Considering the experimental errors and the uncertainties in the activity coefficients, the values for the degree of aggregation probably can be considered accurate to about ±10%. This appears to be about comparable to that obtained by measurements on sedimentation equilibria in the centrifuge with Schlieren optics.[5]

NOTE ADDED IN PROOF.—Since the completion of this work, H. A. Levy, M. D. Danford and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959), have published results of an X-ray diffraction study of hydrolyzed 5.81 monomolar Bi(III) solutions. The data can be explained by assuming one aggregate containing six bismuth ions which has cubic symmetry. This would explain the absence of depolarization which was noted in this work.

[CONTRIBUTION FROM LABORATORY OF PHOTOCHEMISTRY AND SPECTROSCOPY, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Temperature Dependence of Photoisomerization Equilibria. Part I. Azobenzene and the Azonaphthalenes

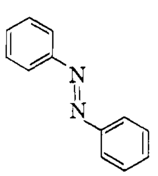
BY ERNST FISCHER

RECEIVED OCTOBER 26, 1959

On irradiation of solutions of azobenzene or the azonaphthalenes with light at specific wave lengths, a photoequilibrium between the respective *cis* and *trans* isomers is established. It is found that, in the absence of *thermal* isomerization, cooling shifts the photoequilibrium toward the *trans* isomer to an extent depending on the nature of the compound, the solvent, and the wave length of the photoactive light. Thus photoequilibration at 365 mμ of 2,2′-azonaphthalene results in 20% *trans* at −20° and in 82% at −125°. The results indicate that the quantum yields of photoisomerization strongly depend on temperature.

Previous reports from this Laboratory[1,2] and from Zimmerman and co-workers[3] described the dependence of the *cis-trans* photoisomerization equilibria of azocompounds on the wave length of the light used in photoequilibration, at one temperature.

The present paper shows how the photoequilibrium, reached by irradiation at certain wave lengths, changes with the temperature at which the irradiation is carried out. All irradiations were performed at temperatures sufficiently low to stop any *thermal* isomerization, *i.e.* below 0° for azobenzene (I) and 2,2′-azonaphthalene (II) and below minus 20° for 1,1′-azonaphthalene (III).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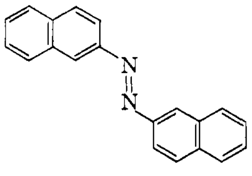
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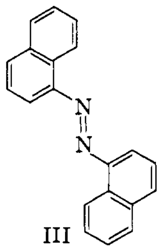
III

Experimental

Reagents. Azobenzene.—Eastman Kodak white label azobenzene was recrystallized from ethanol and from hexane.

1,1′-Azonaphthalene and 2,2′-azonaphthalene were prepared as described previously.[4] No *cis* isomers were separated for the purpose of the current investigation.

Solvents.—Methylcyclohexane, methylcyclopentane and isononane were purified by passage through columns of activated silica and activated alumina (Woelm, basic, activity I).[5] In the experiments with azonaphthalenes these solvents were distilled from a potassium–sodium alloy, in a high vacuum, into the optical cell containing the solute. The cell was then fused-off under vacuum.[6] The same procedure was used with tetrahydrofuran and 2-methyl-tetrahydrofuran. A 1:1 mixture of the two served as solvent in some cases. 1-Propanol was freshly distilled from potassium hydroxide.

Photochemistry and Spectrophotometry.—Irradiations and spectrophotometric measurements in a wide range of temperatures were carried out in a Cary Model 14 spectrophotometer, as described previously.[6] Photoisomerization was investigated for each compound in a temperature range limited upwards by the required absence of *thermal cis* → *trans* isomerization and downwards by the freezing points of the solvents used. Each experiment started with a solution of the respective *trans* isomer. Absorption spectra were recorded at the various required temperatures. This was followed by irradiation, at each temperature, with light from an a.c. operated Philips Spectral lamp No. 93110 mercury arc, at several wave lengths corresponding to the mercury emission "lines." These were isolated by the usual Corning filter combinations[3] (for the 578, 546, 436 and 365 mμ bands), a Balzer interference filter (for the 405 mμ band) and a combination of a solution of nickel chloride and Corning filters 9863 and 0620 (for the 313 mμ band).[7] The light beam filled practically 100% of the cell windows. The number of light quanta at 365 mμ incident on the solution in the cell was determined by iron oxalate actinometry in the same cells, at room temperature, as approximately 4 × 10^{17} quanta/minute. The solutions had a volume of three ml. and were not stirred. Unless stated otherwise, cells had a cross section of 10 × 10 mm.

