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Mechanisms of Elimination Reactions. 32. Tritium Isotope Effects and Tunnel Effects in the Reaction of 2,2-Diphenylethyl-*2-t* Derivatives with Various Bases[1]

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Abstract: Primary tritium isotope effects as a function of temperature have been determined for the E2 reaction of 2,2-diphenylethyl-*2-t* tosylate with ethoxide in ethanol and *tert*-butoxide as well as the anions derived from imidazole, 2-methylimidazole, and 2,4,5-trimethylimidazole in *tert*-butyl alcohol. The temperature dependence of the tritium isotope effect has also been determined for the E2 reaction of 2,2-diphenylethyl-*2-t* bromide with ethoxide in ethanol and *tert*-butoxide in *tert*-butyl alcohol. Observed k_H/k_T values at 50 °C ran from 17.6 to 31.3, and the ratios of Arrhenius preexponential factors, A_{aH}/A_{aT}, from 0.15 to 0.74, indicating moderate tunneling. A temperature dependence calculated from the Bell theory of tunneling was fitted to the observed temperature dependence to obtain tunnel corrections, Q_{tH}/Q_{tT}, ranging from 1.3 to 2.5 at 50 °C. Observed isotope effects are larger with *tert*-butoxide in *tert*-butyl alcohol than with ethoxide in ethyl alcohol for both the tosylate and the bromide, but the difference arises primarily from tunneling. Isotope effects are larger with the imidazole anions than with *tert*-butoxide. There is no marked effect of methyl substitution in the imidazole anion on either the observed isotope effect or the tunnel effect, even with the sterically hindered 2,4,5-trimethylimidazole anion. The semiclassical (without tunneling) isotope effects run approximately 80–100% of the maximum values predicted by the treatment of Melander and Westheimer. The proton thus seems to be nearly symmetrically located in the transition states, and the contribution of heavy-atom motion to the reaction coordinates cannot be large.

Our recent studies of the temperature dependence of deuterium isotope effects in E2 reactions have revealed that moderate tunneling is quite common.[2-4] To explore further the occurrence of tunneling in E2 reactions and its relation to reactant structure and reaction conditions, we chose to determine tritium isotope effects in reactions of 2,2-diphenylethyl-*2-t* tosylate and bromide with bases of varying strength and steric requirements. Because tritium isotope effects are greater than the corresponding deuterium isotope effects, changes in their magnitude should be easier to measure precisely. Tritium isotope effects are also well suited for temperature dependence studies, since the competitive method permits measurement over a wide range of rates, without the deterioration of precision at the extremes often encountered in diirect rate measurements. The only limitation to the intermolecular competitive procedure used here is that mixing of reagents must be fast compared to the rate of reaction so as to avoid local depletion of the faster reacting isotopic species.

The desired tritium label was introduced by refluxing diphenylacetic acid with tritiated water in the presence of excess sodium hydroxide.[5] The recovered acid was reduced to 2,2-diphenylethanol-*2-t* with lithium aluminum hydride. Oxidative degradation to benzophenone showed that less than 0.1% of the activity of the alcohol resulted from tritium in the benzene rings. The alcohol was tosylated by standard procedures or converted to the bromide by the method of Wiley et al.[6]

Because k_H/k_T is large, the molar activity of unreacted starting material after partial reaction depends very little on the magnitude of k_H/k_T[7]. Precise measurement of k_H/k_T requires determination of the molar activity of the radioactive product of the reaction, which in the present case is the solvent, *tert*-butyl alcohol or ethanol.[8] Spectrophotometric measurement of the fraction of reaction, F, and determination of the specific activity of the solvent permit calculation of the molar activity of that fraction of the solvent formed by the reaction. In the work on the tosylate, we carefully recovered all of the solvent activity from the reaction mixture by chasing with inactive solvent but later discovered that distillation of about 30% of the total resulted in no measurable tritium fractionation. This procedure for determining k_H/k_T does have the disadvantage that uncertainty in F affects not only F but R_p (molar activity of the product) as well. The isotope effect is, however, not very sensitive to small errors in R_p.[7]

