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HIGH PRESSURE STUDIES. XI. VISCOSITY AND PRESSURE TESTS FOR CAGE RETURN. p-NITROPHENYLAZOTRIPHENYLMETHANE.[1]

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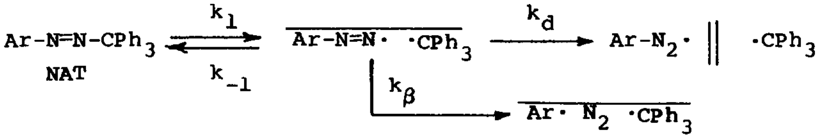
Thermal decomposition of the unsymmetrical azo compound p-nitrophenylazotriphenylmethane (NAT) is retarded by increasing solvent viscosity.[2] This has led Pryor to propose that it decomposes by a one-bond scission mechanism (Scheme I) characterized by substantial (> 20%) internal return (k_{-1}). Until recently, little evidence has been available to support the intermediacy of diazenyl radicals ($ArN_2\cdot$) and most data for decomposition of azo compounds suggest that they are bypassed in favor of direct expulsion of molecular nitrogen.[3]



Scheme I

We now wish to report that the observed activation volumes calculated from rates of decomposition of NAT in three different solvents (Table I) are exceptionally large and must be interpreted in terms of one-bond scission (Scheme I) with significant cage return (k_{-1}). We believe that the values of ca. +18, +20, and +21 cc/mole for ΔV^*_{obs} in n-octane, cumene, and tert-butylbenzene, respectively, are the largest values yet reported for a homolytic scission reaction.

As discussed extensively elsewhere,[1a,4] values of ΔV^*_{obs} for homolytic scission will be larger than the volume change for bond breaking (ΔV^*_1) by an amount related to the pressure dependence of the ratio of return to other cage processes when return (k_{-1}) competes with the other reactions. Specifically for Scheme I, equation 2 obtains.

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

There is a fair amount of data supporting the generalization that values of ΔV_1^*, in the absence of polar effects, will be about +4 to +5 cc/mole.[4,5] Particularly clean examples are provided by decomposition of azocumene and p,p'-dimethylazocumene (Table II) which give values of ΔV_{obs}^* in this range: azocumene, +5.0 (cumene), +4.3 (chlorobenzene); dimethylazocumene, +4 (cumene). Azocumene has been studied in media of varying viscosity and its decomposition rate appears to be insensitive to this parameter.[2] This is in complete agreement with a two-bond scission mechanism[6] and the assignment of ΔV_{obs}^* solely to ΔV_1^*. Thus, the differential term of eq. 2 could be on the order of +15 cc/mole for NAT.[5,7]

The largest values of ΔV_{obs}^* previously reported for one-bond homolytic scission (ca. +13 cc/mole) were those for di-tert-butyl peroxide,[8] pentaphenylethane,[9] and tert-butyl perbenzoate[4a] decompositions. While the limited data preclude firm generalizations, they suggest that the larger values of ΔV_{obs}^* for NAT may be due to β-scission being competitive with separative diffusion. In the above cases, and others previously studied, unimolecular β-scission is either not possible or generally presumed to be substantially slower than diffusion.[4e] If β-scission is competitive with separative diffusion at low pressure in NAT decompositions, increasing pressure should retard this process as well as diffusion, leading to a particularly large (and positive) differential term (eq. 2).

Viscosity studies also indicate that cage return is a significant process of unsubstituted phenylazotriphenylmethane (PAT).[2] Thus, it seems that early data and their rationales for substituent and solvent effects on $X\text{-}PhN_2CPh_3$ decomposition[10,11] require reevaluation. A particularly surprising observation in these studies was that the rates of decomposition of the meta and para isomers for a particular group X were virtually the same. Additionally, all substituents other than methyl led to decreased rates independent of their electronic properties. Such results are consistent with a significant dependence of k_{obs} on k_d. The variation in the rate of separative diffusion should depend on the mass of the radical $X\text{-}PhN_2\cdot$, but relatively little on the site of substitution of X. The solvent effects have been interpreted in terms of an isokinetic relationship between activation enthalpies and entropies; an explanation seemingly incompatible with Scheme I. For these reasons we are continuing our studies on other isomers of the general structure ArN_2CPh_3.

