Nuclear Magnetic Resonance Study of the Effect of Alkali Metal Ions on the Configuration of the Acetylacetonate Anion

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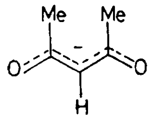
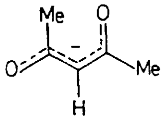
Summary The equilibrium between *ZZ*- and *EZ*-sodium acetylacetonate is shifted toward the chelated (*ZZ*) form by increased concentrations of alkali metal ions.

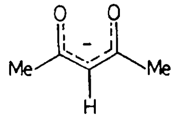
THE acetylacetonate anion can adopt three configurations: *EE*-, *EZ*-, and *ZZ*-(**1**). The low-temperature n.m.r. spectrum of sodium acetylacetonate in CD_3OD (Figure a) demonstrates that *EZ*- and *ZZ*-(**1**) are both present in equilibrium. The single resonance at δ 1·80 derives from the *ZZ*-configuration, while the equally intense resonances at δ 1·89 and 2·27 must be associated with the diastereotopic methyl groups of the *EZ*-configuration. It is noteworthy that the isomer which is capable of chelation [*ZZ*-(**1**)] represents only a minor portion (*ca.* 23%) of the total enolate anion in methanol solution.† The non-chelated *EZ*-(**1**) accounts for most of the anion. Apparently, methanol solvent competes favourably with the *ZZ*-enolate anion as a ligand for sodium, and chelation of sodium by the enolate anion is relatively unimportant in methanol solvent. With pyridine as solvent, a greater preference for the *ZZ*-form is observed, even in the presence of a crown ether. Thus, a ratio of 7 : 3 for *ZZ*-(**1**) to *EZ*-(**1**) is found at −50 °C for sodium acetylacetonate in pyridine solution containing 1·6 equiv. of 18-crown-6.‡



EE-(1)



EZ-(1)



ZZ-(1)

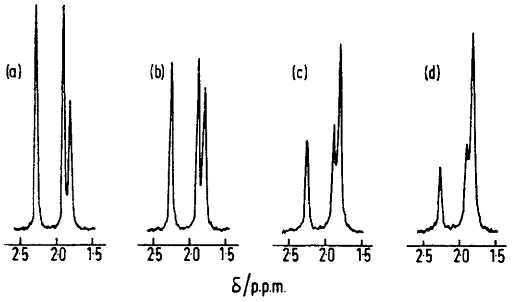
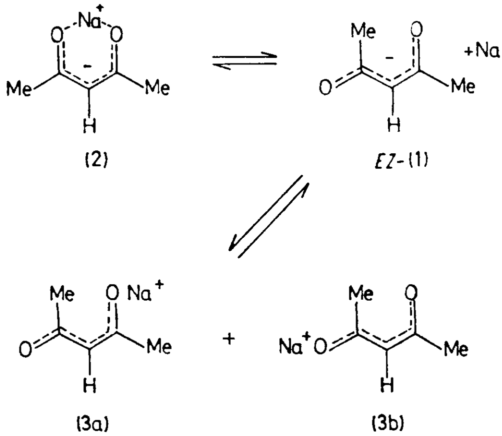


FIGURE. ^{1}H N.m.r. spectra (60 MHz) of sodium acetylacetonate at −57 °C in CD$_3$OD, illustrating the effect of added sodium iodide: (a) no added salt; (b) 0·453 equiv. of NaI; (c) 1·79 equiv.; (d) 2·45 equiv.

Additional sodium ion in the form of sodium iodide has a dramatic effect upon the $EZ \rightleftharpoons ZZ$ equilibrium in methanol (Figure). As the sodium ion concentration is increased, the amount of the *ZZ*-form increases from only 23% with no added salt to 31, 43, 53, and 63% when 0·45, 1·18, 1·79, and 2·45 equiv. of sodium iodide are added. This shift in the ratios reflects a mass action effect from the addition of sodium ion and allows an important conclusion to be made about the degree of dissociation of the *EZ*-form: the *EZ*-isomer must exist substantially in dissociated form, in contrast to the *ZZ*-isomer, in which association with sodium ion (chelation) occurs. If the equilibrium between *EZ*-(**1**) and (**3**) overwhelming favoured (**3**), then no mass action effect would be observed; an equilibrium between (**2**) and (**3**) should be insensitive to added sodium ion.§



The ability of *ZZ*-(**1**) to compete with methanol as a ligand depends on the identity of the alkali metal involved. As a consequence, the ratio of chelated to dissociated forms changes when the metal ion is changed. Considerably less of the *ZZ*-isomer (11%) was observed for potassium acetylacetonate, as compared with the sodium salt at the same concentration and temperature. On the other hand, lithium ion is so strongly chelated that dissociation of lithium acetylacetonate is negligible in methanol under the conditions used in this study.¶

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† While the assignment of the *EZ*-configuration to one of the isomers rests upon symmetry arguments, the isomer which gives rise to a single resonance at δ 1·80 is assigned the *ZZ* configuration on the basis of experiments with added sodium ion and crown ether which indicate that it is capable of chelation, *vide infra*. The concentration and volume of the sample used were 0·376 M and 0·5 ml at room temperature. The volume decreases at the lower temperatures where measurements were made. The relative amounts of *ZZ*-(**1**) and *EZ*-(**1**) are sensitive to the concentration of (**1**). At lower concentrations, the proportion of *ZZ*-(**1**) is even lower. This concentration dependence is obviously related to the dependence on sodium concentration discussed below.

‡ Further n.m.r. experiments have demonstrated that the low-field methyl resonance observed for sodium acetylacetonate in pyridine solution containing 18-crown-6 derives from the *EZ* configuration, rather than the *EE* configuration, as previously reported (E. A. Noe and M. Raban, *J. Amer. Chem. Soc.*, 1974, **96**, 6184). The *EZ* form gives rise to two methyl singlets, one of which overlaps with the intense peak due to crown ether.

§ The exclusive involvement of two species, undissociated (**2**) and dissociated *EZ*-(**1**) in equilibrium, implies an equilibrium constant of the form $K_{eq} = [\mathrm{Na}^+][EZ\text{-}(\mathbf{1})]/[(\mathbf{2})]$. The data obtained do not quantitatively fit this equation but instead furnish an equilibrium constant which declines with increasing sodium ion concentration, particularly when the sodium ion concentration becomes large. This might reflect a lack of ideality due to the high concentrations and changing ionic strength, or might indicate that some (**3a**) or (**3b**) is present.

¶ The order of relative abilities to form chelates observed in this work (Li > Na > K) has also been found by other workers for related systems. (S. M. Esakov, Al. A. Petrov, and B. A. Ershov, *Zhur. org. Khim.*, 1973, **10**, 849; 1975, **11**, 680; Al. A. Petrov, S. M. Esakov, and B. A. Ershov, *ibid.*, 1973, **10**, 1336; 1974, **10**, 1988; J. Terpinski, *Roczniki Chem.*, 1973, **47**, 537; O. Siiman, J. Fresco, and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 2347).