Cyclofragmentation of Bis-(*N*-methylanilinomethyl) Peroxide: Mechanism of Hydrogen Extrusion

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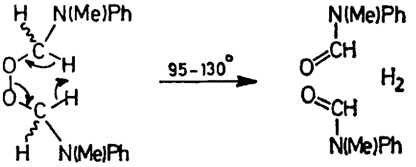
Summary Activation energy parameters, solvent effect, and kinetic isotope effect indicate a novel concerted mechanism for the fragmentation of the title substance.

The expulsion of molecular hydrogen (H_2) from a strictly organic precursor under mild conditions is rarely encountered,[1] although from consideration of the strength of the H–H bond (103 kcal mol^{-1}) it ought to be useful synthetically. We have examined the mechanism of fragmentation of bis-(*N*-methylanilinomethyl) peroxide (**1**) to *N*-methylformanilide and hydrogen,[2] with a view to establishing concertedness within the transition state, and have obtained the following evidence:

(1) Kinetics for the disappearance of peroxide from xylene solutions of (**1**) have been examined over the temperature range 94·4—130·0°. Good first-order rates were observed (duplicate determinations) to at least 80% completion [k (130·0°) = $92·6 \times 10^{-5}$ s^{-1}].[†] A least-squares fit ($r = -0·994$) of log k *vs.* $1/T$ yielded $\Delta G^{\ddagger}_{130°} = 29·5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 28·6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2·3$ cal K^{-1} mol^{-1}. Such a negative entropy of activation is consistent with a constrained (cyclic) transition state. Analogous synchronous reactions possessing transient six-membered rings have similar values.[3] Considering that thermolysis of (**1**) yields three components with attendant gain in translational degrees of freedom, the value of $\Delta S^{\ddagger}$ suggests an early, concerted transition state.

(2) The fragmentation was examined in more polar solvents than xylene, with a view to detecting ionic intermediates. Clean, first-order decomposition was no longer observed. However, the initial rates in benzonitrile and dimethyl formamide were, respectively, 1·2 and 3·4 times as fast as in xylene at the same temperature (130°). Such a small effect does not support possible charge separation in the transition state. Radical chain processes may similarly be excluded.[2] A concerted mechanism is therefore more plausible.

(3) In view of the likelihood of a cyclic mechanism, the tetradeuterium labelled peroxide (**2**) was prepared (from 98 atom % $CD_2{=}O$). The possibility of a large kinetic isotope effect was anticipated, stemming from synchronous cleavage of two C–(H,D) bonds. In xylene the rate of fragmentation of (**2**) relative to (**1**) (k_{2CH}/k_{2CD}) was 4·3 at 130·0°. This is acceptable for a primary deuterium kinetic effect, but is somewhat less than might be realized for full extension of two sigma bonds in a synchronous transition state.[4]



(1)

Ph(Me)NCD$_2$OOCD$_2$ N(Me)Ph

(2)

We conclude that fragmentation of (**1**) is a concerted $[_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s]$ pericyclic process. We postulate an early transtition state (based on $\Delta S^{\ddagger}$ and k_{2CH}/k_{2CD}), driven both by scission of the weak peroxide linkage and to a lesser extent by the strength of the incipient hydrogen–hydrogen bond. The formation of two stable amide linkages probably also contributes to the velocity of the reaction; the small solvent effect observed may be associated with solvation of these groupings.

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[†] Additional rate constants (temp., $k \times 10^5$ s^{-1}): 125·0°, 58·8; 115·0°, 20·8; 108·0°, 11·0; 106·0°, 9·4; 94·4° 2·8. Each value is the average of duplicate determinations.

[1] (a) L. J. Durham, C. F. Wurster, Jr., and H. S. Mosher, *J. Amer. Chem. Soc.*, 1958, **80**, 332; (b) L. J. Durham and H. S. Mosher, *ibid.*, 1960, **82**, 4537; 1962, **84**, 2811; (c) R. J. Ellis and H. M. Frey, *J. Chem. Soc.* (*A*), 1966, 553; (d) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 1967, **63**, 985.

[2] L. Horner and K. H. Knapp, *Annalen*, 1959, **622**, 79.

[3] G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, 1971, **8**, 75; M. R. Willcott, R. L. Cargill, and A. B. Sears, *ibid.*, 1972, **9**, 25; S. J. Rhoads in 'Molecular Rearrangements,' Part 1, ed. P. de Mayo, Interscience, New York, 1963, p. 655; see also ref 1b, but note criticism of that work: R. Hiatt and S. Szilagyi, *Canad. J. Chem.*, 1970, **48**, 615.

[4] Assuming a negligible secondary isotope effect due to the geminal deuterium atoms and disregarding C–H bending modes (R. A. M. O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 785), each participating C–D bond should maximally contribute a rate retarding factor of *ca.* 4·2 at 130°; K. B. Wiberg, *Chem. Rev.*, 1955, 713.