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# Reexamination of the Secondary α-Deuterium Isotope Effect in Thermolysis of 1,1'-Diphenylazoethane. Mechanistic Consequences for Related Compounds

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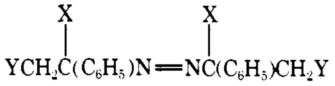
**Abstract:** Secondary α-deuterium isotope effects were obtained for the thermal decomposition of 1,1'-diphenylazoethane (I) and 1,1'-diphenylazoethane-*1,1'*-$d_2$ (I-$d_2$) at 103.90°. Samples of I and I-$d_2$ prepared by (a) $LiAlH_4$ and $LiAlD_4$ reduction of 1,1'-dichloro-1,1'-diphenylazoethane are designated as I-1 and I-$d_2$-1, respectively, and (b) catalytic hydrogenation and deuteration of acetophenone azine are specified as I-2 and I-$d_2$-2, respectively. An α effect of 1.195 ± 0.006 was obtained from I-1 and I-$d_2$-1 upon correction of $k_H/k_D = 1.191 \pm 0.006$ for 0.040 ± 0.002 atoms of α protium. An α effect of 1.198 ± 0.014 was obtained from I-2 and I-$d_2$-2 upon correction of $k_H/k_D = 1.159 \pm 0.010$ for 0.415 ± 0.016 atoms of α protium and 0.245 ± 0.105 atoms of β deuterium. Thus, the isotope effect in thermolysis of I is 1.194 rather than 1.27 at 105.28°. Nitrogen evolution experiments verified that I-1 and -2, I-$d_2$-1 and -2, I-*ring*-$d_{10}$, *meso*-1,1',2,2'-tetraphenylazoethane (IV), *meso*-IV-$d_2$, 1,1'-diphenylazobutane (V), V-$d_2$, 2,2'-dimethoxy-1,1'-diphenylazoethane (VI), and VI-$d_2$ undergo 98–100% decomposition. The previous conclusion that a simultaneous one-step mechanism obtains for thermolysis of these compounds is consistent with an α effect of 1.195 for I. The α effects previously obtained for IV–VI are reinterpreted in terms of the result obtained for I. For I, the transition state model which reproduces an α effect of 1.27 and the primary nitrogen effect should be consistent with a $k_H/k_D$ of 1.195 if the H–C–N bending force constant is ca. 0.33 mdyn Å/(rad)$^2$ rather than 0.23 mdyn Å/(rad)$^2$.

In a series of classic experiments, Seltzer[2] and Seltzer and Dunne[3] utilized α-secondary deuterium isotope effects to demonstrate (1) a concerted mechanism for pyrolysis of 1,1'-diphenylazoethane[4] (I) and (2) a change in the pyrolysis mechanism from symmetrical to unsymmetrical one-step cleavage to two-step cleavage in the series I, 1-methyl-1'-phenylazoethane (II), and (1-phenylethyl)azomethane (III). "Exact" analysis[5] of the α-deuterium and primary nitrogen[6] effects in pyrolysis of I, II, and III and the carbon effect[3] at the methyl group of III resulted in a quantification of these conclusions.[6] Also, the deuterium isotope effects in thermolysis of I-*methyl*-$d_6$[7] and I-*ring*-$d_{10}$[8] demonstrate for the transition state of I that hyperconjugative stabilization is of little importance[7] and that delocalization of the incipient odd electron produces a negligible perturbation of the aromatic CH force constants.[8]

To investigate the influence of molecular structure on the potential-energy hypersurface for pyrolysis, α effects were measured for decomposition of *meso*- and *dl*-1,1',2,2'-tetraphenylazoethane[9] (IV), 1,1'-diphenylazobutane[10] (V), and 2,2'-dimethoxy-1,1'-diphenylazoethane[10] (VI). Using structure-reactivity relationships, the α effects for *meso*- and *dl*-IV (1.224 and 1.207) and for V (1.200) compared with that for I (1.27) were plausibly explained in terms of more reactant-like transition states for each of the former than for the latter.[9-11] However, the α effect for VI (1.188) could not be similarly rationalized; i.e., such considerations appeared to predict a $k_H/k_D$ of ca. 1.27.[10,11] Furthermore, thermolysis of 3,12,15,24-tetraphenyl-1,2,13,14-tetraza-1,13-cyclotetracosadiene (VII) yielded an α effect of 1.20[12] rather than a value of ca. 1.27.



$$YCH_2\overset{X}{\overset{|}{C}}(C_6H_5)N{=}N\overset{X}{\overset{|}{C}}(C_6H_5)CH_2Y$$

I, Y = X = H
I-$d_2$, Y = H; X = D
*meso*-IV, Y = $C_6H_5$; X = H
*meso*-IV-$d_2$, Y = $C_6H_5$; X = D
V, Y = $CH_3CH_2$; X = H
V-$d_2$, Y = $CH_3CH_2$; X = D
VI, Y = $CH_3O$; X = H
VI-$d_2$, Y = $CH_3O$; X = D

Because the magnitude of the α effect for I is of singular importance in interpreting the ones obtained for related compounds, we have redetermined its value. The extent of pyrolysis which could affect the magnitude of $k_H/k_D$ was also determined for the samples of protiated and α-deuterated I, *meso*-IV, V, and VI and of I-*ring*-$d_{10}$ used in the isotope effect determinations.

