the absorption curve of α-[Co(acac)(trien)]$^{2+}$ in the presence of *N*-chlorosuccinimide.

(1) In spite of the very low concentrations of the substrates and electrophiles in this experiment, the halogenation is, as a whole, unexpectedly fast. Therefore, it suggests that, in the syntheses of the halogenated complexes, the reaction temperature need not be raised over 40°C, in order to avoid unnecessary side reactions.

(2) The chlorination is the slowest. The bromination and the iodination are comparable, although an exact comparison must be performed at a lower temperature.

(3) The rate of chlorination of the *fac(N)*- and the *mer(N)*-*i*-DTMA complexes, which are unipositive, are not necessarily faster than those of the others, which are dipositive. Thus, the charge of complex ions is not a dominant factor determining the chlorination velocity. This observation is thought to be important, since it seems to have been believed that this kind of substitutions are strongly influenced by the electric charge of the substrates.[3]

Table 1. Fraction of the chlorinated species at 40 min of the reaction.

$(NH_3)_4$-	54 %
$(en)_2$-	68 %
α-trien-	47 %
β-trien-	74 %
fac(N)-*i*-DTMA-	63 %
mer(N)-*i*-DTMA-	44 %

All the complexes were brominated and iodinated over 90 % at the condition described in the text.

References and Footnote:

1) K. Yoshitani, K. Kunigita, K. Watanabe, and K. Kuroda, This Letters, **1975**, 573.

2) The spectra of the acac- and Bracac-complexes have been drawn in ref. 1). The spectra of the Clacac- and Iacac-complexes are similar to that of the Bracac-complex in each group with a same amine or ammine, as in Fig. 1.

3) *e. g.* Y. Fujii, E. Kyuno, and R. Tsuchiya, Bull. Chem. Soc. Japan, **42**, 1301 (1969).

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