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On the Use of Tetraphenylborate as a Phase Transfer Agent for Acid Catalysis

Sir:

Phase transfer catalysis has proven a remarkably versatile technique for facilitation of reactions involving anions.[1] A recent communication on catalysis by sodium tetraphenylborate for the acid hydrolysis of an ester suggested the potential extension of the phase transfer approach to reactions involving cations.[2] We report here, however, that this intriguing potential remains to be demonstrated, for the initial observations are attributable to decomposition of the tetraphenylborate rather than hydrolysis of an ester.

In the previous study[2] the hydrolysis of *p*-nitrophenyl acetate was followed spectrophotometrically at 865 nm. In a two-phase cyclohexane–HCl (1.5 N) system no reaction was observed in 48 h at 25 °C in the absence of sodium tetraphenylborate, but with added NaBPh$_4$ a rapid color change occurs which was attributed to the hydrolysis of *p*-nitrophenyl acetate. Our attempts to extend this result, however, led quickly to the observation that the same color is produced at the same rate with or without the *p*-nitrophenyl acetate present.

To a stirred solution of 222 mg of *p*-nitrophenyl acetate in 25 mL of cyclohexane was added 25 mL of 1.5 N HCl and 346 mg of sodium tetraphenylborate. A yellow orange color appeared within 30 s which reached maximum intensity in 3 min. In the control reaction containing no *p*-nitrophenyl acetate, the color change was identical. The UV–visible spectrum (Beckman Acta M-VI) of the control reaction showed a broad maximum at 408 nm; the sum of this spectrum with that of pure *p*-nitrophenyl acetate in cyclohexane reproduced identically the spectrum of the assumed hydrolysis reaction. The reactions with and without *p*-nitrophenyl acetate also showed no differences at 865 nm (Spectronic 20).

To confirm the stability of *p*-nitrophenyl acetate, the reaction was repeated on a slightly larger scale. The organic phase was separated after 15 min, washed with dilute bicarbonate, and evaporated to constant weight at high vacuum. From an initial 546 mg of *p*-nitrophenyl acetate was obtained 658 mg of a gummy solid which integrated for 80% *p*-nitrophenyl acetate by NMR.[3] The amount of crude *p*-nitrophenyl acetate is thus $\sim$96%; crystallization from cyclohexane gave an isolated recovery of 445 mg (81.5%).

The instability of tetraphenylborate to acid is well established.[4,5] Our results indicate that acid decomposition of tetraphenylborate is significantly faster than hydrolysis of *p*-nitrophenyl acetate. The utility of tetraphenylborate as a proton phase transfer agent would thus appear limited; those substrates reactive enough to compete with the decomposition of tetraphenylborate are likely to be easily reacted by other means.[6]

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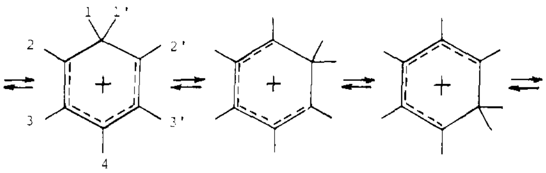
Elucidation of Chemical Exchange Networks by Two-Dimensional NMR Spectroscopy: The Heptamethylbenzenonium Ion

Sir:

For the investigation of chemical exchange processes, nuclear magnetic resonance (NMR) has proved to be a powerful and versatile technique. Much of the present detailed knowledge on chemical and biological rate processes is due to NMR investigations.[1,2] Exchange processes have been studied by three types of techniques: (a) line-shape analysis,[1-5] (b) spin echo experiments,[6] and (c) saturation transfer studies.[7-10] These techniques, in particular (a) and (b), do not always lead to an intuitive grasp of the exchange network because the results are obtained through a computer least-squares fit.

We demonstrate in this letter a novel technique, recently proposed by Jeener,[11-13] which is based on the concept of two-dimensional (2D) spectroscopy.[14-15] It leads to a particularly vivid representation of the exchange network ideally suited for a qualitative analysis of exchange networks by inspection.

We select as an example the well-investigated rearrangement of heptamethylbenzenonium ion.[16-18] This ion undergoes an alkide shift which makes all seven methyl groups equivalent at sufficiently high temperature:



There has been some discussion whether this shift is intramolecular involving either a 1–2 shift or a random shift with jumps, between all possible positions, or whether it is intermolecular. NMR line-shape analysis[16] indicated in agreement with many further systems of similar structure[2] that the dynamics is governed by an intramolecular 1–2 methyl shift. Although the least-squares fit gives an unambiguous result, the visual evidence for this conclusion is just a slight line distortion for intermediate exchange rates.[16] The mechanism has been verified also by a saturation transfer study.[18]

A two-dimensional exchange spectrum of heptamethylbenzenonium ion is shown in Figure 1. It can be interpreted as

