

# The Role of Cage Return in the Determination of the Solution Phase Deuterium Isotope Effect during Hydrogen Abstraction Reactions of Bromine Atoms

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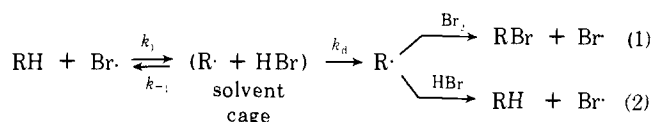
**Abstract:** The intermolecular deuterium isotope effect for the photoinitiated bromination of cyclohexane and perdeuteriocyclohexane has been determined in the vapor phase and in solution. Under conditions where the radicals formed do not transfer with hydrogen or deuterium bromide, a value for the vapor phase reaction of  $k_{RH}/k_{RD} = 5.4 \pm 0.2$  (20.8°) was found. In solution at concentrations of bromine (0.07–3.6 M) which are high enough to stop the transfer of the radicals that are free of the solvent cage, with the low concentrations of hydrogen or deuterium bromide formed at low conversion, the value obtained for  $k_{RH}/k_{RD} = 4.3 \pm 0.2$ . The difference between the vapor phase and solution results is attributed to a cage reversal reaction, between the radical hydrogen bromide pair, that is competitive with diffusion. At concentrations of molecular bromine (10–18 M) that are high enough to scavenge radicals from the solvent cage, the value obtained for  $k_{RH}/k_{RD}$  is the same as that found in the vapor phase. Under conditions where mixtures of the reactants ( $C_6D_{12}:C_6H_{12}:Br_2$ , 1:1:1) were allowed to completely react the value determined for  $k_{RH}/k_{RD} = 3.1 \pm 0.01$  can be attributed to both internal and external reversal reactions.

In order to rationalize our observation that a number of relative rates of bromination of alkanes and substituted alkanes showed a dependence on the concentration of molecular bromine used, it was suggested that one possible explanation for this dependence was not only the incursion of reversible hydrogen abstraction by the "free" radicals but also the possibility of internal return of the abstracted hydrogen to the radical in the solvent cage (Scheme I).<sup>2</sup> In this study, we report our preliminary attempts to substantiate the suggestion that cage return must be considered in the evaluation of solution phase bromination mechanisms.

Although the rate has not been measured directly, the transfer of an alkyl radical with molecular bromine in solution has been assumed to be a diffusion-controlled process.<sup>3</sup> This assumption must be nearly correct since vapor phase values of  $E_a$  and  $A$  assigned to this transfer process will place the solution reactions, within an order of magnitude, in the diffusion-controlled range.<sup>4–6</sup> Since it is apparent that reversible abstraction with hydrogen bromide<sup>3,4</sup> is competitive with the transfer reactions with molecular bromine, these hydrogen transfer reactions must also, within an order of magnitude, be governed by diffusion.

Concentrations within the cage can be estimated as corresponding to bulk concentrations<sup>7</sup> and it is, therefore, very probable that the rates of reaction of the geminate pair ( $R\cdot + HBr$ ) in the cage will occur at a rate which is competitive

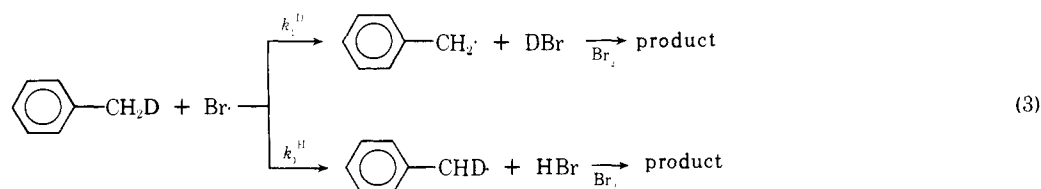
## Scheme I



with diffusion. Cage return will intercede in the mechanism before product formation. In comparing the reactivity of different C–H bonds in both intermolecular and intramolecular competition reactions, if the reverse reactions of the two radicals formed are of a different rate and are competitive with radical diffusion, then the ratio of products formed (or of the reactants that disappear) will be affected by cage filtering.