## Experimental Section

**Azo Compounds.** 1,1'-Diphenylazoethane and 1,1'-diphenylazoethane-*1,1'*-$d_2$ were prepared by two methods. Samples prepared by $LiAlH_4$ and $LiAlD_4$ reduction of 1,1′-dichloro-1,1′-diphenylazoethane[13] are designated I-1 and I-$d_2$-1, respectively. Samples prepared by catalytic hydrogenation and deuteration of acetophenone azine[2a] are designated I-2 and I-$d_2$-2, respectively. Palladium on charcoal (5%), 3 g, suspended in 150 ml of purified benzene[10] was equilibrated with deuterium gas, and 11.0 g (0.047 mol) of azine was then reduced at atmospheric pressure; 4 hr were required for uptake of 0.094 mol of $D_2$. After filtration, the crude hydrazine was oxidized at room temperature with yellow mercuric oxide[9] (40 g). Crude I-$d_2$-2 was repeatedly recrystallized from methanol, mp 71.5–72.5°.

Previously prepared samples of I-2,[8] I-*ring*-$d_{10}$,[8] *meso*-IV,[9] *meso*-IV-$d_2$,[9] V,[10] V-$d_2$,[10] VI,[10] and VI-$d_2$[10] were recrystallized as described.

**Kinetics.** The isotope effects were determined by simultaneously measuring the rates of decomposition of the protium and deuterium compounds in purified ethylbenzene as previously described.[9] Temperature was determined as previously described[9] except that a NBS-calibrated copper–constantan thermocouple was used in place of the NBS-calibrated thermometer.

**Quantitative Nitrogen Evolution.** Ampoules were constructed as follows. A 90 × 22 mm section of glass tubing was closed at one end. A 90 × 4 mm section of thick-walled glass tubing bearing a 10/30 inner joint and a 90 × 10 mm section of glass tubing containing a break seal and bearing a 12/30 outer joint were fused to the other end. A weighed amount of azo compound (ca. 0.1 mmol) was dissolved in 5 ml of purified ethylbenzene[9] and the resulting solution quantitatively transferred to an ampoule. The solution was degassed at Dry Ice temperature under high vacuum (<1 μm) using a freeze–thaw procedure; the procedure was repeated until the pressure was that of ethylbenzene. The ampoule was then sealed under vacuum by allowing the tube heated below the 10/30 joint to collapse. After the sample had been decomposed for a minimum of 10 half-lives in a constant temperature bath, the ampoule was cooled in a Dry Ice–chloroform–carbon tetrachloride slurry and connected by two liquid nitrogen cooled radiator traps to a quantitative gas analysis system. Before the ampoule was opened, the volume above the break seal was evacuated. The noncondensable gases were Toepler-pumped to the calibrated gas buret. To ensure complete recovery of nitrogen, the contents of the ampoule was subjected to at least five warming-cooling-pumping cycles. Pressures were then recorded for three different gas volumes; the moles of nitrogen were calculated for each set of *PV* data and then averaged.

For a number of samples, the gas was then transferred to a glass loop. Subsequent gas chromatographic analysis verified that the noncondensable gas was nitrogen.

**Deuterium Content and Correction of Isotope Effects.** The deuterium content of I-$d_2$-1 and I-$d_2$-2 was determined respectively by combustion[14] and by combustion and NMR. The NMR measurements involved a minimum of three independent determinations of the proton ratios for labeled and unlabeled compounds by integration following repetitive scanning with a Varian C-1024. Spectra of all samples were taken in chloroform-*d* (100 atom % D). Assuming no excess deuterium in the phenyls, the atom fraction of deuterium was calculated by comparison of the proton ratios in the deuterated compounds with the corresponding ratios in the protium sample.

