[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, BRYN MAWR COLLEGE]

The Photochemical Isomerization of Azobenzene[1]

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The photochemical *cis* → *trans* and *trans* → *cis* isomerizations of azobenzene solutions in isoöctane have been studied. Quantum yields for both processes have been determined with precisions of from 5 to 10% over wide ranges of wave length, concentration and light intensity. The quantum yield depends only on wave length and is approximately constant throughout a single absorption band. The average quantum yields are as follows: for the ultraviolet band, *cis* → *trans* 0.42 ± 0.04, *trans* → *cis* 0.11 ± 0.01; for the visible band, *cis* → *trans* 0.48 ± 0.05, *trans* → *cis* 0.24 ± 0.02. The results suggest that the isomerization takes place as an ordinary thermal reaction of an electronic excited state.

Introduction

We have studied the photochemical *cis–trans* isomerization of azobenzene dissolved in isoöctane over a wide range of concentration, of light intensity and of energy per photon. Several other investigators[3–5] have made quantitative measurements of the photoisomerization of azobenzene, but only in one case[4] have quantum yields for both directions been obtained, along with analogous quantum yields for a number of substituted derivatives. We feel that the present data for azobenzene are both more accurate and more extensive. In particular, we found that in order to obtain quantum yields of meaningful accuracy, it was important that the irradiating light contain less than 1% of stray light, *i.e.*, light of wave lengths other than the mercury lines used as sources.

If any mixture of the two isomers is irradiated with steady visible or ultraviolet light, the isotopic composition changes with time, approaching asymptotically the *same* photostationary composition regardless of initial composition or light intensity (over wide ranges), but depending strongly on wave length. In the stationary state the photochemical *trans-cis* rate must be equal to the photochemical plus the thermal *cis-trans* rates. In general, for any irradiated solution at any time all three rate processes are taking place simultaneously. We feel that any satisfactory analysis of experimental data should account quantitatively for the entire behavior in time of any solution.

Experimental

Reagents.—*trans*-**Azobenzene.**—Eastman Kodak Co., white label azobenzene was recrystallized three times from ethanol in red light, with previous refluxing in the dark.

cis-**Azobenzene.**—The method of preparation of Hartley[6,7] was used without change; the final product was estimated to contain less than 0.02% of *trans*-isomer (*vide infra*).

Isoöctane and Benzene.—Eastman spectro grade was redistilled in a 20 t.p. packed column.

Analysis.—The isomeric composition was determined by careful determination of optical densities with a Beckman DU spectrophotometer. Solutions were thermostated at 25.0 ± 0.1° for all work. The absorption spectra of both isomers in isoöctane (see Fig. 1) were determined carefully using a number of concentrations. For the *cis* isomer, because of the thermal *cis-trans* reaction, it was found necessary to measure the times between dissolving the pure crystalline *cis* isomer and making a reading on the spectrophotometer. Knowing the first-order rate constant (*vide infra*) for the thermal reaction, the optical density at zero time could be calculated. All points on the *cis* absorption curve were obtained by this sort of extrapolation. To check the purity of the crystalline *cis* isomer, this procedure was repeated for six successive recrystallizations at the most sensitive wave length (340 mμ). The residual variations in the extrapolated density indicated the purity mentioned above. The rate constant, $k = 1.37 \pm 0.01 \times 10^{-4}$ min.$^{-1}$ for the thermal reaction was obtained from a least squares slope of the straight line obtained by plotting ln $(D_\infty - D)$ *vs.* t. (D = optical density, t = time.)

Photochemistry.—Solutions of total azobenzene concentration, c_0, from 10^{-3} to 10^{-5} m were irradiated in a fused cylindrical quartz cell, thermostated at 25.0 ± 0.1°. The solutions had a volume of 6.204 cc. and were stirred with a small magnetic stirrer lying just below the almost parallel beam of light. The beam filled about 80% of the cell windows and was produced by one of two Hanovia quartz mercury arc lamps, normally operated with 60 cycle a.c. from a constant voltage transformer. To isolate "lines" the standard Corning glass filter combinations[8] were used and in addition a Balzer interference filter for 405 mμ and a Cl_2 gas filter plus Corning 9863 for 254 mμ. The purity of the radiation was tested in each case photographically with a small quartz Hilger spectrograph, and the relative intensities of the several components of the compound lines were estimated microphotometrically. These relative intensities were needed to calculate the proper average absorption for a compound line.

