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Photoisomerizations of 3,3′-Dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene

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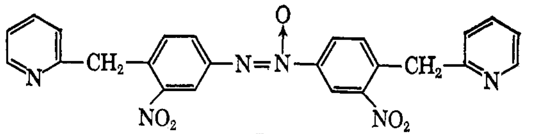
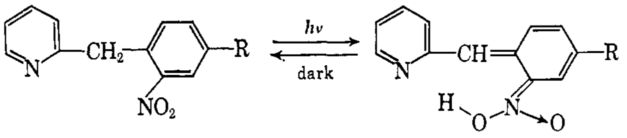
It is reported that, on irradiation with ultraviolet light, 3,3′-dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene (I) undergoes simultaneously *aci*-nitro–nitro tautomerization and geometrical isomerization. Kinetic data at several temperatures are reported for the dark reverse reactions. The thermodynamic properties of the dark reactions are also given.

In a previous paper,[1] the preparation of 3,3′-dinitro-4,4′-di(2-pyridylmethyl)azoxybenzene (I) was reported. It was observed that, when cooled crystals are exposed to ultraviolet light, a photochromic change from yellow to blue-green occurs. In room light the crystals fade to their original color. A reversible photochromism of cooled ethanol solutions of the compound was also noted. This behavior is similar to that observed for other *o*-nitrobenzylpyridines[1,2–6] and related compounds.[4,6–8] It is believed that the color change is due to the formation of the *aci*-nitro tautomer.[3–5,7]



I



In addition to the above structural change, I, on ultraviolet irradiation, might also undergo geometrical isomerization around the –N=N– bond. It was considered of interest to determine whether both photoisomerizations could be detected and isolated by spectrophotometric techniques, and, if so, to determine the kinetic and thermodynamic properties of the dark reactions.

Results and Discussion

Spectroscopic Studies.—The ultraviolet and visible spectra of an ethanol solution of I before and after exposure to ultraviolet light are shown in Fig. 1. The absorption band at 610 mμ, observed on irradiation of the cooled solution, is similar in shape to the visible band reported[3,4] for the photoisomer of 2-(2,4-dinitrobenzyl)pyridine. This band decays rapidly when the exciting radiation is removed.

In the ultraviolet spectrum of the unirradiated sample, absorption bands are observed at 330 and 260 mμ. The effect of ultraviolet light on these bands can be observed at room temperature. The band at 330 mμ decreases markedly in intensity, while the absorbance at 260 mμ increases slightly. After irradiation the spectrum slowly reverts to that originally observed. The ultraviolet spectra before and after exposure closely resemble those reported[9] for the pure *trans* and *cis* isomers, respectively, of azoxybenzene and several of its derivatives. This geometrical photoisomerization also occurs at low temperatures.

The ultraviolet spectra of unirradiated ethanol and cyclohexane solutions of I were not temperature dependent. In these solutions the compound exists essentially in the *trans* configuration. Evidence for an equilibrium mixture of *cis* and *trans* forms was observed in the spectrum of an unirradiated ethanol solution of azoxybenzene. Exposure to ultraviolet light enriched the solution with respect to the *cis* isomer. The original equilibrium was restored when irradiation was discontinued.

Kinetics.—First-order kinetics was observed for the fading reaction of the photoisomer of I absorbing at 610 mμ. Although many aromatic azoxy compounds undergo a molecular rearrangement to *o*-hydroxyazo compounds on prolonged irradiation with ultraviolet light,[10,11] and 2-(2,4-dinitrobenzyl)pyridine decomposes on extended exposure,[3,4] no detectable irreversible change occurred during the short exposure times utilized in the rate measurements reported in this study. For example, the same value for the first-order rate constant was obtained after each of several exposures of an ethanol solution to radiation in the flash photolysis experiments at room temperature.