$$V \pm \sigma_V = (X \pm \sigma_X)^{Y \pm \sigma_Y} \tag{1}$$

Equation 1 was used either to correct an isotope effect to maximum number of atoms of D or to compute an isotope effect given a specific number of atoms of D. In the former computations, $V$ is the corrected effect, $X$ is the effect to be corrected, and $Y \pm \sigma_Y = Z/(W \pm \sigma_W)$ where $Z$ and $W$ are the maximum and experimental number of atoms of D, respectively, for the position of interest. In the latter computations, $V$ is the isotope effect calculated for $Y$ experimental atoms of D at a position given the isotope effect $X$ per D for that position. In both cases, $\sigma_i$ represents the associated standard deviations. For calculations involving data for I-$d_2$-1, the standard deviation in the experimental number of atoms of D ($W$) was replaced by the average deviation. The standard deviation in $V$ was calculated by eq 2, which was derived from the expression $\sigma_V = \pm[(\partial V/\partial X)^2\sigma_X{}^2 + (\partial V/\partial Y)^2\sigma_Y{}^2]^{1/2}$.[15]

$$\sigma_V = V[(Y\sigma_X)^2/X^2 + (\sigma_Y \ln X)^2]^{1/2} \tag{2}$$

## Results

Excellent first-order kinetics were observed for decomposition (a) of I-1 and I-$d_2$-1 prepared by reduction of 1,1′-dichloro-1,1′-diphenylazoethane with $LiAlH_4$ and $LiAlD_4$,[13] respectively, and (b) of I-2 and I-$d_2$-2 prepared by catalytic hydrogenation and deuteration, respectively, of acetophenone azine. At the completion of all kinetic determinations, the samples exhibited no absorption in the region centered around 360 mμ. The rate constant 4.50 ± 0.03 × $10^{-3}$ $min^{-1}$ for decomposition of I-1 in ethylbenzene at 103.90 ± 0.04° is in good agreement with the value 4.56 ± 0.09 × $10^{-3}$ $min^{-1}$ obtained for I-2 at 103.9 ± 0.2°.

Table I presents the observed and corrected (2 atoms of α-D) isotope effects and the deuterium content of I-$d_2$-1 determined by combustion and of I-$d_2$-2 determined by both combustion and NMR (proton ratios determined by integration following repetitive scanning with a Varian C-1024). For I-$d_2$-2, the value for atoms of deuterium by combustion, 1.810 ± 0.003, differs on the average by only 1.1% from the NMR value 1.830 ± 0.106 (1.585 ± 0.016 atoms of α- and 0.245 ± 0.105 atoms of β-D). The standard deviation in the atoms of β-D, which clearly dominates σ in the total atoms of D, reflects for our Varian XL-100 the difficulty in reproducing with high precision absorption bands of protons having chemical shifts less than ca. δ 1.7. For any one experiment, σ in the methyl proton ratio was less than 0.105, but the number of these protons was found to be dependent upon the power used to lock-in on the tetramethylsilane absorption band. Thus, the average value obtained for each determination of the individual methyl proton ratio for I-2 and I-$d_2$-2 was used to arrive at the value 0.245 ± 0.105 without regard to the σ for each methyl determination.

For I-$d_2$-1, an α effect of 1.195 ± 0.006 is obtained upon correction of $(k_H/k_D)_{obsd}$ to 2 atoms of α-D. The $(k_H/k_D)_{obsd}$ for I-$d_2$-2 was corrected to 2 atoms of α-D as follows. The contribution of α deuterium to the experimental $k_H/k_D$ for I-*methyl*-$d_6$[7] was calculated to be 1.0027 ± 0.0013 by eq 1, where $X \pm \sigma_X$ equals 1.195 ± 0.006 and $Y \pm \sigma_Y$ equals 0.0150 ± 0.0075.[7] The $k_H/k_D$ for 5.891 ± 0.005 atoms of β-D[7] is thus $(1.112 \pm 0.005)^7/(1.0027 \pm 0.0013)$ or 1.109 ± 0.005. Equation 1 then yields a β effect of 1.018 ± 0.001 per atom of β-D. An identical value is obtained if the α effect for I-$d_2$-1 is first extrapolated from 103.90 to 105.20°, the temperature at which $k_H/k_D$ was determined for I-*methyl*-$d_6$.[7] Equation 1 in which $Y \pm \sigma_Y$ = 0.2449 ± 0.1049 then gives a calculated value of 1.0043 ± 0.0019 for the contribution of β deuterium to $(k_H/k_D)_{obsd}$. For 1.585 ± 0.016 atoms of α-D, $k_H/k_D$ is (1.1590 ± 0.0104)/(1.0043 ± 0.0019) or 1.1540 ± 0.0106 which when corrected to 2 atoms of α-D yields an α effect of 1.198 ± 0.014 for I-$d_2$-2.