Table I. Tritium Isotope Effects for the Reaction of 2,2-Diphenylethyl-*2-t* Tosylate with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol

T, °C	k_H/k_T	T, °C	k_H/k_T
40	30.59	60	23.71
40	31.30	70	20.99
50	27.12	70	20.28
50	26.40	80	18.56
60	22.77	80	18.29

The quantities F, R_p, and the molar activity of the original reactant, R_o, can be combined to give the isotope effect[7]

$$\frac{k_H}{k_T} = \frac{\log (1 - F)}{\log [1 - (FR_p/R_o)]} \tag{1}$$

A typical set of results is shown in Table I. In nearly all cases duplicate results agree with each other to within 1–3%. The k_H/k_T values at 50 °C and the Arrhenius parameters for all of our reactions are summarized in the first five columns of Table II.

On the basis of a simple three-center model for proton transfer, the same reasoning that gives a lower limit for A_{aH}/A_{aD} of 0.5 in the absence of tunneling gives 0.33 for A_{aH}/A_{aT}.[9] This figure is almost certainly unrealistically low.[3] Model calculations suggest realistic lower limits of 0.7–0.9 for A_{aH}/A_{aD}.[10,11] Comparable calculations have not been done for A_{aH}/A_{aT}, but a reasonable

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Table II. Activation Parameters, Tritium Isotope Effects, and Tunnel Corrections for the Reaction of 2,2-Diphenylethyl-*2-t* Derivatives with Base[a]

leaving group	base[b]/solvent	A_{aH}/A_{aT}[c]	$E_{aT} - E_{aH}$[c]	k_H/k_T[d]	Q_{tH}/Q_{tT}[e]	$(k_H/k_T)_s$[f]
OTs	*t*-BuO⁻/*t*-BuOH	0.314 ± 0.039	2.85 ± 0.08	26.72	2.04	13.10
OTs	Im⁻/*t*-BuOH	0.344 ± 0.048	2.90 ± 0.09	31.32	1.89	16.57
OTs	MIm⁻/*t*-BuOH	0.153 ± 0.025	3.41 ± 0.11	30.74	2.52	12.20
OTs	TMIm⁻/*t*-BuOH	0.278 ± 0.063	3.00 ± 0.15	29.80	2.10	14.19
OTs	EtO⁻/EtOH	0.600 ± 0.089	2.21 ± 0.10	18.86	1.69	11.16
Br	*t*-BuO⁻/*t*-BuOH	0.463 ± 0.095	2.42 ± 0.12	20.11	1.65	12.19
Br	EtO⁻/EtOH	0.738 ± 0.110	2.57 ± 0.35	17.60	1.27	13.86

[a] The temperature range was 40–80 °C at 10 °C intervals for all reactions of the tosylate, 30–65 °C for the bromide with *t*-BuO⁻, and 20–70 °C for the bromide with EtO⁻. [b] Im⁻ = imidazole anion, MIm⁻ = 2-methylimidazole anion, TMIm⁻ = 2,4,5-trimethylimidazole anion. [c] From least-squares fits of the data to the Arrhenius equation. Deviations are standard deviations. [d] Calculated from the Arrhenius parameters at 50 °C. [e] Tunnel correction to the isotope effect obtained by fitting a temperature dependence calculated from the first term of the Bell equation to the observed temperature dependence at 50 °C (see text). [f] The semiclassical isotope effect at 50 °C, $(k_H/k_T)/(Q_{tH}/Q_{tT})$.

estimate would be 0.6 to nearly 0.9. For fairly large k_H/k_D values, the calculated A_{aH}/A_{aD} is very close to unity (1.0 ± 0.1) and so, presumably, is A_{aH}/A_{aT} for k_H/k_T values of the size reported here. By these criteria, all or nearly all of the reactions in Table II show definite evidence of tunneling.

