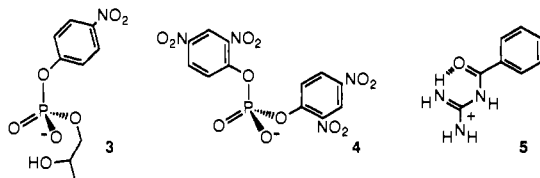


Figure 2. Release of 4-nitrophenol in the reaction of **3** and (a) no receptor and (b) **1** [30 mM].

stabilize the trigonal-bipyramidal intermediate via four hydrogen bonds with concomitant charge neutralization, as in Figure 1. Furthermore, the reduced pK_a of acylguanidinium (~ 8) compared to guanidinium (~ 14)¹² should facilitate proton transfer from the receptor to the leaving group and so promote the second step in Scheme I.¹⁴

The intramolecular phosphoryl transfer reactions of **3**¹⁵ were followed through at 324 nm the release of 4-nitrophenol. The receptors were used as their bis(tetraphenylborate) (mono- in the case of **5**) salts and the diesters **3** and **4** as their barium¹⁶ and pyridinium salts, respectively. All kinetic runs were carried out in CH_3CN with an initial concentration of diester of 1×10^{-4} M; the receptor (see Table I) and lutidine (1.25×10^{-2} M), as a general base, were present in excess. The phosphoryl-transfer reactions followed pseudo-first-order kinetics, and their rate constants¹⁷ and conditions are collected in Table I.



The rate of release of 4-nitrophenol in the intramolecular reaction of **3** is greatly increased (Figure 2) in the presence of **1**. Comparison of the first-order rate constant with that of the uncatalyzed reaction ($k_{\text{obsd}}/k_{\text{uncat}}$) gives a rate acceleration of 700-fold.¹⁸ The reaction follows Michaelis-Menten kinetics, showing

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(13) Alternative interaction geometries can be envisioned including binding to the three groups (O⁻, O⁻, OR) in the trigonal plane or proton transfer from the guanidiniums to the more basic O atoms in the intermediate.

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saturation behavior as the concentration of receptor increases (Table I). An Eadie-Hofstee plot ($R = 0.988$) gave values for $k_{\text{cat}} = 3.8 \times 10^{-4} \text{ s}^{-1}$ and $K_m = 1.2 \times 10^{-2} \text{ M}$. This corresponds to a maximum rate acceleration for the receptor ($k_{\text{cat}}/k_{\text{uncat}}$) of 10^3 and a k_{cat}/K_m of $3.2 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. The high value of K_m ($K_a = 85 \text{ M}^{-1}$) in these experiments, compared to the value for **2** in CH_3CN , presumably reflects the increased polarity of the medium which contains excess lutidine ($1.25 \times 10^{-2} \text{ M}$),¹¹ and this is supported by complexation studies under similar conditions. The binding arrangement provided by two guanidiniums in **1** is crucial for this large rate enhancement. An analogue **5** (10 mM), containing only one guanidinium, caused a 2.5-fold acceleration in the reaction of **3** whereas receptor **1**, at half the concentration (5 mM), increased the rate of the reaction by almost 300-fold.¹⁹ Similar, although less dramatic, effects are seen with the bimolecular reaction between phosphodiester **4**²¹ and ethyl mercaptoacetate ($1.25 \times 10^{-2} \text{ M}$), as added nucleophile.²² Addition of receptor **1** (at 5 mM) caused a 36-fold increase in the rate of the intermolecular thiolysis reaction.

In summary, we have shown that substantial rate enhancements in phosphodiester cleavage reactions can be achieved by a very simple receptor containing both hydrogen bonding and electrostatic complementarity to the trigonal-bipyramidal intermediate. We are currently investigating further the mechanism of this process as well as incorporating additional functionality into the receptor to increase the catalytic activity.

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Registry No. **1**, 137695-71-7; **3**, 4286-25-3; **4** (pyridinium salt), 76215-45-7; **5** (BPh₄), 137945-61-0; SN, 9013-53-0; ethyl mercaptoacetate, 623-51-8.

