BRIDGE—TERMINAL EXCHANGE OF ALUMINUM TRIALKYL DIMERS

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Summary

The kinetic parameters of the bridge—terminal interconversion of triethylaluminum (TEA) in cyclopentane and in toluene as well as of tri-n-propylaluminum (TPA) in cyclopentane are obtained from the total line shape analysis of ^{13}C NMR spectra with proton-decoupling. The enthalpies and entropies of activation of these aluminum alkyls and of trimethylaluminum (TMA) in both solvents are nearly the same, but the interconversion is faster in toluene than in cyclopentane, and also becomes faster as the alkyl chain of the aluminum compounds becomes longer. From these data and the heats of dissociation obtained thermochemically by M.B. Smith [J. Phys. Chem., 71 (1967) 365; J. Organometal. Chem., 21 (1970) 273, 46 (1972) 31 and 211], a possible mechanism of the bridge—terminal exchange is elucidated, in which the exchange proceeds "intramolecularly" for TMA and presumably TEA in cyclopentane. For the aluminum alkyls in toluene and for TPA in cyclopentane, on the other hand, the exchange may proceed "intermolecularly" with only a little contribution from an "intramolecular process".

Introduction

Aluminum trialkyl dimers occupy a unique position in structural chemistry because of their electron deficiency [1], and many spectroscopic studies have been made on these compounds, in which the bridge—terminal exchange in aluminum trialkyls has been studied by PMR spectroscopy [2—9]. Muller and Pritchard [2] first found the bridge—terminal exchange phenomenon in trimethylaluminum (TMA) by PMR, and proposed two possible mechanisms for the exchange as depicted in Scheme 1.

Structure I involves a deformation of the molecule in which no bonds are broken, while structure II requires breaking of one Al—C bond.

Later Ramey and others [4] studied this exchange system quantitatively by PMR and found the enthalpy of activation in the bridge—terminal exchange of TMA in cyclopentane to be 15.6 kcal/mole. They proposed the mechanism via structure II for the bridge—terminal exchange of TMA, from the study of

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SCHEME 1
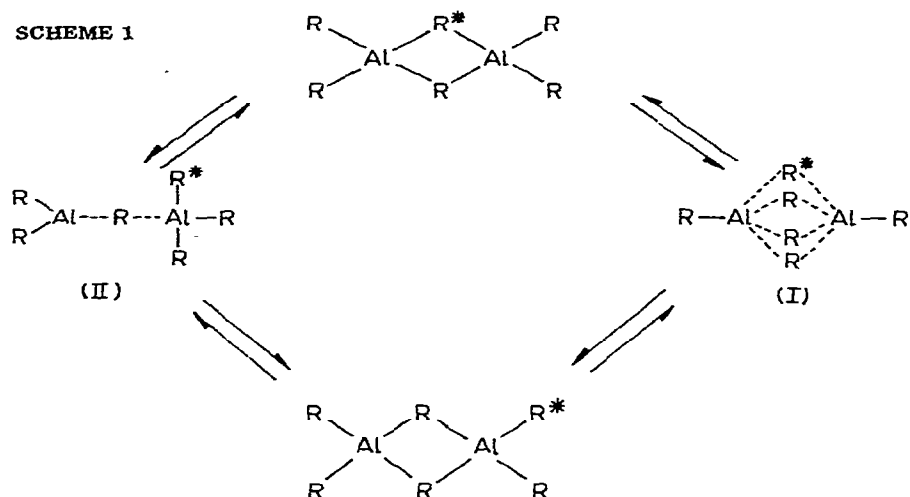
alkyl exchange in mixed aluminum alkyl systems. Williams and Brown [5] proposed another mechanism for the bridge—terminal interconversion from the study of the alkyl exchange between TMA and monomeric trimethyl-gallium and -indium in cyclopentane and toluene. The proposed mechanism assumes solvent-caged monomers through which the alkyl exchange can take place.

Jeffery and Mole [7] also studied the same systems, and generally agreed with Williams and Brown on the mechanism for the bridge—terminal exchange of TMA, although the mechanism for the exchange between TMA and trimethyl-gallium differs in detail from that of Williams and Brown. They assumed a "monomer pair", the role of which is similar to the solvent-caged monomers of Williams and Brown. On the other hand Matteson [8] indicated that for the interpretation of the data obtained for the exchange between TMA and trimethyl-gallium there is no need to rely upon the assumption of a solvent-cage effect. He also suggested that the bridge—terminal interconversion of TMA proceeds by way of complete dissociation to two AlMe$_3$ groups. Later Brown and Murrell [9] supported Matteson's postulate.

