Use of ^{13}C $T_{1\rho}$ Measurements to Study Dynamic Processes in Solution

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Summary Experimental requirements for making ^{13}C $T_{1\rho}$ measurements for studying dynamic processes in solution and the utility of these measurements are pointed out; the method is used to study internal reorientation of the CHO group of benzaldehyde and *p*-methoxybenzaldehyde, the measurements providing useful exchange rate data some 100—120 K above the coalescence temperature.

It has been pointed out that relaxation effects in the rotating frame are a potentially powerful means of studying dynamic processes in solution.[1] In this regard, ^{13}C $T_{1\rho}$ measurements should be particularly useful, as dynamic processes at many different sites in a molecule can be studied by Fourier transformation of the free induction decay following the spin-locking pulse. Also the contribution to $T_{1\rho}$ from chemical exchange [equation (1)],[2] $T_{1\rho}$ (C.E.), depends on $(\Delta\omega)^2$ (where $\Delta\omega$ is the shift separation in rad s^{-1}); for ^{13}C, this can be large even when working with low field n.m.r. spectrometers. In equation (1), $\tau_e{}^{-1}$

$$[T_{1\rho}(\text{C.E.})]^{-1} = \tfrac{1}{4}\,(\Delta\omega)^2[\tau_e/(1 + \omega_1{}^2\tau_e{}^2)] \qquad (1)$$

is the exchange rate constant, ω_1 the strength of the spin-locking field, and exchange between two equally populated sites is assumed. The contribution from exchange to the measured $T_{1\rho}$ can be found from the measured difference $(T_{1\rho}^{-1} - T_1^{-1})$.† The interesting feature of the method is that it potentially allows the determination of exchange rates significantly faster than can be reliably obtained from high-resolution linewidth or spin-echo measurements.[2] We now point out one vital experimental requirement for high-resolution ^{13}C $T_{1\rho}$ measurements and demonstrate the utility of the technique by measuring the barrier to rotation of the CHO group in benzaldehyde (**1**) and *p*-methoxybenzaldehyde (**2**). For these compounds we demonstrate that $T_{1\rho}$ measurements provide useful exchange rate data some 100—120 K above the coalescence temperature.

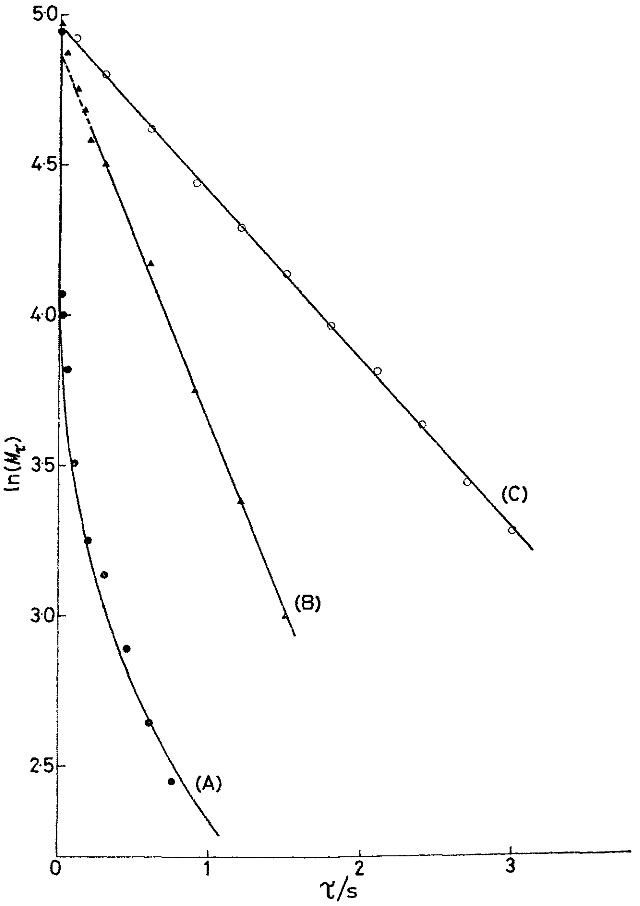

FIGURE 1. Semi-log plot of $\ln(M_\tau)$ *vs.* τ for the carbon resonance of ethylene glycol determined at 22·63 MHz, 300 K, and sample containing *ca.* 20% D_2O under conditions of: (A) Proton heteronuclear decoupling and $\omega_1 = 1{\cdot}74 \times 10^4$ rad s^{-1}. (B) Proton heteronuclear decoupling and $\omega_1 = 4{\cdot}08 \times 10^3$ rad s^{-1}. The 'apparent' $T_{1\rho}$ determined from the solid line is 0·81 s (correlation coefficient for least squares regression 0·999). (C) Decoupler gated off during spin locking pulse and $\omega_1 = 1{\cdot}74 \times 10^4$ rad s^{-1}. $T_{1\rho}$ is 1·80 s (correlation coefficient 1·000). In all cases, the carrier is set 73 Hz off-resonance. T_1 is measured as 2·01 s.

