2 H, CH_2), 5.8 (br m, 1 H, =CH).

Other labeled ethers, $CD_3OCH_2CH{=}CH_2$, $CH_3OCD_2CH{=}CH_2$, $CD_3OC_2H_5$, and $CH_3OC_2D_5$, were prepared respectively from $CH_2{=}CHCH_2OH$, $CH_2{=}CHCD_2OH$,[16a] C_2H_5OH, and C_2D_5OD (99.5% *d*) by reaction with CD_3I or CH_3I in the presence of silver oxide and dimethylformamide.[6] Yields were in the range of 68–92%. **3-Oxapentane-*1,1,2,2,2-d*$_5$** was prepared in 67% yield from a solution of ethyl-d_5 alcohol-*d* (99.5% *d*, 1.4 g, 27 mmol) and sodium metal (0.13 g, 5.65 mmol) and iodoethane (0.92 g, 5.9 mmol). Methyl ether labeled with ^{18}O was prepared from ^{18}O-labeled methanol by reaction with iodomethane and silver oxide in dimethylformamide. The labeled methanol was obtained by the hydrolysis of tri-*n*-butyl orthoformate with $H_2{}^{18}O$ (99% ^{18}O)[20] followed by reduction of the *n*-butyl formate-^{18}O so formed with LAH in diglyme.[21] This method gave more than 98% isotopically pure ^{18}O-labeled methanol.

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Registry No. **1**, 23653-97-6; **1a**, 78638-90-1; **1b**, 44652-30-4; **1c**, 78638-91-2; **2**, 10152-76-8; **3**, 627-40-7; $CD_3SCH_2CH{=}CH_2$, 68345-75-5; $CH_3SCD_2CH{=}CH_2$, 41865-20-7; $CH_3SCH_2CH{=}CD_2$, 68388-59-0; $CD_3OCH_2CH{=}CH_2$, 78638-92-3; $CH_3OCD_2CH{=}CH_2$, 78638-93-4; $CH_3OCH_2CH{=}CD_2$, 78656-88-9; $CD_3OCH_2^+$, 78638-94-5; $CH_3OCD_2^+$, 78638-95-6; $CH_3CH_2OCH_2^+$, 43730-63-8; $CH_3CH_2OCD_2^+$, 78638-96-7; $CH_3CD_2OCH_2^+$, 78638-97-8; $CD_3CD_2OCH_2^+$, 78638-98-9.

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Mechanisms of Elimination Reactions. 34. Deuterium and Nitrogen Isotope Effects and Hammett Correlations in the Reaction of (2-Arylethyl)trimethylammonium Ions with Hydroxide Ion in Mixtures of Water and Dimethyl Sulfoxide[1,2]

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When (2-phenylethyl)trimethylammonium and (2-phenylethyl-*2,2-d*$_2$)trimethylammonium bromides are treated with sodium hydroxide in aqueous dimethyl sulfoxide at 60 °C, increasing the dimethyl sulfoxide concentration leads to an increase in the elimination rate ($>10^3$ between 17.1% and 57.1% Me_2SO). There is also an increase in k_H/k_D from 3.22 at 17.1% Me_2SO to 5.21 at 34.3%, followed by a decrease to 3.83 at 57.1%. The nitrogen isotope effect (k_{14}/k_{15}) decreases initially from ca. 1.009 (estimated from data at 97 °C) in water to 1.007 in 22.8% Me_2SO but thereafter remains essentially constant around 1.006–1.007 up to 57.1% Me_2SO. When substituted (2-phenylethyl)trimethylammonium bromides (substituents *p*-Cl, H, *p*-Me, and *p*-MeO) are used, the rates fit the Hammett equation. The Hammett ρ is +3.11 in 17.1% Me_2SO, but after an initial rise it remains essentially constant ($+3.38 \pm 0.09$) from 30% to 50.6% Me_2SO. Both the nitrogen isotope effects and the Hammett ρ values indicate a transition state that becomes somewhat more reactant-like with increasing dimethyl sulfoxide concentration. The deuterium isotope effects are consistent with this picture but suggest a greater shift in transition-state structure.

