

PROTON TRANSFER BETWEEN ELECTRONEGATIVE ATOMS: RATE-DETERMINING OR NOT?

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Abstract - Several carbonyl group reactions which involve rate-determining proton transfer between electronegative atoms, as evidenced by biphasic Bronsted plots and detailed kinetic analysis, also give kinetic hydrogen isotope effects which change rapidly with the pKa difference between the proton donor and the protonated proton acceptor (ΔpK) and peak sharply at $\Delta pK=0$. This indicates that the proton transfer component of the overall proton transfer process (encounter of reactants, proton transfer, and separation of products) is at least partly rate-determining in these systems, but it is so only over a narrow region of ΔpK about $\Delta pK=0$. Kinetic isotope effects on the base-catalyzed decomposition of nitramide as well as the shape of the Bronsted plots for this reaction and the deprotonation of the conjugate acid of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene indicate that proton transfer involving nitrogen is intrinsically slower than that involving oxygen and is therefore (partly) rate-determining over a wider, albeit still rather limited, range of ΔpK .

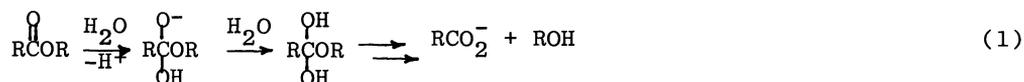
INTRODUCTION

It is a tenet of long standing in mechanistic chemistry that proton transfer between electronegative atoms such as oxygen and nitrogen is seldom if ever rate-determining in a reaction where such transfer and changes in bonding between heavy atoms must take place. This idea is stated especially clearly in a Solvation Rule laid down by Swain, Kuhn and Schowen (1), who said:

A proton being transferred from one oxygen (or nitrogen) to another in a reaction which requires heavy atom reorganization "should lie in an entirely stable potential at the transition state and should not form reacting bonds nor give rise to primary isotope effects".

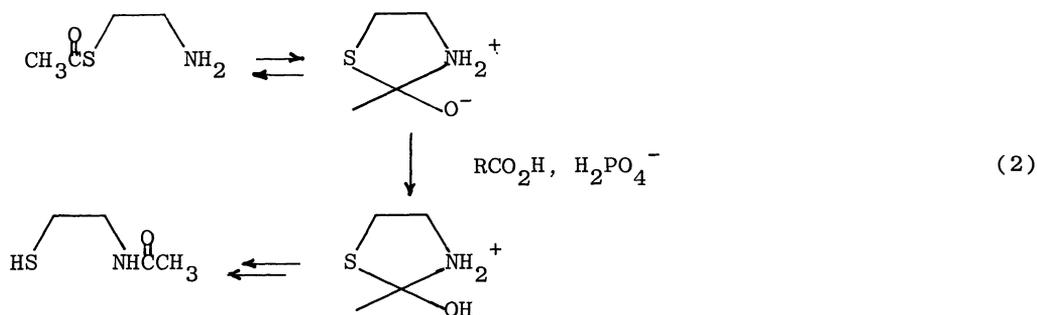
The origin of this idea is obscure, but it was undoubtedly fostered by the fact that rates of proton transfer between electronegative atoms, i.e. "normal" [in the Eigen sense (2)] acid-base centers, were for a long time too fast to measure. When appropriate fast reaction techniques were invented and the rates of normal acid-base reactions were finally measured and found to be very fast indeed (2), the idea was reinforced.

Heavy atom reorganization, however, can also be very fast. An early indication that it might be fast enough to compete with proton transfer between electronegative atoms came from studies of oxygen-18 exchange during the hydrolysis of carboxylic acid esters which suggested that proton transfer from solvent water to the negatively charged oxygen atom of the tetrahedral intermediate formed in this reaction (eq. 1) might in some cases be kinetically significant (3). This requires reversal of tetrahedral intermediate

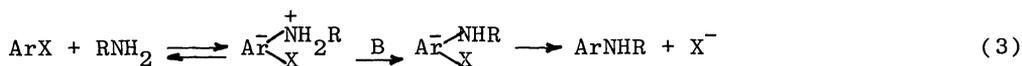


formation, which involves bonding changes between oxygen and carbon, to be either faster than or at least of the same velocity as proton transfer between two oxygen atoms. Firm evidence that breakdown of tetrahedral intermediates can be faster than subsequent protonation of these species was

later provided by detailed kinetic study of the intramolecular acetolysis of S-mercaptoethylamine, which showed that protonation by oxygen acids of the zwitterionic intermediate formed in this reaction (eq. 2) is rate-determining under certain conditions (4).



