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Ligand Isotopic Exchange Kinetics of Tris(acetylacetonato)-titanium(IV) Perchlorate in Acetonitrile

Masato NISHIZAWA, Hiroaki KIDO, Isamu KINOSHITA, Yoshikuni SOMA,* and Kazuo SAITO
Chemistry Department, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai, 980

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Synopsis. The rate of isotopic exchange between tris(acetylacetonato)titanium(IV) ions and acetylacetone-$^{14}C_3$ in enol form is measurable at −20 °C in acetonitrile. Water, free ligand and a strong acid catalyse the exchange.

The tris(acetylacetonato)titanium(IV) ion [Ti(acac)$_3$]$^+$ has been known as salts of various anions[1–3] and the absorption spectrum examined.[4,5] Its dynamic behavior is, however, not known.[6] We have examined the isotopic exchange of this complex ion with free acetylacetone (Hacac) labelled with ^{14}C in acetonitrile and obtained some information concerning the kinetics.

Experimental

Materials. *The Complex Perchlorate*: Dichlorobis(acetylacetonato)titanium(IV)[7] (3.9 g) was dissolved in chloroform (20 ml), mixed with ethanol (10 ml), concentrated to *ca.* 10 ml, and trented with barium perchlorate trihydrate (4.8 g) in ethanol (15 ml). The precipitate was filtered off, washed with chloroform (60 ml) and the filtrate and washings were concentrated to 20 ml together with Hacac (15 ml) at 30 °C and 50 mmHg. Addition of hexane (10 ml) gave [Ti(acac)$_3$]ClO$_4$, which was recrystallized by dissolving in chloroform and Hacac, and adding hexane. The orange needles decomposed at 180 °C. Anal. Found: C, 40.62; H, 4.83%; Calcd for $C_{15}H_{21}O_{10}ClTi$: C, 40.51; H, 4.76%. IR spectrum in Nujol mull gave a very similar pattern to those of [Si(acac)$_3$]ClO$_4$[8] and [Ge(acac)$_3$]ClO$_4$.[9] NMR pattern in deuterochloroform coincided with that in literature.[10] This method gives a higher yield (*ca.* 60%) and a purer product than solvent extraction[3] and direct synthesis from titanium (IV) sulfate and Hacac.[10]

Other Reagents: Acetylacetone-$^{14}C_3$(2,4-pentenedione-1,3,5-$^{14}C_3$) was prepared as in literature.[11] Acetonitrile (AN) was refluxed with phosphorus pentoxide and distilled. The water content was 3 to 5×10^{-3} M. Hexane was washed with sulfuric acid and alkali solution, dried with phosphorus pentoxide and distilled.

Measurements. The UV spectrum was recorded with a Hitachi 323 Spectrometer in the presence of varying amounts of water (≤0.1 M). The radioactivity was recorded with a Unilux IIA of Nuclear Chicago Co., in anisole containing 0.4% *p*-terphenyl and 0.01% POPOP. The enol/keto ratio of free Hacac was determined from UV absorption at 273 nm.[12]

Kinetic Runs. The complex solution ($\simeq10^{-2}$ M) in AN (5 ml) and Hacac-^{14}C ($\simeq10^{-2}$ M) in AN (5 ml) were placed in the two sections of a glass-stoppered test tube with a branched side bottom. The tube was kept in a thermostat at −21.3 °C and both solutions mixed. One ml portions were taken out at appropriate time intervals and poured into chilled hexane (5 ml, −50 °C) in a thin test tube within 10 s. (The UV spectra showed that only the enol tautomer of free Hacac was extracted into the hexane layer while the AN solution flows down.). After 30 s 2 ml portions were pipetted out of the middle part of hexane layer. One ml was dissolved in the anisole scintillator (14 ml) for β-activity counting. The other one ml was diluted with hexane (9 ml) and the extinction measured at 273 nm to find the concentration of Hacac. The water content of the AN solution was determined in the reaction tube by Karl Fischer titration.

