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HIGH PRESSURE STUDIES. XII. DECOMPOSITION OF A CYCLIC AZO COMPOUND.[1]

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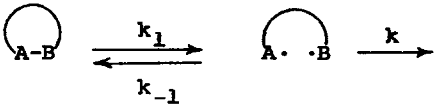
Rates of one-bond homolytic scission reactions characterized by cage return are sensitive to medium viscosity if separative diffusion is a competing process. Many examples are available.[3] This test cannot be applied, however, to cyclic systems (eq. 1) for the latter condition does not pertain; the radical centers are connected.

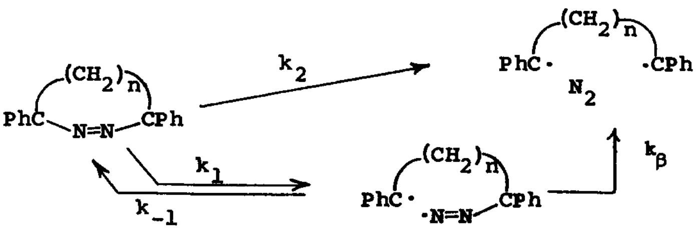


(1)

Pressure effects on the observed decomposition rate constants might provide information about such return processes in cyclic systems (eq. 2). The

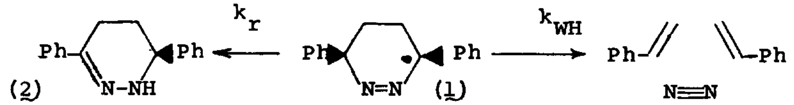
$$\Delta V^*_{obs} = \Delta V^*_1 + RT\partial \ln(1 + k_{-1}/k)/\partial P \qquad (2)$$

observed decomposition activation volume will depend not only on that for homolytic scission, but the pressure dependence of the competing processes k_{-1} and k (eq. 2).[4] We have chosen to investigate a series of cyclic azo compounds which could conceivably decompose via two diradical mechanisms.[5] Our beginning



hypotheses were that the pressure dependences of the one and two-bond scission steps (k_1 and k_2) would be similar to each other and comparable to the values in open chain systems; while the pressure dependence of k_{-1}/k_β (i.e., k_{-1}/k, eqs. 1 and 2) would make ΔV^*_{obs} significantly greater than either ΔV^*_1 or ΔV^*_2.[1a,4]

We have examined a "six-ring" member of this series (n=2), <u>cis</u>-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (1), and the results are reported here.[6] Decomposition is complicated by the facile rearrangement (k_r) to the cyclic hydrazone (2) and the possibility of an allowed concerted opening (k_{WH}) giving styrene and molecular nitrogen.[6b,7] The latter products, which are observed,

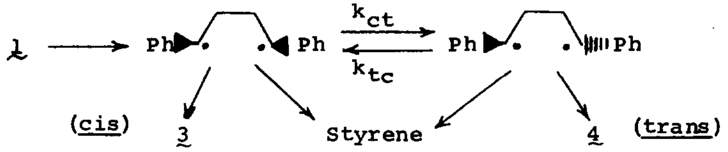


might also be expected via the diradical mechanisms along with the additionally observed <u>cis</u>- and <u>trans</u>-1,2-diphenylcyclobutane (3 and 4, respectively).

Decomposition of 1 (toluene, 60°) monitored by loss of the azo absorbance in the UV (383 mμ) was retarded by increasing pressure (Table I). The apparent ΔV^* from these data is in the range of +2 to +3 cc/mole. Inspection of the UV spectra, and the hydrocarbon product yields (Table II), however, indicate that hydrazone formation (k_r) is substantially competitive with the other possible decomposition modes. Decomposition rate constants corrected for this process (Table I) give a value of ΔV^*_{obs} of about +5 cc/mole. This value is remarkably similar to others determined for simultaneous scission of two-bonds during decomposition of acyclic azo compounds.[1a,4]

Yields of each hydrocarbon product were determined by glpc analyses of completely decomposed samples of 1 in toluene (60°) (Table II). The total hydrocarbon yield seems to decrease with increasing pressure and analyses of UV traces of totally decomposed samples indicated a concomitant increase in the yield of cyclic hydrazone.[8] As far as we could ascertain, these products were the only ones present in significant yield; however, it is worth noting that low yields (<u>ca</u>. 0.5%) of 1-phenyltetralin were observed in each run.[9]

As noted previously,[6b] the products are consistent with a diradical mechanism and so are their pressure dependences. The relatively large (<u>cis</u>)/(<u>trans</u>) ratio at atmospheric pressure presumably reflects entry into the <u>cis</u> diradical and the increase of the ratio with pressure would be consistent with



an acceleration of diradical closure and/or retardation of the isomerization process (k_{ct}). However, if ring closure is accelerated by pressure, scission should simultaneously be retarded. The relatively small (and opposite) variations in (*cis*)/(styrene) and (*trans*)/(styrene) do not fit this behavior; but they are in agreement with relatively minor differences in volume between the high energy diradicals and their closure and scission transition states. Intramolecular rotation, on the other hand, might be expected to possess pressure dependence characteristics more akin to those of diffusion and "rotational diffusion" processes.[4,10] We thus favor a pressure retardation of diradical isomerization as the explanation for the marked increase in (*cis*)/(*trans*) with pressure.