The α effect for I-$d_2$-1 (1.195 ± 0.006) is in excellent agreement with the value for I-$d_2$-2 (1.198 ± 0.014). The standard deviation in the latter primarily reflects the magnitude of σ in $(k_H/k_D)_{obsd}$. In the I-2/I-$d_2$-2 measurements, difficulty was encountered in achieving long-term temperature stability. However, these measurements were not repeated because of the excellent agreement in the α effects.

It is important to note that the β effect per D is 1.018[7] regardless of whether $(k_H/k_D)_\alpha$ of 1.27 or 1.195 is used to correct the experimental $k_H/k_D$ for I-*methyl*-$d_6$ for α-deuterium.

Quantitative nitrogen evolution studies were undertaken because appreciably incomplete azo compound decomposition could yield erroneous isotope effects. Table II tabulates the results. The uncertainty in the percentage nitrogen

Table I. Isotope Effect in the Decomposition of 1,1′-Diphenylazoethane-*1,1′*-$d_2$ in Ethylbenzene at 103.90°[a]

| Compd | Atoms of α-*d* | $\langle k_H/k_D\rangle_{obsd}$[b] | $\langle k_H/k_D\rangle_{corr}$[c] |
|---|---|---|---|
| I-1/I-$d_2$-1 | 1.960 ± 0.002[d] | 1.1912 ± 0.0062[e,f] | 1.195 ± 0.006 |
| I-2/I-$d_2$-2 | 1.585 ± 0.016[g] | 1.1590 ± 0.0104[h,i] | 1.198 ± 0.014 |

[a] Deviations are standard deviations except where noted. Column three is not rounded for computation purposes. [b] Measured simultaneously. [c] $k_H/k_D$ observed corrected to 2 atoms of α-*d*. [d] Calculated from average atom % D obtained from duplicate combustion analysis; atom % D found: 10.88 and 10.90. Deviation is average deviation. [e] Average of six determinations. [f] $\Delta T = \pm 0.04°$. [g] Determined by NMR. Atoms of β-*d* by NMR are 0.2449 ± 0.1049. Total atoms of D by NMR and duplicate combustion are 1.830 ± 0.106 and 1.810 ± 0.003, respectively. [h] Average of five determinations. [i] $\Delta T = \pm 0.2°$.

evolved is ca. 1.5–2% from consideration of the standard deviation in the *PV* products and of solution preparation. The results obtained for both preparations of I and I-$d_2$ agree with the nitrogen yield obtained for I by Seltzer and Mylonakis;[6] the nitrogen yields obtained for *meso*-IV and *meso*-IV-$d_2$ agree with the values obtained for *meso*-IV by Mylonakis, Scheppele, and Seltzer.[16] Thus, in all instances, the kinetic data and, hence, the isotope effects reflect 98–100% decomposition.

## Discussion

The α-deuterium isotope effect for decomposition of I is (a) 1.195 rather than 1.27[2a] and (b) comparable in magnitude to those obtained for IV through VII.[9,10,12] To consider the implications of this result, α effects for decomposition of I through VII are shown in Table III. For purposes of comparison, the α effects have been extrapolated to 105.28° on the assumption that $A_H/A_D = 1$.[17] Various experimental[18] and theoretical studies[5,19] have shown that the difference in loss of zero-point energy between protio and deuterio compounds in the ground states and transition states is principally responsible for the α effect.[20] However, an $A_H/A_D$ somewhat less than unity is indicated for α effects in unimolecular decompositions. For the unimolecular decomposition of the *tert*-cumyloxy-β-$d_3$ radical, a least-squares fit of log $k_H/k_D$ vs. $1/T$ for $\Delta T$ of 84° yields an $A_H/A_D$ of 0.93 ± 0.02[18b] or 0.976 per D. Seltzer and Hamilton[7] performed "exact" calculations for decomposition of I-$d_2$ and I-*methyl*-$d_6$. An $A_H/A_D$ of 0.960 per α-D is calculated from the α effect computed for transition-state model-I (the reason for choosing model-I is given below) at 273 and 373 K. For the model system $CD_3X \rightarrow CD_3{\cdots}X^{\ddagger}$, "exact" calculations for the temperature range 300–325 K lead to an $A_H/A_D$ of 0.94, 0.97, or 0.93 depending upon the magnitude of the decrease in the HCX bending force constant, $f_{HCX}$,[21] in passing from the reactant to the transition state; these values give an average $A_H/A_D$ of 0.982 per α-D. The possible consequence of such results on the extrapolation of the experimental α effects in Table III was investigated by extrapolating the α effects for II and III at the benzylic position and for VI assuming $A_H/A_D$ values of 0.973 (average of above values) and 0.960 per D. These $A_H/A_D$ values increase the α effects at 105.28° by 0.01 or less per atom of deuterium.

