Found: C, 74.93; H, 8.28; mol wt (osmometrically in benzene), 388.

The photolysis of 2-benzylidenedioxolane in the normal fashion resulted in the formation of a white insoluable solid. The solid (22% yield) was purified by vacuum sublimation and found to melt at 213–215°.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21; mol wt, 324. Found: C, 74.19; H, 6.29; mol wt (osmometrically in acetone), 329.

The liquid residue from the photolysis of 2-benzylidenedioxolane

was distilled to give some starting material and unidentified liquids having no nmr signals above τ 7.2. From the distillation residue another 21% of crude solid melting over a wide range was obtained.

The crude lactone from 2-benzylidene-*m*-1,3-dioxane was isolated by distillation and had bp 132–138° (0.4 mm). The crude material was chromatographed on silica gel and eluted with 1:1 benzene–chloroform. The liquid was flash distilled to give pure compound having n^{20}D 1.5511.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.86. Found: C, 74.30, 74.99; H, 6.80, 7.07.

The Secondary β-Deuterium Isotope Effect and the Cage Effect in the Thermal Decomposition of Azobis-α-phenylethane[1]
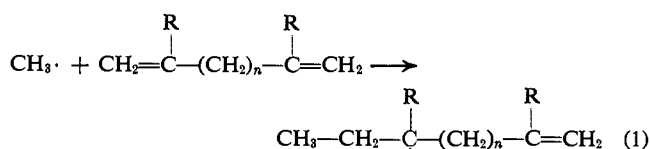
Stanley Seltzer and Edwin J. Hamilton, Jr.

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received April 5, 1966

Abstract: Azobis-α-phenylethane-β,β,β-d_3 was prepared and its rate of decomposition in ethylbenzene at 105° was compared to that for the natural compound. Calculations indicate that approximately one-fourth of the rate retardation is due to the effect of increased mass on the ratio of imaginary frequencies. The residual β effect in the formation of the α-phenylethyl radical is about one-fourth as large as the comparable β effect in the formation of the α-phenylethyl carbonium ion and suggests that hyperconjugative stabilization in the radical is somewhat diminished in comparison with the ion. In addition the cage effect was measured in the absence of scavengers.

The stabilization of carbonium ions by delocalization of charge on neighboring β-hydrogen atoms is well known and has received considerable attention.[2] Hyperconjugation in radical transition states or intermediates has not been as well established. The best evidence arises from electron spin resonance spectra.[3] Contributions of hyperconjugative resonance forms to the electronic structure, for example, of the ethyl radical allows an explanation for the approximately 5% of free spin density in each of the methyl hydrogen 1s orbitals.[4]

Support for hyperconjugation in radicals from kinetic studies is weaker and less obvious. In a study of the polymerization of *p*-alkyl-substituted styrenes initiated by azobisisobutyronitrile, the relative rates were found to follow the Baker–Nathan order, methyl > ethyl > *t*-butyl.[5] The ratio of rates between the fastest and slowest, however, was only a factor of 1.2. The addition of methyl radicals to isolated dienes also exhibits a small rate enhancement when R is changed from H to CH_3 (eq 1).[6] For example, the rate of methyl addition

$$CH_3 \cdot + CH_2{=}\overset{R}{\underset{|}{C}}{-}(CH_2)_n{-}\overset{R}{\underset{|}{C}}{=}CH_2 \longrightarrow$$

$$CH_3{-}CH_2{-}\overset{R}{\underset{|}{C}}{-}(CH_2)_n{-}\overset{R}{\underset{|}{C}}{=}CH_2 \quad (1)$$

to 2,4-dimethylhexadiene-1,5 is 10–15% faster than to the unsubstituted hexadiene. Similarly, addition to 2,3-dimethylbutadiene is about 7% more rapid than to butadiene itself. This increase in rate has been attributed to hyperconjugative stabilization of the radical-like transition state.[6] A possible reason for the very small enhancement may be the resemblance of the transition state to the reactant state rather than to the product radical.[7]

One way to investigate the degree of involvement of hyperconjugative stabilization is the study of secondary β-deuterium isotope effects. This tool has already been used extensively by Shiner[8a] and Lewis[8b] in studies of carbonium ion formation although Robertson[8c] has suggested a different mechanism for secondary β-deuterium effects.[8d]

As the first part of an investigation of hyperconjugative stabilization of radicals we describe here the study of the secondary β effect in the thermal decomposition of azobis-α-phenylethane. Since we also have at hand the hexadeuterio azo compound, we have measured the cage effect in the absence of scavengers in ethylbenzene solution.

Experimental Section

Aceto-d_3-phenone Azine. To a solution of 5.34 g (0.0434 mole) of aceto-d_3-phenone[9] in 8 ml of absolute ethanol-d^{10} was added 1.63 g

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) "Conference on Hyperconjugation," Pergamon Press Inc., New York, N. Y., 1959; (b) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.

(3) M. C. R. Symons, *Tetrahedron*, 18, 333 (1962).

(4) D. B. Chesnut, *J. Chem. Phys.*, 29, 43 (1958); A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958).

(5) M. Imoto and K. Takemoto, *J. Polymer Sci.*, 19, 205 (1956).

(6) A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc.* (London), A251, 394 (1959).

(7) M. Field, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, 84, 4451 (1962).

(8) (a) V. J. Shiner, *Tetrahedron*, 5, 243 (1959); (b) E. S. Lewis, R. R. Johnson, and G. M. Coppinger, *J. Am. Chem. Soc.*, 81, 3140 (1959); (c) K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *Chem. Ind.* (London), 259 (1961); (d) see also E. A. Halevi, "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 109.

(9) Supplied by Merck Sharp and Dohme of Canada, Ltd.

(10) S. Seltzer, *J. Am. Chem. Soc.*, 87, 1534 (1965); the ethanol-*d* was dried by azeotropic distillation from a benzene–alcohol–water mixture.

