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CHELATION EFFECTS ON THE RATE OF THE METHYL-PROTON EXCHANGE IN ALKALI ACETOPHENOLATES

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The rate of the hydrogen-deuterium exchange of acetyl-methyl groups was determined for the alkali-metal salts of three acetophenolates by means of NMR measurement of the rate of the disappearance of the methyl-signals in D_2O. The chelation of o-hydroxyacetophenone with the alkali-metal ions was found to influence the reaction rate.

The reactions of coordinated ligands have aroused interest widely and a considerable amount of investigations exists concerning the reactivity of C-H bonds in metal-chelate compounds. However, they are almost related to the activation of protons bound to carbon atoms which are members of chelate rings,1) and the reactivity of C-H bonds out of chelate rings has been rarely investigated.2) The reactivity of the acetyl-metyl groups in β-dicarbonyl compounds is, thus, of great interest. The author has measured the H-D exchange-rate constants of the acetyl-methyl protons in the thallous or sodium salts of β-dicarbonyl compounds and the related compounds by means of NMR measurement in D_2O.3) In most case of the β-dicarbonyl compounds, however, there was some uncertainty to measure the rate constant, because C-C cleavage in the ligands occurred during the measurement. The salts of o-hydroxyacetophenone turned out to be very effective in revealing chelation effects on such a proton dissociation. This paper will deal with cation effect on the rate of the methyl-proton exchange in alkali o-acetophenolates.

The hydroxyacetophenones used were commercially available; their alkali-metal salts were prepared by mixing each of the alkali hydroxide solutions in a small quantity of water with each of the hydroxyacetophenone solutions in methanol. The salts obtained were almost hygroscopic; their purities were confirmed by the elemental analyses. All the NMR spectra of the alkali salts were taken at 35.5°C in 0.13 ± 0.02 M solution in D_2O(99.75 %); the integrated values of the NMR signal intensities were measured at appropriate time intervals. Because such a H-D exchange reaction in D_2O follows a rate law of first order dependence on the amount of protons in acetyl-methyl groups, the rate constant can easily be determined from the slope of the logarithm of the methyl-signal intensity vs. time plots. The integration values due to the aromatic protons were used as references for the methyl-signal intensities.

Figure 1 shows such plots for the sodium salts of o-hydroxyacetophenone(OOA), m-hydroxyacetophenone(MOA), and p-hydroxyacetophenone(POA) in D_2O. The NMR peak due to acetyl protons appeared at τ 7.37 for OOA-Na, at τ 7.43 for MOA-Na, and at τ 7.55 for POA-Na, respectively. By use of the mixture of OOA-Na, MOA-Na, and POA-Na in D_2O, the rate constants for the three salts could be measured at the same time. In such a condition, the amount of OD^- ion, which influences the reaction rate for the salts, is equivalent. Although each of the rate constants measured in the mixed solution was larger than the corresponding one obtained from Fig. 1, the decreasing order of the

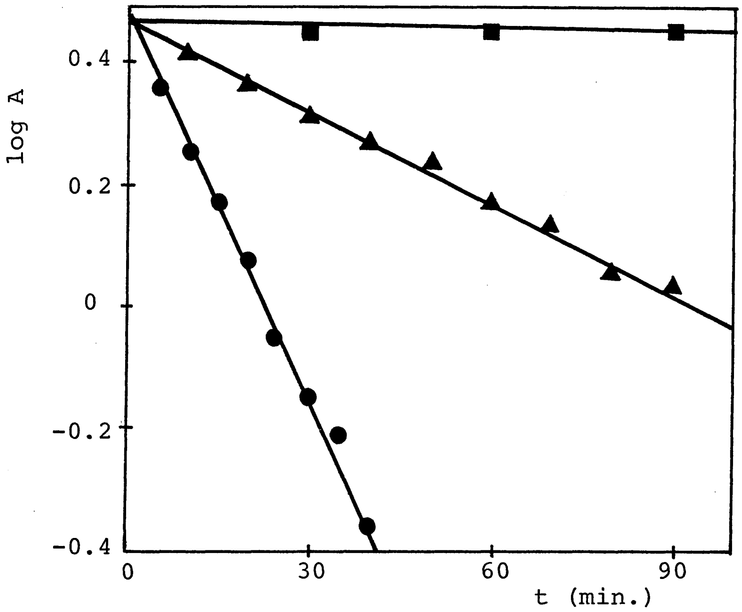

Fig. 1. Correlations of methyl-signal intensity(A) with time(t) at 35.5°C.
●, OOA-Na; ▲, MOA-Na; ■, POA-Na.