2-Phenylethyl derivatives have played a key role in investigations of transition-state structure in bimolecular elimination (E2) reactions[3] and have more recently also figured in the study of tunneling in E2 reactions.[4] In this paper we provide further evidence on the effects of solvent and base on the transition states for E2 reactions of (2-arylethyl)trimethylammonium salts.

Previous workers have shown that these substances react with ethoxide ion in ethanol with a k_H/k_D of only 3.0[5] at 50 °C, a Hammett ρ of +3.8[6] at 30 °C, and a nitrogen isotope effect, k_{14}/k_{15}, of 1.013[7] at 40 °C. The nitrogen isotope effect is well below the maximum value of 1.040–1.045 from model calculations,[8] which in conjuction with the high ρ value indicates a transition state with a relatively strong C–N bond (at least 70% of normal) and a high degree of carbanion character at the β carbon. The low k_H/k_D could indicate that proton transfer is considerably more than half complete in the transition state, though more recent work[4] suggests that the unsymmetry

Table I. Rate Constants for the Reaction of (2-Arylethyl)trimethylammonium Bromides with Sodium Hydroxide in Aqueous Dimethyl Sulfoxide at 60 °C[a]

Me_2SO, mol %[b]	10^4k_2, s^{-1} M^{-1} for isotope, substituent[c]				
	H, *p*-Cl	H, H	H, *p*-Me	H, *p*-MeO	D, H
17.1	6.87	1.29	0.390	0.189	0.400
22.8		4.03			1.04
30.0	12.1	21.7	5.23	2.23	4.57
34.3	223.0	34.0	11.0	4.17	6.53
37.1	430.0	73.3	23.8	7.73	
40.6	830.0	163.0[d]	46.0	16.1	33.0
44.5	1560.0	282.0	92.3	31.7	58.3
50.6	4700.0	710.0[e,f]	240.0	80.7	160.0
57.1		1660.0			433.0
69.5				930.0[g]	

[a] Substrate ca. 0.004 M, base ca. 0.05 M. Measured as pseudo-first-order rate constants and divided by the base concentration to calculate k_2. [b] Mole fractiom times 100. [c] Each value is the average of at least two runs; reproducibility ±1.5%. [d] 163.0 with KOH as base. [e] 780.0 with KOH as base. [f] 550.0 in the presence of 0.4 M tetrabutylammonium bromide. [g] 1390.0 with KOH as base.

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

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Table II. Hammett ρ Values for the Reaction of (2-Arylethyl)trimethylammonium Bromides with Sodium Hydroxide in Aqueous Dimethyl Sulfoxide at 60 °C[a]

Me_2SO, mol %[b]	ρ	$\log k_0$	r[c]
17.1	3.11 ± 0.02	−3.406 ± 0.006	0.99997
30.0	3.47 ± 0.08	−2.219 ± 0.029	0.9995
34.3	3.39 ± 0.13	−1.960 ± 0.049	0.998
37.1	3.39 ± 0.20	−1.654 ± 0.076	0.996
40.6	3.36 ± 0.18	−1.347 ± 0.069	0.997
44.5	3.29 ± 0.18	−1.073 ± 0.069	0.997
50.6	3.43 ± 0.19	−0.640 ± 0.071	0.997

[a] From a linear least-squares fit using rate constants from Table I. Deviations are standard deviations. [b] Mole fraction times 100. [c] Correlation coefficient.

