# *cis*-Intermediates in Azo-compound Photolysis

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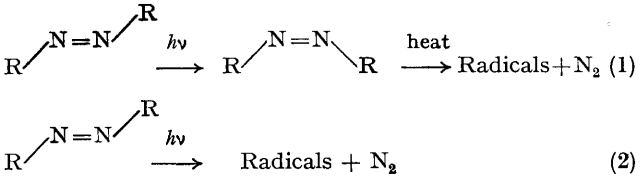
*Summary* Two mechanisms, radical formation and isomerization, have been identified for the thermal decomposition of unsymmetric *cis*-azo-compounds; the photochemical behaviour of *trans*-azo-compounds is dependent on the thermal behaviour of the corresponding *cis*-azo-isomer.

Two mechanisms are possible for azo-photolysis: (i) *trans*–*cis* isomerization of the azo-compound followed by thermal decomposition of the unstable *cis*-isomer to give free radicals [equation (1)]; (ii) photodecomposition of the azo-compound to radicals and molecular nitrogen occurring directly from the *trans*-azo-compound [equation (2)]. The first mechanism has been suggested to account for the photochemical behaviour of symmetric[1] and unsymmetric[2] azo-compounds. The second mechanism has been frequently put forward but infrequently supported by experimental evidence.

We report here on the thermochemistry of the *cis*-isomers of the azo-compounds (**1**)—(**4**)† and on the photochemistry of the *trans*-isomer of (**4**). The thermal decomposition of *cis*-(**1**)—(**4**) was monitored by u.v. spectroscopy. The decomposition was first order in each case and the rate of decomposition was unaffected by addition of the radical scavenger, di-t-butyl nitroxide. The kinetic parameters obtained for *cis*-(**1**)—(**4**) are given in the Table.

*cis*-Azobenzene decomposes by a non-radical route (bond rotation or linear inversion of the azo-linkage) to give *trans*-azobenzene as the sole product.[3] The behaviour of the *cis*-azo-compound (**4**) is analogous to that of *cis*-azobenzene in that: (a) it is converted solely into *trans*-(**4**) without radical decomposition products, (b) no CIDNP signals are observed during the *cis–trans* conversion of (**4**), (c) an isosbestic point in the u.v. spectrum is observed at 382 nm during the *cis–trans* conversion, and (d) an $A$ value (*ca.* $10^{12}$), typical of azobenzene isomerizations, is found for (**4**).

The thermal behaviour of *cis*-(**2**) and (**3**) contrasts with that of (**1**) and (**4**). With the former, large $A$ values ($10^{14}$) typical of azo-decomposition to free radicals[4] are obtained. Free-radical decomposition products are found in the decomposition of *cis*-(**2**) and -(**3**). For example, *cis*-(**3**) decomposes thermally to give *trans*-(**3**) and the radical rearrangement product (**5**)[2b] as well as products derived from the coupling of dimethylallyl radicals. Further, the comparative activation energies of (**2**) and (**3**) are consistent with radical-pair formation. The greater stability of the dimethylallyl radical as compared to the cumyl radical[5] is reflected in the low $E_a$ found for (**3**) compared with that found for (**2**).



Ph–N=N–R

| | R |
|---|---|
| (**1**) | Ph |
| (**2**) | $CMe_2Ph$ |
| (**3**) | $CMe_2CH{=}CH_2$ |
| (**4**) | $Bu^t$ |
| (**5**) | $CH_2CH{=}CMe_2$ |

Two different mechanisms are therefore possible for the *cis*-azo-compounds studied. If the potential radical is stabilized sufficiently, as is the case with (**2**) and (**3**), the decomposition occurs *via* a radical-pair mechanism. If the potential radical is not stabilized as is the case with the phenyl and t-butyl radicals, then the azo-compound is diverted to the isomerization pathway and radical formation is avoided.

The photochemical behaviour of the *trans*-isomers of (**1**)—(**3**) is consistent with the photoisomerism mechanism described by equation (1). It appears that the photochemical act of consequence in these compounds is *trans–cis* isomerization and that the dissociation to radicals involves simply the thermal decomposition of the unstable *cis*-isomer. Thus, *trans*-azobenzene does not photolyse since the *cis*-isomer does not decompose to radicals but only re-isomerizes back to *trans*. On the other hand, *trans*-(**2**) and -(**3**) photodecompose to radicals *via* the unstable photoisomer. This mechanism [equation (1)] fails to explain the photochemical behaviour of (**4**) (*vide infra*).

Photolysis of *trans*-(**4**) at −85, 0, and 25° with 380 nm light results in a rapid *trans–cis* isomerization accompanied by a slow conversion of the photoequilibrated azo-compound into hydrocarbon products. The primary volatile products produced in the photolysis of *trans*-(**4**) in pentane were identified as benzene and t-butylbenzene, the expected free-radical decomposition products. Similarly, photolysis of *cis*-(**4**) leads to rapid *cis–trans* isomerization and to the same hydrocarbon products formed from *trans*-(**4**) photolysis.

The two-step sequence for photodecomposition [equation (1)] is ruled out as a possible mechanism for decomposition of (**4**) since the corresponding *cis*-isomer does not decompose to radicals thermally. Therefore, the decomposition of (**4**) must involve a truly photolytic decomposition of *cis*- and/or *trans*-(**4**) [equation (2)] rather than a simple thermal decomposition of the *cis*-azo-compound.

TABLE

*Activation parameters for thermal decomposition of* cis-*azo-compounds in octane*

| | $E_a$/kcal mol$^{-1}$ | log $A$ |
|---|---|---|
| (**1**) | 22·8[a] | 12·87[a] |
| (**2**) | 23·3 ± 0·4 | 14·11 |
| (**3**) | 21·8 ± 0·3 | 14·29 |
| (**4**) | 22·2 ± 0·3 | 12·43 |

[a] See J. Halpern, G. W. Bradyard, and C. A. Winkler, *J. Canad. Research*, 1950, **28**, 140.

We suggest that there are at least two possible modes for photodecomposition of unsymmetric aryl/alkyl azo-compounds. The first, which requires light only as an isomerization agent, occurs when the potential radical is suitably stabilized. The second pathway (a much less efficient decomposition pathway) is followed when thermal decomposition of the *cis*-isomer to radicals is impossible.

We thank the National Science Foundation for financial support.

(*Received, 17th January* 1973; *Com.* 066.)

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† The *cis*-azo-compounds were prepared as previously described.[2a]

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