Soon thereafter further examples of rate-determining protonation or deprotonation of tetrahedral intermediates on oxygen or nitrogen by oxygen and nitrogen acids and bases were discovered (5). More recently, proton transfer to oxygen and nitrogen bases from the ammonio nitrogen atom of the intermediate formed in nucleophilic aromatic substitution by amines (eq. 3) was shown to be rate-determining in some circumstances (6).



In each of these examples, proton transfer between an external normal acid or base and an electronegative atom of the substrate must be slower than the atomic reorganization which accompanies certain bonding changes between heavy atoms in the substrate. Proton transfer itself, however, is a multistage process that includes some transport steps which themselves require heavy atom reorganization. In its most simple formulation, the process consists of 1) encounter of the substrate with the proton donor (or acceptor) to form a reaction complex (eq. 4), 2) proton transfer within this complex (eq. 5), and 3) separation of the proton transfer products (eq. 6). Any one of these



steps could be rate-determining, and, if the rate-determining step should happen to be either encounter or separation, then the heavy atom reorganization required in such a transport step would be slower than proton transfer. In this way, proton transfer between electronegative atoms (eq. 5) could be faster than heavy atom reorganization (eq. 4 or 6) while the overall proton transfer process (eqs. 4, 5, and 6) still remained the rate-determining stage of a complex reaction scheme. Whether or not this could be the case is the question we set out to answer several years ago.

The isotope effect criterion

A classic method of determining whether a given atom is in flight or is an entirely stable potential at the rate-determining transition state of a chemical reaction is to measure the effect of isotopic substitution on reaction velocity. It was, in fact, the general absence of kinetic hydrogen isotope effects significantly greater than estimated secondary and solvent values, and therefore unmistakably primary in origin, on reactions involving proton transfer between electronegative atoms which lead to the formulation of the Solvation Rule (1).

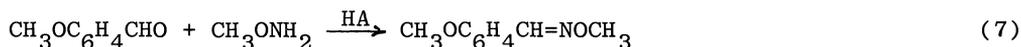
Primary isotope effects, however, can be quite small. Isotope effect theory leads to the expectation that primary effects will vary in magnitude with transition state structure, and will be large only when the transition state is appreciably symmetrical in the sense that the partial bonds holding the atom being transferred are of approximately equal strength (7). A number of examples of such behavior are now known for slow proton transfers to or from carbon (8). These isotope effects pass through maximum values when the

strengths of the two bases between which the proton is moving are equal, as judged, for example, by the difference in pKa of their conjugate acids: $\Delta pK=0$ [$\Delta pK = pK_a(\text{donor}) - pK_a(\text{acceptor})$]. The variation of isotope effect with ΔpK in these slowly reacting systems is very gradual and the maxima are broad. This indicates that the symmetry of the transition states of these reactions does not change with ΔpK very rapidly, a feature which is characteristic of intrinsically slow reactions (9).

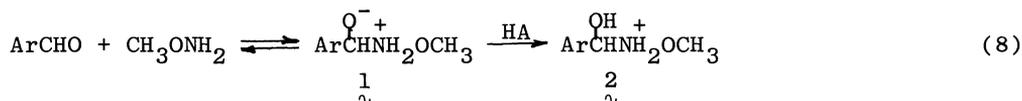
Proton transfers between electronegative atoms, however, are intrinsically very fast, and the symmetry of their transition states will consequently change much more rapidly with ΔpK . Isotope effects on these reactions should therefore show much sharper maxima, and effects large enough to be identified unmistakably as primary might be missed unless the pKa's of the proton donor and the proton acceptor are closely matched. A search for primary isotope effects on proton transfer between electronegative atoms should therefore concentrate in the region immediately about $\Delta pK=0$.

Tetrahedral intermediates

We began our search for such isotope effects by examining the reaction between *p*-methoxybenzaldehyde and methoxylamine in the presence of acidic catalysts (eq. 7). A previous detailed study of this system had shown that,



under certain conditions of pH and catalyst concentration, proton transfer from oxygen and nitrogen acids to the alkoxide oxygen atom of the first-formed zwitterionic intermediate, 1 (eq. 8), is rate-determining (10). The



pKa of the hydroxyl group of the cationic intermediate in this reaction, 2, had been estimated as 9.0, and $\Delta pK=0$ should therefore occur at $pK_a(\text{catalyst}) = 9$. This is confirmed by the fact that this reaction gives a biphasic Bronsted plot of the type first found by Eigen for normal acid-base reactions, and that the break in this Bronsted plot comes at $pK(\text{catalyst}) = 9$; such Bronsted plots are expected to break at $\Delta pK=0$ (2).

