

# The Possibility of Energy Transfer through a Hydrocarbon Chain during Thermal Decomposition of an Azo Compound<sup>1</sup>

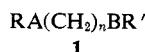
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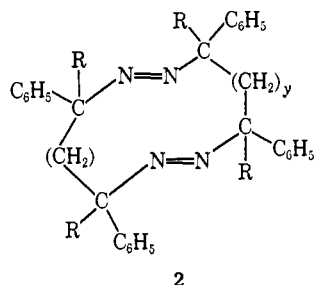
**Abstract:** The mechanism of the thermal decomposition of a 24-membered ring with two azo groups has been studied by kinetics and the secondary  $\alpha$ -deuterium isotope effect. A concerted loss of both nitrogen molecules is ruled out on the basis of the isotope effect,  $k_H/k_D = 1.20$  (four atoms of D). A crossover experiment indicates that the biradical, formed after the expulsion of the first nitrogen molecule, couples to reclose the ring before the second nitrogen molecule is lost. Because there are eight methylene groups between the two azo groups, it is unlikely that vibrational excitation is transferred between azo groups. Rather, it is probable that the two azo groups act independently.

The mechanism by which energy is transferred between molecules is still under investigation.<sup>2</sup> The process and the timing of energy transfer from one part of a molecule to another also requires further elucidation. When this excess energy is in the form of electronic excitation, intramolecular energy transfer has been shown to take place by the partial overlap of chromophores.<sup>3</sup> It appears that vibrationally excited intermediates, deriving their energy through chemical reaction, quickly distribute their internal energy from the reaction center to other bonds in the intermediate.<sup>4</sup> Of course competing with this process is the removal of energy from the reaction center by collisional deactivation. Even at high pressures, however, the distribution of internal energy is not completely quenched.<sup>5</sup> Consequently, it might be expected that excess energy which a molecule in solution receives by chemical reaction or by collision would be partially distributed before collisional deactivation. This study is concerned with the possibility of intramolecular distribution of internal energy.

More specifically, if the bonds to A and B in **1** are



labile, how small does  $n$  have to be so that energy deposited at or near A can migrate to B and cause rupture of bonds at both A and B? The requirement that both A and B be labile groups can be met when these are both azo groups in a molecule such as **2**. As the first sys-



**2**

tem in a series that we hope to investigate, we chose a molecule where  $x$  and  $y$  are large enough to make it improbable that some of the vibrational energy deposited by collision in one azo group be transmitted to the other through the methylene chain. Fortunately, Overberger and Lapkin<sup>6</sup> have already prepared **2a** ( $R = H$ ) where  $x = y = 8$ .

In previous studies, the secondary  $\alpha$ -deuterium effect has been shown to be a powerful tool in determining the detailed sequence of thermally induced bond rupture of aralkyl azo compounds.<sup>7</sup> This same technique has been applied here. In this study we report the synthesis of the tetradeuterated analog, **2b** ( $R = D$ ), the isotope effect in the thermal decomposition, and the results of a crossover experiment.

## Experimental Section

**3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosadiene** was prepared and purified by catalytic reduction, at atmospheric pressure, of 3,12,15,24-tetraphenyl-1,2,13,14-tetraaza-2,12,14,24-cyclotetracosatetraene according to the reported method;<sup>8</sup> mp 131–132° (lit.<sup>6</sup> 130–131°);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  359 m $\mu$  ( $\epsilon$  82),  $\lambda_{\text{min}}^{\text{CHCl}_3}$  323 m $\mu$  ( $\epsilon$  35) (lit.<sup>6</sup>  $\lambda_{\text{max}}$  355 and 357 m $\mu$  ( $\log \epsilon$  2.1)).

**3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosadiene-3,12,15,24-d<sub>4</sub>** was prepared in similar fashion by catalytic reduction with deuterium in ethanol-*d*<sup>8</sup> as solvent, mp 131–132°;  $\lambda_{\text{max}}^{\text{CHCl}_3}$  358 m $\mu$  ( $\epsilon$  78);  $\lambda_{\text{min}}^{\text{CHCl}_3}$  323 m $\mu$  ( $\epsilon$  41). The atom per cent of deuterium in the cyclic azo compound was determined both by nmr analysis of the natural and deuterated compound and by mass spectral analysis of the hydrogen gas derived from the compound upon combustion and subsequent reduction of the water.<sup>9</sup> The average concentration in each of the four benzylic hydrogen positions was found to be 93.45  $\pm$  0.28% by combustion and 94.9  $\pm$  4.7% by nmr. The nmr peaks for phenyl, methylene, and benzylic hydrogens were all very broad and therefore analysis by nmr integration is difficult and leads to a large error.

