II. Photochemistry of Azobenzene and its Derivatives

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1 Introduction

The discovery of the first azo-dye was made by Martius in 1863, and in the following year Griess reported the coupling reaction of diazonium compounds. These momentous discoveries led to the development of the azo-dyes, now the most important and versatile class of coloured organic compounds to find use as dyes and pigments. One of the most important requirements for a commercially viable dye is good light stability, yet although the azo-dyes have been known for over a century, only relatively recently has their photochemistry received the close attention it deserves. Probably the first fully elucidated photochemical reaction of an azobenzene derivative was reported by Krollpfeiffer and coworkers in 1934, who succeeded in isolating and identifying the fading products of an *o*-aminoazo-compound.[1] A further significant discovery was made three years later by Hartley, who observed for the first time the photochemical *trans* $\rightleftharpoons$ *cis* isomerization of azobenzene,[2] and in following years the photochemistry of the azobenzenes has been the subject of a great deal of research.

Few other chemical classes exhibit as wide a variety of photochemical reactions which are at the same time of major technological significance. As a result, the photochemistry of azobenzene and its derivatives is of interest to the photochemist, the technologist, and the non-specialist chemist. The following discussion will deal with the major reaction classes of the azobenzenes, namely photoisomerization, photocyclization, and photoreduction, and will briefly consider the fading reactions of azo-dyes on polymeric substrates. It is useful, however, to consider first the light absorption properties and excited states of the azobenzenes.

2 Electronic Absorption Spectra and Excited States

For a full understanding of the photochemical reactions of a compound, a knowledge of its excited states is essential. Although the azobenzenes have received considerable attention from the theoreticians, the experimental data available concerning their excited states are limited, and are largely confined to the singlet states obtained by direct absorption of radiation. The light absorption properties of *cis*- and *trans*-azobenzene have been calculated by MO

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[1] F. Krollpfeiffer, C. Mühlhausen, and G. Wolf, *Annalen*, 1934, **508**, 39.
[2] G. S. Hartley, *Nature*, 1937, **140**, 281.

methods with varying degrees of sophistication,[3] and in general good agreement with experiment is obtained.

cis- and *trans*-azobenzene have three accessible excited singlet states, corresponding to three absorption bands in the visible and near-u.v. spectrum, and these can best be discussed with reference to the simple orbital diagram shown in the Figure. The three highest occupied and three lowest unoccupied π-orbitals of the azobenzene system are shown, and the non-bonding atomic orbitals of the azo-nitrogen atoms are considered to interact to give the two orbitals depicted by n_a and n_s.

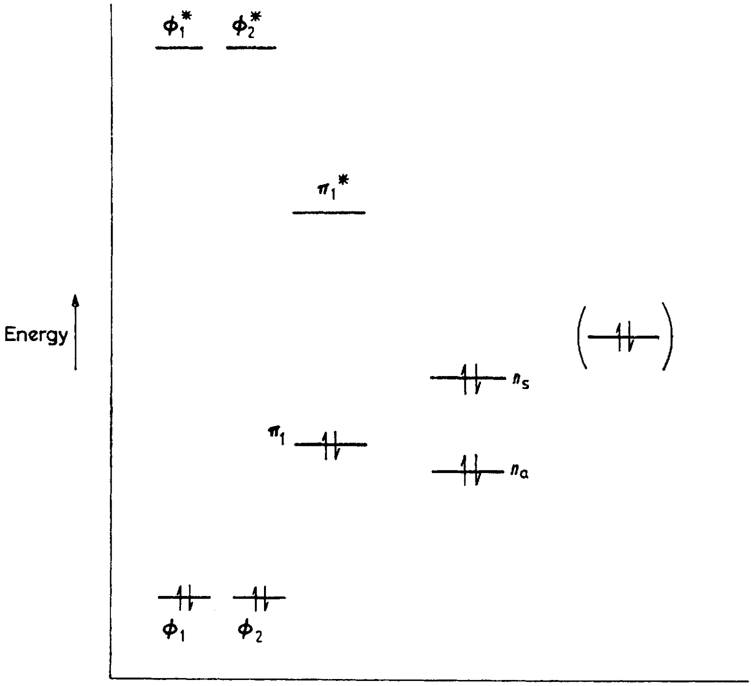

Figure *Crude MO energy diagram for the azobenzene system. The orbital in parentheses is present in azobenzenes containing a substituent with lone-pair electrons in conjugation with the π-electron system.*

The lowest-energy transition occurs at approximately 440nm ($\epsilon \sim 500$) and

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[3] D. L. Beveridge and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1966, **88**, 1948; J. Kroner and H. Bock, *Chem. Ber.*, 1968, **101**, 1922; H. H. Jaffe, S.-J. Yeh, and R. W. Gardner, *J. Mol. Spectroscopy*, 1958, **2**, 120.