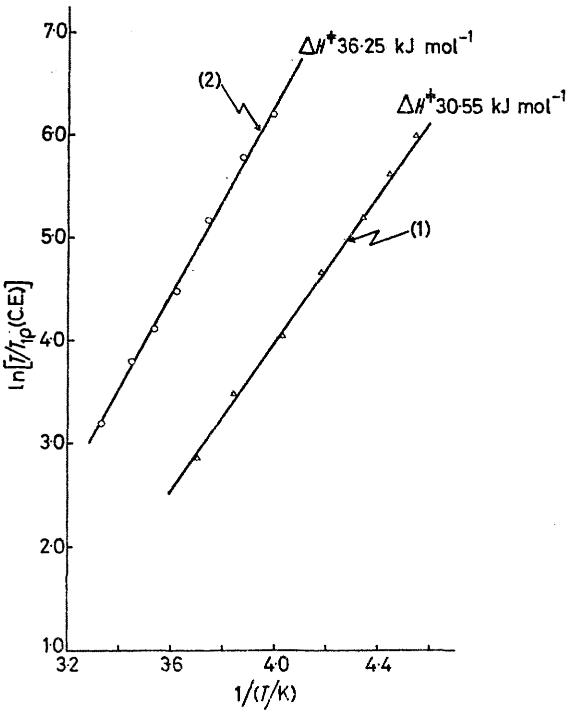

FIGURE 2. Semi-log plots of ln $[T/T_{1\rho}(\text{C.E.})]$ *vs.* T^{-1} for C(2) resonance of benzaldehyde (**1**) (correlation coefficient 1·000), and *p*-methoxybenzaldehyde (**2**) (correlation coefficient 0·99).

Instrumentally the $T_{1\rho}$ pulse sequence is well known,[3] but for ^{13}C studies in particular, there have been very few $T_{1\rho}$ measurements reported and it is not appreciated that the use of proton heteronuclear decoupling, a requirement for obtaining simplified ^{13}C spectra, introduces experimental difficulties. However, Freeman and Hill alluded to these problems in their reports on ^{13}C T_2 measurements;[4] briefly, the problem arises from magnetic resonances in the rotating frame[5] where 'stirring' of the proton spins results in rapid (and often non-exponential) relaxation of the ^{13}C

TABLE. Temperature dependence of T_1 and $T_{1\rho}$ (in s) for the C(2) resonance in benzaldehyde and *p*-methoxybenzaldehyde.

Benzaldehyde			*p*-Methoxybenzaldehyde[a]		
T/K	T_1	$T_{1\rho}$	T/K	T_1	$T_{1\rho}$
220	1·11	0·37	240	0·73	0·19
230	2·08	0·79	250	1·05	0·34
240	2·81	1·29	260	1·45	0·65
250	3·43	2·06	270	1·97	1·04
260	4·46	2·96	280	2·65	1·65
270	5·61	4·09	290	3·35	2·24
290	8·03	6·76	300	3 93	2·97
Coalescence temperature[b]					
	168			213	

[a] C(2) is *ortho* to the CHO group. [b] Ref. 7.

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† This analysis assumes that chemical exchange is the only contribution to $T_{1\rho}$. Although this is a reasonable assumption here, in general, $T_{1\rho}$ should be measured as a function of applied field strength to determine the chemical exchange contribution. Accordingly, we have developed the instrumental capabilities[6] to perform 10·45 MHz ^{13}C $T_{1\rho}$ measurements as a complement to the 22·63 MHz measurements reported herein.

spin *via* scalar coupling.[6] Accurate ^{13}C $T_{1\rho}$ measurements can only be performed by gating the decoupler *off* during the spin locking pulse. Figure 1 summarises measurements on ethylene glycol illustrating the difficulties.

In the table we list T_1 and $T_{1\rho}$ values for the C(2) carbon resonances of (**1**) and (**2**) obtained as a function of temperature and Figure 2 shows a plot of ln $T(T_{1\rho}^{-1} - T_1^{-1})$ *vs.* T^{-1}. We obtained $\Delta H^{\ddagger}$ values of 30·55 and 36·25 kJ mol^{-1} for (**1**) and (**2**), respectively, in good agreement with previous measurements.[7] The significant experimental observation (Table) is that experimentally meaningful exchange rate data are obtained some 100—120 K above the coalescence temperature.

It is clear that ^{13}C $T_{1\rho}$ measurements properly performed will be an important means of probing low-energy dynamic processes in solution.

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