To obtain a quantitative measure of tunneling, we applied a procedure of fitting to the observed temperature dependence a calculated temperature dependence based on the Bell theory of tunneling.[9] We used the program of Caldin and Mateo[12] on our k_H/k_T values for the tosylate but subsequently found that a simpler and faster method gave equivalent results when the first term of the Bell equation was adequate,[3] which is the case for all of the results reported here. Consequently our k_H/k_T values for the bromide were fitted by the simpler procedure. The resulting tunnel corrections, Q_{tH}/Q_{tT} and semiclassical isotope effects, $(k_H/k_T)_s$, are given in the last two columns of Table II. We have discussed previously the justification for using the Bell theory in deriving tunnel corrections to hydrogen isotope effects in reactions such as these.[3]

Before considering the results further, we should set them in the context of our earlier investigations of tunnel corrections to k_H/k_D values.[2-4] The commonly used relationship between k_H/k_D and k_H/k_T (eq 2)[13] does not take tunneling into account and so

$$\ln (k_H/k_T)_s/\ln (k_H/k_D)_s = 1.44 \qquad (2)$$

applies strictly only to semiclassical isotope effects. Model calculations indicate, however, that the inclusion of tunneling has very little effect on the relationship.[14] To determine how well an expression like eq 2 might apply to the tunnel corrections alone, we used the first term of the Bell equation (eq 3) and assumed

$$Q_t = (u_t/2)/\sin (u_t/2) \qquad (3)$$

that u_{tH}, u_{tD}, and u_{tT} were in the ratio $1:1/\sqrt{2}:1/\sqrt{3}$. Values of u_{tH} from 0.5 to 5.5 at intervals of 0.5 were used, and the ratio of eq 4 was calculated. The ratio t was not quite constant but

$$\frac{\ln (Q_{tH}/Q_{tT})}{\ln (Q_{tH}/Q_{tD})} = t \qquad (4)$$

varied from 1.33 at $u_{tH} = 0.5$ to 1.22 at $u_{tH} = 5.5$. Thus the appropriate value of t for any given u_{tH} can be obtained by interpolation, and the Q_{tH}/Q_{tH} values in Table II can then be shown to correspond to Q_{tH}/Q_{tD} values ranging from 1.2 to 2.1. The Q_{tH}/Q_{tD} values found for the reactions of 2-arylethyl and 2-aryl-1-propyl derivatives were in the range 1.3–2.1 at 50 °C.[3] Application of eq 2 to our $(k_H/k_T)_s$ values of 11.2–16.6 converts them to $(k_H/k_D)_s$ values of 5.3–7.0. These are in a higher range than the values of 2.0–5.3 observed for 2-arylethyl and 2-aryl-1-propyl derivatives.[3]

The semiclassical isotope effects in the 2,2-diphenylethyl system correspond to roughly 80–100% of the maximum values expected from a simple three-center model as well as more elaborate models for hydrogen transfer.[15,16] Such large semiclassical isotope effects indicate that all of these reactions proceed *via* transition states in which the proton is nearly symmetrically located between the β-carbon and the attacking base. In addition, no substantial amount of heavy-atom motion (C–C contraction and C-OTs or C–Br extension) can be coupled with the proton transfer in the reaction-coordinate motion, for such coupling should also diminish the primary hydrogen isotope effect.[2,3,16,17] Thus the reactions appear to be near the ElcB-like end of the spectrum of E2 transition states,[18] with relatively little double-bond character or extension of the bond to the leaving group.

In contrast, semiclassical isotope effects with 2-phenylethyl-*2,2-d*$_2$ derivatives run considerably lower relative to the maximum values. 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium bromide reacts with hydroxide ion in H_2O–Me_2SO mixtures and with ethoxide in ethanol to give $(k_H/k_D)_s$ values that are only 30–50% of the maximum, even under conditions in which the proton is almost certainly symmetrically located in the transition state.[3] As noted above, the range for all E2 reactions of 2-arylethyl and 2-aryl-1-propyl derivatives examined so far is 2.0–5.3, or 30–80% of the maximum, barely up to the lower limit for the reactions of the 2,2-diphenylethyl derivatives. On average, at least, E2 reactions of 2-arylethyl derivatives seem to have more concerted and less ElcB character than those of 2,2-diarylethyl derivatives.