430 nm ($\epsilon \sim 1500$) in *trans*- and *cis*-azobenzene, respectively, corresponding to excited singlet states of about 66 kcal mol^{-1} in energy. The transitions are most probably due to the partly forbidden $n_s \rightarrow \pi_1{}^*$ process, as indicated by the low intensity and hypsochromic shifts of the bands in polar solvents.† As they are the lowest in energy, these states will be the singlet states most likely to be involved in solution-phase photochemical reactions. Of course, each state will have an associated $n\pi^*$ triplet state which may play an even more important role in these reactions.

The second transition occurs in the u.v. region of the spectrum, *cis*-azobenzene absorbing at *ca.* 280 nm ($\epsilon \sim 5100$), and *trans*-azobenzene at 314 nm ($\epsilon \sim 17000$), (approximately 102 and 92 kcal mol^{-1}, respectively). The marked difference between the two isomers is due to the non-planar configuration of the *cis*-isomer. The transitions are allowed and are due to the process $\pi_1 \rightarrow \pi_1{}^*$. The bands suffer bathochromic shifts in polar solvents, and are particularly sensitive to substituent effects. The positions of the corresponding $\pi\pi^*$ triplet states have yet to be ascertained, and may be even lower in energy than the $n\pi^*$ triplet states.

The highest-energy transition is due to the process $\phi \rightarrow \phi^*$, and because of the close association of the ϕ-orbitals with the benzene rings, the transition may be regarded as localized in these rings. The bands occur in the region 230—240 nm for both isomers, and because of their high energy (*ca.* 120 kcal mol^{-1}) the corresponding singlet states are unlikely to be involved in the solution-phase reactions of azobenzene.

If the azobenzene system is substituted with an electron-releasing group with lone-pair electrons (*e.g.* OH or NH_2) the simple orbital diagram has to be modified by the inclusion of an additional π-orbital containing two electrons, as indicated in the Figure by the orbital in parentheses. Since this may be regarded as a non-bonding orbital it lies close to the zero-energy level, and consequently the first $\pi \rightarrow \pi^*$ transition will be of much lower energy than in azobenzene itself. Thus the overall effect of such substituents, or auxochromes, is to provide intense absorption bands in the visible spectrum. In many cases the $\pi\pi^*$ singlet state may in fact be lower in energy than the $n\pi^*$ singlet state (which is insensitive to substituent effects), and thus the photochemical properties may differ from those of simpler azobenzenes.

The absence of triplet-state energy data for the azobenzenes is due largely to their inability to exhibit phosphorescence. Hammond and Jones have placed a maximum value of 45 kcal mol^{-1} on the lowest triplet state of azobenzene by using energy-transfer methods,[4] but these results require further investigation, and it is to be hoped that more work in this important area will be carried out in the near future.

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†The $n_a \rightarrow \pi_1{}^*$ process is generally believed to occur at much shorter wavelength (M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, 1962, **36**, 580; G. Kortüm and H. Rau, *Ber. Bunsengesellschaft phys. Chem.*, 1964, **68**, 973).

[4] L. B. Jones and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 4219.

3 Photochemical *cis–trans* Isomerization

The azobenzenes normally exist in the stable *trans*-form, and the *cis*-isomers cannot be made by the usual chemical methods. The possibility of *cis–trans* isomerism in the azobenzenes had been considered for many years before the first discovery of the *cis*-isomer of azobenzene by Hartley in 1937.[2] During a spectroscopic study of the solubility properties of *trans*-azobenzene, he noted that solutions exposed to sunlight underwent a colour change which could be reversed by keeping the solutions in the dark. Using a tedious solvent-distribution technique, he was able to isolate the product responsible for this change, and succeeded in measuring its physical and chemical properties. This new compound thermally reverted to *trans*-azobenzene by a first-order process, and Hartley correctly inferred that it was the previously unknown *cis*-isomer of azobenzene. In the following year the generality of the photoismerization reaction was demonstrated by the synthesis of other *cis*-azobenzene derivatives,[5] and a simpler isolation procedure using column chromatography was described.[6] Subsequently this aspect of azobenzene photochemistry has attracted much interest and a large number of *cis*-azobenzenes and their naphthalene or heterocyclic equivalents have now been described.

