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The Secondary α-Deuterium Isotope Effect: The Mechanism of the Thermal Decomposition of Azo-bis-α-phenylethane[1]

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The secondary α-deuterium isotope effect in the free radical cleavage of azo-bis-α-phenylethane-α,α'-d_2 in ethylbenzene as solvent, was found to be 1.27 ± 0.03 at 105°. A large body of data on secondary α-deuterium isotope effects indicate that an average value of 1.12, at this temperature, corresponds to a system where only one bond is being broken in the slow step. Since the measured effect is about twice as large, it appears that both carbon–nitrogen bonds are being broken simultaneously in the transition state. This method represents a new method of differentiating between a simultaneous and stepwise two-bound rupture. Comparison of the deuterium content in the solid product, meso-2,3-diphenylbutane-2,3-d_2, with that of the starting azo compound, indicates that hydrogen abstraction by the intermediate α-phenylethyl radical from ethylbenzene, does not occur.

Introduction

There has been interest for some time in the mechanism of homolytic cleavage of R–X–R′, where R and R′ are alkyl or aryl derivatives and X is an azo group (—N=N—) or a metallic element like mercury or zinc. In the case of the azo compounds, detailed discussions have been advanced by Cohen and Wang[2] and Overberger and DiGiulio[3] on the question of whether carbon–nitrogen cleavage is simultaneous or stepwise.

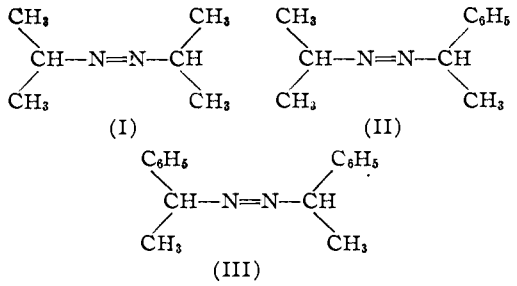
$$R{-}N{=}N{-}R' \longrightarrow R\cdot + R'\cdot + N_2 \qquad (1)$$

or

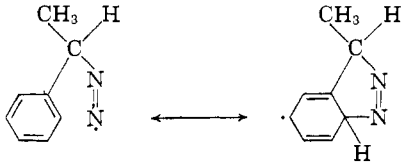
$$R{-}N{=}N{-}R' \longrightarrow \underset{(A)}{R{-}N{=}N\cdot} + R'\cdot \qquad (2)$$

$$R{-}N{=}N\cdot \longrightarrow R\cdot + N_2 \qquad (3)$$

Comparisons of activation energies and rates of reaction were made for the decomposition of azoisopropane (I), α-phenylethylazoisopropane (II) and azo-bis-α-phenylethane (III). Because the activation energy decreased about



4 kcal./mole each time a phenyl group replaced a methyl group in this series and because the ratio of rates for compounds (III) and (II) was greater than a statistical factor of two, these authors concluded that both carbon–nitrogen bonds break simultaneously. The increase in rate and decrease in activation energy is due to the phenyl group aiding in the delocalization of a lone electron in the transition state. This is a strong argument only if it can be shown that the presence of an α-phenyl group cannot also stabilize the formation of intermediate (A) (equation 2) in the transition state. If decomposition occurred by steps 2 and 3 the intermediate could possibly be stabilized by delocalization of the free electron as shown in equation 4.



(4)

In order that the phenyl group participate in this manner, it is necessary that the ortho hydrogen be displaced somewhat out of the plane of the benzene ring as the reactant molecule moves along its path to the transition state.

Another way in which to investigate this problem is to measure the magnitude of the secondary α-deuterium isotope effect to see if one or two carbon–nitrogen bond-scissions are involved in the rate determining step.

It has been shown previously[4–8] that the rate of SN1 solvolysis, for compounds having α-deuterium atoms at the site of substitution, is slower by about 15% at room temperature. Conversely, reactions which involve addition of a fragment to a trigonal reaction site, bearing α-deuterium atoms, proceed at a faster rate than their protium analogs.[9–11] Furthermore, there have been indications[7,12] that the isotope effect for two deuterium atoms at a reaction site is twice that for one atom of deuterium. It therefore seemed reasonable that two α-deuterium atoms, at separate reaction sites, would produce an isotope effect similar to that observed for two atoms of deuterium at one reaction site, if both centers of reaction were undergoing change simultaneously in the rate controlling step.

