Stereochemical Consequences of Ionic Bonding in Alkali Metal Acetylacetonates[1a,b]

Morton Raban,* Eric A. Noe, and Gaku Yamamoto[1c]

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received September 28, 1976

Abstract: The proton NMR spectra of alkali metal (lithium, sodium, and potassium) acetylacetonates [M(acac), M = Li, Na, K] in methanol solvent were measured at low temperatures (ca. −60 °C) where rotation about carbon–carbon partial double bonds is slow on the NMR time scale. The spectra indicate that species with different configurations of the acetylacetonate moiety are present (*Z,Z* and *E,Z*). Experiments in which the concentration of Na(acac) is varied or in which NaI is added indicate that the *Z,Z* form is a chelated ion pair while the *E,Z* form is dissociated. The amount of chelation decreases with the increasing ionic radius of the metal ion, Li > Na > K. Tetramethylammonium acetylacetonate, prepared and studied in situ, was overwhelmingly in the dissociated *E,Z* form. The dependence of configuration upon the state of association permitted the "configurational titration" of Na(acac) with LiClO$_4$ and 18-crown-6. The first of these experiments indicated that lithium prefers to chelate with two acac anions when the concentration of lithium is low, forming a complex anion Li(acac)$_2$⁻. The second of these experiments demonstrates that the competition between 18-crown-6 and acac anion can be monitored by observing the NMR spectra of the acac moiety. The free energy of activation at the coalescence point for topomerization of the acac anion was determined by complete line shape analysis, 13.7 kcal/mol, and compared with the barriers previously measured for the nitrogen and oxygen analogues, diacetamide and formic anhydride.

The structures of enolate anions derived from β-dicarbonyl compounds and the interactions between these anions and metal cations have long been of interest to organic and inorganic chemists.[2-18] The configurational equilibria of these anions, which can be studied by low-temperature NMR spectroscopy, can provide useful information about ionic interactions as well as other structural features in these and related molecules.[15-17] This paper describes our measurements on the barrier to configurational interchange of the acetylacetonate anion and the configurational equilibria, in methanol as solvent, with the alkali metal cations, Li⁺, Na⁺ and K⁺, and the tetramethylammonium ion as gegenions. We also describe the changes in the configurational equilibrium attendant upon the addition of cations and crown ether and show how these experiments can be used to make configurational assignments and to define the kinds of interactions involved.

The acetylacetonate anion, **1**, like the related systems with isoelectronic π systems, the imides,[20] anhydrides,[21] and pentadienide anion,[22] can exist in three configurations corresponding to combinations of the *E* and *Z* configurations at the

E,E-1   *E,Z*-1   *Z,Z*-1
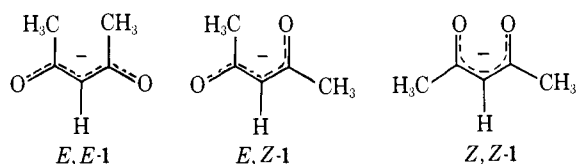
two carbon–carbon partial double bonds. The acetylacetonate anion differs from its neutral analogue diacetamide in that a gegenion is required for charge neutrality and this gegenion can perturb the configurational equilibrium. Thus, *Z,Z*-**1** is expected to be quite unfavorable as the free anion because of the considerable coulombic repulsion between the two proximate oxygen atoms, which together bear most of the negative charge. However, chelation to a metal ion can overcome this repulsion and stabilize this configuration, if the ionic bonding to the metal is sufficiently strong.

Exchange of metal ions is rapid enough that the NMR signals which are associated with the *Z,Z* configuration could arise not only from the free anion but also the chelated form and other complexes which have this configuration. Thus, each of the configurations does not necessarily represent one structure but could reflect the time-averaged properties of a set of free, solvated, and complexed ions which are in rapid equilibrium. Nevertheless, if particular species can be pre-

dominantly associated with different configurations, as is the case under some conditions, vide infra, the energy barrier to configurational interchange forms energy wells which allow species which differ in solvation or complexation to be separately observed and the equilibrium constant to be measured.

Results and Discussion

At low temperatures, the methyl region of the proton NMR spectrum of sodium acetylacetonate (Na(acac)) in methanol-d_4 (Figure 1a) features three singlets, two of which are of equal intensity, indicating that more than one of the three configurations of **1** are present in equilibrium. The two equally intense singlets at δ 1.89 and 2.27 can be assigned to the *E,Z* configuration on symmetry grounds. The singlet which appears at higher field (δ 1.80) can be shown to be associated with the *Z,Z* configuration by experiments in which the concentration of Na(acac) is varied or other species are added.