Results and Discussion

Absorption Spectrum. The complex perchlorate has three absorption peaks in AN at 364, 257, and 225 nm with log ε values 3.91, 4.34, and 4.30, respectively. When the water content in the solution was $\simeq10^{-3}$ M (the same order as the complex in a 0.1 mm thick cell), the peak heights decreased little (by *ca.* 2% within 30 min.). When the water concentration was $\simeq10^{-1}$ M in $\simeq10^{-5}$ M complex solution, the absorbancy at 364 and 225 nm decreased rapidly, and after several minutes two shoulders were observed with log ε *ca.* 3.4 and 3.6, respectively. Simultaneously a new shoulder appeared at $\simeq$270 nm with log ε *ca.* 3.9, which seemed to be due to free Hacac. The peak at 257 nm gave only a small shift to 259 nm and a very little decrease in absorbancy. When a large excess of Hacac ($\simeq10^{-1}$ M) was added, the log ε at 364 nm increased and the pattern gradually approached that of freshly prepared solution. It seems the change in absorption in the presence of overwhelming amount of water is caused by partial hydrolysis of the complex. The absorption data given in literatures[4,5] may represent those of partially hydrolysed products.

Isotopic Exchange. The experimental results were calculated by McKay's formula,

$$R = -2.3[3ab/(3a+b)][\log(1-F)/t] \qquad (1)$$

where *a* and *b* are the concentrations of the complex and free Hacac, respectively, and *t* is the lapse of time. *F* is the fraction of reaction and is known from $(x_0-x_i)/(x_0-x_\infty)$, where x_0, x_i, and x_∞ are the specific counting rates at time 0, *t* and infinity, respectively.

Acetylacetone is in tautomeric equilibrium and *ca.* 67% is in enol form in AN at −10 °C. The interchange between keto and enol form is much slower (*ca.* $10^{-5}s^{-1}$) than the present isotopic exchange. The *R* can be calculated in two ways by considering the participation of either the enol tautomer or total Hacac in the exchange. The experimental x_∞ values come in between the values calculated in the two ways. The x_i *vs.* *t* diagrams are simulated by considering that the keto tautomer exchanges with the ligand at a much smaller

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* Present address: Research Institute, Mitsui Petrochemical Co. Ltd., Iwakuni Yamaguchi-ken.

rate than the enol does (*e.g.* in 0.02 M complex solution containing 0.03 M water and 0.015 M Hacac, the ratio $R_{\text{enol}}/R_{\text{keto}}$ is *ca.* 30.). Hence the following discussion is made on the assumption that only the enol form exchanges with the ligand. McKay plots made in this way gave straight lines at the initial stage of exchange ($F <$ *ca.* 0.5). The UV absorption of the reaction mixture remained unchanged for at least 100 min. These facts indicate that the R values thus calculated give rates of the following isotopic exchange.

$$[\text{Ti(acac)}_3]^+ + \text{Hacac(enol)}^* \rightleftarrows [\text{Ti(acac}^*\text{)(acac)}_2]^+ + \text{Hacac(enol)} \quad (2)$$

Attempts have been made to elucidate the influence of various factors upon R. However, only limited information was obtained because of experimental difficulty, especially in adjusting the water concentration, and the discussion is very much limited.

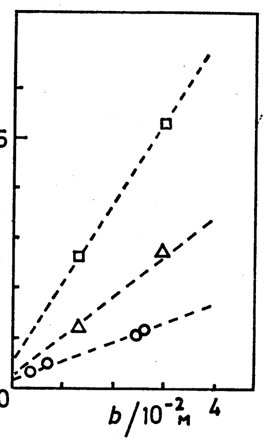

Fig. 1. Dependence of the exchange rate constant on the concentration of Hacac in enol form.
$[H_2O]$=○ 0.016, △ 0.037, □ 0.079 M.