(0.0291 mole) of hydrazine hydrate-d_6[9] and one drop of glacial acetic acid. The solution was refluxed for about 50 hr. The solvent and excess hydrazine hydrate were removed by evaporation and the solid azine was recrystallized from natural ethanol, yield 4.81 g, 91.5%, mp 122.3–123.3°, lit.[11] mp 124° (natural azine). The nmr spectrum[12] of the azine in chloroform-d revealed only two broad aromatic proton signals. The natural azine in carbon tetrachloride displays two broad aromatic signals with centers at τ 2.15 and 2.65 and a singlet methyl signal at 7.68. Integration of the τ 7.68 region relative to the aromatic signal sets an upper limit of 0.8 ± 0.4 hydrogen atom % in the methyl groups.

Azobis-α-phenylethane-β,β,β-d_3. The deuterated azine (4.81 g) was catalytically hydrogenated to the hydrazine at atmospheric pressure in 50 ml of Spectrograde dioxane and 1.6 g of 5% palladium on charcoal. After the uptake of hydrogen ceased the solution was filtered and the solvent was removed under vacuum. The hydrazine was oxidized with 10 g of yellow mercuric oxide in benzene solution at room temperature. Benzene was removed from the filtered solution and the residue was recrystallized three times from methanol, ultraviolet yield 1.70 g, ultraviolet ϵ_{355} 48.1, mp 72.0–72.7°. The nmr spectrum of the natural azo compound in carbon tetrachloride is composed of a doublet ($J = 7$ cps) at τ 8.56, a quartet ($J = 7$ cps) centered at 5.43, and a multiplet at 2.78. The corresponding spectra of the azobis-α-phenylethane-β,β,β-d_3 lacked the CH$_3$ doublet at τ 8.56 with replacement of the quartet at 5.43 by a singlet (width at half-height equals 3 cps) at 5.47. Integration of the signals in the deuterated azo compound and comparison with the natural azo compound indicate that there are a total of 0.109 ± 0.005 atoms of hydrogen in the methyl groups of the deuterated azo compound. Because of the slight loss (0.061 atom/molecule) of deuterium from the methyl groups during catalytic hydrogenation of the azine there can be no more than 0.031 ± 0.0145 atom of deuterium in both α positions.

Azobis-α-phenylethane was prepared as reported previously,[13] ultraviolet ϵ_{355} 48.6.

Base- and Acid-Catalyzed Hydrogen Exchange of Acetophenone Azine. Acetophenone azine (7.5 g) was heated for 48 hr in a refluxing mixture of 50 ml of ethanol-d containing sodium ethoxide formed from about 0.29 g of sodium. The infrared spectrum of the recovered azine lacked absorption in the region of the C–D stretching frequency. The sodium ethoxide concentration was increased to approximately twice the starting concentration and refluxing of the mixture was continued. After about 100 hr less than 7% of the methyl hydrogen atoms exchanged.

Acetophenone azine (7.5 g) was heated for 95 hr in a refluxing mixture of 50 ml of 0.13 M sulfuric acid-d_2 in ethanol-d. An infrared spectrum indicated considerable loss in intensity of the C–H stretching bands at 2920 and 2950 cm^{-1} with concurrent appearance of bands in the C–D stretching region. It appeared that about 65% of the methyl hydrogens exchanged under these conditions.

Ethylbenzene (Distillation Products, Inc.) was passed through a 12-in. neutral alumina (Woehlm) column. The refractive index was measured: $n^{25.0}$D 1.4934 (lit.[14] n^{25}D 1.4933). For the runs designed to determine the cage effect, ethylbenzene was distilled from sodium at atmospheric pressure, n^{25}D 1.4932.

Kinetics. Before starting a series of kinetic runs, both the natural and deuterated azobis-α-phenylethane compounds were sublimed under vacuum at about 60° and stored at about −10°. Solutions of each azo compound, 0.02 to 0.03 M in ethylbenzene, were prepared and also stored at −10°.

Vacuum tight, 1-cm quartz cells to which standard taper joints had been sealed were partially filled with azo compound in ethylbenzene solution. The solution was degassed under high vacuum while the quartz cell was bathed in a Dry Ice–chloroform–carbon tetrachloride mixture and the cell was sealed with a torch.

All kinetic runs were carried out in pairs, i.e., a cell containing the natural azo compound and one containing the deuterated compound were both placed in the thermostat at the same time and measurements of the optical density at 355 mμ were recorded almost simultaneously on a Beckmann DU spectrophotometer.

A self-contained, fully enclosed, thermostat was constructed

(11) S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Am. Chem. Soc.*, 72, 3947 (1950).

(12) All nmr spectra were recorded on a Varian A-60 spectrometer.

(13) S. Seltzer, *J. Am. Chem. Soc.*, 83, 2625 (1961).

(14) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishing Co., Inc., New York, N. Y., 1955, p 77.

from 0.050-in. copper sheet. Copper tubes for the light path, for the fastening screws that connect the phototube housing to the monochromator, and for the carriage positioning rod were inserted and welded to the walls of the tank. Holes were drilled in the cover to allow three heaters, a stirrer shaft, a thermometer, and a thermistor to be inserted. The copper tank was fully surrounded by a 0.5-in. Bakelite box but between the copper and Bakelite walls there was placed about a 0.5-in. layer of vermiculite. The outside dimensions of the box are 12 × 9.5 × 12 in. To reduce heat losses, Teflon connecting rods were introduced between the hot inner and cool outer portions of the stirrer shaft and cell-carriage positioning rod. Mineral oil was used.

Because of the increased distance of the cell and photomultiplier from the monochromator, a quartz lens[15] with a focal length of 3 in. was placed about 3 in. from the monochromator.

Determination of Cage Effect. Approximately equal quantities of azobis-α-phenylethane and azobis-α-phenylethane-β,β,β-d_3 were added to about 20 ml of purified ethylbenzene in a 50-ml flask fitted with a 10/30 standard taper joint. The contents were degassed on a high-vacuum line while the solution was cooled to −78° and the flask was sealed under vacuum. The resulting solution was approximately 0.02 M in total azo compound. Similar solutions containing only the natural or the hexadeuterio azo compound were prepared and all three flasks were submerged in a constant temperature bath at 105.5° for 24 hr.

