bond closely approximates that gained through rotation of the amide group and subsequent coordination with the iron atom.

Little, *et al.*, found that both acetoxyferrocene and phenoxyferrocene were not only oxidized more readily than expected, but also were irreversibly oxidized. We suggest that coordination of the acetoxy and phenoxy substituents with the positive iron atom in the oxidized species may have provided a pathway for decomposition. It would seem that more research is indicated to determine why methoxyferrocene is stable and acetoxy- and phenoxyferrocenes unstable under oxidation conditions. Apparently, the urethano- and acetamidoferrocenes do not have a similar pathway for facile decomposition when oxidized.

In conflict with the present study wherein acetamido- and urethanoferrocenes are oxidized at anomalously low quarter-wave potentials, Tirouflet and Komenda observed no unusual behavior for acetamidoferrocene in a polarographic study.[11] The data point for this compound fell very nearly on the correlation line in their plot of the oxidation potentials of 17 ferrocene derivatives *vs.* σ_p. Unless the ethanol–water solvent used in the study of Tirouflet and Komenda minimized the effect of internal solvation by the acetamido group as compared with the effect in acetonitrile, we are at a loss to explain the conflicting results. It is our feeling that a polar hydroxylic solvent system should not completely mask an internal solvation phenomenon. This problem should be investigated further.

Tirouflet and Komenda also reported that their data did not correlate nearly as well with σ_m or Taft's polar constants. It is interesting to note that in their σ_p plot the point for aminoferrocene fell off the correlation line in the same direction that the point for methoxyferrocene did in our own study. Here again it seems that the electron-donating effect of substituents is overestimated by σ_p.

Acknowledgment. We are indebted to Professor J. H. Richards and Professor F. C. Anson for their helpful comments and for financial assistance during the course of this investigation. The financial assistance was derived in part from the U. S. Army Research Office (Durham) under Grant No. DA-ARO(D)-31-124-G315 and in part from the National Science Foundation under Grant No. NSF-GT5190.

Rates and Isotope Effects in the Proton Transfers from 2-Nitropropane to Pyridine Bases[1]

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Abstract: The reaction between pyridine bases and 2-nitropropane in the presence of iodine is uncomplicated in *t*-butyl alcohol–water mixtures. In the absence of excess iodide ion and with only a small fraction of the pyridine converted to its conjugate acid, the reversibility can be neglected, and the reaction is apparently free from solvent and lyate ion catalysis. Steric retardation from 2- and 6-alkyl groups in the pyridine is significant, and comparable in magnitude to the acceleration resulting from the increase in base strength. Isotope effects measured when using 2-nitropropane-2-*d* are large and variable, increasing not only with base strength but also with steric hindrance from a value of $k_H/k_D = 9.8$ at 24.88° for pyridine catalysis to $k_H/k_D = 24.2$ for 2,4,6-trimethylpyridine catalysis at the same temperature. Reasons for the unusually large isotope effects are considered; both tunneling and extensive loss of zero-point energy are invoked.

The proton transfer reaction is one of the most important reactions of chemistry, because of the prevalence of hydrogen and also because of the widespread use of hydroxylic solvents, which serve as both proton donors and acceptors. Aliphatic nitro compounds are experimentally desirable as proton donors to bases because the slow reaction is not susceptible to acid catalysis, so that the interpretation of measured rates is simplified. In previous work[3] aqueous ethanol was used as a solvent, and complications resulting from the side reactions with iodine were significant. In the present work *t*-butyl alcohol–water was used as a solvent to avoid this difficulty, and the extent of the reverse reaction, the existence of which has been established,[3,4] was reduced by minimizing the concentrations of inorganic products, acid, and iodide ion.

Results

The rates of reaction 1 were followed by disappearance of iodine measured spectrophotometrically in a

$$\mathrm{Py} + (CH_3)_2CHNO_2 + I_2 \longrightarrow \mathrm{PyH}^+ + I^- + (CH_3)_2ClNO_2 \quad (1)$$

system containing *ca.* 0.1 *M* pyridine base, *ca.* 0.1 *M* 2-nitropropane, and *ca.* 10^{-4} *M* iodine in a solvent consisting of six volumes of *t*-butyl alcohol made up to ten with water. The small amount of perchloric acid used in previous studies[3,5] is not necessary, but was usually

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[1] A portion of this work has been published before in preliminary form: L. Funderburk and E. S. Lewis, *J. Am. Chem. Soc.*, **86**, 2531 (1964). From the Ph.D. Thesis of L. H. Funderburk, 1964.

