However, the reaction is synthetically useful in that it provides a convenient high yield route to the tetraselenometalates and their derivatives.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are grateful to Jim Ibers for preliminary communication of results.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles of all atoms, anisotropic thermal parameters, and H atom coordinates for $[(C_6H_5)_4P]_2[MoSe_4]$, $[(C_6H_5)_4P]_2[WSe_4]$, and $[(C_6H_5)_4P]_2[MoSe_9]$ (3 pages); listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

Intramolecular Exchange Effects in Multiple Quantum Spectroscopy

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Received October 27, 1987

The effects of exchange processes in high resolution NMR spectroscopy have been investigated extensively, from both a theoretical and an experimental standpoint.[1] The sensitivity of NMR spectroscopy to exchange effects has provided a very powerful means to elucidate the exchange pathways and measure the rates for various types of chemical reorganization processes; NMR techniques which have been employed include line shape analysis,[2] double resonance methods such as saturation transfer,[3] pulse experiments such as spin echo studies,[4] and two-dimensional exchange spectroscopy.[5] In the present communication, we would like to take a different perspective and demonstrate a possibility for recovering spectral information which is often lost due to exchange effects; this method is based on the insensitivity of certain multiple quantum coherences to some intramolecular exchange processes.

To illustrate this unique and potentially very useful feature of multiple quantum NMR spectroscopy,[6,7] consider as a simple example a linear AMX spin system (J_{AX} coupling is not resolved) in which the A and X spins are undergoing mutual exchange. It is well known that if two spins are exchanging sites, their individual resonances will first broaden and then coalesce into an exchange-narrowed, single peak as the exchange rate k increases from slow to fast relative to the frequency separation of the unperturbed resonances, $\Delta\nu$. Due to substantial line-broadening, it is sometimes difficult to detect the NMR signal from exchanging spins when $k \sim \Delta\nu$; this is particularly true in many types of coherence transfer experiments where the resonances have antiphase multiplets and are thus severely attenuated due to self-cancelation when the line width is large compared to the active scalar coupling. In a 2D correlation experiment for instance, such as COSY[8] or double quantum-filtered (DQF) COSY,[9] the cross peaks expected for an AMX system will be extremely weak in the case where spins A and X are mutually exchanging at an intermediate rate. It is in this situation that multiple quantum spectroscopy has a unique advantage. As discussed by Braunschweiler et al.,[7] it is possible to excite a so-called "remote" double quantum coherence between spins A and X in a linear AMX system through their mutual scalar coupling to spin M. The frequency of this 2Q transition is the sum of the single quantum frequencies of the A and X spins, which is *independent* of the mutual exchange of these spins. This AX 2Q coherence, unaffected by the A ↔ X exchange process, can subsequently be transferred back to single quantum transitions of the M spin (which also are not exchange-broadened). As a result, in a 2D double quantum spectrum a remote peak at $\omega_1 = \Omega_A + \Omega_X$ and