The isotope effects we found for this system are shown in Fig. 1 (11). They describe a clearly defined maximum which peaks at $pK(\text{catalyst}) = 8-9$. This maximum is indeed quite narrow and isotope effects only a few pKa units away from $\Delta pK=0$ are small enough to be classified as purely secondary or solvent effects. (The reacting hydrogen in this system exchanges rapidly with the solvent, and isotope effect determinations therefore require measurements in D_2O solution.) The isotope effects at $\Delta pK=0$, however, must be primary because secondary and solvent effects are expected to vary monotonically with ΔpK and should not show extrema such as the maximum found here.

This isotope effect maximum is defined by a series of ammonium ion catalysts. The maximum value, $k_H/k_D = 3$, however, falls considerably short of the isotope effect expected for N-H bond-breaking through a symmetrical transition state. This indicates that the proton transfer step (eq. 5) of the overall proton transfer process (eqs. 4, 5, 6) is in this case not fully rate-determining and that the transport steps (eqs. 4, 6) are kinetically significant even at $\Delta pK=0$. In fact a model in which encounter, proton transfer, and separation occur at equal rates at $\Delta pK=0$ fits the data well. Because proton transfer is not fully rate-determining at $\Delta pK=0$, it quickly becomes not rate-determining at all when ΔpK moves away from zero in either direction. This leaves a rather narrow "window" through which the isotope effect on the proton transfer step (eq. 5) may be viewed. This window is in fact in this case too small to allow the dependence of this isotope effect on ΔpK to be determined, and, although the relationship between the observed isotope effect, i.e. that on the combination of all three steps of the proton transfer process (eqs. 4, 5, 6), and ΔpK gives a sharp maximum, it does not necessarily follow that the isotope effect on the proton transfer step goes through a sharp maximum as well (12).

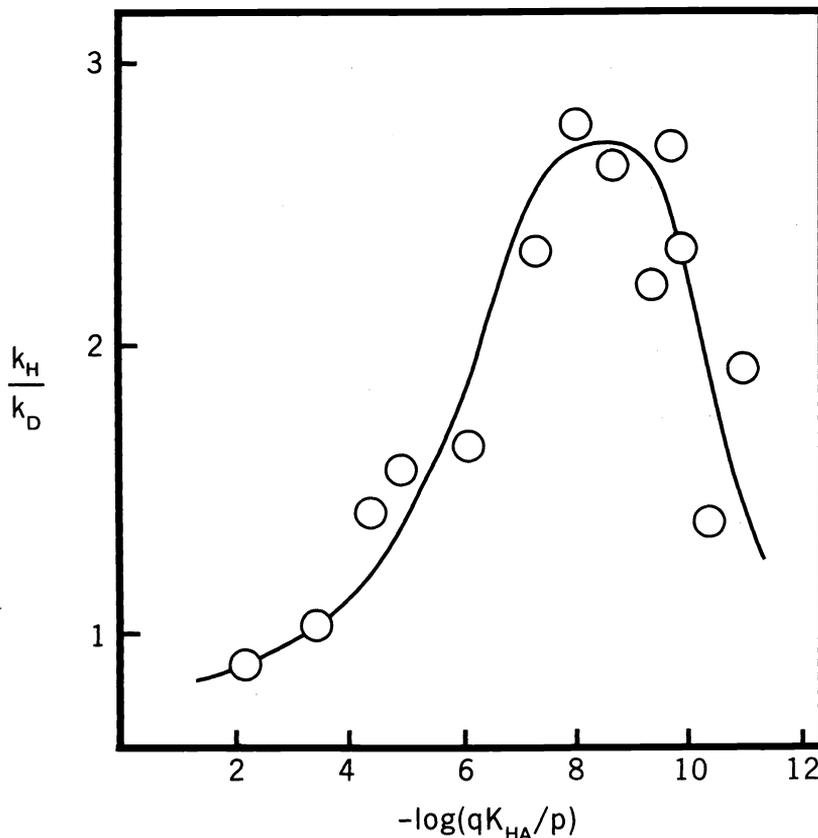
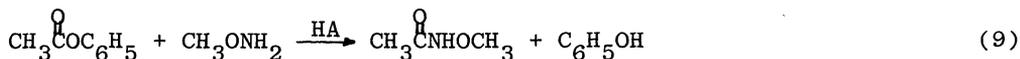


Fig. 1. Isotope effects on proton transfer to the zwitterionic intermediate formed by addition of methoxylamine to p-methoxybenzaldehyde.