Although there are some differences in the mechanism proposed by these authors, recent works are in general agreement that the bridge—terminal exchange of TMA proceeds by an intermolecular rather than an intramolecular process.

Recently Smith [10—13] obtained precise values of heats of dissociation of aluminum trialkyl dimers in aliphatic and aromatic solvents. The heat of dissociation of TMA in the liquid phase obtained by Smith [12] is 19.4 kcal/mole, which is greater than the enthalpy of activation of TMA obtained from PMR by Ramey and others. Since the difference seems to be outside the range of experimental errors, this fact is contradictory to the assumption that the bridge—terminal exchange of TMA in cyclopentane proceeds through completely dissociated monomers. Smith [13] further found that the heat of dissociation of TMA is reduced by about 4 kcal/mole in aromatic solvents. But the enthalpy of activation of TMA in toluene obtained by Williams and Brown [5] is essentially the same as that in cyclopentane. Smith [13] suggested that the mechanisms of the exchange may be different for the two different solvent systems.

Smith [11,12] also obtained the heats of dissociation of triethylaluminum (TEA) in aliphatic and aromatic solvents. These heats are considerably lower than those for TMA, probably because of the bulkiness of the alkyl group. Thus it seemed of interest to obtain the enthalpies of activation for exchange in higher aluminum alkyls from NMR and to compare them with the heats of dissociation obtained thermochemically. PMR spectra of higher aluminum alkyls are complicated due to spin multiplicity [2] and are inconvenient for obtaining the kinetic parameters. On the other hand, ^{13}C NMR (CMR) spectra with proton-decoupling have recently been proved to be very useful for this purpose because of the simplicity of the spectra even for the compounds having many protons coupled with each other [14].

We have obtained the kinetic parameters of the bridge—terminal interconversion of triethylaluminum in cyclopentane and in toluene, as well as of tri-n-propylaluminum (TPA) in cyclopentane from the CMR spectra with proton-decoupling, and we have attempted to define a mechanism which is consistent with all the data obtained by NMR and thermochemical methods.

Results and discussion

Chemical shifts and the general features of the CMR spectra of TEA and TPA

The chemical shifts of TEA and TPA referred to TMS are summarized in Table 1. Reflecting the low electronegativity of the Al atom, the α-carbon signals are at the highest field, in which the signal of the terminal carbon is at a higher field than that of the bridge carbon. For the β-carbon (and also the γ-carbon in TPA) the opposite is true, i.e. the terminal carbon shows its resonance at a lower field side than the bridge carbon. In TPA, the γ-carbon signal is at the lowest field. This assignment was confirmed by the partially decoupled spectra.

Detailed discussion of the chemical shift is not the subject of this paper and will be published elsewhere together with those of the other aluminum alkyl derivatives. Here we merely point out that the chemical shift data in Table 1 suggest the formation of a π-complex of TEA with toluene, because the high field shift of the bridge α-carbon in toluene can be explained in terms of a dona-

TABLE 1

^{13}C CHEMICAL SHIFTS OF TEA AND TPA (ppm)
(referred to TMS) b, bridge; t, terminal