In many cases the *cis*-isomers are too unstable to permit isolation, and their detection has usually relied on spectroscopic techniques. A typical example is the aminoazobenzene derivative (1); this is very unstable in the *cis*-form, but under conditions of continuous irradiation the u.v. spectrum clearly reveals the presence of the *cis*-isomer.[7] In general, *cis*-azobenzenes absorb at shorter wavelength than the *trans*-isomers and thus detection is greatly simplified. Exceptionally unstable *cis*-isomers can be observed by flash-photolytic or low-temperature techniques. In some instances photoisomerization is completely inhibited, and this can be attributed to azo–hydrazone tautomerism, *e.g.* (2) $\rightleftharpoons$ (3), in which the compound exists almost completely in the hydrazone form. Thus, for example, the naphthalene derivative (3) does not exhibit photoisomerization.[7]

In a few cases, particularly where *ortho*-substituents are present, the *cis*-isomer is unusually stable, a notable example being the fluoro-derivative (4), which retains its configuration for relatively long periods at room temperature.[8] When more than one azo-group is present in the molecule, the various possible geometric isomers can be isolated, and, for example, the unstable *cis,cis*- and *cis,trans*-isomers of 4-phenylazoazobenzene have been identified.[9] From a practical viewpoint the preparation of *cis*-azobenzenes is usually a simple process, and provided that the wavelength of radiation is chosen to ensure that the *trans*-isomer absorbs a high proportion of the light, high conversions can be

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[5] G. S. Hartley, *J. Chem. Soc.*, 1938, 633.

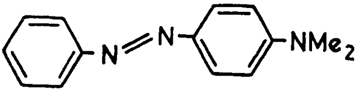
[6] L. Zechmeister, O. Frehden, and P. Fischer Jörgensen, *Naturwiss.*, 1938, **26**, 495; A. H. Cook, *J. Chem. Soc.*, 1938, 876.

[7] W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4641.

[8] M. J. Namkung, N. K. Naimy, C. A. Cole, N. Ishikawa, and T. L. Fletcher, *J. Org. Chem.*, 1970, **35**, 728.

[9] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1939, 1309.

obtained. Isolation of the products is most easily effected by column chromatography, carried out in the dark and with cooling if necessary.



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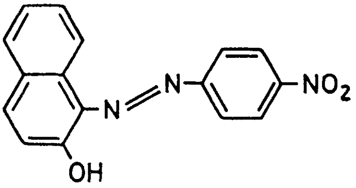

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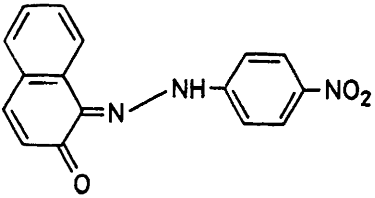

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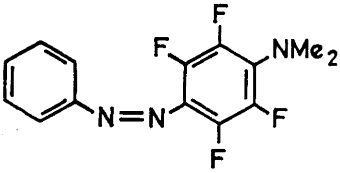

(4)

Mechanistic Studies.—Although much interest has been shown in the photoisomerization reaction, the detailed mechanism of the process is still a subject of debate. Stilbene, the hydrocarbon analogue of azobenzene, is understood much more fully, and presumably the additional $n\pi^*$ states of azobenzene contribute to the difficulties associated with mechanistic studies of this compound. The main features of the mechanism of azobenzene photoisomerization have been elucidated, however, and in certain instances these have been used to practical advantage.

As with all *cis–trans* photochemical conversions, irradiation of *trans*-, or *cis*-azobenzene ultimately produces the same photostationary state in which the relative proportions of the two isomers are invariant with exposure time. Under these conditions the rate of photochemical formation of the *cis*-isomer is equal to the rate of its photochemical destruction. The proportion of the *cis*-isomer at equilibrium should thus be increased if the wavelength of light used is not absorbed strongly by the *cis*-isomer, but is strongly absorbed by the *trans*-isomer. This wavelength effect was first demonstrated by Fischer, Frankel, and Wolovsky,[10] who showed that with light of wavelength 365 nm the proportion of *cis*-azobenzene at the photostationary state increased to 91%, compared with 37% when unfiltered u.v. light was used. At 365 nm the *trans*-isomer has a much higher extinction coefficient than the *cis*-isomer. This general wavelength effect has proved to be of great preparative value.

