α SECONDARY DEUTERIUM ISOTOPE EFFECTS IN RADICAL REACTIONS

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EFFECTS IN RADICAL REACTIONS

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To my mother and father who have sacrificed so much for me.

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CHAPTER I

INTRODUCTION

The rate of S_N1 solvolysis of cyclopentyl tosylate is reduced by about 15% at 60° when an α hydrogen is replaced by an α deuterium[1]. This α secondary deuterium isotope effect was mainly attributed to a large decrease in one of the carbon-hydrogen bending frequencies in passing from the reactant to the transition state. The sp^3 reactant carbon-hydrogen bond frequencies are ca. 2890 cm^{-1} (stretching motion) and 1340 cm^{-1} (an approximately doubly degenerate bending motion). In the transition state the hybridization of the α carbon is intermediate between sp^3 and sp^2. The aldehydic hydrogen of acetaldehyde was chosen as a model for the carbon-hydrogen bond in the transition state[1]. This bond has a stretching frequency of 2800 cm^{-1}, an in-plane bending frequency of 1340 cm^{-1} and an out-of-plane bending frequency of 800 cm^{-1}. The magnitude of the isotope effect for complete change from tetrahedral to trigonal coordination is calculated to be ca. 1.38 using Eq. 1[1], which is an approximate form of the Bigeleisen equation[2] in which

$$\nu_{H,i}/\nu_{D,i} = \nu_{H,i}^{\neq}/\nu_{D,i}^{\neq} = 1.35.$$

$$k_H/k_D \cong \pi_i \exp\left[(0.187/T)(\nu_{H,i} - \nu_{H,i}^{\neq})\right] \qquad (1)$$

The lower observed value of the isotope effect probably results from incomplete rupture of the bond between the α carbon and the leaving

group in the transition state. Consequently, the maximum decrease in the frequency of the out-of-plane bending mode is not realized. A decrease of ca. 300 cm^{-1} would be consistent with the observed isotope effect. The decrease in the carbon-hydrogen leaving group bending force constants has been shown to account for the frequency decrease[3]. Exact calculations suggest that the difference in the loss of zero point energies between the protio and deutero compounds upon passing from the reactant to the transition state is the principal cause of the α effect[3]. This has been confirmed by the observed temperature dependence of the α effect in the thiocyanate-catalyzed isomerization of maleic acid[4] and the formation of methyl radicals from the thermal decompositon of tert-cumyl hypochlorite[5].

There has been interest for some time in the mechanism of thermal decomposition of azo compounds of the general formula R_1-N = N-R_2. Cohen and Wang[6] and Overberger and DiGiulio[7] have discussed in detail the question of whether carbon-nitrogen scission is simultaneous or stepwise: Eq. 2 and 3 and 4 respectively.

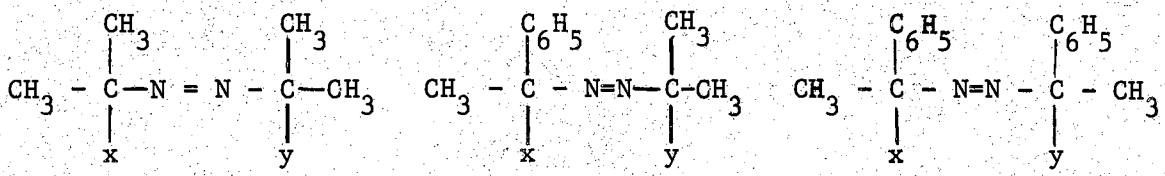
$$R_1 - N = N - R_2 \rightarrow R_1 + R_2\cdot + N_2 \qquad (2)$$

or

$$R_1 - N = N - R_2 \xrightarrow{\text{slow}} R_1 - N = N\cdot + R_2\cdot \qquad (3)$$

$$R - N = N\cdot \xrightarrow{\text{fast}} R_1\cdot + N_2 \qquad (4)$$

The activation energies, Ea, and the rates of decomposition of azoisopropane (I), 1-(isopropylazo)-1-phenylethane (II) and 1,1'-diphenylazoethane (III) are listed in Table I. The data in Table I shows



I x = y = H

II x = y = H
IIa x = D, y = H
IIb x = H, y = D

III x = y = H
IIIa x = y = D

that Ea is decreased about 4 kcal/mole for each phenyl group substituted for methyl in this series and that the ratio of the rates for compounds II and III is greater than the statistical factor of two. Consequently, it was argued that both carbon-nitrogen bonds of III break simultaneously [6,7]. The rate increase is due to aid from the phenyl groups in the delocalization of the incipient odd electron in the transition state.

TABLE I

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR COMPOUNDS I, II AND III

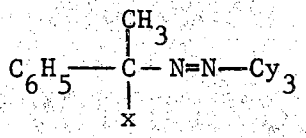
Compound	Ea(kcal/mole)[a]	k x 10^4 sec^{-1}[a,c]	$\Delta S^{\neq}$[a] (eu.)
I	40.9 (51.9)[b]	.00001	1
II	36.5	.132	9.3
III	32.6	4.85	7

a - Values from Ref. 7 except as otherwise noted
b - See Ref. 19
c - @ 120°

The "simultaneous" mechanism was confirmed by comparison of the pyrolysis rate of III with IIIa[8]. In unimolecular reactions proceeding via a "classical" transition state, a normal isotope effect is 1.12 - 1.15 for

each α-D[8]. Consequently, if III undergoes simultaneous rupture of both carbon-nitrogen bonds an α effect (k_{III}/k_{IIIa}) of ca. 1.27(1.12 - 1.15)[2] would be predicted. If the mechanism of decomposition were stepwise an isotope effect of 1.12 would be expected[9]. The observed value of 1.27 confirms the "simultaneous" mechanism.

The magnitude of the α effect is affected by the degree of bond rupture in the transition state for pyrolysis of unsymmetrical azo compounds. Deuterium isotope effects in the decomposition of II (IIa and IIb) and 1-(methylazo)-1-phenylethane IV (IVa and IVb) are presented in Table II[10].



