molecular electron–nuclear dipolar and scalar interactions. The longitudinal relaxation times can be accounted for solely in terms of the dipolar interaction while the scalar interaction makes a large contribution to the transverse relaxation times in the concentration region below about 1 *M*. The field dependence of the relaxation times is accounted for by the frequency-dependent dipolar term.

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Photochemical and Thermochemical Cis–Trans Isomerization of Azoxybenzene

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Abstract: A study has been made of thermal and photochemical isomerization of azoxybenzene. The activation energy of the cis to trans thermal isomerization was found to be 25 kcal/mol in 95% ethanol and 19 kcal/mol in heptane. Quantum yields for the photoisomerization were determined as 0.11 for trans to cis isomerization and 0.60 for cis to trans isomerization and were the same in heptane and ethanol and independent of the wavelength of the exciting light from 330 to 370 nm.

The cis–trans isomerization of stilbene and of azobenzene has been studied extensively; for the photochemical isomerization process, photostationary states have been established by direct irradiation,[1,2] as well as by photosensitization.[3,4] In the structurally similar compound, benzalaniline, photoisomerization has been observed only in flash photolysis.[5] The formation of *cis*-azoxybenzene from the trans isomer was first demonstrated in this laboratory.[6] We have now undertaken a study of the cis–trans isomerization of azoxybenzene.

Upon irradiation of *trans*-azoxybenzene (I) in solution, a number of reactions and equilibria need to be considered: (1) the photochemical cis–trans isomerization of I; (2) the thermochemical reconversion of the cis isomer (II) to I; (3) the Wallach rearrangement to form hydroxyazobenzene (III) [the reaction is known to proceed by acid catalysis to 4-hydroxyazobenzene (4-III), but irradiation of I is known to produce the 2 isomer (2-III)]; (4) cis–trans isomerizations of 2-III and also 4-III, if formed [fortunately, in both cases the cis compounds (2-IV and 4-IV) appear to be so *rapidly* reconverted to 2-III and 4-III that the cis compounds can be ignored safely]; (5) equilibrium of III with a keto form V (however, in view of the small amounts of III formed in the present work, the equilibria with V have had no bearing on the results).

With this multiplicity of competing reactions, we have decided to start our investigation with those reactions which appear to be the most rapid, and hence the least complicated, by these competitions. Consequently we have investigated the thermo- and photochemical cis–trans isomerization of azoxybenzene.

Results and Discussion

Thermal Reaction. The rate of the rearrangement of *cis*-azoxybenzene to its trans isomer was followed spectrophotometrically at 324 nm. The reaction is first order. Rate constants obtained at 5, 25 and 35° in ethanol, and at 5, 15 and 25° in heptane, are shown in Table I.

Table I. Rate Constants for the Thermal Cis → Trans Conversion of Azoxybenzene

Solvent	Temp, °C	k, sec^{-1} $\times 10^{-6}$	Std dev $\times 10^{-6}$
Ethanol	5	0.638	0.092
	25	14.6	0.37
	35	48.7	0.57
Heptane	5	15.65	0.73
	15	51.0	
	25	165	13

The most striking feature of these results is the tremendous difference in rates between solutions in ethanol and heptane; the difference in rate constants is almost one power of 10 at 25° and 25-fold at 5°. In azobenzene, the difference is reported to be threefold.[7] Activation parameters are shown in Table II.

Table II. Activation Parameters for the Thermal Cis → Trans Isomerization of Azoxybenzene

Solvent	E_a, kcal/mol	A, sec^{-1}
Ethanol	24.8	2.1×10^{13}
Heptane	19.4	2.4×10^{10}

