

A HAMMETT STUDY ON THE TERMINATION STEP OF THE INDIRECT PHOTO-
OXYGENATION OF TRANS-4,4'-DISUBSTITUTED- α,α' -DIMETHYLSTILBENES

by

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IN MEMORY OF MY PARENTS

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ABSTRACT

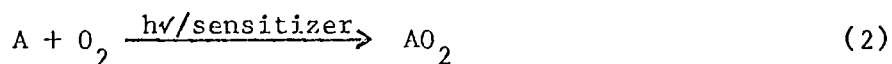
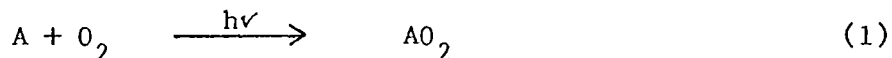
The type II indirect photooxygenation of 4,4'-disubstituted- α,α' -dimethylstilbenes was studied. The substituents ($-\text{NO}_2$, $-\text{Cl}$, CH_3 , and $-\text{OCH}_3$) selected allowed a meaningful application of the Hammett equation in determining the sensitivity of this type of reaction series to ring substitution (indicated by ρ). The ρ (-0.60) calculated indicated a significant sensitivity to ring substitution. Product studies suggest that a concerted-type mechanism is operative. Consistent with this assumption, and the ρ determined in this study, a transition state with little molecular reorganization was drawn.

A significant rate enhancement, which was linear within the reaction series, was recorded with the change of reaction solvent from methanol to acetonitrile. This rate enhancement can be rationalized by a change in the lifetime of $^1\text{O}_2$, or a change in the reactivity of substrate toward $^1\text{O}_2$, or both.

INTRODUCTION

The photochemically induced attack of molecular oxygen (O_2) on organic substrates has been extensively studied over the last decade. The present study involves the use of 4,4'-disubstituted- α,α' -dimethylstilbenes in elucidating the mechanistic implications of the termination step in type II indirect photooxygenation reactions.

Photooxygenation is an oxygenation reaction requiring light, and may be either a direct or an indirect process. In the direct process (1), light is absorbed by A (substrate) or O_2 , while in the



indirect process (2), light is absorbed by molecules other than A or O_2 , that is, by a photosensitizer (Gollnick 1968a).

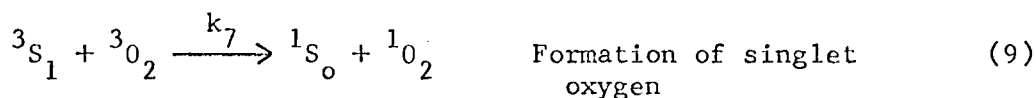
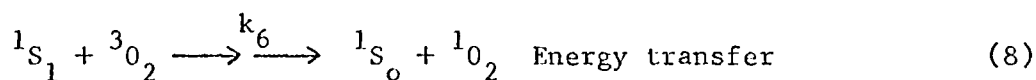
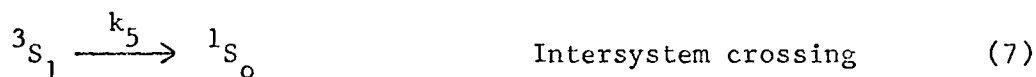
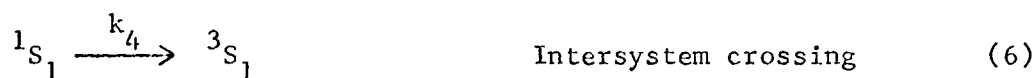
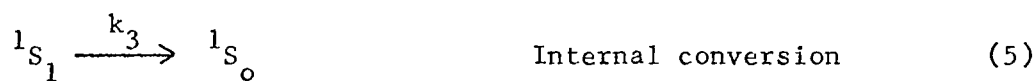
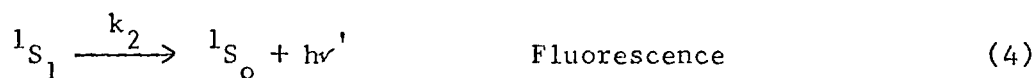
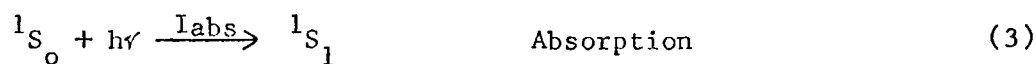
Intermediates involved in these reactions may be either free radicals or molecules in electronically excited states. Photooxygenation reactions may therefore be further subdivided into type I processes, in which free radicals and electronically excited molecules occur as intermediates, or type II processes in which only electronically excited molecules occur as intermediates (Schenck 1963).