At the end of this time the flasks were removed, cooled, and opened. Each solution was concentrated to about 1.5 ml by distillation of the excess ethylbenzene through a 12-in. vacuum-jacketed column at atmospheric pressure. The remaining ethylbenzene was separated from the hydrocarbon product, 2,3-diphenylbutane, by vapor phase chromatography on a 2-m silicone grease column (Perkin-Elmer column "O") at 190° with a helium pressure of 20 psi.

Since large amounts of racemic and *meso*-2,3-diphenylbutanes were not well resolved both of these were collected in the same trap cooled to 0°. The collection tubes fitted with a ball joint and break-seal, were degassed under high vacuum while cooled to liquid nitrogen temperature, and then sealed. The ball joint of the sample tube was connected to a G.E. analytical mass spectrometer without the intervention of a leak. The vapor pressure of 2,3-diphenylbutane is sufficiently low to allow the determination of mass spectra at room temperature.

To see if the fragmentation pattern of the *meso-dl* mixture was different from that of pure *meso* isomer, ethylbenzene was removed from a portion of the concentrated solution of 2,3-diphenylbutane-1,1,1,4,4,4-d_6 by passing a stream of nitrogen over it for a few hours. The remaining oil was taken up in hot methanol and the deuterated *meso* compound crystallized when the solution was cooled. The solid was recrystallized twice and then sublimed. The sample was analyzed by mass spectrometry in the manner described above. Ion currents in the parent region were small indicating that the *meso* isomer would be present to a small extent in a *meso-dl* vapor mixture at room temperature.

The procedure for the decomposition in ethylbenzene of a degassed sample of azobis-α-phenylethane-β,β,β-d_3 was repeated. Isolation and purification of the *meso* isomer was accomplished by crystallization and sublimation, mp 123.8–124.8°. The deuterated *meso* isomer (3.014 mg) was mixed with 58.556 mg of natural *meso*-2,3-diphenylbutane. The mixture was dissolved in hot methanol and cooled, and the solvent was removed in a stream of nitrogen. The solid was finally sublimed and analyzed for deuterium by combustion;[16] atom % D: 1.30$_5$, 1.30, 1.31. This corresponds to 17% of the α-phenylethyl radicals exchanging with solvent. The thermal decomposition of the hexadeuterio azo compound was repeated in ethylbenzene that had been purified by distillation from sodium. The *meso* isomer was again purified by recrystallization and sublimation. The deuterated 2,3-diphenylbutane (4.083 mg) was diluted with natural material (83.339 mg) and the mixture was analyzed for deuterium; atom % D: 1.47$_7$, 1.48$_7$, 1.48$_0$. This corresponds to a maximum of 0.5% exchange of α-phenylethyl radicals with the solvent.

Results and Discussion

In exploratory experiments, natural acetophenone azine was heated in refluxing ethanol-d containing about 0.2 M sodium ethoxide as well as in refluxing

(15) Supplied by Republic Lens Co., Inc., New York, N. Y.

(16) S. Seltzer, *J. Am. Chem. Soc.*, 83, 1861 (1961).

ethanol-d, 0.1 M in sulfuric acid. In both of these media, exchange was relatively slow with the acidic conditions catalyzing the exchange to a greater degree. Even though exchange proceeded slowly it was decided to carry out the synthesis of the aceto-d_3-phenone azine in a solvent rich in deuterium. The azine was formed from aceto-d_3-phenone and hydrazine hydrate-d_6 in a solution of ethanol-d to which was added a trace of natural glacial acetic acid. Integration of the nmr spectrum of the azine indicated that less than 0.8 $\pm$ 0.4 atom% of hydrogen was present in the methyl groups.

Conversion of azine to the hydrazine was accomplished through catalytic hydrogenation in dioxane as solvent. It was previously shown that very little methyl hydrogen exchange results during catalytic reduction of this azine in ether.[13] That this is also true for dioxane as solvent was shown by the nmr spectrum of the azo compound derived from the hydrazine. The nmr spectrum of a sample of azobis-α-phenylethane-β,β,β-d_3 indicated that about 1% (see the Experimental Section) of the deuterium in the methyl group was lost during catalytic hydrogenation. Because of the almost stoichiometric amount of hydrogen gas present in the reservoir during reduction, the deuterium lost from the methyl groups (0.061 atom) represents an upper limit to the deuterium bonded to the nitrogen and α-carbon atoms in the hydrazine. A fourth of this (0.015 atom), therefore, represents the upper limit of the amount of deuterium in each α-hydrogen position. Consequently, the observed rate of thermal decomposition for this sample of azobis-α-phenylethane-β,β,β-d_3 must be corrected for this small amount of deuterium in the α position.

Kinetics. The rates of thermal decomposition of the azo-d_6 and azo-d_0 compounds were determined separately but simultaneously side by side in the same thermostat. In an individual run, the decrease in optical density at 355 mμ vs. time was determined on about 3 ml of approximately a 0.02 M solution of azo compound in ethylbenzene in a sealed, degassed quartz cell. An average of 45 observations were made while the optical density decayed to about 1% of the initial reading. The data were fitted by means of a nonlinear least-squares program, as described previously,[13] to the first-order rate law. First-order rate constants are shown in Table I.