The cell holder was arranged so that it could be alternately irradiated for a measured time interval and examined in the Beckman spectrophotometer to determine the isomer composition. The Beckman wave length setting was fixed for a given total concentration, c_0, and was chosen to give the maximum precision for the analysis; *e.g.*, 410 mμ for $c_0 = 10^{-3}$ m, 315 mμ for $c_0 = 2.5 \times 10^{-5}$ m. The intensity of the light incident upon the solution, I_0, was determined by uranyl oxalate actinometry for all except the green and yellow lines. Relative intensity measurements with an Eppley thermopile, used in conjunction with a Liston–Becker breaker amplifier and an Esterline–Angus recording milliammeter, were used to check the actinometry and to obtain values for the green and yellow lines. During a photochemical run the relative light intensity was monitored by reflecting a small portion of the light on to a Weston Photronic cell which, in turn, was checked periodically against an incandescent lamp maintained at a constant voltage.

Results

The experimental results are best expressed as fraction of *cis* isomer, y, as a function of time for each I_0, c_0 and wave length, as shown in Figs. 2 and 3. For most wave lengths the stationary state was approached from both sides—for example, in Fig. 3 a solution, initially pure *trans*, was irradiated with wave length 313 mμ, and after reaching the steady composition, $y_\infty = 0.80$, was then irradiated with wave length 546 (or 436) giving the descending curve and reaching a new stationary state. The

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[3] I. Hausser, *Naturwissenschaften*, **36**, 35 (1949); *Z. Naturforsch.*, **5a**, 56 (1950).

[4] P. P. Birnbaum and D. W. G. Style, *Trans. Faraday Soc.*, **50**, 1192 (1954).

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

[6] G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

[7] G. S. Hartley and R. J. W. LeFevre, *ibid.*, 531 (1939).

[8] G. Zimmerman, *J. Chem. Phys.*, **23**, 825 (1955).

stationary state compositions which are given in Table I (y_∞) depended only on wave length and not on I_0 or c_0 for the ranges studied. It was found that the infrared radiation present in the light sources and the presence of dissolved O_2 (from about 10^{-2} to 2×10^{-7} *m*) in the solutions had no observable effect on the photoisomerization. In all cases the isomerization was completely reversible, in agreement with previous work[4] where fairly drastic tests failed to show the presence of any side reactions. In no case (including gaseous *trans* isomer at low pressures) was luminescence of any sort observed.

Analysis of Data.—The differential equation for the rate processes occurring assuming monochromatic light, complete stirring, Beer's law and that the quantum yields in both directions are independent of I_0 and concentrations, can be written

$$\frac{dy}{dt} = \frac{I_0 l}{VF}\left[\phi_x \epsilon'_x (l - y)\right] - \frac{I_0 l}{VF}\left[\phi_c \epsilon'_c y\right] - ky \quad (1)$$

where

l = path length through soln. (cm.)
ϕ_x = quantum yield for *trans-cis*; subscripts x and c refer, respectively, to *trans* and *cis*
ϵ' = molar absorption coeff. } defined by the relation
D' = optical density }
$\ln_e(I_0/I) = D' = c_0 l[\epsilon'_x + (\epsilon'_c - \epsilon'_x)y]$
V = volume in soln. in liters.
$F = \dfrac{D'}{1 - e^{-D'}}$
t in min.; I_0 in Einsteins/min.

The first two terms on the right are the photochemical rates in the two directions and the third term is the thermal *cis-trans* rate. Setting $dy/dt = 0$ for $t = \infty$, solving for ϕ_c, and substituting into (1) gives

$$\frac{dy}{dt} = \frac{A}{F}(y_\infty - y) - ky(F_\infty/F - 1) \qquad (2)$$

where $A = I_0 l \phi_x \epsilon'_x / V y_\infty$. For all experimental conditions used, a careful numerical comparison shows that the second term in (2) can be neglected compared with dy/dt, giving the equation

$$dz/dt = -\frac{A}{F}z \qquad (3)$$

where $z = (y_\infty - y)$. If we let $I(z) = \int F\,dz/z$ then we can write $I(z) = -At +$ Constant, and a plot of $I(z)$ against t gives the constant, A, and hence $I_0\phi_x$. In order to find $I(z)$, the function F can be represented as the power series[9]

$$F(D') = 1 + D'/2 + D'^2/12 - D'^4/720 + \ldots\ldots. \qquad (D' < 5)$$

For $D' > 5$ it is a good enough approximation to write $F(D') = D'$. For various ranges of D' values one obtains the following valid approximations for $I(z)$

