Interpretation of Nuclear Magnetic Resonance Kinetics of Two-Step Exchange of Methyl Groups between Hexamethyldialuminum and Trimethylgallium

Sir:

Two independent research groups have studied the exchange of methyl groups between hexamethyldialuminum and trimethylgallium by means of proton nmr spectra but have failed to find a fully satisfactory kinetic expression for the observed rates.[1,2] The derivation presented here avoids problems in symbolism encountered with equilibrium kinetics. The result supports the two-step mechanism of eq 1 and 2 without requiring the postulation of solvent-cage effects to achieve a good first approximation to the observed kinetics.

$$Al_2(CH_3)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Al(CH_3)_3 \qquad (1)$$

$$Al(CH_3)_3 + Ga(CH_3)_3 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (CH_3)_2Al(CH_3)_2Ga(CH_3)_2 \qquad (2)$$

The concentrations of $Al(CH_3)_3$ and $AlGa(CH_3)_6$ are low. Although it is possible to use the steady-state approximation that $d[Al(CH_3)_3]/dt = 0$,[1] there are two pitfalls. First, the equations must be rewritten in terms of the units actually measured by nmr, which are methyl groups (protons) and not molecules. Otherwise, the derived kinetic expression will have the right form but (usually) wrong k values because the number of methyl groups transferred may differ at each step of the reaction. Second, the forward and reverse paths must somehow be distinguished and the steady-state treatment applied to only one of them at a time. If all four processes outlined in eq 1 and 2 are put into the steady-state treatment and the symbols interpreted literally, calculations lead to the dead end $0 = 0$ because there is no net change in the concentration of anything. The different approach which follows takes advantage of the equilibrium condition from the start.

The equilibrium condition provides the equations

$$k_1[Al_2(CH_3)_6] = k_{-1}[Al(CH_3)_3]^2 \qquad (3)$$

$$k_2[Al(CH_3)_3][Ga(CH_3)_3] = k_{-2}[AlGa(CH_3)_6] \qquad (4)$$

Let Q represent the (unknown) fraction of the methyl groups in $Al(CH_3)_3$ which have come from $Ga(CH_3)_3$. Then each dimerization of $Al(CH_3)_3$ results in net, measurable transfer of $6Q$ methyl groups from $Ga(CH_3)_3$ to $Al_2(CH_3)_6$ and the rate is

$$-d[(CH_3)_{Ga}]/dt = 6Qk_{-1}[Al(CH_3)_3]^2 = 6Qk_1[Al_2(CH_3)_6] \qquad (5)$$

Half the dissociations of $AlGa(CH_3)_6$ result in transfer of one methyl group from $Al(CH_3)_3$ to $Ga(CH_3)_3$, and the fraction of these methyl groups originating from $Al_2(CH_3)_6$ is $(1 - Q)$. Taking eq 4 into account, the rate may be written

$$-d[(CH_3)_{Al}]/dt = \frac{1}{2}(1 - Q)k_2[Al(CH_3)_3][Ga(CH_3)_3] \qquad (6)$$

The forward and reverse rates, eq 5 and 6, must be equal. Expressing $[Al(CH_3)_3]$ as $(k_1/k_{-1})^{1/2}[Al_2(CH_3)_6]^{1/2}$ from eq 3, equating (5) and (6), and solving for Q yields

$$Q = \frac{[Ga(CH_3)_3]}{[Ga(CH_3)_3] + \frac{12k_{-1}}{k_2}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Al_2(CH_3)_6]^{1/2}} \qquad (7)$$

The observable pseudo-first-order rate constant $1/\tau_{Ga}$ is $-d[(CH_3)_{Ga}]/dt$ from eq 5 divided by the number of methyl groups in $Ga(CH_3)_3$ and its molarity (eq 8). It can also be shown that for each dissociation–recombination of $Al_2(CH_3)_6$, the chance that a given terminal methyl group will exchange to a bridge site is $(1/3)(1 - Q)$ and the chance it will go to a gallium site is Q. The reciprocal lifetime is therefore

$$\frac{1}{\tau_{Ga}} = \frac{2Qk_1[Al_2(CH_3)_6]}{[Ga(CH_3)_3]} \qquad (8)$$

$$\frac{1}{\tau_{Al(t)}} = k_1\left[\frac{1}{3} + \frac{2}{3}Q\right] \qquad (9)$$

Similarly, for the bridge methyl groups

$$\frac{1}{\tau_{Al(b)}} = k_1\left[\frac{2}{3} + \frac{1}{3}Q\right] \qquad (10)$$