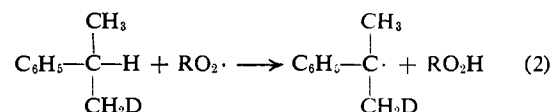Table I. First-Order Rate Constants for Thermal Decompositions[a]

CH₃—CH₃ head	CD₃—CD₃ head	
C₆H₅CN=NCC₆H₅ (H,H)	C₆H₅CN=NCC₆H₅ (H,H)	
$k \times 10^6$ sec^{-1}	$k \times 10^5$ sec^{-1}	k_{H_6}/k_{D_6}
8.470 $\pm$ 0.020[b]	7.655 $\pm$ 0.016[b]	1.106 $\pm$ 0.003
8.455 $\pm$ 0.019[b]	7.577 $\pm$ 0.016[b]	1.116 $\pm$ 0.003
8.515 $\pm$ 0.021[b]	7.677 $\pm$ 0.016[b]	1.109 $\pm$ 0.004
8.453 $\pm$ 0.031[b]	7.584 $\pm$ 0.016[b]	1.115 $\pm$ 0.005
Av 8.473 $\pm$ 0.029[c]	7.623 $\pm$ 0.050[c]	1.112 $\pm$ 0.005
	$k_H/k_D = 1.018 \pm 0.001$	

[a] In ethylbenzene at 105.02°. [b] Standard deviation within a kinetic run. [c] Standard deviation in the average rate constant.
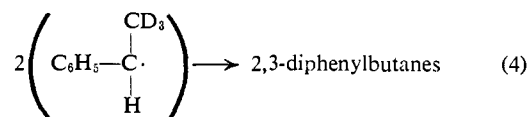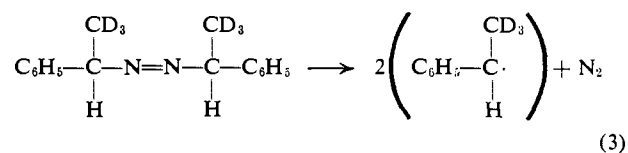
In order to calculate the secondary β-deuterium isotope effect it is first necessary to correct the rate ratio for the very small quantity of deuterium in the α positions of azobis-α-phenylethane. The isotope effect in the thermal decomposition of the α-deuterated isomer has already been measured under almost identical conditions.[13] The ratio of first-order rate constants is $k_H/k_D = 1.27 \pm 0.03$ when deuterium replaces the two α protons. If it is assumed that the effects are cumulative, the contribution of the α-D impurity to the decrease in observed rate is $(1.27 \pm 0.03)^{0.015 \pm 0.0075}$ or 1.0035 ± 0.0020. The rate ratio attributed only to β substitution is then $(1.112 \pm 0.005)/(1.0035 \pm 0.0020) = 1.108 \pm 0.004$ for 5.89 atoms of deuterium or $k_H/k_D = 1.0175 \pm 0.001$ per D atom.

While this work was in progress, Koenig and Brewer[17a] reported in a preliminary communication that t-butyl α-phenylperpropionate homolytically decomposed to α-phenylethyl radical at a 3% faster rate than a preparation deuterated to 70% in the β-methyl group. While their result is in harmony with ours, the isotope effect unfortunately is slightly larger than their reported error.

The only other report concerned with the measurement of secondary β-deuterium effects and the role of hyperconjugative stabilization in radical reactions was carried out by Boozer and co-workers on the autoxidation of cumene.[17b,c] These workers claimed to have isolated the propagation step

$$\underset{\substack{| \\ CH_3 \\ C_6H_5-C-H \\ | \\ CH_2D}}{} + RO_2\cdot \longrightarrow \underset{\substack{| \\ CH_3 \\ C_6H_5-C\cdot \\ | \\ CH_2D}}{} + RO_2H \quad (2)$$

by adding phenolic inhibitors to the medium. Under these conditions the rate was decreased about 10% for each methyl D atom. The mechanism, however, is still incompletely understood.[18] Thus an observed effect of deuterium substitution might be a combination of effects for propagation and termination steps. This uncertainty is avoided in the decomposition of azobis-α-phenylethane-β,β,β-d_3.

$$\underset{\substack{CD_3 \quad CD_3 \\ | \quad | \\ C_6H_5-C-N=N-C-C_6H_5 \\ | \quad | \\ H \quad H}}{} \longrightarrow 2\left(\underset{\substack{CD_3 \\ | \\ C_6H_5-C\cdot \\ | \\ H}}{}\right) + N_2 \quad (3)$$

$$2\left(\underset{\substack{CD_3 \\ | \\ C_6H_5-C\cdot \\ | \\ H}}{}\right) \longrightarrow 2,3\text{-diphenylbutanes} \quad (4)$$

In ethylbenzene, the thermal decomposition is clearly first order to at least 99% reaction and has been suggested to involve simultaneous rupture of both carbon–nitrogen bonds.[13] Therefore, the approximate sixth root of the corrected β effect corresponds to the isotope effect (1.018) per D atom.

(17) (a) T. W. Koenig and W. D. Brewer, Tetrahedron Letters, 2773 (1965); (b) C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wightman, III, J. Am. Chem. Soc., 78, 1506 (1956).

(17c) NOTE ADDED IN PROOF. An indirect method has recently been used by W. A. Pryor, R. W. Henderson, R. A. Pastiga, and N. Carroll ibid., 88, 1199 (1966)] to determine the secondary β-deuterium effect in the polymerization of styrene. Our observations are in aggreement with their results.

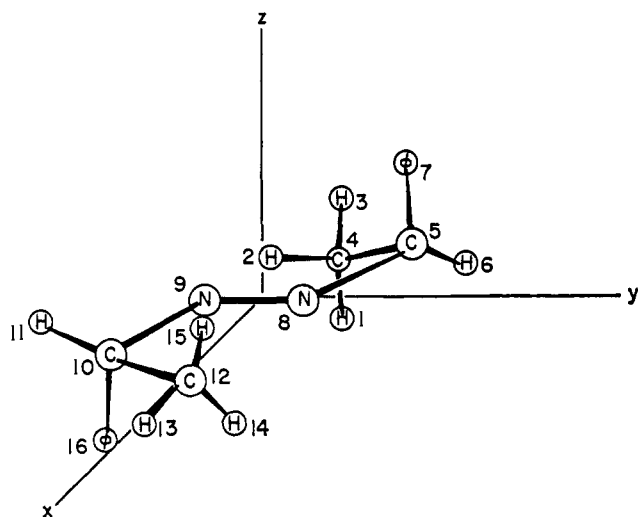(18) P. D. Bartlett and T. G. Traylor, ibid., 85, 2407 (1963).