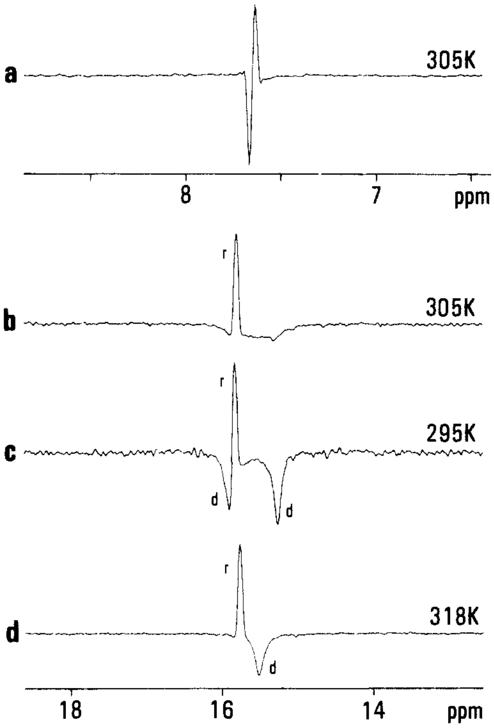

Figure 1. Slices taken from 2D ^1H NMR spectra at the ω_2 chemical shift of the aromatic 4-H of Phe-45 in BPTI (in ^2H_2O, 15 mM, pH 4.6) for (a) a double quantum-filtered COSY experiment and (b)-(d) double quantum experiments, at the temperatures indicated. In the DQF-COSY spectrum only a diagonal peak is detected, providing no information concerning the 3,5-H resonance frequencies. In the 2Q spectra the remote and direct peaks are labeled 'r' and 'd', respectively. (A ppm scale is the most convenient for interpreting the multiple quantum spectra, but note that it is not a chemical shift scale; the origin of this scale is such that $\omega_1 = 0$ Hz corresponds in ppm to twice the chemical shift of the transmitter frequency in the ω_2 dimension.) For each of the 2Q spectra shown, two adjacent slices from the 2D maps have been co-added because in the ω_2 dimension the direct and remote peaks have opposite phase characteristics[15] (absorption/dispersion) and different multiplet component intensities so that the maxima occur at slightly different ω_2 frequencies. Note also that a multiple quantum excitation period of 30 ms was chosen, which is about optimum for the direct peaks but results in the remote peak having approximately half its maximum intensity. All experiments were run at 500 MHz on a Bruker AM500 spectrometer. The standard pulse sequence was used for the DQF-COSY experiment,[9,12] while the conventional sequence for 2Q experiments[7] (with 90° 'read' pulse) was modified by employing $(385^\circ_x - 325^\circ_{-x} - 25^\circ_x)$ composite 90° pulses[16] and EXORCYCLE phase-cycling[17] of the 180° refocussing pulse to eliminate ω_1 phase errors arising from off-resonance effects.

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$\omega_2 = \Omega_M$ is readily observed, regardless of the rate of exchange of A and X, thereby establishing the connectivity of the AMX system.

A more quantitative treatment of the exchange effects described above can be realized by considering the evolution of the density matrix $\rho(t)$ in the presence of an intramolecular exchange process[10]

$$\frac{d\rho(t)}{dt} = i[\rho,H] + k(P\rho P - \rho) \qquad (1)$$

where H is the time-independent Hamiltonian for the spin system, k is the exchange rate, and P is an exchange operator which is defined such that if $\Psi(t)$ is the wave function of the system before an exchange, then $P\Psi(t)$ describes the system after an exchange event. Thus, the evolution of a density matrix element ρ_{ij} is unaffected by exchange whenever $\phi_i = P\phi_i$ and $\phi_j = P\phi_j$, where the ϕ_i are the basis states on which ρ and P are defined.

To demonstrate these exchange effects experimentally, proton NMR spectra were recorded for the protein basic pancreatic trypsin inhibitor (BPTI). Wagner and co-workers[11] have established that for a temperature range centered around 30 °C the aromatic ring of phenylalanine-45 is flipping at an intermediate rate, causing significant broadening of the 2,6-H and 3,5-H resonances. Figure 1a is a slice from a DQF-COSY[9,12] spectrum (32 °C) taken parallel to the ω_1 axis at the ω_2 frequency of the Phe45 4-H resonance, showing only the autocorrelation peak for the 4-H. Since no coherence transfer from the 3,5-protons is observed, their resonance frequencies remain undetermined. In fact, if the diagonal peak had been lost due to overlap with other resonances, there would have been no indication of the presence of the spin system at all. Figure 1b is an ω_1 slice through a double quantum spectrum at the Phe45 4-H ω_2 frequency and reveals both a relatively sharp resonance and a very broad, weak peak. The sharp resonance is the remote peak arising from 2Q coherence between the 3-H and 5-H which is transferred to 1Q transitions of the 4-H. Such a peak allows the chemical shift of the 4-H and the sum of the shifts of the 3-H and 5-H resonances to be determined. The broad peak is a direct connectivity resulting from 2Q coherence between the 4-H and 3,5-H; it is observable in this spectrum due to the in-phase character of the multiplet components.[13] Figure 1c shows a slice from a 2Q spectrum recorded at 22 °C; separate resonances are observed (negative peaks) for the direct connectivity of the 4-H to the 3-H and 5-H, due to the decreased exchange rate. Figure 1d is the result obtained at 45 °C, where the 4-H to 3,5-H direct connectivities have coalesced and are starting to become exchange-narrowed. Note that at all three temperatures the remote connectivity has remained relatively sharp. It should also be noted that while the direct peaks in Figure 1 (parts c and d) are quite strong, their partners appear only very weakly at the ω_2 shifts of the 3,5-H resonances (data not shown), due to antiphase multiplet structure in the ω_2 dimension.