The previous conclusion[2,3,6] that the decomposition mechanism changes from symmetrical to unsymmetrical one-step cleavage to two-step cleavage in the series I, II, and III is entirely consistent with an α effect of 1.195 ± 0.006 for I. Consideration of the data for III, II, and I in terms of the mechanisms presented in eq 3, 4, and 5 establishes the validity of this conclusion.

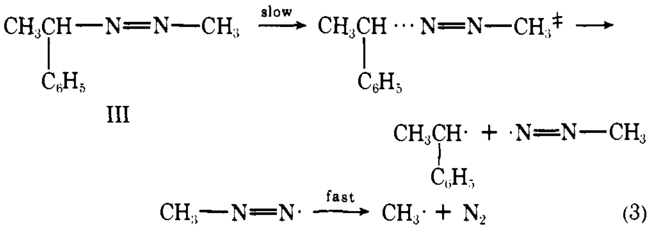
Table II. Percentage Nitrogen Evolved in Azoalkane Pyrolysis in Ethylbenzene

| Compd | *T*, °C | Compd, mmoles × 10² | $N_2$, mmoles × 10² | % $N_2$ evolved |
|---|---|---|---|---|
| I-1 | 155 | 9.986 | 10.08 | 100.9 |
| I-2 | 155 | 10.15 | 10.16 | 100.1 |
| I-$d_2$-1 | 158 | 9.819 | 9.763 | 99.4 |
| I-$d_2$-2 | 160 | 9.861 | 9.958 | 101.0 |
| I-*ring*-$d_{10}$ | 155 | 9.541 | 9.276 | 97.2 |
| *meso*-IV | 155 | 10.17 | 9.962 | 98.0 |
| *meso*-IV-$d_2$ | 155 | 10.06 | 9.848 | 97.9 |
| V | 155 | 9.849 | 9.614 | 97.6 |
| V-$d_2$ | 155 | 9.243 | 9.037 | 97.8 |
| VI | 158 | 10.22 | 10.20 | 99.8 |
| VI-$d_2$ | 158 | 10.02 | 10.18 | 101.6 |

Table III. α-Secondary Deuterium Isotope Effects for Thermolysis of Azoalkanes

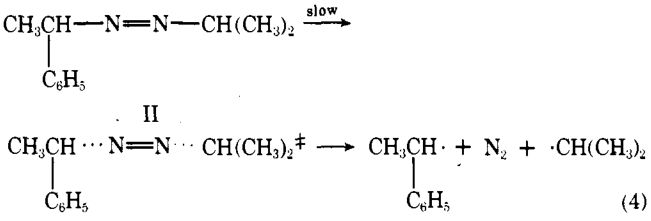
| Compd | $(k_H/k_D)_{exp}$[a] | *T*, °C | Position of D | $(k_H/k_D)$[b] at 105.28° | $(k_H/k_D)$[c] per α-D at 105.28° |
|---|---|---|---|---|---|
| I | 1.195 ± 0.006 | 103.90 | Benzyl | 1.194 | 1.093 |
| II | 1.148 ± 0.012[d] | 143.20 | Benzyl | 1.164 | 1.164 |
|  | 1.036 ± 0.007[d] | 143.20 | Propyl | 1.040 | 1.040 |
| III | 1.13 ± 0.01[e] | 161.00 | Benzyl | 1.151 | 1.151 |
|  | 0.97 ± 0.01[e] | 161.00 | Methyl | 0.966 | 0.989 |
| *meso*-IV | 1.224 ± 0.006[f] | 106.47 | Benzyl | 1.225 | 1.107 |
| *dl*-IV | 1.202 ± 0.006[f] | 106.47 | Benzyl | 1.203 | 1.097 |
| V | 1.194 ± 0.008[g] | 106.68 | Benzyl | 1.201[i] | 1.096 |
|  | 1.206 ± 0.014[g] | 107.35 |  |  |  |
| VI | 1.188 ± 0.004[g] | 118.09 | Benzyl | 1.195 | 1.093 |
| VII | 1.20 ± 0.02[h] | 112.95 | Benzyl | 1.204 | 1.097[j]<br>1.048[k] |

[a] Corrected to maximum atoms of D at the indicated position. [b] For maximum atoms of D at the indicated position. [c] Calculated by taking the $n^{-1}$ root of the value in column five where *n* is the number of atoms of D at a specified position. [d] See ref 2b. [e] See ref 3. [f] See ref 9. [g] See ref 10. [h] See ref 12. [i] Average of two extrapolated values, 1.195 and 1.208. [j] $k_H/k_D$ per 2-α-D. [k] $k_H/k_D$ per α-D.