(19) Simple acid-base effects are not responsible for the acceleration. Addition of a 1:1 mixture of lutidine/lutidinium tetraphenylborate (12.5 mM) caused no significant effect on the reaction.²⁰

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Rearrangement of Pentacoordinated Carbonium Ions over Zeolite Y

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Zeolites are acidic aluminosilicates widely used for cracking of high-boiling oils into gasoline and LPG.¹ Although carbenium ions are believed to be the intermediates in the cracking process, their initial formation from alkanes over the zeolite surface is still a matter of controversy.² Recently, there appeared reports which

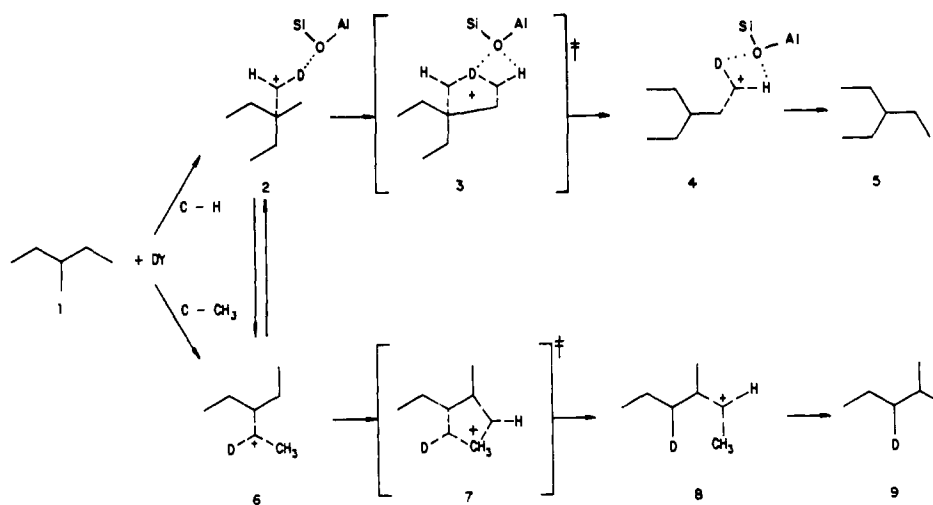
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[‡] Universidade Federal do Rio de Janeiro.

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Scheme I



suggest that zeolites can donate protons to the σ bonds of an alkane to form pentacoordinated carbonium ions.³⁻¹⁰ However, due to the high temperatures involved (ca. 400–500 °C), some authors prefer to attribute the methane and hydrogen formation in cracking reactions to the involvement of radical species.^{11,12} On the other hand, the H–D exchange between superacids and alkanes can occur under mild conditions and as an event prior to formation of carbenium ions.¹³ This evidence has been used to support the involvement of pentacoordinated carbonium ion as intermediates in alkane reactions in superacids.^{14,15} We have recently reported an infrared study of the surface H–D exchange between deuterated zeolite Y and 3-methylpentane under mild conditions (no cracking).¹⁶ We now wish to report preliminary results showing the incorporation of deuterium into the 3-methylpentane which indicate that pentacoordinated carbonium ions are readily formed and rearrange on the zeolite surface.

About 550 mg of acidic steam dealuminated zeolite Y¹⁷ (framework Si/Al = 4.5, residual Na₂O = 0.5 wt %) was pre-treated with dry N₂ (38 mL/min) at 500 °C for 30 min. Deuteration was carried out with 3 mol % of D₂O/N₂ at 200 °C for 60 min followed by an N₂ purge of 15 min. The alkane (ca. 6 mol % in N₂) was passed (20 mL/min) over the zeolite at 100 °C. The hydrocarbon was condensed in a dry ice–acetone trap. The sample collected after 60 min (15-min N₂ purge) was then

analyzed by ²H NMR (Varian VXR 300) and GC/MS (HP 5988 A).