The advantages of multiple quantum spectroscopy for studying exchanging systems are not restricted to 2Q experiments. For example, a strong signal which arises from a 3Q coherence actively involving the Phe45 3-, 4-, and 5-H can be observed in a 3Q spectrum of BPTI; this transition is independent of the exchange of the 3,5-H and can be transferred to easily detected single quantum transitions of the 4-H. It should also be pointed out that multiple quantum spectroscopy can be useful for identifying exchanging systems when the traditional strategy of changing the temperature to move the exchange rate to the slow or fast limit, where exchange-broadening is minimized, is not feasible due to thermal degradation of the sample. Another form of 2D spectroscopy which can also be very useful for identifying coupling partners in exchanging systems is the TOCSY experiment;[14] the advantage of this technique is that the multiplet components have in-phase character in both dimensions, thus avoiding the loss of intensity suffered by antiphase peaks due to self-cancellation in the presence of exchange broadening. However, the presence of peaks arising from an exchanging system but not broadened by the exchange is unique to multiple quantum spectroscopy.

Acknowledgment. I thank Claudio Dalvit for pointing out the presence of an unusual remote peak in the 2Q spectrum of BPTI, which initiated this project; Linda Tennant is thanked for the sample preparation, Pearl Tsang for helpful comments, and Dennis Hare for supplying his software. This work was supported by the National Science Foundation (Grant DMB-8517959).

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Radical Cation Cyclization of 1,5-Hexadiene to Cyclohexene via the Cyclohexane-2,5-diyl Radical Cation Intermediate

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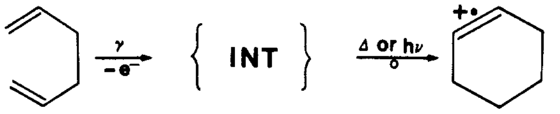
Received September 11, 1987

The classical example of a neutral carbon-centered radical cyclization reaction is the regioselective 1,5-ring closure (exo-cyclization) of the 5-hexenyl radical to the cyclopentylcarbinyl radical.[1] Here we report the title reaction, a comparable addition process whereby an α,ω-diene radical cation reacts by endo-cyclization and hydrogen shift(s) to produce a cycloolefin radical cation.

By using the Freon method for the radiolytic generation of radical cations at low temperatures,[2] we have observed the title reaction by ESR spectroscopy in $CFCl_3$, CF_3CCl_3, $CF_2ClCFCl_2$, and $CFCl_2CFCl_2$. In $CFCl_3$, only the cyclohexene radical cation is present immediately after γ irradiation at 77 K of dilute solid solutions (ca. 1 mol %) of 1,5-hexadiene (99.9% from Wiley Organics and 99% from Aldrich). However, when γ-irradiated 1,5-hexadiene solutions in the other three matrices are examined between 77 and 100 K, an intermediate is also observed, and representative results for CF_3CCl_3 solutions will now be described.



As shown in Figure 1, the ESR spectrum of this intermediate species consists of seven equally spaced lines with nearly binomial intensity ratios. Evidence that this signal carrier is the precursor of the cyclohexene radical cation comes from both photobleaching and thermal annealing studies. First, a comparison of the spectral

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