Kinetics of the thermal decomposition was followed by observing the loss of absorption at 355 m $\mu$ . Ethylbenzene was distilled from sodium,  $n_D^{20}$  1.4932 (lit.<sup>10</sup> 1.4933). Ethylbenzene solutions of the azo compound in quartz uv cells were degassed on a vacuum line by repeated freeze-pump-thaw cycles. The cell was then sealed under vacuum and placed in a self-contained thermostated cell compartment attached to a Beckman DU spectrophotometer.<sup>11</sup>

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

(2) See, e.g., B. S. Rabinovitch and M. C. Flowers, *Quart. Rev. (London)*, **18**, 122 (1964); W. H. Flygare, *Accounts Chem. Res.*, **1**, 121 (1968).

(3) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 2322 (1965).

(4) R. E. Harrington, B. S. Rabinovitch, and H. M. Frey, *J. Chem. Phys.*, **33**, 1271 (1960).

(5) B. S. Rabinovitch and R. W. Diesen, *ibid.*, **30**, 735 (1959).

(6) C. G. Overberger and M. Lapkin, *J. Amer. Chem. Soc.*, **77**, 4651 (1955).

(7) S. Seltzer, *ibid.*, **83**, 2625 (1961); **85**, 14 (1963); S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

(8) S. Seltzer, *ibid.*, **87**, 1534 (1965).

(9) S. Seltzer, *ibid.*, **83**, 1861 (1961).

(10) A. Riddick and E. E. Toops, Jr., "Techniques of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955, p 77.

(11) S. Seltzer and E. J. Hamilton, *J. Am. Chem. Soc.*, **88**, 3775 (1966).

The kinetics of decomposition of the natural and tetradeuterated azo compound was measured at the same time in the same cell compartment. In this way errors due to thermal fluctuation are minimized. The temperature at which the kinetics were measured,  $112.95 \pm 0.02^\circ$ , was determined with a Rubicon potentiometer and a thermocouple, previously calibrated against an NBS thermometer. All rate data were fitted to a first-order rate equation by a nonlinear least-squares computer program.<sup>4</sup>

**Test for Intermolecularity.** In preliminary experiments the solutions used to measure the kinetics of decomposition and originally containing the natural azo compound, **2a**, were combined after nitrogen evolution. The solvent was removed by vacuum distillation. The residue from 0.4502 g of azo compound was chromatographed on neutral alumina (column dimensions: diameter, 1 cm; length, 41 cm) and eluted with chloroform; two fractions were collected. The first, fraction A, 0.3122 g (76%), was molecularly distilled at  $212^\circ$  at  $1 \mu$  (0.2752 g). The compound was apparently 1,2,11,12-tetraphenylcycloicosane, as reported previously.<sup>6</sup> *Anal.* Calcd for  $C_{44}H_{56}$ : C, 90.35; H, 9.65. Found: C, 89.88; H, 9.60. The second fraction (B) amounting to 0.1061 g appeared to be a mixture. Elemental analysis of either fraction indicated nitrogen to be absent. Fraction B could be separated further into a white crystalline fraction and a yellow waxy solid. Further identification of these fractions was not attempted because of the very small amount of material available.

The thermal decomposition and separation of products were repeated for a reaction mixture containing initially 0.2000 g of the natural cyclic azo compound, **2a**, and 0.2000 g of the tetradeuterated cyclic azo compound, **2b**, in 40 ml of ethylbenzene. Prior to thermolysis the solution was degassed and the ampoule sealed under vacuum. The reaction was allowed to proceed for 55 hr (greater than 20 half-lives) at  $113^\circ$ . Chromatographic separation yielded 0.296 g (74%) of fraction A. The molecular distillate, 0.207 g, was subjected to mass spectral analysis on an Atlas CH-4 instrument by the direct inlet procedure.<sup>12</sup> Mass spectral analyses were obtained similarly for the molecular distillates of fraction A of the products of thermolysis from solutions containing initially only the natural or tetradeuterated azo compound.

## Results and Discussion

Overberger and Lapkin<sup>6</sup> studied the kinetics of decomposition of **2a** in xylene by measuring the volume of nitrogen evolved. They noted a very short rapid rate followed by a slower first-order rate for at least one half-life. In the present study, the rate of decomposition was followed by the loss of azo linkage absorption at  $355 \mu\mu$  of degassed solutions of the azo compound in ethylbenzene. Contrary to the observations of the previous workers we find a slightly slower rate for the first 10–15 min ( $\sim 0.1$  half-life) followed by excellent first-order kinetics to at least 95% decomposition. Since the reaction is started by placing the reaction cell which is initially at ambient temperatures into the cell compartment thermostated to  $113^\circ$ , it is entirely reasonable that the rate for the first 15 min be lower because of incomplete temperature equilibration. The rate constants obtained from nonlinear least-squares fitting<sup>4</sup> of the rate data are shown in Table I.