The relative amounts of the two configurations exhibit a significant dependence on the nominal concentration of Na(acac). Thus, a solution which was 0.376 M in Na(acac) contained 23% of the *Z,Z* form, while a 0.63 M solution contained 35% of the *Z,Z* form. This concentration dependence is indicative of different degrees of association of the two forms of the enolate anion with sodium ion. The *Z,Z* form, whose relative amount increases with increasing concentration, must be less dissociated than the species which has the *E,Z* configuration. In the limit, this situation is expressed by an equilibrium between a chelated complex *Z,Z*-**2** and the dissociated ions *E,Z*-**2.** Indeed, our data seem in qualitative accord with

Scheme I

Z,Z-2   *E,Z*-2
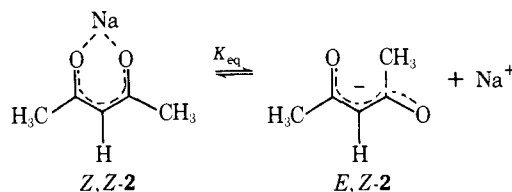
this kind of equilibrium. The equilibrium constant *K* can be obtained from eq 1, where *N* is the nominal concentration of Na(acac) and *R* is the ratio of *Z,Z* to *E,Z* configurations. The equilibrium constants calculated from our data were
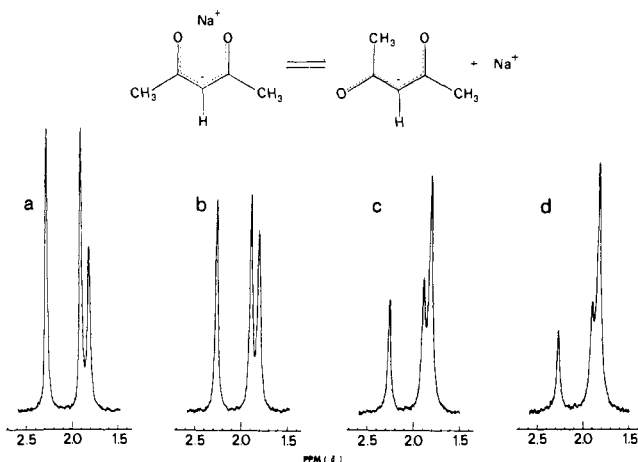
Figure 1. ^{1}H NMR spectra (60 MHz) of sodium acetylacetonate at −57 °C in CD$_3$OD, illustrating the effect of added sodium iodide: (a) no added salt; (b) 0.453 equiv of NaI; (c) 1.79 equiv of NaI; (d) 2.45 equiv of NaI.

$$K_{eq} = \frac{[Na][E,Z\text{-}1]}{[Z,Z\text{-}2]} = \frac{N}{R(1 + R)} \qquad (1)$$

$K = 0.76$ at $N = 0.65$ M and $K = 0.96$ at $N = 0.376$ M. While our data are not sufficiently accurate to define the degree of dissociation of E,Z-2 exactly, they do indicate that it is predominantly dissociated at these concentrations, and it appears that Scheme I provides a useful picture. It is noteworthy that the isomer which is capable of chelation (Z,Z-2) represents only a minor portion of the total enolate anion in methanol solution. The nonchelated E,Z-2 accounts for most of the anion. Apparently, methanol competes favorably with the enolate anion as a ligand for sodium, and chelation is relatively unimportant in this solvent.

A more dramatic demonstration of the effect of mass action on this equilibrium is provided by the effect of added sodium cation (Figure 1). Upon the addition of sodium iodide to a solution of Na(acac), the equilibrium in Scheme I is shifted to the left (Table I). Thus, the percentage of the Z,Z configuration increases from only 23% with no added salt to 63% when 2.45 equiv of sodium iodide are added. This shift in the ratios reflects a mass action effect and confirms that the E,Z isomer must exist substantially in dissociated form, in contrast to the Z,Z isomer, in which association with sodium ion (chelation) occurs. Modification of eq 1 to accomodate for the effect of added sodium ion leads to eq 2, where A is the number of equivalents of added NaI relative to Na(acac). Equation 2 reduces to (1) when A is zero. The equilibrium constants, calculated using eq 2 and given in Table 1, decline as the