The intramolecular deuterium isotope effect for bromine atom abstraction from toluene- $\alpha$ - $d_1$  has been carefully studied in both solution<sup>8</sup> and vapor phase.<sup>9</sup> Both groups were careful to exclude observable reversal reactions (i.e., reactions in solution corresponding to reactions of radicals free of the solvent cage). The value,  $k_H/k_D$ , in solution was found to be  $4.59 \pm 0.03$  (77°), while the value obtained in the vapor phase was calculated,  $k_H/k_D = (1.08 \pm 0.25) \exp(1430 \pm 110)/RT$ , to be 8.2 (77°). If one assumes cage reversal to be the major difference between the solution and vapor phase reactions, in the absence of external reversal, then the two mechanisms may be formulated by eq 3 and 4.

### Vapor phase



### Solution

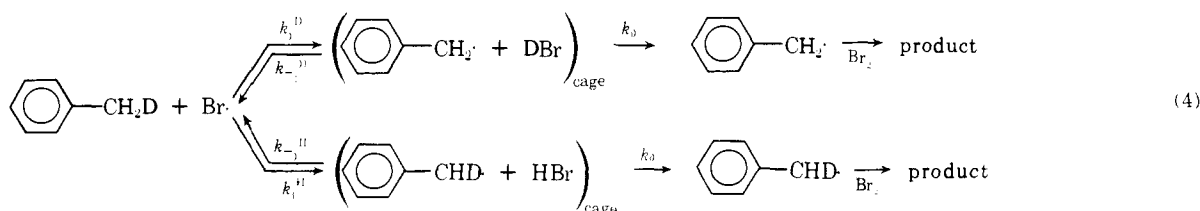


Table I. Competitive Photobrominations of Cyclohexane and Perdeuteriocyclohexane

Reaction no.	Conditions (temp, °C)	Concentration, $M \times 10^5$					External reversal <sup>a</sup>	$k_{RH}/k_{RD}$ <sup>b</sup>	Average $k_{RH}/k_{RD}$
		$[C_6H_{12}]^0$	$[C_6D_{12}]^0$	$[Br_2]^0$	$[C_6H_{12}]^f$	$[C_6D_{12}]^f$			
1	Gas phase (22)	5.25	5.10	41.1	0.560	3.30	None	5.14	5.38 ± 0.11
2	Gas phase (21)	5.25	5.10	41.1	1.35	3.98	None	5.48	
3	Gas phase (21)	5.25	5.10	41.1	1.20	3.88		5.40	
4	Gas phase (21)	5.25	5.10	80.8	2.26	4.38	None	5.54	
5	Gas phase (21)	5.25	5.10	81.3	0.985	3.73		5.35	
Concentration, $M \times 10^3$									
6	Bromine (21)	180	190	18300	45.7	145		5.07	5.33 ± 0.20
7	Bromine (21)	180	190	18300	46.6	150	None	5.72	
8	Bromine (21)	186	190	18200	31.6	136		5.30	
9	Bromine (21)	186	190	18200	73.3	159		5.23	5.34 ± 0.25
10	Freon 113 (21)	23.2	22.8	10200	2.44	14.6		5.05	
11	Freon 113 (21)	23.2	22.8	10200	3.44	16.1		5.49	
12	Freon 113 (21)	23.2	22.8	10200	6.24	18.1		5.69	
13	Freon 113 (21)	23.2	22.8	10200	6.55	17.8		5.11	
14	Freon 113 (21)	23.2	22.8	7710	4.03	15.9		4.86	4.67 ± 0.14
15	Freon 113 (21)	23.2	22.8	7710	4.25	16.0		4.79	
16	Freon 113 (21)	23.2	22.8	7710	3.35	15.2		4.77	
17	Freon 113 (21)	23.2	22.8	7710	1.92	13.1		4.50	
18	Freon 113 (21)	23.2	22.8	7710	8.78	18.3		4.42	
19	Freon 113 (21)	23.2	22.8	7710	7.32	17.8		4.66	4.32 ± 0.10
20	Freon 113 (21)	23.2	22.8	3630	7.58	17.7		4.42	
21	Freon 113 (21)	23.2	22.8	3630	12.8	19.8		4.22	
22	Freon 113 (21)	4.79	4.87	1030	2.14	4.01		4.15	
23	Freon 113 (21)	4.79	4.87	1030	2.24	4.05	None	4.12	
24	Freon 113 (21)	4.91	4.99	149	2.29	4.16	None	4.19	4.30 ± 0.18
25	Freon 113 (21)	4.91	4.99	149	2.85	4.42	None	4.48	
26	Freon 113 (20)	5.61	5.71	103	2.38	4.69		4.36	
27	Freon 113 (20)	5.61	5.71	103	2.38	4.62		4.05	
28	Freon 113 (21)	4.75	4.83	68.6	2.29	4.14	None	4.73	
29	Freon 113 (21)	4.75	4.83	68.6	2.52	4.17	None	4.31	4.52 ± 0.21
30	Freon 113 (21)	4.96	5.04	33.6	2.80	4.31	Obsd	3.65	
31	Freon 113 (21)	732	726	652	442	617	Obsd	3.10	3.12 ± 0.01
32	Freon 113 (21)	732	726	652	447	620	Obsd	3.13	

