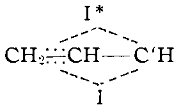
do observe, there must be an additional transition state of slightly lower free energy that leads to exchange without isomerization. Such a transition state could be represented as XI. Of course our



$$\underset{\mathrm{I}}{\overset{\mathrm{I}^*}{\mathrm{CH_2{\cdots}CH{-}C'H_2}}} \qquad \mathrm{XI}$$

data provide no information as to whether the two iodines in XI are on the same or on opposite sides of the plane determined by the three carbon atoms, but XI could revert to IX and then dissociate to cause iodine exchange without carbon isomerization. If dissociation of IX took place about as easily as rearrangement to a symmetrical species like IV or X, all of our observations of both atomic and molecular mechanisms could be accommodated to the reversible formation of π-complexes in which iodine exchange is easier than the formation of species containing more conventional valence bonds. These mechanisms somewhat resemble other reactions like the hydration of olefins[20] in which significant free energy barriers apparently oppose the rearrangements between π-complexes and conventionally bound species.

Acknowledgments.—Professor Robert F. Nystrom of the University of Illinois provided the allyl alcohol-1-C^{14} without which this study would have been impossible.

Professor Robert R. Becker of Columbia University provided valuable advice and facilities in connection with counting carbon-14, and Dr. Alfred P. Wolf of the Brookhaven National Laboratory carried out some measurements that helped in the characterization of our material.

During some of the period of this investigation, William Cain held a special teaching assistantship provided by the du Pont Chemical Corporation. The research also was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314.

[20] P. Riesz, R. W. Taft, Jr., and R. H. Boyd, THIS JOURNAL, **79**, 3724 (1957).

EUGENE, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Kinetics of the Photolysis of 2,2'-Azo-bis-isobutyronitrile

BY P. SMITH AND A. M. ROSENBERG[1]

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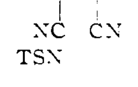
The kinetics of the photolysis of 2,2'-azo-bis-isobutyronitrile, AZO, in deaerated benzene solution at 25.00 ± 0.02° have been investigated employing 366 mμ radiation, isolated from the output of a medium pressure, mercury-quartz lamp with Corning filters C.S. No. 7-37 and 0-52. The initial concentration of AZO was varied between 0.0144 and 0.0699 *M* and the reaction pursued to as far as *ca.* 80% destruction of AZO in some cases. The reaction course was followed spectrophotometrically over the 290–400 mμ range. All changes in optical density observed agree with the supposition that the only reaction product that absorbs radiation at 290–400 mμ is dimethyl-N-(2-cyano-2-propyl)-ketenimine, DKI. Throughout every run $-R[\mathrm{AZO}] = \phi I_{\mathrm{abs}}$, where ϕ is 0.47 ± 0.02 mole einstein^{-1}, and the fractional molar conversion, f, of AZO into DKI did not vary detectably, *viz.*, $+R[\mathrm{DKI}] = f\phi I_{\mathrm{abs}}$. The value of f has been estimated to be 0.59 ± 0.02 and 0.58 ± 0.02 by two different methods. For the purpose of settling some of the aforementioned points, a specimen of DKI, 99.3 ± 0.6 mole % pure, was prepared by the thermal decomposition of AZO. Its absorption spectrum in benzene solution over the 290–404 mμ range is reported. As previously suggested by Talât-Erben and Bywater, its extinction coefficient about 360–380 mμ is small. Finally, the results obtained are discussed.

Introduction

The simple photolysis of 2,2'-azo-bis-isobutyronitrile, AZO, has had little attention. Its likely similarity to the much investigated, thermally induced decomposition and its possible suitability as an actinometric reaction prompted the present work. There appears to have been only one attempt so far to investigate the kinetics of this process.[2] This was in benzene solution at 25° using impure 366 mμ mercury radiation. The reported results refer to only one initial concentration of AZO. The reaction course was followed spectrophotometrically at one wave length, 345 mμ. Evidence was given that thermally decomposing AZO in benzene solution can form material that absorbs appreciably at 345 mμ. In view of the liklihood that photochemically decomposing AZO might display a similar effect, no greater accuracy was claimed for the results obtained.

The thermal decomposition of AZO in solution has been studied extensively over the 30–105° range. It follows simple first-order kinetics at about the same rate in a variety of solvents, with no evidence of induced chain processes. The evolution of nitrogen is quantitative and in unreactive media, such as carbon tetrachloride or toluene, the final organic products are tetramethylsuccinonitrile, TSN, and small amounts of material thought to arise from disproportionation of 2-cyano-2-propyl radicals, R·, for example, isobutyronitrile. Leaving aside these disproportionation products, the reaction stoichiometry is



$$\underset{\text{AZO or } \mathrm{RN_2R}}{(\mathrm{CH_3})_2\underset{\mathrm{CN}}{\mathrm{C}}\mathrm{N{=}N}\underset{\mathrm{CN}}{\mathrm{C}}(\mathrm{CH_3})_2} \longrightarrow \mathrm{N_2} + \underset{\mathrm{TSN}}{(\mathrm{CH_3})_2\underset{\mathrm{NC}}{\mathrm{C}}{-}\underset{\mathrm{CN}}{\mathrm{C}}(\mathrm{CH_3})_2} \qquad (1)$$

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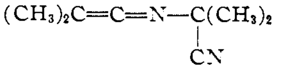
[1] This paper is based partly upon a thesis submitted by A. M. Rosenberg in partial fulfillment of the requirements for the degree of Master of Science at Purdue University, January, 1958.

[2] R. Back and C. Sivertz, *Can. J. Chem.*, **32**, 1061 (1954). There has also been a study of the scavenging action of molecular iodine in this system, J.-C. Roy, J. R. Nash, R. R. Williams and W. H. Hamill, THIS JOURNAL, **78**, 519 (1956).

A recent, spectrophotometric investigation of the thermal breakdown of AZO in deaerated toluene solution at 70–105°, by Talât-Erben and Bywater,[3a] has shown that dimethyl-N-(2-cyano-2-propyl)-ketenimine, DKI



$$(CH_3)_2C{=}C{=}N{-}\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2 \qquad (2)$$

is a reaction intermediate, which decomposes at about the same rate as does AZO; DKI is probably the only material produced during the breakdown of AZO that absorbs light in the 310–390 mμ range, the absorption of reaction mixtures at 360–380 mμ being claimed[3b] to be due only to AZO.