The position of the photoequilibrium reached on irradiation of any solution with light at any particular wave length was found to be independent of the isomeric composition before irradiation (*cf.* Fig. 2), the intensity of the light incident on the solution (down to $^1/_4$ of the value given above), the concentration of the solutions (*cf.* caption to Fig. 3 E) and the absorbance of the solutions (up to 1.2). These points are important since, in the absence of stirring and rapid diffusion, light which is strongly absorbed may not even reach the deeper layers of the solution, making it impossible to attain true photoequilibrium.

The present investigation aimed primarily at the determination of photoequilibria, and only crude measurements of the rates of photoequilibration were made in some cases. The results of these kinetic experiments are expressed as half-life times, *i.e.*, the time required to achieve one half of the total change in isomeric composition resulting from irradiation with light at a particular wave length.

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

[2] E. Fischer and Y. Frei, *ibid.*, **27**, 328 (1957).

[3] G. Zimmerman, THIS JOURNAL, **80**, 3528 (1958), and earlier literature listed there.

[4] M. Frankel, R. Wolovsky and E. Fischer, *J. Chem. Soc.*, 3441 (1955).

[5] G. Hesse and H. Schildknecht, *Angew. Chem.*, **67**, 737 (1955).

[6] Y. Hirshberg and E. Fischer, *Rev. Sci. Irst.*, **30**, 197 (1959).

[7] R. E. Hunt and W. Davis, THIS JOURNAL, **69**, 1415 (1947).

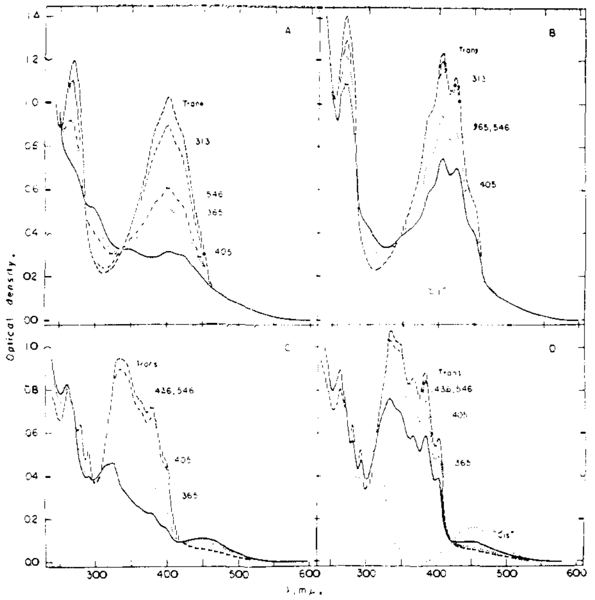

Fig. 1.—Absorption spectra at various temperatures, before and after photoequilibration with light at the indicated wave lengths: 1,1′-azonaphthalene in 1-propanol, 15 mg./l., at (A) −20° and (B) −120°; 2,2′-azonaphthalene in 1-propanol, 7 mg./l., at (C) −40° and (D) −100°. The '*cis*' curves in (B) and (D) are explained in the text. Concentrations of solutions are expressed as mg./l. at room temperature.

