and direct the stereochemistry of a reaction. Thus, the nature of the ligands in a chiral complex could have a profound effect on its chiroptical properties.

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Registry No. **1**, 80422-24-8; **2a**, diasteriomer A, 80422-25-9; **2a**, diasteriomer B, 80446-90-8; **2b**, 80422-26-0; **2c**, 80422-27-1; **3**, diasteriomer A, 80422-29-3; **3**, diasteriomer B, 80446-92-0; **4**, 80422-30-6; **5**, diasteriomer A, 80422-31-7; **5**, diasteriomer B, 80446-93-1.

Long-Range Proton–Carbon-13 NMR Spin Coupling Constants

Ad Bax

Department of Applied Physics
Delft University of Technology
Delft, The Netherlands

Ray Freeman*

Physical Chemistry Laboratory
Oxford University, Oxford, England

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We propose a new NMR technique for the detection and assignment of long-range proton–carbon-13 spin coupling constants. It is based on an existing two-dimensional Fourier transform[1,2] experiment which detects carbon-13 spin echoes modulated by heteronuclear spin–spin coupling,[3-5] but it uses a frequency-selective 180° radio frequency pulse applied to an isolated proton resonance. The resulting carbon-13 spin multiplets are simple, well-defined, and readily assigned, and the sensitivity of this experiment can be higher than in the corresponding conventional proton-coupled carbon-13 spectrum. The technique provides precise measurements of long-range CH couplings, useful for studies of molecular conformation and for the assignment of carbon-13 spectra, particularly the quaternary sites.

Spin echoes are modulated by spin–spin coupling provided that both coupled spins experience the effects of the 180° refocusing pulse.[3-5] This phenomenon permits proton–carbon couplings to be separated from carbon-13 chemical shifts[6-8] by making use of the extra frequency dimension provided by two-dimensional Fourier transform NMR spectroscopy. A carbon-13 spin echo is generated at the end of a variable evolution period (t_1) and the second half of the echo detected under conditions of broadband proton decoupling. The new frequency dimension (F_1) displays the fine structure due to all the proton–carbon couplings.

The innovation is to make the 180° proton pulse frequency selective (Figure 1) by reducing its intensity ($\gamma B_1/2\pi = 25$ Hz) and increasing its duration (20 ms).[9,10] Its effectiveness for spin inversion is thereby restricted to a frequency range of the order ±25 Hz about the exact resonance condition for a chosen proton so that the outer satellite lines due to $^1J_{CH}$ are unaffected while the inner satellites due to long-range coupling are inverted. The proton site is selected so as to have a resonance frequency well separated from other proton lines, usually at least 50 Hz away. Thus only long-range couplings to this chosen proton modulate the carbon-13 spin echo, and there is *only one* such splitting on each carbon-13 resonance. No large one-bond CH couplings are involved so that very fine digitization can be used to display these spin multiplets, giving precise values for the long-range couplings. The process is then repeated to characterize long-range coupling to another proton site.

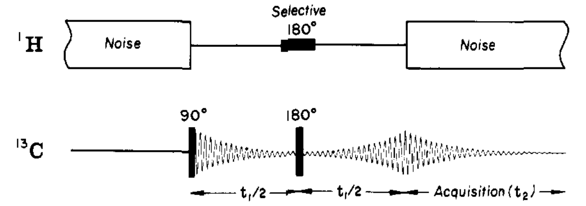

Figure 1. Pulse sequence used to detect long-range CH couplings.