The work reported here was therefore carried out at 25° employing highly purified mercury 366 mμ band radiation with benzene as solvent. The conditions were comparable to those employed previously[2] and calculated to favor the accumulation of DKI, if it were formed. After completion of this study, a method of preparing relatively pure DKI became available. This enabled the results gained to be more fully interpreted.

Experimental

Materials. 2,2′-Azo-bis-isobutyronitrile.—Eastman Kodak, White Label material was recrystallized four times from absolute ethanol below 40° in subdued light and stored *in vacuo* in the dark at *ca.* −10° until use, m.p. (uncor.) 101° with decomposition. The products of the third and fourth recrystallizations had identical absorption spectra over the 250–400 mμ range, taken in 0.010 *M* absolute ethanol, path length 10 cm., λ_{max} 345 mμ, ϵ^4_{max} 13.0 ± 0.1; and over the 290–700 mμ range for 0.05–0.10 *M* benzene solution, path length 1–10 cm., λ_{max} 345 mμ, ϵ_{max} 15.0 ± 0.1 (lit. λ_{max} 345 mμ, ϵ_{max} 14.9[3] and 14.7[2] for toluene and benzene, respectively). The values for ε in benzene over the whole 300–400 mμ range agreed with those already reported,[2] Beer's law being obeyed. Within the 430–700 mμ region ε was $\gg$0.05. This AZO was used for all purposes save the preparation of TSN and DKI. In the case of TSN, unpurified Eastman material was employed. Porophor N (Recrystallized), Westville Laboratories, Monroe, Connecticut, was used without further purification for the DKI preparation.

Tetramethylsuccinonitrile.—AZO, 20 g., was refluxed in benzene solution under nitrogen (Linde, High Purity, Dry) for 48 hr., the solvent then removed by vacuum distillation, and the residue, 84% crude yield, recrystallized[5] twice from methanol, m.p. (uncor.) 170° (lit. 169°,[2] 167–167.5°[5]). The progress of purification was followed spectrophotometrically over the 250–400 mμ range in 0.03 *M* absolute ethanol solution, path length 1 cm. The product of the first recrystallization showed a slight absorption at 330–360 mμ, corresponding to ε $\gg$0.3. This disappeared after the second recrystallization but reappeared in 0.20 *M* benzene solution examined over the 280–404 mμ range, ε $\gg$ 0.05 at 330–360 mμ, which was otherwise diactinic, *i.e.*, ε $\gg$0.02. It may be supposed that this small absorption results from an impurity, possibly AZO. These observations agree with expectation for a substance such as TSN and with the claim,[3] by Talât-Erben and Bywater, that TSN does not absorb appreciably at 320 mμ.

Dimethyl-N-(2-cyano-2-propyl)-ketenimine.—A procedure suggested by Dr. George S. Hammond of Iowa State College was followed. Two liters of cyclohexane was placed in a three-liter, three-neck round bottom flask fitted with a stirrer, a reflux condenser (with protecting drying tube) and a nitrogen bubbler. After a preliminary purging of the liquid with nitrogen (Linde, High Purity, Dry), it was heated to reflux temperature and 133 g. of AZO quickly dissolved. Refluxing was then carried out for 145 minutes, the flask next being quickly stoppered and immersed in an ice–salt bath. The resultant crystals were removed by filtration at *ca.* 10° with the exclusion of moisture. The combined filtrates from five such operations were concentrated at reduced pressure. The brown residue was distilled with a Claisen head at 3 mm. pressure, the fraction at 35–40° being collected, about 100 ml. of colorless liquid, f.p. 13.1°. This was followed by three further distillations at 0.5 mm. pressure, with a pot temperature of 35° and collecting the middle 80% fraction. The course of purification was followed by determination of the freezing point using a precision recording Pt resistance thermometer arrangement.[6] The results obtained were 13.52, 13.97 and 13.99°, respectively. ΔH of fusion for DKI may be taken[6] as 3 ± 1 kcal. mole^{-1}. The purity of the final distillation product is then estimated as 99.3 ± 0.6 mole % ($n^{30.0}_D$ 1.444_9). The freezing point data given are minimum values and may be low by a few tenths of a degree, on account of the form of the cooling curve in the early stages of freezing. This uncertainty does not affect the purity estimate very much and, in any case, is allowed for in the quoted result. When not in use, DKI was stored *in vacuo* in the dark at *ca.* −10°. Solutions in benzene of the freshly distilled DKI, up to 0.06 *M* in 1–10 cm. quartz cells, were spectrally examined over the 290–404 mμ range. Beer's law was obeyed. λ_{max} 291 mμ, ϵ^7_{max} 150.5 ± 1.6. From 290 to 400 mμ at 10 mμ intervals ε is, respectively,[7] 150.3 ±1.6, 131.2 ± 1.5, 84.5 ± 0.9, 42.3 ± 0.6, 17.4 ± 0.2, 6.37 ± 0.07, 2.29 ± 0.05, 0.79 ± 0.04, 0.31 ± 0.04, 0.15 ± 0.04, 0.10 ± 0.04 and 0.09 ± 0.04.

Solvents. Benzene.—A dry sample prepared by Mr. S. Carbone[8] was used, $n^{20.0}_D$ 1.5010_2, m.p. 5.53°, 99.97 ± 0.03 mole % purity determined from the cooling curve taken with the recording Pt resistance thermometer arrangement mentioned earlier.[6] The method of purification employed, starting with technical quality material, was essentially that of Rybicka and Wynne-Jones.[9] This benzene was used for all purposes except in the preparation of TSN, where technical grade material was employed.

Other Solvents.—All were dried and simply distilled before use.

Apparatus. The Reaction Vessel.—This was a rectangular Pyrex absorption cell of all-fused construction and external dimensions 12 × 12 × 46 mm., Beckman Type 2097, the light path being measured as 10.0 mm. To its open end was fused a 5-ml. capacity bulb by way of a 10 cm. length of

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(3) (a) M. Talât-Erben and S. Bywater, THIS JOURNAL, **77**, 3710, 3712 (1955). These two papers give a full literature survey on this reaction. See also C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 511; J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958). (b) It was stated that individual measurements of the optical density of reaction mixtures at 360, 370 and 380 mμ and at different reaction times agreed with the assumption that only AZO was absorbing, the rate constants for AZO removal calculated on the basis of these measurements being shown to agree with those obtained by the nitrogen evolution method. Both the spectrally and gasometrically determined data show some scatter, hence the cited claim was considered to be perhaps slightly stronger than the given facts but hardly likely to be very far from the truth; this view is supported by the results of the present study, *e.g.*, see Table I.