The correlation of log k values with $1/T$, shown in Fig. 2, appears to be linear over a temperature range of 132°. The values of the Arrhenius activation energy, entropy of activation, and frequency factor were found to be 5.9 ± 0.1 kcal./mole, -39 e.u., and 4.2×10^4 sec.$^{-1}$, respectively. These values are consistent with those previously found for the thermal fading reaction

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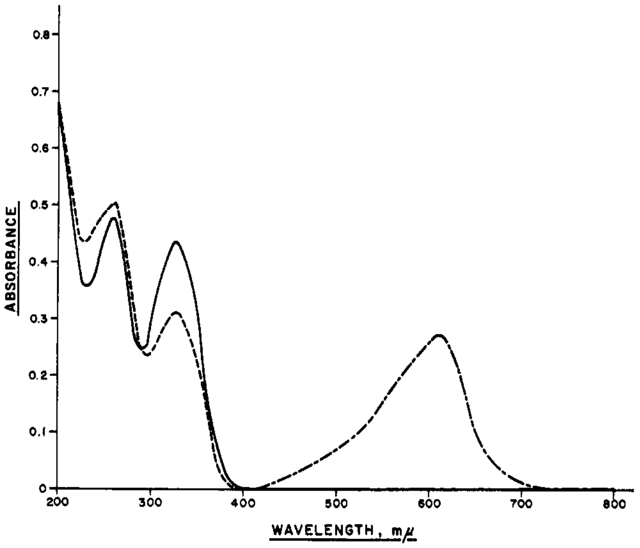

Fig. 1.—Absorption spectra of an ethanol solution of 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene: ———, ultraviolet and visible spectra before irradiation; – – – –, ultraviolet spectrum after irradiation for 3 min. at 25.0°; –·–·–·, and visible spectrum after irradiation for 1 min. at –90.0°.

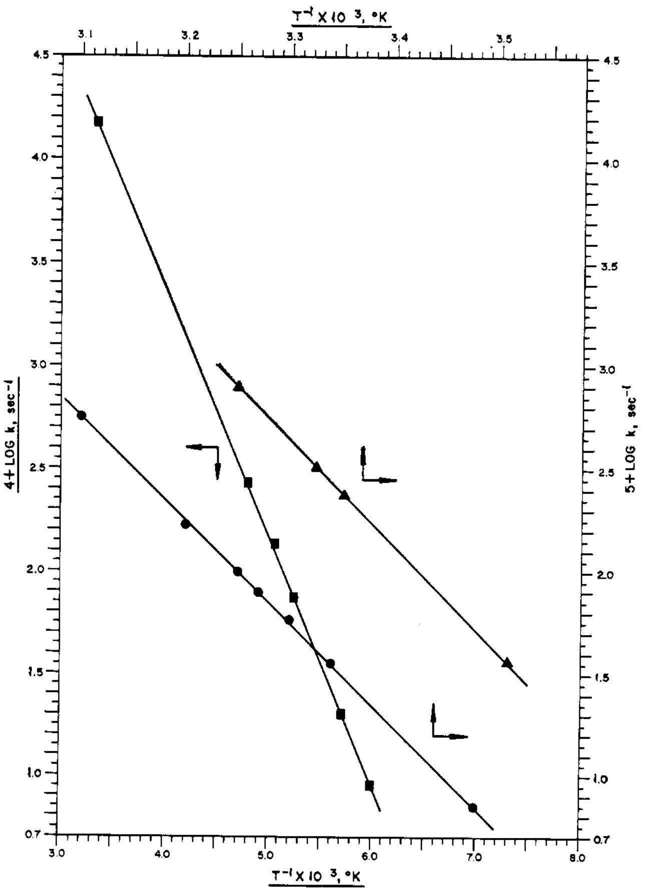

Fig. 2.—Plots of log k values *vs.* $1/T$ for 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene: □, *aci*-nitro–nitro tautomerization in ethanol (room temperature value is from flash photolysis experiments); ○, *cis–trans* isomerization in ethanol; and △, in cyclohexane.

