43.8°.[28] The sharpness of the melting point and the near-theoretical deuterium analyses argue against significant contamination.

Cyclohexyl ethyl ether was obtained by treatment of an ether suspension of the sodium salt of cyclohexanol (prepared from cyclohexanol and sodium hydride in dry ether) with ethyl bromide. Filtration and distillation, followed by treatment with sodium metal and fractionation, gave a product of bp 148–149.5° (lit.[29] 148.5–149°).

Cyclohexyl *t*-butyl ether was prepared in the same manner as cyclohexyl ethyl ether, using *t*-butyl bromide instead of ethyl bromide. The product had bp 60–62° (12 mm) (lit.[30] 55–57° (10 mm)).

Kinetics of the Base-Promoted Elimination Reactions of the Cyclohexyl *p*-Toluenesulfonates. Anhydrous ethanol was prepared by the method of Lund and Bjerrum.[31–33] Anhydrous *t*-butyl alcohol was obtained by distilling Eastman Kodak White Label grade material twice from sodium. Gas chromatograms (15-ft Carbowax column) of both alcohols showed less than 0.05% of water. Standard solutions of alkoxides were obtained by dissolving the clean metal in the alcohol and were stored in polyethylene bottles. Standardization was performed just before each use. Standard aqueous sodium hydroxide and hydrochloric acid were prepared from carbonate-free water and standardized in the usual manner.

Reactions were run in a modified 50-ml volumetric flask with side arm as previously described.[2] Temperature control was good to ±0.02°, and the thermometer was calibrated against one calibrated by the National Bureau of Standards. In about 25 ml of the alcohol, 0.005 mole of the cyclohexyl *p*-toluenesulfonate was dissolved, the solution equilibrated for 1 hr or more, 25 ml of 0.6 *M* alkoxide (also equilibrated) added, and the volume adjusted to the mark. Aliquots of 3.89 ml were withdrawn with a calibrated syringe, quenched in 10 ml of standard aqueous hydrochloric acid, and back titrated with standard sodium hydroxide. Deuterated and undeuterated materials were run at the same time. Rate constants were calculated from the integrated second-order rate equation.

Attempted Detection of Substitution Products. The reaction mixture (10–12 ml) was diluted with an equal volume of water and extracted with three 20-ml portions of ligroin. The solution was dried over sodium sulfate, reduced to about 5 ml by fractionation through a 6-in. Vigreux column, and analyzed by gas chromatography on a 5-ft Carbowax column (flow rate *ca.* 50 cc/min and oven temperature *ca.* 100° for the products in ethanol–ethoxide and *ca.* 155° for the products in *t*-butyl alcohol–*t*-butoxide). Simulated reaction mixtures containing 97.5% of cyclohexene and 2.5% of the cyclohexyl alkyl ether in the appropriate alcohol were subjected to the same treatment and gave peaks corresponding in retention times to the cyclohexyl alkyl ethers. The actual reaction mixtures gave no peaks corresponding to the cyclohexyl alkyl ethers.

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Mechanisms of Elimination Reactions. VIII. The Effect of Added Dimethyl Sulfoxide on Rates, Isotope Effects, and Substituent Effects in the Reaction of 2-Arylethyl Bromides with Potassium *t*-Butoxide in *t*-Butyl Alcohol[1]

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Abstract: Rates of elimination have been determined for the reactions of 2-arylethyl bromides with potassium *t*-butoxide in *t*-butyl alcohol containing varying concentrations of dimethyl sulfoxide. Kinetic deuterium isotope effects were determined using 2-phenylethyl and 2-phenylethyl-2,2-d_2 bromides. Hammett reaction constants were determined with the *para* substituents methoxyl, methyl, hydrogen, and bromine. The temperature range was 30–50°, and the dimethyl sulfoxide concentration was varied between 0 and 2.23 *M*, most measurements being made in the 0–0.965 *M* region. The rate of reaction increases markedly as dimethyl sulfoxide is added—about 120-fold from 0 to 2.23 *M*. In fact, the rate increases much faster than the basicity of the medium as measured by an H– function. In contrast to the effect on rate, neither k_H/k_D nor ρ is changed appreciably by added dimethyl sulfoxide. Possible explanations of these results are discussed. It is suggested that usual definitions of equilibrium or kinetic basicity are not suitable when discussing the effect of "basicity" upon transition-state structure in these elimination reactions.