In our initial study of energy transfer along a hydrocarbon chain we chose **2** as a molecule where we could expect unsuccessful energy transfer between the two azo groups. The chain of eight methylene groups would be able to accommodate 66 vibrational modes and thereby provide a good sink for vibrational excitation. The observation that the loss of azo groups follows excellent first-order kinetics is consistent with a concerted loss of both nitrogen molecules. It is also consistent with other mechanisms that will be discussed below. To help us differentiate between a concerted or stepwise loss of two nitrogen molecules, we turned to a study of the magnitude of the secondary  $\alpha$ -deuterium

(12) We thank Professor Carl Djerassi for providing the mass spectra.

**Table I.** First-Order Rate Constants for the Thermal Decomposition of 3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosadiene and 3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetracosadiene-3,12,15,24- $d_4$  in Ethylbenzene at  $112.95^\circ$

<b>2a</b> $k_H \times 10^6, \text{sec}^{-1}$	<b>2b</b> $k_D \times 10^6, \text{sec}^{-1}$
8.852	7.513
8.747	7.323
8.597	7.517
8.847	7.268
Av 8.761 $\pm$ 0.119 <sup>a</sup>	7.405 $\pm$ 0.129 <sup>a</sup>
$(k_H/k_D) \text{ obsd} = 1.183 \pm 0.026^a$	

<sup>a</sup> Standard deviation.

isotope effect on thermal decomposition. The tetradeuterated isomer, **2b** ( $R = D$ ), was synthesized by a similar route as that leading to **2a**. Ultraviolet spectra of the two compounds are very similar. Analysis by combustion and by nmr indicates that on each of the four carbon atoms that are bonded to nitrogen there are 0.935 atom of deuterium. First-order rate constants for loss of azo absorption from **2a** and **2b** are shown in Table I.

Based on our previous work,<sup>4,13</sup> it is most probable that the two carbon–nitrogen bonds to one azo group in **2** rupture in a concerted manner. If all four carbon–nitrogen bonds in **2** ruptured in concerted fashion we would expect the secondary deuterium effect to be about  $(1.12)^4$  or 1.57 at  $105^\circ$ . The observed effect at this temperature, corrected for complete deuteration at each benzylic hydrogen position, is  $1.20 \pm 0.02$ . The measured effect is only consistent with a stepwise loss of the two nitrogen molecules assuming that the two carbon–nitrogen bonds to one azo link break simultaneously. As expected, energy transfer between the two azo linkages is too inefficient.

The first-order kinetics that is observed is consistent with a stepwise mechanism where  $k_2 \gg k_1$  for eq 1 and 2. A is the starting molecule containing two azo



groups. B is an intermediate containing only one azo linkage. A mechanism whereby  $k_1$  and  $k_2$  are of the same order of magnitude would not lead to apparent first-order kinetics except in the special case where  $k_1 = 2k_2$ . That is to say, except for a statistical factor of 2, the energetics of the loss of the first nitrogen molecule is exactly the same as for the loss of the second even though the second may be from an opened diradical or reclosed ring. This assumes that the extinction coefficient of the molecule containing two azo linkages is exactly twice that of the intermediate containing only one azo group. That a series first-order reaction with these restrictions leads to apparent first-order kinetics follows from the general treatment below. Here A and B refer to concentrations and the other letters have their

$$A = A_0 e^{-k_1 t} \quad (3)$$

$$B = \frac{k_1}{k_2 - k_1} A_0 (e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

(13) S. Seltzer and S. G. Mylonakis, *J. Am. Chem. Soc.*, **89**, 6584 (1967).

usual meaning. The optical density at time  $t$  is given by

$$\text{OD}_t = A\epsilon_A + B\epsilon_B \quad (5)$$

If spectrophotometric measurements are made at a wavelength that is sensitive to the concentration of azo linkages,  $\epsilon_A \neq \epsilon_B$ . Therefore let  $\epsilon_A/\epsilon_B = R$  and  $k_1/k_2 = S$ . Then by substitution of eq 3 and 4 into 5 we obtain

$$\text{OD}_t = R\epsilon_B A_0 e^{-k_1 t} + \frac{Sk_2}{k_2 - Sk_2} \epsilon_B A_0 (e^{-k_1 t} - e^{-k_2 t}) \quad (6)$$

which reduces to

$$\text{OD}_t = \frac{S}{S-1} \epsilon_B A_0 e^{-k_2 t} \quad (7)$$

when

$$R = \frac{S}{S-1} \quad (8)$$

A plot of  $\log \text{OD}_t$  vs.  $t$  will appear to support first-order kinetics if  $S > 1$  and eq 8 is obeyed.<sup>13a</sup> For the special case where  $R = S = 2$ , both of the above conditions are satisfied, and  $k_2$  will be the observed apparent first-order constant. The condition that  $R = S = 2$  implies that the two azo groups act independently of one another.