Azo-bis-α-phenylethane-α,α'-d_2 has been synthesized and its rate of decomposition in ethylbenzene has been measured and compared to that for the natural compound under identical conditions.

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

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(12) V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRAL ANALYSIS OF NATURAL AND DEUTERATED MESO-2,3-DIPHENYLBUTANE

	Integrated areas				
	Phenyl	CH	CH_3	Total H	
Meso-2,3-diphenylbutane[a]	563	117	344	1024	
	564	115	346	1025	
	563	116	347	1026	
Average	563.3	116	345.7	1025	1025/18 = 56.94/H
Meso-2,3-diphenylbutane-2,3-d_2[b]	558	28	326	912	
	556	31	322	909	
	558	27	326	911	
Average	557.3	28.7	324.7	910.7	
Normalized average[c]	576.0	29.7	335.6		
% H[d]	101 ± 1	26 ± 3	98.2 ± 0.8		

[a] 99.9 mg. dissolved in 729.5 mg. of $CDCl_3$. [b] 98.9 mg. dissolved in 740.7 mg. of $CDCl_3$. [c] Normalized to correct for differences in concentration and molecular weights. [d] The errors are those suggested by Dr. LeRoy Johnson of Varian Associates.

Experimental[13]

Azo-bis-α-phenylethane.—Acetophenone azine was prepared as described by Cohen, *et al.*[14]; m.p. 122.2–123.0°, $\epsilon_{350m\mu}$ = 1054[15,16] and $\epsilon_{359m\mu}$ = 490 (both in ethylbenzene). The ketazine was dissolved in 100 ml. of purified dioxane and 1.5 g. of 5% palladium on charcoal (Baker and Co.) was added. The reduction was accomplished in a Paar hydrogenation apparatus. The initial pressure was 18 p.s.i. After about 2 hr. the required amount of hydrogen was taken up and the reduction was stopped. The mixture was filtered and the dioxane evaporated off at reduced pressure. The oxidation of the hydrazine was carried out with yellow mercuric oxide according to the method of Cohen and Wang[17]; m.p. of azo compound, 72.3–72.9°.

Azo-bis-α-phenylethane-α-α′d_2.—The deuteriated azo compound was prepared in the same way except that the reduction was carried out at atmospheric pressure in ether solution. Twelve hours were needed for the uptake of two moles of deuterium (> 99.5% D, Stuart Oxygen Co.) in the reduction of 9.34 g. of acetophenone ketazine dissolved in 50 ml. of ether catalyzed by 2.0 g. of 5% palladium on charcoal, m.p. of azo compound, 71.8–72.7°.

Ultraviolet Spectra.—A sample of the natural azo compound was dissolved in distilled ethylbenzene and its ultraviolet spectrum determined from 305 to 420 mμ. The largest peak was found to be at 359 mμ with a log ε = 1.68.

Solutions of varying concentrations of the azo compound in ethylbenzene were prepared and their optical densities determined. The data are: 0.0163 *M*, 0.743; 0.00978 *M*, 0.446; 0.00587 *M*, 0.276; 0.00352 *M*, 0.168; 0.00211 *M*, 0.101; 0.00127 *M*, 0.065. A plot of these points indicates that Beer's Law is obeyed.