Hammett reaction constants[2–4] and kinetic deuterium isotope effects[5] have been used to study transition-state structure in elimination reactions of 2-arylethyl bromides. The only solvents used so far have been ethanol and *t*-butyl alcohol. No significant change in ρ is observed,[4] but k_H/k_D is larger with *t*-butoxide in *t*-butyl alcohol than with ethoxide in ethanol. Interpretation of these results is rendered difficult by the fact that both solvent and base are varied simultaneously.

We felt that the use of potassium *t*-butoxide in *t*-butyl alcohol–dimethyl sulfoxide mixtures might enable us to dissect better the factors influencing rate and transition-state structure in these reactions. While dimethyl sulfoxide has a substantially greater dielectric constant than *t*-butyl alcohol, the E_T and Z values are nearly identical for the two solvents.[6] Consequently,

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[1] This work was supported by the National Science Foundation.

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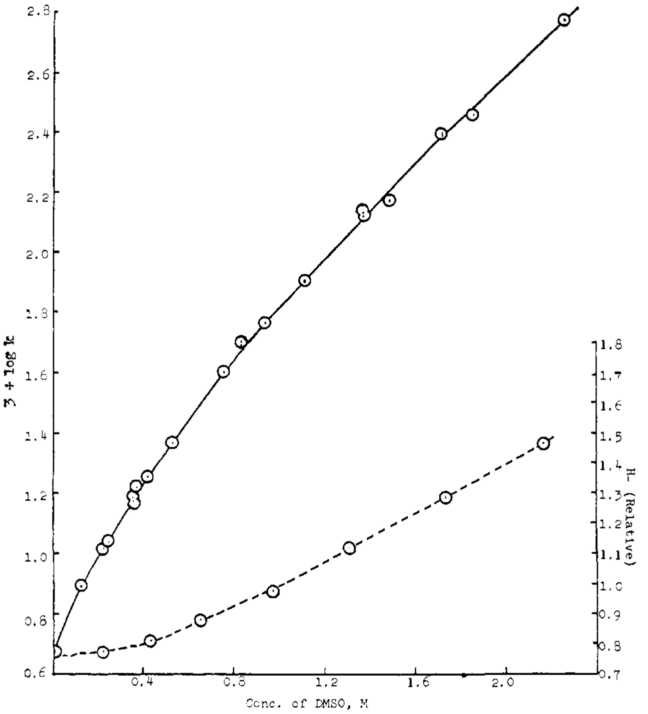

Figure 1. Effect of added dimethyl sulfoxide (DMSO) on rate of reaction (solid line) of 2-phenylethyl bromide with potassium *t*-butoxide in *t*-butyl alcohol and on the basicity (dashed line) of the medium. Rate constants are second order (l./mole sec) for substrate 5 × 10^{-5} *M*, base 4.2 × 10^{-2} *M*. H_- = 0 for half-ionized 4-chloro-2-nitroaniline. H_- measured with 4-amino-4′-nitroazobenzene at a fixed concentration of 1.68 × 10^{-2} *M* potassium *t*-butoxide.

there should not be large differences in solvating ability toward the neutral alkyl bromide and the charge-dispersed transition state. This leaves the effect on basicity of the *t*-butoxide, which can be determined separately from measurements of an H_- function.[7]

Since calculation of k_H/k_D and ρ at different dimethyl sulfoxide concentrations and temperatures required determination of a large number of rate constants, we needed a rapid and simple method. The procedure used was to follow appearance of styrene or substituted styrene spectrophotometrically in the thermostated cell compartment of a Beckman DU spectrophotometer, using a large excess of base and later converting the pseudo-first-order to second-order rate constants. The results are recorded in Table I.