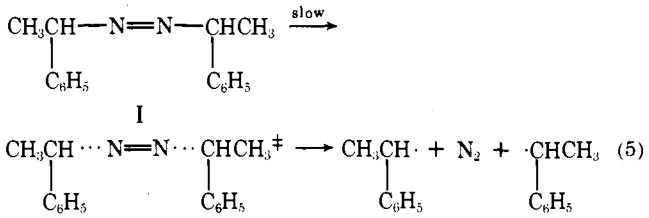
III

$$CH_3CH(C_6H_5)-N{=}N-CH_3 \xrightarrow{\text{slow}} CH_3CH(C_6H_5){\cdots}N{=}N-CH_3^{\ddagger} \longrightarrow CH_3\dot{C}H(C_6H_5) + {\cdot}N{=}N-CH_3$$
$$CH_3-N{=}N{\cdot} \xrightarrow{\text{fast}} CH_3{\cdot} + N_2 \qquad (3)$$



II

$$CH_3CH(C_6H_5)-N{=}N-CH(CH_3)_2 \xrightarrow{\text{slow}} CH_3CH(C_6H_5){\cdots}N{=}N{\cdots}CH(CH_3)_2^{\ddagger} \longrightarrow CH_3\dot{C}H(C_6H_5) + N_2 + {\cdot}CH(CH_3)_2 \qquad (4)$$



I

$$CH_3CH(C_6H_5)-N{=}N-CH(C_6H_5)CH_3 \xrightarrow{\text{slow}} CH_3CH(C_6H_5){\cdots}N{=}N{\cdots}CH(C_6H_5)CH_3^{\ddagger} \longrightarrow CH_3\dot{C}H(C_6H_5) + N_2 + {\cdot}CH(C_6H_5)CH_3 \qquad (5)$$

**(1-Phenylethyl)azomethane** (III). "Exact" calculations in model chemical systems have shown that the magnitude of the α effect is dependent upon the change in the hydrogen-carbon leaving group bending force constant (HCX); i.e., $\Delta f_{HCX} = f_{HCX} - f_{HCX}{}^{\ddagger}$, in passing from the reactant state to the transition state.[5] Thus, the $\alpha$ effect reflects the extent of bond rupture between the $\alpha$ carbon and the leaving group at the saddle point. Consequently, the $\alpha$ effect for III at the benzylic position ($k_H/k_D$ = 1.13 at 161°, see Table III) demonstrates homolysis of the 1-phenylethyl carbon-to-nitrogen bond.[3] On the other hand, the $\alpha$ effect of 0.97 at the methyl position suggests a slightly stronger $CH_3$–N bond in the transition state than in the reactant state.[3] The 13-carbon effect at the methyl group ($k_{12}/k_{13}$ = 1.0068 at 161°) is also consistent with the latter conclusion; i.e., the experimental effect is less than $\nu_{1l}/\nu_{2l}$[3,6] (the classical mechanical contribution to the isotope effect). For a reaction mechanism (potential-energy reaction hypersurface) to be valid, absolute reaction rate theory requires that it quantitatively reproduce (predict) the kinetic isotope effect for any molecular position. Thus, the fact that the "exact" analysis of the isotope effects for III yields a transition-state model for which the force constants are numerically consistent with the qualitative interpretation of the experimental data constitutes a significant interpretative result.[11] The observation[22] that optically active III racemizes faster than it extrudes nitrogen is also consistent with the two-step mechanism shown in eq 3.

**1-Methyl-1′-phenylazoethane** (II). For decomposition of II at 143.20°, the $\alpha$ effects of (a) 1.15 at the 1-phenylethyl position and (b) 1.036 at the 1-methylethyl position show that homolysis of both C–N bonds is occurring in the rate-controlling step.[2b] The conclusion concerning rupture of the $(CH_3)_2CH$–N bond follows from the fact that $k_H/k_D$ exceeds the value of $\nu_{1l}/\nu_{2l}$ = 1.004 calculated for a two-step mechanism (analogous to eq 3) by the mass fragment approximation.[23] Also "exact" analysis of both $\alpha$-secondary deuterium and of the primary nitrogen isotope effects leads to a set of transition-state force constants consistent with eq 4. The diminution in the energy and entropy of activation in going from III ($E_a$ = 38.6 kcal/mol, $\Delta S^{\ddagger}$ = 14.0 eu)[3] to II ($E_a$ = 36.5 kcal/mol, $\Delta S^{\ddagger}$ = 9.3 eu)[4b] is consistent with some rupture of and restricted rotation about the $(CH_3)_2CH$–N bond in the activated complex.[3,24] The results are mutually consistent with an unsymmetrical one-step mechanism for pyrolysis of II; the difference in degree of rupture of the two C–N bonds parallels the difference in stabilities of the 1-phenylethyl and 1-methylethyl radicals.