$$K_{eq} = \frac{N}{R(R + 1)} + \frac{NA}{R} \qquad (2)$$

amount of added sodium ion increases. This trend argues against a substantial amount of complexation of E,Z-2 to give
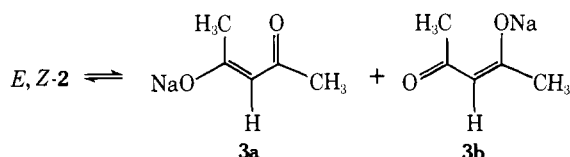
3. If **3** were present in substantial amounts, the apparent equilibrium constant should increase at higher sodium ion concentrations, contrary to the observed trend. The deviation of the percentage of the Z,Z form observed from the ideal value obtained using eq 2 and $K = 0.96$ actually increases with the concentration of addend. One explanation for this trend is that

Table I. Effect of Concentration and Addends on the Configurational Equilibrium of Sodium Acetylacetonate

[Na-(acac)], M[23]	Temp, °C	Addend	Addend concn, M	% ZZ (obsd)	% ZZ (calcd)[a]	K
0.38	−57			23		0.96
0.38	−57	NaI	0.16	31	30	0.94
0.38	−57	NaI	0.45	43	41	0.89
0.38	−57	NaI	0.68	53	48	0.76
0.38	−57	NaI	0.93	63	54	0.59
0.63	−58			35		0.76
0.69	−57	18-Crown-6	0	34		
0.69	−57	18-Crown-6	0.19	24		
0.69	−57	18-Crown-6	0.35	17		
0.69	−57	18-Crown-6	0.52	7		
0.66	−57	18-Crown-6	0.70	3		
0.69	−57	18-Crown-6	1.12	0		
0.63	−58	LiClO$_4$	0.02	36		
0.63	−58	LiClO$_4$	0.05	46		
0.63	−58	LiClO$_4$	0.09	57		
0.63	−58	LiClO$_4$	0.13	68		
0.63	−58	LiClO$_4$	0.16	72		
0.63	−58	LiClO$_4$	0.27	91		
0.63	−58	LiClO$_4$	0.49	~100		
0.63	−58	LiClO$_4$	0.62	100		
0.63	−58	LiClO$_4$	0.71	100		
0.63	−58	LiClO$_4$	0.82	100		
0.63	−58	LiClO$_4$	1.42	100		

[a] Calculated values for % Z, Z were obtained using eq 2 and $K = 0.96$ (see text).

the activity coefficient for sodium ion is increased as the concentration of salt is increased because of a reduced ability of methanol solvent to sufficiently solvate ions at these fairly high concentrations.

This effect can be illustrated by modification of Scheme I to account for interactions with solvent (Scheme II), where we

Scheme II
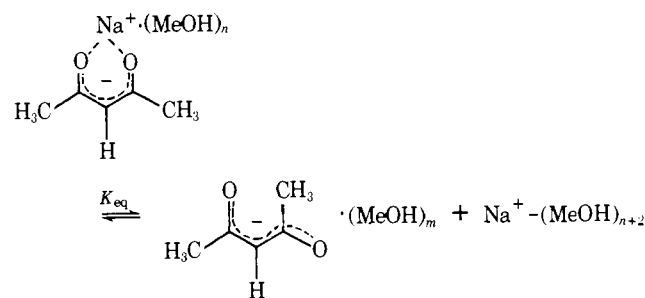
have assumed that unchelated sodium ion is solvated by two additional methanol molecules.[24] Since more methanol molecules are required for solvation of the E,Z form, the equilibrium will be shifted to the left when the activity of methanol is lowered at higher salt concentrations.

