Comparison of the proton and carbon lanthanide-induced shifts for isoborneol is most informative. A reasonable chemical-shift correspondence between nuclei in similar geometric positions relative to europium evidences that the lis experiment is dominated by a pseudocontact phenomenon governed by an equation of the form[8,9]

$$A = a + \frac{3\cos^2\theta - 1}{3r^3}(g_{\parallel} - g_{\perp})\beta g_N \beta_N \qquad (1)$$

where A is the observed contact shift. When scalar coupling a is small, A is directly proportional to the gyromagnetic ratios of interacting nuclei and is usually referred to as the pseudocontact shift. If A is expressed in field-independent units (parts per million) and if axial symmetry about europium is maintained, then values for all nuclei are predicted and observed to be proportional to $\langle 1/r^3 \rangle$. Deviations between ^{13}C and ^{1}H shifts in isoborneol would arise from small differences in position relative to europium. This demonstrated effect should be quite general for all similar multinuclear nmr experiments.[8]

In summary, apnmr supplies ^{13}C spectra with improved sensitivity, while retaining and measuring *all, true* ^{13}C–H coupling constants and directly identifying methyl, methylene, methine, or quaternary carbons. Lis methods apply to cmr and provide spectra which, when compared with proton lis spectra, can facilitate assignment of ^{13}C resonances. In particular, the two nearly equivalent geminal methyl signals and the quaternary carbons of isoborneol were assigned. We further note that selective decoupling of dispersed proton resonances while observing the ^{13}C lis spectrum simplifies measurement of ^{13}C–H coupling constants. The apnmr–lis methods in conjunction are new and most powerful tools for structure determination.

Acknowledgment. The authors acknowledge research support from the Robert A. Welch Foundation.

[8] Implicit in this statement is that the McConnell relationship (eq 1) holds. Herein, we suggest only that its validity is sufficient to permit use of lis reagents in cmr.

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Rate Processes and Carbon-13 Magnetic Resonance Spectra. Hindered Internal Rotation of *N,N*-Dimethyltrichloroacetamide

Sir:

Carbon-13 magnetic resonance (cmr) is a well-established method for determination of molecular structure in solution.[1] However, no studies have as yet been performed to investigate the utility of cmr techniques for study of rates of fast chemical exchange processes although such applications of proton magnetic resonance (pmr) are common.[2] Perhaps the most often and accurately studied exchange reaction is hindered internal rotation about carbon–nitrogen bonds in substituted acid amides.[3] One particular molecule, *N,N*-dimethyltrichloroacetamide, has proven most amenable to pmr studies. The presence of only protons participating in chemical exchange allows use of spin–echo as well as high-resolution nmr to determine the energy barrier to internal rotation.[4] This, together with the presence of two carbon atoms exchanging between two chemically different sites, let us initiate this, the first reported cmr study of a kinetic process. We wish to demonstrate that cmr methods are at least as useful as pmr techniques in that nmr signal-shape analysis following the Gutowsky–Holm formulation[5] provides rate constants and activation energies at least as accurately as pmr studies and that, in many cases, cmr studies will prove more accurate than pmr studies.

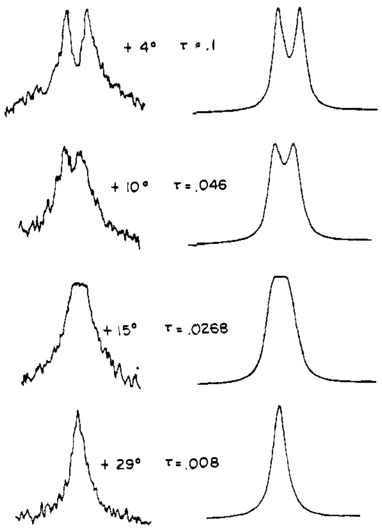

Figure 1. Actual and computer-simulated carbon-13 nmr spectra of the methyl reasonances of *N,N*-dimethyltrichloroacetamide at several temperatures (°C). The τ values reported are obtained from computer-simulated signal-shape analysis.

Measurements of ^{13}C spectra were performed operating a Brücker HFX-10 nmr spectrometer at 22.6 MHz using the usual Fourier transform signal enhancement methods[6] in conjunction with broad band proton decoupling.[7] Solutions were 70% DMTCA-30% 1,2-dibromotetrafluoroethane (DFTE), the latter serving as an 84-MHz ^{19}F lock signal. Sample temperature was measured by directly inserting a small thermometer into the 10-mm diameter sample tube spinning in a dewared insert. A thermocouple fixed near the bottom of the freely rotating sample tube serves to regulate a flow of cooled nitrogen gas. Control of temperature was accurate to ±0.5°. A similar 10-mm insert was used for proton measurements at 90 MHz. Our 60-

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Table I. Rate Constants and Activation Energies for Hindered Internal Rotation of *N*,*N*-Dimethyltrichloroacetamide as Determined by Proton and Carbon Magnetic Resonance