Where comparison is possible, we are in excellent agreement with Saunders and Edison.[5] Our values run consistently *ca.* 20% lower than those of DePuy and Bishop,[4] who report that low values are obtained unless the *t*-butyl alcohol was distilled twice from sodium. Our *t*-butyl alcohol was distilled twice from potassium and handled in a drybox, so the discrepancy appears to arise from some other factor in either their work or ours. While we used lower concentrations than the earlier work,[4,5] we established that a fivefold variation in base concentration caused no significant drift in the second-order rate constants.

The effect of added dimethyl sulfoxide on rate is sufficiently strong that measurement was feasible only over a rather limited range of concentrations. By the time 0.965 *M* dimethyl sulfoxide is added, a 12-fold rate increase occurs for 2-phenylethyl bromide at 30°, and bringing the dimethyl sulfoxide up to 2.23 *M* gives a total rate increase of 120-fold. The results are presented graphically in Figure 1, which also contains (dashed line) a plot of H_- *vs.* dimethyl sulfoxide concentration.[7] It is evident that the increase in rate far exceeds the increase in basicity, which is only about sixfold over the range covered. A less spectacular example of the same phenomenon is the 2.6-fold decrease in rate when sodium *t*-butoxide is substituted for potassium *t*-butoxide, as compared to about a twofold decrease in basicity of the medium.[7] The difference in rate between sodium and potassium *t*-butoxides, incidentally, is much less with *p*-nitrophenylethyl bromide (1.2-fold). Considerably lower base concentrations were used because of the high reactivity of this compound, however, so we cannot say whether this behavior is characteristic of the substrate or the base concentration.

To devise an explanation of this interesting dependence of rate on basicity in which any confidence can be placed will require considerably more information. That the result is not general is shown by several pieces of data.

Preliminary work on 1-phenylethyl bromide at 40° shows a slower increase, about sevenfold, in rate constant over a range of dimethyl sulfoxide concentrations in which the 2-phenylethyl bromide rate increases tenfold and the basicity 1.8-fold.[8]

When the reaction of 1-phenylethyl bromide is carried out with sulfolane instead of dimethyl sulfoxide as the additive, the rate increase over a similar range of sulfolane concentrations (0–0.92 *M*) is about eightfold and the basicity increase, as measured by H_-,[7] is also about eightfold. Evidently the rate increase parallels additive concentration better than it does H_- where these two different additives are involved. In another example, the action of potassium *t*-butoxide in *t*-butyl alcohol–sulfolane on 9-bromo-9,9′-bifluorenyl,[7] the rate actually increases considerably *less* than basicity.

The relation between H_- and rate for rate-determining proton transfers has been derived for aqueous solutions[9] and is given by eq 1 from which a plot of $H_- + \log C_{H_2O}$ *vs.* $\log k_{obsd}$ is expected to be linear. In the

$$\log k_{obsd} = \log k_2K_w + H_- + \log C_{H_2O} \qquad (1)$$

mixed media which we employ the situation is complicated by probable variations in the autoprotolysis constant of the solvent. This effect may be the main reason for the differences noted when dimethyl sulfoxide and sulfolane are the additives. The differences in steepness of dependence on H_- for different substrates, however, undoubtedly arises from failure of the activity coefficients to behave as required by the correlation (eq 2 for our cases).

$$f_{t\text{-BuOH}}f_{\text{RBr}}/f^* = f_{\text{ArNH}_2}/f_{\text{ArNH}^-} \qquad (2)$$

In particular, the charge distribution in $ArNH^-$ will differ considerably from that in the E2 transition state. The negative charge in $ArNH^-$ will be mainly on the