IV x = y = H

IVa x = D, y = H

IVb x = H, y = D

TABLE II

PRIMARY AND SECONDARY ISOTOPE EFFECTS AND ACTIVATION PARAMETERS FOR COMPOUNDS II, IIa, IIb, III, IIIa, IV, IVa AND IVb

Compound	k_H/k_D	k_{14}/k_{15}[a]	Ea(kcal/mole)	$\Delta S^{\neq}$(eu.)
III/IIIa	1.27	1.0229	32.6	7
II/IIa	1.15	1.0152[b]	36.5	9.3
II/IIb	1.04	—	—	—
IV/IVa	1.15	1.0132[c]	—	—
IV/IVb	0.97	—	—	—

a) Refers only to unlabelled compound. b) Average (benzylic and isopropyl). c) Ref. 10.

The isotope effects II/IIa, 1.15 and II/IIb, 1.04, indicate that in the transition state both carbon-nitrogen bonds break simultaneously but that the α-phenylethyl carbon-nitrogen bond is stretched considerably more than the isopropyl carbon-nitrogen bond. The α effects, IV/IVa, 1.15 and IV/IVb, 0.97, show that IV decomposes in two discrete steps. Consistent with the fact that the methyl radical is 25 kcal/mole less stable than the α-phenylethyl radical[11], the slow step is rupture of the benzylic carbon-nitrogen bond in IV followed by scission of the methyl carbon in a fast second step. The inverse deuterium isotope effect observed for the decomposition of IVb together with the very small methyl ^{13}C isotope effect of 1.0068[10] in the decomposition of IV suggests that the methylazo carbon-nitrogen bond tightens a small amount during the stretching of the benzylic carbon-nitrogen bond[10]. Rationalization for the behavior of II can be found in the relative stabilities of the incipient radicals, the isopropyl radical being more stable than the methyl radical but less stable than the α-phenylethyl radical. Primary nitrogen isotope effects were obtained for the decomposition of II, III and IV (Table II). It was possible to obtain a set of consistent transition state force constants to account for both the α effects and the primary nitrogen isotope effects[10].

The magnitude of the α isotope effect reasonably reflects the extent of decrease in the α carbon-hydrogen bending force constants and, hence, the extent to which bond breaking has occurred in the transition state. The sooner the transition state of a reaction occurs along the reaction coordinate the more "reactant-like" it appears[12]. Since the degree of bond rupture will be small, the decrease in the α-carbon-hydrogen force constants will be small and, hence, a small isotope

effect is expected. Conversely, the further along the reaction coordinate the transition state occurs, the greater the degree of bond breakage and the less "reactant-like" the transition state. This results in a larger decrease in the force constants and one therefore expects a larger isotope effect. The magnitude of the isotope effect therefore provides a means of measuring the progression of the transition state along the reaction coordinate.

The α isotope effects in the decomposition of meso- and d,l-1,1',2,2'-tetraphenylazoethane, V, are 1.224 and 1.202 respectively[13]. These values for the isotope effect correspond to a 5 and 7% reduction in the α effect of V as compared to III. Three possible interpretations for the observed results were considered: a) substitution of phenyl for hydrogen markedly affects the force constants of the α benzylic hydrogens, b) steric interference is present between the ends of V, and c) the β-phenyl group participates in the rupture of the α carbon-nitrogen bond. It has been shown that substitution does not alter force constant values in alkanes[14] and since the rates of decomposition of III and V are very similar, steric acceleration did not appear to be entirely responsible for the large decrease in the isotope effect. Consideration of all the data suggested neighboring group participation to be the better explanation. The isotope effect may, therefore, be a more sensitive means of detecting neighboring group participation in compounds which are structurally related than comparison of rate constants.

The question now arises as to whether for a given reaction the α effect responds to movement of the transition state along the reaction coordinate resulting from changes in substitution. A related question is whether substituents move the transition state along the reaction

coordinate. If the former is valid, a correlation may exist between the magnitude of the isotope effect and the inductive, resonance, steric and neighboring group effect of the substituents. We have examined a system in which only steric and inductive and/or resonance effects were operative. It has been shown[15-17] that the rates of α-alkyl-substituted azo nitriles, 1,1'-(4,4'-disubstituted)-diarylazoethanes and 1,1'-(3,3' and 4,4'-disubstituted)-azocumenes are influenced by steric, resonance and inductive factors.

In order to study the inductive effects of substituents on the isotope effect we studied a series of 1,1'-(3,3' and 4,4'-disubstituted)-diphenylazoethanes. 1,1'-Diphenylazopentane and 3,3'-dimethyl-1,1'-diphenylazobutane were chosen for study of the steric influence on the α effect.

CHAPTER II

RESULTS AND DISCUSSION

Kinetics

The kinetics of the thermal decomposition of the protium-containing compounds in this study, excepting for 1,1'-bis(3-methylphenyl)azoethane and 1,1'-diphenylazopentane, have already been determined by measuring the rate of nitrogen evolution[15]. In this study the decrease in the optical density due to the azo chromopnore at λ_{max} was measured as a function of time. A plot of log O.D. vs. time was made and the rate constant estimated from the slope of the straight portion of the plot. The data were programmed and solved for the best fit to the following equation using the method of

$$y = A + Be^{-kt}$$

nonlinear least squares by an I.B.M. 360/50 computer. The values of A, B and k were estimated from the plot of log O.D. vs. time. No residual absorptions were observed at the end of each kinetic run indicating that a) complete decomposition had occurred and b) the products of decomposition did not absorb in the area of λ_{max}.