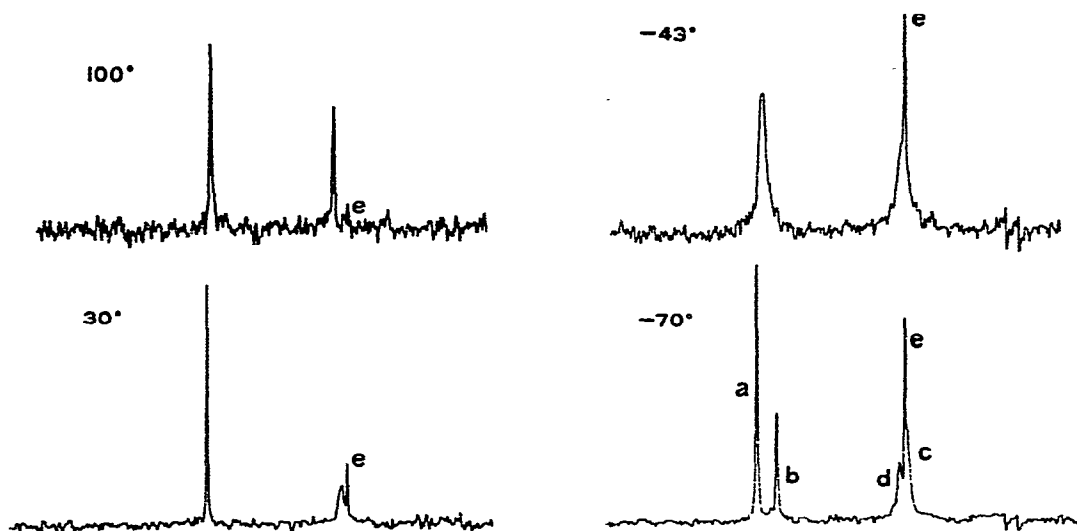| TEA		TPA		In cyclopentane	In toluene
α-CH$_2$	b			1.1	0.5
	t			0.0	0.0
β-CH$_3$	b			8.3	8.2
	t			9.2	9.4
		α-CH$_2$	b	14.0	13.5
			t	12.6	12.5
		β-CH$_2$	b	18.8	18.4
			t	19.6	19.5
		γ-CH$_3$	b	20.5	20.3
			t	21.5	21.3

Fig. 1. CMR spectra of TEA in toluene at various temperatures: (a) terminal CH_3, (b) bridge CH_3, (c) terminal CH_2 and (d) bridge CH_2 carbon signals, and (e) standard TMS.

tion of π-electrons of the solvent to the electron deficient α-carbon. The same trend is also found in the proton spectra [15].

As an example indicating the general features of ^{13}C NMR spectra of aluminum alkyls, Fig. 1 shows a spectrum of TEA in toluene at several temperatures. The line-width of the α-carbon signal is much broader even at room temperature. This is probably due to the residual spin—spin coupling with ^{27}Al, which has spin 5/2, and thus a non-zero quadrupole moment. In the absence o the quadrupole relaxation of the latter nucleus, the ^{13}C NMR signal of the α-ca bon would be a sextet. The multiplet broadens as the quadrupole relaxation ra becomes faster [16]. Higher rates of relaxation cause the multiplet to coalesce into a broad line; the signal becomes a sharp singlet for more rapid relaxation. Thus the signal of the α-carbon is subject to dual broadening effects, i.e. by chemical exchange and by ^{27}Al quadrupole interaction. At about $-40°$, the tw broadening effects are most significant for the α-carbon. When the temperature is raised and the correlation time for molecular rotation becomes shorter to reduce significantly quadrupolar relaxation of ^{27}Al, the α-carbon signal would be a sharp multiplet if the chemical exchange were slow enough. But because the exchange becomes rapid, the α-carbon spins lose their coupling with partic ular spin states of ^{27}Al, which results in the coalescence of the multiplet into a single line. At room temperature this coalescence effect is not yet complete, and the α-carbon signal is much broader than that of the β-carbon which has n spin coupling with ^{27}Al. (The chemical shift differences between the terminal and the bridge carbons are approximately the same for α- and β-carbons, so tha the line broadening of the averaged signals would be about the same for the tw peaks if the α-carbons were not coupled with ^{27}Al.) At $100°$, the rate of the chemical exchange is fast enough to average out the α-carbon signal almost completely, as shown from the approximately equal line-widths of the α- and β-carbons.

As a result of the above considerations, we cannot use the α-carbon signal in the line shape analysis to extract accurate kinetic parameters. Thus only the methyl carbon signal for TEA, and the methyl and β-methylene signals for TPA were used.

Kinetic parameters for the bridge—terminal exchange of TEA and TPA

The line shape analysis was carried out in the conventional method based on the modified Bloch equations [14]. The fits of calculated and observed spectra are satisfactory. As an example, the temperature-dependent line shapes of TPA are given in Fig. 2. The rate constant k is related to the life time τ by equations 1 and 2 [4] where τ_t and τ_b are the mean life times of the carbon atoms at the terminal and the bridge positions, respectively. From the plots the kinetic parameters can be calculated in the usual way and are summarized in Table 2. In Table 2 the heats of dissociation $\Delta H_d^o(l)$ of aluminum alkyls obtained thermochemically by Smith are also listed for further discussion.