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Table I. Rate Constants for Reaction of 2-Arylethyl Bromides with Potassium *t*-Butoxide in Butyl Alcohol–Dimethyl Sulfoxide[a]

Temp, °C[b]	DMSO, *M*	Subst[c]	$k_2 \times 10^2$, l./mole sec[d]	Temp, °C[b]	DMSO, *M*	Subst[c]	$k_2 \times 10^2$, l./mole sec[d]
30	...	...	0.774[g]	40	...	...	1.55
30	...	...	0.295[f]	40	...	2,2-d_2	0.196
30	...	2,2-d_2	0.0948[h]	40	...	*p*-MeO	0.485
30	...	*p*-MeO	0.185[i]	40	...	*p*-Me	0.794
30	...	*p*-CH_3	0.308	40	...	*p*-Br	5.96
30	...	*p*-Br	3.40	40	0.483	...	5.98
30	...	*p*-NO_2	1110[l]	40	0.483	2,2-d_2	0.811
30	...	*p*-NO_2	934[m]	40	0.483	*p*-MeO	1.84
30	0.249	...	1.73	40	0.483	*p*-Me	2.96
30	0.249	2,2-d_2	0.203	40	0.483	*p*-Br	25.8
30	0.249	*p*-MeO	0.472	40	0.724	...	10.2
30	0.249	*p*-Me	0.811	40	0.724	2,2-d_2	1.28
30	0.249	*p*-Br	8.26	40	0.724	*p*-MeO	3.18
30	0.344	...	2.42	40	0.724	*p*-Me	4.48
30	0.344	2,2-d_2	0.296	40	0.724	*p*-Br	48.3
30	0.416	...	2.88	40	0.965	...	15.4
30	0.416	*p*-MeO	0.782	40	0.965	2,2-d_2	1.99
30	0.416	*p*-Me	1.31	40	0.965	*p*-MeO	5.02
30	0.416	*p*-Br	15.4	40	0.965	*p*-Me	7.67
30	0.483	...	3.29[e]	40	0.965	*p*-Br	75.7
30	0.483	2,2-d_2	0.402[e]	50	...	...	3.07[j]
30	0.724	...	5.85[e]	50	...	2,2-d_2	0.450
30	0.724	2,2-d_2	0.714[e]	50	...	*p*-MeO	0.964[k]
30	0.950	...	9.13	50	...	*p*-Me	1.48
30	0.950	2,2-d_2	1.13	50	...	*p*-Br	10.4
30	0.950	*p*-MeO	2.62	50	0.483	...	10.4
30	0.950	*p*-Me	4.53	50	0.483	2,2-d_2	1.49
30	0.950	*p*-Br	54.2	50	0.483	*p*-MeO	3.46
30	0.965	...	9.68[e]	50	0.483	*p*-Me	5.28
30	0.965	2,2-d_2	1.18[e]	50	0.483	*p*-Br	58.1
30	1.36	...	21.1	50	0.724	...	17.2
30	1.36	2,2-d_2	2.56	50	0.724	2,2-d_2	2.57
30	1.72	...	39.0	50	0.724	*p*-MeO	5.06
30	1.72	2,2-d_2	4.87	50	0.724	*p*-Me	8.55
30	1.72	*p*-MeO	9.96	50	0.965	...	28.2
30	1.72	*p*-Me	17.5	50	0.965	2,2-d_2	3.86
30	2.23	...	94.1	50	0.965	*p*-MeO	8.67
30	2.23	2,2-d_2	11.4	50	0.965	*p*-Me	12.8