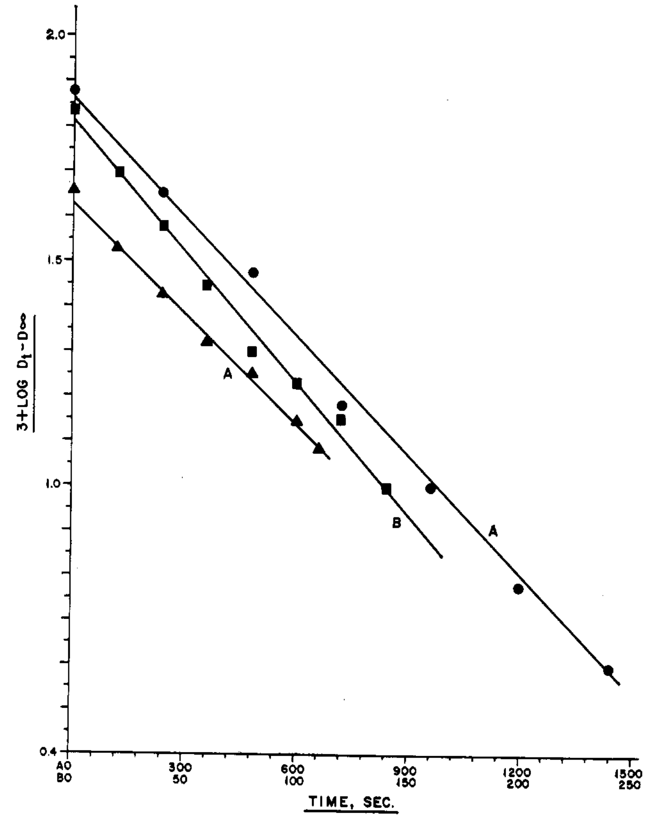

Fig. 3.—The dark reactions of 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene: □, *aci*-nitro–nitro tautomerization in ethanol at –75.5°; ○, *cis–trans* isomerization in ethanol at 39.1°; and △, in cyclohexane at 27.6°.

of the photoisomers of 2-(2,4-dinitrobenzyl)pyridine[4] and other *o*-nitrobenzyl compounds.[6]

The thermal *cis–trans* isomerization of I in ethanol and cyclohexane follows first-order kinetics. Log k values are given in Fig. 2 and thermodynamic data are presented in Table I.

TABLE I

THERMODYNAMIC PROPERTIES OF THE *cis–trans* ISOMERIZATION OF 3,3'-DINITRO-4,4'-DI(2-PYRIDYLMETHYL)AZOXYBENZENE

Solvent	E_{exp}, kcal./mole	ΔS^*, e.u.	A, sec.$^{-1}$
Ethanol	23.1 ± 0.1	0.79	2.6×10^{13}
Cyclohexane	23.6 ± 0.1	6.7	4.9×10^{14}

The values of E_{exp} agree closely with those found by Luner and Winkler[12] for the isomerization of pure *cis*-azoxybenzene and *cis-p,p'*-azoxytoluene in the same solvents. For azoxybenzene in ethanol, the energy of activation was found to be 22.9 kcal./mole, the same value as that reported by the above workers.

The rate of isomerization of I in cyclohexane is almost ten times as fast as in ethanol. At 34.5°, for example, the values of k in cyclohexane and ethanol were found to be 8.04×10^{-3} and 9.83×10^{-4} sec.$^{-1}$, respectively. This rate change arises from the almost tenfold difference in entropies of activation. The smaller value of ΔS^* observed for ethanol solutions probably signifies that, due to solvation, there is in this solvent more restriction to rotation about the nitrogen–nitrogen single bond in the activated state.

Experimental

Materials.—3,3'-Dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene[1,13] was purified by recrystallization from 2:1 ethanol–water,

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[12] P. Luner and C. A. Winkler, *Can. J. Chem.*, **30**, 679 (1952).

[13] The n.m.r. spectrum, measured in deuteriochloroform, was consistent with the assigned structure.

and melted at 135–136°. Azoxybenzene (Eimer and Amend) was recrystallized from methanol and melted at 36°, lit.[14] m.p. 36°. Spectro Grade cyclohexane and absolute alcohol were used as solvents in the kinetic measurements.

aci-**Nitro–Nitro Tautomerism.**—Rate studies at low temperatures in the range -106.4 to $-64.8°$ were carried out in a 2.5-cm. cell maintained at the required temperature in a specially constructed cryostat.[15] Ethanol solutions $(10^{-3}\ M)$ cooled in the cryostat were exposed for 30 sec. to the unfiltered radiation from a General Electric H3FE 85-watt mercury lamp with a Pyrex glass envelope. Uniform coloring of the solutions was observed. The cryostat was quickly transferred to the sample cell compartment of a Cary Model 14 spectrophotometer, and the decrease in absorbance of the visible absorption band at 610 mμ was followed with respect to time. A matched cell containing pure solvent was in the reference beam.[15] In all cases, the absorbance of the system ultimately fell to zero. In order to obtain all the kinetic data reported in this paper, at least three runs were made at each temperature.

