

### The Mechanism of the Intramolecular Rearrangements of Aluminum $\beta$ -Diketonate Complexes

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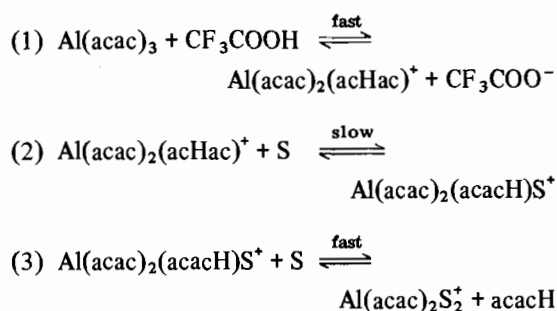
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The rearrangement reactions of Al(III)  $\beta$ -diketonates have been studied in some detail [1–4]. They clearly proceed by an intramolecular mechanism since the rates of rearrangement are much greater than the rates of ligand exchange [5, 6]. However, in spite of detailed analyses, it has not been possible to unambiguously distinguish between various twisting and bond rupture mechanisms. Bond rupture mechanisms would be ruled out if the rate of ligand exchange were determined by the breaking of the first metal–oxygen bond rather than by breaking of the second bond as suggested by Saito and Masuda [6]. It is the purpose of the present communication to present evidence that the breaking of an aluminum oxygen bond to form a dangling ligand intermediate is a slow process and that rearrangement must therefore occur without bond rupture. However we also wish to argue that rearrangement does not necessarily occur by any of the simple twisting mechanisms usually considered.

Saito and Masuda [5, 6] measured the rates of ligand exchange of  $\text{Al}(\text{acac})_3$  (acac = acetylacetonate) and found that the reaction was catalysed by water and by acids. They suggested that protonation occurs on the oxygen of the ligand and leads to the rapid formation of a dangling ligand intermediate of “considerably long lifetime”. If this is the case it should be possible to obtain NMR evidence for the intermediate. Our experiments have been directed towards this end.

The NMR spectra obtained by the addition of trifluoroacetic acid to  $\text{Al}(\text{acac})_3$  have been examined using a number of different solvents. The results depend markedly on the solvent. However all of the results can be accommodated by the reaction scheme:



In this scheme acHac represents the keto form of acetylacetonate, acacH the enol form and S a solvent molecule.  $\text{Al}(\text{acac})_2(\text{acacH})\text{S}^+$  is the dangling ligand intermediate of Saito and Masuda.

In good coordinating solvents such as THF and DMSO equilibrium 1 is to the left and equilibrium 3 to the right. As a result, the NMR spectrum shows only the resonances of  $\text{Al}(\text{acac})_3$  and the final products  $\text{Al}(\text{acac})_2\text{S}_2^+$  and acetylacetonate. The lines for  $\text{Al}(\text{acac})_3$ , acacH and acHac are sharp and not shifted from their positions in the absence of acid. The spectrum of  $\text{Al}(\text{acac})_2\text{S}_2^+$  (S = THF) agreed well with that given by Movius and Matwiyoff [7] and with spectra of the same species obtained by other reactions in this laboratory. Conductivity and  $^{19}\text{F}$  NMR measurements showed that  $\text{CF}_3\text{COO}^-$  was not coordinated to the metal. It is apparent that neither of the intermediates are present in sufficient concentration to affect the spectra.

In poor coordinating solvents such as benzene and nitromethane the initial result of adding acid was a considerable broadening of the C–H resonance of  $\text{Al}(\text{acac})_3$ . At high acid concentrations (0.5 M) weak lines from the free ligand appeared. These lines showed small but significant shifts from their expected positions. Equilibria 2 and 3 have been displaced to the left resulting in a sufficient concentration of  $\text{Al}(\text{acac})_2(\text{acHac})^+$  to give line broadening by equilibrium 1 and of rapid exchange of free ligand by equilibrium 3. It is possible that in benzene S represents small amounts of water added with the acid.

Chloroform and methylene chloride show intermediate behaviour as solvents.  $\text{Al}(\text{acac})_2\text{S}_2^+$  is formed and both broadening of the C–H resonance and shifts of the free ligand lines are observed. These shifts cannot be accounted for by adding either  $\text{Al}(\text{acac})_3$  or  $\text{CF}_3\text{COOH}$  alone. Chemical shift data is given in Table I.

The reactions 1–3 provide a pathway for ligand exchange essentially the same as that suggested by Saito and Masuda. Protonation occurs on the carbon rather than on the oxygen, which is perhaps not unexpected in the light of the observations of Brouwer [8] on the effect of electron withdrawing substituents on the protonation of  $\beta$ -diketonates. Modifications of the scheme are possible, e.g., reaction 2 could occur without transferring the proton from carbon to oxygen, but the three basic steps of a) protonation b) breaking the first Al–O bond and c) breaking the second Al–O bond must be present. Since the overall reaction is slow, one of these steps must be slow.