Like Cohen and coworkers[15] (Table III), we observed an increase in the rates of decomposition when the parent compound, 1,1'-diphenylazoethane, was substituted with electron-donating groups in the meta and

para positions. Table IV lists the rate constants and activation parameters obtained. The isotope effect was obtained by measuring the rates

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS OBTAINED BY COHEN[15]

$[x-C_6H_4-\underset{R}{\underset{\vert}{C}}H-N=]_2$		k x 10^{-2} min^{-1} t=100.4°	k x 10^{-2} min^{-1} t=110.3°	Ea (kcal/mole)
x =	R =			
p-H	CH_3	.327	1.014	32.6 ± 0.5
p-H	CH_3CH_2	.141	.432	32.3 ± 2.8
p-CH_3	CH_3	.354	1.110	32.9 ± 1.8
p-H	$(CH_3)_2CHCH_2$	.456	1.452	33.3 ± 1.0
p-CH_3O	CH_3	.429	1.488	35.8 ± 1.0

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS OBTAINED FOR PROTIATED SPECIES IN PRESENT STUDY

$[x-C_6H_4-\underset{R}{\underset{\vert}{C}}H-N=]_2$		Temp., °C	Average k x 10^{-3} min^{-1}	Ea (kcal/mole)	$\Delta S^{\neq}$ (e.u.)
x=	R=				
p-H	CH_3	112.91 ± .03	1.280 ± .012	32.60[a] 32.87[b]	6.615[a] 7.334[b]
p-CH_3	CH_3	112.91 ± .03	1.465 ± .040	32.86[a] 32.48[b]	7.6289[a] 4.877[b]
m-CH_3	CH_3	112.91 ± .03	1.287 ± .013	32.69[b]	6.906[b]

TABLE IV (Continued)

$[x-C_6H_4-\underset{R}{\underset{\vert}{CH}}-N=]_2$		Temp., °C	Average k x 10^3 min^{-1}	Ea (kcal/mole)	$\Delta S^{\neq}$ (e.u.)
m-CH_3	CH_3	93.43 ± .03	.1336 ± .003		
p-OCH_3	CH_3	112.91 ± .03	1.756 ± .018	35.76[a] 36.88[b]	15.7785[a] 18.360[b]
p-H	$CH_3CH_2CH_2CH_2$	113.21 ± .08	1.153 ± .003	32.24[b]	5.463[b]
p-H	$CH_3CH_2CH_2CH_2$	93.02 ± .03	.1135 ± .013		
p-H	$(CH_3)_2CHCH_2$	113.32 ± .03	2.070 ± .030	33.3[b]	9.327[b]

a) Calculated using data from Table III.

b) Calculated using data from Table IV and V.

of decomposition of the protium- and deuterium-containing azo compounds simultaneously. The results are presented in Table V.

TABLE V

RATE CONSTANTS FOR PROTIUM- AND DEUTERIUM-CONTAINING COMPOUNDS AND OBSERVED ISOTOPE EFFECTS

$[x-C_6H_4-\underset{R}{\overset{CH_3}{\vert}}-N=]_2$		Temp., °C	Average k x 10^3 min^{-1}	Relative Rates	Observed k_H/k_D
x=	R=				
p-H	H	105.35	5.447 ± .06	1.00	
p-H	D	105.35	4.713 ± .04		1.155 ± .005
p-CH_3	H	105.13	6.146 ± .004	1.13	
p-CH_3	D	105.13	5.577 ± .033		1.095 ± .0097

TABLE V (Continued)

$[x-C_6H_4-\overset{CH_3}{\underset{R}{C}}-N=]_2$		Temp., °C	Average k x 10^3 min^{-1}	Relative Rates	Observed k_H/k_D
m-CH_3	H	105.35	5.442 ± .010	1.00	
m-CH_3	D	105.35	4.937 ± .014		1.102 ± .009
p-OCH_3	H	105.13	7.372 ± .014	1.35	
p-OCH_3	D	105.13	6.2248 ± .087		1.184 ± .016

It is clear from the data presented in Tables III, IV and V that the presence of para-methoxyl and para-methyl groups increases the rate of decomposition. Table V shows the rate increase to be 35% and 13% at 105.35° and 105.13°, respectively, while the presence of a meta-methyl group produces a negligible effect on the rate. The effects of these groups on the rate of reaction are probably due to their electron-releasing properties, which may stabilize the incipient radical. The suggestion that electron release is operative in the case of para-methoxyl is tantamount to invoking p orbital expansion on oxygen, i.e., that oxygen can accommodate the incipient odd electron in one of its anti-bonding orbitals[23]. The 33% increase in the reaction rate caused by substitution of a pair of α methyl groups by a pair of isobutyl groups is probably steric in origin[15] (Table III), but the reason for the 10% reduction in reaction rate observed by substitution of n-butyl groups (Table IV) for a pair of α methyl groups is not clear. Interestingly, a 56%[16] and a 23%[18] decrease in reaction rate was observed when a pair of α methyl groups were substituted by a pair of ethyl and n-propyl

groups respectively; thus, as expected, the steric factors[15-17] become increasingly important as the α n-alkyl chain length is increased.

Calculations based on Cohen's rate measurements (Table III) were made using the temperatures at which our rate data was determined, in order to obtain the value of the rate constants Cohen would predict at our temperatures; Tables IV and V are compared in Table VI. It is seen that excepting for 1,1'-bis(4-methoxyphenyl)azoethane generally good agreement is obtained.

TABLE VI

COMPARISON OF PREDICTED RATE CONSTANTS WITH VALUES OBTAINED

$[x—C_6H_4—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—N=]_2$, x=	Calculated $k \times 10^3$ min^{-1}	Experimental $k \times 10^3$ min^{-1}	Temp., °C	% Diff.
p-H	5.406[a]	5.447 ± .016	105.28	0.8
p-OCH_3	7.908	7.372 ± .044	105.15	7.3
p-CH_3	6.171	6.146 ± .004	105.20	0.4
p-H	1.255	1.280 ± .012	112.91	1.95
p-OCH_3	2.044	1.756 ± .018	112.91	15.3
p-CH_3	1.486	1.466 ± .040	112.91	1.3

a) Value obtained by Seltzer, Ref. 8.

b) @ 105.34°

In the decomposition of 1,1'-bis(4-methoxyphenyl)azoethane an induction period of about 40-50 min. was observed. Plots on semilogarithmic graph paper of the $OD_t - OD_\infty$ as a function of time show a

pronounced curvature up to 50 min. after which a straight line is obtained. This induction period has been attributed to gas shrinkage caused by reaction of the radicals with traces of oxygen[15]. Our method of following the decrease in the optical density of the azo chromophore in degassed, sealed u.v. cells excludes any such effect of gas shrinkage. Furthermore, this short induction period was observed in many of the reactions[15] while we observed it only in the case of 1,1'-bis(4-methoxyphenyl)azoethane. Measurements of thermally induced decompositions regardless of method are always erratic for the first part of the reaction owing to the necessity that the reaction mixture attain thermal equilibrium. Consistent data was obtained for the first 20-25 min. in each of the reactions studied excepting for that of 1,1'-bis(4-methoxyphenyl)azoethane. While the reason for this behavior is not obvious it may account for the large deviation encountered in the comparison of our experimentally determined rate constants at 105.15° and 112.91° to the values extrapolated from Cohen's data.