Another isotope effect maximum on proton transfer between electronegative atoms in a different system which was discovered at the same time as that of Fig. 1 is more informative (13). This reaction, the methoxyaminolysis of phenyl acetate (eq. 9), occurs by a preassociation mechanism rather than by



the trapping mechanism of eq. 8, and that gives this system a somewhat wider window for viewing the proton transfer step. The data cannot be fitted by a gradually changing isotope effect on this step, but rather require this isotope effect to be a very sharp function of ΔpK . This, however, once again does not prove that isotope effects on proton transfer between electronegative atoms give narrow maxima, for these data can also be fitted by a constant isotope effect modified by a switch from rate-determining proton transfer to a rate-determining change in solvation (14).

Nitramide decomposition

Previous to the discovery of these two isotope effect maxima for proton transfer between electronegative atoms, an isotope effect maximum was reported for the decomposition of nitramide catalyzed by a series of aryloxy ions (15). The generally accepted mechanism for this reaction consists of rapid isomerization of nitramide to its aci-nitro form followed by slow elimination of H^+ and OH^- from this species (eq. 10); the process therefore



involves proton transfer from nitrogen to oxygen. In an attempt to extend this work, we were unable to corroborate the original findings, but we did

obtain further interesting information about proton transfer between electronegative atoms (16).

The base-catalyzed decomposition of nitramide is a much-studied reaction which has figured prominently in investigations of acid-base catalysis over the past half-century. It was, for example, the system used by Bronsted and Pedersen in their classic work which led to the discovery of the Bronsted relation (17). In all of this previous work the reaction was followed by monitoring the evolution of N_2O gas. This becomes a cumbersome method, prone to error, when used with moderate to strongly basic catalysts, such as the aryloxide ions employed in the study reporting an isotope effect maximum. We found, however, that nitramide decomposition can be followed by standard spectroscopic techniques, and that this method gives highly accurate results with bases of any strength.

Using this method we determined the isotope effects shown in Fig. 2. These

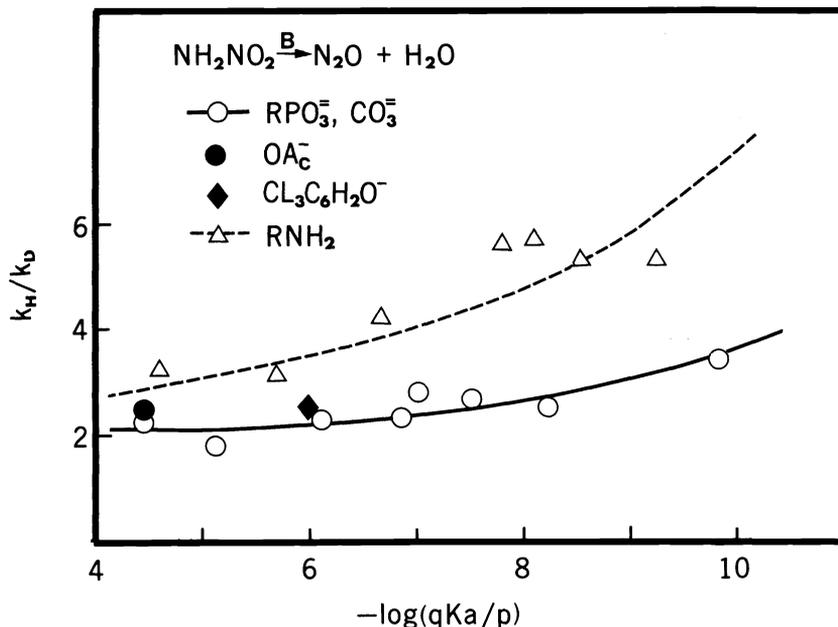


Fig. 2. Kinetic isotope effects on the base-catalyzed decomposition of nitramide.

are generally lower than those reported before and are ostensibly constant in the region of the previously claimed maximum about $pK(\text{catalyst}) = 6$. Our isotope effects do begin to increase, however, as $pK(\text{catalyst})$ approaches 10, and the rise is more pronounced for nitrogen than for oxygen bases.