Table III. Nitrogen Kinetic Isotope Effects (k_{14}/k_{15}) for the Reaction of (2-Phenylethyl)trimethylammonium Bromide with Sodium Hydroxide in Aqueous Dimethyl Sulfoxide at 60 °C

Me_2SO, mol %[a]	F[b]	k_{14}/k_{15}	av k_{14}/k_{15}[c]
0			1.0087[d]
17.1	0.111	1.0077	
	0.098	1.0086	
	0.204	1.0082	
	0.057	1.0085	1.0082 ± 0.0002
22.8	0.136	1.0078	
	0.114	1.0068	
	0.125	1.0063	1.0070 ± 0.0004
27.0	0.268		1.0060[e]
30.0	0.130	1.0057	
	0.290	1.0061	
	0.120	1.0048	1.0055 ± 0.0004
30.5	0.087		1.0063[e]
31.5	0.152	1.0068	
	0.089	1.0068	1.0068 ± 0.0000
34.3	0.109	1.0071	
	0.139	1.0063	
	0.087	1.0083	1.0072 ± 0.0006
37.4	0.094	1.0072	
	0.131	1.0061	1.0066 ± 0.0006
44.5	0.140	1.0066	
	0.138	1.0065	1.0066 ± 0.0001
57.1	0.073	1.0067	
	0.080	1.0066	1.0066 ± 0.0001

[a] Mole fraction times 100. [b] Fraction of reaction based on the yield of trimethylamine. [c] Deviation is the standard deviation of the mean. [d] Extrapolated from 1.0078 at 97 °C[7] by assuming an exponential temperature dependence with $A_{14}/A_{15} = 1$. [e] Single measurement.

of the position of the proton in the transition state may not be as great as originally thought.

Studies on the reaction of (2-arylethyl)dimethylsulfonium salts with hydroxide ion in mixtures of dimethyl sulfoxide and water indicate definite changes in transition-state structure as the solvent composition is changed. The Hammett ρ rises from +2.1 in water to +2.6 in 60% Me_2SO, while k_H/k_D goes through a maximum of about 6.2 at 40 °C in the vicinity of 40% Me_2SO.[9] At the same time, the sulfur isotope effect, k_{32}/k_{34}, decreases from 1.0074 at 40 °C in water to 1.0025 in 43% Me_2SO.[10,11] The most reasonable interpretation of these results is that the increasing basicity of hydroxide ion as dimethyl sulfoxide is added[12] causes the transition state to become more reactant-like. The present studies were undertaken to test the generality of these conclusions.

Table I shows that increasing the concentration of dimethyl sulfoxide sharply increases the rate of reaction of the quaternary ammonium salt, by about 10^3 from 17.1% to 50.6% Me_2SO. The effect of dimethyl sulfoxide on the rate is comparable to that found with the corresponding sulfonium salt.[9,10] Both effects probably result mainly from the increase in basicity of hydroxide ion as the concentration of dimethyl sulfoxide increases.[12] Ion-pairing effects seem to become significant at higher concentrations of dimethyl sulfoxide. Sodium and potassium hydroxide are equally effective bases in 40.6% Me_2SO, but the reaction is 10% faster with potassium hydroxide in 50.6% Me_2SO and 49% faster in 69.5% Me_2SO (Table I, footnotes *d*, *e*, and *g*). Added 0.4 M tetrabutylammonium bromide causes a 23% rate decrease in 50.6% Me_2SO (Table I, footnote *f*). Added salts should sharply reduce the rate of reaction between oppositely charged ions.[13] The rather modest decrease actually observed suggests competition from a rate-enhancing specific effect in which ion-paired sodium hydroxide is converted at least partly to tetrabutylammonium hydroxide, which should be a more effective base by virtue of less or no ion pairing.[6]

The Hammett ρ values (Table II) behave with changing solvent composition very much like those for the corresponding sulfonium salts.[9] At first there appears to be a slight increase in ρ with added dimethyl sulfoxide, but for a range extending from 30% to 50.6% Me_2SO ρ remains constant at +3.38 ± 0.09. This is substantially larger than the figure of +2.6 in 19.4–60.3% Me_2SO for the corresponding sulfonium salts,[9] indicating more carbanion character in the transition states for the ammonium salts.