The equilibrium could also be observed under conditions where the effective sodium ion concentration was lower than the concentration of acetylacetonate anion. This was accomplished by the addition of 18-crown-6, which complexes sodium ion and makes it incapable of chelation. As indicated in Table I and Figures 2 and 3, the addition results in a gradual decrease in the concentration of the Z,Z configuration. The complete absence of the Z,Z configuration observed when excess crown is added indicates that the free ion overwhelmingly prefers the E,Z configuration. As in the case of the imides,[20] the coulombic repulsion between the two negatively charged oxygen atoms significantly destabilizes the Z,Z configuration relative to the E,Z configuration. For the same reason, we can also
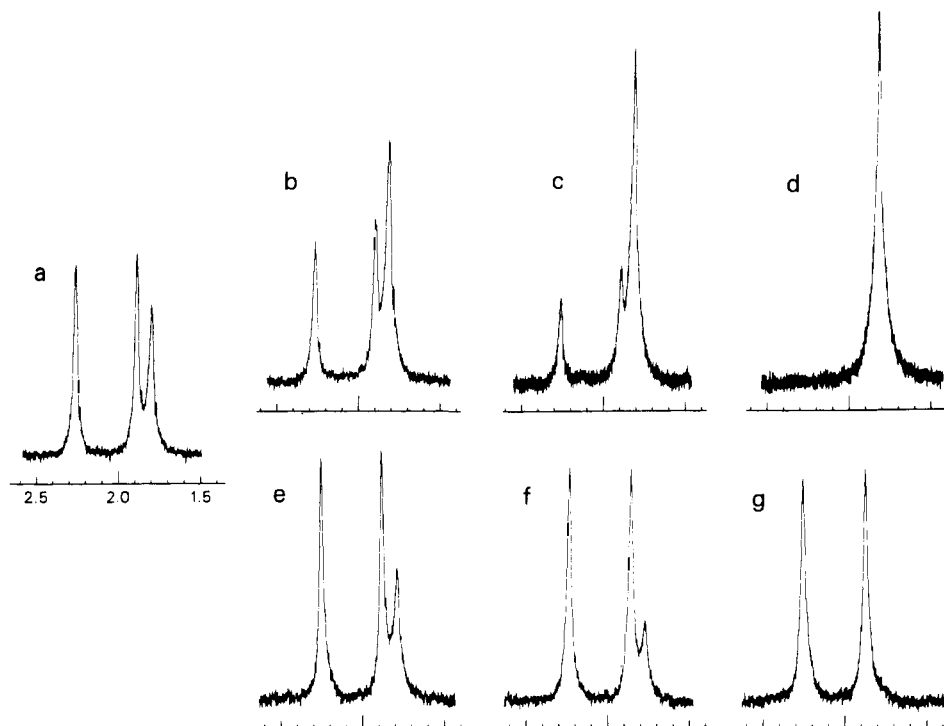
Figure 2. ^{1}H NMR spectra (60 MHz) of sodium acetylacetonate in CD_3OD illustrating the effect of added lithium perchlorate (b,c,d) and 18-crown-6 (e,f,g); (a) no addend, (b) 0.08 equiv of $LiClO_4$; (c) 0.20 equiv of $LiClO_4$; (d) 2.25 equiv of $LiClO_4$; (e) 0.19 equiv of 18-crown-6; (f) 0.35 equiv of 18-crown-6; (g) 1.12 equiv of 18-crown-6.
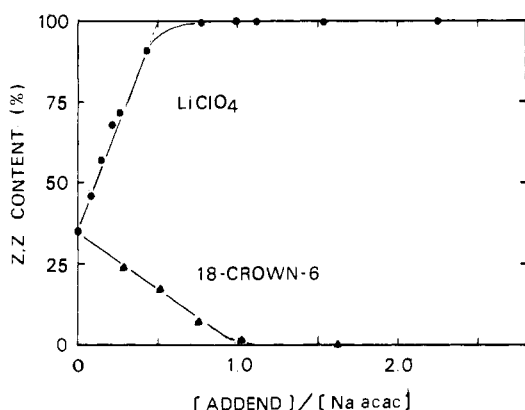

Figure 3. Percentage of acetylacetonate with Z,Z configuration as a function of added $LiClO_4$ or 18-crown-6.

Figure 4. ^{1}H NMR spectra (60 MHz) of alkali metal acetylacetonates.

conclude from this result that the Z,Z form observed in the absence of crown ether derives exclusively from the chelate and that dissociation to the free Z,Z anion is negligible under the conditions of these experiments. The amount of Z,Z form observed with the addition of 1 equiv of 18-crown-6 is very small (only ca. 3%), indicating that crown ether competes very effectively with acetylacetonate anion, in contrast to the behavior in pyridine where a substantial amount of the Z,Z form is observed even when 1 equiv of crown is present.[25]

The configurational equilibrium is also strongly dependent on the nature of gegenion. The equilibrium represents a measure of the relative abilities of the acetylacetonate anion and methanol to complex with the gegenion. The complexation of potassium cation by acetylacetonate is less favorable than that of sodium.[13,15-17] Thus, the NMR spectrum (Figure 4) indicates a lesser amount of the Z,Z configuration (11%) as compared with the 23% observed for the sodium ion at the same concentration and temperature. The dissociation constants obtained for Na(acac) and K(acac) in methanol using eq 1 (0.96 and 2.7, respectively), measured in this way, follow the