This behavior suggests the presence of an isotope effect maximum above $pK(\text{catalyst}) = 10$, a region not directly accessible because of the incursion of a second reaction. It implies further that the maximum is broader for nitrogen than for oxygen bases. This inference is supported by the Bronsted plot for this reaction (Fig. 3), which consists of a long linear portion followed by the beginning of a break near $pK(\text{catalyst}) = 10$: the break starts earlier with nitrogen than with oxygen bases. This behavior is also consistent with the expected pK_a of the N-H bond of aci-nitramide, which puts $\Delta pK=0$ in the region above $pK(\text{catalyst}) = 10$.

These phenomena can be understood in terms of a three-step expansion of the slow stage of the mechanism of eq. 10:

- 1) encounter of aci-nitramide with the basic catalyst (eq. 11),
- 2) proton transfer (eq. 12), and 3) expulsion of OH^- and formation of N_2O before the proton transfer products can separate (eq. 13). [This reaction scheme in reverse would be an acid-catalyzed (BH^+) preassociation mechanism enforced by the short lifetime of the adduct formed by nucleophilic attack of OH^- upon N_2O (18).] When the catalyst is a weak base (Fig. 4, left side),

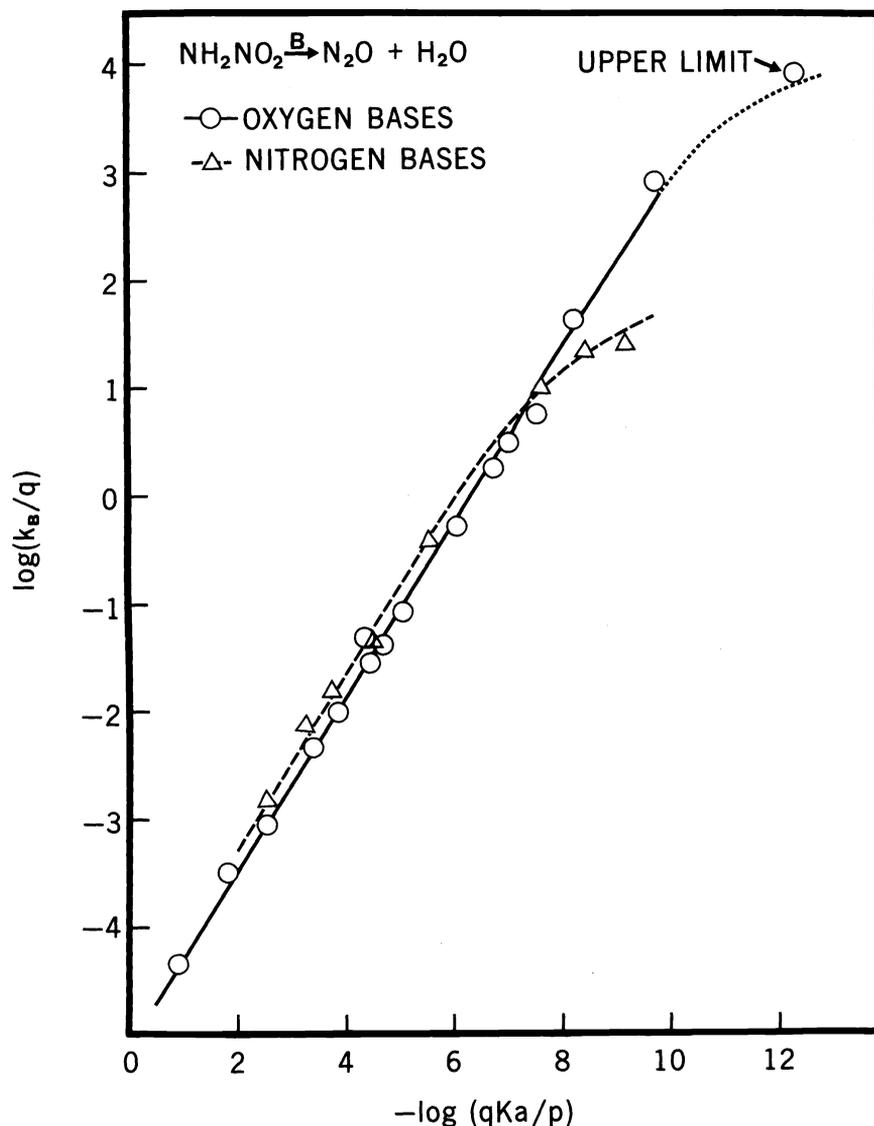


Fig. 3. Bronsted plot for the base-catalyzed decomposition of nitramide.