Kinetic Runs.—Eastman ethylbenzene was distilled from sodium and the middle fraction, having a 0.4° b.p. range, was taken. The azo compound (0.3–0.6 g.) was dissolved in about 90 ml. of ethylbenzene in a 100 ml. volumetric flask. Prepurified nitrogen was bubbled through the solution for about 20 minutes at room temperature. While there was still a nitrogen atmosphere above the solution, the flask was stoppered with a rubber serum cap which was further tightened with wire. The flask was then placed in a constant temperature bath at 105.28 ± 0.05°. After about 5 minutes the gas above the solution was brought to atmospheric pressure by inserting a hypodermic needle through the serum cap for a very short period of time. After the contents came to temperature-equilibrium with the bath, generally about ten minutes, samples were taken. Sampling was accomplished by using a hypodermic syringe with a 10 inch needle. The syringe and needle were filled with about 4–5 ml. of prepurified nitrogen. The cap was punctured; the nitrogen discharged; and a sample of approximately 4 ml. was withdrawn. This was put into a stoppered test tube and allowed to cool to room temperature. The optical density at 359 mμ of each sample was determined in a Beckman DU spectrophotometer thermostated at 30°. Rate constants were determined by programming the data on the IBM 704 computer.

Meso-2,3-diphenylbutane.—α-Phenylethyl chloride was prepared from styrene and dry hydrogen chloride as described by Kharasch, *et al.*[18] Meso-2,3-diphenylbutane was prepared by treating α-phenylethyl chloride with magnesium according to the method of Barber, *et al.*,[19] m.p. 125.3–125.9°.

Meso-2,3-diphenylbutane-2,3-d_2 from Kinetic Runs.—The solutions of azo-bis-α-phenylethane-α,α′-d_2 in ethylbenzene that remained in the reaction flask at the end of several kinetic runs were combined. The ethylbenzene was distilled off and the meso isomer of 2,3-diphenylbutane-2,3-d_2 separated from the racemic form by alternate recrystallizations from methanol and sublimations.

Meso-2,3-diphenylbutane-2,3-d_2.—Azo-bis-α-phenylethane-α,α′-d_2 (690 mg.) was placed in a heavy walled tube. The tube was flushed with nitrogen, evacuated and then sealed off. The tube was then heated to 110° for 24 hr. (99.999% decomposition) after which it was opened and the solid in the tube was recrystallized from methanol. It was then sublimed, recrystallized from methanol and sublimed once again yielding 206 mg. of meso-2,3-diphenylbutane-2,3-d_2, m.p. 125.0–126.2°.

Benzoic Acid-*d*.—The deuteriated azo compound (0.287 g.) was dissolved in 75 ml. of glacial acetic acid. Then 1.37 g. of CrO_3 was added and the mixture refluxed for 90 minutes after which it was diluted with an equal volume of water and extracted continuously with *n*-pentane for 48 hr. The pentane was evaporated and the acid was recrystallized three times from water and then sublimed under vacuum, yield 0.088 g.; m.p. 121.2–122.2°. Toluene-3,4-d_1, when oxidized to benzoic acid-3,4-d_1 under the same conditions, does not exchange ring-hydrogens.

Deuterium Analysis.—An analysis for atom % D was carried out by the method described previously.[20] In the case of meso-2,3-diphenylbutane-2,3-d_2, the n.m.r. spectra were analyzed by Dr. LeRoy F. Johnson of Varian Associates. It was compared with the spectrum for the natural compound in order to determine the atom % D in the three different functional groups.

Results and Discussion

Azo-bis-α-phenylethane-α,α′-d_2 was synthesized by a route involving catalytic reduction of acetophenone azine. There always exists the possibility of deuterium exchange while the compound is in contact with a hydrogenation catalyst.[21] For this reason, a partial degradation of the azo compound was undertaken. In addition, the deuterium content in the three functional groups of meso-2,3-diphenylbutane-2,3-d_2, the product of azo-bis-α-phenylethane-α,α′-d_2 thermolysis, was determined

(13) All melting points are uncorrected.

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(18) M. S. Kharasch and M. Kleiman, *ibid.*, **65**, 11 (1943).

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by nuclear magnetic reasonance in the laboratory of Varian Associates.[22a] This provides a check on the total deuterium content in addition to the amount of deuterium in the phenyl group. The results of the n.m.r. analysis are shown in Table I.[22b]

The combined deuterium analyses are listed in Table II. As can be seen from the data in Table II, analysis by n.m.r. and by conventional means yield essentially the same data. The advent of precise area integrators in conjunction with n.m.r. spectrometers offers a new and easy method of analyzing for atom % deuterium in different parts of a complicated molecule.