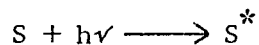
In type II indirect photooxygenation reactions we may distinguish an acceptor-activation mechanism from an oxygen-activation mechanism depending on whether the substrate or the oxygen,

respectively, is activated when it enters the termination reaction which leads to the final product(s) AO_2 (Figure 1, Gollnick 1968a).

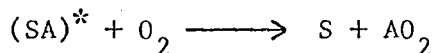
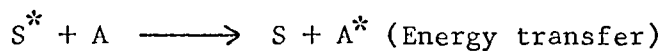
Type II photooxygenation reactions can be distinguished from type I in that type II processes have been found to occur with quantum yields (Φ = no. of molecules undergoing a particular process/no. of quanta absorbed by the system) which do not exceed unity and which are independent of the absorbed light intensity (Livingston 1961). In addition, free-radical intermediates, present in type I, can be excluded on the basis of product analysis, since olefins, for example, produce different products in type II than in type I photooxygenation processes (Gollnick 1968a).

The following reaction sequence has been found to occur in type II indirect photooxygenation reactions:





1. Acceptor-activation mechanism



2. Oxygen-activation mechanism

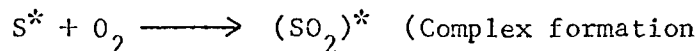
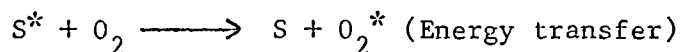
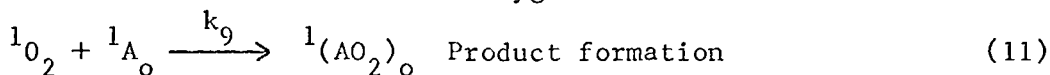
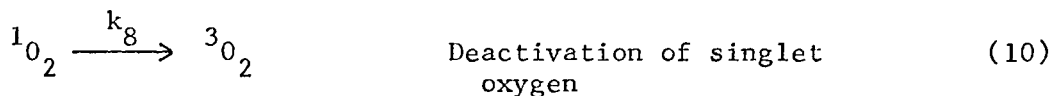


Figure 1. Type II Indirect Photooxygenation Reactions.

A = Substrate; A^* = Singlet or triplet excited A,
 S = Sensitizer; S^* = Singlet or triplet excited S;
 $(SA)^*$, $(SO_2)^*$ = electronically excited complexes.

Only in cases where the exciting photons possess wavelengths shorter than 2000 Å must reaction $O_2 + h\nu \longrightarrow O_2^*$ be considered.



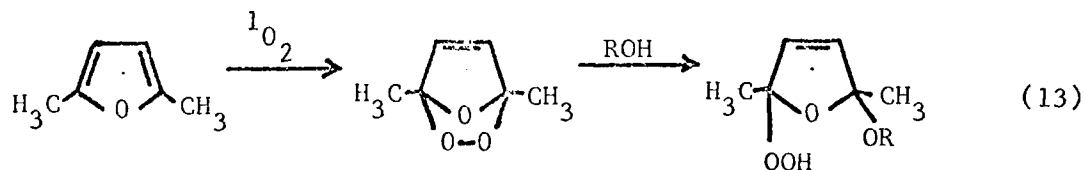
with S = photosensitizer; 1S_o , 1S_1 , and 3S_1 = singlet ground state, first excited singlet state, and first excited triplet state of S, respectively; 1A_o and ${}^1(AO_2)_o$ = singlet ground states of A and AO_2 , respectively; 3O_2 = triplet ground state oxygen, 1O_2 = excited singlet oxygen which is either ${}^1\Delta_g O_2$ or ${}^1\Sigma_g^+ O_2$ (Gollnick 1968a).