[2] Robert A. Welch Foundation Predoctoral Fellow, 1962–1964. We thank this Foundation for this and other support of this work.

[3] E. S. Lewis and J. D. Allen, *J. Am. Chem. Soc.*, **86**, 2022 (1964).

[4] R. P. Bell and E. Gelles, *Proc. Roy. Soc.* (London), **A210**, 310 (1952).

[5] R. G. Pearson and F. V. Williams, *J. Am. Chem. Soc.*, **75**, 3073 (1953).

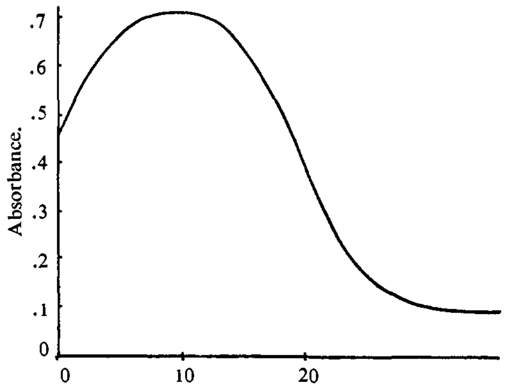

Figure 1. The time dependence of absorbance at 360 mμ for iodine, 2-nitropropane, and 2,4,6-trimethylpyridine in aqueous *t*-butyl alcohol.

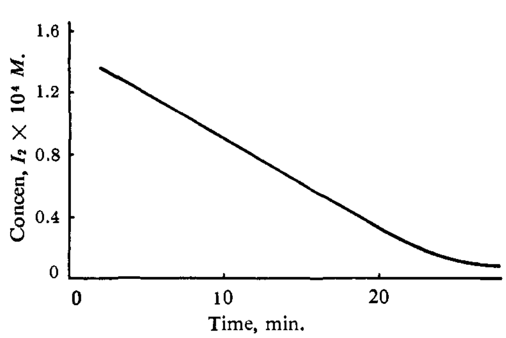

Figure 2. The time dependence of total iodine concentration as measured by the extinction coefficients and the absorbance shown in Figure 1.

used. The disappearance of iodine follows a zero-order course, but a plot of optical density *vs.* time is far from linear, because both the reagent pyridine base and the product iodide ion react reversibly with iodine to alter the extention coefficient, but not the kinetics. In earlier work,[3] excess iodide ion was used to make the extinction coefficient constant, but in this case the experimental simplification is not worth the added complexity of interpretation introduced by extensive reversal. Figure 1 shows the absorbance plotted against time for a reaction with 2,4,6-trimethylpyridine as the base. The curvature results entirely from variation of extinction coefficient, and this one is extreme since it was measured at 360 mμ. Most measurements were made at 468 mμ, where this effect is less marked but still present. This plot, obtained directly from the recording spectrophotometer, was then converted to a plot of concentration of iodine (including all its complexes) as a function of time using appropriate extinction coefficients. The plot so obtained from the data of Figure 1 is shown in Figure 2, and the good linearity down to large extents of completion is shown. The reaction in this linear portion is thus zero order in iodine. The reversal indicated by the non-zero final concentration of iodine was neglected, since data were used before the appearance of significant curvature.

The second-order rate constants were obtained by dividing the zero-order rate constant by the product of the initial 2-nitropropane and free base concentrations. Since the rate expression has been explored before, no searching experiments were done to verify it. No results were incompatible with this rate law except for the blank reaction mentioned elsewhere, for which correction was made. We therefore consider only one important term in the rate expression, that shown in eq 2 (2NP = 2-nitropropane, Py = a pyridine base).

$$-\mathrm{d}(\mathrm{I_2})/\mathrm{d}t = k_2(\mathrm{Py})(\mathrm{2NP}) \qquad (2)$$

