Additional and subsequent measurements in this laboratory have shown that the value of M_0 is mainly determined by two factors: (1) the signal-to-noise of the initial point of the FID and (2) the accuracy of the rf phases. Furthermore, when larger data averagings are used to improve $(S + N)/N$ and rf phases are critically adjusted, the value of this dc offset is reduced substantially.

Finally, Table II contains the ^{29}Si chemical shifts of silyl ether model compounds and other compounds used in this research. Nuclei were excited via the JCP technique. The values of shifts are tabulated with respect to Me_4Si_2 and negative shifts are downfield.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division under contract No. W-7405-eng-82.

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Determination of NMR Spin Coupling Constants Using *J*-Cross Polarization. A Comment on "*J*-Cross Polarization in Silanes" [1]

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Received February 9, 1979

Abstract: In NMR, a coupled I and S spin system can interchange polarizations by *J*-cross polarization (JCP). If the S spectrum is observed without I decoupling, the relative phases of the lines within the S multiplet vary with cross-polarization time. A PCJCP sequence (phase corrected *J*-cross polarization) is demonstrated which removes the phase variation; this facilitates determination of the spin coupling constant *J* directly from the cross-polarization spectrum.

Introduction

To scrutinize the theory of the transfer of spin polarization during *J*-cross polarization, Murphy[1] et al. (preceding paper) extract the NMR spin coupling constant *J* by curve fitting their experimental data to the theoretical relation. They find good agreement and are able to infer the magnitude of Hartmann-Hahn[3] mismatch from their effective value of *J*. They hasten to add that such a procedure can be time consuming when contrasted to the more conventional determination of *J* and recommend using *J*-cross polarization without (I) spin decoupling at a single value of cross-polarization time τ.

We have found[4] certain complications when the S cross-polarized magnetization is observed without decoupling. In the coupled spectrum (i.e., without I decoupling), during cross polarization the magnetization associated with each line in the S multiplet does not necessarily grow just along the rf axis. In fact, the magnetization is complex, with a longitudinal component along the rf axis and a transverse component perpendicular to both the rf and static field B_0 directions. The transverse magnetization arises from correlations between the I and S polarizations. We find that, for $I = 1/2$, the transverse components are equal and opposite for S resonances associated with up and down I spins;[4] that is, the respective upfield and downfield lines have equal and opposite transverse magnetizations. These transverse components will cancel under I decoupling but manifest themselves in the coupled spectrum as phase shifts of the multiplet resonance lines which are, in general, dependent on cross-polarization time τ.

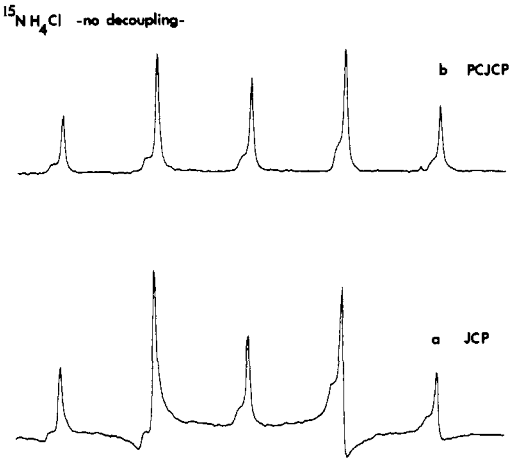

Figure 1. ^{15}N resonance via the JCP pulse sequence with τ = 4 ms in aqueous NH_4Cl. No proton decoupling is used during signal acquisition. In the conventional JCP experiment (a), the relative phases of the lines in the multiplet vary with cross-polarization time τ. In PCJCP at the end of the cross-polarization process, application of an additional $\pi/2$ pulse to I spins (as in (b)) or S spins removes the out-of-phase component so that the relative phases are independent of cross-polarization time. This facilitates measurement of spin coupling constant *J* with the PCJCP sequence. Note also that, in JCP and PCJCP, the multiplet amplitudes are not in the usual quintet ratio of 1:4:6:4:1. In (b) the I extension pulse is in phase with the I cross-polarization rf; if the extension pulse is shifted by 90°, the multiplet amplitudes are altered from (b) but their phases are still independent of τ.