The quantum yield of ${}^1(AO_2)_o$ formation is given by

$$\phi_{AO_2} = \frac{[O_2]}{k_2 + k_3 + k_4 + k_6[O_2]} \left(k_6 + k_4 \cdot \frac{k_7}{k_5 + k_7[O_2]} \right) \frac{k_9[A]}{k_8 + k_9[A]} \quad (12)$$

in which the state symbols are omitted for simplicity and the rate constants correspond to the processes as given above (Gollnick 1968a).

Gollnick and Schenck (1964) have done extensive kinetic studies on the photooxygenation of 2,5-dimethylfuran (2,5-DMF) in alcoholic solutions sensitized by xanthene dyes (rose bengal, erythrosin, etc.). For kinetic studies 2,5-DMF is a convenient substrate in that the total oxygen consumption is one mole of O_2 per mole of substrate, and that the rate of oxygen consumption is independent of the concentration of 2,5-DMF (i.e., zero-order) as long as it is greater than 10^{-3} M (Gollnick 1968a). The photooxygenation of 2,5-DMF (13) yields the ozonide of 1,2-dimethylcyclobutadiene which undergoes a facile cleavage by the alcoholic solvent to the corresponding 2-alkoxy-5-hydroperoxy-2,5-dimethylfuran derivative (Foote et al. 1967).



The quantum yield of product formation (ϕ_{AO_2}) in the photooxygenation of 2,5-DMF is equal to the quantum yield of singlet oxygen formation ($\phi_{^1\text{O}_2}$) and is given by

$$\phi_{\text{AO}_2} = \frac{[\text{O}_2]}{k_2 + k_3 + k_4 + k_6[\text{O}_2]} \left(k_6 + k_4 \frac{k_7}{k_5 + k_7[\text{O}_2]} \right) = \phi_{^1\text{O}_2} \quad (14)$$

since

$$[\text{A}] \gg k_8/k_9 \quad \text{when} \quad [\text{A}] > 0.001 \text{ M (Gollnick 1968a)}.$$

In order to establish the validity of a general mechanism for indirect photooxygenation reactions, substrates other than 2,5-DMF have been studied. The quantum yield of product formations for these reactions is given by the general equation

$$\phi_{\text{AO}_2} = \phi_{^1\text{O}_2} \left\{ \frac{[\text{A}]}{([\text{A}] + \beta)} \right\} \quad (15)$$

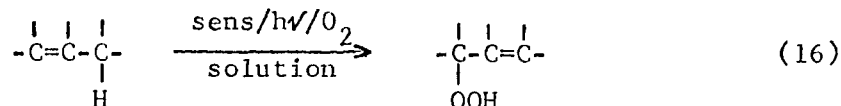
with $\beta = k_8/k_9$ and $\phi_{^1\text{O}_2}$ being obtained from the photooxygenation of 2,5-DMF. It should be here noted that most substrates are less reactive than 2,5-DMF toward singlet oxygen, so that $[\text{A}] \gg k_8/k_9$ [i.e., the assumption made in eq. (14)] is not valid even at relatively large substrate concentrations (Gollnick 1968a). It has been shown by Schenck and Gollnick (1963) that β is independent of the nature of

sensitizer but slightly dependent on solvent. On the other hand, ϕ_{1O_2} of the sensitizers remained practically unaffected by the change of solvents. Consequently, the change of β with solvents may be due either to a change of the lifetime of the singlet oxygen ($1/k_8$) or a change of the reactivity of the substrate toward singlet oxygen (k_9), or both (Gollnick 1968a).