The ²H NMR spectrum of recovered 3-methylpentane (in CDCl₃) showed three broad singlets centered at ca. 0.9, 1.2, and 1.4 ppm (relative intensities of 1.6:1:1, respectively). These peaks were assigned to primary, secondary, and tertiary deuterium, respectively, in 3-methylpentane (no methyl resolution). GC/MS analysis showed a small degree of monodeuteration (ca. 6%) with the remaining 3-methylpentane being undeuterated. About 2.5 wt % of 2-methylpentane was found showing a higher index of monodeuteration (ca. 67%)¹⁸ than 3-methylpentane. These results are surprising when compared to the observation that, in superacid solutions, exchange occurs only at the tertiary position.¹⁹ No trace of olefin was detected in either the starting material or the product. The possibility that the exchange was due to attack in primary and secondary C–H bonds was eliminated by demonstrating that *n*-hexane does not exchange under these reaction conditions. Thus, we explain the incorporation in these positions by invoking the rearrangement of deuterium within the pentacoordinated carbonium ions. Rearrangement of pentacoordinated carbonium ions has been previously suggested for the gas-phase protonation of propane.^{20,21}

To obtain more information about these processes, the experiment was repeated with methylcyclohexane. The ²H NMR spectrum of the recovered cycloalkane again showed three peaks at ca. 0.7, 1.1, and 1.5 ppm, but with 2.4:0.1:1 relative intensities. The strong preference for incorporation in the primary position compared to secondary suggests that there is a critical stereo-orientation in the transition state for rearrangement and that there is probably a need for eclipsing the two electron pairs in the TS, which is easy from the protonated axial tertiary C–H to the methyl but almost prohibited with the equatorial secondary C–H (Figure 1).

A reasonable representation of the species involved in the rearrangement to form the deuterated products and the 2-methylpentane is shown in Scheme I. The deuterium migration to primary or secondary positions requires some binding of the intermediate 2 to the zeolite. This causes asymmetry between the three-center bond and the zeolite making the exchange at the tertiary position difficult. Migration of deuterium to primary or secondary adjacent positions would lead to carbonium ion 4 in

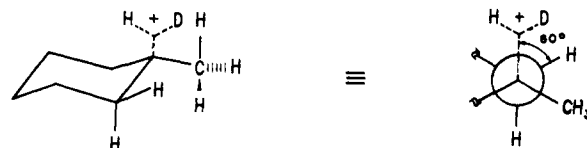


Figure 1.

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which release of hydrogen to the zeolite seems to be more favorable. These data stress the importance of the binding of protonated species to the zeolite framework, as has already been demonstrated for carbenium ions.^{22,23} The current model for rearrangement of carbonium ions gives emphasis to the rearrangement of nuclei (positively charged species) within electron clouds as opposed to the normal model for rearrangement of carbenium ions, which rearranges electrons (negatively charged species) to electron-deficient centers.

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Registry No. 1, 96-14-0; 1-H⁺, 138093-65-9; 2-methylpentane, 107-83-5; methylcyclohexane, 108-87-2; methylcyclohexane conjugate acid, 138093-66-0; hydrogen, 1333-74-0.

Supplementary Material Available: Mass spectra for standard 2-methyl- and 3-methylpentane and for both after H-D exchange, ²H NMR spectra for recovered methylcyclohexane and 3-methylpentane, and an X-ray diffractogram for zeolite Y (7 pages). Ordering information is given on any current masthead page.

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Homonuclear Deuterium Correlation Spectroscopy in the Rotating Frame

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High-resolution deuterium NMR has some attractive features in spite of poor sensitivity. Chief among these is the fact that each chemically distinct site in a perdeuterated molecule leads to exactly one resonance because of the small homonuclear ²H-²H couplings, which are invariably less than 0.5 Hz. In addition, the quadrupolar ²H nucleus normally has higher effective relaxation rates than does ¹H, enabling faster pulse sequence repetition for signal averaging. In recent years, some interest has focused on NMR applications involving deuterium: polarization transfer from ²H to ¹³C is a significant example.^{1,2} 2D homonuclear ²H-²H correlation is another important application,³ performed with a COSY sequence optimized for small couplings.⁴ While it is gratifying that correlation is at all possible in such cases of unresolved couplings, it is the purpose of this work to show that homonuclear deuterium correlation—as well as relayed correlation—can be performed with surprisingly high efficiency, far superior to the optimized COSY experiment.