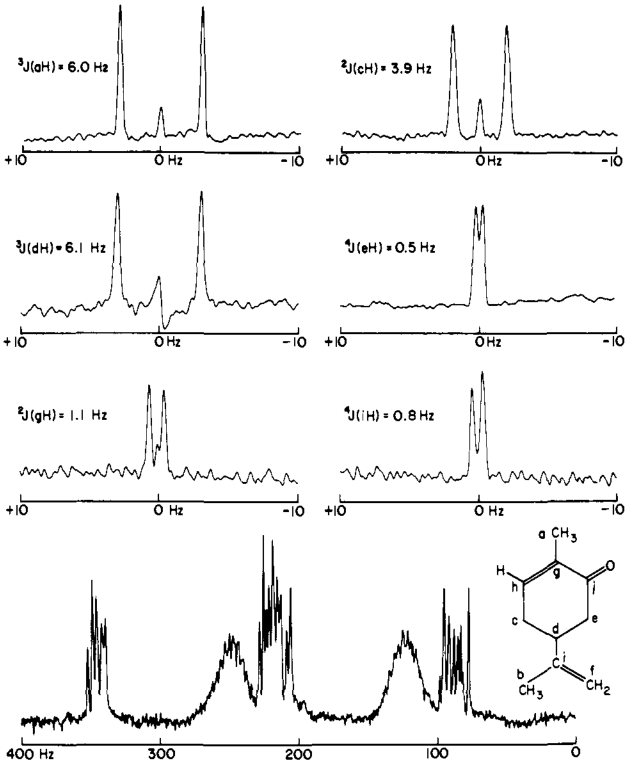

Figure 2. Long-range CH couplings observed between the various carbon sites of carvone (inset) and the proton at site h. The bottom trace shows the conventional proton-coupled carbon-13 spectrum for sites d and e obtained in the same total experimental time.

The pulse sequence (Figure 1) contains a preparation period for establishment of a nuclear Overhauser enhancement (8 s in practice) followed by a variable evolution period incremented in 64 equal steps up to a maximum of 3.2 s, giving a spectral width in the F_1 dimension of ±10 Hz. After the first Fourier transformation the data matrix contains useful information only at the carbon-13 chemical shift frequencies, known from an earlier conventional spectrum; the second Fourier transformation is therefore restricted to these sections through the data matrix, thus displaying only those F_1 traces which carry the desired coupling information. A complete two-dimensional spectrum is not computed.

Carbon-13 spectra were recorded at 50 MHz on a Varian XL-200 spectrometer, using carvone (Figure 2) to illustrate the technique, concentrating on the long-range CH couplings to the proton at site h. The assignment follows Bohlmann et al.[11]

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Resolution enhancement by Lorentzian to Gaussian conversion[12] was employed in the F_1 dimension, sacrificing some sensitivity but giving line widths of less than 0.5 Hz. Six long-range couplings are evident in Figure 2, any others being judged to be less than about 0.2 Hz from the absence of broadening on the appropriate carbon-13 resonances. The weak artifacts at $F_1 = 0$ are due to pulse imperfections and the tails of nearby carbon-13 lines. An indication of the complexity of the conventional proton-coupled carbon-13 spectrum is provided by the multiplets from sites d and e (bottom trace).

Although two-dimensional spectra may have somewhat poorer sensitivity than the corresponding one-dimensional spectra acquired in the same total time,[13] this is more than offset in the present experiment by the considerable reduction in the number of times a given carbon-13 resonance is split. However, a single two-dimensional experiment of this kind measures long-range coupling to only one proton site, so the experiment may need to be repeated, and not all proton sites are necessarily accessible. Strong coupling effects are evident in the conventional carbon-13 spectrum (particularly at the methylene sites), but it is expected that the corresponding distortions of the two-dimensional spectrum will be less serious since only one proton is flipped.[14] Nevertheless, care should be exercised in interpreting the observed CH splittings when the protons are strongly coupled.

The proposed technique looks promising for precise measurements of long-range heteronuclear spin–spin coupling constants and for their assignment. The key factor is the simplicity of the multiplets (doublets, triplets, quartets) since each long-range coupling is displayed separately. Sensitivity can be higher than the conventional proton-coupled spectrum.

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Registry No. Carvone, 99-49-0.

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Bridging the Gap between the Gas Phase and Solution: Transition in the Kinetics of Acid–Base Reactions

Diethard K. Bohme,* Asit B. Rakshit, and
Gervase I. Mackay

Department of Chemistry, York University
Downsview, Ontario M3J 1P3, Canada

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Recent gas-phase investigations of ion–molecule reactions have provided an important new dimension to the acid–base chemistry of anions in solution; it has become possible to execute solution acid–base reactions of type 1 in the complete absence of solvent

$$B^- + AH \rightleftarrows A^- + BH \qquad (1)$$

and to scrutinize the influence of solvent as a function of stepwise solvation with studies of reactions of type 2. Equilibrium constant

$$B^-{\cdot}S_n + AH \rightleftarrows A^-{\cdot}S_n + BH \qquad (2)$$

measurements for reactions of type 1 have allowed the determination of relative intrinsic acidities of molecules[1] whereas similar measurements for reactions of type 2 have provided a means to follow changes in relative acidities with added solvent.[2] Here we report the first attempt to follow systematically the transition in the *rate* of acid–base reactions which ensues from the stepwise solvation of B^-. Hydrated hydroxide ions and methoxide ions solvated with methanol were chosen for study because of their importance as bases in solution. Their gas-phase reactivities are followed from the total absence of solvent to solvation with up to three molecules of solvent. The acids chosen as substrates have allowed us to establish trends in reactivity when relative acidity is preserved and to observe the abrupt change in rate which accompanies a reversal in relative acidity upon solvation.