The nitrogen isotope effect, k_{14}/k_{15} (Table III), shows a significant decrease at first as dimethyl sulfoxide is added, but by 22.8% Me_2SO the effect levels off between 1.006 and 1.007 and shows no further change up to 57.1% Me_2SO. The seemingly low value in 30% Me_2SO appears to be within experimental error of other values in the same region of dimethyl sulfoxide concentration. The *t* test[14] shows that it does not differ significantly at the 90% confidence level from the values in 22.8% and 34.3% Me_2SO.

Maximum k_{14}/k_{15} values at 25 °C have been estimated from model calculations to be 1.040–1.045.[8] Assuming that the isotope effect lies entirely in the exponential term ($A_{14}/A_{15} = 1$), these correspond to 1.036–1.040 at 60 °C. Alternatively, Arrhenius parameters for a model with the C–N bond 90% broken predict a slightly steeper temperature dependence and give a k_{14}/k_{15} of 1.036 under these conditions.[15] Thus, even k_{14}/k_{15} in water corresponds to less than 25% cleavage of the C–N bond in the transition state, and the k_{14}/k_{15} values found from 22.8% to 57.1% Me_2SO correspond to only 15–20% cleavage. The percentage represents simply $(((k_{14}/k_{15}) - 1)/((k_{14}/k_{15})_{\mathrm{max}} - 1))100$, but it can be approximately equated to $(1 - (F^{*}_{\mathrm{CN}}/F^{0}_{\mathrm{CN}}))100$, where the F's are stretching force constants of the C–N bond in the transition state and in the reactant, respectively.

A comparison of these results with those for the corresponding sulfonium salt at 40 °C is instructive. Extrapolation of calculations at 25–40 °C gives a k_{32}/k_{34} of 1.010–1.012,[8,16] while Arrhenius parameters for a model

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Table IV. Kinetic Isotope Effects (k_H/k_D) for the Reaction of (2-Phenylethyl-*2,2-d*$_2$)trimethylammonium Bromide with Sodium Hydroxide in Aqueous Dimethyl Sulfoxide at 60 °C

Me_2SO, mol %[a]	k_H/k_D	Me_2SO, mol %[a]	k_H/k_D
17.1	3.22	40.6	4.94[c]
22.8	3.88	44.5	4.84
30.0	4.75[b]	50.6	4.44[d]
34.3	5.21	57.1	3.83

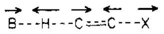
[a] Mole fraction times 100. [b] Arrhenius parameters in ref 4 give 4.16. [c] Arrhenius parameters in ref 4 give 5.01 for 40% Me_2SO. [d] Arrhenius parameters in ref 4 give 3.55 for 50% Me_2SO.

with the C–S bond 90% broken give a k_{32}/k_{34} of 1.011 at 40 °C.[15] The experimental value of 1.0074 in water at 40 °C thus corresponds to about 60–75% cleavage of the C–S bond in the transition state, and the value of 1.0025 in 43% Me_2SO still corresponds to 20–25% cleavage.[10,11] C–S cleavage is substantially more advanced than C–N cleavage in the transition state in water. There is, however, a substantially faster decrease in the sulfur than in the nitrogen isotope effect as the dimethyl sulfoxide concentration increases. Thus the difference between the extents of C–S and C–N cleavage in the transition state narrows markedly as the dimethyl sulfoxide concentration approaches 43%, the highest concentration at which the sulfur isotope effect was determined.

The variation in the deuterium isotope effect (Table IV) appears to provide an excellent example of the k_H/k_D maximum predicted by Melander[17] and Westheimer[18] for a proton-transfer transition state in which the proton is half transferred from substrate to base. This picture ascribes a key role to the symmetric stretching vibration of a linear three-center transition state. When the proton is symmetrically located, the frequency of that vibration is insensitive to isotopic substitution at hydrogen. When the proton is not symmetrically located, isotopic substitution does lead to a change in vibrational frequency of that mode and hence a difference in zero-point energy. That difference partly cancels a corresponding difference in the reactant and thus diminishes k_H/k_D.