proton transfer is a strongly uphill process; its reverse (eq. 12, back reaction) is therefore very fast [Hammond postulate (19)] and heavy atom reorganization (eq. 13) is rate-determining. This gives a linear Bronsted plot and only secondary isotope effects; the latter, however, are appreciable ($k_H/k_D = 2-3$) because the transferred hydrogen is held in a strong hydrogen bond (20). As the catalyst becomes stronger (Fig. 4, right side) and the barrier for proton transfer in the forward direction decreases, that for its reverse increases (Hammond postulate); proton transfer then begins to be at least partly rate-determining. This introduces curvature into the Bronsted plot and adds a primary component to the isotope effect.

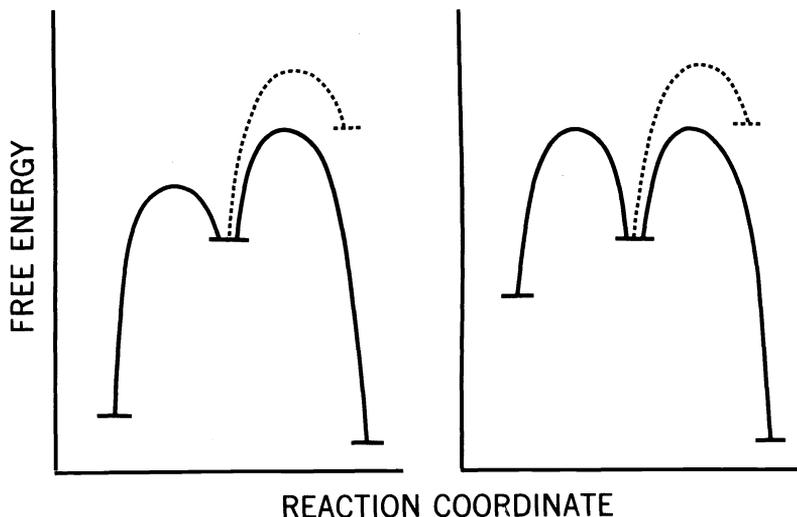


Fig. 4. Schematic representation of nitramide decomposition catalyzed by weak (left side) and strong (right side) bases. The solid line denotes proton transfer (eq. 12) and heavy atom reorganization (eq. 13), and the broken line shows separation of the proton transfer products.

The earlier Bronsted plot curvature and greater isotope effects observed for nitrogen bases imply that proton transfer to nitrogen begins to become rate-determining sooner than proton transfer to oxygen bases, and that it is therefore more fully rate-determining at $\Delta pK=0$. In other words, proton transfer to nitrogen is intrinsically slower than proton transfer to oxygen, and this gives a wider window through which the characteristics of the proton transfer step may be viewed. This difference is in accord with the hypothesis that formation of a strong hydrogen bond is a prerequisite for very fast proton transfer (2) and the fact that nitrogen bases are poorer hydrogen bond acceptors than oxygen bases (21).

Super sponge

Further indication that proton transfer to nitrogen is intrinsically slower than proton transfer to oxygen comes from our investigation, not yet complete, of the acid-base reactions of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene or "Super Sponge" (22). This substance is related to 1,8-(dimethylamino)naphthalene (Proton Sponge), whose remarkable basicity was discovered just over a decade ago (23). The pK_a of the conjugate acid of Proton Sponge is 12.03 (24), which is 7 pK units greater than the pK_a of protonated 1-(dimethylamino)naphthalene; this makes Proton Sponge a stronger base than simple aliphatic amines.

Proton Sponge is a strained molecule: interaction of the large groups in the peri-positions distorts the naphthalene ring (25). This strain is relieved in part upon protonation (26), and that, plus the fact that the acidic proton in protonated Proton Sponge is situated on one nitrogen atom and is hydrogen-bonded to the other in a particularly strong intramolecular hydrogen bond (26), is believed to be responsible for its great basic strength (23). These factors also make the rate of proton transfer from protonated Proton Sponge much slower than it would otherwise be. For example, downhill proton transfer to the hydroxide ion has a rate constant of only $k_{HO^-} = 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, which is 5 orders of magnitude below the encounter-limited rate constants usually found for comparable reactions of simple ammonium ions (27). Super Sponge is even less reactive: $k_{HO^-} = 8 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ [in 70% DMSO-30% H_2O] (28).