[a] Pseudo-first-order rate constants determined spectrophotometrically (see Experimental Section) and converted to second-order rate constants. Usual conditions were substrate 5–10 × 10^{-5} *M*, base *ca.* 4 × 10^{-2} *M*. There was no significant change in k_2 over a fivefold variation in base concentration. [b] Controlled to ±0.1° or better. [c] Dots refers to unsubstituted 2-phenylethyl bromide. [d] Single runs only for most substituted reactants, average of two or three runs for 2-phenylethyl and 2-phenylethyl-2,2-d_2 bromides with average deviations usually 1–2%. Gross errors in single runs excluded by requirement that rate constants for each reactant fall reasonably near the smooth curve in plots of log *k* *vs.* DMSO concentration. [e] Extrapolated from other DMSO concentrations using a plot of log *k* *vs.* DMSO concentration. [f] The base was sodium *t*-butoxide; the concentration was 0.123 *M*. [g] Saunders and Edison[5] report 0.776 × 10^{-2} l./mole sec, DePuy and Bishop[4] report 0.911 × 10^{-2} l./mole sec. [h] Saunders and Edison[5] report 0.0985 × 10^{-2} l./mole sec. [i] DePuy and Bishop[4] report 0.249 × 10^{-2} l./mole sec. [j] DePuy and Bishop[4] report 0.369 × 10^{-2} l./mole sec. [k] DePuy and Bishop[4] report 1.12 × 10^{-2} l./mole sec. [l] Potassium *t*-butoxide, concentrations of 9–24 × 10^{-4} *M*. [m] Sodium *t*-butoxide, concentrations of 13–52 × 10^{-4} *M*.

amino group and the nitro group, and considerable ion pairing with the potassium ion seems likely. In a truly concerted E2 transition state the negative charge will be very diffuse and ion pairing or solvation less important. In such cases, the poor solvating ability of dimethyl sulfoxide for negative ions will not be important, and its good solvating ability for positive ions[10] can be utilized by the freer potassium ions. The ArNH⁻ ions thus should be less affected than the E2 transition state by added dimethyl sulfoxide. Other E2 transition states could have different charge distributions. In an E1-like transition state, for example, negative charge will still be concentrated on alkoxide to a considerable extent, and a less steep response to H_- might be expected. That the variations we observe are not limited to mixed solvents is shown by the results of O'Ferrall and Ridd[11] in methanol containing sodium methoxide. The E2 rate for 3,3-dimethylbutyl chloride is strictly proportional to methoxide concentration, but that for 2-phenylethyl chloride rises faster than methoxide concentration. The dependence of rate on H_- may prove to be an effective measure of transition-state structure as long as conditions are not varied too widely.

The Hammett ρ values (least-squares procedure of Jaffé),[12] derived from rates with the *para* substituents methoxyl, methyl, hydrogen, and bromine, and the kinetic deuterium isotope effects with 2-phenylethyl-2,2-d_2 bromide are given in Table II. The k_H/k_D value at 30° in the absence of dimethyl sulfoxide agrees well with that of Saunders and Edison.[5] The ρ value is distinctly higher than that of DePuy and Bishop[4] for

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Table II. Hammett Correlations and Deuterium Isotope Effects for Reaction of 2-Arylethyl Bromides with Potassium *t*-Butoxide in *t*-Butyl Alcohol–Dimethyl Sulfoxide[a]

Temp, °C	DMSO, *M*	ρ^b	r^c	k_H/k_D
30	...	2.529 ± 0.086[d]	0.999	8.16[f]
30	0.249	2.456 ± 0.158	0.996	8.52
30	0.344	...	...	8.18
30	0.416	2.572 ± 0.197	0.994	...
30	0.483	...	...	8.18
30	0.724	...	...	8.19
30	0.950	2.589 ± 0.252	0.991	8.08
30	0.965	...	...	8.20
30	1.36	...	...	8.24
30	1.72	2.220 ± 0.106[e]	0.999	8.20
30	...	2.296 ± 0.036[d,e]	0.999	...
30	2.23	...	...	8.25
40	...	2.149 ± 0.126	0.996	7.91[g]
40	0.483	2.270 ± 0.157	0.995	7.37
40	0.724	2.384 ± 0.204	0.993	7.97
40	0.965	2.343 ± 0.218	0.991	7.74
50	...	1.875 ± 0.009[e]	0.999	6.82
50	0.483	1.769 ± 0.042[e]	0.999	6.98
50	0.724	1.958 ± 0.043[e]	0.997	6.69
50	0.965	1.920 ± 0.068[e]	0.999	7.31