Figure 1. Representation of the assumed geometry of the reactant.

The activation energy for abstraction of hydrogen from cumene is lower than that for the thermal cleavage of azobis-α-phenylethane by some 20 kcal/mole.[11,19] It might be argued then that of the two aralkyl species present at the transition states in these two reactions, the one formed in the thermal decomposition of the azo compound should resemble more a fully formed radical. Assuming this to be true, hyperconjugative stabilization of the transition state should be just as or more important in this case of azo decomposition than in hydrogen abstraction of cumene. Although the two systems differ, we feel that the disagreement lies in the inability to completely isolate the propagation step from the over-all autoxidation kinetics.

Calculations. Based on a program written by Schachtschneider[20] to calculate normal harmonic vibrational frequencies from given force constants, masses, and positions of atoms, Wolfsberg[21] has developed a computer program to calculate isotope effects in reactions of multiatom molecules. By *assuming* force constants for the transition state and from a knowledge of the corresponding force constants for the reactant state, kinetic effects can be calculated.[22]

Azobis-α-phenylethane was assumed to have the *trans*-azo configuration and because of its symmetry the *meso* isomer (Figure 1) was chosen in order to simplify calculation of the coordinates of each atom. The important bond lengths and angles of the reactant and transition state are given in Table II;[23] tetrahedral angles are assumed for those not particularly specified. The G matrices of the reactant and transition state were calculated for the natural, the fully methyl-deuterated, and the bis-α-deuterated compounds.[20]

(19) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1, 107 (1961).

(20) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 19, 117 (1963).

(21) M. Wolfsberg and M. Stern, *Pure Appl. Chem.*, 8, 225 (1964); 8, 325 (1964).

(22) These have been termed "exact" calculations. It should be emphasized that this refers to the precision in the calculation rather than to its relation to "exact" reality.

(23) Bond lengths and angles for the reactant were those found for similar molecules published in H. J. M. Bowen, J. Donohue, D. G. Jenkin, O. Kennard, P. J. Wheatley, and D. H. Whiffen, Special Publication No. 11, The Chemical Society, London, 1958. Bondlengths and angles for the transition state were taken as intermediate between the reactant and product. In cases where the bond is nonexistent in the product, its length was just increased by about 15%.

Table II. Assumed Bond Angles and Lengths for Azobis-α-phenylethane

Angle position	Angle, deg	
	Reactant	Transition state
$(C_6H_5)_7-C_5-N_8$	112	101
$H_6-C_5-C_4$	106	111
$C_5-N_8-N_9$	120.2	105
$H_2-C_4-C_5$	109.5	109.5
	Lengths, A	
C_5N_8	1.47	1.71
$(C_6H_5)_7C_5$	1.52	1.52
C_5H_6	1.10	1.10
C_4C_5	1.54	1.54
C_4H_1	1.10	1.10
N_8N_9	1.24	1.17

A choice of force constants for the reactant was arrived at by comparison with those known for other molecules and for the most part they were identical with those used for the transition state. In order to convert the reactant molecule to a transition state, the force constant for each carbon–nitrogen stretch was reduced arbitrarily to half its original value and an interaction force constant was introduced so that both carbon–nitrogen bonds stretched simultaneously. By allowing the left side of eq 5 to equal -0.0001, a value close to

$$f_{\text{α-CN stretch}} f_{\text{α'-CN'stretch}} - f^2_{\text{interaction}} = -0.0001 \quad (5)$$

zero and yet still negative, an almost flat barrier is produced.

In addition, the nitrogen–nitrogen stretching constant was increased 25% since a triple bond is being formed. All bending force constants associated with the leaving groups were reduced to about 55% (model I), 40% (model II), or 25% (model III) of their original value. These include the α-H–C–N, C_6H_5–C–N, C (of methyl)–C–N, and the C—N═N bending constants. *No force constants involving either the stretching or bending modes of hydrogen in the methyl groups were changed.* To check that these assigned changes bear some resemblance to what might be happening during thermolysis, the isotope effect for substitution of two α-deuterium atoms for hydrogen was calculated. As shown in Table III, model II, in which all bending force constants associated with nitrogen have been reduced in the transition state to 40% of their original value, fits best with the observed α effect. It is interesting to note that the ratio of imaginary frequencies, ν_{1L}^*/ν_{2L}^*, is 1.006 by this method and 1.005 using the reduced masses of the separating fragments.[24a] Using these same force fields, the effect of substitution of six atoms of deuterium for hydrogen in the methyl groups was examined. These results are shown in the last three columns of Table III.

Because the observed β effect is so small in this system, the effect of the change in mass on the ratio of imaginary frequencies must be calculated before we can attribute the observed β effect solely to hyperconjugative stabilization. As shown in the last three columns of Table III, the ratio of imaginary frequencies is 1.026 and independent of which of the three models is chosen. This is about one-fourth of the total observed β effect. The remainder, about 1.3% per atom of deuterium, is the maximum portion of the effect that can

Table III. Calculated Secondary Deuterium Isotope Effects in the Decomposition of Azobis-α-phenylethane

Temp, °K	α-$(k_H/k_D)^a$			β-$(k_H/k_D)^b$		
	Model			Model		
	I	II	III	I	II	III
273	1.311	1.455	1.591	1.031	1.032	1.033
373	1.193	1.274	1.347	1.028	1.028	1.029
2000	1.014	1.017	1.020	1.026	1.026	1.026
$\nu_{1L}*/$ $\nu_{2L}*{}^c$	1.006	1.006	1.006	1.026	1.026	1.026
$\nu_{1L}*/$ $\nu_{2L}*{}^d$	1.005	1.005	1.005	1.014	1.014	1.014

^{a} Values for two α-deuterium atoms. Observed effect is 1.27 at 378°K. ^{b} Values for six β-deuterium atoms. ^{c} Wolfsberg–Schachtschneider program. ^{d} From the reduced masses of the fragments.[24a]

be attributed to a weakening of the methyl carbon–hydrogen bonds.