Results and Discussion

The experimental results are expressed as percentage of *trans* isomer in the isomeric mixture. The isomeric composition of mixtures was estimated from the height of the narrow bands or shoulders at about 335 mμ for azobenzene, 400 mμ for 1,1′-azonaphthalene and 380 mμ for 2,2′-azonaphthalene, assuming that at the indicated wave lengths the absorption of the *cis* form is negligible as compared with that of the *trans* form. (*Cf.* the absorption curves calculated accordingly for the pure *cis* isomers in Figs. 1B and 1D.) The position of these absorption bands depends somewhat on the temperature and the solvent and is only approximately indicated by the above wave lengths.

In each series of experiments the absorption curves of the *trans* isomer and of the same solution after photoequilibration with light at several wave lengths were taken at each temperature, as shown in Fig. 1 for some typical experiments. Incidentally, these curves show that the *cis* isomers lack the spectral fine structure of the *trans* isomers at low temperatures. The same observation was made with *trans* and *cis* stilbene.[8] Fig. 2 indicates how the isomeric composition changes during irradiation with light of one wave length, at different temperatures. Half-life values for the process of photoisomerization, calculated from these and similar curves, are summarized in Table I.

Fig. 3 summarizes the results for the temperature dependence of the photoequilibria attained for each of the three compounds investigated, in several solvents and with light at several wave lengths. The latter were chosen so as to represent the two main absorption bands of the azocompounds, in the visible and near ultraviolet regions, respectively.

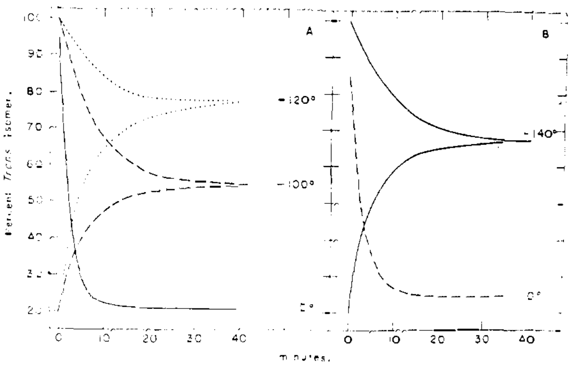

Fig. 2.—Change of isomeric composition with time of irradiation, at the indicated temperatures: (A) 2,2′-azonaphthalene in methylcyclohexane, irradiated at 365 mμ, (B) azobenzene in 1-propanol, irradiated at 313 mμ.

TABLE I

RATES OF PHOTOISOMERIZATIONS AT VARIOUS WAVE LENGTHS λ, AND TEMPERATURES *T*, EXPRESSED AS PHOTOEQUILIBRATION HALF-LIVES τ

Compound	λ, mμ	*T*, °C.	τ, min. *cis* → *trans*	τ, min. *trans* → *cis*
Azobenzene in 1-propanol	313	0	. .	2
		−120	. .	4
		−140	3.8	7
	436	0	1.8	. .
		−120	1.5	. .
		−140	1.6	. .
Azobenzene, in methylcyclopentane	313	0	. .	3
		− 40	. .	3.2
		− 80	. .	3.4
		−140	. .	6.8
	436	0	2	. .
		− 40	2	. .
		− 80	2	. .
		−140	2	. .
2,2′-Azonaphthalene in methylcyclohexane	365	0	. .	1.5
		−100	3.7	6
		−115	. .	8
		−120	3.6	. .
	546 + 578	0	4.5	. .
		−100	4.5	. .
2,2′-Azonaphthalene, in 1-propanol	365	0	. .	1
		−100	. .	6
		−145	2.3	. .
	546 + 578	0	8	. .
		−100	11	. .
2,2′-Azonaphthalene, in "tetrahydrofuran"[a]	365	−140	4	4
	405	−140	15	. .

[a] A 1:1 mixture of tetrahydrofuran and its 2-methyl derivative.