It is interesting that the difference in $(k_H/k_D)_s$ values between the 2-arylethyl and the 2,2-diphenylethyl derivatives is not accompanied by any difference in Q_{tH}/Q_{tD} values, which are in virtually identical ranges for the two series (see above). One might have expected that a smaller effective mass along the reaction coordinate, resulting from less heavy-atom motion, and a more sterically hindered β-carbon should both contribute to more tunneling in the reactions of the 2,2-diphenylethyl derivatives. Evidently effective mass along the reaction coordinate is not a decisive factor nor is there any clear-cut relation between steric hindrance and tunneling (see below) in the present results. The magnitude of the tunnel correction depends upon barrier height, barrier width, and effective mass along the reaction coordinate,[9] and differences in one of these factors between the 2-arylethyl and 2,2-diphenylethyl systems may be counteracted by compensating differences in another. A plausible ad hoc explanation is that steric effects do narrow the barrier and that the effective mass is smaller in the reactions of the 2,2-diphenylethyl derivatives but that two β-aryl groups lead to a lower barrier than one because of greater stabilization of a carbanion-like transition state. It is certainly clear that no single factor stands out as decisive for the magnitude of the tunnel correction.

We now turn to the comparison of the present results with each other. Although they confirm our earlier observations[2-4] of virtually ubiquitous tunneling in E2 reactions, there are almost no

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clear-cut trends in either isotope effects or tunnel corrections. The most obvious regularity is that the overall k_H/k_T is larger for *tert*-butoxide in *tert*-butyl alcohol than for ethoxide in ethyl alcohol for both the tosylate and the bromide, but this difference is caused mainly or entirely by a larger tunnel correction with *tert*-butoxide in *tert*-butyl alcohol. The same generalization also holds for E2 reactions of 3-methyl-2-butyl *p*-nitrobenzenesulfonate.[4] The greater steric requirements of *tert*-butoxide and *tert*-butyl alcohol may be responsible. The former could lead to a narrower potential barrier and the latter to less effective solvation of the proton in transit, both of which are factors expected to enhance tunneling.[19-21]

In view of this evidence, it is surprising that the tunnel effect for the reaction of 2,4,5-trimethylimidazole anion with 2,2-diphenylethyl-*2-t* tosylate is not the largest of the tunnel effects for the E2 reactions of the same substrate. This base was expected to be sterically very similar to 2,6-dimethylpyridine, which does give unusually large isotope effects in its reaction with 2-nitropropane-*2-d* and *-2-t*.[19,20] The bond angles, and hence the shielding of nitrogen by the methyl groups, are slightly different in 2,4,5-trimethylimidazole anion and 2,6-dimethylpyridine, but it is difficult to believe that these minor differences would have much effect. Another factor is that the two bases differ in charge type, which could affect the NH and CH bond distances in the transition states and thereby the sensitivity to steric effects. Finally, the solvent remains the same with *tert*-butoxide and all of the imidazole anions, so the extent of solvation and hence the effective mass of the proton in transit may not vary significantly.

It is difficult to make much of the relatively small variations in the semiclassical isotope effects. The imidazole anion (pK_a = 14.2[22]) is a weaker base than *tert*-butoxide ion (pK_a = ca. 20) and gives a larger $(k_H/k_T)_s$ value. On the other hand, the two methylated imidazole anions are unlikely to differ greatly in pK_a from the parent anion and give $(k_H/k_T)_s$ values comparable to those with *tert*-butoxide. Ethoxide, also a weaker base than *tert*-butoxide, gives a smaller $(k_H/k_T)_s$ value with the tosylate but a larger one with the bromide. More or less plausible ad hoc explanations might be adduced for at least some of these results, but the $(k_H/k_T)_s$ values are probably uncertain by at least ±1, and that fact makes the significance of the observed order doubtful except for values at the two extremes. Under these circumstances it seems best to limit interpretation to the claim already made, that the proton is close to half transferred in the transition states of all of these reactions.