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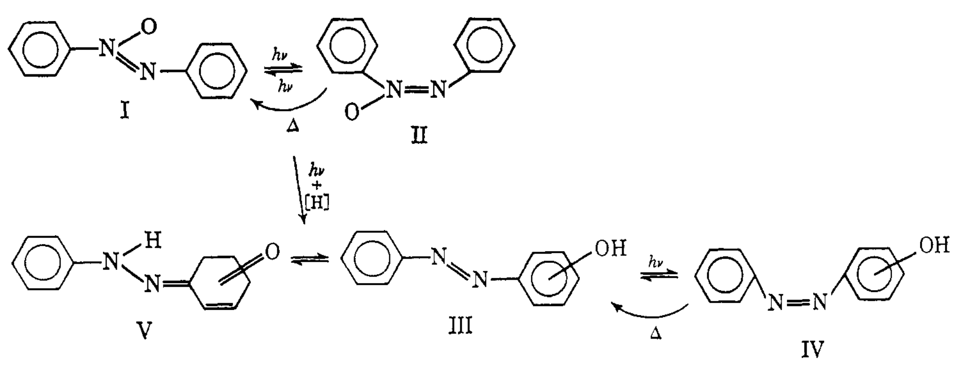

Table III. Quantum Yields for the Isomerization of Azoxybenzene at 5°

	λ, nm											
	330	340		350		360			370	Average		
Solvent	EtOH	EtOH	C_7H_{16}	EtOH	C_7H_{16}	EtOH	C_7H_{16}	C_7H_{16}[a]	C_7H_{16}	EtOH	C_7H_{16}	Both
Q_t[b]	0.13	0.11	0.11	0.11	0.10	0.13	0.10	0.12	0.12	0.12	0.11	0.11
Q_c[c]	0.67	0.53	0.71	0.49	0.65	0.56	0.54	0.67	0.68	0.56	0.64	0.60
Q_t/Q_c	0.19	0.21	0.15	0.22	0.15	0.23	0.19	0.18	0.18	0.21	0.17	0.19
	1.50	1.20		0.82			0.44		0.19			
	0.35	0.34		0.29			0.22		0.15			
x_t		0.68		0.69			0.75		0.83			
x_c		0.32		0.31			0.25		0.17			

[a] Not degassed; not included in averages. [b] Quantum yield for the trans → cis reaction. [c] Quantum yield for the cis → trans reaction.

The facts that the energy of activation increases and the entropy of activation is more positive in alcohol, relative to heptane, suggest that the solvent effect consists of a much stronger solvation of the highly polar azoxybenzene in the polar solvent. This explanation is also consistent with a much smaller solvent effect in the much less polar azobenzene.

Photochemical Isomerization. In order to obtain systematic information about the photochemical isomerizations, we have determined quantum yields for both the forward and reverse process as a function of wavelength in both heptane and ethanol. In ethanol, quantum yield determination was complicated by the fact that the Wallach rearrangement, reaction 3 above, was fast enough that measurable fractions of substrate had undergone this reaction by the time the photostationary state was established. Consequently, usual techniques of quantum yield (Q) determination were not readily applicable, and the Q was determined by the method of initial slopes. In heptane, the Wallach rearrangement can also be observed but it is so slow that a photostationary state can be established without measurable rearrangement occurring, as shown by the demonstration that the spectral changes induced by irradiation were quantitatively reversible thermally. On the other hand, in heptane the thermal cis → trans conversion is fast enough, even at the temperature of these experiments, 5°, that corrections for this reaction were required.

Quantum yields in heptane were calculated by a modification of Zimmerman's equation[8] (*cf.* Experimental Section). The most striking result of Table III is that Q for the photoisomerization is constant and independent of the wavelength in the range 330–370 nm, *i.e.*, throughout the first absorption band of both isomers of azoxybenzene. Also, Q seems to be the same in the two solvents. The quantum yield for the cis → trans reaction is not as readily determined, and hence the constancy is not as well documented.

The composition of the photostationary state appears to conform to the usual relation

$$x_c/x_t = Q_t\epsilon_t/Q_c\epsilon_c$$

where x_c and x_t are mole fractions for cis and trans isomer, respectively, the ϵ's are the absorbancies of the two species, and Q_t and Q_c are the quantum yields for trans → cis and cis → trans conversion, respectively. The thermochemical cis → trans conversion is too slow to noticeably affect this relation. Since Q_t and Q_c are effectively wavelength independent, so is their ratio, and we have

$$x_c/x_t \propto \epsilon_t/\epsilon_c$$

At 324 nm ϵ_t/ϵ_c is at a maximum (this wavelength was chosen for analysis for this reason) and, at this wavelength, the photostationary state is richest in cis isomer.