If k_1 were rate controlling, Q would approach unity and eq 8 would approach first order in $[Al_2(CH_3)_6]$ and zero order in $[Ga(CH_3)_3]$. If k_2 were rate controlling, Q would be small and eq 8 would approach half-order in $[Al_2(CH_3)_6]$ and first order in $[Ga(CH_3)_3]$. Neither extreme prevails. The values $k_1 = 9\ sec^{-1}$ and $12(k_{-1}/k_2)(k_1/k_{-1})^{1/2} = 0.5$ in eq 7–10 yield calculated $1/\tau$ values within 2–3 sec^{-1} of the observed values at $-47°$ tabulated by Jeffery and Mole.[2] Since a 3-sec^{-1} error corresponds to an increment of only 1 Hz in the half-intensity line width, this seems reasonable agreement. The $1/\tau_{Ga}$ data of Williams and Brown[1] are correlated $\pm 1\%$ if k_1 is 7.5 and $[Ga(CH_3)_3]$ is 0.3 M, which was not specified precisely. Twofold dilution of one of the mixtures used by Williams and Brown would reduce $1/\tau_{Ga}$ by only 15% according to eq 8, which appears to agree with their general statement that dilution did not affect the rates.

These results indicate that the bridge–terminal exchange of $Al_2(CH_3)_6$ proceeds by way of complete dissociation to two $Al(CH_3)_3$ groups as postulated by Williams and Brown.[1] Although Jeffery and Mole similarly favored the dissociation mechanism,[2] their kinetic treatment required postulation of such an unusual solvent-cage effect that it might better have been construed as favoring a partially opened intermediate $(CH_3)_2Al–CH_3–Al(CH_3)_3$. However, such a single-bridged transition state recently found in the case of μ-*tert*-butoxy-pentamethyldialuminum has grossly different characteristics,[3] and the present treatment removes any anomaly from the behavior of $Al_2(CH_3)_6$.

The relative magnitudes of the k values required by the kinetic expressions and observations are consistent with expected trends in reactivity. Observations that $k_1 \simeq 9\ sec^{-1}$ and $12(k_{-1}/k_2)(k_1/k_{-1})^{1/2} \simeq 0.5$ require that $k_{-1} \simeq 2 \times 10^{-4}k_2^2$, which makes k_{-1} for the recombination of two $Al(CH_3)_3$ groups greater than k_2 for the reaction of $Ga(CH_3)_3$ with $Al(CH_3)_3$ if both k's are above 5×10^3, as expected. Also, it can be shown that the concentration of $AlGa(CH_3)_6$ would be too low to detect if $k_{-2} > 10^4\ sec^{-1}$, which seems reasonable.

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[1] K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 5460 (1966).

[2] E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **22**, 1129 (1969).

[3] E. A. Jeffery and T. Mole, *ibid.*, **23**, 715 (1970).

The foregoing kinetic analysis has been for lines separated only by chemical shifts. Such an excursion as that of a methyl group from $Ga(CH_3)_3$ to short-lived $Al(CH_3)_3$ and back to $Ga(CH_3)_3$ will not contribute to line broadening, in accord with the Gutowsky–Holm equation.[4] If collapse of a spin multiplet were involved, such excursions would contribute to $1/\tau$ and would have to be taken into account. The present method of kinetic analysis can be extended to multistage reactions by assigning a different fraction Q_1, Q_2, ..., Q_n to each intermediate and solving for the Q's by means of the equilibrium relationships.

(4) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

DEPARTMENT OF CHEMISTRY
WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163
DONALD S. MATTESON

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Electron Spin Resonance of Copper Bis(dibenzoylmethane). Superhyperfine Anomalies[1]

Sir:

Recently So and Belford[2] commented on the report of Kuska, *et al.*,[3] about the esr spectra of frozen solutions of bis(1,3-diphenyl-1,3-propanedionato)copper {$Cu(dbm)_2$}. Kuska, *et al.*, attributed the complicated "superhyperfine structure" which is observed in frozen chloroform solutions to a delocalization of the unpaired electron over the phenyl groups leading to a substantial interaction with the protons of these rings. So and Belford showed that the same compound exhibits a completely normal esr spectrum if the solutions are prepared with commercial grade chloroform at room temperature. Spectra similarly complicated as those of Kuska, *et al.*, were obtained as soon as the solution was boiled before taking the esr spectrum.

So and Belford postulated from this observation that an unidentified radical species is formed upon boiling the chloroform solution. They also observed a diminution of these extra hyperfine lines when toluene is added to a boiled chloroform solution. They attribute this effect to a sensitivity of the "radical species" toward toluene.