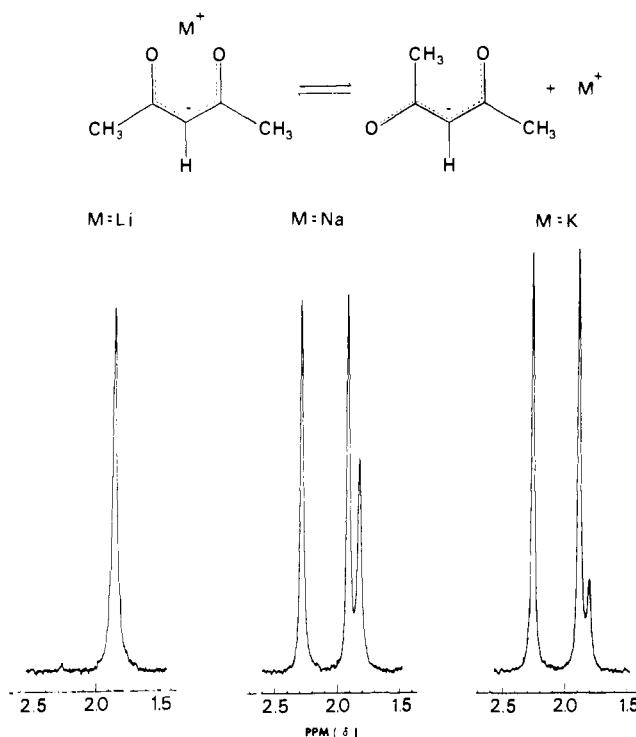same trend but indicate a significantly greater degree of dissociation than those obtained indirectly using pK_a measurements.[13] By contrast, the lithium cation shows a much greater tendency for chelation.[13,15-17] Lithium acetylacetonate exists almost completely in the chelated form, with a methyl resonance at δ 2.25 (Figure 4). A dissociation constant of 6×10^{-4} can be calculated using this datum and eq 1. although as discussed below, Scheme I does not provide an accurate picture of the equilibrium and this value is not quantitatively signifi-

cant. 18-Crown-6 (up to 2.55 equv) did not have sufficient complexing ability for lithium cation to compete with the acetylacetonate anion.

The much weaker tendency for chelation of sodium with respect to lithium suggested another means for studying the effect of lithium ion in small concentrations. It was possible to use NMR spectra to monitor the titration of Na(acac) by LiClO$_4$. The chelation of lithium is sufficiently more favorable that the addition of lithium cation (LiClO$_4$) can displace sodium cation when added to a solution of Na(acac). This displacement has a dramatic effect on the NMR spectrum. The amount of the chelated configuration increases until all of the acac anion is present in the Z,Z configuration in the presence of excess lithium cation (Figure 2d). This change in configuration as a function of lithium ion concentration permits the "configurational titration" of Na(acac). The initial points in the plot of the fraction of the acac anion in the Z,Z configuration as a function of the amount of LiClO$_4$ added are quite linear (Figure 3). Extrapolation yields a line which intersects the 100% line at a point corresponding to 0.5 lithium atoms per acac. Thus, lithium cation prefers to coordinate with two acac anions in solution as well as in the solid state[18] even in the presence of excess methanol as an alternative ligand. Although a hexacoordinate anion [Li(acac)$_2$(MeOH)$_2$]$^-$ cannot be excluded, the most probable form for the lithium chelate formed with small amounts of added lithium would seem to be the tetracoordinate complex anion **4**, with square-planar (D_{2h}) geometry or more likely distorted tetrahedral (D_{2d}) geometry at lithium.[18]

Examination of spectra at higher lithium ion concentrations indicated that either **4** or the monochelate Li(acac)(MeOH)$_n$ is present even in the presence of excess lithium cation. If a complex cation **5**, analogous to one used to explain solubility

4

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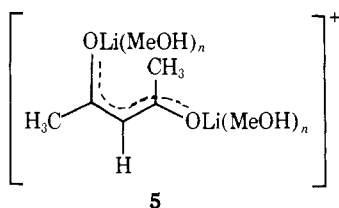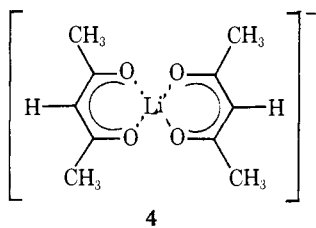
data in acetonitrile,[14] were formed, the amount of the Z,Z configuration should decline at higher lithium ion concentrations.