Shiner, Lewis and their co-workers[8a,b] have attributed secondary β-deuterium effects to hyperconjugative stabilization of developing carbonium ions in SN1 solvolysis of substituted alkanes. Their systems show decreases in rate of from 10 to 20% per deuterium atom for alkyl systems and about 7% per deuterium atom in the SN1 limiting solvolysis of α-phenylethyl-β,β,β-d_3 chloride.[24b] The latter effect, when corrected to 105°, is about four times greater than that observed in the present reaction. If this is an index of hyperconjugative stabilization, it appears that the α-phenylethyl radical derives its greatest stabilization through delocalization of the lone electron in the ring. Evidence for this has been given by Cohen.[25] He has drawn attention to the change in activation energy of thermal decomposition on substitution of phenyl for methyl in azobis-2-propane. Each substitution of phenyl decreases the activation energy about 4 kcal/mole in these systems. The lack of hyperconjugative stabilization of the incipient α-phenylethyl radical does not preclude, of course, its occurrence in systems lacking neighboring conjugation.[26]

The Cage Effect.[27] Radical products from the photochemical or thermal decomposition of azo compounds are known not to be completely efficient in initiating polymerization. A large fraction of the radical pairs produced are locked together by solvent and combine before they can diffuse apart to enter in other reactions. The portion that find their way out is often determined by the use of scavengers: I_2, Br_2, galvinoxyl, diphenylpicrylhydrazyl, etc. All of the product radicals cannot be forced to combine with scavenger and that fraction that does not is the caged portion. It is of some consequence whether there may be some induced decomposition of the parent azo compound in the presence of scavenger, thereby limiting the normal cage fraction. Moreover, the stability of the scavenged product under the conditions of the experiment is an important consideration.

Because we had a highly deuterated sample, we thought it worthwhile to determine the cage effect in the

(24) (a) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 30 (1958); (b) B. L. Murr, Ph.D. Thesis, University of Indiana, 1961.
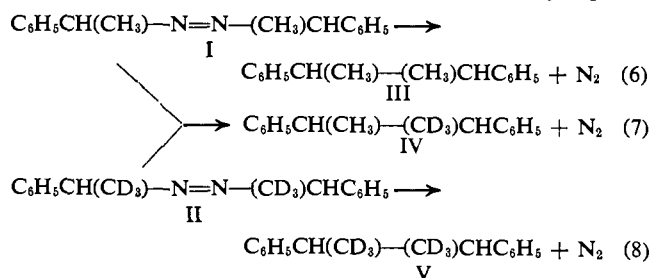(25) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, 77, 3628 (1955).
(26) Unpublished calculations by S. Ehrenson and M. Wolfsberg suggest hyperconjugation in the ethyl radical to be more important than in α-phenylethyl radical in stabilization.
(27) For a leading reference see: H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 1911 (1964).

absence of scavenger. Approximately equal quantities of the natural and hexadeuterated azo compounds were dissolved in ethylbenzene to a total concentration of about 0.02 M. The compounds were allowed to thermolyze in the absence of air, for 9.5 half-lives of the deuterated compound.

Three different isotopically substituted 2,3-diphenylbutanes are formed. We could not observe any separa-

$$C_6H_5CH(CH_3)-N=N-(CH_3)CHC_6H_5 \longrightarrow$$
$$I$$
$$\searrow \quad C_6H_5CH(CH_3)-(CH_3)CHC_6H_5 + N_2 \quad (6)$$
$$III$$
$$\searrow \longrightarrow C_6H_5CH(CH_3)-(CD_3)CHC_6H_5 + N_2 \quad (7)$$
$$\diagup \quad IV$$

$$C_6H_5CH(CD_3)-N=N-(CD_3)CHC_6H_5 \longrightarrow$$
$$II$$

$$C_6H_5CH(CD_3)-(CD_3)CHC_6H_5 + N_2 \quad (8)$$
$$V$$

tion of III, IV, or V when the mixture was vapor phase chromatographed on a 2-m silicone grease column but each compound separated into equal quantities of *rac* (or *threo*) and *meso* (or *erythro*) isomers. The relative quantities of III, IV, and V were determined from the intensities of the peaks in the parent region of the mass spectrum.

When a mixture of equal amounts of I and II is thermalized, the composition of the butanes will be 25% III, 50% IV, and 25% V if there is a zero cage effect in the reaction. As the portion of radicals trapped in a cage increases the quantity of III and V increases with concomitant decrease in the quantity of IV. The relative quantities of butanes are given by eq 9–11 where α is the fraction of caged molecules and a and b are the initial concentrations of I and II, respectively. These equations hold if I and II decompose

$$[III] = \alpha a + \frac{(1 - \alpha)a^2}{(a + b)^2}(a + b) \tag{9}$$

$$[IV] = \frac{2(1 - \alpha)ab}{(a + b)^2}(a + b) \tag{10}$$

$$[V] = \alpha b + \frac{(1 - \alpha)b^2}{(a + b)^2}(a + b) \tag{11}$$

at identical rates. If, on the other hand, the two compounds decompose at very different rates it is clear that the concentrations of III and V will increase and IV will decrease. So as not to confuse this behavior with a true cage effect, the importance of different rates on the distribution of III, IV, and V was investigated. The kinetic equations used for this calculation are given in the Appendix. Numerical integration was carried out with the aid of an IBM 7094 computer using 1000 intervals. The variation of the ratio of cross-product to noncross-product as a function of the ratio of first-order rate constants, in the absence of a cage effect, is shown in Figure 2. It is assumed here that the secondary isotope effect in radical coupling is negligible. The utility of these results is not confined to a study of isotopic isomers but is important in estimating the amount of cross-product to be expected when the two starting materials differ more markedly.[28] Nevertheless, for the present case, an isotope effect of 11% does