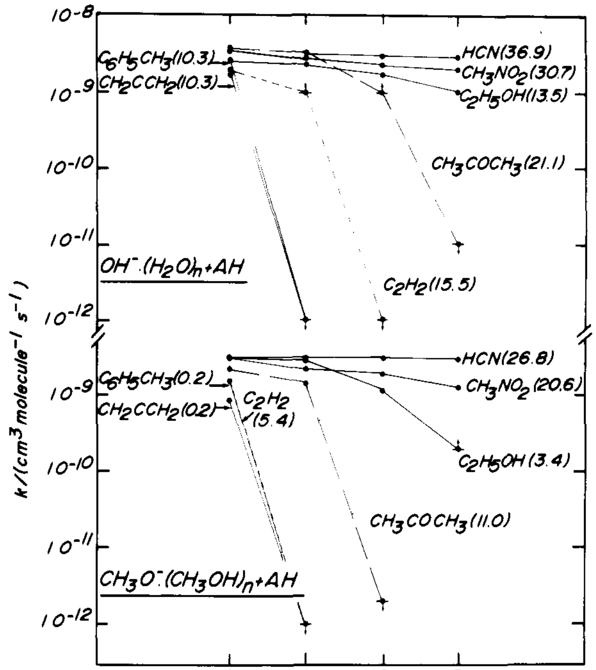

Figure 1. Observed variations in the rate constants at 298 K for acid–base reactions in the gas phase between the acids AH = allene, toluene, ethanol, acetylene, acetone, nitromethane, and hydrogen cyanide and hydrated hydroxide ions (top) and methoxide ions solvated with methanol (bottom). The reactions with acetone and hydrogen cyanide in the upper graph involve $OD^-{\cdot}(D_2O)_n$. The accuracy of the rate constants is better than ±50%. The values indicated in parentheses correspond to the relative intrinsic acidities, in kcal mol^{-1}, i.e., $-\Delta G°$ for the solvent-free reactions at 298 K. For all of the reactions with $k \geq 10^{-10}$ cm^3 molecule^{-1} s^{-1}, formation of product ions of the type $A^-{\cdot}S_n$ was observed concomitant with the disappearance of the reactant ions $OH^-{\cdot}(H_2O)_n$ or $CH_3O^-{\cdot}(CH_3OH)_n$.

The measurements were carried out with the flowing afterglow technique.[3] Hydroxide (or OD^-) ions and methoxide ions were generated by electron impact on H_2O (or D_2O) and CH_3OH upstream in a flowing He or H_2 plasma at total pressures of ca. 0.4 torr. The ions were solvated by reactions of type 3 and

$$B^-{\cdot}S_n + S + He(H_2) \rightarrow B^-{\cdot}S_{n+1} + He(H_2) \qquad (3)$$

thermalized by collisions with the buffer molecules prior to the reaction region. Partial pressures of added solvent were in the range 0.005–2 mtorr. The decays of the $B^-{\cdot}S_n$ ions and the formation of the $A^-{\cdot}S_n$ ions were monitored as a function of the additon of AH (in order of increasing intrinsic acidity): allene, toluene, ethanol, acetylene, acetone, nitromethane, and hydrogen cyanide. Rate constants were derived in the usual manner from the observed decays of $B^-{\cdot}S_n$.[4] The results are indicated in Figure 1.

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[4] The initial relative population of the cluster ions, $B^-{\cdot}S_n$, was dependent on the amount of added solvent vapor. Complications which arose due to the depletion of the precurser ions, $B^-{\cdot}S_{n-1}$, were taken into account in the analysis of the decay of $B^-{\cdot}S_n$. Also contributions to the measured ion signals due to the presence of the impurity ions $^{35}Cl^-{\cdot}(H_2O)_{n-1}$ were taken into account in the measurements of $OH^-{\cdot}(H_2O)_n$; the $^{37}Cl^-{\cdot}(H_2O)_{n-1}$ signals were measured concomitantly.

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