[10] E. Fischer, M. Frankel, and R. Wolovsky, *J. Chem. Phys.*, 1955, **23**, 1367.

The role of the various excited states of azobenzene in the reaction has attracted close attention, but because of the lack of triplet-energy-level data the situation is still unclear. Excitation of the $n \rightarrow \pi^*$ bands of *cis-* and *trans-*azobenzene results in isomerization with quantum yields of 0.70 and 0.20, respectively. Thus the $n\pi^{*1}$, $n\pi^{*3}$, or $\pi\pi^{*3}$ states could be involved in the reaction. However, $\pi \rightarrow \pi^*$ excitation is also accompanied by isomerization, and this state could also be involved. In the latter case, quantum yields of 0.44 and 0.10 are observed for the *cis-* and *trans-*isomers, respectively.[11] The multiplicity of the excited state involved in the photoisomerization of stilbene has been clearly defined as a triplet state by sensitization studies. When similar methods were applied to azobenzene, however, conflicting results were obtained. Hammond and Jones[4] found that in the presence of triplet sensitizers of energy higher than 45 kcal mol^{-1} the composition of the photostationary state differed markedly from that in the unsensitized reaction, and thus it was concluded that triplet states were not involved in the direct photoisomerization. On the other hand, Fischer found identical photostationary state compositions for the sensitized and unsensitized reactions, indicating that triplet states could play a part in the unsensitized photoisomerization reaction.[12] Obviously further work is needed to clarify this important aspect of the reaction. Theoretical considerations, based on MO calculations[13] or spectroscopic studies,[14] suggest that isomerization is more likely to occur from a triplet state.

A particularly interesting feature of the reaction is the existence of a temperature effect on the composition of the photostationary state.[11,15] In all the cases studied the proportion of the *trans-*isomer increases at lower temperatures, although this is only observed for $n \rightarrow \pi^*$ excitation and not for $\pi \rightarrow \pi^*$ excitation. Separate examination of the *cis-* and *trans-*isomers shows that only the rate of the *trans* → *cis* reaction is temperature dependent and that one of the intermediate steps in this conversion must have an activation energy of 0.7 kcal mol^{-1}.[11] If the reaction occurs from a triplet state this could be sufficiently long-lived to permit thermal equilibration with the surroundings, and thus a temperature effect could be observable. The absence of a similar effect for the rate of *cis* → *trans* isomerization can most easily be accounted for if the *cis-*triplet is of higher energy than the corresponding *trans-*triplet.

It should be noted that comparative studies of solvent and substituent effects on the photoisomerization of azobenzene and stilbene revealed that they differ in many fundamental respects, and thus mechanistic parallels should not be drawn between the two systems.[16]

The thermal reversion of *cis-*azobenzenes to their *trans-*isomers has been shown to be a first-order process with an activation energy close to 24 kcal mol^{-1}

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[11] S. Yamashita, H. Ono, and O. Toyama, *Bull. Chem. Soc. Japan*, 1962, **35**, 1849.

[12] E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 796.

[13] D. R. Kearns, *J. Phys. Chem.*, 1965, **69**, 1062.

[14] R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, 1962, **36**, 2326.

[15] E. Fischer, *J. Amer. Chem. Soc.*, 1960, **82**, 3249; S. Malkin and E. Fischer, *J. Phys. Chem.*, 1962, **66**, 2482.

[16] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 3907.

for a wide range of derivatives.[17,18] The reaction can, however, be catalysed by a variety of reagents. In the case of *o*-hydroxyazobenes, much lower activation energies have been found, and this is presumed to be due to azo–hydrazone tautomerism, the hydrazone tautomer providing a low-energy pathway from the *cis*- to the *trans*-isomer.[19] The normal activation energy of 24 kcal mol^{-1} is some 13 kcal lower than that observed for isomerization of the stilbenes, and it has been suggested that the thermal isomerization of *cis*-azobenzene involves a linear transition state, in which one or both of the nitrogen atoms are sp^1 hybridized, rather than a twisted transition state.[17]

Because of the often pronounced colour change accompanying photoisomerization of the azobenzenes, this reaction is of practical importance in connection with the azo-dyes. This aspect of the reaction will be considered in more detail in Section 6.

