PRESSURE EFFECTS IN A [2+2] PHOTOCYCLOADDITION AND -REVERSION[1]

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Summary: Evidence is presented to support the conclusion that the [2+2] photocycloaddition
of acrylonitrile to naphthalene has a late transition state similar in volume to
those in concerted thermal cycloadditions.

It is a well-established fact now that thermally allowed [2+4] and [4+6] cycloadditions
have late transition states, which occupy small volumes comparable to those of the products.[2]
Conversely, molecules undergoing thermal [2+2] cycloaddition by way of a diradical inter-
mediate occupy a relatively large space in the transition state.[3]   This knowledge has been
derived from the pressure coefficients of the rate constants of these reactions via the re-
lationship

$$\partial(\ln k)/\partial p) = -\Delta V^{\ddagger}/RT$$

and in competing reactions from

$$\partial(\ln r)/\partial p) = (V_A^{\ddagger} - V_B^{\ddagger})/RT$$

where r is the ratio of the products B/A. The principal reason for this difference in volume
is thought to be the extra bond which is allowed to form in the concerted reactions. In view
of these results it seemed of interest to learn the volume relationships in a photocycloaddi-
tion reaction.

Although it has long been predicted[4] that hydrostatic pressure may become a valuable tool
in photochemical investigations, little or no work has been published which begins to realize
these expectations.[5] One of the problems is that very little is known about the pressure de-
pendence of the fundamental steps that characterize photochemistry; another, that accurate
knowledge of absolute rate constants in photochemistry is difficult to come by even at atmos-
pheric pressure. However, useful insights can be gained from the effect of pressure on product
distributions.

McCullough and co-workers have made a very thorough study[6] of the [2+2] photocycloaddition
of acrylonitrile to naphthalene, a process which features competition by a photosubstitution:

(1)   (2)
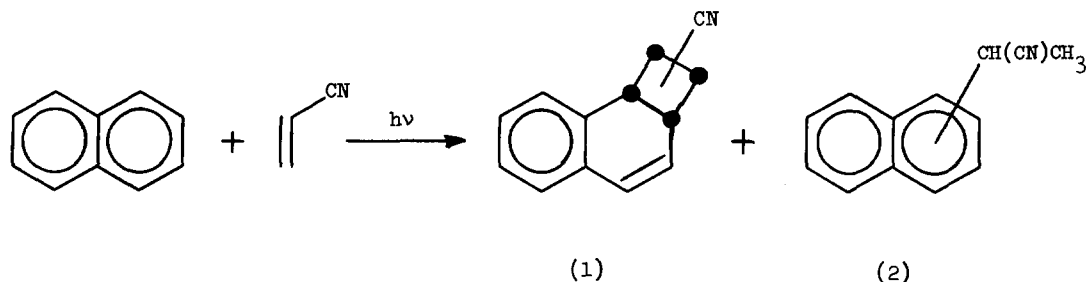
The latter reaction is greatly favored by the use of polar solvents. Thus, while only (1) obtains in benzene, mixtures are formed in more polar media, and in formic acid only (2) can be detected; a good correlation was found between the product ratio and the solvent parameter Z.[6a] It was also noted that the cycloaddition is stereospecific: only the endo-products form, although at least one of them is demonstrably less stable than its epimer.[6b] Their formation can be photochemically reversed, and the reversion can be quenched by the addition of 2,3-dimethylbutadiene (3).[6a] The reaction is known[6c] to originate with the first excited singlet state of naphthalene, which either undergoes concerted cycloaddition to acrylonitrile, or which forms a highly dipolar exciplex with it; the latter reaction is followed by protonation, and finally, irreversible formation of (2).

In our experiments, use was made of a Hanovia 450 W lamp with Pyrex filter. The high pressure optical vessel and the cell have been described elsewhere;[7] the pressure range was 1500 atm. A glycerine-water mixture (20-80 by volume) was used as hydraulic fluid and methanol as the solvent; the solutions were initially 0.03 M in naphthalene and 2 M in acrylonitrile, and enough (3) was added (0.1 M) to prevent the reversal of the cycloaddition. The temperature was 25°; analysis was done by means of vpc, and known mixtures were used to calibrate the technique. The result is that the product distribution in the forward direction is independent of pressure; the ratio (2)/(1) equals 0.491 ± 0.005 over the entire range. This means that the transition states leading to these products have partial volumes equal to within 0.3 cc/mole. This at first seems surprising, since reactions favored by the use of polar solvents are invariably also promoted by the application of pressure due to solvation (electrostriction).[8] Since the transition state for the formation of (2) should be highly compact due to solvation of the charges, the activated complex on the way to (1) must have an alternative feature accounting for its small volume. The only other factor known to cause this is an advanced state of bonding. It is reasonable to postulate concerted bond formation on this basis.