Range of D'	Approximation for F	$I(z)$
$D' < 0.02$	$F = 1$	$\log \lvert z\rvert$
$0.02 < D' < 0.2$	$F = 1 + D'/2$	$p \log \lvert z\rvert - jz$
$0.2 < D' < 2.0$	$F = 1 + D'/2 + D'^2/12$	$s \log \lvert z\rvert - rz + uz^2$
$D' > 5$	$F = D'$	$q \log \lvert z\rvert - bz$

The various coefficients are all positive numbers depending on c_0, l, ϵ_x', ϵ_c', y. Figure 4 shows various plots of $I(z)$ against t using the appropriate approximation. In all cases good straight lines were obtained, omitting the last 2 or 3 points close to z_∞ where the uncertainty becomes very large. Table I gives the values of $I_0\phi_x$ obtained in this way. The values of ϕ_c were calculated from the steady state equation; here the term containing the thermal reaction constant k cannot be neglected. Alternatively and more generally it was found possible to use the differential equation directly by fitting an empirical function to the experimental data and then differentiating. This procedure was much more lengthy and gave the same results

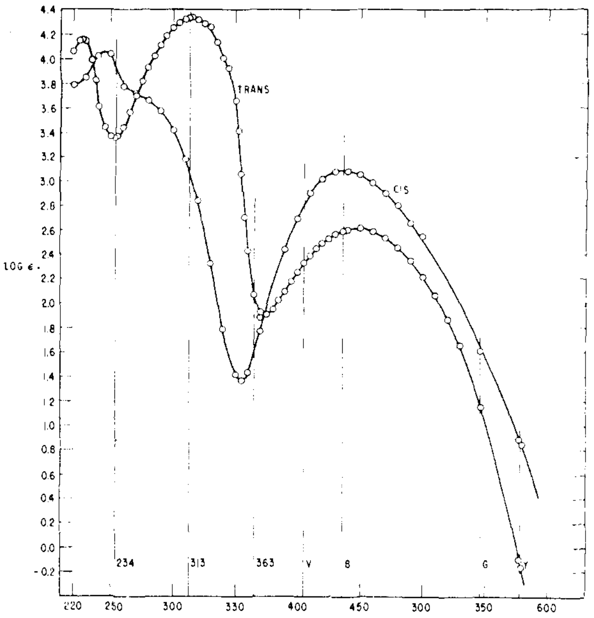

Fig. 1.—Absorption spectra of *cis*- and *trans*-azobenzene, at 25°, dissolved in isoöctane (in this fig. only, ε is defined using base 10 logs instead of natural logs as in the text).

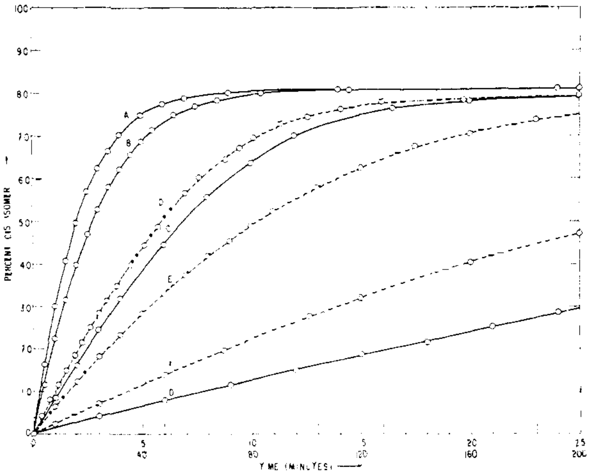

Fig. 2.—Change of isomeric composition with time for solutions irradiated with wave length 313 mμ: A, B, C and D are for the same light intensity, I_0, and for $c_0 = 10^{-5}$, 2.5 × 10^{-5}, 10^{-4}, and 10^{-3}, respectively; D′ is the same as D except using the lower time scale. E and F are for c_0 = 2.5 × 10^{-5}, and $I_0/3$ and $I_0/10$, respectively.