Mechanism. The mechanism of the cis–trans photoisomerization of stilbene remains controversial.[9–12] Although some authors have proposed a singlet mechanism,[9] the most generally accepted interpretation seems to involve triplet mechanism.[10–12] It has been proposed that the photoisomerization of azobenzene proceeds *via* a different path than that of stilbene. While for stilbene there appears to be only one possible path, rotation about the central double bond, it

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Table IV. Quantum Yields of Stilbene, Azobenzene, and Azoxybenzene Isomerization

Stilbene				Azobenzene				Azoxybenzene			
λ	Solv[a]	Q_t	Q_c	λ	Solv[a]	Q_t	Q_c	λ	Solv[a]	Q_t	Q_c
253[b]	HEX	0.67	0.28	254[d]	IO	0.13	0.44				
313[b]	HEX	0.59	0.32	313[d]	IO	0.11	0.41				
313[b]	MCH/IH	0.50	0.35								
313[c]	EtOH	0.50	0.35								
				365[d]	IO	0.11	0.41	360	HEPT	0.10	0.54
				436[d]	IO	0.28	0.55				

[a] Solvents: HEX, hexane; IO, isooctane; HEPT, heptane; MCH/IH, methylcyclohexane–isohexane (3:1); EtOH, ethanol. [b] H. Stegmeyer, *J. Phys. Chem.*, **66**, 2555 (1962). [c] E. Fischer, *et al.*, *J. Amer. Chem. Soc.*, **90**, 12 (1968). [d] Reference 8.

has been suggested that, in azobenzene,[7] as in imines,[13] an in-plane flipping of a phenyl ring from the position in one isomer to that in the other is the favored process. A recent investigation[14] has revealed a significant difference in the azobenzene photoisomerization depending on which singlet state, n → π* or π → π* ($^1W \leftarrow {}^1A$ or $^1B \leftarrow {}^1A$), is excited; the difference lies principally in the ratio Q_t/Q_c.

The quantum yields for the azoxybenzene reaction measured in this work closely resemble the data reported for azobenzene, *cf.* Table IV; hence it seems likely that the mechanisms of these two reactions are very similar. The insensitivity of the azoxybenzene photoisomerization to oxygen (*cf.* the undegassed experiment reported in Table III) suggests that the mechanism involves only singlet states, *i.e.*, that isomerization is more rapid than intersystem crossing. This conclusion agrees with that of Tanigaka,[15] who found that photosensitization of azoxybenzene results in reduction to azobenzene, not isomerization.

Tanigaka[15] has found that the yield of *cis*-azoxybenzene from photoisomerization is lower in hexane than in alcohol. Since, for each compound, the absorptivities in the two solvents above 280 nm seem to be identical, and the quantum yields are the same (*cf.* Table III), we must conclude that Tanigaka's results are due to the thermochemical cis → trans isomerization, which is much more rapid in heptane.

Experimental Section

Photochemical Apparatus. The apparatus used for the photochemical experimnets was of standard design. A continuous spectrum of light (about 330–430 nm) from a 150-W XBO xenon lamp was focused by a lens on the entrance slit, set at 2.5 mm, of a Bausch and Lomb monochromator, Model 33-86-01. The monochromatized beam passes through an exit slit at 1.0 mm and through a filter made of a solution of 10% w/v of $CuSO_4 \cdot 5H_2O$ in a 1-cm quartz cell. A quartz plate at 45° serves to deflect 14% of the light beam which is focused on the window of a Photovolt photomultiplier, used to monitor the light intensity of the xenon lamp. The undeflected beam falls into a sample cell, a 1.0-cm quartz cell thermostated to 5°. Condensation on the cell windows is controlled by drying agent.

Actinometry. The ferrioxalate actinometer of Hatchard and Parker[16] was used to determine absolute flux.