(4) Decadic molar extinction coefficient, $\epsilon = ([AZO]l)^{-1} \log_{10} (I_0/I)$, [AZO] in mole l.$^{-1}$ and l in cm.

(5) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

(6) K. L. Nelson, *Anal. Chem.*, **29**, 512 (1957).

(7) The impurity present was taken to be TSN, which is transparent to 290–404 mμ radiation. The quoted uncertainties in ε include that for the purity of the DKI. Liquid DKI rapidly turns yellow on exposure to dry air. The extent of the chemical reaction at *ca.* 20° over a period of 1–2 hr. was undetectable by freezing point measurements. In any event, the spectral measurements were carried out in such a way as to minimize interference on this score, no effect being noticeable in the 290–404 mμ region. This yellow coloration is probably related to the similar one, followed by formation of a brown precipitate, observed when benzene solutions of AZO containing air were allowed to stand in Pyrex bottles at room temperature in sunlight. In this connection it might be noted that R. Back and C. Sivertz, ref. 2, do not mention whether air was excluded from the reaction mixture during their kinetic investigation; furthermore, J. P. Van Hook and A. V. Tobolsky, ref. 3a, have noticed that thermally decomposing AZO in benzene solution, at 60° with air present, forms material that absorbs appreciably at 360–380 mμ, in contrast to the results obtained with air absent.

(8) S. Carbone, M.S. Thesis, Purdue University, January, 1958.

(9) S. M. Rybicka and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 3671 (1950).

TABLE I

PURITY OF THE LIGHT BEAM

Wave length, mμ	Lamp[a,b] output, %	Filter[c] trans., %	ϵ_{AZO},[d] cm.$^{-1}$ M^{-1}	ϵ_{DKI},[d] cm.$^{-1}$ M^{-1}
546–623	11.7	0.05	$\ngtr$0.05	...
436–496	4.3	.05	$\ngtr$0.05	...
391–404	3.6	.05	1.9–0.5	$\ngtr$0.1
366	7.4	16.8	9.65 ± 0.05	0.46 ± 0.04
334	0.8	$\ngtr$0.006	13	11
313	5.1	$\ngtr$ .00005	5	69
303–230	11.6	$\ngtr$ .00004	3	117

[a] On an energy basis. [b] % of total output, taken from data supplied by the maker. These data are accurate to ±5, ±8 and ±15% for the visible, strong bands in the ultraviolet and weak bands in the ultraviolet, respectively. There is presumably some radiation occurring between the mercury lines and tending to render the conclusions based on this table to be more qualitative than the numbers themselves would suggest. [c] Calculated from the transmissions of both Corning filters, examined separately against air, together with estimated data for the front face of the reaction vessel, obtained by spectral measurements on the reaction vessel against a like cell made of quartz, both vessels containing distilled water. [d] The data at 366 mμ relate to 365.6 mμ; those at 303–230 mμ, to 303 mμ. The absorption of DKI beyond 404 mμ was not determined. Pure DKI appears colorless and ϵ_{DKI}^{404} is 0.07 ± 0.04, hence the absorption in the visible beyond 404 mμ is probably negligible. About 55% of the lamp's energy is in the infrared. This was assumed to be essentially removed, mainly by the 7–37 filter and the (see Irradiation Procedure) *ca.* 8 cm. of bath-water before the reaction cell.

8 mm. o.d. Pyrex tubing which bore also a short sidearm carrying a constriction and terminating in a ₸ 10/30 outer joint. With the reaction vessel upside down, reaction mixture was pipetted into the 5-ml. bulb through the ₸ 10/30 joint which was next used for attaching the whole unit to a high vacuum line so that the reaction mixture could be degassed. This was done by repeated cycles of freezing at the temperature of liquid nitrogen, evacuation and careful thawing to 8 ± 2° in subdued light. Three evacuations proved sufficient to remove all detectable traces of gas, hence, after the third evacuation, the unit was detached from the vacuum line by sealing off the constriction at a pressure of less than 10^{-6} mm. All the reaction mixture, after thawing, was then poured into the reaction vessel by inverting the unit.

The Optical Bench Assembly.—The light source, a 330 watt Hanovia Model No. AE50A12 quartz-mercury arc, ran from a 220 volt d.c. generator and in series with a variable, water cooled, 50 ohm resistance. Its output was adjusted and maintained constant using a negative-feedback, photo-regulator device. This relied upon fluctuations of the arc intensity to cause changes in the output of a regulating, "blue sensitive" phototube from a Beckman Model DU Spectrophotometer, exposed to filtered light from the lamp, to effect changes in the grid potentials of a bank of ten RCA 1625 amplifier tubes in parallel with the lamp, so compensating for the original fluctuations. The arc operated at 15° to the horizontal, and the arc center was at the focus of a fused quartz lens of aperture 80 mm. and focal length 130 mm., the arc itself being in the focal plane. The roughly parallel beam produced passed through a second lens of the same type, placed 10 cm. from the first one, and was concentrated further by a third lens of aperture 55 mm. and focal length 65 mm. placed 195 mm. from the second lens. The beam then passed normally in turn through a light filter and two plane, circular, fused quartz windows, 3 in. diameter, set in two opposite sides, 7 in. apart, of a rectangular, water thermostat-bath, made of welded nickel and with all metal parts therein either of nickel or nickel-plated. From there it arrived at a monitoring RCA 935 phototube, the output of which was measured using a stable, bridge-balanced amplification unit, of tested linear response, running from a Sola constant voltage transformer, Cat. No. 30806. The above components, save for the thermostat bath, were mounted on a Gaertner Model L357 double rod optical bench with the monitoring and regulating phototubes at opposite ends. The output of the two phototubes remained constant to ±1.0% over 24 hours of operation without resetting of the controls.