These unusual reactivities pose an interesting mechanistic problem. It has been found that rates of proton transfer from intramolecularly hydrogen-bonded acids are generally several orders of magnitude slower than those in comparable systems where the internal hydrogen bond is absent. This difference was attributed to a reaction mechanism in which the intramolecular

hydrogen bond is first broken to give an acid externally hydrogen-bonded to solvent; this unstable intermediate then reacts with the proton acceptor in a rapid reaction, but the overall rate is slowed because of the unfavorable pre-equilibrium (2). It has been pointed out, however, that single-stage proton transfer directly out of the intramolecular hydrogen bond should also give reduced rates because the transition state for such a process would have a tri-coordinated proton with an unfavorable non-linear arrangement of the forming and breaking bonds (29).

A choice between these two mechanisms is difficult, but it might be made on the basis of the fact that the proton transfer step of the pre-equilibrium mechanism is a simple proton transfer reaction between non-internally hydrogen-bonded acids and bases; it should therefore display features characteristic of such a reaction, e.g. a biphasic Bronsted plot and a sharp isotope effect maximum. These features, however, will not appear where the overall pK difference between donor and acceptor, as measured by the conventional pK_a of the intramolecularly hydrogen-bonded acid, ΔpK , is zero, but rather where the actual pK difference for the proton transfer step, $\Delta pK'$, is zero (eq. 14). Because of the unfavorable pre-equilibrium, $\Delta pK'=0$ will be



displaced from $\Delta pK=0$ in the uphill direction by an (appreciable) amount corresponding to the value of the pre-equilibrium constant (Fig. 5).

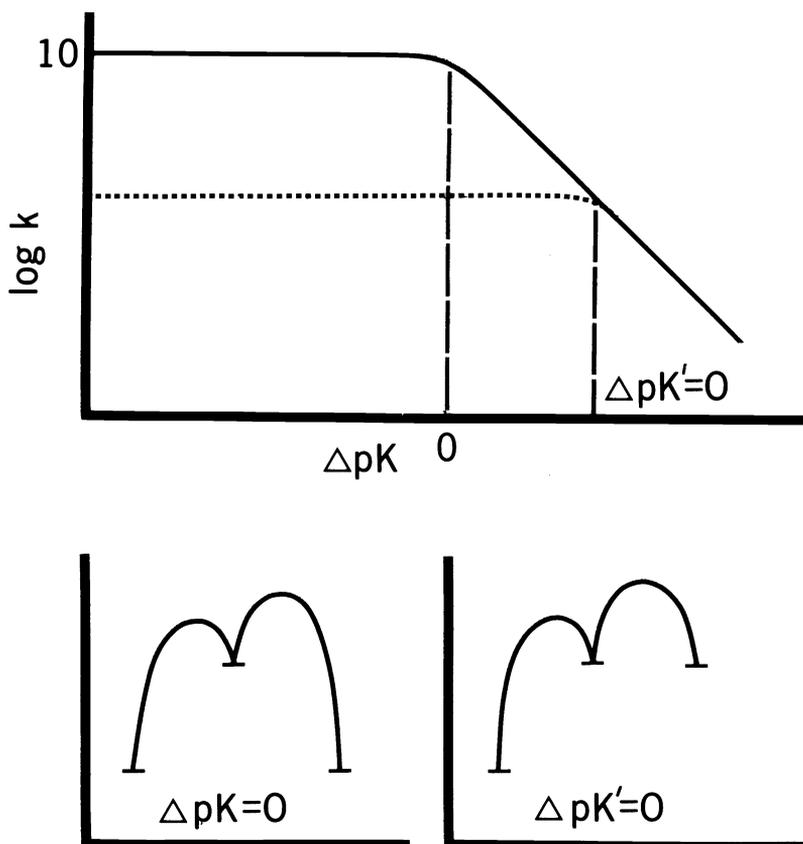
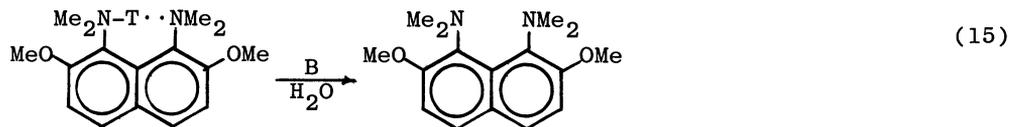


Fig. 5. Schematic representation of Bronsted plot (upper drawing) and free energy vs. reaction coordinate diagrams (lower drawings) for proton transfer from intramolecularly hydrogen bonded acids by the pre-equilibrium mechanism. The solid line in the Bronsted plot denotes proton transfer from a normal non-hydrogen bonded acid.