In the termination step of type II indirect photooxygenation reactions, singlet oxygen reacts with a suitable substrate producing an oxygenation product. The quantum yield of the product formation is given by equation (15), as long as the substrates do not act as quenchers of the excited singlet or triplet light absorbers. β values can be obtained from the variation of ϕ_{AO_2} with concentrations of A. However, since the rate of product formation equals the rate of singlet oxygen consumption, and is proportional to ϕ_{AO_2} , β values are more conveniently obtained from the change of the rate of singlet oxygen consumption with the variation in substrate concentration. β values (k_8/k_9) for various substrates under similar reaction conditions reflect only the change in k_9 as a function of substrates, since k_8 remains unchanged. Consequently, a comparison of β values gives some information on the relative reactivities of various substrates toward singlet oxygen.

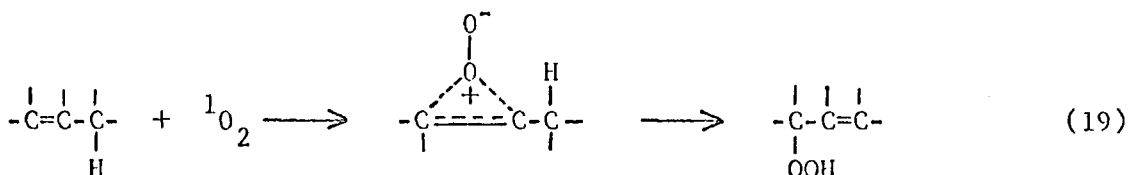
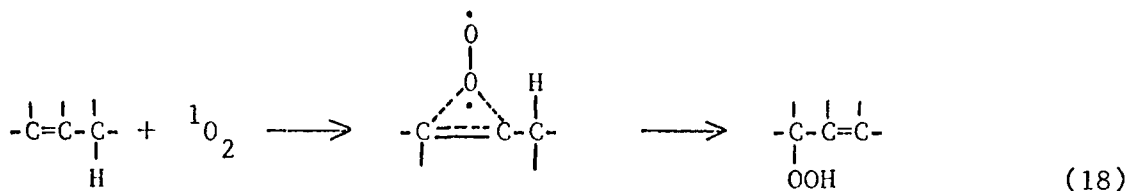
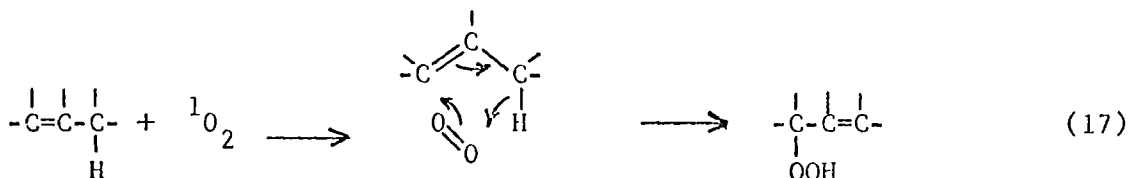
The photosensitized oxygenation of olefins which leads to the formation of α,β -unsaturated hydroperoxides was discovered by Schenck (1948). The Schenck reaction (16) may be described as occurring in three steps: (1) attachment of the oxygen molecule to one of the

carbon atoms of the double bond, (2) shift of the double bond into the allyl position, and (3) migration of the allyl hydrogen atom to the terminus of the peroxy group (Gollnick 1968a). Schenck et al. (1964)



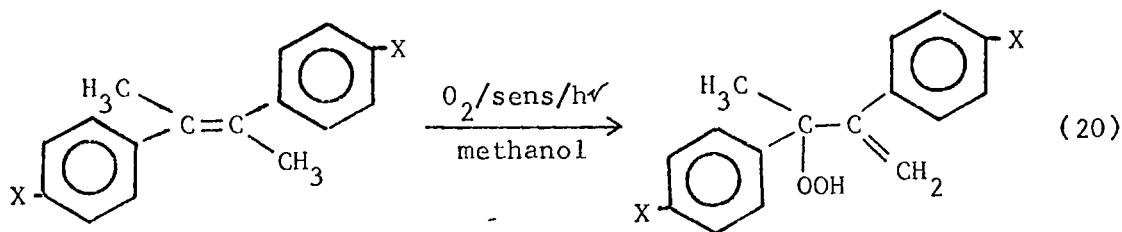
in recent investigations have found that this photosensitized hydroperoxidation reaction to be a type II process.