TABLE II

DEUTERIUM ANALYSES

	Atom %D	Atoms D relative to azo compound Total	ϕ_2	$(CH)_2$	$(CH_3)_2$
Azo-bis-α-phenyl-	8.57	1.54			
ethane-α,α′-d_2	8.65	1.56			
Benzoic acid-d	0.07		0.0084		
	0.07		0.0084		
Meso-2,3-diphen-	8.80	1.58			
ylbutane-2,3-d_2[a]	8.72	1.57			
Meso-2,3-diphen- ylbutane-2,3-d_2[b]		1.59	0	1.48	0.11

[a] Obtained from the remaining solutions from kinetic runs. [b] N.m.r. analysis; see Table I.

By n.m.r. analysis and partial degradation, it was found that deuterium was in the desired positions. There was a very small amount of deuterium incorporation in the phenyl group and only 1.8 atom % in the methyl group. Aromatic hydrogen exchange would involve the addition of a deuterium atom to the ring with some loss of aromaticity. Apparently the activation energy is too large for this process to occur. On the other hand, exchange in the methyl group presumably occurs by addition of a deuterium molecule (or atom) to a carbon–nitrogen double bond (in conjugation with a phenyl group), elimination of HD (or a hydrogen atom) forming the terminal olefin and then the addition of D_2 to this double bond. Methyl–hydrogen exchange would therefore be expected to have a lower activation energy and proceed at a faster rate than aromatic hydrogen exchange.

Kinetics.—The kinetics of the thermal decomposition of azo-bis-α-phenylethane in ethylbenzene have already been determined by Cohen, *et al.*,[2] by measuring the rate of nitrogen evolution. In this research, the change in optical density of the azo compound at 359 mμ (—N=N— absorption) was measured as a function of time; the data were programmed and solved for the best fit to the equation $(O.D.)_t = (O.D.)_0\, e^{-kt}$ + const., by the IBM 704 computer. The constant term, amounting from 1–5% of the initial optical density reading, is small and probably due to a trace of acetophenone azine resulting from oxidation of the azo compound. The azine exhibits an extinction coefficient at 359 mμ, ten times that for azo-bis-α-phenylethane. Sample kinetic data are shown plotted in Fig. 1. Here the optical density at $t = \infty$ was subtracted from each

(22) (a) The meso isomer was analyzed because it is a solid and therefore easier to handle on a small scale. The *dl*-mixture is expected to give the same results. (b) The n.m.r. spectra of natural and deuteriated meso-2,3-diphenylbutane may be obtained on request.

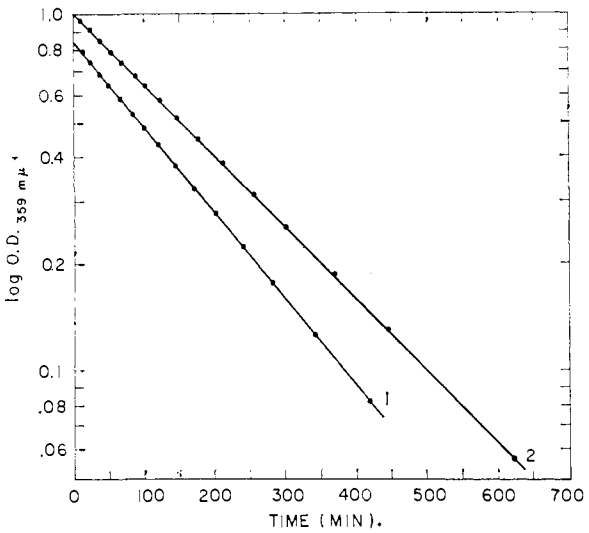


Fig. 1.—Sample first order plot of the decomposition of (1) azo-bis-α-phenylethane and (2) azo-bis-α-phenylethane-α,α′-d_2 in ethylbenzene at 105.3°.

reading before plotting. The correctness of this treatment is proved by the linearity of the line of $\log(O.D.)_t$ *vs.* time and indicates that the impurity (0.1–0.5%, if acetophenone azine) is not changing in concentration during the run. First order rate constants, derived by plotting and those obtained by the more exact electronic computation method,[23] differ by not more than 1%. A summary of the rate data is presented in Table III.