[a] Using the least-squares procedure of Jaffé[12] and data from Table I. [b] Hammett reaction constant with standard deviation. Based on the *para* substituents MeO, Me, H, and Br unless otherwise noted. [c] Correlation coefficient. Given as 0.999 for all values of 0.999 or greater. [d] DePuy and Bishop[4] report 2.08 ± 0.02 for the substituents *p*-MeO, H, *m*-Br, and *p*-Cl. [e] Based on the three *para* substituents MeO, Me, and H. [f] Edison[5] reports 7.89 ± 0.46. [g] Other runs at 0.055, 0.110, and 0.221 *M* potassium *t*-butoxide plus this value (0.041 *M*) gave an over-all average of 7.85.

Table III. Activation Parameters for Reaction of 2-Arylethyl Bromides with Potassium *t*-Butoxide in *t*-Butyl Alcohol–DimethylSulfoxide[a]

Subst[b]	DMSO, *M*	$\Delta H^{\ddagger}$, kcal/mole[c]	$\Delta S^{\ddagger}$, cal/mole deg[c]	A_H/A_D[d]
...	...	12.8 ± 0.2[e]	−17.8 ± 0.5[e]	
2,2-d_2	...	14.5 ± 0.8	−16.4 ± 2.7	0.46
p-Me	...	14.7 ± 1.5	−13.4 ± 4.9	
p-MeO	...	15.4 ± 1.2[f]	−11.9 ± 4.0[f]	
p-Br	0.483	10.3 ± 0.2	−23.2 ± 0.6	
...	0.483	10.5 ± 0.1	−22.4 ± 0.1	
2,2-d_2	0.483	12.1 ± 0.3	−21.4 ± 0.9	0.58
p-Me	0.483	11.0 ± 0.1	−22.2 ± 0.1	
p-MeO	0.483	12.4 ± 0.1	−19.0 ± 0.4	
p-Br	0.483	10.5 ± 2.9	−19.4 ± 9.3	
...	0.724	9.9 ± 0.1	−23.6 ± 0.1	
2,2-d_2	0.724	11.8 ± 0.8	−21.3 ± 2.7	0.38
p-MeO	0.724	10.8 ± 1.2	−23.0 ± 3.7	
p-Me	0.724	10.2 ± 1.2	−23.8 ± 3.8	
...	0.965	9.8 ± 0.9	−23.0 ± 3.0	
2,2-d_2	0.965	10.9 ± 1.0	−23.5 ± 3.2	1.32
p-MeO	0.965	10.9 ± 0.3	−21.5 ± 1.0	
p-Me	0.965	9.2 ± 0.3	−26.3 ± 1.0	
...	...	17.0 ± 1.0[g]	−11.7 ± 3.4[g]	
2,2-d_2	...	18.6 ± 0.1[g]	−10.6 ± 0.1[g]	0.56

[a] Calculated by a least-squares plot of log *k vs.* $1/T$ using data at 30, 40, and 50° from Table I. Temperature for calculation of $\Delta H^{\ddagger}$ from E_a and $\Delta S^{\ddagger}$ from log *A* was 40°. [b] See footnote *c*, Table I. [c] Deviations are standard deviations and are given as 0.1 if too small to calculate by the least-squares program used. [d] Ratio of the preexponential factors for undeuterated and deuterated species. [e] DePuy and Bishop[4] report $\Delta H^{\ddagger} = 13.0$ kcal/mole, $\Delta S^{\ddagger} = -25.0$ cal/mole deg from data at 30 and 50°. [f] Depuy and Bishop[4] report $\Delta H^{\ddagger} = 14.0$ kcal/mole, $\Delta S^{\ddagger} = -24.3$ cal/mole deg from data at 30 and 50°. [g] From pseudo-first-order rate constants compared at constant H_-, so that these figures incorporate the temperature dependence for ionization of the indicator was 4-chloro-2-nitroaniline and any change in intrinsic basicities of the alkoxide solution with temperature.