The "configurational titration" could also be accomplished using N(CH$_3$)$_4$(acac) as a substrate. Tetramethylammonium acetylacetonate was prepared in situ and its NMR spectrum was examined, although attempts to prepare crystalline material were not successful. Weighed amounts of tetramethylammonium hydroxide pentahydrate (ca. 3% excess) and acetylacetone were dissolved in anhydrous methanol-d_4 in an NMR sample tube. At −57 °C, three singlets were observed in the methyl region: δ 1.80 (Z,Z), 1.89 and 2.27 (E,Z). The fraction in the Z,Z form appears to be independent of concentration within experimental error: 4% at 0.72 M and 3% at 0.32 M. The origin of this small amount of the Z,Z form is not clear. It seems unlikely that it arises from ion pairing with N(Me)$_4$$^+$, or from the free anion, since none of the Z,Z form can be detected for samples of Na(acac) in the presence of

excess 18-crown-6. It seems more likely that some other species is responsible for this small amount of chelation. The 6 equiv of water present or small amounts of sodium cation leached from glass vessels are two possibilities.

Addition of 0.03 and 0.25 equiv of lithium perchlorate to this solution increased the Z,Z content to 11 and 54%, respectively. A plot of the Z,Z content as a function of added lithium perchlorate gave a line which also intersected the 100% line at 0.5 equiv of LiClO$_4$, again indicative of the presence of Li(acac)$_2$$^-$.

Since this preparation (in the absence of lithium ion) is composed nearly exclusively of free acac anion, it was selected as the most suitable for measuring the free energy of activation for topomerization of the diastereotopic methyl groups of the E,Z configuration. When the temperature was elevated, the small peak at δ 1.80 disappeared (at ca. −47 °C) giving rise to a slightly distorted doublet which coalesced (T_c = −2 °C) into a singlet. The rate constant for the coalescence (k_c) of an uncoupled AB spectrum with the appropriate chemical shift difference and half-width was evaluated by complete line shape analysis: 48 s^{-1}. Assuming that the experimental system closely resembles this model, the free energy of activation for topomerization obtained using the Eyring equation with a transmission coefficient of unity is 13.7 kcal/mol. This value can be compared with the value of the isoelectronic but neutral nitrogen analogue, diacetamide (N-acetylacetamide): $\Delta G_c^{\ddagger}$ = 10.8 kcal/mol at −60 °C in dichloromethane.[20]

As one expects, the free energy of activation is somewhat higher for the acac anion. The barrier is a measure of the energy required for deconjugation of one of the carbonyl groups,[26] resulting in a less delocalized anion at the transition state. Conjugation would be expected to have a greater effect on the stabilization of the acac anion by delocalization of the negative charge. By contrast, in diacetamide, only delocalization of the nitrogen lone pair is involved. While the direction of this change is as expected, the magnitude of the difference seems smaller than might have been anticipated, especially considering the much lower barrier measured for the oxygen analogue, formic anhydride, viz., 4.4 kcal/mol.[21] Although the differences in atom electronegativities between oxygen and nitrogen and between nitrogen and carbon are nearly the same on the Pauling–Allred scale,[27] and the tendency toward electron pair donation of carbon in the acac anion is further increased by the negative charge, the carbon and nitrogen compounds fall fairly close together.

The much lower barrier of the oxygen compound would not seem to be due to electronegativity differences alone. This compound differs from the other two compounds in another respect as well, which may be responsible for its much lower barrier. Oxygen in formic anhydride bears an additional lone pair of electrons; conjugation with both lone pairs is possible and could stabilize the transition state for topomerization, lowering the free energy of activation for the process.

Experimental Section

NMR spectra were obtained using a Varian A-60A spectrometer equipped with a variable temperature accessory. The spectra were calibrated by the side-band technique, using a Hewlett-Packard 523B counter. Chemical shifts are reported in δ units, relative to internal tetramethylsilane. Percentages of the minor isomer were obtained by electronic integration or by weighing of 10 Xerox copies of the expanded sweep width spectra. These values were reproducible within a range of ±2%. Temperatures were measured by replacement of the sample tube with an open tube containing a suitable solvent and a copper–constantan thermocouple. The melting point of n-pentane was used to assure the calibration of the thermocouple–potentiometer system in the low-temperature range. Temperatures measured in this way are estimated to be accurate to ±2 °C.