Since the energies of activation for each of the compounds studied are within 2 kcal/mole of each other, no variation in the mechanism of decomposition is indicated.

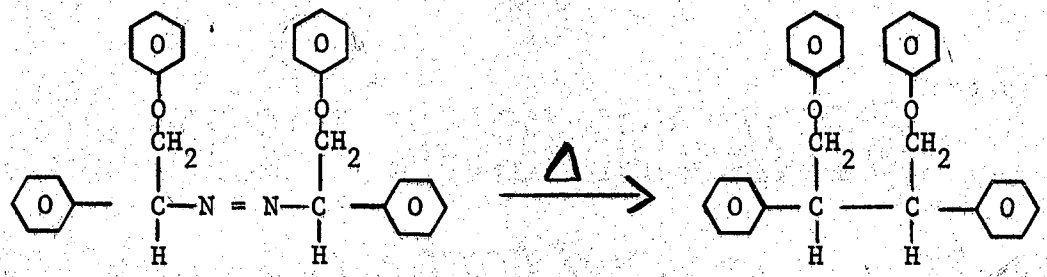
1,1'-Diphenylazomethane

1,1'-Diphenylazomethane was exceedingly difficult to purify and could only be obtained in pure form by sublimation. The compound was found to be quite unstable at room temperature; crystals placed on a watch glass turned to an oil in less than 1 hour. Even at 0° the compound decomposed relatively rapidly and was visibly contaminated with yellow material within 36 hours. The decomposition product had the odor

of benzaldehyde, suggesting that the decomposition of 1,1'-diphenylazomethane proceeds via air oxidation. Further work on this compound was therefore discontinued.

1,1'-Diphenyl-2,2'-diphenoxyazoethane

The thermal decomposition of 1,1'-diphenyl-2,2'-diphenoxyazoethane (VI) at 120° produced a white solid and a yellow oil. The mass spectrum of the solid showed an ion at m/e = 394, corresponding to the molecular weight of 1,1'-diphenyl-2,2'-diphenoxyethane (VII), which results from the dimerization of the radicals formed on decomposition of the azo compound.

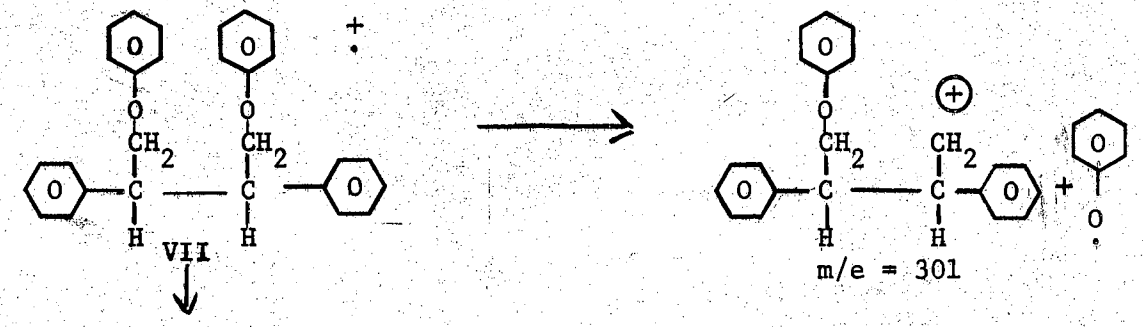


(VI) (VII) m/e = 394

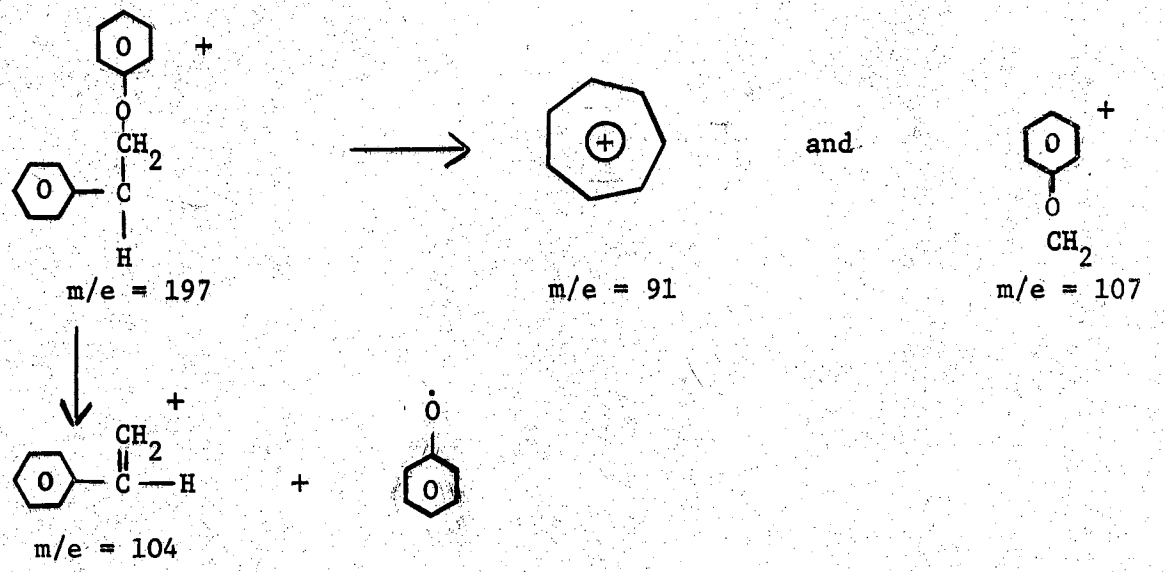
Other major peaks in the spectrum were at m/e = 301, m/e = 197, m/e = 104, m/e = 107 and m/e = 91 and are attributed to the postulated fragmentations presented in Scheme I.