Experimental Section

Solvents. Absolute ethanol was refluxed over magnesium with a trace of iodine for 6 h and then distilled. The first 10% of the distillate was discarded. *tert*-Butyl alcohol was dried over grade 3A molecular sieves (Linde), refluxed over potassium *tert*-butoxide for 3 h, and distilled. The first 10% of the distillate was discarded.

Bases. Sodium ethoxide was prepared by scraping sodium clean under hexane, washing it twice in dry ethanol, and dissolving it in dry ethanol. Potassium *tert*-butoxide was prepared in an analogous manner from potassium metal and dry *tert*-butyl alcohol. Solutions of the imidazole anions in *tert*-butyl alcohol were prepared by mixing solutions of the imidazole and potassium *tert*-butoxide such that the final solution was 0.04 M in the imidazole anion and 0.04 M in the imidazole. Imidazole (Eastman Organic Chemicals) and 2-methylimidazole (Aldrich) were recrystallized from benzene prior to use.

2,4,5-Trimethylimidazole was prepared from 2,3-butanedione and ammonia.[23] The hydrochloride was isolated by passing dry hydrogen chloride gas into a dried ether extract of the crude product. The hydrochloride was purified by recrystallization from ethanol; mp 312–315 °C (lit.[24] mp 316 °C). The free imidazole was liberated from an aqueous solution of the hydrochloride with potassium carbonate and extracted with ether and the extract dried over magnesium sulfate. Removal of the ether and recrystallization from ether gave 2,4,5-trimethylimidazole, mp 131–2 °C (lit.[25] mp 132.5–133 °C).

Table III. Arrhenius Parameters for the Rates of Reaction of 2,2-Diphenylethyl Derivatives with Base[a,b]

leaving group	base[a]/solvent	E_{aH}[a]	log A_{aH}[a]
OTs	*t*-BuO⁻/*t*-BuOH	16.8 ± 1.9	9.381 ± 1.249
OTs	Im⁻/*t*-BuOH	19.6 ± 1.3	9.642 ± 0.835
OTs	MIm⁻/*t*-BuOH	16.9 ± 0.5	8.554 ± 0.348
OTs	TMIm⁻/*t*-BuOH	18.9 ± 0.6	10.599 ± 0.369
OTs	EtO⁻/EtOH	22.1 ± 0.4	12.511 ± 0.277
Br	*t*-BuO⁻/*t*-BuOH	14.6 ± 0.4	8.553 ± 0.278
Br	EtO⁻/EtOH	17.2 ± 0.4	10.140 ± 0.287

[a] See footnotes *a*–c in Table II. [b] From approximate rate constants obtained as described in the Experimental Section.

Diphenylacetic-2-*t* Acid. Diphenylacetic acid (6.3 g, 0.030 mol) was refluxed with 10 mL of tritiated water (1 mCi/mL, diluted from ICN Biological Grade, 100 mCi/mL) and sodium hydroxide (2.05 g, 0.050 mol) for 64 h. The solution was cooled and neutralized with 10% sulfuric acid. The precipitated acid was removed by filtration, washed with water, and dried to give a 98% yield of material of mp 146–148 °C (lit.[26] 146 °C), activity 11.55 μCi/mmol.

2,2-Diphenylethanol-*2-t* was obtained by the reduction of diphenylacetic-2-*t* acid with lithium aluminum hydride in ether, followed by the workup procedure of Amundsen and Nelson.[27] 2,2-Diphenylethanol-2-*t* was obtained in 70–90% yields; mp 51–52 °C (lit.[28] mp 52.5–54 °C).

2,2-Diphenylethyl-*2-t* Tosylate. The procedure was essentially that of Tipson,[29] except that the product was precipitated by adding 10% sulfuric acid with cooling (ice bath) to the reaction mixture. The product was obtained in 95% yield; mp 116–117 °C (lit.[30] mp 116 °C).