TABLE 1. Exchange-rate constants(k_{H-D}, $min.^{-1}$) at 35.5°C for the alkali-metal salts of OOA and POA

Alkali salt	OOA-Li	OOA-Na	OOA-K	POA-Li	POA-Na	POA-K
Conc. (M)	0.14	0.13	0.13	0.13	0.13	0.11
k_{H-D}($min.^{-1}$)	4.0×10^{-2}	5.0×10^{-2}	5.4×10^{-2}	1.6×10^{-4}	1.6×10^{-4}	1.6×10^{-4}

rate constants, OOA-Na > MOA-Na > POA-Na, remained in both series. In the previous paper,[4)] it has been reported that such a methyl-proton exchange was decelerated by the effect of resonance in a chelate ring in which the acetyl carbonyl took part. Strong resonance including acetyl-carbonyl bonds results in the decreased covalency of the carbonyl bonds. In the same sense, it is reasonable that the rate constant of POA-Na is smaller than that of MOA-Na. The covalency of the carbonyl bond in POA-Na is diminished by the through-conjugation of the p-hydroxybenzene ring. If the effect of the through-conjugation is similar to the chelation effect discussed before, it is worthwhile noting that the rate constant of OOA-Na is much larger than that of POA-Na. Moreover, even the value of MOA-Na in which such conjugation can not be considered is smaller than that of OOA-Na. This is clearly due to the proximity effect of the hydroxyl group in OOA.

Intra molecular bonding, with consequent stabilization, is possible only in the salt of OOA; this could be confirmed by cation effects on the ultraviolet absorption spectra of the alkali-metal salts of OOA and POA by the method of H. E. Zaugg and A. D. Schaefer.[5)] Hypsochromic shifts observed in going from DMF to water were 8.1 Kcal/mol for OOA and 7.0 Kcal/mol for POA, respectively. These values showing ground-state hydration were plotted against their respective aqueous pK values, 10.82 for OOA[6)] and 8.05 for POA.[7)] The anionic ground-state hydration for many phenols and enols with no chelating ability had been known to be proportional to anion basicities. The plot of POA fell close to a straight line shown in the literature.[5)] In the case of OOA, like β-dicarbonyl compounds capable of forming chelate compounds, such a plot fell off the line.

Table 1 shows cation effects on the exchange-rate constants of the alkali-metal salts of OOA and POA. The order of relative abilities of alkali-metal ions to form chelates, Li > Na > K, has been found for related systems.[8,9)] The rate constants of the salts of OOA were found to be inversely proportional to the cationic radii. The observed bathochromic shifts of the UV absorptions of the salts of OOA were also in inverse proportion to the cationic radii, showing the absence of appreciable covalency interactions with the alkali metals as had been shown in the literature.[5)] On the contrary, these cation effects were not observed in the salts of POA.

Another case of the cation effects on the exchange-rate constant for OOA-Na was exhibited by a mass action effect from the addition of sodium ion. The exchange rate of OOA-Na decreased with increasing sodium ion concentration; the rate constant changed from 5.0×10^{-2} min.$^{-1}$ to 4.8×10^{-2}, 4.6×10^{-2}, and 4.4×10^{-2} min.$^{-1}$ when

0.9, 3.9, and 5.9 equiv. of sodium iodide were added. Based on the low-temperature NMR spectra of sodium acetylacetonate in CD_3OD, E. A. Noe and M. Raban have reported the effect of alkali metal ions on the configuration of the acetylacetonate anion.9) The cation effects on the exchange rate in this study should be discussed by considering the change in the relative amount of associated and dissociated species in the equilibrium of OOA-Na in D_2O.

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