Since the ionization of nitro compounds is presumably subject to general base catalysis, one should also be concerned about the terms $k_3(\mathrm{OR^-})(\mathrm{2NP})$ and $k_4 \cdot (\mathrm{ROH})(\mathrm{2NP})$. Following Pearson and Williams,[5] we attempted to suppress the k_3 term by adding some acid. The lack of important contribution of this term is indicated by an experiment in which the acid was omitted, using 2,6-dimethylpyridine as the base. No significant change in rate was noted, which suggests that the lyate ion term becomes negligible with only the amount of acid produced in the first few per cent of the reaction of the iodine, which occurred before measurements were started. The absence of the solvent term was not rigorously demonstrated, but if this term had contributed heavily, the rate would not have been proportional to the concentration of free base, and a significant rate in the absence of base would have been noted. The rate constants determined as described above are shown in Tables I and II. The tabulated values of the rate constant for deuterated species, k_D, include a correction, suitable when the extent of reaction is small, for contamination by the protonated species by eq 3, in which k_obsd is the observed rate constant for the deuterated compound, and *f* is the fraction

Table I. Rates and Isotope Effects for the Iodination of 2-Nitropropane in the Presence of Pyridine Bases

Pyridine subst	pK_a[a]	10^4k_H,[b] M^{-1} min^{-1}	10^4k_D,[c,d] M^{-1} min^{-1}	$k_\mathrm{H}/k_\mathrm{D}$
None	5.17[e]	1.12 ± 0.02	0.122 ± 0.003	9.8
3-Methyl	5.68[e]	1.56 ± 0.03	0.153 ± 0.003	10.2
2-*t*-Butyl	5.76[e]	0.0585[c]	*f*	. . .
2-Methyl	5.97[e]	2.70 ± 0.02	0.232 ± 0.001	10.2
4-Methyl	6.02[e]	2.24 ± 0.06	0.211 ± 0.002	10.6
3,5-Dimethyl	6.19[g]	2.20 ± 0.02	0.207 ± 0.004	10.6
2,5-Dimethyl	6.48[h]	4.23 ± 0.10	0.387 ± 0.002	10.9
3,4-Dimethyl	6.53[h]	3.07 ± 0.09	0.303 ± 0.01	10.1
2,6-Dimethyl	6.75[e]	1.73 ± 0.04	0.0717 ± 0.002	24.1
2,4-Dimethyl	6.79[i]	5.93 ± 0.06	0.403 ± 0.005	14.6
2,4,6-Trimethyl	7.59[j]	4.83 ± 0.07[k]	0.199 ± 0.011[k]	24.3

[a] pK_a of $\mathrm{PyH^+}$ measured in water. [b] The indicated errors are average deviations of several runs made in aqueous *t*-butyl alcohol at 24.88° and measured at 468 mμ. Blank corrections not more than 2%. [c] Corrected for blank reaction of not more than 10%, otherwise as in *b*. [d] Corrected for 1.3% light hydrogen content; the uncertainty of this correction is not included in the figures following ±. [e] H. C. Brown and X. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955). [f] Too slow for adequate separation from blank reaction. [g] J. M. Essery and K. Schofield, *J. Chem. Soc.*, 3939 (1961). [h] Estimated from the pK_a of pyridinium ion by adding 0.80 for each 2-$\mathrm{CH_3}$ group, 0.51 for each 3-$\mathrm{CH_3}$ group, and 0.85 for each 4-$\mathrm{CH_3}$ group. This estimate reproduces the published values in the table within 0.03 pK_a unit. [i] L. Saceoni, D. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **82**, 3828 (1960). [j] H. C. Brown, S. Johnson, and H. Podall, *ibid.*, **76**, 5556 (1954). [k] Measurements made at both 468 and 360 mμ.

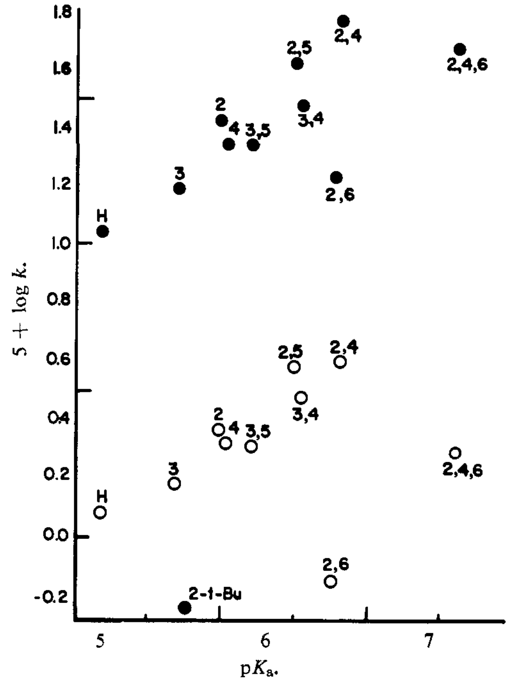

Figure 3. Brønsted plots for the reaction of pyridine bases with 2-nitropropane, ●, and 2-nitropropane-2-*d*, O, in aqueous *t*-butyl alcohol. Numbers indicate positions of substituents, methyl except where otherwise stated.