Two mechanisms have been proposed to account for the type II indirect photooxygenation reaction outlined above. Gollnick and Schenck (1964) have proposed a one-step concerted-type mechanism (17), while Sharp (1960) and Kopecky and Reich (1965) have suggested a two-step mechanism via either a diradical (18) or an ionic species (19). In considering a two-step mechanism the first step must be the attack of



oxygen on the double bond. This may give rise to either a diradical or an ionic species, which in a second step rearrange to the α,β -unsaturated hydroperoxide via hydrogen atom or proton migration, respectively (Gollnick 1968a). Gollnick has suggested excluding the two-step mechanism [(18) and (19)] since product studies have indicated no preference to the attack of O_2 on the nonsterically hindered carbon atom, which would be expected if the most stable alkyl radical or carbonium ion is to be formed. It is assumed that in the cyclic "onium" ions the attacking cation is more strongly bonded to the carbon with the smallest number of alkyl substituents (Roberts and Caserio 1965).

Suitable substrates for the Schenck reaction (20) are 4,4'-disubstituted- α,α' -dimethylstilbenes. When selecting appropriate



substituents (X), these substrates via the application of the Hammett equation can be used to study the electronic effects, if any, on the termination step [eq. (11)] of type II indirect photooxygenation reactions.

The Hammett equation (Hammett 1940) gives an almost quantitative relationship between structure and reactivity. That is, it relates structure to both rate constants and equilibrium constants for the reactions of meta- and para-substituted benzene derivatives. In the application of the Hammett equation two parameters are necessary,

ρ and σ . The σ value for a substituent is found by measuring the effect of that substituent on the ionization of benzoic acid in water at 25°, and is given by

$$\sigma = \log (K_{X-C_6H_4-CO_2H} / K_{C_6H_5-CO_2H}) \quad (21)$$

where $K_{X-C_6H_4-CO_2H}$ and $K_{C_6H_5-CO_2H}$ are the ionization constants for the substituted and unsubstituted benzoic acids, respectively. σ is consequently defined on the basis of this arbitrarily chosen standard reaction for which ρ is fixed at unity. σ is characteristic of the substituent and is a reflection of its inductive and resonance effects. A positive σ value indicates a group which is a stronger electron attractor than hydrogen, while a negative σ value indicates a group which is a weaker electron attractor than hydrogen. ρ , on the other hand, is characteristic of the reaction series at hand and is a measure of the sensitivity of this type of reaction series to ring substitution. The Hammett equation is written

$$\log (k/k_0) = \rho \sigma \quad (22)$$

where k and k_0 are the rate constants for the reaction of the substituted and unsubstituted compound, respectively. A positive ρ value indicates the reaction is aided by an electron withdrawing group, while a negative ρ value indicates the reaction is made more difficult by an electron withdrawing group.

DISCUSSION

The rate constants for the photooxygenation of the 4,4'-disubstituted- α,α' -dimethylstilbenes and the α,α' -dimethylstilbene (which is the standard) have been compiled in Table I.¹ The photooxygenation of

Table I. Rate Constants for the Photooxygenation of 0.00833 M Solutions of Dimethylstilbenes.

Compound	$k_1 \times 10^4 \text{ sec}^{-1}$ a in methanol	$k_1 \times 10^3 \text{ sec}^{-1}$ a in acetonitrile
4,4'-dinitro- α,α' -dimethylstilbene	0.14 ^b	0.24
α,α' -dimethylstilbene	1.59	
4,4', α,α' -tetramethylstilbene	2.20	4.05
4,4'-dimethoxy- α,α' -dimethylstilbene	5.03	8.44

a. Calculation outlined in the Experimental section.

b. Determined from the proportionality constant K avg as outlined in the Experimental section.