4 Photocyclization

The photochemical conversion of stilbene into phenanthrene has been known for many years, but it was not until 1960 that an analogous photocyclization reaction was observed with azobenzene. Lewis[20] noted that solutions of azobenzene in concentrated sulphuric acid were readily decolorized by sunlight, and he showed that the major product was benzo[*c*]cinnoline (8), a heterocyclic analogue of phenanthrene. In the same year a group of Swiss chemists discovered a similar reaction using ferric chloride as catalyst,[21] and thus it appeared that, unlike stilbene, azobenzene required protonation or complexation for cyclization to occur. Lewis suggested the mechanism shown in the Scheme,[22] in which monoprotonated *cis*-azobenzene is the reactive species (for obvious steric reasons the *trans*-isomer cannot be involved). Although it was not possible to detect any difference between the rates of photocyclization of pure *cis*- and pure *trans*-azobenzene, this could be accounted for by the observation that the *trans* → *cis* photoisomerization occurred about one hundred times more rapidly than cyclization.[23]

Protonation of the azo-group probably results in inversion of the $n\pi^*$ and $\pi\pi^*$ singlet states, and the latter lower-energy state should, by analogy with stilbene, be favourable for cyclization. It is also likely that protonation provides a charge distribution in the excited state which facilitates the reaction. Complexation of the azo-group with ferric chloride would be expected to have the same effect. The multiplictiy of the excited state involved has not been investigated, and it is possible that triplet states could be involved. After formation of the

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[17] E. R. Talaty and J. C. Fargo, *Chem. Comm.*, 1967, 65.

[18] D. Schulte-Frohlinde, *Annalen*, 1958, **612**, 138.

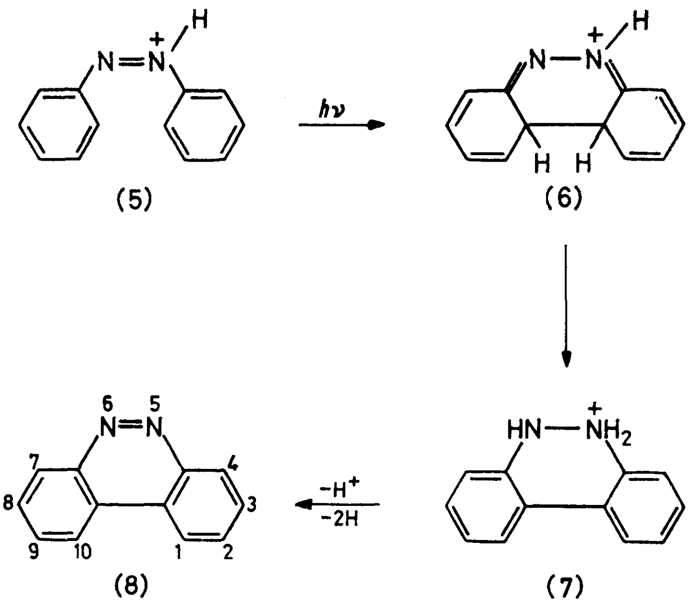
[19] E. Fischer and Y. F. Frei, *J. Chem. Soc.*, 1959, 3159; G. Wettermark, M. E. Langmuir, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1965, **87**, 476; G. Gabor and E. Fischer, *J. Phys. Chem.*, 1962, **66**, 2478.

[20] G. E. Lewis, *Tetrahedron Letters*, 1960, no. 9, 12.

[21] P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.

[22] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1966, **19**, 643.

[23] G. E. Lewis, *J. Org. Chem.*, 1960, **25**, 2193.



Scheme

intermediate (6) from (5), rapid conversion into the more stable (7) can occur by two prototropic shifts. Benzo[*c*]cinnoline is then formed by dehydrogenation of (7). The nature of this last oxidation step has been investigated in some detail, and it was found that in 98 % sulphuric acid the solvent was the effective dehydrogenating agent, being reduced during the reaction to sulphur dioxide. Frequently, reactions of this type were characterized by providing near-quantitative yields of the cyclized product.[24] In weaker acids, however, dehydrogenation was caused by monoprotonated azobenzene in the reaction

$$(7) + \mathrm{Ph\overset{+}{N}H{:}NPh} \rightarrow (8) + \mathrm{Ph\overset{+}{N}H_2{\cdot}NHPh}$$

Thus for every molecule of benzo[*c*]cinnoline formed, one molecule of hydrazobenzene is produced, and consequently the yield of the former compound cannot exceed 50 %. Under the acidic conditions employed, hydrazobenzene is efficiently isomerized to benzidine, and Lewis has shown in many instances that where the yields of cyclized product do not exceed 50 %, benzidine products are also formed in similar yields.[25] It is thus evident that for preparative purposes 98 % sulphuric acid should be used as solvent, provided that the stability of the starting material will permit its use.

