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Association of Alkali Metal Ions with Anions of β-Diketones in Methanol and Ethanol

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The pK_a values of a number of β-diketones (acetylacetone, benzoylacetone, dibenzoylmethane, 2-thenoyltrifluoroacetone, and dimedone) in anhydrous methanol and ethanol have been determined, and, in addition, the interaction of the anions of these diketones with alkali metal cations in the same solvents has been studied. The pK_a values in these solvents for each of the diketones are similar and much higher than the corresponding value in water. For the anion of any of the diketones studied except dimedone, the pK values for the dissociation of the complexes with alkali metal ions generally decrease, as expected, with increasing cationic size. Values for pK are higher in ethanol than in methanol. No clear correlation was found between the pK_a values of the diketones and the dissociation constants of the complexes in either solvent.

Introduction

Although a large number of complexes of alkali metal ions with anions of β-diketones have been prepared, little quantitative data exist on the dissociative stability of such complexes. Van Uitert, Haas, Fernelius, and Douglas[1] found that in aqueous dioxane β-diketones containing two aromatic rings, such as dibenzoylmethane, gave the strongest complexes with sodium ion, β-diketones containing methyl groups formed complexes of lesser stability, and dimedone (1,1-dimethyl-3,5-cyclohexanedione) did not appear to complex at all. Dimedone differs from the other diketones studied in that steric factors do not permit simultaneous bonding of both oxygens to the metal ion. Fernelius and Van Uitert[2] found that the stability of alkali metal ion complexes with the anion of dibenzoylmethane in 75% dioxane–25% water decreases with increasing cationic size. The stability constants reported seemed surprisingly large in view of the high water content of the solvent mixture. Thus log K values ranging from 5.95 (for Li^+) to 3.42 (for Cs^+) were obtained.

In the present communication we report the results of a study of the stability of complexes of alkali metal ions with the anions of a variety of β-diketones in essentially anhydrous methanol and ethanol. It was expected that the relative absence of water in these solvents would enhance markedly the extent of complex formation over that exhibited in the dioxane–water medium cited above.

Experimental

Materials.—Methanol and ethanol were purified by treatment with calcium hydride and potassium borohydride, followed by fractional distillation through a 4-ft. column packed with glass helices. The fraction collected for each solvent boiled within a 0.3° range. Analysis by the Karl Fischer method showed the water content of each solvent to be less than 2×10^{-2} M. Practical grade acetylacetone (Fisher Scientific Co.) was purified according to the method of Steinbach and Freiser.[3] Benzoylacetone and dibenzoylmethane, both Eastman White Label, were used without further purification. The former, after being dried *in vacuo* at room temperature, melted at 57–58°, and the latter, after drying *in vacuo* at 65°, melted at 77–78.5°. 2-Thenoyltrifluoroacetone, Fisher Certified Reagent, dried *in vacuo*, melted at 44–45° and was used without further purification. Dimedone, obtained from Matheson Coleman and Bell, was purified by sublimation *in vacuo* at 100°; m.p., 148–149°. All melting points are uncorrected and agree well with literature values.[4] Tetrabutylammonium hydroxide titrant, purchased from Southwestern Analytical Chemicals, was 1 M Titration Grade in methanol. This was diluted to 0.1 M concentration with methanol or ethanol and the resulting solution was standardized by titration of primary standard potassium acid phthalate to a phenolphthalein end point. Reagent grade lithium perchlorate, sodium perchlorate, potassium iodide, potassium thiocyanate, sodium benzoate, and benzoic acid were all dried at 110° just prior to use. Tetraethylammonium bromide (Eastman White Label) was recrystallized three times from acetonitrile before use. Lithium salicylate, obtained by neutralization of lithium hydroxide with salicylic acid and evaporation to dryness, was dried at 110° before use. Tetrabutylammonium perchlorate was precipitated by the addition of perchloric acid to tetrabutylammonium iodide (Eastman White Label) in water. The crude salt was filtered, washed with water, and dissolved in acetone. The resulting solution was treated with silver perchlorate to remove iodide impurity. After filtration of silver iodide, a small amount of water was added to the acetone solution and excess silver ion removed by controlled potential electrolysis at −0.2 v. *vs.* s.c.e. The solution was then evaporated almost to dryness, and the tetrabutylammonium perchlorate was

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(1) L. G. Van Uitert, C. G. Haas, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 455 (1953).