This picture has been questioned by Bell, Sachs, and Tranter,[19] who argue on the basis of an electrostatic model that the isotopic zero-point energy difference associated with the symmetric stretching frequency changes too little with transition-state symmetry to account for observed changes in k_H/k_D. They prefer to ascribe the variation in k_H/k_D to tunneling. Recent work in which the tunnel correction, Q_{tH}/Q_{tD}, was estimated from studies of the temperature dependence of k_H/k_D[4] fails to support this picture. Within the precision of the method, the maximum remains in $(k_H/k_D)_s$, the semiclassical isotope effect, after the influence of tunneling is factored out. There is not significant variation in Q_{tH}/Q_{tD} from 30 to 50% Me_2SO. A study on [2-[(*p*-trifluoromethyl)phenyl]ethyl]trimethylammonium ion under similar conditions does give an apparent maximum in Q_{tH}/Q_{tD},[20] but the differences between it and values at other Me_2SO concentrations are not beyond experimental error, and variation in Q_{tH}/Q_{tD} accounts for only a part of the variation in the observed k_H/k_D. Although more work is needed on this point, there is so far no *experimental* justification for ascribing k_H/k_D maxima wholly or largely to variations in Q_{tH}/Q_{tD}.

It is becoming increasingly obvious, however, that k_H/k_D is influenced by factors other than the isotopic zero-point energy difference in the symmetric stretch. Tunneling appears to contribute to k_H/k_D in many elimination reactions.[4,20-22] Another important factor is the contribution of heavy-atom motion to the reaction coordinate motion[4,8,23] arising in the case of the E2 reaction from the C═C contraction and C- - -X extension that must accompany motion of the proton in the transition state (1). This factor depresses k_H/k_D, as demonstrated by the low value of $(k_H/k_D)_s$ at the maximum in the reaction presently under discussion. Again, there is no experimental evidence on whether or in what way this contribution varies with the extent of proton transfer.



1

Nonlinear proton transfers are predicted to occur with smaller isotope effects than corresponding linear ones.[24,25] There seems to be no reason to suspect nonlinearity in the present reaction and no reason in general to expect variation in the degree of nonlinearity as reaction conditions are varied with a single reactant.

There remains one other possible cause of variation in k_H/k_D: changes in the frequencies of bending modes of the B- - -H- - -C system (there will be two degenerate modes for a three-center system, but the analogous modes in a more complex system such as 1 need not be degenerate).[26] Such evidence as there is suggests that the isotopic zero-point energy difference from such modes approximately cancels that due to bending modes in the reactant.[27,28] This does not exclude the possibility of some variation, which could depend on transition-state symmetry in such a way as to contribute to a maximum in k_H/k_D.

A maximum in k_H/k_D can in principle be ascribed either to a single cause that has an extremum at the maximum or to a combination of two or more causes that vary in different ways for a given change in reaction conditions or reactant structure. While we cannot entirely exclude the possibility that the second explanation applies to some or all cases of k_H/k_D maxima, we see no evidence that supports or even suggests such a conclusion. Under the circumstances, we prefer to adopt the simpler hypothesis that a single factor produces the k_H/k_D maximum, and there seems to be no persuasive reason for abandoning the Melander–Westheimer model. This is not to argue that tunneling or the influence of bending frequencies cannot reinforce the Melander–Westheimer maximum or that these or other factors cannot alter the magnitude of the maximum or the shape of the curve or cause scatter from a smooth curve. In spite of all of the possible complications, it still seems reasonable to conclude that a k_H/k_D or k_H/k_T maximum strongly suggests a transition state

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(16) We exclude as unrealistic one model in ref 7 that predicts a maximum k_{32}/k_{34} of a little over 1.02. It assumes a flat potential barrier, which is inconsistent with the significant tunnel correction in the E2 reaction of (2-phenylethyl)dimethylsulfonium ion with ethoxide in ethanol.[4]

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with a symmetrically located proton.