<sup>a</sup> See Table II. Reactions with blank entries were not checked by mass spectrometry. <sup>b</sup> Calculated from the equation  $k_{RH}/k_{RD} = \ln([C_6H_{12}]^0/[C_6H_{12}]^f) / \ln([C_6D_{12}]^0/[C_6D_{12}]^f)$ .<sup>14</sup>

If in solution  $k_{-1}^H$  is near the diffusion-controlled limit, then the inequality  $k_{-1}^H > k_{-1}^D$  would make cage filtering of the radicals leading to products observable. Using the steady state approximation for the concentration of the radicals in the cage, assuming that both benzyl radicals and monodeuterated benzyl radicals diffuse at the same rate, and that the bulk concentrations of caged hydrogen bromide,  $[HBr]$ , and deuterium bromide,  $[DBr]$ , are the same, a relationship for the cage effect can be obtained (eq 5). This derivation further assumes that solvent effects play a negligible role in determining the relative rates of abstraction of deuterium or hydrogen, i.e.,  $(k_1^H/k_1^D)^{sol} = (k_1^H/k_1^D)^{vp}$ .

$$\left( \log \frac{[RH]^0}{[RH]^f} / \log \frac{[RD]^0}{[RD]^f} \right)^{sol} = \left( \frac{k_1^H}{k_1^D} \right)^{vp} \left( \frac{k_{-1}^D[DBr] + k_d}{k_{-1}^H[HBr] + k_d} \right) = \left( \frac{k_{RH}}{k_{RD}} \right)^{sol} \quad (5)$$

The value of  $(k_{-1}^D[DBr] + k_d)/(k_{-1}^H[HBr] + k_d)$  for toluene- $\alpha$ - $d_1$  is found to be  $\sim 0.56$  and hence  $k_{-1}^H > k_{-1}^D$ . The exact value for the cage relationship determined in this manner assumes that none of the cage reversal is effected by processes which scavenge radicals from the cage.

It is interesting to note that, in studies of the solution and vapor phase deuterium isotope effect for the chlorination of deuterated toluene, where reversal, both internal and external, is energetically unfavorable ( $E_a > 18$  kcal/mol), the values of  $k_H/k_D$  were found to be the same.<sup>10</sup>

Considering a similar set of schemes to those proposed for toluene (eq 3 and 4), we have determined the intermo-

lecular deuterium isotope effect for the bromination of cyclohexane and perdeuteriocyclohexane under a variety of conditions. Since abstraction of deuterium from perdeuteriocyclohexane involves contributions from both  $\alpha$  and  $\beta$  secondary deuterium isotope effects, the intramolecular isotope effect,  $(k_H/k_D)$ , cannot be determined and, although these secondary effects should be small,<sup>8</sup> the values obtained are reported as  $k_{RH}/k_{RD}$  and not  $k_H/k_D$  (see Table I).

The intermolecular deuterium isotope effect found in the vapor phase (reactions 1–5),  $k_{RH}/k_{RD} = 5.4$ , was obtained using a sufficiently high concentration of bromine so that reversal of the radicals formed would not compete with transfer with molecular bromine. Mass spectral analysis of the unbrominated substrates before and after the reaction confirmed the absence of reversal (see Table II).<sup>11</sup>

In solution, the observed value of  $k_{RH}/k_{RD}$  was found to be variable and dependent on the concentration of molecular bromine. Under conditions similar to those used by other workers<sup>12</sup> to obtain relative rates of reactions of hydrocarbons with bromine (reactions 31–32), the value  $k_{RH}/k_{RD} = 3.1$  was found. Since the reaction was carried out to the complete consumption of bromine (at  $>50\%$  of the reaction, the ratio of  $[HBr]/[Br_2] > 1$ ), reversal should be an important reaction. The unbrominated substrate recovered after the reaction was found to have undergone extensive reversal (see Table II). If a mechanism similar to that proposed for toluene takes place for cyclohexane (eq 4), the low value of  $k_{RH}/k_{RD}$  observed under these conditions will be due to external reversal (observed by scrambling of D for H and H for D) and internal return (which is not detectable).