Field strength, MHz, nucleus	Method	Solvent	E_a, kcal/mol	T_c,[b] °C	$\Delta F^{\ddagger}(T_c)$,[c] kcal/mol	$k(T_c)$, sec^{-1}
60, proton	Ss[a]	30% DFTE[f]	16.4 ± 0.8	13	17.5	0.027
90, proton	Ss	30% DFTE	17.4 ± 0.8	~21	18.3	0.0168
22.6, carbon	Ss	30% DFTE	16.6 ± 0.8	15	17.6	0.0268
26.9, proton	Se	Neat	14.6 ± 0.6	~18.5	18.0[d]	0.0167[e]

[a] Ss = signal-shape analysis. Se = spin echo. [b] T_c = coalescence temperature. [c] $\Delta F^{\ddagger}$ = free energy calculated at coalescence temperature. [d] Calculated using rate constant at 17° obtained from spin-echo measurements; ref 4. [e] Rate constant at 17° from spin-echo measurements; ref 4. [f] DFTE is 1,2-dibromotetrafluoroethane.

MHz pmr spectra were observed on a Varian A-56/60 spectrometer with a calibrated "standard" methanol sample used to determine temperature. The DMTCA was prepared and purified according to Brintzinger's method.[8]

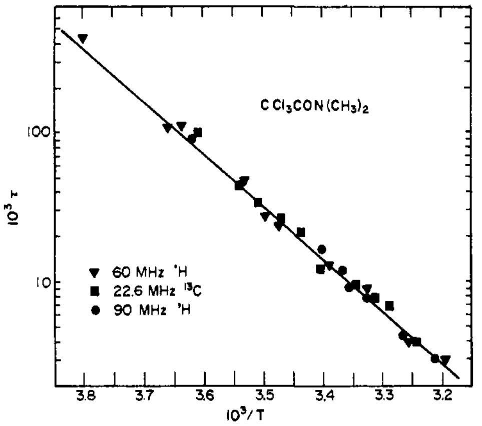

Figure 2. Arrhenius activation energy plot for hindered internal rotation of *N*,*N*-dimethyltrichloroacetamide. The τ values are relaxation times measured from computer-fitted 60-, 90-, and 22.6-MHz spectra.

Proton and carbon spectra were obtained throughout the temperature range −10 to +50°. Several actual and computer-simulated cmr spectra from which reported relaxation times (τ) were determined are presented for comparison purposes in Figure 1. Rate constants, $k = 1/2\tau$, and activation energies listed in Table I were calculated using multiple linear regression analysis program No. 1971A on a Wang 700 programming calculator.

Free energies of activation, ΔF, were obtained from exchange rates at pmr, cmr coalescence temperatures and compare quite well with those measured from spin-echo nmr by Allerhand and Gutowsky. Agreement among pmr and cmr activation energies measured in this work is excellent and is within 10% of the spin-echo value measured for neat DMTCA. Figure 2 is an Arrhenius plot of all data measured at 60, 90, and 22.6 MHz, which firmly establishes the validity of cmr as a method for kinetic studies.

Several experimental caveats are necessary. First, spectra reported are presently the absolute limit of cmr sensitivity. Several thousand repetitive pulses were necessary. We anticipate the need to use ~10% ^{13}C-enriched materials for other measurements. Secondly, as lines broaden or as measurements are performed at higher temperatures on, for example, *N*,*N*-dimethylformamide (DMF), sensitivity drops dramatically for two reasons: (a) Boltzman populations readjust, (b) large, low-temperature shift differences between the two methyls of DMF (5.3 ppm) cause broadening and coalescening over a large spectral area. Large shift differences make data collection more difficult, but the wider temperature range over which cmr data may be obtained will provide activation energies more accurate than those obtained by pmr methods.

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Crystal Structure of Potassium Tris(oxalato)rhodate(III)

Sir:

We have undertaken the determination of the structure of $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$ in order to establish whether all oxalato groups are bis chelated or, as some earlier studies seemed to indicate, the complex should be written as $K_6[Rh(C_2O_4)_3][Rh(C_2O_4)_2(C_2O_4H)(OH)]\cdot 8H_2O$. The latter formulation denotes that one oxalato group per two Rh(III) centers is singly bonded to rhodium, the remaining coordination site being occupied by a hydroxyl group or by a water molecule. This formulation was suggested (a) by a study of the solid-state broad-line proton magnetic resonance spectrum,[1] in which certain peaks, at temperatures varying from −196 to 45°, were assigned to protons in waters (or hydroxyls) directly coordinated to the rhodium center; (b) by dehydration data;[1] and (c) by consideration of the kinetics of the oxalate exchange and aquation reactions of the complex in solution, in which a monoaquated tris(oxalato)rhodate(III) ion was postulated to preexist.[2] More recent support for a dangling oxalate in the solid was cited by Gillard, *et al.*,[3] who interpret their dta curves at 200° in terms of the removal of one-half of a constitutional water molecule per Rh.

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