$-43.6°$ $k = 1.735$

$-45.0°$ 1.581

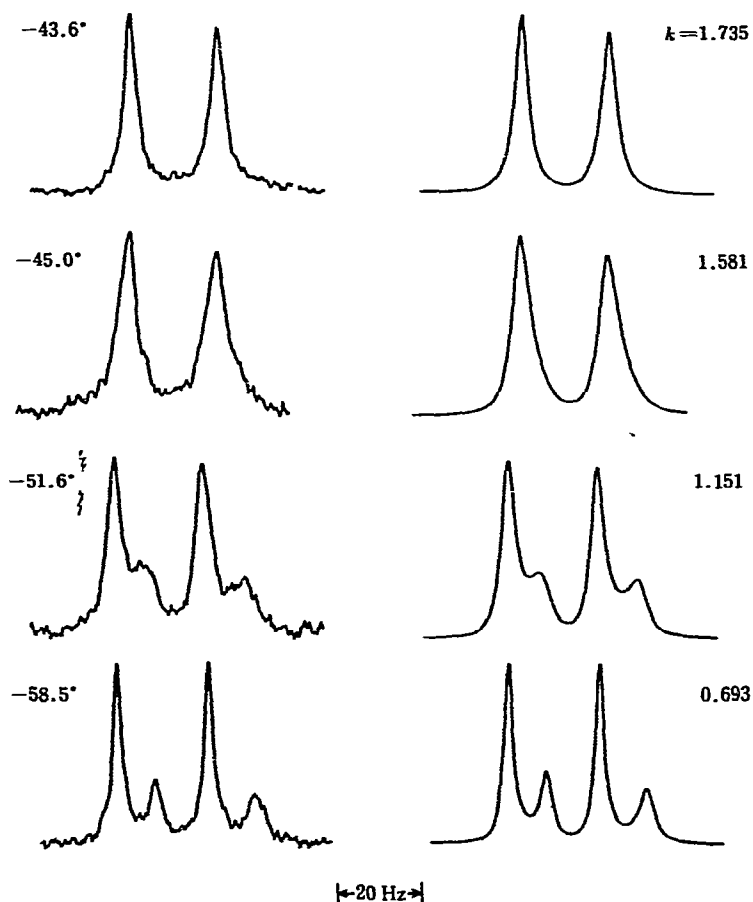$-51.6°$ 1.151

$-58.5°$ 0.693

|←20 Hz→|

Fig. 2. Observed (left) and calculated (right) CMR spectra of TPA in cyclopentane at various temperatures. Left and right signals in a spectrum are those of γ-CH$_3$ and β-CH$_2$ carbons, respectively.

TABLE 2

KINETIC PARAMETERS AND THERMOCHEMICAL DATA FOR TMA, TEA AND TPA

	Solvent	E_a^a	$\Delta H^{\ddagger a}$	$\Delta G^{\ddagger a}$	$\Delta S^{\ddagger a}$	$\Delta H_d^0(l)^b$	$\Delta S_d^0(l)^b$
TMA	Cyclopentane^c	16.0 ± 1.5	15.5 ± 1.5	10.7 ± 0.2	15.9	19.4	29.3
	Toluene^d	15.4	14.8			15.6 ± 1.4^e	
TEA	Cyclopentane	15.4 ± 0.8	14.9 ± 0.8	11.1 ± 0.2	12.6 ± 3.6	16.9	32.2
	Toluene	15.6 ± 0.8	15.0 ± 0.8	10.2 ± 0.3	16.1 ± 3.7	13.6^e	
TPA	Cyclopentane	15.5 ± 1.0	14.9 ± 1.0	10.5 ± 0.3	14.8 ± 4.3		

^{a}kcal/mole and cal mol/K at 298 K. ^{b}Ref.10—13; kcal/mole and cal mol/K, respectively. ^{c}Recalculated from the data of ref.4 to obtain the values at 298 K. ^{d}Ref.5. ^{e}Estimated values according to ref.13.

$$k = \tfrac{2}{3}\tau_e \tag{1}$$

$$\tau_e = \frac{\tau_b \cdot \tau_t}{\tau_b + \tau_t} \tag{2}$$

The kinetic parameters obtained are substantially the same for TEA and TPA in cyclopentane, and TEA in toluene. They are also the same as those for TMA in both solvents reported by the other authors. An inspection of Fig. 3 together with similar plots for TMA in cyclopentane and in toluene shows that the rate of interconversion is faster in toluene than in cyclopentane, and also shows that the rate becomes faster as the alkyl chain becomes longer. Thus the rate of the bridge—terminal exchange depends upon the alkyl chain length as well as the solvent system, while the height of the potential barrier does not.