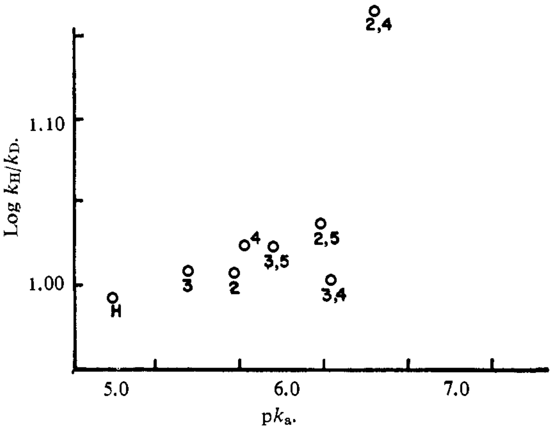

Figure 4. Plot of log k_H/k_D *vs.* pK_a for the reactions of substituted pyridines with 2-nitropropane. The points for 2,6-dimethylpyridine and 2,4,6-trimethylpyridine are off scale.

of the protium in this compound. The value used for proton content of the deuterated species was 1.3%.

$$k_D = (k_{obsd} - fk_H)/(1 - f) \qquad (3)$$

Discussion

The results in Table I can be used to show that there is significant steric hindrance in some of these reactions. Brønsted plots of the data for both the protium and deuterium compounds are shown in Figure 3.

The Brønsted correlation is rough, but the deviations of the points for the 2,6-dimethyl-, 2,4,6-trimethyl-, and 2-*t*-butylpyridines (amounting to a factor of about 5 too slow a rate for the first two bases, and about 30 for the third) are clear and can be understood in terms of steric hindrance to proton transfer. There is no obvious deviation with any of the other 2-methyl substituents. We shall discuss the results with the the apparently unhindered bases first.

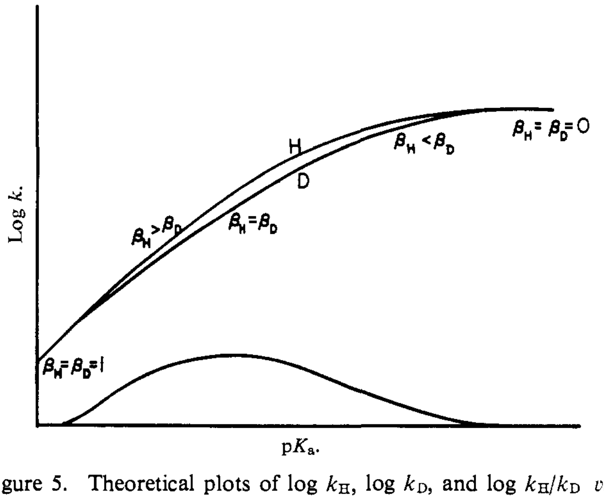

Figure 5. Theoretical plots of log k_H, log k_D, and log k_H/k_D *vs.* pK_a for a proton transfer reaction.

The slopes (β) of the Brønsted plots are not well defined, but that for the deuterium compound is about 0.4. A small difference in the Brønsted slope between the hydrogen compound and the deuterium is not obvious from this plot, but is more conspicuous in Figure 4, in which log k_H/k_D is plotted against pK_a of the pyridinium ion, the bases with serious steric effects being off scale. A correlation with base strength is indicated, and most of the 8 points fall reasonably on a line with a slope of 0.04, indicating that the Brønsted β for unhindered cases is perhaps 10% larger for the proton transfer than for the deuteron transfer reaction. This increase in isotope effect with base strength of the attacking species has often been observed before (a few of the many examples are cited in ref 3); it is clear that it cannot continue over a wide range of base strengths, for the isotope effects would become unreasonably large. Thus, this increase of 0.04 in log k_H/k_D per pK unit would predict k_H/k_D = 50 with a hypothetical base with conjugate acid pK_a of 20. Such isotope effects are unreasonable and not in accord with either experience or any theory of isotope effects. The Brønsted relationship runs into a limitation when reactions are diffusion controlled, but for this same base with conjugate acid pK_a = 20, the rate constants k_D and k_H predicted by the Brønsted coefficients of 0.40 and 0.44, respectively, are k_D = 0.2 and k_H = 10 l./mole sec, which are well below the diffusion-controlled limit. In order to reconcile experience and theory with this extrapolation, it is clear that the extrapolation must give way, and the Brønsted relation for either the proton