Table II. Isotopic Composition of the Parent Ions from Cyclohexane and Perdeuteriocyclohexane before and after Bromination<sup>a</sup>

Reaction no.	M <sup>+</sup> , %					M <sup>+</sup> , %			
	<i>d</i> <sub>12</sub>	<i>d</i> <sub>11</sub>	<i>d</i> <sub>10</sub>	<i>d</i> <sub>9</sub> - <i>d</i> <sub>0</sub>	<i>d</i> <sub>12</sub> - <i>d</i> <sub>3</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>0</sub>	
<i>b</i>	94.0	6.0	0.0	0.0	0.0	0.0	0.0	100.0	
<i>b</i>	93.7	6.0	0.3	0.0	0.0	0.0	0.0	100.0	
<i>b</i>	93.7	6.3	0.0	0.0	0.0	0.0	0.0	100.0	
1	93.8	6.0	0.2	0.0	0.0	0.0	0.0	100.0	
2	94.0	5.8	0.2	0.0	0.0	0.0	0.0	100.0	
4	93.9	6.1	0.0	0.0	0.0	0.0	0.0	100.0	
7	94.2	5.8	0.0	0.0	0.0	0.0	0.0	100.0	
23	94.1	5.9	0.0	0.0	0.0	0.0	0.0	100.0	
24	93.6	6.1	0.3	0.0	0.0	0.0	0.6	99.4	
25	93.8	6.2	0.0	0.0	0.0	0.0	0.0	100.4	
28	94.0	6.0	0.0	0.0	0.0	0.0	0.1	99.9	
29	94.2	5.8	0.0	0.0	0.0	0.0	0.0	100.0	
30	93.4	6.6	0.0	0.0	0.0	0.0	0.3	99.7	
31	83.2	14.3	2.5	0.0	0.0	0.6	8.4	91.0	
32	84.6	14.9	0.5	0.0	0.0	0.6	9.0	90.4	

<sup>a</sup> Values reported are corrected for C<sup>13</sup> natural abundance.

<sup>b</sup> Starting material.

An estimation of the magnitude of the cage contribution,  $(k_{-1}^D[\text{DBr}] + k_d)/(k_{-1}^H[\text{HBr}] + k_d)$ , could be obtained by a study of the variation of the observed value of  $k_{RH}/k_{RD}$  as a function of the concentration of bromine (reactions 6-32). By monitoring the amount of external exchange (mass spectral scrambling) as the concentration of bromine is increased, it could be shown that, at approximately 0.07-3.6 M bromine, when the concentration of bromine to hydrogen bromide was always  $\gg 1$ , the external exchange could be eliminated and the observed  $k_{RH}/k_{RD}$  was equal to 4.3. The difference between 5.4, the vapor phase value, and 4.3 is attributable, presumably, to cage reversal. Applying eq 5,  $(k_{-1}^D[\text{DBr}] + k_d)/(k_{-1}^H[\text{HBr}] + k_d) = 0.80$ . The magnitude of the cage filtering process, as would be predicted, is found to be closer to unity for the exothermic, less selective, cage transfer of a cyclohexyl radical than that observed for the near thermoneutral transfer reactions of the more stable, more selective, benzyl radicals.

In the classic studies by Hammond on the effect of cage recombination upon the yield of "free" radicals obtained from the decomposition of AIBN, it was found that molecular bromine could act as an effective scavenger of radicals free of the solvent cage. It was further found when the AIBN decomposition was carried out in liquid bromine (~18 M) that cage recombination was completely eliminated by scavenging of the radicals from the solvent cage.<sup>13</sup>

When the concentration of bromine was increased to 7.7 M (39% liquid bromine, reactions 14-19, Table I), it was anticipated that the observed value of  $k_{RH}/k_{RD}$  would increase due to cage scavenging of the radicals by the high concentration of molecular bromine. In accord with this expectation, the observed values were increased and were intermediate between the vapor phase values and the solution values (reactions 20-29). The intermediate values represent, presumably, incomplete scavenging of the radicals from the solvent cage. When the concentration of molecular bromine was increased further to  $>10$  M and  $[\text{Br}_2]/[\text{HBr}] \gg 1$ , then not only is external reversal eliminated but scavenging from the cage is essentially complete and the value for the observed  $k_{RH}/k_{RD}$  (reactions 6-13, Table I) is equal to that obtained in the vapor phase (reactions 1-5, Table I).