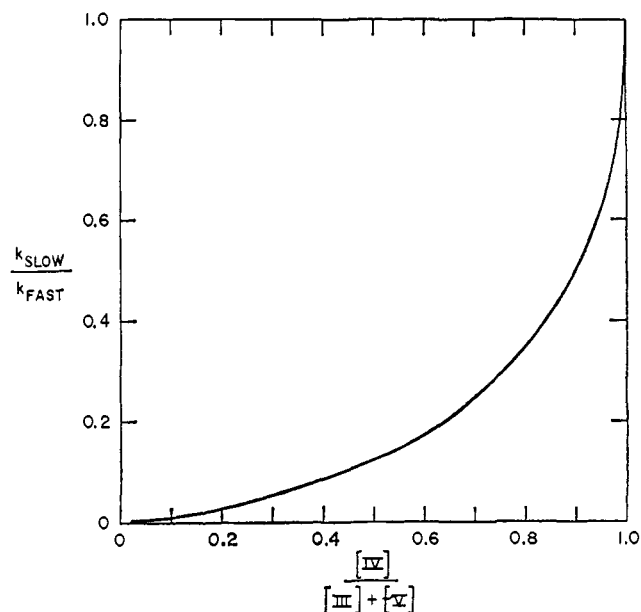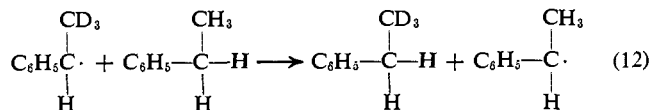(28) See, *e.g.*, D. V. Banthorpe and E. D. Hughes, *J. Chem. Soc.*, 2860 (1964).

Figure 2. A plot of the ratio of rate constants *vs.* the ratio of cross-product to the sum of noncross-product for equal concentrations of starting material.

Table IV. Parent Region Mass Spectrum of 2,3-Diphenylbutane from Thermolysis of Azobis-α-phenylethane in Ethylbenzene

	Relative intensities		
m/e	From I	From II[a]	From I + II[b]
216		100.0	84.1
213		43.3	100.0
211	19.4	19.4	
210	100.0		97.9
209	0.92		
208	0.60		
207	1.70		

[a] Ethylbenzene purified by percolation over alumina. [b] Ethylbenzene distilled from sodium. Average of four spectra from a ratio, $[II]_0/[I]_0 = 1.007$.

not change the distribution of products significantly; $[IV]/[III] + [V] = 0.9967$.

In initial experiments, thermolysis of the hexadeuterated azo compound was accompanied by about 17% exchange of the α-phenylethyl radicals with the solvent.

$$C_6H_5\overset{\underset{\displaystyle |}{CD_3}}{\underset{\displaystyle |}{C}} \cdot + C_6H_5\overset{\underset{\displaystyle |}{CH_3}}{\underset{\displaystyle |}{C}}-H \longrightarrow C_6H_5\overset{\underset{\displaystyle |}{CD_3}}{\underset{\displaystyle |}{C}}-H + C_6H_5\overset{\underset{\displaystyle |}{CH_3}}{\underset{\displaystyle |}{C}} \cdot \quad (12)$$

That this reaction operates is shown in the third column of Table IV by the decrease in parent mass in units of three and by a simultaneous deuterium analysis by combustion of the product from thermolysis of I. These results run counter to those previously published[13,29] and appear to be due to the method of solvent purification.[30]

The thermolysis of an almost equimolar mixture of I and II was repeated in ethylbenzene that was shown not to exchange (see the Experimental Section). The results are shown in the last column of Table IV.

Although almost equal quantities of I and II were present during thermolysis, equal ion currents at mass 216 and 210 are not observed. This discrepancy may be due to (a) different vapor pressures for III and V, and/or (b) slightly different sensitivities and fragmentation patterns for d_6-, d_3-, and d_0-diphenylbutanes. At temperatures between the boiling point and melting point, however, deuterated hydrocarbons generally have a vapor pressure higher than their fully protonated counterparts.[31] Because the reverse is observed here, the source of the discrepancy probably lies in the

assumption that the three diphenylbutanes behave identically, in a quantitative sense, toward an electron beam. If it is assumed that the deviation is a linear function of the degree of deuteration, and s is the sensitivity (ion current per unit partial pressure) for the d_0 compound, then $(s - \Delta s)$ and $(s - 2\Delta s)$ are the sensitivities for the d_3- and d_6-diphenylbutanes, respectively. By taking the ratio $2[IV]/([III] + [V])$ to determine α, the cage effect, the deviation Δs falls out.

If l, m, and h are the ion currents for mass 210, 213, and 216, respectively, then $l = [III]s$, $m = [IV](s - \Delta s)$, and $h = [V](s - 2\Delta s)$.

$$\frac{2m}{l + h} = \frac{2[IV](s - \Delta s)}{[III]s + [V](s - 2\Delta s)} =$$

$$\frac{2[IV](1 - \Delta s/s)}{([III] + [V])\left(1 - \frac{2[V]}{[III] + [V]}\frac{\Delta s}{s}\right)} \quad (13)$$

If the difference in vapor pressures between the d_0- and d_6-diphenylbutanes is negligible and the initial concentrations of I and II are very nearly equal, then $[V] \simeq [III]$. Under these conditions, eq 13 reduces to

$$\frac{2m}{l + h} = \frac{2[IV]}{[III] + [V]} \quad (14)$$

Combining eq 9–11 with eq 14 and substituting values for l, m, and h from Table IV, a value for α can be obtained. By this method, it is found that 29.1% of the total geminate phenylethyl radicals that eventually dimerize do so before diffusing apart.
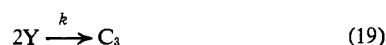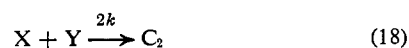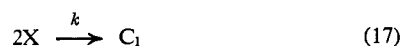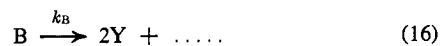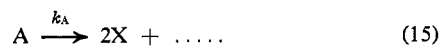
Unfortunately, a value for the cage effect in the decomposition of azobis-α-phenylethane in ethylbenzene at 105° obtained from the use of scavengers has not been published. Recently, however, an extensive study of the factors affecting the cage effect in azocumene decomposition has been reported.[32] An extrapolation of the data indicates that about 21% of the cumyl radicals is caged in toluene as solvent as determined by the use of di-*t*-butyl nitroxide as scavenger. However, considerable variations in the cage effect were found to be brought about by changing the solvent. These variations were shown to be independent of the viscosity of the medium. So it appears that a direct comparison of the two systems in different solvents may be dangerous at this time and will have to await further work.