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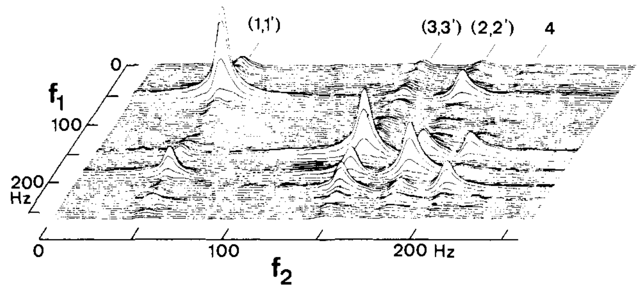

Figure 1. 2D exchange spectrum of heptamethylbenzenonium ion in 9.4 M H_2SO_4 obtained by a 2D Fourier transformation from 64 free induction decays with t_1 values ranging from 0 to 142 ms, and with τ_m = 280 ms (60-MHz proton resonance on a modified Varian DA60 spectrometer, 40 °C sample temperature).

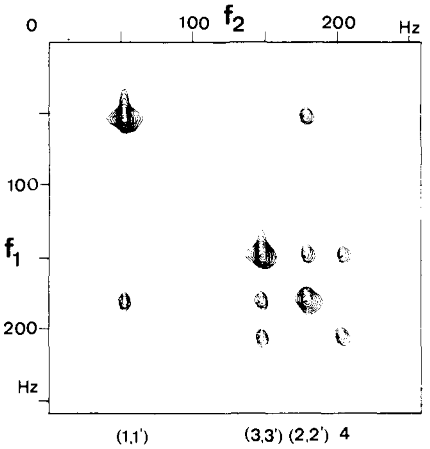

Figure 2. Contour plot based on the same data as used for Figure 1.

follows. The signal peaks of the four nonequivalent methyl groups (1,1′, 3,3′, 2,2′, and 4) are found along the main diagonal (upper left to lower right) with the proper intensity ratio 2:2:2:1. Note the order of chemical shifts of the four classes of methyl groups: 1, 3, 2, 4. The essential information is contained in the off-diagonal peaks. The appearance of such a peak indicates exchange taking place between the two methyl groups connected by this off-diagonal peak. The cross peaks between groups 1 and 2, 2 and 3, and 3 and 4 lead immediately to the exchange network $1 \rightleftarrows 2 \rightleftarrows 3 \rightleftarrows 4$, which is consistent with a 1-2 alkide shift mechanism.

Instead of presenting the data in a pseudo-three-dimensional representation, it is often convenient to give contour line plots as shown in Figure 2. It is based on the same data set as Figure 1 and gives a particularly clear representation of the experimental facts.

The basic experiment leading to a 2D exchange spectrum can be considered as a modulation transfer experiment with the initial z magnetization, frequency modulated by the resonance frequency of each site. Owing to the frequency labeling of the magnetization components, it is possible to follow them through the complex exchange process. The frequency-modulated z magnetization is created as follows (Figure 3): by a $\pi/2$ pulse, transverse magnetization is generated for all involved nuclei. After precession for a time t_1, the x components, modulated by the precession angles, are rotated back along the z axis by a second $\pi/2$ pulse. The amplitude-modulated z magnetizations form the initial conditions for the exchange process taking place during the following exchange period of length τ_m.

At the end of the exchange period, the z components are converted again into observable transverse magnetization and the resulting free induction decay is recorded as a function of t_2. The virtue of this experiment is the possibility to determine after exchange the origin of each observed magnetization component and to trace back the exchange pathways. However, a single experiment with fixed length of the evolution period is not sufficient for the unequivocal correlation of initial and final sites of an exchanging chemical group. The experiment is repeated for a sequence of equidistant t_1 values.

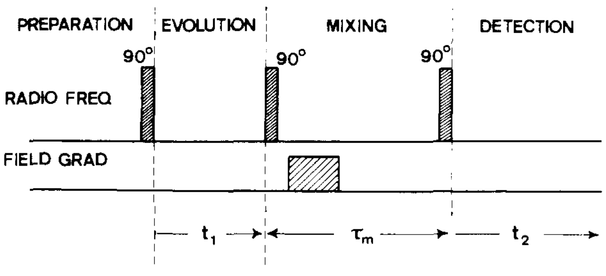

Figure 3. Experimental scheme of 2D exchange spectroscopy. During preparation, transverse magnetization is created. The evolution period serves to "label" the magnetization components with the precession frequencies to allow after exchange the determination of their origin and to trace out the exchange pathways. The magnetic field gradient pulse has the purpose to destroy transverse interference between evolution and detection periods.

The resulting data matrix $s(t_1,t_2)$ is converted by a two-dimensional Fourier transformation into a 2D spectrum $S(\omega_1,\omega_2)$ in which the frequency coordinates ω_1 represent the precession frequencies during the evolution period and characterize the initial state before exchange while the frequency coordinates ω_2 display the precession frequencies during the detection period and identify the final state after exchange.

2D exchange spectra can become a powerful tool for the organic chemist and for the biochemist to explore complex exchange networks. A more detailed description and analysis of this technique will be given at another place.[12]

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