4,4'-dinitro- α,α' -dimethylstilbene was performed in acetonitrile due to its lack of solubility in methanol. In order to determine if there was any rate enhancement due to solvent change, photooxygenation reactions were run for 4,4', α,α' -tetramethylstilbene and 4,4'-dimethoxy- α,α' -dimethylstilbene in both methanol and acetonitrile. A significant rate

1. It is peculiar, and not explainable as of this writing, that in the photooxygenation of 4,4'-dichloro- α,α' -dimethylstilbenes the $^1\text{O}_2$ consumption was negligible.

enhancement was discovered which was linear within the reaction series. As a result, a proportionality constant K avg (17.6 ± 0.8) was determined, where

$$K = \frac{k_1', X \text{ (in acetonitrile)}}{k_1', X \text{ (in methanol)}}$$

K avg was then used to determine the k_1' in methanol for 4,4'-dinitro- α,α' -dimethylstilbene. The rate enhancement can be rationalized by a change in the lifetime of 1O_2 , or a change in the reactivity of substrate toward 1O_2 , or both.

β values for the dimethylstilbenes were determined from the k_1' 's above, and have been compiled in Table II. From these β 's, a plot was made of the $\log \beta_H/\beta_X$ (i.e., $\log k_9, X/k_9, H$, where k_9 is the termination step) vs. σ 's for the substituents (Jaffe 1953) and the slope (ρ , $\rho = -0.60$) was determined. ρ is a measure of the sensitivity of the termination step in the photooxygenation of the dimethylstilbenes

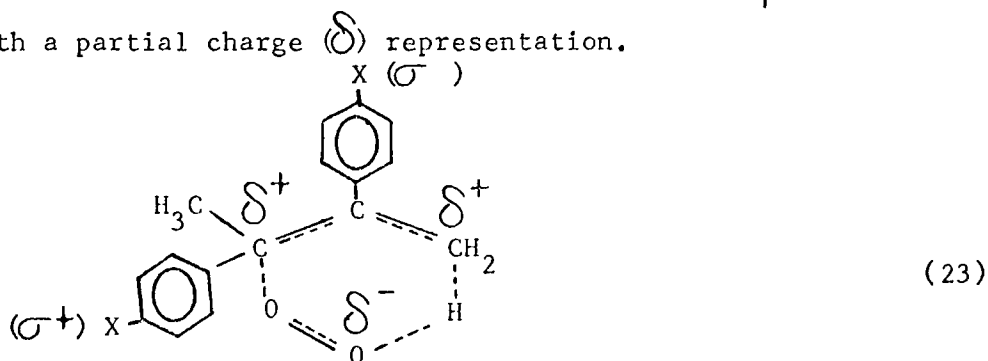
Table II. β Values.

Compound	a moles/liter
4,4'-dinitro- α,α' -dimethylstilbene	7.65
α,α' -dimethylstilbene	0.69
4,4', α,α' -tetramethylstilbene	0.50
4,4'-dimethoxy- α,α' -dimethylstilbene	0.21

a. Calculation outlined in Experimental section.

to ring substitution. The magnitude of ρ indicates a significant correlation between ring substitution and the relative reactivity of these substrates toward singlet oxygen (n.b., $^1O_2 + A \xrightarrow{k_9} AO_2$). The negative sign associated with ρ indicates, as has been recorded in Table II, that the attack of singlet oxygen on the substrates has been made more difficult by the presence of an electron withdrawing group in the para position.

The concerted nature of the Schenck reaction is indicated by the fact that a Markovnikoff-type directing effect is essentially absent. That is, secondary and tertiary products are formed in nearly equal amounts from unsymmetrically substituted olefins (Gollnick 1968a). Gollnick (1968b) presents a convincing summary of product studies which are consistent with a concerted mechanism. Assuming a concerted mechanism, a transition state (23) with little molecular reorganization would not be inconsistent with a ρ of the magnitude (-0.60) found in this study. In the drawing of the transition state, the sign of ρ suggests the charge distribution, while the magnitude of ρ is consistent with a partial charge (δ) representation.