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[24] G. M. Badger, C. P. Joshua, and G. E. Lewis, *Austral. J. Chem.*, 1965, **18**, 1639.

[25] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1963, **16**, 1042.

Quantum-yield studies have shown that photocyclization is a relatively inefficient process (the quantum yield for azobenzene is approximately 0.015), although the efficiency can be increased slightly in weaker acids.[22] It is suggested that under very strongly acidic conditions diprotonation can occur, which inhibits the reaction. Both 4-chloro- and 4-methyl-azobenzene have lower quantum yields than azobenzene, indicating the absence of a simple substituent effect.

The synthetic utility of the reaction has been studied extensively by Lewis and co-workers, and a wide range of substituted benzo[*c*]cinnolines can be made by this process. Certain aminoazobenzenes are exceptional and do not cyclize, as exemplified by 4-(dimethylamino)azobenzene, probably because diprotonation of these compounds occurs in strong acids.[24] Generally, 4-substituted azobenzenes give the 2-substituted benzo[*c*]cinnoline [see (8)], whereas 3-azobenzene derivatives give mixtures of the 1- and 3-substituted heterocycle, the latter predominating for steric reasons.[25,26] Azobenzenes with substituents in the 2-position give, in addition to the expected 4-derivative, small amounts of the unsubstituted (8), owing to cyclization occurring to an occupied carbon atom with subsequent elimination of the substituent.[25,27] In certain cases migration of the substituent can occur.[26] Photocyclization also occurs readily with several azobenzenes in which the chromophore is extended by conjugation, giving complex benzo[*c*]cinnolines.[28]

In general, the photocyclization reaction provides a very useful route to the benzo[*c*]cinnoline system, and is of particular value because of the ready availability of the starting materials and the simplicity of the experimental procedures involved. Where 98% sulphuric acid can be employed, very high yields can often be obtained.

5 Photoreduction

Photoreduction of the azobenzenes is of particular interest as it is the only common photochemical reaction that ultimately results in irreversible destruction of the azo-linkage. In spite of the possible significance of this process in the irreversible fading of azo-dyes, relatively few systematic studies have been made in this area. Sufficient data have been accumulated, however, to show that reduction can occur in two mechanistically distinct ways. The first of these involves direct excitation of the azobenzene chromophore to give an excited state that abstracts hydrogen from the solvent, whereas the second process requires excitation of the solvent to give a species capable of reducing azobenzene in its ground state. The second reaction type is not a true photochemical reaction of the azobenzene system, and thus will only be mentioned briefly.

A. Hydrogen Abstraction by an Excited State of the Azobenzene.—In 1949

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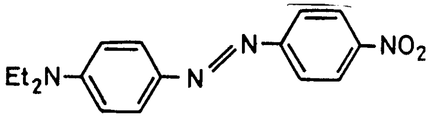
[26] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1964, **17**, 1036.

[27] C. P. Joshua and G. E. Lewis, *Austral. J. Chem.*, **1967**, **20**, 929.

[28] G. M. Badger, N. C. Jamieson, and G. E. Lewis, *Austral. J. Chem.*, 1965, **18**, 190; N. C. Jamieson and G. E. Lewis, *ibid.*, 1967, **20**, 321.

Blaisdell investigated the photochemical fading of azobenzene in various solvents. On the basis of spectroscopic evidence he concluded that the fading was a reductive process, and that the reduction products were hydrazobenzene and aniline.[29] Direct chemical evidence confirming these results was obtained several years later by Hashimoto and co-workers,[30] who carried out a similar reaction in acidified propan-2-ol. The primary reduction product was hydrazobenzene, which under the acidic conditions employed was converted into benzidine in high yield; aniline was also detected in the reaction products. The hydrazobenzene is presumably formed by abstraction of hydrogen from the solvent by an excited state of the azobenzene, and, as in the photoreduction of ketones, the efficiency of the reaction was found to be markedly solvent dependent. Propan-2-ol was the most effective solvent studied.