TABLE III

FIRST ORDER RATE CONSTANTS OF THERMAL DECOMPOSITION[a]

Azo-bis-α-phenylethane, $k_1 \times 10^5$ sec.$^{-1}$[b]	Azo-bis-α-phenylethane-α,α′-d_2, $k_1 \times 10^5$ sec.$^{-1}$[b]
9.25 ± 0.07	7.68 ± 0.04
9.00 ± .05	7.54 ± .04
9.01 ± .07	7.64 ± .05
9.02 ± .07	
8.80 ± .02	
Average	
9.01 ± 0.14[b]	7.62 ± 0.06[b]

[a] In ethylbenzene at 105.28 ± 0.05°. [b] Errors given are standard deviations.

The observed isotope effect, where only 0.72 atoms of deuterium are in each α-position is $k_H/k_D = 1.18 \pm 0.02$. The isotope effect for two fully deuteriated α-positions would be 1.27 ± 0.03.[24]

There are now several published cases of secondary α-deuterium isotope effects; a tabulation of most of these is presented in Table IV. The data presented are for reactions which involve a rate

(23) In the case of the graphical treatment the constant term is that from direct measurement at one point. Electronic computation, on the other hand, fits the equation $(O.D.)_t = (O.D.)_0 e^{-kt}$ + const. at every point while minimizing the deviations.

(24) If a = atom fraction of D in the tertiary-hydrogen position and A = the total concentration of all azo molecules at any time, then

$$-dA/dt = k_{2H}(1-a)^2A + k_{H,D}2(1-a)aA + k_{2D}a^2A$$

where k_{2H}, k_{HD} and k_{2D} are the first order decomposition rate constants for the molecules having no, one and two tertiary-deuterium atoms, respectively. Then $k_{obsd.} = (1-a)^2k_{2H} + 2a(1-a)k_{H,D} + a^2k_{2D}$. The equation can then be solved for k_{2D} if it is assumed that $k_{H,D} = 1/2(k_{2H} + k_{2D})$.

TABLE IV

SECONDARY α-DEUTERIUM ISOTOPE EFFECTS IN BOND-BREAKING SYSTEMS

Reaction	k_H/k_D	Atoms D	T, °C.	k_H/k_D, corr.[a]	Ref.
Acetolysis of cyclopentyl-1-*d* tosylate	1.15	1.07	50	1.13	4
Formolysis of 2-phenylethyl-1,1-d_2 tosylate	1.17	1.83	75.3	1.09	5
Solvolysis of 1-*p*-tolylethyl-1-*d* chloride in water–acetone	1.10	1.00	..	1.08	6
Solvolysis of 1-methylheptyl-1-*d* *p*-bromobenzenesulfonate in methanol	1.10	1.00	..	1.09	[b]
Acetolysis of isopropyl-2-*d* *p*-bromobenzenesulfonate	1.12	1.01	70.0	1.11	7
Acetolysis of benzyl-α-*d* tosylate	1.12	1.00	50.0	1.10	7
Acetolysis of benzyl-α-d_2 tosylate	1.25	2.06	50.0	1.10	7
Acetolysis of cyclohexyl-1-*d* tosylate	1.19	1.03	75.4	1.17	7
Acetolysis of cyclodecyl-1-*d* tosylate	1.17	1.05	25.0	1.13	7
Ethanolysis of cyclopropyl-methyl-α-d_2 tosylate	1.42	1.88	20.0	1.15	8
Acetolysis of cyclopropyl-methyl-α-d_2 tosylate	1.34	1.88	20.0	1.13	8
Base catalyzed hydrogen-deuterium exchange of toluene-α-d_3 *vs.* toluene-α-*d* in cyclohexylamine	1.30	2	50	1.12	[c]

[a] The isotope effect is corrected here to 105.3° and for only one deuterium atom at the reaction site by using the equation $(RT/n) \ln (k_H/k_D) = \Delta(\Delta F)$.[6] In cases where more than the theoretical number of atoms of deuterium was present, the theoretical value for n was used. [b] See ref. 2 in ref. 6. [c] A. Streitwieser, Jr., "Abstracts of the 16th National Organic Chemistry Symposium of the American Chemical Society," June 15–17, 1959, Seattle, Wash., p. 74.