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[9] B. O. Peirce, "A Short Table of Integrals," 3rd Ed., Ginn and Co., New York, N. Y., 1929, No. 764, p. 90.

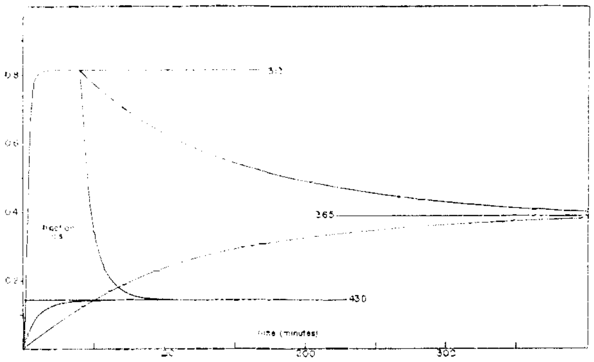

Fig. 3.—Change of isomeric composition with time for different wave lengths and initial compositions; in all cases, $c_0 = 2.5 \times 10^{-5}$.

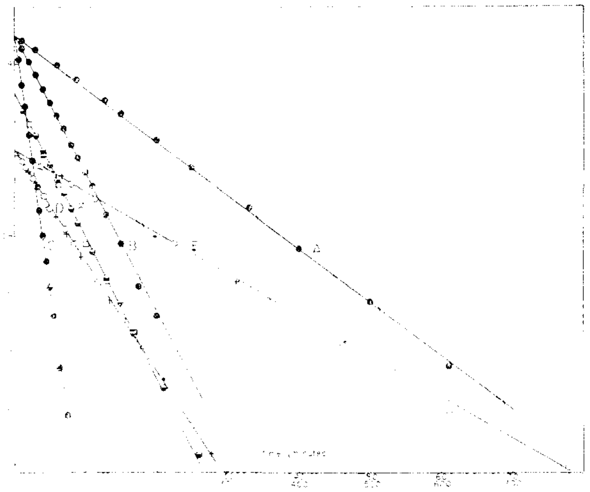

Fig. 4.—Plots of $I(z)$ vs. time; the intercepts for zero time have been chosen arbitrarily for convenience. Curves A, B and C correspond to curves B, E and F in Fig. 2. Curves D and F each correspond to the two curves for 365 and 436 mμ respectively in Fig. 3. Curve E is for 578 mμ and $c_0 = 2.5 \times 10^{-5}$ *m*: ●, +, ◒ represent y increasing with time; ○, □ represent y decreasing with time.

as integration and hence was used only as a check on a few runs.

It is interesting to note that, below a certain value of c_0, y as a function of time becomes independent of c_0, *e.g.*, for wave lengths 546 and 578 mμ for both $c_0 = 10^{-3}$ and 10^{-5} the photochemical conversion takes place at the same rate. Azobenzene solutions (or perhaps azonaphthalene solutions,[5] which absorb much more strongly in yellow and red light) could be used for actinometry extending almost to red light; the solutions are chemically stable (to O_2), have slowly varying and fairly large quantum yields and seem to be relatively insensitive to temperature variations. The results of interest are summarized in Table I. Each entry for $c_0 = 10^{-3}$ and 2.5×10^{-5} is an average of several individual runs. Figure 5 shows the quantum yields as a function of wave length, the other variables investigated being without substantial effect.

TABLE I

QUANTUM YIELDS FOR ISOMERIZATION OF AZOBENZENE IN ISOÖCTANE AT 25°

λ	c_0	$I_0 \times 10^7$	ϕ_x	ϕ_c	y_∞	$\phi_x + \phi_c$
254	2.5×10^{-5}	0.468	0.13	0.44	0.075	0.57
313	10^{-3}	5.99	0.10	0.42	0.796	0.52
	10^{-4}	4.76	.11	.43	.794	.54
	2.5×10^{-5}	4.77	.10	.41	.805	.51
	2.5×10^{-5}	1.43	.10	.41	.803	.51
	2.5×10^{-5}	0.48	.11	.43	.793	.54
	2.5×10^{-5}	4.20[a]	.10	.40	.810	.50
	10^{-6}	4.70	.12	.40	.812	.52
365	10^{-3}	7.34	.12	.48	.388	.60
	2.5×10^{-5}	6.90	.12	.48	.390	.60
405	10^{-3}	2.75	.21	.51	.133	.72
	2.5×10^{-5}	2.74	.23	.55	.125	.78
436	10^{-3}	3.81	.27	.55	.147	.82
	2.5×10^{-5}	3.73	.28	.55	.143	.83
	10^{-3}	3.50	.26[b]	.46[b]	.174[b]	.72
546	10^{-3}	17.9	.24	.40	.192	.64
	2.5×10^{-5}	18.1	.24	.40	.188	.64
578	2.5×10^{-5}	23.1	.23	.44	.045	.67