(29) C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957); E. L. Eliel, P. H. Wilken, F. T. Fang, and S. H. Wilen, *ibid.*, **80**, 3303 (1958).

(30) In earlier experiments,[13] ethylbenzene, distilled from sodium, does not exchange with α-phenylethyl radicals. In the present experiment, ethylbenzene, purified by percolation through an alumina column, exchanges with α-phenylethyl radicals. A repetition of the earlier conditions gives no exchange. The mechanism of this exchange is under current investigation.

(31) I. B. Rabinovich, *Usp. Khim.*, **31**, 101 (1962).

(32) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

Acknowledgments. The authors wish to thank Drs. Stern and Wolfsberg for invaluable help with exact calculations. They would also like to express their appreciation to Mr. Ted Middleton and Mrs. Kay Paul for mass spectrometric and deuterium analysis. Thanks are especially due to Mr. Ronald Withnell for aid in modifying the optics of the spectrophotometer.

Appendix

Consider the following reactions

$$A \xrightarrow{k_A} 2X + \ldots \ldots \tag{15}$$

$$B \xrightarrow{k_B} 2Y + \ldots \ldots \tag{16}$$

$$2X \xrightarrow{k} C_1 \tag{17}$$

$$X + Y \xrightarrow{2k} C_2 \tag{18}$$

$$2Y \xrightarrow{k} C_3 \tag{19}$$

where A and B are natural and hexadeuterated azo compounds, X and Y are natural and trideuterated α-phenylethyl radicals, and the C's are the corresponding isotopically substituted 2,3-diphenylbutanes. The simplifying assumption is made that the rate constants for reactions 17–19 are equal since these are very rapid reactions. For the present case there is no doubt that $k \gg k_A$ or k_B. Neglecting cage effects, the small concentrations of X and Y formed during dt are $d[X] = 2k_A[A_0]e^{-k_A t}dt$ and $d[Y] = 2k_B[B_0]e^{-k_B t}dt$ where $[A_0]$ and $[B_0]$ refer to the initial concentrations of A and B, respectively.

An approximate method can be introduced here to simplify the calculation considerably. The small increments in X and Y are calculated from 0 to t. X and Y are coupled statistically according to reactions 17–19 and the quantities C_1, C_2, and C_3 are determined from eq 20–22.

$$dC_1 = \frac{(d[X])^2}{(d[X] + d[Y])} \tag{20}$$

$$dC_2 = \frac{2d[X]d[Y]}{(d[X] + d[Y])} \tag{21}$$

and

$$dC_3 = \frac{(d[Y])^2}{(d[X] + d[Y])} \tag{22}$$

The interval is changed from t_1 to t_2 and the quantities C_1, C_2, and C_3 are recalculated. The sums of C_1, C_2, and C_3 are obtained over at least 10 half-lives of the slowest rate and 1000 time intervals. No significant change is produced when the number of intervals is increased by a factor of 10. The results obtained by this method are identical with those from a more rigorous treatment which would require too much space to reproduce here.

A Study of the Deoxygenation of Some o-Alkylnitro- and o-Alkylnitrosobenzenes in Triethyl Phosphite[1]

R. J. Sundberg

Contribution from the Department of Chemistry, Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia 22903. Received April 25, 1966

Abstract: The deoxygenation of four o-alkylnitrobenzenes in excess triethyl phosphite gives mainly triethyl N-arylphosphorimidates, but also significant amounts of amines, some of which are the result of apparent C–H insertion reactions involving the adjacent alkyl side chain. The deoxygenations of three o-alkylnitrosobenzenes have been investigated and compared with the corresponding nitro deoxygenations. Deoxygenation of o-alkylnitrosobenzenes in excess triethyl phosphite has been found to give rearranged products containing the pyridine ring. The mechanism of the H-abstraction reaction which occurs during nitro deoxygenation and azide pyrolysis is briefly considered.

In recent years several investigations have established that aromatic nitro and nitroso compounds are deoxygenated by the action of trivalent derivatives of phosphorus. Depending upon the structure of the substrate and reaction conditions, the deoxygenated fragments have been isolated as azoxy compounds,[2–4] as heterocyclic nitrogen compounds,[2,4–6] as derivatives of phosphorimidic acid,[2,6] and as tars.[5,6]

Although the formation of most of these types of products can be rationalized by invoking monovalent, electron-deficient nitrogen intermediates, arylimidogens,[7] there is little firm evidence supporting such a proposal. In the case of deoxygenation of o-nitrostyrene derivatives, evidence has been presented which indicates that a major path to the indoles observed as products does not involve a monovalent intermediate.[6] The present study of o-alkyl-substituted nitro- and nitrosoaromatics was undertaken to determine if deoxygenation gives intermediates capable of reacting with adjacent saturated side chains to give C–H insertion

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(3) S. A. Buckler, L. Doll, F. K. Lind, and M. Epstein, *J. Org. Chem.*, 27, 794 (1962).

(4) A. C. Bellaart, *Tetrahedron*, 21, 3285 (1965).

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(6) R. J. Sundberg, *J. Org. Chem.*, 30, 3604 (1965).

(7) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 149 (1964).