The facts discussed so far make fairly clear qualitatively how the transition state responds to change in the proportion of dimethyl sulfoxide in the medium. For (2-phenylethyl)trimethylammonium ion, the proton transfer is beyond the halfway point, and carbon–nitrogen cleavage is much less than half complete in water, resulting in a markedly carbanion-like transition state. Addition of dimethyl sulfoxide causes a decrease in the extents of both proton transfer and carbon–nitrogen cleavage in the transition state, though change in the latter levels off rather early. For the (2-phenylethyl)dimethylsulfonium ion a similar description applies, except that carbon–sulfur cleavage in the transition state is more than half complete in water, and the carbanion character is thus less. As dimethyl sulfoxide is added, the extent of proton transfer in the transition state decreases, though less rapidly than for the ammonium salt, and the extent of carbon–sulfur cleavage decreases more rapidly than does the extent of carbon–nitrogen cleavage in the ammonium salt.

Whether these qualitative conclusions can be expressed in quantitative terms is more problematical. It is somewhat troubling, particularly with the quaternary ammonium salt, that the Hammett ρ value remains virtually unchanged over the entire range of solvent composition except for the small rise in the lowest range of dimethyl sulfoxide concentration. In particular, k_H/k_D shows that the extent of proton transfer is decreasing, and k_{14}/k_{15} shows that the extent of carbon–nitrogen cleavage remains essentially constant from 30% to 57% Me_2SO. This should be accompanied by a decrease in ρ, which was not observed.

More or less plausible ad hoc explanations of the insensitivity of ρ to change in solvent composition come to mind. Hammett[29] suggested that ρ should vary inversely with the dielectric constant of the medium. If so, the constant ρ could reflect a balance between an increase from this cause and a decrease from decreasing carbanion character as dimethyl sulfoxide is added. It is also conceivable that the carbon–hydrogen bond order (n_{CH}) is varying relatively little and that the change in k_H/k_D results from a more rapid change in the oxygen–hydrogen bond order (n_{OH}). Such an explanation implies that the total bond order to hydrogen, $n_{CH} + n_{OH}$, can drop significantly below unity in the transition state. There is no good evidence either for or against this hypothesis. Finally, ρ may simply be a less sensitive measure of the extent of proton transfer than k_H/k_D.

Comparison of the k_H/k_D values in Table IV with calculated curves[8] suggests a marked change in the extent of hydrogen transfer: from 0.70–0.75 in 17.1% to 0.15–0.20 in 57% Me_2SO. The calculations[8] do not, however, take account of tunneling and assume a particular form for variation of the bending frequencies, so these values should not be ascribed too much quantitative significance. Curiously, the variation in k_H/k_D is much slower for the (2-phenylethyl)dimethylsulfonium ion as the solvent changes: the extent of hydrogen transfer estimated as above changes only from 0.5 in water to 0.3 in 68.9% Me_2SO.[9] It should be noted that in the calculations the carbon–hydrogen and base–hydrogen bonds become of equal strength at an "extent of hydrogen transfer" of 0.38, because a full O–H bond is stronger than a full C–H bond, and so the k_H/k_D maximum corresponds to this point rather than to 0.5. The extent of hydrogen transfer corresponds to the order, n_{OH}, of the forming bond if constant total bonding to hydrogen ($n_{OH} + n_{CH} = 1$) is assumed.[30,31]

The apparent inconsistency between the Hammett ρ values and k_H/k_D raises the more general question of the relationship to be expected between kinetic isotope effects, which measure strength of bonding in the transition state relative to reactants, and structure–reactivity parameters such as the Hammett ρ, the Brønsted β, and the Jencks β_{lg} and β_{nuc}[32] parameters, which measure electron distribution in the transition state. More systematic comparisons than have so far been made would be highly desirable. In the meantime, a few caveats are in order.