Unfortunately, the region around $\Delta pK'=0$ is not accessible by the usual kinetic methods which use spectrophotometric detection. For example, T-jump measurements can only be made in a range up to 2-3 pK units to either side of $\Delta pK=0$. Such determinations nevertheless have been done, and they have produced the near-unity isotope effects (30) and rate constants independent of ΔpK (28) expected for the pre-equilibrium mechanism in this region.

In order to obtain information in the more diagnostic region about $\Delta pK'=0$, we have turned to a tritium tracer method of following the reaction. We place the tritium initially in the nitrogen-hydrogen bond of protonated Super Sponge and then monitor its loss to the solvent in the presence of basic catalysts (eq. 15). Although these reactions are strongly uphill and



therefore quite reversible in a chemical sense, the overwhelmingly large pool of hydrogen in the wholly aqueous solvent employed renders detritiation essentially non-reversible.

The rate constants we determined for this system are shown in Fig. 6 as a Bronsted plot. This plot is decidedly biphasic, as expected at $\Delta pK'=0$ for the pre-equilibrium mechanism, and this confirms that this mechanism is operating here. But the rate constants also show a systematic difference between oxygen and nitrogen bases, with nitrogen bases reacting a full order of magnitude more slowly at $\Delta pK'=0$. Part of this difference is probably the result of an electrostatic effect, which favors reaction of the positively charged substrate with negatively charged oxygen bases over neutral nitrogen bases. Most of the reactivity difference, however, as well as the more gradual curvature shown by the nitrogen bases at $\Delta pK'=0$ must be due to an intrinsically slower proton transfer step with the nitrogen proton acceptors.

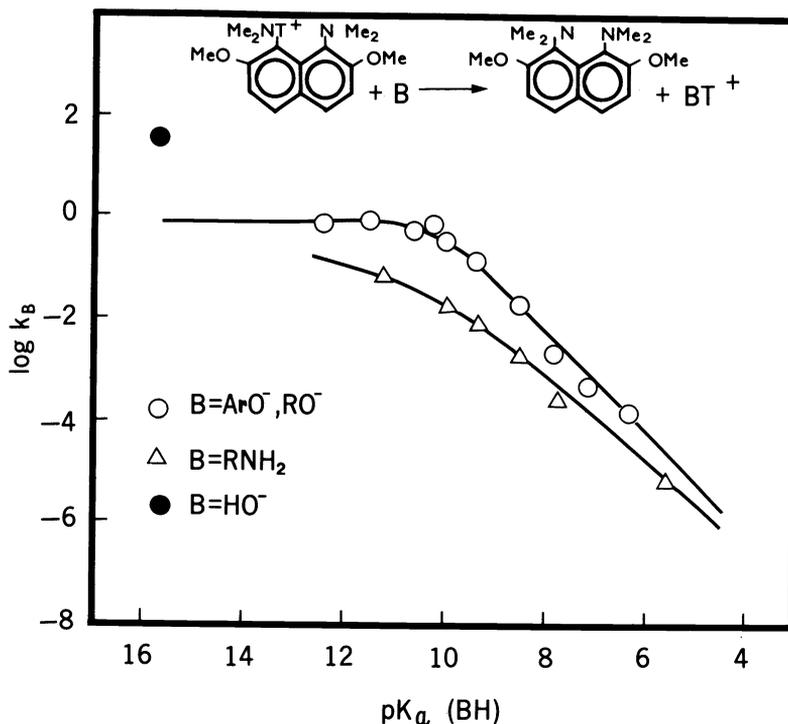


Fig. 6. Bronsted plot for proton transfer from the conjugate acid of Super Sponge.

in such reactions, however, over only a very narrow range of ΔpK about $\Delta pK=0$, and outside of this region it does lie in an entirely stable potential and does eschew formation of reacting bonds.

Proton transfer between electronegative atoms is intrinsically faster the greater the electronegativity of the atoms between which the proton is moving; this order is determined by the strength of the hydrogen bond formed between proton donor and proton acceptor. Consequently, proton transfers involving nitrogen are slower, and (partly) rate-determining over a wider range of ΔpK , than are those limited to oxygen, and proton transfers involving phosphorus are slower yet.

Acknowledgement - This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, the Petroleum Research Fund of the American Chemical Society, and the University of Toronto.

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