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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 ~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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References and Notes

(1) C. M. Starks and C. Liotta, "Phase Transfer Catalysis, Principles and Techniques", Academic Press, New York, 1978; W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis", Springer-Verlag, Berlin, 1977.
(2) D. W. Armstrong and M. Godat, *J. Am. Chem. Soc.*, **101**, 2491 (1979).
(3) The NMR spectrum of the crude material showed only aromatic protons and the methyl singlet at 2.4 ppm. The percentage of *p*-nitrophenyl acetate was calculated by assuming that the 20% excess aromatic area relative to the methyl area is proportional to the weight of impurities. To the extent that the percentage of hydrogen is greater in phenylboron derivatives than in *p*-nitroacetate, this assumption would underestimate the recovery of *p*-nitrophenyl acetate.
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(6) Professor Armstrong has informed us that tetraphenylborate exhibits varying stability to metal ions and may facilitate certain reactions involving metal cations.

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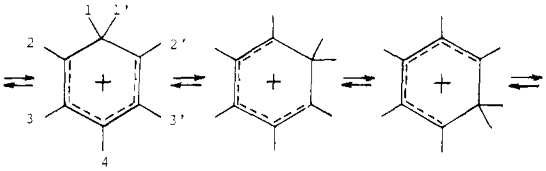
Elucidation of Chemical Exchange Networks by Two-Dimensional NMR Spectroscopy: The Heptamethylbenzenonium Ion

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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