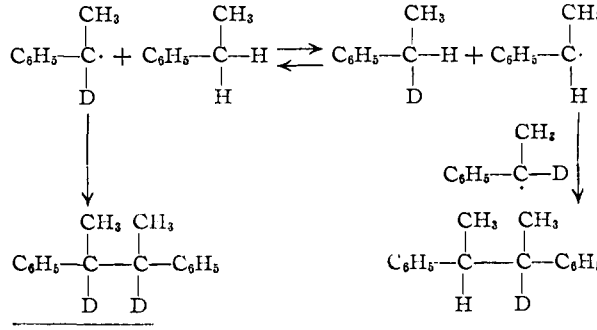
controlling *unimolecular* bond scission. The secondary α-deuterium isotope effects, when corrected for temperature and the number of deuterium atoms, are remarkably constant; the average value being 1.12 at 105°. These data all involve reaction at only one center. If two atoms of deuterium are at the reaction center the effect is about twice as large as can be seen by reactions 6, 7, 10 and 11.

As has been shown previously,[4] the secondary α-deuterium isotope effect can be accounted for by consideration of only the zero point energy differences between the protio- and deuterio-compounds in the ground and transition states. The constancy of this isotope effect, observed in these cases, stems from the similarity in the changes of the α-carbon–hydrogen vibrational frequencies in going from their respective ground states to transition states. This is not surprising. It is known that complex molecules, differing in several respects, exhibit similar vibrational frequencies characteristic of certain functional groups.[25] The carbon–hydrogen group frequencies are sensitive to the degree of unsaturation at that carbon but relatively insensitive to the chemical nature of substitution at that carbon atom. As the distance between the leaving group and the carbon atom increases with concurrent alterations in the α-carbon-hydrogen frequencies, it is expected that these frequencies similarly will be unaffected by the nature of the leaving group or other substituents at that carbon atom. Because of these similarities, systems which undergo reaction where a bond is broken in a unimolecular-rate controlling process generally should exhibit a secondary α-deuterium isotope effect with a magnitude in the range of those listed in Table IV.

The thermal decomposition of azo-bis-α-phenylethane involves two centers of reaction if both carbon–nitrogen bonds break simultaneously. If only one bond breaks in the slow step and the second bond breaks in a faster succeeding step, the deuterium atom at the other reaction site will not be expected to contribute to a decrease in the rate of reaction. Therefore an isotope effect of 1.12 at 105° is expected if azo-bis-α-phenylethane-α,α'-d_2 decomposes along a stepwise path. However, if both bonds break simultaneously the value of 1.24 is expected at this temperature. The isotope effect, $k_H/k_D = 1.27$, after normalization for two atoms of deuterium, corresponds to a transition state where both carbon–nitrogen bonds are undergoing simultaneous cleavage.

There is one question that arises when comparing the magnitude of isotope effects and that is the nature of the species involved in the transition state. In the thermolysis of azo-bis-α-phenylethane radicals are being formed, while in the solvolysis charges are developing. The evidence that the methyl radical is planar[26] (most probably having sp^2-hybridization) and the relative difficulty of forming the tertiary-bridgehead-radical of bicyclo [2.2.1]hepta-2,5-diene,[27] strongly suggests that the α-phenylethyl radical has approached planarity in the transition state. Furthermore calculations, accounting for the magnitude of secondary α-deuterium isotope effects, involve the use of carbon–hydrogen vibrational frequencies of neutral molecules with no corrections for charges or solvation effects. It would therefore be expected that radicals would fit better the models used for calculation. The effect of charge-development is considered to be a second order effect.[28]

The Identity Reaction.—The solid product, meso-2,3-diphenylbutane-2,3,-d_2, from the thermal



(25) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, 1958, p. 13.

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(27) A. Rajbenbach and M. Szwarc, *Proc. Chem. Soc.*, 347 (1958).