**1,1′-Diphenylazoethane** (I). First, the results for II and III render a two-step pyrolysis mechanism for I implausible. However, a priori estimation of $k_H/k_D$ for two-step and concerted thermolysis of I/I-$d_2$ is difficult because the activation energy for I ($E_a$ = 32.6 kcal=mol)[25] suggests a more reactant-like transition state and, hence, a smaller $\Delta f_{HCX}$ per C–N bond rupture for I than for either II or III. However, for decomposition of I via a two-step mechanism, the $\alpha$ effect for III at the benzylic position predicts a $k_H/k_D \leq$ 1.15–1.16 for thermolysis of I/I-$d_2$ at 105.28°. Alternatively for thermolysis via a concerted mechanism, since $\Delta f_{HCX}$ is determined by the decrease in two $f_{HCN}$, the $k_H/k_D$ for I/I-$d_2$ at 105.28° would necessarily be predicted to be larger than the extrapolated benzylic $\alpha$ effects for II and III. The experimental result ($k_H/k_D$ = 1.195) is greater than the values obtained upon extrapolating (giving reasonable consideration to the possibility that $A_H/A_D$ may be less than unity, vide supra) the observed benzylic $\alpha$ effects for II and III to 105.28° and, hence, is qualitatively most consistent with a concerted mechanism. From a quantitative viewpoint, it is significant that "exact" analysis of both the $\alpha$-deuterium and primary nitrogen isotope effects results in a model for the activated complex in which the reaction coordinate is the symmetric stretch of both carbon–nitrogen bonds[6] (as discussed below, a $k_H/k_D$ = 1.195 is not inconsistent with the "exact" analysis[6]). Other kinetic evidence which favors a concerted mechanism is as follows. The entropy of activation for decomposition of I is 7.0 eu.[25] Thus both $E_a$ and $\Delta S^{\ddagger}$ for I are in harmony with an activated complex involving delocalization of two incipient p electrons over two aromatic $\pi$ systems attendant with restricted rotation of the phenyl groups. The absence of a viscosity dependence on the rate of thermolysis of the structurally related azoalkane 1,1′-dimethyl-1,1′-diphenylazoethane also constitutes indirect supporting evidence.[26] Considered together, these results provide, in the absence of any other data, compelling evidence for a concerted one-step mechanism for I. Similarly the $\alpha$ effects for IV through VII and the activation parameters for both diastereomers of IV,[9] V,[10] and VI[10] are entirely consistent with a concerted mechanism for thermolysis of these compounds.[9–11]

For decomposition of I, the magnitude of the decrease in $f_{HCN}$ upon passing from the reactant state to the transition state must be less than the decrease required to produce $k_H/k_D$ = 1.27. Seltzer and Mylonakis[6] describe two transition-state models (IVa and IVb) which produce an $\alpha$ effect of 1.27; in both models, $f^{\ddagger}_{HCN}$, $f^{\ddagger}_{CH_3CN}$, $f^{\ddagger}_{C_6H_5CN}$, and $f^{\ddagger}_{CNN}$ are 40% of the corresponding reactant-state values. Model-IVb, which gives the better fit to $k_{14}/k_{15}$, differs from model-IVa in the magnitude of $f^{\ddagger}_{CN}$ and the interaction force constant $f^{\ddagger}_{ij}$. Transition-state model-I, described by Seltzer and Hamilton,[7] appears to be identical with model-IVa except that the bending force constants are ca. 55 rather than 40% of the reactant-state values. It is important to note that model-I predicts an $\alpha$ effect of 1.193 at 373 K. Thus, it appears reasonable to conclude that model-IVb, in which $f^{\ddagger}_{HCN}$, $f^{\ddagger}_{CH_3CN}$, $f^{\ddagger}_{C_6H_5CN}$, and $f^{\ddagger}_{CCN}$ are ca. 55 rather than 40% of the reactant-state values, still constitutes a reasonable description of the bonding in the transition state for decomposition of 1,1′-diphenylazoethane.