Preparation of *cis*-Azoxybenzene and Determination of Its Spectra. A general procedure for the preparation of *cis*-azoxybenzene by a photochemical method has been established in this laboratory.[6] A solution of *trans*-azoxybenzene, prepared by dissolving 6.0 g of recrystallized material in 20 ml of benzene, was irradiated for 20 hr while the temperature of the solution was maintained below 0°. This treatment was followed by chromatography on a silicic acid column which was precooled and maintained below 0° by circulating a cold mixture of methanol and water. The column was eluted with cold 20% ether–ligroin (40–60°). After *trans*-azoxybenzene had been collected, the cis compound was eluted with 80% ether/ligroin. The cis solution was evaporated to dryness in the dark, keeping the temperature below 0°, and the resulting crystals were stored in the Dry Ice box. The melting point was determined as 76°, compared with a value of 71° reported in the literature.[17]

The spectrum of *cis*-azoxybenzene was determined in 95% ethanol and heptane of spectrograde. To prevent thermal conversion in heptane, a solution of the cis compounds of roughly proper concentration was prepared immediately before the measurement of absorbance, and the actual concentration was determined after complete thermal conversion to the trans isomer in the dark, since the molar extinction coefficients of the trans isomer can be determined accurately.

Kinetic Measurement of the Thermal Conversion. Kinetic measurements have been carried out at 5, 25, and 35° for alcohol solution and 5, 15, and 25° in heptane. The reaction vessel was painted black and wrapped with aluminum foil to keep out light. The solution was kept in a constant temperature bath, and the absorbance of the solution was measured after predetermined intervals at 324 nm, the wavelength at which the difference between molar extinction coefficients of the cis and trans isomer is at a maximum.

Deoxygenation of Solvent. The "Stick Vacuum" technique of Linschitz,[18] *et al.*, was employed. The degassed solution was carried to a dry box with a nitrogen atmosphere. The nitrogen gas was purified by passing through a heated coil of copper at 700–800° in a furnace. Then the solution was filled into a cell of premeasured volume, and the cap of the cell was sealed.

Quantum Yield Determination. To determine the quantum yields in heptane solution we used the Zimmerman equation[8] with some minor modifications. This equation, for a photochemical process complicated by a thermochemical process, in which the photoproduct of concentration y disappears in a first-order process with rate constant k, is

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{I_0Lm}{V}[Q_t\epsilon_t(1 - y) - Q_cG_cy] - ky \qquad (1)$$

where I_0 is the incident light intensity, L is the path length of the reaction cell of volume V, and $m = (1 - 10^{-A})/A$, where A is the absorbance.

Using the photostationary state condition, $\mathrm{d}y/\mathrm{d}t = 0$, we may eliminate Q_c from eq 1. Calling the values of m, I_0, and y at the stationary state m^∞, I_0^∞, and y^∞, respectively, and introducing the symbol $a = (\epsilon_tQ_tL)/(2.303V)$, we obtain

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \left[\frac{2.303amI_0}{y^\infty} + k\left(1 - \frac{mI_0}{m^\infty I_0^\infty}\right)\right]y = 2.303amI_0 \qquad (2)$$

$mI_0/m^\infty I_0^\infty$, under the conditions of our experiments, was always very close to unity, and hence the coefficient of k in eq 2 was small; as a result, the second term in the brackets of eq 2 could safely be neglected relative to the first term. The changes of m and of I_0 through a run are slow and nearly linear. We have assumed that, in an interval of time from t_i to t_j, m can be replaced

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by an average value m_{ij}, and we have integrated eq 2 over many such intervals to give

$$-\log (y^{\infty} - y)/y^{\infty} = a\sum m_{ij}I_0\int_{t_i}^{t_j} I\mathrm{d}_0 t$$

where the integrals are proportional to areas under the photomultiplier plots of the split beam. Then, a plot of log ($y^{\infty} - y$) *vs.* $\Sigma m_{ij}\int_{t_i}^{t_j} I_0 \mathrm{d}t$ gave straight lines. From the slopes, obtained by the method of least squares, Q_t is readily calculated.