The Light Filters.—These were the same for both the initiating and controlling light beams so as to ensure close regulation. They comprised the Corning combination C.S. No. 0-52 plus 7-37 with transmission properties as listed in Table I. For the present investigation [AZO] ranged between 0.07 and 0.007 *M* and [DKI] never was greater than 0.02 *M*. Ignoring for the moment the presence of DKI, the data in Table I show that $\ngtr$ *ca.* 0.06% of the absorbed energy is outside the 366 mμ region, the major contamination being at 391–404 mμ. Allowing for the presence of the DKI does not cause the above claim to be modified, even for the most extreme example, *viz.*, the case where [AZO] and [DKI] are, respectively, 0.007 and 0.02 *M* (the final stage of run D). Again, with regard to the energy absorption solely by the DKI, not more than *ca.* 0.3% occurs outside the 366 mμ region.

Actinometry.—The potassium ferrioxalate system was employed. The quantum yield for ferrous ion production at 25.0° and *ca.* 366 mμ was taken[10] as 1.21 mole einstein^{-1}. The procedures of Hatchard and Parker[10] were followed, potassium ferrioxalate being recrystallized three times from conductivity water after preparation by mixing 1.5 *M* solutions of reagent grade potassium oxalate (Baker and Adamson) and ferric chloride (Baker). Irradiations were carried out in the reaction cell using 3.00 ml. of actinolyte, 0.00600 *M* and 0.10 *N* in potassium ferrioxalate and sulfuric acid (Baker and Adamson, C.P.), respectively, a slow stream of nitrogen (Linde, High Purity, Dry), purified by bubbling first through Fieser solution[11] and then aqueous lead acetate, being used for stirring. The exposed solution now was made up to 25 ml. with buffer, etc., before spectral examination. A check of the absorption of the actinolyte over the 300–700 mμ range was made using 1 cm. quartz cells and 0.10 *N* H_2SO_4 as the blank. The data obtained, the fact[10] that the actinolyte absorbs essentially completely for radiation of wave length less than 300 mμ, the dependence of the quantum yield on wave length[10] and the information in Table I show that the correction to the actinometrically determined light intensity at 366 mμ, to allow for extraneous radiation and incomplete absorption at 366 mμ, is negative and small,[13] *ca.* 0.1–0.3%. The cited range for this % arises from the unknown relative contribution for the components of the 436–496 mμ band.

Spectrophotometry.—Spectral measurements in the case of irradiated reaction mixtures, benzene solutions of DKI and AZO, the reaction vessel when containing water, and the actinometry were carried out with a Beckman model DU spectrophotometer fitted with a thermojacketed cell compartment at 25.0°. A Cary Recording Spectrophotometer Model 10-11 M was used for benzene solutions of DKI and AZO and for all the other spectral work. Both machines were calibrated with respect to wave length, over the 290–404 mμ range, and optical density using mercury arcs and conventional optical density standards, respectively. Readings with the Beckman at any given wave length were taken always at the same half-intensity band width to ensure maximum precision. The Cary was run at slit control and high voltage control settings 10 and 4, respectively. Unless stated otherwise, quoted ε values refer to Cary determined data. The reported checks of Beer's law were carried out with both spectrophotometers.

Irradiation Procedure.—All photolyses were effected without stirring at 25.00 ± 0.02° (N.B.S. thermometer). The reaction cell was located midway between the two quartz windows of the bath, *i.e.*, *ca.* 8 cm. from each quartz window. It was held upright by means of the 8 mm. o.d. tubular neck with its clear faces normal to the axis of the light beam. The reaction course was followed by withdrawing the cell at convenient time intervals and examining the reaction mixture spectrophotometrically after thorough agitation. It was not considered likely that the absence of stirring during reaction would have much effect on the results because of the expected simplicity of the process and the fact that, except for the solutions most dilute in AZO, the total AZO concentration fall for one irradiation period was generally 5–10% of the AZO concentration at the start of that period. This prediction is well supported by the concordance of the results obtained. Readings were taken

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(10) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*), **A235**, 518 (1956).

(11) L. F. Fieser, THIS JOURNAL, **46**, 2639 (1924).

generally at 10 mμ intervals, or more frequently, over the 290–400 mμ region. The blank was purified benzene, degassed and sealed in another reaction vessel, benzene in contact with air having variable optical densities at about 300 mμ, perhaps because of the presence of an oxygen complex.[12]

The runs carried out are listed in Table II.

TABLE II

SUMMARY OF RUNS CARRIED OUT

Run	A	B	C	D	E	F
$[\text{AZO}] \times 10^2$, mole l.$^{-1}$	1.44	3.04	3.26	3.31	6.78	6.99
$I_0 \times 10^{-14}$, qu. sec.$^{-1}$ cm.$^{-2}$	2.50	2.50	2.96	2.67^a	2.96	2.09

^{a} Estimated from Fig. 2, the reaction mixture volume in this case being *ca.* 3.5 ml., some 20% larger than for all the other runs and for the actinometry (3.00 ml.).

Results

Figure 1 gives a typical family of curves showing the variation of D over the 290–400 mμ range for one reaction mixture after different irradiation times at constant incident light intensity. At shorter wave lengths there is a rise in D with time, at longer wave lengths, a fall. The isosbestic wave length corresponding to constant D was the same for all runs, namely, 329.1 ± 0.2 mμ, and did not change detectably with irradiation time. It would appear that the new light absorbing material produced during the photolysis is not affected appreciably by further irradiation. This view is supported by the excellent linear variation of D for any given reaction mixture, taken at 10 mμ intervals over the 290–400 mμ range, with that at 345 mμ during the full course of irradiation. Use was made of this reproducible linear dependence to establish the initial reaction rate law, by measuring initial reaction rates in terms of variation of D with time in the shorter wave length region, where D varies relatively rapidly. Figure 2 illustrates the results obtained, the initial rate of change of D at 310 mμ being linearly dependent upon the initial absorbed light intensity, $(I_{\text{abs}})_0$, which was varied by changing both the initial concentration of AZO, $[\text{AZO}]_0$, and the incident light intensity, I_0.