Although this reductive process could be involved in the fading of commercial azo-dyes, only one complex azobenzene derivative has been studied in this context. The red dye (9) was observed to fade when irradiated at 254 nm in alcohol solvents, giving the unstable hydrazo-compound (10).[31] The reaction is inefficient and solvent dependent, the quantum yield falling from approximately 5×10^{-4} in propan-2-ol to less than 1×10^{-6} in benzene. The excited state responsible for hydrogen abstraction is probably a triplet, although sensitization studies proved to be of little value in establishing this point. High-energy triplet sensitizers such as naphthalene had little effect on the quantum yield, indicating that if a triplet state were involved, inefficient intersystem crossing could not be the cause of the low quantum yield for hydrogen abstraction. When ketone triplet sensitizers were used, reduction of the sensitizer to ketyl radicals occurred, and these rapidly reduced the dye.[32] The azo-compound (9) also exhibits a novel



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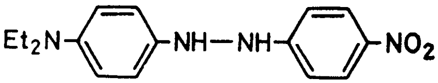

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[29] B. E. Blaisdell, *J. Soc. Dyers and Colourists*, 1949, **65**, 618.

[30] S. Hashimoto, J. Sunamoto, and H. Fujii, *Kogyo Kagaku Zasshi*, 1967, **70**, 699 (*Chem. Abs.*, 1967, **67**, 116375p).

[31] G. Irick and J. G. Pacifici, *Tetrahedron Letters*, 1969, 1303.

[32] J. G. Pacifici and G. Irick, *Tetrahedron Letters*, 1969, 2207

type of photoreduction in amine solvents, giving products derived from reduction of the nitro-group rather than the azo-group.[33]

It has been mentioned that photoreduction to hydrazobenzenes can result in irreversible cleavage of the azo-linkage, and this arises from an interesting photochemical or thermal disproportionation reaction of hydrazobenzenes. In this process, two molecules of the hydrazo-compound are converted into one molecule of the azo-compound and two molecules of an amino-compound:

$$2\text{ArNH}\cdot\text{NHAr} \rightarrow \text{ArN:NAr} + 2\text{ArNH}_2$$

Thus eventually the azo-compound is completely and irreversibly converted into the arylamine.

B. Reduction by Photochemically Produced Hydrogen Donors.—In certain cases azobenzenes can be rapidly reduced to hydrazo-compounds in the presence of substrates which absorb the incident radiation.[34] In this process, activated substrate molecules are formed, *e.g.* ketyl radicals from ketones, which act as hydrogen donors and reduce the azobenzene in its ground state. Many substrates will effect reduction of this type, particularly carbonyl compounds and chlorophyll and its derivatives, and it has been suggested that the reductive fading of azo-dyes on polymeric substrates could occur by this method. This interesting possibility, however, has yet to be demonstrated experimentally.

6 The Photochemical Fading of Azo Dyes on Polymeric Substrates

The photochemistry of the azobenzenes is of particular technological importance in connection with the photochemical fading of the azo-dyes. Light fastness has always been one of the prime considerations in the evaluation of dyes intended for commercial exploitation, and as a result the testing of photochemical stability has been a largely empirical process, with little attention directed towards the theoretical aspects of fading. A better understanding of the photochemistry of fading is essential if the search for new dyes is to be carried out with greater efficiency than it has been to date. In recent years some progress along these lines has been made, but a great deal more work remains to be done.

Attempts to study the detailed chemistry of the fading reactions on substrates is fraught with experimental difficulty, as a superficial glance at empirical light-fastness results will show. For example, a dye may suffer rapid photochemical degradation on one substrate, only to show superior light fastness on another. Even on one substrate variable results can be obtained, and it is now known that several factors can influence the fading process. Particularly important variables are the physical form of the dye, the moisture content of the substrate, the availability of oxygen within the substrate, and the chemical structure of the substrate itself. Even when all these factors can be controlled, difficulty is encountered in identifying the primary fading products, mainly because of their

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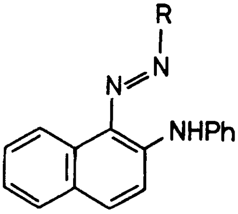
[33] J. G. Pacifici, G. Irick, and C. G. Anderson, *J. Amer. Chem. Soc.*, 1969, **91**, 5654.