The curves in Fig. 3 show that cooling causes a pronounced shift of the photoequilibrium toward the *trans* isomer, the extent of this shift depending on the compound, the solvent and the wave length of the light used for photoequilibration. At the same time it is seen from the kinetic data given in Fig. 2 and in Table I that the rate of the *cis* →

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[8] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953), where previous references are listed.

trans photoisomerization is practically independent of temperature, while the *trans* → *cis* rate is lowered considerably on cooling. Photoisomerization takes place rapidly even at the lowest temperature investigated. The results with 2,2′-azonaphthalene at −145° are particularly striking since in this case irradiation with light at 365 mμ transforms the *cis* into the *trans* isomer rapidly and almost completely, although at this wave length the absorption of the *trans* form is at least twenty times higher than that of the *cis* form.

Analysis of Results.—Photoequilibrium is achieved when the rates of the *cis* → *trans* and *trans* → *cis* photoisomerizations are equal. Following Zimmerman's analysis[3] we have at photoequilibrium, achieved with light at a certain wave length

$$\varphi_c\epsilon_c(1 - x) = \varphi_t\epsilon_t x \qquad (1)$$

where the left and right terms are proportional to the rates of the *cis* → *trans* and *trans* → *cis* photoisomerizations, respectively. φ_c and φ_t are the quantum yields for these photoisomerizations, ϵ_c and ϵ_t are the molar extinction coefficients of the *cis* and *trans* isomers, and x is the fraction of *trans* isomer at photoequilibrium. φ and ϵ refer to the wave length of the light used for photoisomerization. Solving (1) for x gives

$$x = \varphi_c\epsilon_c/(\varphi_c\epsilon_c + \varphi_t\epsilon_t) \qquad (2)$$

or

$$1/x = 1 + (\varphi_t/\varphi_c)(\epsilon_t/\epsilon_c) \qquad (3)$$

Equations 2 and 3 describe the dependence of the isomeric composition, at photoequilibrium, on the relative spectral absorption of the two isomers and on the relative quantum yield of their photochemical interconversion. Since x and ϵ_t/ϵ_c are found experimentally, values of φ_t/φ_c can thus be calculated. Table II summarizes some typical results, based on the observations that ϵ_t/ϵ_c changes only slightly with temperature.

TABLE II

OBSERVED PHOTOEQUILIBRIA AND RELATIVE SPECTRAL ABSORPTIONS FOR PHOTOISOMERIZATION AT VARIOUS WAVE LENGTHS λ AND TEMPERATURES T, AND RELATIVE QUANTUM YIELDS CALCULATED THEREFROM BY EQUATION 3

Compound	λ, mμ	ϵ_t/ϵ_c	T, °C.	x	φ_t/φ_c
Azobenzene in methylcyclopentane	313	18	0	0.22	0.20(0.25)[a]
			−100	.33	.1
			−140	.60	.037
	436	0.31	0	.88	.45(0.51)
			−100	.92	.29
			−140	.97	.10
2,2′-Azonaphthalene in methylcyclohexane	365	21	− 20	.20	.19
			−100	.53	.04
			−120	.78	.013
	436	0.43	− 20	.86	.37
			− 80	.92	.21
			−100	.98	.05

[a] Values in parentheses are calculated from φ_t and φ_c observed by Zimmerman[3] at 25°.

The observed shift of the photoequilibrium in favor of the *trans* isomer on cooling is thus seen to be due to a decrease of φ_t/φ_c, *i.e.*, the proportion between the rates of the *trans* → *cis* and *cis* → *trans* photoconversions. From the results in Table I it appears that a decrease of φ_t is mainly to blame, since the rate of the *cis* → *trans* conversion is practically constant, whereas that of the *trans* → *cis* conversion is diminished on cooling.