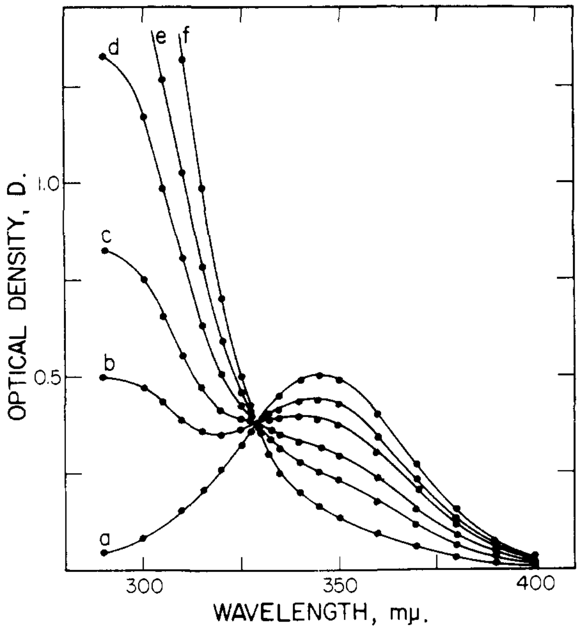

Fig. 1.—Dependence of the optical density D over the 290–400 mμ range upon irradiation time: run D; a, b, c, d, e and f refer to 0, 4.45, 7.96, 15.12, 22.43 and 39.66 × 10^4 sec., respectively. Readings were taken at five other times (see Fig. 3) but are omitted for the purpose of clarity.

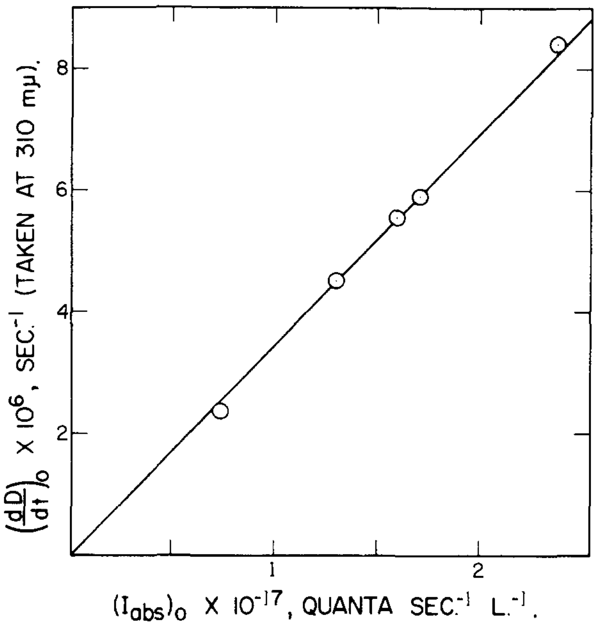

Fig. 2.—Dependence of the initial reaction rate, taken as $(\mathrm{d}D_{310}/\mathrm{d}t)_0$, on the initial absorbed light intensity, $(I_{\text{abs}})_0$; in order of increasing rate, runs A, B, C, F and E, respectively.

The initial reaction rate law so established is

$$(-R[\text{AZO}])_0 = \phi(I_{\text{abs}})_0 \tag{3}$$

where

$$(I_{\text{abs}})_0 = 10^3\, l^{-1}\, I_0\,(1 - 10^{-\epsilon l[\text{AZO}]_0})(1 + g\, 10^{-\epsilon l[\text{AZO}]_0}) \tag{4}$$

and[13] l, ϵ, and ϕ are, respectively, the reaction vessel

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(12) D. F. Evans, *J. Chem. Soc.*, 345 (1953); 1351 (1957).

(13) It is assumed throughout the above analysis that extinction coefficients and also ϕ and g are constants. The factor g is 0.042 and was inserted to allow for the reflection of the light beam back into the reaction mixture as, and after, it emerged therefrom. The reflections at the benzene/Pyrex and water/Pyrex interfaces were shown to be 0.01 and 0.3%, respectively. For these estimates the refractive indexes over the 656–434 mμ region for the materials involved ("International Critical Tables," Vol. II and VII, McGraw-Hill Book Co., New York, N. Y., 1927 and 1930) were extrapolated to 366 mμ and the light beam taken to be parallel. The reflection at the air/fused quartz/water interfaces, for the back window of the thermostat bath, was assumed to be 3.9% ("The Photochemistry of Gases," W. A. Noyes, Jr., and P. A. Leighton, Reinhold Publ. Corp., New York, N. Y., 1941, p. 84). Subsequent reflections at the RCA 935 phototube and its blackened housing were judged to be negligible in view of the geometry of the setup. Hence the total percentage reflection is 4.2%, and may be assumed to remain constant throughout irradiations.

In the case of the actinometry, the reflection corrections are small. This is a consequence of the fact that the actinolyte transmits less than *ca.* 0.06% at 366 mμ for a 1.00 cm. path length. Also, the reflection at the actinolyte/Pyrex interface for the front face of the reaction vessel, taking the refractive index of the actinolyte to be that of 0.1 N H_2SO_4 is 0.3%, whereas the corresponding reflection for the case of the kinetic runs with benzene solutions is 0.01%. The implied positive correction of 0.3% to the actinometric data was not invoked because it is somewhat offset by the negative correction arising from other sources (see Actinometry).

path length in cm., $\epsilon^{366}_{\mathrm{AZO}}$ in cm.^{2} mole,$^{-1}$ and the quantum yield for AZO removal in mole einstein,$^{-1}$ the units of I_0 being einstein cm.$^{-2}$ sec.$^{-1}$. Equation 4 leads to the integrated rate expression

$$(1 + g)^{-1} \log_{10} \left\{ \frac{(10^D - 1)(10^D + 1)^g}{(10^{D_0} - 1)(10^{D_0} + 1)^g} \right\} = - \phi 10^3 I_0 \epsilon t \quad (5)$$

where D and D_0 relate to AZO[14] at 366 mμ, assuming that (4) may be extended to the reaction mixture at all stages, the system being kept well stirred. The same result follows if the integration is effected in more detail. The reaction mixture occupies a rectangular parallelepiped of depth l cm. and front face of area p cm.^{2}. In an infinitely narrow volume element p dx cm.^{3}, taken normal to the incident, supposedly parallel, light beam and x cm. from the front face, the number of moles of AZO destroyed in dt sec. is

$$p \, \mathrm{d}x \, \phi I \alpha \, [\mathrm{AZO}] \, \mathrm{d}t \quad (6)$$

where I, α and [AZO] are, respectively, the light intensity at x, 2.303 $\epsilon^{366}_{\mathrm{AZO}}$ and the molarity of [AZO] in p dx. Assuming the system to be well stirred, I may be replaced by $I_0 e^{-\alpha x[\mathrm{AZO}]}\,(1 + g e^{-2\alpha(l - x)[\mathrm{AZO}]})$ and the total number of moles of AZO destroyed within the entire reaction mixture in dt sec. is then