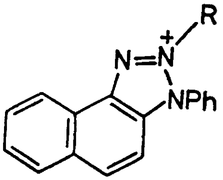
[34] R. Livingston and R. Pariser, *J. Amer. Chem. Soc.*, 1948, **70**, 1510; H. C. A. van Beek and P. M. Heertjes, *J. Phys. Chem.*, 1966, **70**, 1704; *J. Soc. Dyers and Colourists*, 1963, **79**, 661; H. C. A. van Beek, P. M. Heertjes, C. Houtepen, and D. Retzloff, *ibid.*, 1971, **87**, 87.

low concentration and their further degradation to small molecules. Consequently very few reports have appeared where the fading products have been isolated and identified.

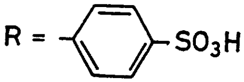
One interesting example is the *o*-aminoazo-dye (11), which fades very rapidly on cellulosic substrates when exposed to light.[1] The major decomposition product was identified as the heterocyclic compound (12), identical to that produced by irradiation of (11) in aqueous solution. The practical value of such experiments was illustrated by the correct prediction that methylation or benzoylation of (11) prevented photocyclization and gave dyes of much greater photochemical stability.



(11)



(12)



Haller and Ziersch[35] isolated 1,2-naphthaquinone from the fading products of 4-arylazo-2-naphthol dyes on cellulose, showing that photo-oxidation can be an important fading process. It is probable that photo-oxidative fading occurs from the hydrazone tautomers of *o*-hydroxyazo-dyes, and that singlet oxygen is involved.[36]

Where identification of degradation products presents great difficulties, studies of substituent effects on rates of fading can provide useful information. Thus for example, various *o*-hydroxyazo-dyes show approximately linear relationships between the logarithm of the fading rate and the Hammett σ constants of substituents in positions *meta* or *para* to the azo-group. On protein substrates (*e.g.* wool) the reaction constant ρ is positive, indicating that electron-withdrawing groups enhance the fading reaction, which is thus probably a reductive process. On a wide range of other substrates the dominant reaction is oxidative, and ρ is negative.[37,38] The reduction reaction on woollen fibres appears to involve

[35] R. Haller and G. Ziersch, *Melliand Textilber.*, 1929, **10**, 951.

[36] J. Griffiths and C. Hawkins, *J.C.S. Chem. Comm.*, 1972, 463.

[37] R. H. Kienle, E. I. Stearns, and P. A. Van der Meulen, *J. Phys. Chem.*, 1946, **50**, 363; H. R. Chipalkatti, N. F. Desai, C. H. Giles, and N. Macaulay, *J. Soc. Dyers and Colourists*, 1954, **70**, 487.

[38] J. W. Cumming, C. H. Giles, and A. E. McEachran, *J. Soc. Dyers and Colourists*, 1956, **72**, 373.

histidine side-chains,[38] and it is possible that the mechanism involves excitation of the substrate, as discussed previously in Section 5B. Similar Hammett correlations were found with 4-arylazo-1-naphthylamine dyes on cellulose acetate, the negative ρ value suggesting an oxidative fading process.[39]

Although reversible fading of azo-dyes is less serious than irreversible fading, nevertheless this phenomenon, usually referred to as phototropy, is an undesirable feature in any intended commercial dye. Phototropy of the azo-dyes is due principally to *cis–trans* photoisomerization, and since the *cis*-isomers absorb at shorter wavelength than the *trans*-isomers, the shade change on exposure to light can be quite pronounced. On polymeric substrates, particularly where the dye is molecularly dispersed within the polymer, the lifetime of the *cis*-isomer can be greatly increased, and thus the control of phototropy is particularly important. By a process of empirical selection, the majority of modern azo-dyes do not exhibit phototropy, and it is interesting to examine the structural features responsible for this. Many of the commercial azo-dyes have predominantly hydrazone structures, or have strongly electron-withdrawing groups *para* to the azo linkage, and, as mentioned in Section 3, these features either inhibit photoisomerization or reduce the lifetime of the *cis*-isomers. Phototropy is also inhibited by strong hydrogen bonding of the dye to the substrate, and thus it is more noticeable on the newer synthetic fibres which are generally devoid of sites for hydrogen bonding.

Although much data have already been accumulated, there are still many gaps in our present understanding of the photochemistry of the azobenzenes. It is to be hoped that future research will help bring closer together mechanistic and empirical studies, and because of the technical importance of the azobenzenes such work is expected to be of both considerable theoretical and practical value.

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[39] E. Atherton and I. Seltzer, *J. Soc. Dyers and Colourists*, 1949, **65**, 629; E. Atherton and R. H. Peters, *ibid.*, 1952, **68**, 64.