From Table 2 it is clear that $\Delta H^{\ddagger}$ for TMA in cyclopentane is smaller than $\Delta H_d^0(l)$, the difference of which does not seem to come from experimental errors. On the other hand, $\Delta H_d^0(l)$ and $\Delta H^{\ddagger}$ of TMA are approximately the same in toluene solution. In TEA $\Delta H^{\ddagger}$ and $\Delta H_d^0(l)$ have closer values in cyclopentane, but $\Delta H^{\ddagger}$ is still smaller than $\Delta H_d^0(l)$. In toluene, on the other hand, $\Delta H^{\ddagger}$ is larger than $\Delta H_d^0(l)$. $\Delta H_d^0(l)$ of TPA in an aliphatic solvent is expected to be decreased to the order of 13—15 kcal/mole from the trend of $\Delta H_d^0(l)$ of TMA and TEA, while $\Delta H^{\ddagger}$ obtained for TPA in cyclopentane still remains at about 15 kcal/ mole.

The large values of entropies of activation suggest that the exchange is a dissociative process, but this does not always mean that the process proceeds by way of complete dissociation. A possible mechanism which is compatible with the data hitherto obtained is the assumption of a transition state intermediate between a dimer and a monomer. The transition state may have a looser structure than II described above, or may be expressed as "solvent-caged monomers" [5] or "monomer pair" [7]. In the case of TMA in cyclopentane, the energy level of the monomer [$\Delta H_d^0(l)$] is higher with respect to the dimer level than that of the transition state ($\Delta H^{\ddagger}$), and the bridge—terminal exchange takes place primarily in the transition state. In this case, the process would be predominantly "intramolecular". Even for a much looser structure, i.e. solvent-caged monomers or the like, the process can be said to be "intramolecular" since if the dissociated monomers are formed from a dimer in the solvent cage the same mono-
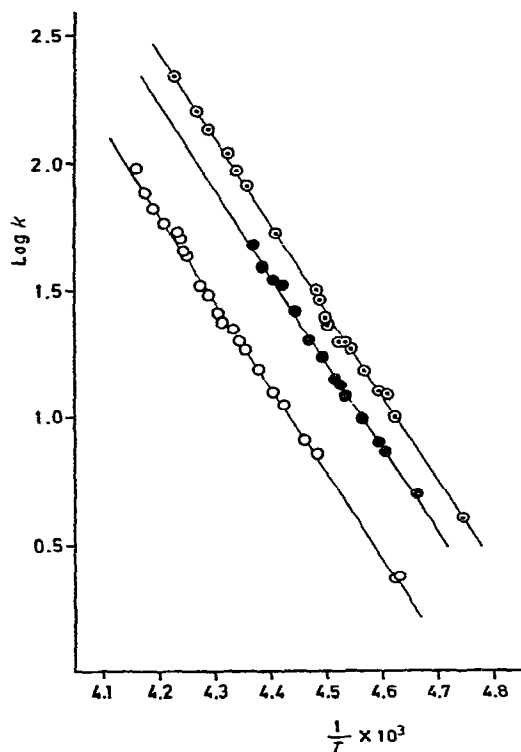
Fig. 3. Arrhenius plots of exchange rates of TEA in cyclopentane (○) and in toluene (◉), and TPA in cyclopentane (●).

mers again recombine to a dimer and other dimers can contribute little to the exchange in the solvent cage.

In toluene solution, the monomers of trialkylaluminum are solvated due to their strong Lewis acid character, so that the monomer energy level with respect to the dimer is lowered by about 3—4 kcal/mole [13]. The dimers are also solvated as indicated by CMR data in this work, but to a much smaller degree (estimated value of the heat of complexation of TEA dimer with mesitylene ≈ —0.4 kcal/mole [13]). The transition state would not be completely dissociated and would be solvated to a much lesser extent than the monomer, thus its energy would not be appreciably lower in toluene. In this case the intermolecular process would also contribute to an appreciate extent. In the transition state, some of the AlR₃ groups may recombine to dimers without going to the monomer level and the alkyl exchange may occur intramolecularly, but a large number of the activated complexes may dissociate to monomers, which, on recombination to dimers, results in an "intermolecular alkyl exchange". In this case the rate of the bridge—terminal exchange may be faster than in the case where there is little contribution of the intermolecular process, as shown from Fig. 3 and the data for TMA [4,5,7].