Table II. Temperature Dependence of the Iodination of 2-Nitropropane with 2,4,6-Trimethylpyridine

Temp, °C	10^4k_H,[a] M^{-1} min^{-1}	10^4k_D,[a] M^{-1} min^{-1}	k_H/k_D
32.08	9.08 ± 0.02	0.425 ± 0.013	21.4
27.03	6.49 ± 0.27	0.265 ± 0.010	24.5
25.01	4.89 ± 0.05	0.197 ± 0.006	24.8
20.45	3.61 ± 0.20	0.138 ± 0.007	26.2

[a] Conditions, corrections, and errors as described in Table I except for temperature.

transfer, the deuteron transfer, or both must fail over this wide range of base strengths. It is absurd to assume a conspicuous failure of the Brønsted relationship for only one isotope; it is more reasonable to have deviation from the relationship in both reactions. A reasonable form for the deviation from linearity is illustrated in Figure 5, which shows the limiting slopes of one and zero as described by Eigen.[6] The difference curve is also plotted (with a magnified scale), showing a maximum in k_H/k_D at some intermediate base strength associated with a Brønsted slope well removed from either limit.

It is difficult to construct any other dependence of isotope effect on pK that does not lead to a rather tortuous Brønsted plot, especially since the kinetic isotope effect can reasonably be expected to be absent in the diffusion-controlled reverse reaction at the left-hand limit.[7]

There is no obvious analytic form to the curves of Figure 5, so that it is not necessary to assume the value $\beta = 0.500$ in the neighborhood of a base giving maximum isotope effect. The observed value of $\beta = 0.4$, which is probably near the maximum since the isotope effects are so large, is reasonable. We would expect further that the Brønsted β would be large for a reaction with isotope effect increasing with base strength, and small when the isotope effect decreases with base strength.

It should be noted that an imaginative reader can actually see a maximum in the isotope effect in Figure 4. If it is assumed that even the single 2 substituent introduces a steric effect which influences the isotope effect, then one should exclude these from Figure 4, and the remaining points show a maximum in isotope effect at pK_a about 6.1. If this is real, then this is the first observation of such an effect with a closely related series of bases.

It is interesting that this maximum in the isotope effect on changing K_a is a consequence only of the dependence of the isotope effect on K_a. The maximum derived from these considerations may be compared to that predicted by Westheimer[8] (and in different language by Melander[9]) for the one-dimensional transition state with hydrogen between two heavier particles. They predict a maximum isotope effect when the force constants to the two particles are equal, and k_H/k_D about unity when either one of these force constants is much greater than the other. The maximum in the isotope effect may then be expected roughly when the reagent base and product base are equal in strength; the transition state should then be about halfway to the products and thus the Brønsted coefficient should be about one-half. It is of interest to see to what extent the present situation fits these expectations. Since the 2-nitropropane anion is probably a stronger base than the pyridine bases, the ionization reaction is endothermic. Hence, following Hammond,[10] the transition state is somewhat product-like but would become more symmetric if the attacking base were stronger. This consideration of basicity would lead to the conclusion that we are on the left-hand side of the maximum in Figure 5. The observed coefficient of 0.4 is then adequately close to the predicted value. There are two complicating factors which should be considered in comparing the present results with any theory. First, the proton is attached to carbon in the reagent and to nitrogen in the product, and the reaction leads to separate charges from neutral reagents. There is thus no reason to believe that the upper curves in Figure 5 should have much symmetry. If a transition state has reached the halfway point in charge separation (the condition expected with $\beta = 0.5$), it need not have attained exactly the halfway point in bond strengths, such that the isotope effect is maximized. Second, the reported Brønsted β is based on pK_a's measured in water, but to use it as a measure of the extent of proton transfer in the reaction under study the pK_a's should be measured in the same solvent as is used in the reaction.