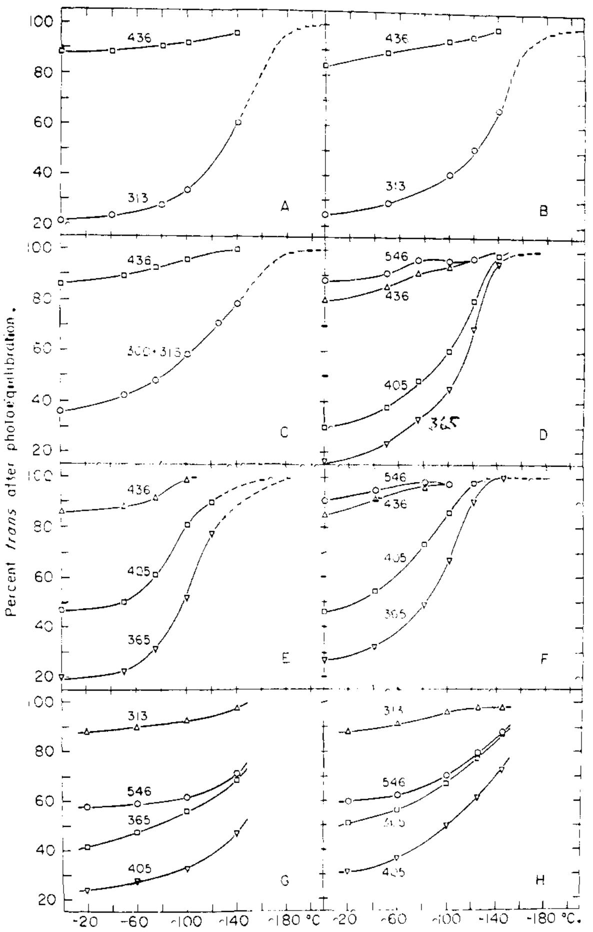


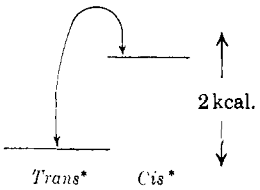
Fig. 3.—Change of isomeric composition, at photoequilibrium, with temperature of photoequilibration carried out at the indicated wave lengths: azobenzene in (A) methylcyclopentane, 8 mg./l.; (B) 1-propanol, 6.3 mg./l.; (C) a 1:1 mixture of methylcyclohexane and isononane, 7 mg./l.; 2,2′-azonaphthalene in (D) tetrahydrofuran/methyltetrahydrofuran, 5.7 mg./l.; (E) methylcyclohexane, 10 mg./l., identical with results in methylcyclohexane, 150 mg./l., and in methylcyclopentane, 2 mg./l.; (F) 1-propanol, 7 mg./l.; 1,1′-azonaphthalene in (G) methylcyclopentane, 13.5 mg./l.; and (H) 1-propanol, 15 mg./l.

Equation 2, applied to results at several wave lengths and one temperature, shows that the observed[1–3] pronounced dependence of the position of the photoequilibria on the wave length of the photoconverting light is due mainly to variations of ϵ_t/ϵ_c, since these variations are very much larger than those of φ_t/φ_c (*cf.* Table II).

The fact that the quantum yields of at least some of the photoisomerizations are strongly affected by changes in temperature indicates that photoisomerization involves thermal steps with sufficiently high potential barriers. Such steps might include the thermal interconversion of electronic excited *cis** and *trans** isomers, as suggested by Zimmerman.[3] (The asterisk denotes excited states.) In this case the above conclusion that φ_t decreases on cooling much more than φ_c implies that the barrier for the *cis** → *trans** conversion is lower than that for the *trans** → *cis** conversion, indicating that the excited level of the *cis* isomer is higher than that of the *trans* isomer. This parallels the situation at the ground level, where the enthalpy difference between the two isomers amounts to 10 kcal./mole for azobenzene.[9]

A semiquantitative approach is possible, if one makes the oversimplified assumption that the variation of φ_t/φ_c with temperature is due solely to variations in φ_t. The values of φ_t/φ_c, such as those given in Table II, may then be assumed to be proportional to the rates of the *trans* → *cis* photoconversion.[10] Application of the Arrhenius equation to these rates at various temperatures leads to values for the activation energy, or potential barrier, for the thermal *trans** → *cis** conversion. Such crude calculations, based on the data of Table II, give about 2 kcal./mole for 2,2′-azonaphthalene in methylcyclohexane.