The first is that direct linear relationships are not generally to be expected and that numeric equality between different measures of the progress of bond making or bond breaking in the transition state is particularly unlikely. Even if one assumes that the Brønsted β is a direct measure of the extent of bond formation between the base and proton (n_{OH} in our case), it will equal the "extent of hydrogen transfer" as defined in isotope-effect calculations[8] only when $n_{OH} + n_{CH} = 1$. Furthermore, $\beta = 0.5$ should not correspond to the k_H/k_D maximum but to a point somewhat beyond it for oxygen and nitrogen bases. For oxygen bases, $\beta = 0.38$ should correspond to the k_H/k_D maximum (see above) under the simplifying assumptions made in this paragraph. In general, β at the k_H/k_D maximum will have a value dependent upon the relative strengths of the full base–hydrogen and substrate–hydrogen bonds, as well as upon the bond orders of both bonds in the transition state.

As another example, Alunni and Jencks[32] report a β_{lg} of −0.35 for the reaction of (2-phenylethyl)quinuclidinium ions with hydroxide ion in water. At first sight this would seem to suggest a greater extent of carbon–nitrogen cleavage in the transition state than the 20–25% estimated from our nitrogen isotope effects. There is, however, evidence that β_{lg} contains a contribution from an inductive effect of the leaving group on the ease of proton removal, and thus β_{lg} is nonnegligible (ca. −0.1 to −0.2) even for irreversible E1cB reactions.[32] Given a reasonable correction for this factor, β_{lg} and k_{14}/k_{15} are in semiquantitative agreement. Again, care must be exercised in comparing two experimental quantities that measure related but not identical properties of the transition state.

In conclusion, all of the experimental results suggest that the transition state for E2 reactions of (2-phenylethyl)trimethylammonium ion with hydroxide ion becomes more reactant-like with increasing dimethyl sulfoxide concentration. The different criteria are not all in agreement on the magnitude of the change, however, and more work is still needed.

Experimental Section

Materials. Distilled water was redistilled from potassium permanganate. Dimethyl sulfoxide was refluxed over calcium hydride and fractionally distilled; bp 35 °C (1 mm). It was redistilled immediately prior to use; mp 18.5 °C (lit.[33] mp 18.5 °C). Mixtures of dimethyl sulfoxide and water were prepared gravimetrically. Base solutions were prepared by weighing the desired volume of standard 1 N sodium hydroxide solution into dimethyl sulfoxide and then adding the required weight of water. The (2-arylethyl)trimethylammonium bromides were prepared as previously described.[6] (2-Phenylethyl-*2,2-d₂*)trimethylammonium bromide was prepared by the method of Saunders and Edison.[5]

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[31] Reference 23, p 68.

[32] Alunni, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2052–60.

[33] Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29–40.

Kinetics. Substrate concentrations of ca. 0.004 M and base concentrations of 0.05 M were used. Base and substrate solutions were equilibrated to 60.00 ± 0.05 °C in separate limbs of a stoppered two-limb vessel, and the solutions were then rapidly mixed. Aliquots were withdrawn by calibrated 1.00-mL pipets and diluted in a known volume (50 or 100 mL) of 95% ethyl alcohol. The absorbance of the solution (A_t) was then recorded at the absorption maximum[34] of the styrene. The absorbance after 10 half-lives was taken as A_∞, and rate constants were determined from the slope of the least-squares plot of log ($A_\infty - A_t$) vs. time. The A_∞ values showed that the (2-arylethyl)trimethylammonium salts are converted quantitatively (102 ● 3.5%) into the corresponding styrenes. The rate constants reported in Table I are the averages of at least two runs each and are reproducible to ±1.5%.