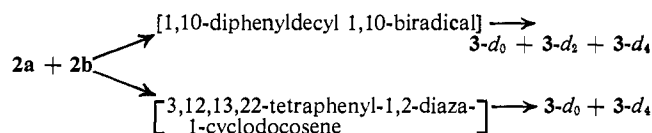
The high yield (72%) of 1,2,11,12-tetraphenylcycloicosane (**3**) from thermal decomposition of **2** led the previous workers to suggest that a single molecule of nitrogen is lost first.<sup>6</sup> The biradical product couples to close the ring before the second molecule is lost. An alternate mechanism whereby loss of the second nitrogen molecule competes with ring closure would lead to the formation of 1,10-diphenyldecyl 1,10-biradical. The fact that a high yield of **3** is obtained is not compelling evidence to choose against the formation of 1,10-diphenyldecyl 1,10-biradical because the preferred reaction of this biradical might be dimerization rather than the characteristically unfavorable cyclization reaction required to form a ten-membered ring.<sup>14</sup>

To determine to what extent 1,10-diphenyldecyl 1,10-biradical is formed and later dimerizes we investigated the possibility of crossover in the formation of **3**. It was hoped that these results might help us to choose between the two stepwise mechanisms that are consistent with both the isotope effects and kinetic measurements, viz.,  $k_1 = 2k_2$  and  $k_2 \gg k_1$ . Approximately equal amounts of **2a** and **2b** were mixed and

(13a) NOTE ADDED IN PROOF. The high experimental precision within each kinetic run (i.e.,  $\pm 0.2\%$  error in the first-order rate constant) would allow us to see easily a deviation of 10% or more from the relation  $R = S = 2.0$ .

(14) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 198-199.

allowed to thermolyze in ethylbenzene. The products were chromatographed on alumina. The 20-membered ring was examined mass spectrometrically in the parent region.



The spectra from this mixture were compared with that for **3-d<sub>0</sub>** and **3-d<sub>4</sub>** obtained from solution containing initially only **2a** and **2b**, respectively.<sup>12</sup> As shown in Table II no **3-d<sub>2</sub>** could be detected. It appears then

Table II. Mass Spectra of the Cyclic Products from Natural (**2a**) and Deuterated (**2b**) 3,12,15,24-Tetraphenyl-1,2,13,14-tetraaza-1,13-cyclotetradecadiene<sup>a</sup>

$m/e$	Reactants		
	<b>2a</b>	<b>2b</b>	<b>2a + 2b</b>
590	<i>b</i>	6.5	<i>c</i>
589	<i>b</i>	52.9	44.0
588	<i>b</i>	100.0 <sup>d</sup>	71.0
587	<i>b</i>	24.1	<i>c</i>
586	7.2	18.2	<i>c</i>
585	46.5	<i>b</i>	50.0
584	100.0 <sup>d</sup>	<i>b</i>	100.0 <sup>d</sup>
583	2.3	<i>b</i>	<i>c</i>
582	<i>b</i>	<i>b</i>	<i>c</i>
581	<i>b</i>	<i>b</i>	<i>c</i>

<sup>a</sup> Normalized parent region patterns. <sup>b</sup> Less than 0.1% of parent peak. <sup>c</sup> Less than 1% of parent peak. <sup>d</sup> Parent ion currents were in the ratio of 10:4:1 for **2a**, **2b**, and **2a + 2b**, respectively.

that ring closure after the loss of the first nitrogen molecule is at least 100 times faster than the loss of the second nitrogen molecule. That this high specificity in coupling is due to a cage effect is unlikely. Such a cage effect would not be expected to be so efficient.<sup>14,15</sup> While our experiments demonstrate the formation of 1,10-biradical to be unlikely, they do not allow a rigorous choice between the two stepwise mechanisms, viz.,  $k_1 = 2k_2$  or  $k_2 \gg k_1$ ; they only place the restriction that  $k_2 \geq 10^4 k_1$  if the latter mechanism operates. Since the ring is so large we would expect little strain in the molecule. It is difficult, therefore, to rationalize why  $k_2$  should be so much larger than  $k_1$ . It appears that a mechanism where the two azo groups are ejected independently (i.e.,  $k_1 = 2k_2$ ) is more probable.

**Acknowledgments.** The authors are indebted to Professor Carl Djerassi for the mass spectra and to Dr. D. R. Christman and Mrs. C. Paul for the deuterium analysis.

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