The Relative Stability of the Alkali Metal Chelates of Dibenzoylmethane

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Brändström¹ has recently discussed the evidence bearing on the relative stability of the sodium and potassium chelates of β -ketoesters. He concludes that K^+ has a stronger tendency than Na^+ to give a chelate ring with the anion of a β -ketoester. Since none of the evidence previously available involves a direct measurement of these tendencies to form chelate rings, it seems worthwhile to consider some recent measurements in our laboratory on the tendencies of the alkali metal ions to form chelate rings with dibenzoylmethane (HCh) which is very closely related to the β -ketoesters.

By making potentiometric measurements in 75 % dioxane—25 % water instead of pure water, it becomes possible to measure differences in chelate stability which are not measurable in water²⁻⁵. Thus, by using tetramethylammonium hydroxide as the titrating agent (the tetramethylammonium ion is a non-chelating ion), it became possible to make measurements which permit the calculation of formation constants (as defined by Bjerrum⁶) for the alkali metal chelates of dibenzoylmethane. The results of such measurements at 30° (4×10^{-3} mole of HCh and 1×10^{-3} mole of M^+ in 100 ml solution) expressed as log K are:

Li ⁺ (LiNO ₃)	5.95	K ⁺ (KCl)	3.67
Na ⁺ (NaCl)	4.18	R ⁺ (RbNO ₃)	3.52
		Cs ⁺ (CsCl)	3.42

The order of variation with atomic number from metal to metal is the same here as for the alkali earths and other periodic groups. Thus the direct measurements obtained here show that the tendency to form the sodium chelate is definitely greater than that for the potassium chelate.

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A Remark to the Paper of W. C. Fernelius and L. G. Van Uitert on the Relative Stability of the Alkali Metal Chelates of Dibenzoylmethane

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The very interesting measurements of Fernelius and Van Uitert¹ on the relative stability of the alkali metal chelates of dibenzoylmethane which were performed in a dioxane-water mixture are in good agreement with the evidence obtained by Brändström²⁻³ given in papers probably not yet accessible to Fernelius and Van Uitert. The paper of Brändström⁴ cited by them deals with the behaviour in solvents of a much lower polarity (toluene and tert-butyl alcohol) where the situation may be quite different from that in a more polar medium⁵ and where unfortunately no exact measurements seem possible.

The interesting high value of the formation constant obtained with Cs⁺ together with the fact that the alkali chelates appear to be of a pure ionic type might give rise to the question if the tetramethylammonium ion is an absolutely non-chelating ion.

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