Table I. Kinetic Data for Decomposition of NAT (60°) in *n*-Octane, Cumene, and *tert*-Butylbenzene.

	k_{obs} x 10^5, sec^{-1}		
Pressure,Atm.	*n*-Octane	Cumene	*tert*-Butylbenzene
1	11.4	11.6	10.3
1240	4.44	4.73	4.03
2110	2.56	2.27	2.07
3200	1.31	1.22	0.968
3840	0.832	0.723	0.444

Table II. Kinetic Data for Decomposition of Azocumene (ACM) and *p,p*'-Dimethylazocumene (DMACM) (55°) in Cumene and Chlorobenzene.

	k_{obs} x 10^5, sec^{-1}		
Pressure, Atm.	ACM Cumene	ACM Chlorobenzene	DMACM Cumene
1	8.10	8.50	8.86
500	7.20	7.61	
1000	6.75	6.88	7.54
2050	5.45	6.03	6.02
3000	4.56		
4100	3.83	4.42	4.47
5200	2.98		
6100	2.62		

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(1) (a) Part X is R. C. Neuman, Jr., and M. Amrich, J. Am. Chem. Soc., In Press. (b) Supported by the National Science Foundation through grant GP-23968. (c) Written during the tenure of RCN as an NIH Special Research Fellow, 1971-72.

(2) (a) W. A. Pryor and W. K. Smith, J. Am. Chem. Soc., **89**, 1741 (1967). (b) W. A. Pryor and W. K. Smith, ibid., **92**, 5403 (1970).

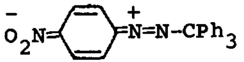
(3) An increasing literature is developing in support of diazenyl radical intermediates: (a) S. Seltzer and F. T. Dunne, ibid., **87**, 2628 (1965); (b) N. A. Porter, M. E. Landis, and L. J. Marnett, ibid., **93**, 795 (1971); (c) K. Takagi and R. J. Crawford, ibid., **93**, 5910 (1971).

(4) (a) R. C. Neuman, Jr., and J. V. Behar, J. Am. Chem. Soc., **91**, 6024 (1969). (b) R. C. Neuman, Jr., Intra-Science Chem. Reprts., **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) Recently obtained results from our laboratory[1a] on a one-bond scission initiator suggest that ΔV_1^* for one-bond scission is essentially the same as that for simultaneous cleavage of two bonds.

(6) See S. F. Nelsen and P. D. Bartlett, J. Am. Chem. Soc., **88**, 137 (1966).

(7) Any polarity in NAT (**1**) ought to be carried over to the product diazenyl radical (**2**) suggesting that significant polar contributions to ΔV_1^* are relatively unlikely.



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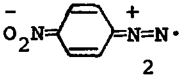

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(8) C. Walling and G. Metzger, ibid., **81**, 5365 (1959).

(9) A. H. Ewald, Discuss. Faraday Soc., **22**, 138 (1965).

(10) (a) S. G. Cohen and C. H. Wang, J. Am. Chem. Soc., **75**, 5504 (1953). (b) M. G. Alder and J. E. Leffler, ibid., **76**, 1425 (1954). (c) M. D. Cohen, J. E. Leffler, and L. M. Barbato, ibid., **76**, 4169 (1954). (d) G. L. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc., 4397 (1956). (e) S. Solomon, C. H. Wang, and S. G. Cohen, J. Am. Chem. Soc., **79**, 4104 (1957).

(11) It should be noted that Davies, Hey and Williams[10d] suggested, using an argument involving energetic considerations, that ArN_2CPh_3 decomposed via one-bond scission. They did not, however, appreciate that cage recombination might occur.