(2) W. C. Fernelius and L. G. Van Uitert, *Acta Chem. Scand.*, **8**, 1726 (1954).

(3) J. F. Steinbach and H. Freiser, *Anal. Chem.*, **25**, 881 (1953).

(4) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1964.

filtered off and washed with water until a suspension of the salt in water was neutral. The salt, dried *in vacuo*, melted sharply at 214° (uncor.); lit.[5] 210.5°. Solutions in methanol (0.1 *M*) of the tetrabutylammonium perchlorate gave satisfactory background scans with the rotating platinum and dropping mercury electrodes.

Procedure.—The titration vessel was an H cell with a side arm attached to the compartment containing the solution under examination. During the course of an experiment, a blanket of nitrogen, presaturated with the solvent, was maintained over the solution. The solution was stirred by means of a magnetic stirring arrangement. A Beckman E-2 blue glass electrode was placed in the solution being studied and an aqueous saturated calomel electrode was placed in the other compartment of the H-cell, with both electrodes being connected to a Leeds and Northrup pH indicator. An adaptor, obtained from the Arthur H. Thomas Co., was employed to connect the Beckman glass electrode to the Leeds and Northrup pH meter.

The pH meter was standardized with the same buffer pairs—sodium benzoate–benzoic acid and lithium salicylate–salicylic acid—as were employed by Izmailov and Aleksandrov.[6]

The applicability of the glass electrode for the study of acid–base equilibria in nonaqueous solvents, including methanol and ethanol, has been demonstrated by a number of investigators.[6–10] This electrode has also been employed for the determination of the formation constants of nickel(II), zinc, cadmium, and manganese(II) acetylacetonates in ethanol.[11] Using the result reported in the last named study for the pK_a of acetylacetone in 0.25 *M* sodium perchlorate in ethanol, uncorrected for the formation of the sodium acetylacetonate complex, and our value for the dissociation constant of sodium acetylacetonate, we have found a value for the pK_a of the diketone which is in excellent agreement with that obtained in our study.

TABLE I

DISSOCIATION CONSTANTS OF COMPLEXES OF ALKALI METAL IONS WITH ANIONS OF β-DIKETONES

	p*K* values in methanol[a]				p*K* values in ethanol[a]			
β-Diketone[b]	H^{+c}	Li^{+d}	Na^{+e}	K^{+f}	H^{+c}	Li^{+d}	Na^{+e}	K^{+g}
Acetylacetone	11.78	2.8	1.6	0.9	11.81	4.6	2.8	2.1
Benzoylacetone	12.02	3.1	1.8	1.2	12.02	3.2	3.2	2.4
Dibenzoylmethane	13.03	4.1	2.4	1.6	13.4	...[h]	...[h]	...[h]
2-Thenoyltrifluoroacetone	8.59	3.2	2.4	1.6	8.20	5.3	4.2	3.2
Dimedone	8.40	1.5	1.5	0.8	8.37	2.1	2.2	1.8

[a] Corrected for ion-pair association of the inorganic salt; correction for KSCN in ethanol was made using data for KI. (Values for the association constants were taken from ref. 9.) [b] The concentration of β-diketone in each case was approximately 2.3×10^{-2} *M*. [c] 0.1 *M* $(C_4H_9)_4NClO_4$ medium. [d] 0.1 *M* $LiClO_4$. [e] 0.1 *M* $NaClO_4$. [f] 0.1 *M* KI (for evaluation of liquid-junction potential difference, 0.1 *M* KBr solution was used; see ref. 8). [g] 0.1 *M* KSCN (for evaluation of liquid-junction potential difference, 0.1 *M* $(C_2H_5)_4NBr$ solution was used; see ref. 8). [h] Values not reported because precision of measurements was poor.