[a] D.c. mercury arc used; in all other cases, 60 cycle a.c.
[b] Benzene as solvent; taken from M. A. thesis of L. Y. Chow, Bryn Mawr College.

Birnbaum and Style[4] using ethanol as the solvent and somewhat greater light intensities, obtained these given values, ours from Table I being listed in parentheses for comparison: ϕ_x at 436 mμ, 0.36 (0.27); ϕ_c at 436 mμ, 0.45 (0.55); ϕ_x at 365 mμ, 0.20 (0.12). The two sets of values for 313 mμ are not comparable because of the polychromatic character of the light used by Birnbaum and Style. These differences *may* be real and due to the different solvents used; in fact, the above change of ϕ_c at 436 mμ is the same as the change in Table I between isoöctane and benzene as solvents. We feel, however, that this change is just barely significant if at all and that the above differences of our results from those of Birnbaum and Style are not serious or possibly not even real.

Discussion

In the absence of appreciable fluorescence it must be assumed that the excited molecules eventually return to the ground state by internal conversion followed by loss of the excess vibrational energy through collisions with the solvent molecules. It seems unlikely that in a condensed phase the vibrationally excited molecules in the process of "cooling off" isomerize appreciably compared with the observed quantum yields. We can apply the same reasoning here as in the case of MnO_4^- decomposition previously discussed.[8] If E represents the excess vibrational energy immediately after internal conversion and e the height of the potential energy barrier separating the two isomers in the ground state, then the probability (hence the quantum yield) of isomerization (by this sort of mechanism) is given approximately by the expression $(1 - e/E)^n$ where n is the number of "classically excited" modes of vibration. This model predicted a strong monotonic decreasing quantum yield with increasing wave length of excitation, which is certainly not the present case. Further, taking $e = 23$ kcal., the average activation energy found for the thermal reaction,[7,10] and $n > 15$,[11] the quantum yields for all wave lengths considered are less than 0.01. This point of view is not consistent with the model of Lewis, *et al.*,[12] for the stilbenes, nor with Olson's model of *cis–trans* isomerization.[13] From the data can be seen at once that there cannot be a single excited state, indistinguishable regardless of which isomer was excited by the radiation, since such a common state would imply that $\phi_x + \phi_c = 1$, which is not the case (Table I, last column).[14] These considerations suggest that isomerization takes place by a normal thermal rate process in an electronic excited state in the potential energy surface of which there is a barrier (probably small—say about 5 kcal.) separating two configurations corresponding approximately to the *cis* and *trans* configurations of the ground state. The simplest kinetic mechanism consistent with this model can be represented by the scheme

$$\mathrm{C} \underset{k_1}{\overset{I_c}{\rightleftarrows}} \mathrm{C}^* \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{X}^* \underset{I_x}{\overset{k_2}{\rightleftarrows}} \mathrm{X}$$

where the asterisk denotes the excited state, the k's first-order rate constants, and the I's the rate of light absorption by each isomer. One would expect the configuration after absorption of a photon to correspond to that of the original absorbing molecule, because of the Franck–Condon principle. The constants, k_3 and k_4, represent thermal isomerization and k_1 and k_2 represent quenching to the ground state with no appreciable loss of configuration. For this case the quantum yields are given by $1/\phi_c = 1 + k_1/k_3\,(1 + k_4/k_2)$ and a symmetrical expression for ϕ_x. Note that if $k_3 << k_1$ then $\phi_c \rightarrow 0$, and similarly for ϕ_x; if k_3 and k_4 are both much larger than k_1 and k_2, then one has the "common state," *i.e.*, C* and X* in equilibrium. In the present case neither extreme applies and, taking average values of the ϕ's for each absorption band, one finds for the ultraviolet band, $k_3/k_1 = 1.0$, $k_4/k_2 = 0.3$, and for the visible band, $k_3/k_1 = 1.8$, $k_4/k_2 = 0.9$; in other words, k_3 and k_4 must be the same order of magnitude as k_1 and k_2. Undoubtedly this is oversimplified insofar as there may well be a different third electronic state responsible for the isomerization itself, and radiationless transitions from the initial singlet excited states to the third state. However, the main features of the kinetics are not changed greatly by such additional complications. One would predict, for example, that at sufficiently low temperatures, other factors (such as solvent viscosity) remaining constant, both ϕ's should vanish.