2,2-Diphenylethyl-*2-t* bromide was prepared by the procedure of Wiley et al.[6] from 2,2-diphenylethanol-*2-t*, triphenylphosphine, and bromine in dry dimethylformamide. After the bromine addition was completed, the reaction mixture was kept at 53 °C for 20 h, cooled, and poured into cold water. The mixture was extracted with 50:50 ether–hexane, and the extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left a syrup that crystallized on cooling. Recrystallization from ethanol afforded 48% of 2,2-diphenylethyl-*2-t* bromide, mp 59–60 °C (lit.[31] 63 °C).

Approximate Rate Constants. In order to decide the time required for a given fraction of reaction in the competitive measurement of k_H/k_T, we determined rough rate constants for the reactions of 2,2-diphenylethyl tosylate or bromide with base. Solutions 0.02 M in substrate and 0.04 M in base were allowed to react under the desired conditions, and 0.2-mL samples were taken at specified times and diluted to 25 mL with absolute ethanol for the determination of absorbance at 253 nm, the absorbance maximum of 1,1-diphenylethylene. Under these conditions the second-order integrated equation for unequal initial concentration can be written as eq 5, where F is the fraction of reaction at time t. The Arrhenius

$$\frac{1}{0.02}\ln\frac{(2-F)}{2(1-F)} = k_2t \tag{5}$$

parameters derived from these k_2 values are recorded in Table III. They reproduce k_2 at any temperature within ±10% of the observed values, but the preexponential factors are too imprecise to give meaningful entropies of activation.

Determination of k_H/k_T. A solution of 2,2-diphenylethyl-*2-t* tosylate (0.074 g, 6.81 μCi/mmol) in 10 mL of *tert*-butyl alcohol was equilibrated for 1 h in a 100-mL flask with a septum cap and potassium *tert*-butoxide (0.4 mL, 1.0 M) injected with a syringe. The initial concentrations were then substrate 0.02 M and base 0.04 M. For reactions with the imidazole and substituted imidazole anions as bases, the potassium *tert*-butoxide was injected into a solution 0.02 M in substrate and 0.08 M in the imidazole, resulting in initial concentrations of 0.04 M imidazole anion and 0.04 M imidazole. The reaction was permitted to proceed to the desired extent of completion. F ranged from 0.25 to 0.70 overall and in

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most runs was 0.40–0.60. No trend in k_H/k_T with F was discernible. Error analysis showed that the relative effect of error in R_p/R_0 on k_H/k_T was independent of F, but the relative effect of error in F on k_H/k_T was greater at higher F, rising slowly at first and then steeply above ca. 0.70. The chosen range of F was thus a compromise between the latter factor and the need to obtain sufficient activity in the solvent for precise counting. Three 0.2-mL samples were withdrawn by syringe for determination of the extent of reaction as described above (approximate rate constants). When the absorbance of unreacted starting material was not negligible, we corrected for it. The remainder of the solution was quenched with 1.0 N hydrochloric acid, centrifuged, and made up to 10.00 ± 0.02 mL.

Subsequent treatment varied somewhat with the nature of the substrate and solvent. In the reactions of the tosylate, 4.00 ± 0.02 mL of the solution was placed in a flask connected to a vacuum manifold, frozen in dry ice and acetone (liquid nitrogen when ethanol was the solvent), degassed by a pump–thaw–freeze–pump cycle, and distilled with the stopcock to the pump closed into a thimble cooled in dry ice and acetone (or liquid nitrogen). Remaining activity was chased into the distillate by repeating the above procedure twice after adding 2-mL portions of inactive solvent to the residue in the flask. The combined distillates were made up to 10.00 ± 0.02 mL. This procedure was shown to remove all of the active solvent within experimental error. 2,2-Diphenylethyl bromide was found to be too volatile for this procedure. Distillation of 3 mL of the total 10 mL of solution was shown by control experiments to result in no significant isotopic fractionation of the solvent (±0.25%) and no distillation of bromide. This was consequently the procedure used for experiments on the bromide.