The rates and the isotope effects with the unhindered cases then present elements of interest, especially with regard to the consequences of an isotope effect that varies with base strength, but do not present any features without precedent from earlier work. The fact that the isotope effects and rates are understood makes them of greater value as a basis for the discussion of the hindered cases, which we shall now consider.

There is no conspicuous evidence for hindrance with only a 2-methyl group. We should then limit this discussion to those bases which deviate markedly from the Brønsted plot, namely 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, and 2-*t*-butylpyridine. In the last case the rate was very low, and the deuterium case was too slow to measure, so that the isotope effect is quite large, but undetermined.

The very large isotope effects with 2,6-dimethylpyridine and 2,4,6-trimethylpyridine are somewhat larger than can be accounted for even by total loss of all the zero-point energy of the C–H and C–D bonds.[11]

The very large isotope effect ($k_H/k_D = 19.5$ at 25°) has also been reported for the 2-nitropropane–2,6-dimethylpyridine reaction in water solution by Bell and Goodall.[12] They also report work of great pertinence to the problem of variation in isotope effect with acid and base strength.

The temperature dependence of the rate for 2,4,6-trimethylpyridine (eq 4) shows that the preexponential factor ratio A_H/A_D is significantly less than unity, so that the activation energy difference is even more difficult to reconcile with zero-point energy effects alone.

$$k_H/k_D = A_H/A_D e^{\Delta E_a/RT} = 0.15e^{3006/RT} \tag{4}$$

The large isotope effect, the large activation energy difference, and the small A_H/A_D factor all suggest, as

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(6) M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

(7) If the reverse reaction has no isotope effect ($k_H/k_D = 1$), then neither does the forward reaction; more strictly, the ratio of the forward and reverse isotope effects is rigorously the equilibrium isotope effect, and this is usually very close to unity. This equilibrium isotope effect is neglected in Figure 5.

(8) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(9) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1962.

(10) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(11) Estimates of the isotope effect attainable under these circumstances depend on the values chosen for the bond vibrational frequencies. The largest estimate in print is about 18, and a smaller maximum value of about 12 arises from a calculation based upon the admittedly inadequately resolved infrared spectra of 2-nitropropane and of 2-nitropropane-2-*d*.

(12) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* (London), **A294**, 273 (1966). We are indebted to Mr. Bell for communicating several of these results to us in advance of publication.

discussed by Bell,[13] that there is a significant tunnel correction, especially to k_H. The existence of a relationship between the steric hindrance and the anomalous isotope effects is strongly indicated, and it is worth considering simple explanations of this relationship.

The simplest picture of the potential barrier to a reaction is a one-dimensional plot of potential energy *vs.* reaction coordinate. The activation energy required is of two sorts; the first is energy required to break bonds or stretch them beyond their equilibrium distance, and the second is that to overcome repulsions between nonbonded atoms. It is clear that steric hindrance falls in the second category. At short interatomic distances, the repulsive energy between atoms, whether bonded or not, rises very rapidly as the distance decreases, so that a potential barrier with an important steric repulsion component can be expected to be very steep in the neighborhood of the maximum. The resulting high barrier, which is difficult to surmount classically, has steep sides and is, therefore, relatively thin at the top; this situation is conducive to significant contribution of tunneling.[14]

It has been pointed out by Johnston[15] that one-dimensional barrier is inadequate to understand tunneling. It is interesting that even with a two-dimensional barrier representing a three-atom linear system there is a factor which will also enhance the fraction of tunneling in sterically hindered cases. Let us consider the familiar energy contours in the plot of r_{AH} *vs.* r_{BH}, and consider that there is in the unhindered case a certain fraction of tunneling direct from some point x on the reaction coordinate to another point y well below the maximum on the other side of the barrier and also on the reaction coordinate. Steric repulsion will raise the entire surface at short interatomic distances, that is, near the origin, but will have little effect when all distances are large. This has a major effect on the transition state but very little effect on the region directly between x and y, not along the reaction coordinate. Thus this tunneling will be relatively unchanged, but the rate of the classical barrier passage will be greatly reduced, and the fraction of tunneling will be increased by this steric repulsion.[16] These explanations, which are not entirely independent, do not allow us to be quantitative, but they do help make these very large isotope effects qualitatively understandable.