It is conceivable that, at high concentrations of molecular bromine, a complex radical ( $\text{Br}_3\cdot$ ) would be more selective than a bromine atom, and that this increased selectivity could account for the higher values of  $k_{RH}/k_{RD}$  observed when the reaction is carried out in liquid bromine. This

suggestion does not, however, explain why the vapor phase value of the isotope effect for both toluene and for cyclohexane brominations are larger than they are in the condensed phase, nor does it explain the coincidence of  $k_{RH}/k_{RD}$  values for cyclohexane in liquid bromine and in the vapor phase.

## Experimental Section

**Materials.** Perdeuteriocyclohexane (Merck, Sharp & Dohme, >99 atom % D) was purified by two preparative GLC collections (20 ft  $\times$  0.25 in. 10% Carbowax 20M TPA or 10 ft  $\times$  0.25 in. 10% UCON 50 LB 550X, glass columns); GLC analysis showed it to be >99.9% pure, and mass spectral analysis (AEI MS9, 12 eV) showed it to contain 99.4 atom % D.

Cyclohexane (Phillips 66, research grade) was washed with concentrated sulfuric acid, water, 5% aqueous sodium carbonate, and water, dried over anhydrous sodium sulfate, and distilled, bp 76.0° (700 mm).

Molecular bromine (Raylo or McArthur Chemical Co., reagent grade) was washed with concentrated sulfuric acid and distilled from phosphorus pentoxide, bp 57.3° (700 mm).

Freon 113 (Matheson) and Freon 112 (PCR) were distilled from phosphorus pentoxide through a 12 in. Vigreux column, bp 45.5 and 88.0° (700 mm), respectively.

**Analysis.** A 24 ft  $\times$  0.25 in. glass column packed with 7.5% UCON 50 LB 550X on Chromosorb P AW, 80-100 mesh, was used to analyze the reaction mixtures. Peak areas were calculated using the peak height-peak width method. Relative reactivities were determined by the method reported previously by this laboratory.<sup>14</sup>

**Gas Phase Competitive Brominations.** Aliquots (0.20 ml) of a solution of cyclohexane (1.312 M), perdeuteriocyclohexane (1.275 M), Freon 112 (1.402 M, internal standard), and bromine (10.25 M) were transferred into Pyrex breakseals, degassed once by the freeze-thaw method, and sealed. The breakseals were attached to a 5-l. reaction bulb and, after the bulb was degassed, the substrates were introduced into the reaction vessel. After 30 min equilibration in the absence of light, the bulb was irradiated (one 100-W incandescent lamp) for sufficient time to ensure at least 12% reaction of cyclohexane-*d*<sub>12</sub>. The contents of the bulb were condensed, and the excess bromine was destroyed with ice-cold 10% sodium bisulfite solution. One milliliter of Freon 113 was added and the Freon solution washed once with water and dried ( $\text{MgSO}_4$ ). Controls on the recovery from the reaction bulb and on the work-up showed that >98% of the substrates and internal standard could be recovered, and that the ratios  $\text{C}_6\text{H}_{12}/\text{Freon 112}$ ,  $\text{C}_6\text{D}_{12}/\text{Freon 112}$ , and  $\text{C}_6\text{H}_{12}/\text{C}_6\text{D}_{12}$  did not change within experimental error ( $\pm 1.8\%$ ). The reaction mixture was then analyzed by GLC.

**Liquid Phase Competitive Brominations.** Aliquots of a Freon 113 solution (see Table I) of cyclohexane, perdeuteriocyclohexane, Freon 112 (internal standard), and bromine were pipetted into Pyrex tubes, degassed five times by the freeze-thaw method, and sealed. The tubes were irradiated at  $21.0 \pm 0.1^\circ$  with two 200-W incandescent lamps until at least 10% of the cyclohexane-*d*<sub>12</sub> had reacted. The reactions were quenched by immersing the tubes in liquid nitrogen, and the excess bromine was destroyed with an ice-cold 10% sodium bisulfite solution. The Freon solution was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and analyzed. The reactions that were 18 M in bromine were run without solvent; after the excess bromine was destroyed, the organic substrates were extracted with Freon 113.