SCHEME I

POSTULATED MASS SPECTRUM FRAGMENTATION



m/e = 301



The complex mass spectrum of the oil indicates it to be a mixture of several compounds, probably formed via a rearrangement rather than dimerization, and no further attempt at identification was made. The possibility exists that the rearrangements which produced the yellow oil ruptured the α carbon-hydrogen bond and, hence, produced a primary isotope effect. Since it would be impossible to separate the total isotope effect into the primary and secondary effects with any degree of accuracy further work on this compound was discontinued.

Thermocouple Calibrations

It was observed that a plot of the voltage (EMF) of the NBS-calibrated thermocouple vs. EMF of the measuring thermocouple did not follow a linear relationship over the temperature range of 80° - 125°. However, a linear relationship was followed over two smaller and overlapping temperature ranges, 80° - 110° and 99° - 125°. The EMF's for each of these narrower temperature ranges were plotted separately. A linear least squares fit for each plot showed deviations from the slope

to be within the experimental error associated with reading the potentiometer, i.e., 1 μ volt. The EMF's corresponding to the temperature at which the isotope effect runs were made were corrected using each of the plots covering the smaller temperature ranges. The difference in the EMF's corrected by the lower temperature plot (80^{o} - 110^{o}) and the higher temperature plot (99^{o} - 125^{o}) was within the temperature fluctuations of the bath, i.e., 0.03^{o}.

The isotope effects presented (Table V) are observed isotope effects only, and as such, have not been corrected for 100% deuterium in the α position. Owing to difficulties experienced over the past several months with instrumentation, it has not been possible to determine the percentage of α deuterium present in the compounds synthesized. Until such time as the amount of α deuterium can be ascertained, no corrected isotope effects can be calculated and, hence, no conclusions can be drawn.

CHAPTER III

EXPERIMENTAL

Preparation of Acetophenone Azine

Sixty grams (0.5 mole) of acetophenone and 8.4g of hydrazine (95%) dissolved in 100 ml. of absolute ethanol containing 10 drops of glacial acetic acid were refluxed for several hours. The reaction mixture was allowed to cool and the crude product collected on a Buchner funnel. The azine was triturated three times with saturated sodium bicarbonate solution and three times with distilled water to remove any traces of acid. Repeated recrystallizations from warm ethanol followed by drying in a vacuum desiccator yielded 49.5g (82.5%) of the azine, m.p. 120.5 - 121.5° (lit. 124°)[15].

Preparation of 1,1'-Diphenylazoethane

Five percent palladium on charcoal, 2.5g, suspended in 225 ml. of benzene was equilibrated with hydrogen gas, and 12g of added acetophenone azine was reduced at room temperature and atmospheric pressure. Seven to eight hours were required for the uptake of 2 moles of hydrogen gas. The reaction mixture was filtered through a fine grade sintered glass funnel under reduced pressure. The resulting colorless solution was transferred to a 500-ml. florence flask and oxidized, with continuous stirring, by addition of yellow mercuric oxide in 10-g portions until no change in the added mercuric oxide was observed. The suspension was

filtered through several layers of #1 filter paper and the benzene evaporated under reduced pressure. The crude azo compound was purified by repeated recrystallizations from methanol; m.p. 71.5 - 72.5° (lit. 72 - 73°)[15], yield 2.5g (20.8%); ε(benzene) 45.76, $\lambda_{max.}$ 359 mμ.

Preparation of 1,1'-Diphenylazoethane-1,1'-d_2

Five percent palladium on charcoal, 5.0g, was suspended in 200 ml. of purified benzene which had been distilled from sodium metal under an argon atmosphere directly into the hydrogenation flask. The Pd/C was equilibrated with gaseous deuterium and 30g of acetophenone azine converted to 4g of 1,1'-diphenylazoethane-1,1'-d_2 by the procedure used for 1,1'-diphenylazoethane. m.p. 71.3 - 72.3° (lit. 71.8 - 72.7°)[8], yield (13.3%); ε(benzene) 46.22, $\lambda_{max.}$ 359 mμ.

Preparation of 1,1'-Diphenylazomethane

Ten grams of benzaldehyde azine was converted to 1,1'-diphenylazomethane using the above procedure. Purification of the crude azo compound was attempted by multiple recrystallizations from absolute methanol, absolute ethanol, hexane, n-heptane, pentane and cyclohexane without success. Purification of 1.5g of the crude azo compound was then attempted by means of column chromatography on (60-200) mesh neutral silica gel (30 x 2 inches). The column was developed with solvent mixtures ranging from 10% petroleum ether - 90% benzene to 50% petroleum ether - 50% benzene. However, the 1,1'-diphenylazomethane appeared to rearrange to benzaldehyde phenylhydrazone on the column and this method of purification was abandoned. Purification was finally achieved by sublimation

at 50° and 3-4 mm. pressure: m.p. 31.5° (lit. 27 - 29°)[22]; ε(benzene) 59.87, $\lambda_{max.}$ 356 mμ.

Preparation of α-Phenoxyacetophenone

α-Phenoxyacetophenone was prepared by the method of Davies and Middleton[20]. Phenol (18.8g, 0.2 mole), phenacyl bromide, (39.8g, 0.2 mole) and anhydrous potassium carbonate (27.6g) were refluxed in 100 ml. of acetone with stirring for 4 hours, then poured into water and cooled. The resultant solid was purified by repeated recrystallizations from ethanol. Yield 25g (61.77%), m.p. 72 - 73°.[21]

Preparation of α-Phenoxyacetophenone Azine

α-Phenoxyacetophenone (15g., 0.07 mole) and 1.18g (0.037 mole) of hydrazine (95%) were combined by the procedure described for acetophenone azine. The crude product was recrystallized from absolute ethanol-benzene: m.p. 165 - 166°.