The first-order rate constant at the coalescence point was obtained by complete line shape analysis using program CLAS, a classical me-

chanical two-site program for exchanging singlets. We regard the uncertainty in free energies of activation obtained in this way to be ca. ±0.2 kcal/mol.

Sodium acetylacetonate was prepared by reaction of acetylacetone with sodium hydride in benzene or pentane and crystallized from ethanol/ether.[3] The potassium salt was prepared using potassium hydroxide in methanol and crystallized from the same solvent mixture.[3] Lithium acetylacetonate was prepared by reaction with *n*-butyllithium in benzene. The precipitated white solid was washed with benzene, filtered, and dried in vacuo. Its infrared spectrum agreed well with that reported earlier.[28] Efforts to obtain pure tetramethylammonium acetylacetonate in crystalline form were not successful and this compound was prepared and studied in situ. Thus, a weighed amount of $(CH_3)_4NOH \cdot 5H_2O$ (2–3% excess), prepared from $(CH_3)_4NCl$ and Ag_2O in aqueous methanol,[29] was dissolved in methanol-d_4 in an NMR sample tube and a weighed amount of acetylacetone was added.

References and Notes

(1) (a) A portion of this work has received preliminary communication: E. A. Noe and M. Raban, *J. Chem. Soc., Chem. Commun.*, 165 (1976); M. Raban, and G. Yamamoto, in press; (b) this work was supported by grants from the National Science Foundation and the National Institute of General Medical Sciences; (c) on leave from the Department of Chemistry, Faculty of Sciences, University of Tokyo.

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(23) The concentrations given in the table and text are approximate nominal molar concentrations obtained by adding weighed amounts of substrate to measured amounts of methanol solvent at room temperature. In order to obtain actual concentrations, these data should be adjusted to take into account the volume change of the solvent upon addition of substrate and the change in temperature. The equilibrium constants were obtained using these nominal concentrations. Since accurate equilibrium constants were not needed in order to evaluate the trends discussed and since the errors introduced should be reasonably small, no effort was made to correct our data for volume changes.

(24) While our results do not permit us to rule out the presence of other species in solution, we believe that most of the compound exists as one of the two forms in Scheme II. The low association constant for the chelate with sodium ion argues against the presence of substantial amounts of a dichelate, $Na(acac)_2^-$, of the type postulated below for lithium ion. We assume here that the association constant for the second acac ion with Na(acac) will be smaller than for the first acac and Na⁺. The mass action results indicate that the *Z,Z* form associates with sodium ion to a greater extent than does the *E,Z* form, and the reasonable agreement between the model (Scheme II) and experimental results is made worse by the inclusion of *Z,Z* species such as $Na(acac)_2^-$, which have a lower Na⁺:acac ratio, or by inclusion of associated *E,Z* species.

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(26) An alternative to rotation about the partial double bonds can be considered for the enolate anions. Protonation of the enolate could lead to the β-diketone, for which only a negligible barrier is expected, or to the enol (β-hydroxy conjugated enone) for which the barrier might be substantial, although it should be lower than that of the enolate. If such a mechanism cannot be ruled out, the measured free energy of activation must be regarded as a lower limit to the torsional barrier. While conversion to the keto form (C protonation) is probably far too slow to account for the topomerization, a referee has argued that protonation to give the enol does occur at a rate comparable to the rate of topomerization and that this mechanism represents a viable alternative if the enol itself has a small torsional barrier at the formal single bond. One piece of experimental evidence argues against this conclusion, although not definitively. We have measured coalescence temperatures of acetylacetonates under two very different conditions: sodium acetylacetonate in pyridine containing 18-crown-6,[25] and in the present case, tetramethylammonium acetylacetonate in methanol. The approximate barrier calculated for the pyridine solution, 13 kcal/mol, is quite comparable to that obtained here, although the rate of protonation must certainly be much greater in methanol solution. This result provides some evidence that topomerization via protonation and torsion does not occur substantially faster than topomerization of the enolate; however, the argument assumes that association of the enolate oxygens with Na⁺ in pyridine (analogous to protonation in methanol) does not substantially enhance the rate of topomerization in this solvent.

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