It should be noted that steric repulsions in the transition state can also increase the loss of zero-point energy. The most easy deformation in the A–H–B system to get rid of repulsions between A and B is to stretch the hydrogen bond itself, and as this is stretched, the bending vibrations will become less stiff and there will be substantial loss of bending zero-point energy, leading to an isotope effect approaching the upper limit accessible from zero-point energy effects alone. We now believe in fact that both tunnel effects and large zero-point energy effects are responsible for these very large isotope effects from results of an independent nature to be published shortly.

No mention has been made of the role of the solvent, nor can we find any evidence of any peculiar feature associated in the solvent in this reaction. Some less precise measurements with somewhat different mixtures of *t*-butyl alcohol and water showed essentially the same large isotope effects. The discrepancy between the isotope effects measured here and those reported in aqueous ethanol solution earlier[3] is therefore worthy of comment. The other measured isotope effects show reasonable agreement; for instance for pyridine k_H/k_D is 10.2 in *t*-butyl alcohol and 10.7 in ethanol, whereas for 2,6-dimethylpyridine we now find that k_H/k_D is 24.1 in *t*-butyl alcohol, but only 10.1 was reported in ethanol. We now believe that the values in aqueous ethanol suffer from an experimental error and possibly an error of interpretation, both of which could reduce the isotope effect. The principal experimental error is the existence of a slow iodine-consuming reaction in the absence of nitropropane which is essentially negligible for the faster reactions but which becomes serious with the slowest reactions. It will be seen from Table I in ref 3 that the slowest reactions are those of the deuterated 2-nitropropane with pyridine and with 2,6-dimethylpyridine. Since the blank reaction is faster when pyridine is substituted (either because iodination of the solvent is catalyzed more effectively by the stronger bases or because the blank reaction is in part iodination of the pyridine side chains), this blank correction is largest for the case in question of 2,6-dimethylpyridine. Our blank corrections were made assuming that this side reaction was zero order in iodine; if the reaction is first order, the correction is too big. Thus uncertainty in this blank correction makes the value of k_D for 2,6-dimethylpyridine the least accurate of all the data reported, and the k_H/k_D value the least reliable.

A possible error of interpretation in the earlier work may arise from the assumption that the terms associated with the general base catalysis in solvent and in lyate ion are negligible. In aqueous *t*-butyl alcohol these terms are indeed negligible, but in water solution both a water term and a hydroxide ion term are reported to contribute markedly.[12] It is therefore possible that these terms also contribute in aqueous ethanol. Since they would very likely have smaller isotope effects, the ratio of gross rates of the hydrogen and deuterium compounds would be less. We are grateful to Mr. R. P. Bell for presenting this suggestion to us before publication of this explanation.[12]

The absence of lyate ion term was demonstrated for pyridine solutions by showing that the rate was insensitive to the concentration of pyridinium ions. This experiment was not tried on the more strongly basic 2,6-dimethylpyridine, where the lyate ion concentration is higher. The solvent term was believed to be small, but the evidence is incomplete. The only pertinent data are rate constants measured at two different base concentrations which might be interpreted as differing by virtue of a solvent term in the rate expression instead of a change in iodine extinction coefficients as originally assumed. The data are inadequate to separate the two effects, and the blank error mentioned above makes it unlikely that it will be possible even with more data. Nevertheless, the presence of solvent and lyate ion

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(13) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(14) A referee suggests that steric hindrance may hold the extreme atoms of a model triatomic system farther apart throughout, thus effectively making the barrier thicker. We have not become convinced that the barrier thickness is this simply estimated, but we present the above argument as a plausible but by no means rigorous possible explanation of the observed experimental result.

(15) H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961).

(16) This suggestion was made to us by Dr. James M. Perry, whom we thank for this idea.

terms with smaller isotope effects would reduce the gross isotope effect substantially in the aqueous ethanol system. We therefore are inclined to weight the new large isotope more heavily than the old in aqueous ethanol and do not feel that a large isotope effect near a factor of 20 in the aqueous ethanol is necessarily excluded. The minimization of all these complications in aqueous *t*-butyl alcohol is doubtless related to the lower basicity and acidity of this solvent and its resistance to halogenation. It was indeed the unreliability of the lowest rates in the aqueous ethanol solution that prompted us to reinvestigate this reaction in aqueous *t*-butyl alcohol.