Lengthening the alkyl group should cause the energy level of the dimer state with respect to the corresponding state of TMA to increase owing to increased bulkiness of the bridging groups. This may be shown, for example, by

the bridge-bonding factor [6] which represents the ratio of the tendency of an alkyl group to occupy the bridge position to that of a methyl group in the mix alkyl aluminum system. In this case the dimer level, as well as that of the trans tion state, will be raised to about the same extent, because some interactions would remain between AlR_3 groups. Thus the heat of activation would be esser tially constant by lengthening the alkyl chain. On the other hand, the rate of interconversion becomes faster as the alkyl chain becomes longer, which seems to reflect changes in the energy level of the transition state.

In conclusion, the bridge—terminal exchange in aluminum trialkyl dimers is a more or less dissociative process through a transition state with a loose stru ture that may be the solvent-caged monomer pair or structure II described earl TMA and presumably TEA in cyclopentane undergo the bridge—terminal exchange "intramolecularly" in the sense that the exchange takes place primarily between one and the same pair of AlR_3 groups even if the monomers were form in the solvent cage, and that this does not mean that the exchange occurs only after the monomers become well separated. On the other hand, the exchange o trialkylaluminum dimers in toluene and probably of TPA in cyclopentane is at least partially "intermolecular" because the monomers are partially stabilized with the solvent or by the bulkiness of the alkyl group, and the solvent-separat monomers can contribute to the exchange. The factor determining which proce is predominant seems to be the stability of a particular monomer in a particula solvent.

Experimental

CMR spectra of aluminum compounds with proton decoupling were obtained at 15.087 MHz on an NV-14 spectrometer of NEVA Co. Ltd., Tokyo, Japan. Six to nine accumulations of the spectra were made by a C-1024 time averaging computer in the CW mode, and the accumulated spectra were punche out on the paper tape through a Talley P-120 high speed puncher by an interface made by Apex Co., Tokyo, Japan. Then the paper tapes were fed into a FACOM 270/30 computer to carry out the line shape analysis for obtaining the exchange rates.

TEA and TPA were commercial samples supplied by Texas Alkyls Inc., U.S.A. After distillation in vacuo, the material was transferred into a high vacuum system, and the sampling was made on the same apparatus to obtain the solution of about 30 vol % of an aluminum alkyl in cyclopentane or in toluene in an 8 mm sample tube.

For cyclopentane solutions the homo-lock mode was adopted with the loc signal of natural abundant ^{13}C of the solvent, while for toluene solutions the deuteromethyl signal of the solvent toluene-d_8 was used as a D-lock signal in the hetero-lock mode.

The line shape analysis was carried out by a Fortran program (EXNMRO) written by the authors [14]. An original signal, obtained in the form of punche paper tape, was fed into the computer, and after SN-enhancement by the matched filter technique [14], was fitted with the calculated spectra in the iter ation mode of the program to obtain the most reliable τ value. In general, the chemical shift of each carbon atom is slightly temperature-dependent. It was

necessary, therefore, to deduce the true chemical shift of each site at any temperature at which the exchange is so fast that only the average value of the chemical shift can be obtained. This was accomplished by extrapolating the chemical shifts of each site at low temperatures, where the exchange is slow enough to obtain the accurate chemical shift values, to the temperature range for the fast exchange rates.

The chemical shift difference between any two exchanging sites is small (ca. 10—15 Hz at 15 MHz) in the aluminum alkyls in CMR spectra, so that a small change in the chemical shift difference will cause a considerable change in τ value, especially at higher temperatures. This would introduce some ambiguity into the τ value obtained in TEA, because only the methyl carbon signal can be used for the line shape analysis. However, careful analysis may overcome this deficiency, and the kinetic parameters obtained seem to be highly reliable. In TPA we have two pairs of exchange sites (i.e. methyl and β-methylene carbons) and thus the ambiguity will be greatly reduced by analysing the line shape over the two pairs of signals simultaneously.

The natural line-width, $1/T_2$, involved in the modified Bloch equations may be introduced so as to obtain the smallest RMS error between the observed and calculated line shapes.

The sample temperatures were determined with a calibrated copper-constantan thermocouple used in conjuntion with a digital voltometer.

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