**Analysis of H in  $\text{C}_6\text{D}_{12}$  and D in  $\text{C}_6\text{H}_{12}$ .** The liquid phase solutions of cyclohexane and cyclohexane-*d*<sub>12</sub> in Freon 113 were concentrated to about 3 ml on a 24 in. Teflon spinning-band column. The gas phase solutions were used without concentration. The unbrominated  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$  were collected, together, by preparative GLC (10 ft  $\times$  0.25 in. 10% UCON 50 LB 550X, 50°). The mixture was analyzed by mass spectrometry (AEI MS9, 12 eV), and the amount of protium in perdeuteriocyclohexane and the amount of deuterium in cyclohexane was calculated by the method of Biemann.<sup>15</sup>

**Acknowledgment.** The authors thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

## References and Notes

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

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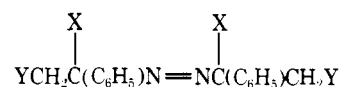
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**Abstract:** Secondary  $\alpha$ -deuterium isotope effects were obtained for the thermal decomposition of 1,1'-diphenylazoethane (I) and 1,1'-diphenylazoethane-1,1'- $d_2$  (I- $d_2$ ) at 103.90°. Samples of I and I- $d_2$  prepared by (a) LiAlH<sub>4</sub> and LiAlD<sub>4</sub> 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  $\alpha$  effect of  $1.195 \pm 0.006$  was obtained from I-1 and I- $d_2$ -1 upon correction of  $k_H/k_D = 1.191 \pm 0.006$  for  $0.040 \pm 0.002$  atoms of  $\alpha$  protium. An  $\alpha$  effect of  $1.198 \pm 0.014$  was obtained from I-2 and I- $d_2$ -2 upon correction of  $k_H/k_D = 1.159 \pm 0.010$  for  $0.415 \pm 0.016$  atoms of  $\alpha$  protium and  $0.245 \pm 0.105$  atoms of  $\beta$  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  $\alpha$  effect of 1.195 for I. The  $\alpha$  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  $\alpha$  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.  $0.33 \text{ m dyn } \text{Å}/(\text{rad})^2$  rather than  $0.23 \text{ m dyn } \text{Å}/(\text{rad})^2$ .

In a series of classic experiments, Seltzer<sup>2</sup> and Seltzer and Dunne<sup>3</sup> utilized  $\alpha$ -secondary deuterium isotope effects to demonstrate (1) a concerted mechanism for pyrolysis of 1,1'-diphenylazoethane<sup>4</sup> (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<sup>5</sup> of the  $\alpha$ -deuterium and primary nitrogen<sup>6</sup> effects in pyrolysis of I, II, and III and the carbon effect<sup>3</sup> at the methyl group of III resulted in a quantification of these conclusions.<sup>6</sup> Also, the deuterium isotope effects in thermolysis of I-methyl- $d_6$ <sup>7</sup> and I-ring- $d_{10}$ <sup>8</sup> demonstrate for the transition state of I that hyperconjugative stabilization is of little importance<sup>7</sup> and that delocalization of the incipient odd electron produces a negligible perturbation of the aromatic CH force constants.<sup>8</sup>

To investigate the influence of molecular structure on the potential-energy hypersurface for pyrolysis,  $\alpha$  effects were measured for decomposition of meso- and dl-1,1',2,2'-tetraphenylazoethane<sup>9</sup> (IV), 1,1'-diphenylazobutane<sup>10</sup> (V), and 2,2'-dimethoxy-1,1'-diphenylazoethane<sup>10</sup> (VI). Using structure-reactivity relationships, the  $\alpha$  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.<sup>9–11</sup> However, the  $\alpha$  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.<sup>10,11</sup> Furthermore, thermolysis of 3,12,15,24-tetraphenyl-1,2,13,14-tetraza-



I, Y = X = H  
 I- $d_2$ , Y = H; X = D  
 meso-IV, Y = C<sub>6</sub>H<sub>5</sub>; X = H  
 meso-IV- $d_2$ , Y = C<sub>6</sub>H<sub>5</sub>; X = D  
 V, Y = CH<sub>3</sub>CH<sub>2</sub>; X = H  
 V- $d_2$ , Y = CH<sub>3</sub>CH<sub>2</sub>; X = D  
 VI, Y = CH<sub>3</sub>O; X = H  
 VI- $d_2$ , Y = CH<sub>3</sub>O; X = D

1,13-cyclotetracosadiene (VII) yielded an  $\alpha$  effect of 1.20<sup>12</sup> rather than a value of ca. 1.27.

Because the magnitude of the  $\alpha$  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  $\alpha$ -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