Experimental Section

Materials. 2-Nitropropane and 2-nitroproane-2-*d* were prepared as before;[3] the protium content of the deuterated species was 1.3% in the 2 position, as measured by the nuclear magnetic resonance spectrum. The substituted pyridines were prepared and purified as described before, and several new ones were commercial materials purified by distillation. Impurity by gas chromatography, which was able to resolve all the compounds available, amounted to no more than 1%. 2,4,6-Trimethylpyridine was purified by distillation from its boron fluoride complex as described before for 2,6-dimethylpyridine[3] to remove unhindered isomers. Tertiary butyl alcohol was a commercial material of good melting point.

Rate Measurements. The solvent was usually made by diluting 1.26 ml of 0.119 *M* aqueous perchloric acid with 30 ml of *t*-butyl alcohol. The carefully weighed appropriate amount of pyridine base (often about 0.4 g) was mixed with the *t*-butyl alcohol solution which was then diluted to 50 ml with water, giving a solution about 0.003 *M* in perchloric acid and 0.1 *M* in pyridine.

The reactions were started by adding a concentrated solution of iodine in aqueous *t*-butyl alcohol to this base solution until the absorbance reached a preselected value (about 0.48) and allowed to come to the thermostat temperature. 2-Nitropropane, about 0.5 g carefully weighed, was diluted to 50 ml with the above base and iodine solution and the resulting solution was placed in a 10-cm absorption cell placed in a recording spectrophotometer set at 468 mμ as rapidly as possible. Since temperatures in the cell compartment were slightly closer to room temperature than the thermostat, because of heat transfer in the circulating system, the temperature changes in dilution and cell filling were in part compensated and the times taken for the cell to come adequately close to the compartment temperature were in fact rather small.

In order to demonstrate absence of serious error from the conversion of absorbances to concentration, the results for 2,4,6-trimethylpyridine were repeated at 360 mμ, using 1-cm cells instead of 10 to compensate for the higher extinction coefficients. The results agreed within 2%.

Controls showed that uncertainty about the reaction temperature was not a significant source of error. Temperatures were measured with a thermistor in the cell compartment with the thermostat itself used frequently as a reference to compensate for drift. The thermostat temperature was determined with a Bureau of Standards calibrated thermometer. Absolute temperatures are probably not accurate to better than ±0.1°, but relative temperatures are limited primarily by reading accuracy and by the precision of bore of the thermometer, leading to an error probably ±0.02°, since the calibration was smooth.

Solutions of known concentration of the base, iodine, and iodide ion in the solvent simulating various extents of reaction were made up, to determine the relation between absorbance and concentration of iodine in all its various complexed states. The record of absorbance *vs.* time from the rates was then converted to a concentration *vs.* time plot, which was linear up to large extents of completion confirming the zero order in iodine and its complexes. There was a residual iodine absorption because of the reversibility of the reaction, but this complication was avoided by using only the linear portion of the curve. The reported second-order rate constants are the slopes of these linear plots, less a blank correction amounting in the largest case to 10% of the observed rate (measured in a solution containing everything but 2-nitropropane and not followed to complete consumption of iodine, since it is so slow) and then divided by the base and nitropropane concentrations. Blank runs with the pyridine base omitted showed negligible reaction, and the measured rates were unchanged by the omission of the small amount of perchloric acid, usually added.

The Importance of the "α Effect" in Amine General Base Catalyzed Ionization of Nitroethane

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Abstract: The conversion of nitroethane to its ion by amine general-base catalysis ($k_{2,B}$) and the retrograde general-acid neutralization of the anion ($k_{2,A}$) have been investigated. Both $k_{2,B}$ and $k_{2,A}$ are correlated by the Brønsted equations for general-acid and general-base catalysis, respectively. Though the log of the rate constants for tertiary, secondary, and primary amines lie on separate Brønsted plots of parallel slope (presumably due to differences of solvation), hydrazine, N-methylhydrazine, hydroxylamine, and methoxylamine show no positive deviations from these plots. Therefore, the so-called α effect does not appear to be operative in the breaking or making of the C–H bond of nitroethane.

The term "α effect" has been used[3] to describe the high reactivity of nucleophiles possessing an unshared pair of electrons adjacent (α) to the nucleophilic atom. This high reactivity is generally noted as a large positive deviation of the log k_{rate} for a nucleophile from a Brønsted plot for nucleophilic displacements by a series of like nucleophiles in aqueous solution. Therefore, the α effect amounts to a nucleophilic (kinetic) parameter not predicted by the thermodynamic affinity of nucleophile for a proton. The various rationales for this kinetic effect have recently been summarized and discussed.[4] They include intramolecular hydrogen

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