Finally, Q_c is obtained from the photostationary state conditions

$$Q_c = \frac{\epsilon_t Q_t}{\epsilon_c}\frac{1 - y^{\infty}}{y^{\infty}} - \frac{kV}{I_0{}^{\infty} m^{\infty} E_0}$$

It should be noted that, in the calculation of Q_c, the thermal rate could not be neglected.

To calculate quantum yields in ethanol solution, the photochemical reaction was run starting with both pure isomers. Plots of concentration of product formed *vs.* time were prepared, and the slope at time zero was estimated and used to calculate the quantum yield.

Photoelectron Spectra of Osmium and Ruthenium Tetroxides

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Abstract: Photoelectron spectra of OsO_4 and RuO_4 have been obtained and the five highest energy filled MO's have been assigned. A Jahn-Teller splitting of the order of 10^2–10^3 cm^{-1} has been detected in the $^2T_2$ ground state of OsO_4^+.

Despite a considerable mass of computational results,[1] the nature and order of energies of the highest energy filled MO's of tetrahedral molecules which are isoelectronic with MnO_4^- remain obscure. It is generally agreed that the five highest energy MO's are $1t_1$, $3t_1$, $2a_1$, $2t_1$, and 1e, with the $1t_2$ and $1a_1$ MO's at considerably lower energies. Apart from this, virtually all possible permutations of the topmost filled five MO's have been suggested at one time or another. Indeed, apart from electronic spectroscopic considerations and inferences drawn therefrom, the only relevant experiment extant is the ESCA results[2] on crystalline $LiMnO_4$, $Mg(MnO_4)_2$, and Li_2CrO_4, which indicates the presence of two groups of ionization events, each group covering only a small energy spread (~3–5 eV).

This work represents an attempt to assign the ionic states of gaseous RuO_4 and OsO_4 and to deduce the nature and order of the highest energy filled MO's. The experimental technique used is photoelectron spectroscopy which, surprisingly enough in view of molecule weight and complexity, generates remarkably well-resolved spectra. Computations are also indulged but are used only in a qualitative vein.

Experimental Section

RuO_4 and OsO_4 (Alfa Inorganics) were repeatedly degassed at reduced temperatures immediately prior to study.

Photoelectron spectra were measured using a Perkin-Elmer Model 18 spectrometer. The resolution was better than 20 MeV. A volatile-probe ionization chamber, in which the tetroxides could be flowed, was used. No significant difficulty was experienced with OsO_4. However, the extreme reactivity of RuO_4, and its tendency to plate out, led to deterioration of instrument characteristics, including the resolution, and necessitated complete instrument overhaul between individual runs. The net result was poorly resolved photoelectron spectra for RuO_4 and a severely malfunctioning electron detector and cathode source which are presently being replaced.

Results

The photoelectron spectra of RuO_4 and OsO_4 are shown in Figure 1. Despite the poor resolution of the RuO_4 spectrum, it is clear that both spectra contain five band systems and that these systems can be correlated in the manner denoted by dashed lines in Figure 1. The correlation of Figure 1 is based on band shapes and relative intensities, as estimated by planimetry. Energies and intensities are given in Table I. An enlarged spectrum of band A of OsO_4 is shown in Figure 2.

Molecular orbital computations were carried out

Table I. Adiabatic Ionization Potentials, Band Areas, and Proposed Assignments[a]

Band	IP, eV	Relative area	Proposed assignment
	RuO_4		
A	12.09	5	$3t_2$
B	12.91	3	$1t_1$
D	13.78	1	$2a_1$
C	13.88	2	1e
E	16.03[b]	2	$2t_2$
	OsO_4		
A	12.32_0	5	$3t_2$
B	13.13_8	3	$1t_1$
C	13.50_2	2	1e
D	14.54_3	1	$2a_1$
E	16.31[b]	2	$2t_2$

[a] Band assignments are cited in terms of that MO from which an electron has been ionized. [b] Energies of band maxima.

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