The unreacted substrate and 1.0-mL samples of the distilled solvent from partial reaction were counted in a toluene-based scintillation cocktail to the ±0.5% (2σ) level of precision on a Beckman LS-100C liquid scintillation counter. Quench corrections were made by the external standard channels ratio method[32] using a Beckman ^3H set (No. 566323) of standard quenched samples to determine the quench correction curve. It was found advantageous to make a least-squares fit of the resulting data to a quadratic equation in the channels ratio to get as precise a value as possible for the percent efficiency. Counting efficiencies were close to 50% for all samples.

Position of Tritiation of Diphenylacetic Acid. In order to determine whether any tritium had been introduced into the aromic rings, we dissolved a 2.0-g sample of 2,2-diphenylethanol-*2-t* in water and treated the solution with 2.0 g of sodium carbonate and portionwise with potassium permanganate until its color persisted (ca. 10 g). After 4 h on the steam bath, the mixture was cooled, treated with sodium sulfite, and acidified to litmus. The mixture was extracted with ether and the extracts washed with sodium bicarbonate and dried. The product left upon removal of the ether was shown to be identical with authentic benzophenone (IR and 1H NMR); mp 47–48 °C (lit.[33] 48.1 °C) after recrystallization from ethanol. Its activity was only 0.083% of that of the 2,2-diphenylethanol-*2-t*, showing negligible tritium incorporation into the aromatic rings.

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Mechanism of Acid-Catalyzed Proton Exchange in Amidinium Ions

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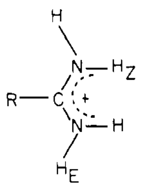
Abstract: In H_2SO_4, H_E of primary amidinium ions exchanges faster than H_Z, as evidenced by two different NMR techniques—line broadening and saturation transfer. This observation is interpreted according to a kinetic scheme that takes into account the competition between deprotonation of the intermediate $RC(-NH_3^+)=NH_2^+$ and rotation about its C—N single bond. Deprotonation is so fast—diffusion controlled—that it is able to compete with rotation because the intermediate is such a strong acid, with a pK_a estimated to be ca. −19. The dependence of protonation and deprotonation rates on angle of rotation is also discussed.

Introduction

In connection with studies on the mechanism of acid-catalyzed proton exchange in amides,[1,2] we were led to study the same reaction in amidinium ions (**1**). It had been observed[3] that



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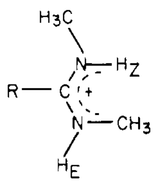

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N,N′-dimethylacetamidinium ion (**2**, R = CH_3) undergoes acid-catalyzed proton exchange in 80% H_2SO_4, via the dication $CH_3C(NH_2^+CH_3)=NH^+CH_3$, and that H_E exchanges 6.4 times as fast as H_Z. Recently this same behavior was also observed, qualitatively, in a gold-carbene complex (**2**, R = $Au_{1/2}^-$).[4] In both these studies the greater reactivity of H_E was accepted as arising from an inherently greater basicity of the nitrogen bearing H_E. Nevertheless, the 6.4-fold greater reactivity of H_E in the first example is too large to be due simply to basicity. For comparison the E/Z ratio in the isoelectronic alkene (3-methyl-2-pentene)[5] is only 1.5, and in the isoelectronic iminium ion (2-butanone *N*-methylimine in CF_3COOH) it is only 1.7 ± 0.2.[6]

We had reason to expect that H_E would exchange faster even in a primary amidinium ion (**1**), where the two nitrogens are necessarily of identical basicity. Indeed, we observed[7] that the protons of benzamidinium ion (**1**, R = C_6H_5) undergo acid-catalyzed exchange at different rates. However, this conclusion was based on only one series of spectra showing differential broadening of NH peaks already broadened by the ^{14}N quadrupole, and we were unable to ascertain that the faster proton was H_E. We now present further evidence that H_E of primary amidinium ions (**1**) does exchange faster, and the significance of that observation.

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