The magnitude of $k_H/k_D$ reflects the reduction in $f_{HCN}$ upon passing from the reactant state to the transition state.[5b,6] Thus, if the force constants associated with the $\alpha$-CH bond in the reactant states are transferable[27] within a few percent,[10] the $\alpha$ effects for *dl*-IV, V, and VI compared with that for I, suggest that substitution of phenyl, ethyl, and methoxy for $\beta$ hydrogen in I does not seriously perturb that part of the potential-energy hypersurface involving motion of the $\alpha$ hydrogen. If such perturbations do occur, they must be compensated by factors such as coupling of vibronic motions and/or curvature in the barrier. As a first approximation, the $\alpha$ effects then indicate only a small substituent effect on the reactant-like-product-like character of the transition state. For *meso*-IV, $k_H/k_D$ and $k_{14}/k_{15}$ (1.0158 at 106.42°)[16] are larger and smaller than the respective values for I ($k_{14}/k_{15}$ = 1.0229 at 105.02°);[6] see also Table III. Previously the $\alpha$ deuterium and primary nitrogen isotope effects were interpreted as favoring a more reactant-like transition state for *meso*-IV than for I.[9–11] However, a problem arises in interpreting the nitrogen effect because the reduction in the C–N force constant is compensated in part by the increase in the N–N stretching constant.[6] Nevertheless, if in passing from the reactant state to the transition state changes in bending force constants are correlated with changes in stretching force constants,[6] and if the consequences[6] of this correlation on $k_H/k_D$ and $k_{14}/k_{15}$ are considered, the isotope effects for *meso*-IV compared with I are consistent with smaller values of $f^{\ddagger}_{HCN}$ and $f^{\ddagger}_{CN}$ and an increased value for $f^{\ddagger}_{NN}$ for the former. Thus, both the deuterium and the nitrogen isotope effects are qualitatively reconcilable with a more radical-like transition state for *meso*-IV than for I.

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# Rearrangements of Toluene and Cycloheptatriene Cations

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**Abstract:** The losses of $CH_3$ and $CH_6$ from the gaseous toluene cation (**1**) have been studied using seven isotopic isomers of **1** and two of cycloheptatriene (**2**) utilizing high resolution (1:50000) measurement of the abundance of the isobaric ionic products. Four distinct isomerization pathways, competitive with other **1** reactions, can be identified: (i) scrambling of the ring hydrogen atoms without involvement of the methyl group; (ii) isomerization **1** ⇄ **2** possibly through norcaradiene (**7**) as an intermediate; (iii) single exchange of an α-H and ring-H, possibly through methylenecyclohexadiene (**8**) as an intermediate; and (iv) complete scrambling of carbon as well as hydrogen atoms, possibly through opening of the aromatic ring. Reaction ii appears to involve the tightest activated complex, and i and ii the lowest activation energy; iii is intermediate, while iv has the loosest activated complex and highest activation energy. An additional pathway for the isomerization of **2**, possibly through bis(methylene)cyclopentene (**10b**), is also indicated.

Most unimolecular decompositions of simple aromatic and related cations are accompanied by extensive rearrangement.[3-9] A number of detailed studies, some utilizing multiple isotopic labeling, have shown that decompositions of benzene,[5] toluene (**1**),[6,8,9] and cycloheptatriene (**2**)[7,8] molecular ions can involve the loss of virtually all positional identity of the carbon as well as the hydrogen atoms. However, the mechanisms of such rearrangements remain obscure;[4] most labeling studies have provided little information of the pathways involved because of the completeness of scrambling in the products. From their recent double-$^{13}$C-labeling study, Davidson and Skell conclude,[7] "This observation leaves in total obscurity the mechanism of carbon scrambling in toluene."

A common suggestion for the behavior of toluene and isomeric $C_7H_8{\cdot}^+$ cations is that their molecular rearrangements involve (Scheme I) isomerization to a common structure such as cycloheptatriene (**2a** or **2b**),[10] or a more symmetrical ion (**3**),[3] with hydrogen scrambling in **2a** involving H migration through **2c**.[5,10-12] The observation[7] that norbornadiene (**4**) undergoes ready loss of $C_2H_2$ with only minor carbon scrambling makes this a less probable intermediate for the isomerization of either **1** or **2**. Recent evidence[8] indicates that the interconversion **1** ⇄ **2** is rapid at the threshold energy for hydrogen loss, making mechanistic studies at these energies difficult. At higher energies, decomposition can take place before such isomerization is complete;[8,12] however, studies at higher energies utilizing hydrogen loss reactions are compromised because the resulting benzyl and tropylium ions of higher internal energies also undergo rapid interconversion.[8]

In this report we conclude that isotopic scrambling arises through at least four competitive pathways (Scheme II) whose relative rates are strongly energy dependent. These conclusions are based on the study of $C_7H_8{\cdot}^+$ decompositions involving the loss of only one carbon atom. Although these product ions are of relatively low abundance, formation of $C_6H_5^+$ and $C_6H_2{\cdot}^+$ require approximately 1 eV less and 5 eV more energy, respectively, than formation of $C_5H_5^+$, the reaction which has been used to demonstrate scrambling in most previous studies. Also an early report by Rylander and Meyerson[13] indicated that $C_6H_5^+$ formation from toluene involves only partial hydrogen scrambling. We wished to probe the scrambling pathways utilizing the isoto-

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