The observed line broadening shows that protonation is fast. The following argument shows that reaction 3 is fast. In THF (the solvent used in Ref. 5) equilibrium 3 is clearly to the right. If the rate con-

TABLE I. Proton Chemical Shifts of Acetylacetonates.<sup>a</sup>

Solvent/Solute	Hacac	acHac	Al(acac) <sub>3</sub>	Al(acac) <sub>2</sub> S <sub>2</sub> <sup>+</sup>
CDCl <sub>3</sub> /Hacac	2.03 <sup>b</sup> , 5.50 <sup>c</sup>	2.22, 3.58 <sup>d</sup>		
CDCl <sub>3</sub> /Al(acac) <sub>3</sub>			1.99, 5.47	
CDCl <sub>3</sub> /Hacac + 0.5 M CF <sub>3</sub> COOH	2.07, 5.55	2.25, 3.64		
CDCl <sub>3</sub> /Al(acac) <sub>3</sub> + 0.5 M CF <sub>3</sub> COOH	2.12, 5.57	2.70, 3.66	2.03, ~5.6 (broad)	2.05, 5.62
C <sub>6</sub> D <sub>6</sub> /Hacac	1.69, 5.12	1.78, 3.06		
C <sub>6</sub> D <sub>6</sub> /Al(acac) <sub>3</sub>			1.76, 5.30	
C <sub>6</sub> D <sub>6</sub> /Al(acac) <sub>3</sub> + 0.25 M CF <sub>3</sub> COOH	1.66, 4.98		1.76, 5.30 (broad)	
DMF/Hacac	2.03, 5.68	2.16, 3.74		
DMF/Al(acac) <sub>3</sub>			1.88, 5.56	
DMF/Al(acac) <sub>3</sub> + 0.5 M CF <sub>3</sub> COOH	2.03, 5.68	2.16, 3.74	1.88, 5.56	1.92, 5.64

<sup>a</sup>Shifts in ppm obtained at 100 MHz, T = 27 °C.<sup>b</sup>CH<sub>3</sub>.<sup>c</sup>CH.<sup>d</sup>CH<sub>2</sub>. Other assignments analogous.

stant for the forward reaction were small, that for the backward reaction would be even smaller. If this were so the backward reaction would be the rate determining step in ligand exchange and the rate would be proportional to ligand concentration. The rate is clearly independent of ligand concentration [5, 6]. The conclusion that reaction 3 is fast is supported by the NMR evidence for rapid exchange involving the free ligand. Breaking of the first Al–O bond (reaction 2 or a modification thereof) must therefore be the slow step. This conclusion is consistent with all the experimental data of Saito and Masuda.

The above discussion applies to acid catalysed ligand exchange. However if the rate of breaking the first bond is slow for the protonated complex it will be even slower for a neutral complex [9, 10]. Data in the literature allow an estimate of this rate for some acetylacetonate complexes. Thus Pearson and Anderson [11] found a rate of  $2 \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$  for the formation of Cu(acac)<sup>+</sup> and concluded that the rate determining step was closure of the six membered chelate ring to form the second M–O bond. Since the equilibrium for most acetylacetonates clearly favours the chelate over the dangling ligand isomer, if closing the ring is slow, opening the ring must be even slower. The formation constant [12] of Cu(acac)<sup>+</sup> is  $\sim 10^{10}$  and that for analogous monodentate ligands [12] (e.g. propionic acid)  $\sim 10^2$ . This gives the rate for dangling ligand to chelate as  $\sim 10^2 \text{ s}^{-1}$  and the equilibrium constant as  $10^8$ , leading to a dissociation rate  $\sim 10^{-6} \text{ s}^{-1}$ . Fortuitously this agrees exactly with the rate of  $6 \times 10^{-5} \text{ min}^{-1}$  reported by Saito and Masuda [5] for the uncatalyzed ligand exchange of Al(acac)<sub>3</sub>. Clearly, though, the observed rate is consistent with the rate determining step being the breaking of the first Al–O bond.

It follows that rearrangement of aluminum β-diketonate complexes cannot occur by a bond rupture mechanism. By analogy this may also be true for the Ga and In compounds but the argument cannot

be applied to V; Zr and Hf complexes since the ligand exchange rates in these cases [13, 14] are not determined by a bond breaking step. However it does not necessarily follow that rearrangement takes place by a simple twisting mechanism. The activation energy for rearrangement must reside in the normal vibrations of the molecule. Each normal coordinate probably corresponds to a complex mixture of bond stretching and bending motions. It seems unlikely that the lowest energy pathway will correspond to the accumulation of all the activation energy in the stretching of a single bond or in a single twisting motion. A more plausible view would be that the transition state of the molecule corresponds to a distorted configuration involving stretching several bonds and distorting several angles. Such a mechanism would be intermediate between a pure twisting and a pure bond rupture process. If this is the case a permutational analysis based on simple model mechanisms [15] must be expected to give ambiguous answers.

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