Results and Discussion

Such a phase shift makes it difficult to measure J from the coupled spectrum. We report here a simple means for removing this phase shift, so that all lines in the multiplet have identical phase. The modification, called by the palindrome PCJCP (phase corrected J-cross polarization), consists of the conventional JCP sequence[1,5,6] in which either the I or S spin locking rf field remains on an additional time t_{90} given by $\gamma_S B_{1S} t_{90} = \gamma_I B_{1I} t_{90} = \pi/2$. As usual, $\gamma_{I,S}$ is the magnetogyric ratio and $B_{1I,S}$ is the rf field strength for the nuclear species I,S. To the extent that it is instantaneous, the S extension pulse flips the transverse S magnetization into the direction of the static field, where it is unobservable. An I extension pulse, either in phase or in quadrature with the cross-polarization rf, can also be used; the explanation in this case is more involved and will appear elsewhere.[4] The operation of this sequence is shown in Figure 1. During cross polarization the multiplet lines grow at different rates[4] and the conventional multiplet intensity ratios are not preserved either in JCP or PCJCP.

The ease of operation suggests that, for a weak resonance of unknown J, one should use a reasonable guess for the cross-polarization time τ to produce a coupled cross-polarization spectrum by PCJCP. The value of J determined is then used to select an optimal τ for maximum cross-polarization signal.

The PCJCP sequence is best used near resonance ($|\omega_0 - \gamma B_0| \ll \gamma B_1$). Operating significantly off resonance introduces amplitude asymmetries in the S multiplet which the $\pi/2$ extension pulse will convert back into phase shifts. In a reciprocal manner, any phase shifts initially present will, under off-resonance operation, be converted by the pulse extension into an asymmetry in the multiplet.

Acknowledgments. Professor B. C. Gerstein and co-workers kindly provided preprints of their results.

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Liquid–Solid–Liquid Triphase Catalysis. Consideration of the Rate-Limiting Step, Role of Stirring, and Catalyst Efficiency for Simple Nucleophilic Displacement[1]

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Abstract: The kinetics of the triphase catalyzed displacement of chloride ion on n-decyl methanesulfonate employing a series of 1% cross-linked polystyrene resins having pendant tri-n-butylphosphonium groups has been investigated. The rate of displacement (1) exhibited a pseudo-first-order dependency on the mesylate concentration, (2) was directly proportional to the amount of catalyst used, (3) was independent of stirring, (4) was characterized by a free energy of activation of ~30 kcal mol^{-1}, and (5) depended on the catalyst-ion concentration in the resin. In addition, reaction was favored at the external portion of the bead. Taken together, these observations provide strong support that a diffusion-limited chemical reaction is the rate-controlling step. When large quantities of polymer were employed, stirring was needed to increase resin contact with the liquid–liquid interface. Consideration of apparent activation energies, and absorption of n-decyl methanesulfonate in the catalysts, supports the conclusion that inefficient use of ionic sites dispersed throughout the resins is responsible for the low activity observed.

Introduction

The use of solid-phase catalysts to accelerate reaction between substances located in organic and aqueous phases (triphase catalysis, TC) is now well established.[2,3] Based on this technique new and attractive synthetic procedures have become available for nucleophilic substitution, dihalocarbene generation, oxidation, and reduction. Simple nucleophilic displacement has received the greatest attention and, in general, reaction rates under triphase catalytic conditions are lower than those for comparable biphase catalytic processes (e.g., phase-transfer catalysis).[4,5] In order to be able to design more active triphase catalysts, it is essential that the rate-controlling step be identified for each particular system. This has not been done in any of the studies reported thus far.

In principle, the rate-limiting step for TC using polymeric catalysts should be (a) diffusion of reactants across a thin liquid layer surrounding the solid phase (Nernst or film diffusion), (b) chemical reaction at the particle surface, or (c) chemical reaction throughout the polymer matrix. If the rate of chemical reaction is much greater than the diffusion of reactants through the Nernst layer, (a) will control the rate. If chemical reaction is much slower, then the rate would be controlled by either (b) or (c). When diffusion of reactants through the resin (matrix diffusion) is very slow relative to chemical reaction and film diffusion is rapid, chemical reaction taking place at the particle surface controls the rate; if matrix diffusion is fast, chemical reaction occurs uniformly throughout the polymer. Finally, when the rate of matrix diffusion is similar to that of chemical reaction, a diffusion-limited chemical reaction is rate determining.

In the present work we have examined in detail the kinetic features of the triphase catalyzed chloride ion displacement

0002-7863/79/1501-4059$01.00/0