This communication prompted us to reproduce the esr spectra of $Cu(dbm)_2$ in frozen solutions, since we had observed similar hyperfine structure anomalies in several esr spectra of frozen solutions of low-spin Co(II) complexes.[4] However, the reason for these anomalies was found to be rather trivial, and we could prove that the anomalous spectra of $Cu(dbm)_2$ can be explained as follows.

We call the appearance of an unexpected and complicated hyperfine pattern in the esr spectrum of a frozen solution in our laboratory jargon the "single-crystal effect." The esr line shape normally observed in frozen solutions or polycrystalline samples is due to

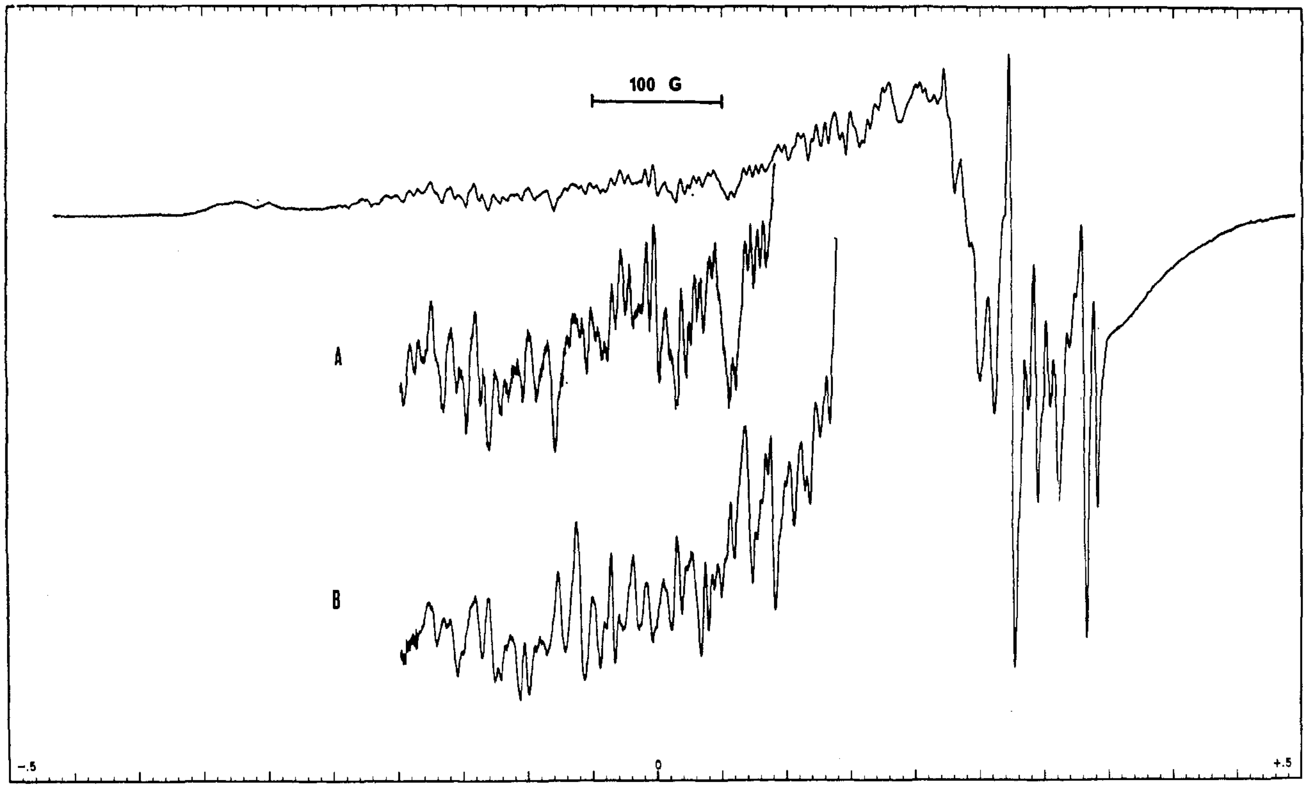

Figure 1.—First-derivative esr spectra of $Cu(dbm)_2$ frozen solutions at 100°K: A, receiver gain 5 times higher than in the upper spectrum; B, rotation of sample tube *ca.* 90° with respect to orientation of trace A.

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[1] Supported by a grant from the Swiss National Foundation for Scientific Research.

[2] H. So and R. L. Belford, *Inorg. Chem.*, **9**, 2194 (1970).

[3] H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967).

[4] H. Fierz and A. von Zelewsky, to be submitted for publication.