The mechanism of photoconversion emerging from the above discussion is shown in the following scheme of the electronic excited levels. The experimental evidence does not allow more far-reaching conclusions and does not exclude the possibility that other, long-lived states may serve as intermediaries between the short-lived excited singlet states. It should also be borne in mind that one may expect large quantitative variations of the described temperature effect with the nature of the compound undergoing isomerization.



The above conclusions might be compared with those reached by Schulte-Frohlinde[11] regarding the *cis* $\rightleftarrows$ *trans* photoisomerization of *p*-methoxy-*p*′-nitrostilbene with light at 365 mμ. He observed that the above photoequilibrium varies strongly with the nature of the solvent used, due to the fact that the solvent has a pronounced effect on the quantum yield of the reverse process. Schulte-Frohlinde suggests that photoisomerization involves passage through a triplet state formed from the excited singlet *cis** and *trans** states. The triplet is sterically much more similar to the *cis** state and therefore is formed from it with greater ease than from the *trans** state. This should make the *trans** → triplet → *cis** conversion more sensitive to environmental effects than the *cis** → triplet → *trans** conversion.

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[9] R. J. Corruccini and E. C. Gilbert, THIS JOURNAL, **61**, 2925 (1939).

[10] This is approximately true when the rate of *trans** → *cis** is small compared with that of *trans** → *trans*. Such is the case in the range of temperatures where $\varphi_t << 1$.

[11] D. Schulte-Frohlinde, *Ann.*, **615**, 114 (1958).

[CONTRIBUTION NO. 1059 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA]

The Phosphorescence of Adsorbed Acriflavine[1]

BY JEROME L. ROSENBERG AND DONALD J. SHOMBERT

RECEIVED OCTOBER 5, 1959

A systematic study of the phosphorescence of acriflavine–silica gel adsorbates has uncovered certain systematic errors in some previous work: sample temperature may be indeterminate in high vacuum under prolonged illumination, and silica phosphorescence may cause appreciable interference unless near ultraviolet is removed from the exciting source. The phosphorescence decay of acriflavine is shown to be non-exponential and strictly first order over an exceptionally wide range of conditions. The postulate that dye–gel attachments occur with a distribution of adsorption energies is consistent with the observed non-exponentiality of triplet decay, with the effect of dye concentration on the decay rate and with the dependence of the decay rate on the wave length of excitation and of luminescence observation. There is an activation energy for populating the triplet state from the excited singlet, but an inefficient crossing from the lowest vibrational level of the excited singlet may occur. The activation energy for α-phosphorescence indicates that greater nuclear displacement occurs in the triplet than in the fluorescent singlet state. The non-radiative decay from triplet to ground has been shown to be less than three times as fast as the direct radiative transition.

Introduction

Early studies of the phosphorescence of acriflavine (3,6-diamino-10-methyl-acridinium chloride) revealed two long-lived radiative processes originating from the photo-excited dye.[2] Accepted interpretations clearly identified these two processes as arising from the same metastable electronic state.[3,4] The longer wave length component, Lewis' β-phosphorescence, represents the direct radiative transition from the metastable state, now identified as a triplet, to the ground singlet state, T → S. The shorter wave length component, Lewis' α-phosphorescence, has the same spectral character as fluorescence because it arises from a thermal activation from the triplet to the first excited singlet, T → S′, followed by the emission, S′ → S.[5] There has been a recent series of experimental and theoretical investigations into the details of dye luminescence,[6,7] prompted by an interest in the role of excited states in photo-

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[1] This work was supported by the National Science Foundation under Grant NSF-G1237. The material presented here is abstracted from a dissertation presented to the University of Pittsburgh by Donald J. Shombert in partial fulfillment of the requirements for the Ph.D. degree in 1959.

[2] P. Pringsheim and H. Vogels, *J. chim. phys.*, **33**, 345 (1936).

[3] A. Jablonski, *Z. Physik*, **94**, 38 (1935).

[4] G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

[5] M. Kasha, *Chem. Revs.*, **41**, 401 (1947).

[6] S. Kato and M. Koizumi, *Bull. Chem. Soc. Japan*, **30**, 27 (1957).

[7] B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).