When a was changed as 1.0, 2.0, and 3.4×10^{-2} M at given concentrations of Hacac (0.029±0.001 M) and water (0.016±0.001 M), R increased linearly, and the quotient R/a was almost equal, *i.e.* 1.6, 1.5, and 1.3×10^{-3} s^{-1}, respectively. The quotient k_0 can be the measure of exchange rate. Figure 1 shows the plot R *vs.* b at given concentrations of water. At a water concentration 0.016±0.001 M, the plot is linear. Not many plots were obtained at higher concentrations of water, but both the gradient and the intercept seem to increase. Hence a kinetic formula, Eq. 3 may be appropriate,

$$R = k_0a = a(k_1+k_2[\text{H}_2\text{O}]+k_3b+k_3'b[\text{H}_2\text{O}]) \quad (3)$$

where b is the concentration of free Hacac in enol form. The dotted lines in Fig. 1 are those calculated on best fitted k values in Eq. 3; *i.e.* $k_1=(1.4\pm0.6)\times10^{-4}$ s^{-1}, $k_2=(5.0\pm1.5)\times10^{-3}$ M^{-1}s^{-1}, $k_3=(7.9\pm2.6)\times10^{-3}$ M$^{-1}\cdot$s^{-1} and $k_3'=(1.9\pm0.1)$ M^{-2}s^{-1} at −21.3 °C. They do not deviate much from the observed plots, and Eq. 3 can be an adequate expression of the kinetics.

The exchange was catalysed by a strong acid (Fig. 2). As the concentration of trichloroacetic acid increases, k_0 increases and then approaches constant. Further increase in water and acid concentration caused decomposition of the complex. The saturation may be due to limited formation of H_3O^+ from the acid and water (0.012 M) rather than to the saturation of protonation of complex cation. Weak acids fail to give such a catalytic action, and the influence of Hacac concentration in Eq. 3 cannot be acid catalysis.

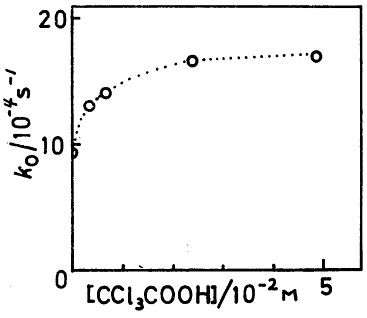

Fig. 2. Influence of the concentration of trichloroacetic acid upon the exchange rate constant.
b=0.024 M $[H_2O]$=0.012 M at −21.4 °C.

It is seen that the isotopic exchange can proceed through several reaction routes. The hydrolysis of $[\text{Ti(acac)}_3]^+$ under the given experimental conditions is much slower ($\simeq10^{-5}$ s^{-1} at +20 °C) than the isotopic exchange and the reaction paths should be different. In the k_3 and k_3' path, an associative contribution of enolic Hacac is feasible in the rate-determining step, whereas k_1, k_2 and acid-catalyzed reaction path may involve dissociative rate-determining step. Further elucidation of the reaction mechanism, however, requires more detailed kinetic studies by more sophisticated methods.

The results, however, provides the first example of kinetic studies of intermolecular substitution reaction of titanium(IV) compounds, and it was made clear that $[\text{Ti(acac)}_3]^+$ undergoes isotopic exchange much faster than $[\text{Si(acac)}_3]^+$ and $[\text{Ge(acac)}_3]^+$ do, and the rate is similar to that of $[\text{Sn(acac)}_3]^+$.[13)]

References

1) W. Dilthey, *Ber.*, **37**, 588 (1904).
2) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, **1964**, 6113.
3) M. L. Reynolds, *J. Inorg. Nucl. Chem.*, **26**, 667 (1964).
4) R. J. Woodruff, J. L. Marini, and J. P. Fackler, *Inorg. Chem.*, **3**, 687 (1964).
5) G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc., A*, **1966**, 723.
6) Kinetic studies have been made only with dihalobis(acetylacetonato)titanium(IV) by NMR; R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **9**, 2048 (1970); also see Ref. 7.
7) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).
8) T. Inoue and K. Saito, This Bulletin, **46**, 2417 (1973).
9) A. Nagasawa and K. Saito, *ibid.*, **47**, 131 (1974).
10) R. C. Fay, and N. Serpone, *J. Amer. Chem. Soc.*, **90**, 5701 (1968).
11) K. Saito and K. Masuda, This Bulletin, **41**, 384 (1968).
12) H. Watarai and N. Suzuki, *J. Inorg. Nucl. Chem.*, **36**, 1815 (1974).
13) K. Saito, *Pure Appl. Chem.*, **38**, 325 (1974).