Preliminary titrations of a number of mixtures of individual β-diketones and alkali metal salts with tetrabutylammonium hydroxide were carried out. It was found from the plots of $\bar{n}$ *vs.* $-\log(\text{RCOCHCOR}^-)$ that only 1:1 complexes were formed even with large ratios of diketone to alkali metal ion. Since poor precision in p*K* values was obtained in the preliminary experiments and since only 1:1 complexes were produced, all other titrations were carried out with large excess of alkali metal ion relative to β-diketone.

The pK_a values for the β-diketones in methanol and ethanol were determined. Approximately 0.7 mmole of diketone was dissolved in either 30 ml. of methanol or ethanol which was 0.1 *M* in tetrabutylammonium perchlorate. The mixture was titrated at 25 ± 1° with a standardized solution of tetrabutylammonium hydroxide in methanol or ethanol. A sufficient number of pH measurements were made to define the titration curve accurately.

For the determination of the dissociation constants of the alkali metal complexes, there were carried out titrations identical with those just described except that the solutions were 0.1 *M* in alkali metal salt rather than in tetrabutylammonium perchlorate.

Results[12]

Values for the dissociation constants of the β-diketones and their 1:1 complexes with alkali metal ions in methanol and ethanol are given in Table I. The pK_a values were determined from the titration data at a number of points before the equivalence point by the use of the expression $\text{pH} = \text{p}K_a - \log[\text{HA}]/[\text{A}^-]$. The results have a precision of ±0.05 unit.

In the determination of the dissociation constants of the alkali metal complexes, the concentration of β-diketone anion was calculated from the amount of diketone used, the quantity of hydroxide ion added, the pH, and the pK_a of the diketone, the latter being corrected for the difference in liquid-junction potential between the tetrabutylammonium perchlorate medium and the alkali metal salt solution.[13] The concentration of alkali metal–diketone complex was obtained from the amounts of hydroxide ion added and diketone anion. The value for uncomplexed alkali metal ion was calculated from the quantities of alkali metal salt originally present and complex formed, with a suitable correction being made for ion-pair association of the inorganic salt. Ion-pair association constants were taken from Davies.[14] Each p*K* value reported is the average of a minimum of six values obtained by the use of three or more points on each of at least two titration curves. The precision of the p*K* values for the complexes was approximately ±0.2 p*K* unit, except for values below 1, which were less precise.

Discussion

The pK_a values in methanol and ethanol for each of the β-diketones studied are similar and considerably

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(5) E. J. Blair and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2459 (1951).

(6) N. A. Izmailov and A. M. Aleksandrov, *J. Gen. Chem. USSR*, **19**, 1405 (1949).

(7) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962).

(8) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962).

(9) D. Wegman, J. P. Escarfail, and W. Simon, *Helv. Chim. Acta*, **45**, 826 (1962).

(10) D. Wegman and W. Simon, *ibid.*, **45**, 962 (1962).

(11) M. C. Day and G. M. Rouayheb, *J. Chem. Eng. Data*, **5**, 508 (1960).

(12) For detailed experimental data, the reader is referred to D. C. Luehrs, Ph.D. Thesis, University of Kansas, 1965.

(13) The difference in liquid-junction potential was evaluated by the use of the half-wave potentials (*vs.* aqueous s.c.e.) for the oxidation of ferrocene. [See (a) I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, **35**, 867 (1963); (b) F. Farha, Jr., and R. T. Iwamoto, *J. Electroanal. Chem.*, **8**, 55 (1964); and (c) D. C. Luehrs, Ph.D. Thesis, University of Kansas, 1965.]

(14) C. W. Davies, "Ion Association," Butterworths, Washington, D. C., 1962, p. 96.

higher than the corresponding value in water (*e.g.*, acetylactone, 8.95[15]; 2-thenoyltrifluoroacetone, 6.38[16]; dimedone, 5.22[17]). Values reported for pK_a in 75 vol. % dioxane–25 vol. % water are somewhat higher than those obtained by us in methanol and ethanol: acetylacetone, 12.70[18]; benzoylacetone, 12.85[18]; dibenzoylmethane, 13.75[18]; 2-thenoyltrifluoroacetone, 8.64[19] and 9.1[18]; and dimedone, 10.16.[17] The values in water and the dioxane–water mixture are not inconsistent with ours when one considers the differences in basic character of the media and the varying dielectric constants —water, *ca.* 78; dioxane–water mixture, *ca.* 15; methanol, *ca.* 33; and ethanol, *ca.* 24.