(28) M. Wolfsberg, private communication.

decomposition of the azo compound in ethylbenzene was analyzed for deuterium. As shown in Table II, the atom % D in the product is the same, within 1.5%, as that in the starting material. From these results it can be concluded that the hydrogen abstraction reaction by a benzylic radical to produce the same benzylic radical does not occur to any measurable extent.

Similar observations have been made on other benzylic systems.[29,30]

Acknowledgments.—I would like to express my thanks to Mrs. Mary Kresge for programming the kinetic data, to Dr. D. R. Christman for deuterium analysis to Dr. Aharon Lowenstein for preliminary n.m.r. determinations and to Dr. Max Wolfsberg for helpful discussions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK]

The Photolysis and Fluorescence of Diethyl Ketone and Diethyl Ketone–Biacetyl Mixtures at 3130 and 2537 Å.[1]

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The photolysis of diethyl ketone and the photolysis and phosphorescence of diethyl ketone–biacetyl mixtures have been studied at 3130 and 2537 Å. The addition of biacetyl at 3130 Å. decreases the photodecomposition of diethyl ketone and increases the phosphorescence of biacetyl. An energy transfer from excited triplet diethyl ketone to biacetyl is proposed and there is evidence that the propionyl radical formed from the singlet state at 3130 Å. is sufficiently "hot" to dissociate into an ethyl radical and carbon monoxide. At 2537 Å. dissociation appears to occur from the initially formed upper singlet state, and there is no evidence that the triplet state intervenes. A detailed mechanism is presented for the primary process in diethyl ketone and for the energy transfer between diethyl ketone and biacetyl.

Introduction

The vapor phase photodecomposition of diethyl ketone at 3130 Å. has been studied[3–12] extensively and a comprehensive review of the primary process in simple ketones published.[13]

The light emission from excited diethyl ketone has not been so well studied although Matheson and Zabor[14] have recorded an emission from 4360 to 5460 Å. with a maximum around 5200 Å. Since the emission is similar to that observed with propionaldehyde, they have ascribed it to the diketone, bipropionyl, formed during radiation. This effect is similar to that observed in acetone where the green emission is due to biacetyl.

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This paper presents the results obtained from an investigation of the primary process involved in the photodecomposition of diethyl ketone and of diethyl ketone–biacetyl mixtures and the energy interchange between excited diethyl ketone and biacetyl.

Experimental

Eastman Kodak diethyl ketone was used. The ketone was distilled under dry nitrogen through about thirty theoretical plates and a middle fraction, constant boiling at 102.7°, retained and stored over anhydrous copper sulfate. The fraction was thoroughly degassed at Dry-Ice temperature in a vacuum line and the middle fraction retained from a bulb-to-bulb distillation. No impurities could be detected in the mass spectrum and vapor phase chromatogram. Eastman white-label biacetyl was dried over Drierite, degassed and fractionated in a bulb-to-bulb distillation. A vapor phase chromatogram gave impurities of less than 1%. Spectro Grade Eastman acetone was dried over Drierite, degassed and distilled in a grease-free vacuum system. No impurities could be detected.

For 3130 Å. radiation, an Osram HBO Super Pressure mercury lamp operating at 76 volts direct current and 6.2 amps was used. A Hanovia S-100 Alpine Burner was used for wave lengths in the region of 2537 Å. The light was collimated and stray radiation prevented from entering the cell by a series of screens. For 3130 Å. the filter arrangement described by Kasha[15] was used, supplemented by a Pyrex plate and a Corning 9700 filter. A filter combination of chlorine, cobalt sulfate-nickel sulfate solution and a Corning 9863 filter was used to give radiation of approximately 2537 Å. The quantum yields for diethyl ketone photolysis were corrected for biacetyl absorption and decomposition.

A T-shaped quartz reaction cell was used for photolysis and light emission measurements. The cell was 125 mm. long with a main window diameter of 38 mm. and a fluorescence window diameter of 23 mm.

Transmitted intensities of the exciting radiation were measured on an R.C.A. 935 phototube connected to a Varian G. 10 Graphic Recorder. Quantum yields were calculated against the CO yield from diethyl ketone at 105° for 3130

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