Room temperature measurements were carried out by flash photolysis techniques previously described.[4]

Geometrical Isomerization.—Rate measurements in the temperature range 11 to 50° were carried out in a 2.5-cm. cell on solutions $(\sim 10^{-5}\ M)$ in ethanol and cyclohexane. Required temperatures were maintained by circulating water from a Haake temperature-regulating bath through a thermostatable cell jacket.[16] Solutions were exposed for 30 sec. to the radiation from the lamp described above, and the cell was quickly transferred to the sample compartment of the spectrophotometer. For both compound I and azoxybenzene, the increase in absorbance of the ultraviolet absorption band at 330 mμ was followed with respect to time. A matched cell containing pure solvent was in the reference beam. In all cases, the absorbance at 330 mμ ultimately returned to its value before irradiation.

Temperature Measurement.—Measurements of temperatures were made by a glass encased copper-constantan thermocouple which dipped into the solutions at the cell neck.

Calculations.—Values of the first-order specific rate constant, k, were calculated from the slope of the straight line obtained in plots of $\log D_t - D_\infty$ *vs.* time, where D_t is the optical density at a given time interval and D_∞ is the optical density after complete isomerization. In the case of the *aci*-nitro–nitro isomerization, D_∞ was equal to zero. The reactions were followed for at least three half-lives. Illustrative plots are given in Fig. 3. The Arrhenius activation energy, E_{exp}, the entropy of activation, ΔS^*, and the frequency factor, A, were calculated by procedures given previously.[4,6]

Ultraviolet and Visible Absorption Measurements.—A Cary Model 14 spectrophotometer was used. Solutions were measured in a 2.5-cm. cell against a reference of pure solvent in a matched cell.

Acknowledgment.—We wish to thank Dr. G. Wettermark for the flash photolysis experiments.

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Thermal Reactions of Trifluoroiodomethane with Halobenzenes

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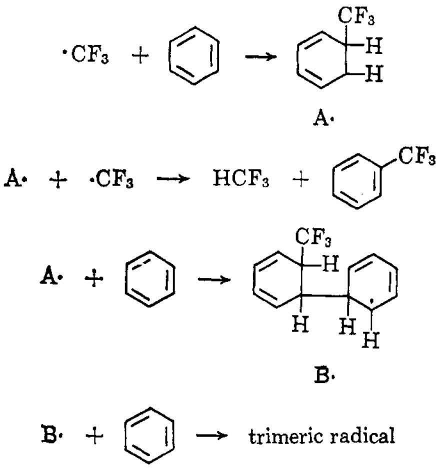
Trifluoroiodomethane reacts with chloro-, bromo-, and iodobenzene at 198° yielding the *o*-, *m*-, and *p*-halobenzotrifluorides, fluoroform, and molecular iodine. A mechanism involving addition of trifluoroiodomethane to the aromatic ring in a free-radical chain reaction followed by elimination of hydrogen iodide which reacts with trifluoroiodomethane to form fluoroform and iodine is proposed for these reactions.

Previous work by others has shown that trifluoromethyl radicals add readily to various aromatic systems. The gas phase reactions of benzene with trifluoromethyl radicals produced by the photolysis of hexafluoroacetone are reported to yield fluoroform, benzotrifluoride, and polymeric oils.[2] The formation of fluoroform and benzotrifluoride was observed to occur at low benzene pressures (less than 10 mm.), but no fluoroform was noted at higher benzene pressures (greater than 40 mm.). The following mechanism which is consistent with these observations is proposed (eq. 1–5).

The cyclohexadienyl radical A· apparently is formed readily as shown in reaction 2, and at higher benzene pressures essentially all of the trifluoromethyl radicals formed by the photolysis react with benzene in this manner. Apparently, only at lower pressures is the concentration of trifluoromethyl radicals great enough for reaction 3, which produces the fluoroform, to occur. Szwarc and his co-workers point out that, in the liquid phase, where the concentration of the aromatic compound is about 3000 times that at 40-mm. pressure,

$$CF_3COCF_3 \xrightarrow{h\nu} 2\cdot CF_3 + CO \qquad (1)$$



(2)

(3)

(4)

(5)

no fluoroform would be expected from a reaction of an adduct radical such as A· with trifluoromethyl radicals.[3] This assumption formed the basis of the method used by Szwarc and his co-workers for determining the relative reactivities of various unsaturates and aromatics toward reaction with trifluoro-

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[1] Taken from the thesis submitted by E. Bedard in partial fulfillment of the requirements for the M.S. degree from the University of Kansas, 1963.

[2] S. W. Charles and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960); S. W. Charles, J. T. Pearson, and E. Whittle, *ibid.*, **57**, 1356 (1961); J. L. Holmes and K. O. Kutsche, *ibid.*, **58**, 333 (1962).

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