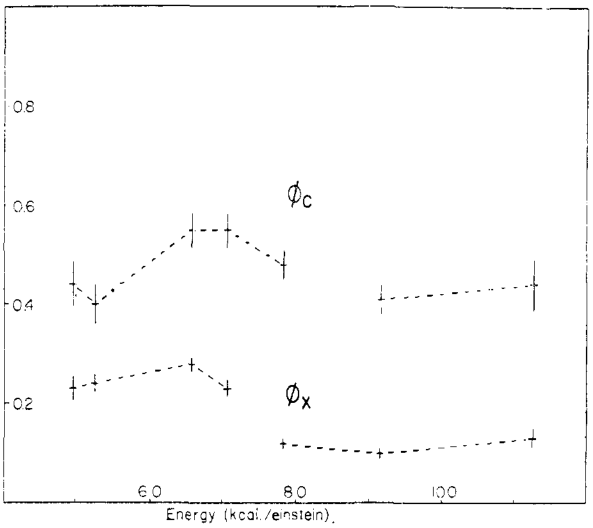

Fig. 5.—Quantum yields as functions of energy per photon; dotted lines connect points lying in the same absorption band. The vertical lines indicate maximum uncertainties.

There has been considerable discussion of the nature of excited electronic states of olefinic compounds[15] and some in the case of azobenzenes.[4] The potential curves for rotation about the N–N bond in the latter case almost always show a fairly small barrier separating the isomers, but it is still only *assumed* that isomerization occurs *via* such a rotation rather than, for example, through a N–N–C angle of 180°.[16]

It has not been the purpose here to try to examine the possible type of electronic state involved in the isomerization but only to point out some general features which the data seem to imply. We plan to look for a possible long-lived triplet state by flash photolysis and also to study the effect of temperature and solvent viscosity over wide ranges, in order to aid, perhaps, in developing a more detailed mechanism.

Acknowledgment.—The authors wish to acknowledge gratefully the help and advice of Doctors Ernst Berliner and W. C. Michels and the Physics Department of Bryn Mawr College.

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(10) R. J. W. LeFèvre and J. Northcott, *J. Chem. Soc.*, 867 (1953); J. Halpern, G. W. Brady and C. A. Winkler, *Canad. J. Res.*, **28B**, 140 (1950).

(11) From examining the heat capacities of a number of hydrocarbons, it seems like a good "rule of thumb" that the number of classically excited vibrations at 25° is about 0.8 to 1.0 times the number of modes of vibration ignoring H atoms; for azobenzene this would mean at least 25 to 30.

(12) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **62**, 2973 (1940).

(13) A. R. Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

(14) Birnbaum and Style (ref. 4) find an average value of about 0.85 for $\phi_x + \phi_c$ and infer a single common state on the basis of this value's lying "close to unity." We feel that this deviation from unity is significant both in their results and also in ours where the average value for $\phi_x + \phi_c$ is about 0.6 and that in all cases a truly common kinetic state is excluded.

(15) See, for example, R. S. Mulliken and C. C. J. Roothaan, *Chem. Revs.*, **41**, 219 (1947).

(16) There does not seem to be entirely convincing evidence yet that thermal isomerization in the ground state proceeds through an intermediate low-lying triplet state. The frequency factor has a normal value (10^{-11} sec.$^{-1}$) and too close an analogy with an olefinic system seems dangerous. See, however, for possible evidence of participation of a triplet state: E. W. Malmberg, M. Kaplan and E. Talaty, Abstracts of Papers, 130th Meeting of the American Chemical Society, No. 135, p. 83-O. It is interesting also in this connection to note the lack of any reaction with oxygen and the constancy of the quantum yields in the p-halogen substituted azobenzenes (see ref. 4, however; see B. E. Blaisdell, *J. Soc. Dyers and Colorists*, **65**, 618 (1949)).