Preparation of 1,1'-Diphenyl-2,2'-diphenoxyazoethane

The α-phenoxyacetophenone azine (4.2g) was converted to azo compound by the procedure used for 1,1'-diphenylazoethane. The meso- and d,l-isomers were separated by fractional recrystallization from methanol. The higher-melting isomer was the less soluble of the two. Both forms were purified by repeated recrystallizations from methanol: meso- m.p. 105 - 106°, ε (benzene) 44.5, λ_{max} 361 and d,l - m.p. 82.5 - 83.5°, ε (benzene) 48.24, λ_{max} 361 mμ.

Decomposition of 1,1'-Diphenyl-2,2'-diphenoxyazoethane

1,1'-Diphenyl-2,2'-diphenoxyazoethane (0.8g) was dissolved in 50 ml. of ethylbenzene and transferred to a 100-ml. round bottom flask. The flask and its contents were degassed by the freeze-thaw technique (see p. 21), sealed, and immersed in a bath at 120°C for 30 hours. This resulted in the production of a yellow colored solution. Since the colored decomposition products could not be identified work on this compound was discontinued.

Purification of Benzene

Reagent-grade benzene was repeatedly shaken in a separatory funnel with concentrated sulfuric acid until the acid layer was colorless. The benzene was then extracted with a) distilled water until the washings were neutral, b) a saturated solution of sodium bicarbonate and distilled water repeatedly until the washings were neutral. The benzene was then dried over magnesium sulfate, filtered, and distilled from sodium metal through an 18-inch Vigreux column.

Determination of Extinction Coefficients

Enough azo compound to produce a solution of optical density ca. 1.00 was weighed into a clean dry 10-ml. volumetric flask. Reagent-grade benzene was added to the mark and an aliquot portion transferred by means of a disposable Pasteur pipet into one of a pair of matched u.v. cells. The spectrum was taken on a Carey 14 recording spectrophotometer. Extinction coefficients and λ_{max} for the protium- and deuterium- containing azo compounds are tabulated in Tables X and XI respectively.

Ethylbenzene

Reagent-grade ethylbenzene was passed through a column (24 x 2.5 inches) containing basic (3 inches), neutral (18 inches), and basic (3 inches) alumina and then distilled from sodium at atmospheric pressure through a silvered vacuum-jacketed column (30 x .5 inches). Only the middle fraction having a 0.4° b.p. range, was collected. A sample of this fraction analyzed by gas chromatography revealed traces of compounds tentatively identified as xylenes.

Kinetic Procedure

Preparation of Solutions for Kinetic Study

The requisite amount of azo compound, calculated from the extinction coefficients in Table VII and VIII, was analytically weighed into a clean dry vial and dissolved in 3 ml. of ethylbenzene. The solution was transferred to a fused quartz u.v. cell fitted with a quartz tube bearing a 10/30 outer joint to a vacuum line for degassing. The cell was immersed in a Dewar flask containing a slurry of finely crushed dry ice suspended in equal volumes of carbon tetrachloride and chloroform. Degassing was accomplished by exposing the cooled cell and its contents to vacuum ($< 1\ \mu$) until the pressure was essentially that of ethylbenzene. With the contents of the cell cut off from the vacuum, and the Dewar flask lowered, the cell was warmed to room temperature with the aid of a hairdryer. The cell was again immersed in the slurry for cooling and degassing. This freeze-thaw procedure was continued until the initial pressure in the system was that of ethylbenzene. The cell was sealed under vacuum by heating the quartz tube below the joint until

it collapsed.

Decomposition Rate Measurements

The sealed u.v. cells were placed in a Beckman D.U. quartz spectrophotometer modified by enclosing the cell compartment in a temperature bath. Time zero was taken to be the placement of the cells in the cell compartment. The rates of the α-protiated and -deuterated azo compounds were simultaneously measured by following the disappearance of the azo chromophore in the u.v. at the maximum absorptions listed in Tables VII and VIII. An average of 80 to 100 points were taken for each run at time intervals corresponding to ca. 0.01 optical density change. The temperature of the cell compartment was taken before and after each run using a copper-constantan thermocouple and a Honeywell model 2745 potentiometer.

Thermocouple Calibrations

The thermocouple was calibrated against an NBS-calibrated thermocouple over the temperature range of the kinetic experiments using a modified Cottrell pump[24]. Solvents, thermocouple readings and corrected thermocouple readings are listed in Table XII. The slopes, intercepts, and associated standard deviations obtained from linear least-square fits of the EMF of the NBS-calibrated thermocouple (y axis) vs. EMF of the measuring thermocouple (x axis) are listed in Table XII.

TABLE VII

PHYSICAL CONSTANTS OF PROTIATED AZO COMPOUNDS[a]

No.	[x–C$_6$H$_4$–CH(R)–N=] x=	R=	m.p., °C	m.p., °C (Lit.)[b]	% Yield	ε	λ_{max} (mμ)
1	p-H	CH_3	71.7-72.5	72-73	20.8	45.76	359
2	p-CH_3	CH_3	77.0-77.5	78-79	21.3	51.50	357
3	m-CH_3	CH_3	36.5-37.5	-----	20.0	49.13	357
4	p-OCH_3	CH_3	91.5-92	91-92	21.3	62.44	357
5	p-H	$CH_3CH_2CH_2CH_2$	48.5-49	-----	7.3	44.79	360
6	p-H	$(CH_3)_2CHCH_2$	83-84	83-84	6.3	48.30	358

a) Recrystallized from abs. methanol

b) Ref. 15

TABLE VIII

PHYSICAL CONSTANTS OF DEUTERATED AZO COMPOUNDS[a]