These data support the diradical mechanism and possibly a two-bond scission initial step. However, firm interpretations of the results must await the completion of studies in progress on higher homologues.

Table I. Kinetic Data for Decomposition of **1** at Several Pressures.[a]

P,atm.	$k_{obs} \times 10^5$, sec^{-1}	% Hydrocarbon	$k_{corr} \times 10^5$, sec^{-1} [b]
1	7.85	85	6.6
1,350	7.19	74	5.3
2,310	6.16	69	4.3
3,300	5.48	74	4.0
4,290	4.62	63	2.9
5,260	4.70	54	2.5

(a) Toluene, 60°; (b) k_{corr} = (%-Hydrocarbon x 10^{-2})xk_{obs}.

Table II. Pressure Dependence of Product Yields from Decomposition of **1**.[a]

P,atm.	(*cis*)/(Styrene)[b]	(*trans*)/Styrene)[b]	(*cis*/*trans*)[c]	% Hydrocarbon[d]
1	0.50	0.20	2.5	85
1,350	0.60	0.21	2.9	74
2,310	0.63	0.18	3.5	69
3,300	0.64	0.16	3.9	74
4,290	0.74	0.18	4.1	63
5,260	0.73	0.16	4.6	54

(a) Toluene, 60°. (b) Ratios of absolutely determined molar yields; *cis* = **3** and *trans* = **4**. (c) Area ratios multiplied by the relative thermal conductivity ratio for the two cyclobutanes. (d) Sum of the absolute yields of styrene and the isomeric 1,2-diphenylcyclobutanes.

References

(1)(a) Part XI is the manuscript by R. C. Neuman, Jr., G. Lockyer, Jr., and M. J. Amrich, directly preceding this part in Tetrahedron Letters. (b) Support by the National Science Foundation (GP-8670 and GP-23968) is gratefully acknowledged. (c) Written during the tenure of RCN as an NIH Special Research Fellow, 1971-72.

(2) NDEA Predoctoral Fellow, 1969-72.

(3) Leading references are given by W. Pryor and W. K. Smith, J. Am. Chem. Soc., **92**, 5403 (1970).

(4)(a) R. C. Neuman, Jr., and J. V. Behar, ibid., **91**, 6024 (1969). (b) R. C Neuman, Jr., Intra-Science Chem. Reports, **3**, 269 (1969). (c) R. C. Neuman, Jr., and R. J. Bussey, J. Am. Chem. Soc., **92**, 2440 (1970). (d) R. C. Neuman, Jr., and J. V. Behar, J. Org. Chem., **36**, 654, 657 (1971). (e) R. C. Neuman, Jr., and G. D. Holmes, J. Am. Chem. Soc., **93**, 4242 (1971).

(5) Some relevant literature is reviewed by R. G. Bergman and W. L. Carter, ibid., **91**, 7411 (1969).

(6)(a) This compound was the subject of an extensive investigation by Kopecky[6b] at atmospheric pressure. Our early attempts to synthesize it were relatively unsuccessful, although great care was taken to explicitly follow reported experimental procedures. Continued attempts led to successful syntheses yielding **1** in high purity as judged by N_2 evolution, product yields, kinetic data, and physical properties. (b) K. R. Kopecky and S. Evani, Can. J. Chem., **47**, 4041 (1969).

(7) See (a) J. A. Berson and S. S. Olin, J. Am. Chem. Soc., **91**, 777 (1969). (b) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, ibid., **91**, 3382 (1969).

(8) λ_{max} for hydrazone is obscured by solvent absorption. Qualitative estimates of its yield were possible at 330 mμ on a steep tail, but quantitative data could not be obtained.

(9)(a) Added 4-ethylstyrene was not changed during the decomposition reactions. (b) Synthesis of an authentic sample of 1-phenyltetralin allowed confirmation of its presence in the reaction mixtures by glpc comparison. It would be expected from a diradical intermediate, but was not observed by Kopecky.[6b]

(10)(a) Diffusion and "rotational diffusion"[10b] processes appear to be very sensitive to medium viscosity and thus to pressure. See R. C. Neuman, Jr., and M. Amrich, J. Am. Chem. Soc., In Press. (b) J. M. McBride, ibid., **93**, 6302 (1971).