Nitrogen Isotope Effects. The procedure was that of Ayrey, Bourns, and Vyas[35] with the exceptions noted below. The trimethylamine from the elimination reaction of ca. 0.01 mol of substrate was converted to an aqueous solution of the hydrochloride prior to Kjeldahl digestion. A selenized granule (Hengar Co.) was used as a catalyst in the Kjeldahl digestion. Titrations were performed with a nitrogen-free indicator (bromcresol green), and the stopcock grease used on the Kjeldahl flask was subjected to a Kjeldahl digestion to ensure that it contained no nitrogen. The nitrogen produced by treatment of the ammonium chloride with sodium hypobromite was passed over traps containing silica gel at dry-ice temperature and ascarite at liquid nitrogen temperature. The resulting nitrogen was transferred by a Toepler pump to a gas buret for measurement and thence to a mass spectrometer sample tube fitted with a break-seal, and the tube was sealed. The nitrogen was shown by mass spectrometry to contain no detectable water or oxides of nitrogen and <0.1% each of carbon dioxide and oxygen. It did not differ measurably in purity from samples that had been purified by repeated cycling over copper and copper oxide at 750 °C.[35] Isotope ratio measurements were performed on an Atlas CH-4 mass spectrometer equipped with dual Faraday cup collectors. The amplifier for the signal from the less abundant isotope was a vibrating-reed electrometer. Samples from a given extent of reaction (varied over 5.7–29% without significant effect on k_{14}/k_{15}) and from 100% reaction were connected to the two inlets of the dual viscous inlet system and the sample sizes adjusted to give nearly the same peak heights (±1%) at *m/e* 28. The isotope ratios were determined alternately on the two samples at least four or five times.

Effect of Nitrous Oxide Formation on the Nitrogen Isotope Ratio. The products of sodium hypobromite oxidation of ammonium chloride were found to be nitrogen (97.5–98.0%), nitrous oxide (1.2–1.5%), and nitrite plus nitrate (0.5%). No attempt was made to determine the $^{14}N/^{15}N$ ratio of the small amount of nitrite plus nitrate, but that of the nitrous oxide was determined as follows. A 1.5-g sample of ammonium chloride (Baker Analyzed Reagent) was dissolved in ca. 10 mL of water, sodium hypobromite solution was added dropwise (10–12 min), and the nitrous oxide was swept into a trap cooled by liquid nitrogen by means of a stream of nitrogen bubbled through a syringe needle into the reaction mixture. The trap was evacuated by a forepump for ca. 10 min to remove any nitrogen and oxygen. It was then transferred to a vacuum line, degassed three times, and transferred to a trap at liquid nitrogen temperature containing ascarite. The yield of nitrous oxide was determined by transferring the gas to a gas buret. The nitrous oxide was then cycled through furnaces containing copper and copper oxide[35] for about 7 h to reduce the nitrous oxide to nitrogen. The latter was measured in a gas buret, passed over silica gel at dry-ice temperature, and sealed in a mass spectrometer sample tube for isotope ratio measurement. The resulting isotope ratio was compared with that of nitrogen from the same sample of ammonium chloride treated as in the isotope effect measurements so as to remove nitrous oxide. In three runs, R_{N_2}/R_{N_2O} ($R = N_2^{29}/N_2^{28}$ ratio) was found to be 1.0048, 1.0048, and 1.0040. The effect of this isotopic fractionation on the nitrogen sample relative to the original ammonium chloride can be shown to be given by the following equation, where N_1 is the mole fraction of nitrogen and N_2 the

$$R_{N_2}/R_{NH_4Cl} = 1/[N_1 + (R_{N_2O}/R_{N_2})N_2]$$

mole fraction of nitrous oxide and assuming $N_1 + N_2 = 1$. In this manner, R_{N_2}/R_{NH_4Cl} was found to be 1.000 04, at least an order of magnitude below the uncertainty in the measurement of R_{N_2}.

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Registry No. (2-Phenylethyl)trimethylammonium bromide, 6068-85-5; (2-(*p*-chlorophenyl)ethyl)trimethylammonium bromide, 6068-86-6; (2-(*p*-methylphenyl)ethyl)trimethylammonium bromide, 19836-63-6; (2-(*p*-methoxyphenyl)ethyl)trimethylammonium bromide, 6948-08-9; (2-phenylethyl-2,2-d_2)trimethylammonium bromide, 1012-70-0.

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