$$p\phi I_0 \alpha[\mathrm{AZO}] \, \mathrm{d}t \int_0^l e^{-\alpha x[\mathrm{AZO}]} \, (1 + g \, e^{-2\alpha(l - x)[\mathrm{AZO}]}) \, \mathrm{d}x = - pl \, 10^{-3} \mathrm{d}[\mathrm{AZO}] \quad (7)$$

where $-$d[AZO] is the change in AZO molarity throughout the reaction mixture. After integration of (7), it follows that

$$\int_{[\mathrm{AZO}]_0}^{[\mathrm{AZO}]} Q^{-1} \, d[\mathrm{AZO}] = - \int_0^t \mathrm{d}t = -t \quad (8)$$

where Q is $I_0 \phi \, 10^3 \, l^{-1}(1 - e^{-\alpha l[\mathrm{AZO}]})(1 + g e^{-\alpha l[\mathrm{AZO}]})$, which yields (5) upon integration. The stirring of the reaction mixture was in fact only intermittent. However, a concentration gradient in [AZO] entirely along the light beam, such as would tend to arise without stirring, would result in no deviation from (5), except insofar as the inner filter effect[14b] of the DKI is stirring dependent. The entire inner filter effect is shown below to be at the most a small one, hence its variation is probably unimportant. The agreement in the values of ϕ obtained by use of (3) and (5), noted later, supports this view.

A maximum limit to the contribution of the inner filter[14b] effect may be set by assuming all the DKI, as formed, to be transferred to an infinitely small solution element at the front face of the reaction mixture. Assuming the reaction mixture and the volume element at the front face to be individually stirred, but not to mix, leads to an

$$\int_{[\mathrm{AZO}]_0}^{[\mathrm{AZO}]} Q^{-1} \, e^{\alpha' l[\mathrm{DKI}]} \, \mathrm{d}[\mathrm{AZO}] = -t \quad (9)$$

expression where Q, α' and [DKI] are, respectively, the same quantity employed in equation 8, 2.303 $\epsilon^{366}_{\mathrm{DKI}}$, and the molarity with respect to DKI for the whole reaction mixture, taking the DKI as being uniformly distributed throughout the entire solution. Now $\alpha' l$[DKI] ranges between zero and 0.02 in this present study, hence the use of equation 5 to evaluate ϕ could not lead to as much as a 2% underestimate, a more probable figure being 1%. The above treatment neglects the effect of the inner filter on the absorption of the reflected beam. This readily may be shown to be insignificant. If the above artifice is not employed and the solution is taken to be uniformly mixed at all times, then I in equation 6 is replaceable by $I_0 e^{-Wx}(1 + g e^{-2Wl})$ where W is $(\alpha[\mathrm{AZO}] + \alpha'[\mathrm{DKI}]$, whence the equation equivalent to (8) becomes

$$\int_{[\mathrm{AZO}]_0}^{[\mathrm{AZO}]} Q^{-1}(1 + G)(1 + GH)^{-1}(1 - J)^{-1} \, \mathrm{d}[\mathrm{AZO}] = -t \quad (10)$$

where G, H^{-1} and J are, respectively, $(\alpha'[\mathrm{DKI}])/(\alpha[\mathrm{AZO}])$, $(1 + (\alpha l[\mathrm{AZO}])/2! + (\alpha l[\mathrm{AZO}])^2/3! \ldots)$ and $(g\alpha' l[\mathrm{DKI}])(g + e^{\alpha l[\mathrm{AZO}]})^{-1}$, the validity of (10) resting on the approximation $e^{-\alpha' l[\mathrm{DKI}]}$ equals $(1 - \alpha' l[\mathrm{DKI}])$ because $\alpha' l[\mathrm{DKI}] \ngtr 0.02$. The term $J \ngtr 8 \times 10^{-4}$ and $(1 + G)(1 + GH)^{-1}$ increases from unity at the reaction start to no more than 1.006 for the case showing the most change. This suggests that ϕ is not as much as 0.7% underestimated by use of equation 5, a likely figure being 0.4%. It seems safe to assume that the percentage underestimation of ϕ resulting from neglect of the inner filter effect is *ca.* 0.4–1.

Figure 3 shows the results for all examined runs plotted to equation 5. The points fall on one straight line, the extent of reaction in some cases being as much as 80%. The quantum yield for AZO removal, ϕ, derived from the slope of this line is 0.47 ± 0.02 mole einstein^{-1}, taking[14c] ϵ as 9.8 ± 0.1. A similar figure for ϕ, 0.45 ± 0.03 mole einstein^{-1}, follows from the slope of the line in Fig. 2 and the ratio[14a] $-\Delta D^{366}/\Delta D^{310}$, 0.215, calculated using a least squares treatment on the results from all runs for the different irradiation times. Figure 4 shows the data used, the changes in D, ΔD, for any one run and wave length being

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(14) (a) The effective wave length for the photolysis was taken as 365.6 mμ, based upon relative intensity data for the 366 mμ band components given in "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929, p. 229. This choice was suggested by the fact that ϵ_{AZO} varies 4% over that band range, as determined with the Cary at high resolution. Nevertheless, for the sake of simplicity, the 366 mμ notation is retained throughout this work. (b) The D_{AZO} values used in equation 5 were calculated from the observed optical densities of the reaction mixtures by correcting for the absorption of the DKI present. For this purpose, the fractional molar conversion of AZO into DKI, $\epsilon^{366}_{\mathrm{AZO}}$ and $\epsilon^{366}_{\mathrm{DKI}}$ were taken as 0.60, 9.8 and 0.5, respectively, the ϵ values being Beckman determined quantities (see ref. 4c). This way of treating the kinetic results assumes that the DKI formed merely acts as an inner filter and that this inner filter effect is negligible. The first assumption implies that photoactivated DKI molecules, or species derived therefrom, do not affect $-R$[AZO]. In view of the deactivating influence of the solvent and the possibility of activated DKI molecules decomposing, the main effect under this assumption probably would arise from the products of photodecomposed DKI. These products are likely to be inert 2-cyano-2-propyl radicals and TSN and hence would have little effect on $-$R[AZO]. In any event, the extent to which DKI is decomposed in this system is small. The second assumption is discussed in the main text. (c) The Beckman and Cary instruments, respectively, gave $\epsilon^{366}_{\mathrm{AZO}}$ as 9.8 ± 0.1 and 9.65 ± 0.05. The Beckman was operated at a comparatively high half-intensity band width (3 mμ), and D values so obtained would be less likely to correspond to irradiation conditions than Cary derived data. It was shown that the quoted ϕ value could be no more than 1% low on account of this discrepancy. On the other hand, it may be deduced from the available data relating to aromatic solvents that the first-order rate constant for the background thermal decomposition of AZO is 5×10^{-8} sec.$^{-1}$, indicating that ϕ is 1% over-estimated on that account.