The pK values for the dissociation of the complexes of alkali metal ions with the anions of the β-diketones generally follow the expected trend relative to metal ion size. Except for dimedone, for any particular β-diketone anion there is a substantial decrease in stability of the complex with increasing size of the alkali metal ion. It is interesting to note that for dimedone there is little difference between the stabilities of the lithium and sodium complexes in methanol or between the same complexes in ethanol. A possible explanation for this fact lies in the structural inability of the anion of dimedone to function as a chelating agent; the pK values of the complexes formed therefore reflect weak nonchelating interactions of the strongly solvated lithium ion and of the more weakly solvated sodium ion with the anion of the diketone.

Examination of the data of Table I shows that for the diketones which can act as chelating agents (all except dimedone) there is no clear correlation between the pK_a values of the ketones and the dissociation constants of the complexes in either solvent. However, all pK values in ethanol are higher than those for corresponding complexes in methanol. This fact is consistent with the lower dielectric constant of ethanol.

In conclusion, although the values reported by Fernelius and Van Uitert[2] for the stability constants of the complexes of alkali metal ions with the anion of dibenzoylmethane in 75% dioxane–25% water originally seemed high relative to the large water content of the mixture, our studies in anhydrous methanol and ethanol indicate that their values are reasonable if no preferential solvation effects by water molecules were operative in their medium.

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[15] R. M. Izatt, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **58**, 1133 (1954).

[16] E. H. Cook and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 6103 (1952).

[17] R. P. Bellad and R. R. Robinson, *Trans. Faraday Soc.*, **57**, 965 (1961).

[18] L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

[19] J. L. Rosenstreich and D. E. Goldberg, *Inorg. Chem.*, **4**, 909 (1965).

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Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Addition Compounds[1]

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The exchange reaction which takes place between trimethylgallium and the trimethylgallium–trimethylamine addition compound has been studied by n.m.r. spectroscopy. The reaction has been shown to proceed through a dissociation step followed by recombination.

$$\mathrm{Ga(C_3H)_3 \cdot N(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ga(CH_3)_3 + N(CH_3)_3}$$

The over-all activation energy for this exchange is 23 kcal./mole. Preliminary investigations have also been carried out on the systems trimethylgallium, trimethylgallium–trimethylphosphine and trimethylgallium, trimethylgallium–dimethyl ether.

There has been growing interest in the exchange reactions of group III alkyls and their addition compounds. A number of studies have been reported on the self-exchange of alkyl groups on aluminum,[3–5] gallium,[6] and thallium.[7] The reports on aluminum have been quantitative with respect to the rate of the exchange reaction and a mechanism has been proposed; however, the other studies have been much more limited in scope. Work has also been reported

[1] Presented in part by J. B. DeRoos, M. T. Emerson, and J. P. Oliver at the 148th National Meeting of the American Chemical Society, Aug. 1964, Abstracts, p. O-21; and by J. B. DeRoos and J. P. Oliver at the 149th National Meeting of the American Chemical Society, April 1965, Abstracts, p. M96.

[2] Recipient of a N.A.S.A. Traineeship for 1964–1965.

[3] E. G. Hoffmann, *Trans. Faraday Soc.*, **58**, 1 (1962).

[4] N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **82**, 248 (1960).

[5] S. Brownstein, B. C. Smith, G. Erlich, and A. W. Laubengayer, *ibid.*, **82**, 1000 (1960).

[6] D. Moy, J. P. Oliver, and M. T. Emerson, *ibid.*, **86**, 371 (1964); J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **24**, 953 (1962).

[7] J. P. Maher and P. F. Evans, *Proc. Chem. Soc.*, 208 (1961).