The basis of our approach is coherence transfer under spin lock,^{5,6,7} also known as isotropic mixing, TOCSY, or HOHAHA. Net in-phase transfer occurs under isotropic mixing (IM), in

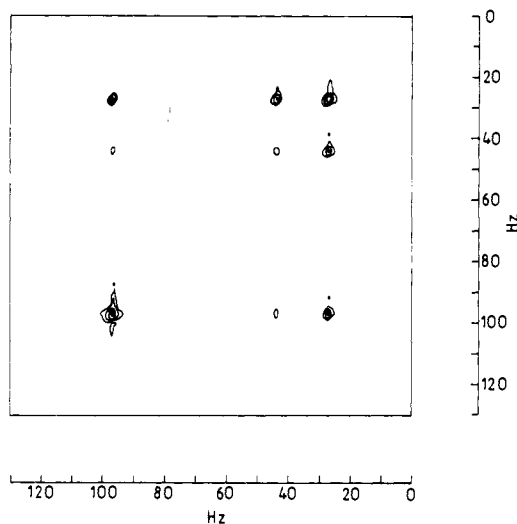


Figure 1. Two-dimensional ²H-²H magnitude mode TOCSY spectrum of pyridine-*d*₅ at 46.073 MHz, acquired in a double-buffered mode. Spectral width, 130 Hz, 64 experiments of 16 scans each; spin lock rf field strength, 1.5 kHz, the spin lock train being issued from the variable phase and amplitude channel of spectrometer modulator. Data processed with shifted sine bell window functions in both dimensions. Mixing time: 1.248 s. The experiments were performed on a Bruker MSL 300 P spectrometer with no hardware designed for high-resolution deuterium work. A 5-mm inverse probe was employed, using the X-nucleus decoupling coil for deuterium excitation, spin lock, and signal detection; field-frequency lock was *not* employed, and the experiments were performed without sample spinning.

contrast to the *basic* INEPT⁸ or DEPT⁹ mechanism that leads to *anti-phase* transfer of coherence. While IM leads to a maximum transfer of 100% for a two-spin-¹/₂ system, which is equivalent to a spin permutation,¹⁰ such is not the case for other systems. One of us (N.C.) has investigated^{11,12} in detail the coherence transfer under isotropic mixing in several general spin-¹/₂ systems. The results for the spin-¹/₂ A₂X₂ system may be adapted to the two-spin-1 problem. It is possible to show by this means or by spin-1 commutator algebra that transverse magnetization of one of the coupled spins in this system goes over into the following observable terms under IM:

$$I_x \rightarrow \frac{1}{2}(1 + \cos 4\pi Jt)I_x + \frac{1}{2}(1 - \cos 4\pi Jt)S_x + \frac{1}{3}[(1 - \cos 2\pi Jt) - (1 - \cos 4\pi Jt)](I_x^2 S_x - I_x S_x^2) + \frac{1}{6}\left(\sin 2\pi Jt + \frac{5}{2}\sin 4\pi Jt\right)(I_y S_z - I_z S_y) \quad (1)$$

Ignoring the anti-phase term, eq 1 predicts that the maximum in-phase coherence transfer efficiency is 77.78% and occurs at a mixing time $t = (4J)^{-1}$. This may be compared with the maximum efficiency for this system under the INEPT mechanism, which amounts to 66.67%^{13,14} anti-phase, also for a duration of $(4J)^{-1}$. This result is easy to visualize since the $m_S = 0$ component of the *I*-spin "multiplet" does not evolve under weak coupling and therefore cannot be transferred: at most two-thirds of the magnetization in the *I* signal can be transferred under INEPT. Under isotropic mixing, on the other hand, the $m_S = 0$ component *does* evolve under the strong coupling induced by spin lock, leading to a higher maximum efficiency of transfer. Most significant, however, from the practical point of view is that the transfer under

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