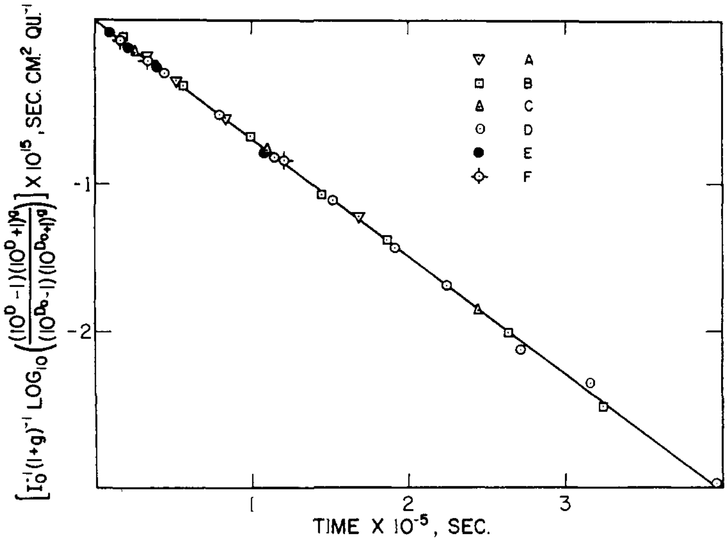

Fig. 3.—Data from all runs plotted to equation 5. Some points corresponding to irradiation times less than 7 × 10⁴ sec. are omitted for the sake of clarity.

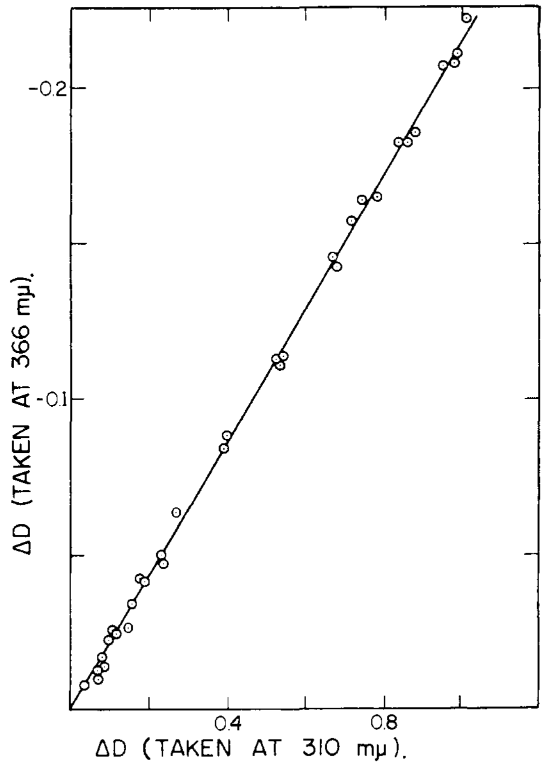

Fig. 4.—Dependence of the change in optical density at 366 mμ with that at 310 mμ for all runs.

obtained by subtracting D_0 at that wave length from the observed D values at the different times. For this purpose D values up to unity were used.

The changes in D over the 290–360 mμ range, when corrected for the contribution from undecomposed AZO, were proportional to the corresponding extinction coefficients of DKI. The concentration of AZO was established from the absorption data at 366 mμ after allowing[14b] for the presence of DKI. Assuming DKI to be the sole light absorbing product,[15] the fractional molar conversion, f, of AZO into DKI was evaluated from the extinction coefficient data for AZO and DKI at the isosbestic region[16] to be 0.594 ± 0.024. Another estimate of f is obtained[16] by way of the relation

$$\Delta D^{366}/\Delta D^{310} = (f\epsilon_{\mathrm{DKI}}^{366} - \epsilon_{\mathrm{AZO}}^{366})/(f\epsilon_{\mathrm{DKI}}^{310} - \epsilon_{\mathrm{AZO}}^{310}) \quad (11)$$

The value so obtained was 0.579 ± 0.013. Similar calculations employing $\Delta D^{366}/\Delta D^{300}$ and $\Delta D^{366}/\Delta D^{320}$ ratios gave f values of 0.579 ± 0.015 and 0.573 ± 0.016, respectively. The data outside the spectral range of these three results were not considered sufficiently precise to justify their use in calculating f.

Discussion

The concentrations of AZO and DKI follow a simple rate law under all investigated conditions, the fractional conversion, f, of AZO into DKI remaining constant to ± 1.5%. The presence of DKI as a reaction product accounts for all the spectral changes observed as AZO decomposes, within the estimated precision of the data. There is no visible fluorescence. This observation is merely qualitative but does agree with the fact that the AZO molecule has many internal degrees of freedom. These data suggest a basic mechanism similar to that of the thermal decomposition[3]

$$\mathrm{AZO} + h\nu \longrightarrow \mathrm{AZO}^*, \quad -R[\mathrm{AZO}] = I_{\mathrm{abs}} \quad (12)$$

$$\mathrm{AZO}^* \longrightarrow \mathrm{AZO}, \quad -R[\mathrm{AZO}^*] = k_{13}[\mathrm{AZO}^*] \quad (13)$$

$$\mathrm{AZO}^* \longrightarrow a\mathrm{DKI} + (1 - a)\,\mathrm{TSN} + \mathrm{N}_2, \quad -R[\mathrm{AZO}^*] = k_{14}[\mathrm{AZO}] \quad (14)$$

AZO* represents an activated entity, such as an electronically excited molecule, a is equal to f, the observed fractional conversion of AZO into DKI, and $k_{14}/(k_{13} + k_{14})$ is numerically equal to the net quantum efficiency for AZO removal. Steps 13 and 14 as written include any free radical contributions, say by way of the initial step

$$\mathrm{AZO}^* \longrightarrow \mathrm{RN}_2\cdot + \cdot\mathrm{R} \quad (15)$$

and together summarize the results of cage and ex-

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[15] It is unlikely that the other conceivable reaction products, such as TSN, methacrylonitrile and isobutyronitrile, would interfere at this wave length. See the Experimental Section and ref. 3a.