It should be pointed out that the lack of any pressure sensitivity of the product ratio cannot be ascribed to a common transition state for both products (‡C in Figure 1). In that case, the inevitable partitioning occurs on the down hill side of the energy profile, and the pressure dependence of the ratio B/A will then be governed by $V(^{\ddagger}A') - V(^{\ddagger}B')$; otherwise, however, nothing changes. A common transition state is not ruled out, but the pressure insensitivity is neither explained nor demanded by it. Furthermore, the solvent effect would remain unexplained.
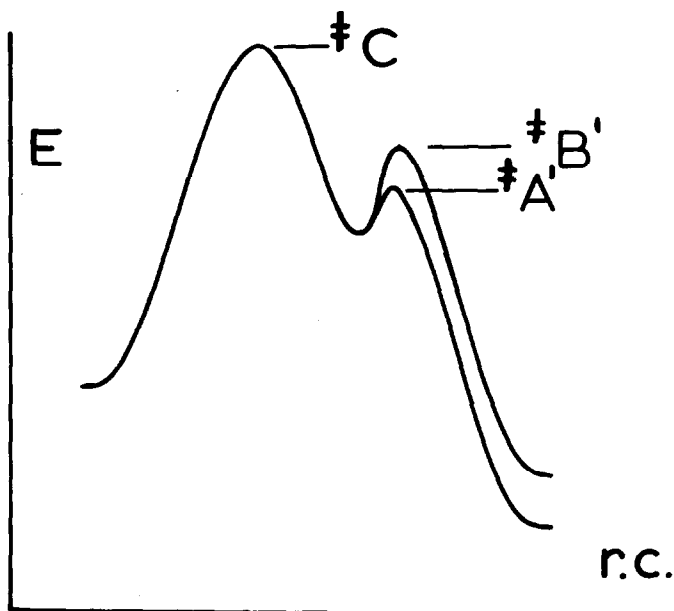
Figure 1.   Reaction profile involving competing reactions with a common intermediate.

In a study of the reverse reaction of (1) (which is of course not the microscopic reverse), a methanolic solution of m-toluic acid was used as a filter (to prevent the forward reaction), and (3) was omitted. Pressure has the effect of suppressing the decomposition reaction; thus, under a given set of conditions the amount decomposed decreases from 43% at ambient pressure to 34% at 1500 atm. The difference in volume between the transition states for decomposition and deactivation is approximately + 4 cm^3/mol. Hammond has shown that sensitization and energy transfer are only modestly sensitive to steric hindrance;[9] it was concluded that, while contact is required, a very close approach is not necessary. On that basis it seems reasonable to assume that $\Delta V^{\ddagger}$ for deactivation is about zero or not much less than that.[10] Accordingly, $\Delta V^{\ddagger}$ for the cycloreversion as an upper limit is about + 4 cm^3/mol. Since the volume difference between pairs of olefinic molecules and their cycloadducts is usually about + 40 cm^3/mol, we conclude that the photocycloreversion has an early transition state.

References and Notes -

1. Paper XLI in the series "Kinetics of Reactions in Solutions under Pressure".

2. For example: W. J. le Noble, H. Guggisberg, T. Asano, L. Cho, and C. A. Grob, J. Am. Chem. Soc., 98, 920 (1976); W. J. le Noble and B. A. Ojosipe, J. Am. Chem. Soc., 97, 5939 (1975), and work quoted in these papers. For review see J. R. McCabe and C. A. Eckert, Accounts Chem. Res., 7, 251 (1974).

3. C. A. Stewart, J. Am. Chem. Soc., 94, 635 (1972). This is not true if zwitterionic inter-mediates are involved; see W. J. le Noble and R. Mukhtar, J. Am. Chem. Soc., 96, 6191 (1974) and 97, 5938 (1975).

4. A. R. Ubbelohde, Nature, 209, 28 (1966).

5. Some examples are: rotating sector studies, A. E. Nicholson and G. W. Norrish, Disc. Faraday Soc., 22, 104 (1956); equilibria involving excited states: S. D. Hamann, J. Phys. Chem., 70, 2418 (1966), and C. O. Leiber, D. Rehm, and A. Weller, Ber. Bunsenges., 70, 1086 (1966); excimer formation: P. Pollmann and A. Weller, Ber. Bunsenges., 77, 1071 (1973); solvation of excited states: K. Tamura, Y. Ogo and T. Imoto, Chem. Lett., 625 (1973), and K. Tamura and T. Imoto, Bull. Chem. Soc. Japan, 48, 369 (1975); diffusion control: T. Tanaka and J. Osugi, Rev. Phys. Chem. Japan, 42, 85 (1972); photodissociation, F. Tanaka, M. Sasaki, and J. Osugi, Rev. Phys. Chem. Japan, 41, 18 (1971). There are of course in-numerable examples of studies of pressure effects on spectra, and of studies employing spectra to determine the effect of pressure on thermal reactions and equilibria.

6. (a) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, J. Am. Chem. Soc., 96, 692 (1974); (b) R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller, and I. Singh, Can. J. Chem., 51, 1060 (1973); (c) R. M. Bowman and J. J. McCullough, Chem. Commun., 948 (1970).

7. W. J. le Noble and A. R. Das, J. Phys. Chem., 74, 3429 (1970); W. J. le Noble and R. Schlott, Rev. Scient. Instrum., 47, 770 (1976). The optical cell is cylindrical, and has a self-adjusting length and constant diameter, so that no compressibility corrections are required.

8. See the following compilations for example: W. J. le Noble, Progr. Phys. Org. Chem., 5, 207 (1967), and S. D. Hamann, Modern Aspects Electrochem., 9, 47 (1974).

9. W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, J. Am. Chem. Soc., 88, 4777 (1966). These authors showed that the cis-trans composition of photostationary states of olefins in the presence of 2,6-dialkylbenzophenones is independent of the nature of the alkyl group un-less this is as bulky as i-propyl.

10. The uncertainty in $\Delta V^{\ddagger}$ for deactivation is compensated somewhat by another problem, namely that our apparatus in its present configuration does not permit the direct irradiation of the entire solution, and hence that decomposition is limited to those molecules that can diffuse into the irradiation zone; since the diffusion rate itself is retarded by pressure, any correction for this problem would tend to reduce the value of + 4 cm^3/mol.