No.	$[x-C_6H_4-\overset{R}{\underset{D}{C}}-N=]_2$ x=	R=	m.p., °C	% Yield	ε	λ_{max}
1	p-H	CH_3	71.3-72.3	13.3	46.22	359
2	p-CH_3	CH_3	76.7-77.3	16.6	52.21	357
3	m-CH_3	CH_3	36.3-37	10.0	49.71	357
4	p-OCH_3	CH_3	90.7-91.2	16.6	63.60	357
5	p-H	$CH_3CH_2CH_2CH_2$	48.5-49	6.0	49.30	360
6	p-H	$(CH_3)_2CHCH_2$	-------	----	-----	---

a) Recrystallized from abs. methanol

TABLE IX

PHYSICAL CONSTANTS OF THE KETAZINES[a]

$[x-C_6H_4-\overset{R}{\overset{\vert}{C}} = N]_2$				
x=	R=	m.p., °C	m.p. °C (Lit.)[b]	% Yield
p-H	CH_3	120.5-121.5	124	82.5
p-CH_3	CH_3	136-137	137-138	75.2
m-CH_3	CH_3	86.5-88	-------	70.0
p-OCH_3	CH_3	198-199	200-202	78.8
p-H	$CH_3CH_2CH_2CH_2$	34-35	-------	75.0
p-H	$(CH_3)_2CHCH_2$	69-70.5	69-71	65.0

a) Recrystallized from abs. ethanol

b) Ref. 15

TABLE X

EXTINCTION COEFFICIENTS OF PROTIATED AZO COMPOUNDS

$[x-C_6H_4-CHRN=]_2$					
x=	R=	ε(benzene)	λ_{max}	Conc.	Amt. Weighed
p-H	CH_3	45.76	359	.0170M	.0406g
p-CH_3	CH_3	51.50	357	.0201M	.0536g
p-CH_3O	CH_3	62.44	357	.0148M	.0440g
m-CH_3	CH_3	49.13	357	.0179M	.0475g
p-H	$(CH_3)_2CHCH_2$	44.79	358	.0191M	.0614g
p-H	$CH_3CH_2CH_2CH_2$	48.30	360	.0187M	.0601g

TABLE XI

EXTINCTION COEFFICIENTS OF DEUTERATED AZO COMPOUNDS

$[x-C_6H_4-\underset{D}{C}\ R\ N=]_2$					
x=	R=	ε (benzene)	λ_{max}	Conc.	Amt. Weighed
p-H	CH_3	46.22	359	.0172M	.0410g
p-CH_3	CH_3	52.21	357	.0192M	.05159
p-CH_3O	CH_3	63.60	357	.0136M	.0408g
m-CH_3	CH_3	49.71	357	.0179M	.0408g
p-H	$(CH_3)_2CHCH_2$	-----	---	-----	------
p-H	$CH_3CH_2CH_2CH_2$	49.30	360	.0187M	.0603g

TABLE XII

THERMOCOUPLE CALIBRATION

Solvent	NBS Thermocouple Readings in mv	Measuring Thermocouple Readings in mv	EMF Measuring Thermocouple (x) vs. EMF NBS Thermocouple (y) Slope	Intercept
		Temperature Range (80-110°)		
Benzene	3.306	3.330	--------	---------
Azeotrope of Dioxane + Water	3.662	3.687	--------	---------
Toluene	4.687	4.723	0.990945 ±.001594	0.0070728 ±.006308
		Temperature Range (99-125°)		
Isooctane	4.187	4.152	--------	---------
Toluene	4.723	4.687	--------	---------
n-Octane	5.445	5.416	1.00498 ±.00279	-0.057581 ±.013408

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APPENDIX A

TABULATION OF RATE DATA OBTAINED

$[x-C_6H_4-\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}-N=]_2$

R'=	R=	x=	Temp., °C	Measured EMF, mv	Calculated EMF, mv	k	Average k
H	CH_3	p-H	112.91	4.886 ± .002	4.85276	1.2930×10^{-2} mins^{-1}	
H	CH_3	p-H	112.91	4.886 ± .002	4.85276	1.2687×10^{-2} mins^{-1}	1.280×10^{-2} mins^{-1}
H	CH_3	p-CH_3	112.91	4.888 ± .002	4.85276	1.5061×10^{-2} mins^{-1}	
H	CH_3	p-CH_3	112.91	4.888 ± .002	4.85276	1.4245×10^{-2} mins^{-1}	1.4655×10^{-2} mins^{-1}
H	CH_3	p-OCH_3	112.91	4.886 ± .002	4.85276	1.7381×10^{-2} mins^{-1}	
H	CH_3	p-OCH_3	112.91	4.887 ± .002	4.85276	1.7774×10^{-2} mins^{-1}	1.756×10^{-2} mins^{-1}
H	CH_3	m-CH_3	112.91	4.887 ± .002	4.85276	1.2692×10^{-2} mins^{-1}	
H	CH_3	m-CH_3	112.91	4.887 ± .002	4.85276	1.2982×10^{-2} mins^{-1}	
H	CH_3	m-CH_3	112.91	4.886 ± .002	4.85276	1.2877×10^{-2} mins^{-1}	1.287×10^{-2} mins^{-1}
H	$CH_3CH_2CH_2CH_2$	p-H	113.13	4.896 ± .002	4.86281	1.1563×10^{-2} mins^{-1}	
H	$CH_3CH_2CH_2CH_2$	p-H	113.21	4.900 ± .002	4.86683	1.1581×10^{-2} mins^{-1}	

APPENDIX A (Continued)