a somewhat different set of substituents. Additional confirmation for our value comes from the work with *p*-nitrophenylethyl bromide. We did not use these data in establishing the line, but they fell very close to it provided σ^- was used, as was expected from the work in ethanol of Saunders and Williams.[2]

Both ρ and k_H/k_D remain constant within experimental error as the dimethyl sulfoxide concentration increases. The only reasonable conclusion one can draw from these data about the transition-state structure is that it remains essentially constant. This result is somewhat surprising when both the equilibrium and kinetic basicities of the medium are obviously increasing considerably. It is generally agreed that transition-state structure in proton-transfer reactions should depend on the basicity of the reagent. A plausible rule[13] predicts that increased base strength should lead to a more reactant-like transition state, since the stronger base can exert from a greater distance enough pull on the proton to remove it.

The problem, we believe, lies in the definition of basicity to be used in the rule. In our case the *nature* of the base is not changing, only its solvation shell and probably the tightness of its pairing with the positive ion. The base must be desolvated to form the transition state, and variation in ease of desolvation will lead to variations in rate, as are observed. Once the transition state is formed, however, the base it contains is substantially the same species (a partially neutralized *t*-butoxide ion) regardless of medium composition. That drastic changes in the medium can alter transition-state structure is evidenced by the work of Froemsdorf, McCain, and Wilkinson,[14] who note variations in olefin proportions from 2-bromobutane when the solvent is changed from pure ethanol or *t*-butyl alcohol to pure dimethyl sulfoxide. Our lesser changes in the medium obviously have no discernible effect. We would predict that transition-state structure will generally be less affected by change in the medium than by change in the nature of the base.

Finally, we turn to the temperature dependence of the reaction rates. As noted before,[4] activation enthalpies are substantially lower, and activation entropies more negative, in *t*-butyl alcohol than in ethanol. There is also a tendency for lower activation enthalpies and more negative activation entropies to be associated with the more electron-withdrawing substituents. For a given substrate, addition of dimethyl sulfoxide to the medium initially produces a marked decrease in activation entropy, but the remaining changes in rate result mainly from the activation energy. Evidently the dimethyl sulfoxide produces a distinct change in solvent structure at the outset, but much less change as more is added.

One point that interested us was the temperature dependence of the isotope effect. Low ratios of the Arrhenius preexponential factors for the hydrogen and deuterium reactions have been taken as evidence for proton tunneling,[15] and such values have been observed in proton abstractions by sterically hindered

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(13) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

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

pyridine bases.[16] The A_H/A_D values in the last column of Table III are near the lower limit (0.5)[15] that one can expect in the absence of tunneling, and do not permit any clear-cut conclusions. The value for 0.965 *M* dimethyl sulfoxide appears out of line and may be in error. Otherwise the results are close to that found by Saunders and Edison[5] in ethanol–ethoxide, and suggest that increased steric requirements of the base do not have the same effect on alkoxide-promoted as on pyridine-promoted proton abstractions.

One final point of interest is treated in the last two lines of Table III. Here results at different temperatures are compared at constant H_- rather than at constant base concentration. The activation parameters are different, of course, because they incorporate the temperature dependence of the ionization of the indicator base used to measure H_-. The A_H/A_D value is, however, unchanged within experimental error. We had considered the hypothesis that unusual A_H/A_D values might arise in part from a change in basicity, and hence of transition-state structure, with temperature, but our results clearly provide no evidence for this hypothesis.

Experimental Section

2-Arylethyl Bromides. Most of these were previously prepared samples[2] which were repurified by distillation or recrystallization. Their properties were as follows.

2-Phenylethyl bromide, bp 93–94° (13 mm), n^{26}D 1.5540 [lit.[2] bp 66° (2 mm), n^{26}D 1.5542].