[16] The isosbestic wave length was taken as 328.9–329.2 mμ, thereby including all observations. It is not, of course, claimed that this range of wave lengths is other than the results observed with a particular Beckman spectrophotometer under fixed operating conditions. The scatter of isosbestic wave length values ruled out conclusions being made as to the direction of change of f during any one run or from run to run. It is to be expected that f might tend to fall during a run on account of the increasing importance of the thermal and the photochemical decomposition of DKI. The observed scatter, amounting to a 3% variation in f, is well able to accommodate the largest change in the over-all value of f expected on these counts, *ca.* 2%, *i.e.*, taking the first-order rate constant for the thermal decomposition of DKI and the quantum yield for the photolysis of DKI at 366 mμ to be, respectively, 10^{-7} sec.$^{-1}$ and 0.4 mole einstein^{-1}, assuming the thermal decomposition of AZO to yield essentially the same proportion of DKI per amount of AZO destroyed as for the photochemical case, and considering the last stages of run D.

Finally, it should be mentioned also that the uncertainty in the DKI purity is included in the uncertainties of all quoted f values. It amounts to ±0.004 in all cases. In general, throughout this work, the cited uncertainties are maximum values.

tra-cage effects. For the thermal decomposition reaction in boiling toluene,[5] small amounts of materials arising from radical disproportionation are formed. In the case of the present study at 25°, such products cannot perhaps be entirely ruled out, for, if the energy of activation of the thermal decomposition reaction,[3] *ca.* 30 kcal. mole^{-1}, is equated to D(RN_2–R), the species formed in step 15 may possess between them some 45 kcal. mole^{-1} in excess of their normal average kinetic energy, on account of the size of the activating quantum. On the other hand, there is the possibility that part of this excess energy might be dissipated as a result of the relatively frequent encounters with solvent molecules, by AZO* before dissociation, yielding a molecule still capable of dissociating, or by the radicals themselves, for example. Such encounters with radicals would be expected to compete favorably with radical–radical collisions. Benzene is also particularly effective in energy transfer processes.[17] The simple kinetics observed exclude the possibility of much disproportionation occurring, or, for that matter, other processes that would tend to cause f to change its value during the reaction, *e.g.*, the thermal decomposition of DKI. It should be emphasized that the claimed isosbestic wave length range,[16] 0.3 mμ, allows a total variation in f of 3%.

The quantum efficiency for AZO removal, 0.47 ± 0.02 mole einstein^{-1}, agrees only moderately well with that found previously,[2] 0.43. This must be considered satisfactory in view of the qualitative nature of the earlier study. The agreement between the two values of ϕ determined, respectively, from Fig. 2 and 3 is good, particularly on account of the fact that Fig. 2 involves initial rate data. The estimated data for f are also in good accord. As discussed above, f might vary slightly during a run, and the figure for f based upon the isosbestic wave length takes this possible change into account. However, the other set of data relies on the assumption that f is time invariant, the ratios $-\Delta D^{366}/\Delta D^{\lambda}$ for the three wave lengths being calculated on the supposition that $-\Delta D^{366}$ varies linearly with ΔD^{λ}. Consequently, these ratios may be more uncertain than their calculated statistical probable errors (which are trivially small). It is hardly likely that the values of f could be more than 1% underestimated on this account.

The fractional molar conversion of AZO into DKI reported here is somewhat larger than the approximate estimate[3a] for this quantity in the case of the thermal decomposition of AZO in the similar solvent toluene at 80.4°, namely, *ca.* 0.3. So far no conversion measurements have been made[18] for the thermal decomposition reaction at 25°. Such measurements would help settle whether the two ways of decomposition are exactly alike, apart from the obvious, formal difference in the primary activation steps producing AZO*, namely, the photolytic process 12 and the thermal reaction

$$\text{AZO} + C_6H_6 \longrightarrow \text{AZO}^* + C_6H_6 \qquad (16)$$

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[17] For example, K. J. Laidler, "The Chemical Kinetics of Excited States," Oxford University Press, London, 1955, Chapter VI. Similar arguments could be given if the primary products of step 15 were two R· radicals and one N_2 molecule.

[18] P. Smith and S. Carbone, unpublished data, have found that the conversion of AZO into DKI at 60–80° for the thermal decomposition in benzene solution is not appreciably different from the photochemically derived results at 25° given in this present study. The DKI formed, of course, decomposes in its turn. The thermally obtained conversions show at the most a slight variation with temperature, suggesting that the photolytic and thermal processes at 25° may have no more than a small difference in conversion.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

A Study on the Absorption Spectra of Ion-pairs[1]

BY ALEXANDER I. POPOV AND RAY E. HUMPHREY[2]

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Ultraviolet absorption spectra and electrical conductances of tetraphenylarsonium chloride were determined in water, acetonitrile, ethylene dichloride, 70% dioxane and 95% dioxane. Ion-pair dissociation constants were determined and were found to be 1.12×10^{-3}, 4.81×10^{-3} and 2.3×10^{-8} for the last three solvents, respectively, the dissociation being essentially complete in water and in acetonitrile. No changes in the position of absorption maxima were observed in different solvents, while relatively slight fluctuations in the intensity of absorbance could not be correlated with the ion-pair formation.

Introduction

The effect of ion-pair formation on the ultraviolet or visible absorption spectra of solutions has been a subject of controversy during the past few years. Several investigators[3–6] have postulated ion-pair formation in aqueous solutions of metal thiosulfates, nitrates and sulfates and have calcu-

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[1] From the Ph.D. Thesis of Ray E. Humphrey, State University of Iowa, June, 1958. Presented at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September 11, 1958.

[2] Eastman Kodak predoctoral fellow.

[3] F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, **51**, 793 (1955).

[4] G. O. Thomas and C. B. Monk, *ibid.*, **52**, 685 (1956).

[5] H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

[6] E. W. Davies and C. B. Monk, *ibid.*, **80**, 5032 (1958).