$[x-C_6H_4-\overset{R}{\underset{R'}{C}}-N=]_2$							
R'=	R=	x=	Temp., ^oC	Measured EMF, mv	Calculated EMF, mv	k	Average k
H	CH_3	p-OCH_3	105.25	4.527 ± .002	4.49200	7.4004×10^{-3} $mins^{-1}$	
D	CH_3	p-OCH_3	105.25	4.527 ± .002	4.49200	6.1259×10^{-3} $mins^{-1}$	
H	CH_3	p-OCH_3	105.13	4.522 ± .005	4.48750	7.3825×10^{-3} $mins^{-1}$	
D	CH_3	p-OCH_3	105.13	4.522 ± .005	4.48750	6.1578×10^{-3} $mins^{-1}$	
H	CH_3	p-OCH_3	105.13	4.522 ± .002	4.48750	7.4483×10^{-3} $mins^{-1}$	
D	CH_3	p-OCH_3	105.13	4.522 ± .002	4.48750	6.444×10^{-3} $mins^{-1}$	
H	CH_3	p-OCH_3	105.13	4.522 ± .002	4.48750	7.3111×10^{-3} $mins^{-1}$	7.3724×10^{-3} $mins^{-1}$
D	CH_3	p-OCH_3	105.13	4.522 ± .002	4.48750	6.1976×10^{-3} $mins^{-1}$	6.2248×10^{-3} $mins^{-1}$
H	CH_3	p-CH_3	105.13	4.522 ± .002	4.487500	6.1485×10^{-3} $mins^{-1}$	
D	CH_3	p-CH_3	105.13	4.522 ± .002	4.48750	5.5271×10^{-3} $mins^{-1}$	
H	CH_3	p-CH_3	105.13	4.522 ± .002	4.48750	6.1530×10^{-3} $mins^{-1}$	
D	CH_3	p-CH_3	105.13	4.522 ± .002	4.48750	5.6194×10^{-3} $mins^{-1}$	
H	CH_3	p-CH_3	105.13	4.522 ± .002	4.48750	6.1416×10^{-3} $mins^{-1}$	6.146×10^{-3} $mins^{-1}$
D	CH_3	p-CH_3	105.13	4.522 ± .002	4.48750	5.586×10^{-3} $mins^{-1}$	5.577×10^{-3} $mins^{-1}$

APPENDIX A (Continued)

$[x-C_6H_4-\underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-N=]_2$

R'=	R =	x =	Temp., °C	Measured EMF, mv	Calculated EMF, mv	k	Average k
H	$CH_3CH_2CH_2CH_2$	p-H	113.32	4.905 ± .002	4.87186	1.1506×10^{-2} mins^{-1}	1.153×10^{-2} mins^{-1}
H	$(CH_3)_2CHCH_2$	p-H	113.32	4.905 ± .003	4.87186	2.0428×10^{-2} mins^{-1}	
H	$(CH_3)_2CHCH_2$	p-H	113.32	4.905 ± .003	4.87186	2.0970×10^{-2} mins^{-1}	2.070×10^{-2} mins^{-1}
H	CH_3	m-CH_3	93.43	3.975 ± .002	3.94608	1.3329×10^{-3} mins^{-1}	
H	CH_3	m-CH_3	93.43	3.975 ± .002	3.94608	1.3383×10^{-3} mins^{-1}	
H	CH_3	m-CH_3	93.43	3.975 ± .002	3.94608	1.3337×10^{-3} mins^{-1}	
H	CH_3	m-CH_3	93.43	3.975 ± .002	3.94608	1.3399×10^{-3} mins^{-1}	1.3362×10^{-3} mins^{-1}
H	$CH_3CH_2CH_2CH_2$	p-H	93.02	3.965 ± .002	3.93617	1.1508×10^{-3} mins^{-1}	
H	$CH_3CH_2CH_2CH_2$	p-H	93.02	3.965 ± .002	3.93617	1.1448×10^{-3} mins^{-1}	
H	$CH_3CH_2CH_2CH_2$	p-H	93.02	3.965 ± .002	3.93617	1.1245×10^{-3} mins^{-1}	1.135×10^{-3} mins^{-1}
H	CH_3	p-H	102.79	4.411 ± .002	4.37813	4.003×10^{-3} mins^{-1}	Not Used
D	CH_3	p-H	102.79	4.411 ± .002	4.37813	3.541×10^{-3} mins^{-1}	Not Used
H	CH_3	p-H	105.35	4.532 ± .002	4.49804	5.405×10^{-3} mins^{-1}	

APPENDIX A (Continued)

$[x—C_6H_4—\underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}—N=]_2$

R'=	R=	x=	Temp., ^oC	Measured EMF, mv	Calculated EMF, mv	k	Average k
D	CH_3	p-H	105.35	4.532 ± .002	4.49804	4.7121×10^{-3} $mins^{-1}$	
H	CH_3	p-H	105.35	4.532 ± .002	4.49804	5.372×10^{-3} $mins^{-1}$	
D	CH_3	p-H	105.35	4.532 ± .002	4.49804	4.6506×10^{-3} $mins^{-1}$	
H	CH_3	p-H	105.35	4.532 ± .002	4.49804	5.5658×10^{-3} $mins^{-1}$	5.447×10^{-3} $mins^{-1}$
D	CH_3	p-H	105.35	4.532 ± .002	4.49804	4.7786×10^{-3} $mins^{-1}$	4.713×10^{-3} $mins^{-1}$
H	CH_3	m-CH_3	105.35	4.532 ± .002	4.49804	5.4352×10^{-3} $mins^{-1}$	
D	CH_3	m-CH_3	105.35	4.532 ± .002	4.49804	4.9913×10^{-3} $mins^{-1}$	
H	CH_3	m-CH_3	105.35	4.532 ± .002	4.49804	5.4577×10^{-3} $mins^{-1}$	
D	CH_3	m-CH_3	105.35	4.532 ± .002	4.49804	4.9482×10^{-3} $mins^{-1}$	
H	CH_3	m-CH_3	105.25	4.527 ± .002	4.49200	5.4353×10^{-3} $mins^{-1}$	5.442×10^{-3} $mins^{-1}$
D	CH_3	m-CH_3	105.25	4.527 ± .002	4.49200	4.8728×10^{-3} $mins^{-1}$	4.937×10^{-3} $mins^{-1}$
H	CH_3	p-OCH_3	105.25	4.527 ± .002	4.49200	7.3197×10^{-3} $mins^{-1}$	
D	CH_3	p-OCH_3	105.25	4.527 ± .002	4.49200	6.1985×10^{-3} $mins^{-1}$	

VITA

2

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