2-(*p*-Tolyl)ethyl bromide, bp 97–99° (6 mm), n^{26}D 1.5472 [lit.[2] bp 103.5–105° (11 mm), n^{22}D 1.5490].

2-(*p*-Anisyl)ethyl bromide, bp 126–128° (6 mm), n^{28}D 1.5571 [lit.[2] bp 63° (0.15 mm), n^{21}D 1.5595].

2-(*p*-Bromophenyl)ethyl bromide, bp 127° (6 mm), n^{25}D 1.5932 [lit.[17] bp 79–80° (0.5 mm), n^{28}D 1.5922. *Anal.* Calcd for $C_8H_8Br_2$: C, 36.40; H, 3.05. Found: C, 36.86; H, 3.15].

2-(*p*-Nitrophenyl)ethyl bromide was recrystallized from 40–60° petroleum ether, mp 69° (lit.[2] 69–69.5°).

2-Phenylethyl-2,2-d_2 bromide was prepared as described by Saunders and Edison,[5] bp 93–94° (14 mm) [lit.[5] bp 94° (15 mm)]. The nmr spectrum showed that the sample contained more than 1.9 atoms of D/molecule.

Styrenes were prepared in quantitative yields by treating the corresponding 2-arylethyl bromides with potassium *t*-butoxide in *t*-butyl alcohol. The absorption maxima and extinction coefficients at the maxima were the same as previously reported for 95% ethanol.[2]

Solvents and Bases. All solvents and solutions for the kinetics were stored and handled in a drybox maintained at 30 ± 1°. Kinetic solutions were prepared at the temperature of the run. *t*-Butyl alcohol was purified by two distillations from potassium metal using a 1-ft, helix-packed column.[7,18] The first 10% of each distillate was discarded, and the material used had mp 25.5°. Dimethyl sulfoxide was purified by two aspirator-pressure distillations from calcium hydride under a nitrogen atmosphere to obtain material of mp 18.5° (lit.[10] mp 18.45°).

Potassium *t*-Butoxide.[7] Potassium metal was thoroughly cleaned in *t*-butyl alcohol, transferred to fresh solvent, and dissolved under reflux in a dry atmosphere. The solution was standardized against 0.1 *M* hydrochloric acid with a phenolphthalein indicator. Sodium *t*-butoxide was prepared by a similar technique. Fresh base solutions were prepared at weekly intervals.

Kinetic Studies. The appearance of styrene or substituted styrene was followed spectrophotometrically. At least a 12-fold (often much greater) excess of base was used and pseudo-first-order rate constants determined from the slope of a plot of log $(D_\infty - D_t)$ against time, where D_t is the absorbance at time *t* and D_∞ the absorbance after at least ten half-lives. Absorbance was in most cases measured at 260 mμ rather than at the absorption maximum of the styrene (near 250 mμ except for *p*-nitro) because absorption due to the base at 250 mμ reduced the precision of measurement. The appearance of *p*-nitrostyrene was followed at 300 mμ. Solutions were prepared in stoppered two-limb cells. In one limb was placed 4.00 ml of base and in the other 0.100 ml of substrate solution (*ca.* 3×10^{-3} *M*). The solutions were thermostated for 0.5 hr, mixed thoroughly, and rapidly transferred to a stoppered silica cell. The cell was placed in the cell compartment of a Beckman DU spectrophotometer. The cell compartment was held to ±0.1° of the stated temperature by circulation of water from a constant-temperature bath. Reactions were followed for three to four half-lives and the pseudo-first-order rate constant based on the best straight line through 20–30 points. Rate constants were reproducible to 1–2% in most cases. Second-order rate constants calculated from these values were satisfactorily independent of base concentration, but the data in Table I are for base concentrations near 0.04 *M* in nearly all cases.

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(18) D. Bethell, *J. Chem. Soc.*, 666 (1963).