An interesting extension of this research would be a study of the photooxygenation of unsymmetrically substituted dimethylstilbenes. The calculation of a new ρ , and a product study of the position of molecular oxygen attack, would illuminate the mechanism in the termination step. The new ρ would indicate to what extent, if any, the σ values of the substituents were additive, and the position of attack would indicate if a statistical pattern of molecular oxygen attack was operative.

EXPERIMENTAL

General

Ultraviolet (uv) spectra of solutions in absolute ethanol were determined with a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance (nmr) spectra of carbon tetrachloride solutions with tetramethylsilane as an external standard were determined with a Varian A-60 nmr spectrometer. Column chromatography was accomplished by using neutral aluminum oxide (Merck and Company). Magnesium sulfate was employed as a drying agent.

trans-4,4'-Dichloro- α,α' -dimethylstilbene

The procedure of Nagai (1961) was employed. Into a 100-ml round-bottomed flask fitted with a reflux condenser were placed 20 g (0.13 mole) of 4-chloroacetophenone, 30 g (0.60 mole) of hydrazine hydrate, and 40 ml of absolute ethanol. The solution was refluxed for one hour on a water bath and cooled on an ice bath. The crude colorless crystals were isolated and twice recrystallized from petroleum ether, yielding 8.6 g (0.052 mole, 40%) of 4-chloroacetophenone hydrazone, mp 50-52°. Nagai (1961) reported the mp as 51-52°.

Into a 2-liter round-bottomed three-necked flask fitted with a dropping funnel, mechanical stirrer, and gas dispersion tube were placed 8.6 g of 4-chloroacetophenone hydrazone, 50 g of lead dioxide, and 250 ml of benzene. The mixture was stirred vigorously for one hour. The solid material was filtered and sulfur dioxide was rapidly

introduced at room temperature to the solution of 1-(4-chlorophenyl)-diazaoethane (reddish) for thirty minutes. The resulting yellowish reaction mixture was distilled almost to dryness. The residue was dissolved in petroleum ether and purified with alumina column chromatography. The stilbene came off with petroleum ether. Isolation and recrystallization yielded 1.25 g (0.0045 mole, 3.5%) of colorless stilbene crystals, mp 132.5-134.5° (reported by Nagai, 132.5-134°). The structure was confirmed by uv (found $\lambda_{\max} = 249 \text{ m}\mu$, $\epsilon = 1.63 \times 10^4$; reported by Nagai, $\lambda_{\max} = 251 \text{ m}\mu$, $\epsilon = 1.48 \times 10^4$).

trans-4,4'-Dinitro- α,α' -dimethylstilbene

The procedure of Nagai (1961) was employed. Into a 200-ml round-bottomed flask fitted with a reflux condenser were placed 33 g (0.2 mole) of 4-nitroacetophenone, 40 g (0.8 mole) of hydrazine hydrate, and 60 ml of absolute ethanol. The solution was refluxed for one hour on a water bath and cooled on an ice bath. The crude yellow crystals were isolated and twice recrystallized from absolute ethanol, yielding 27 g (0.15 mole, 75%) of 4-nitroacetophenone hydrazone, mp 141-145°.

Into a 2-liter round-bottomed three-necked flask fitted with a dropping funnel, mechanical stirrer, and gas dispersion tube were placed 27 g of 4-nitroacetophenone hydrazone, 200 g of lead dioxide, and 1 liter of benzene. The mixture was stirred vigorously for three hours. The solid material was filtered and sulfur dioxide was rapidly introduced at room temperature to the solution of 1-(4-nitrophenyl)-diazaoethane (reddish) for thirty minutes. The resulting yellowish reaction mixture was distilled almost to dryness. The residue was

dissolved in acetone and twice recrystallized, yielding 10 g (0.034 mole, 17%) of the yellow stilbene crystals, mp 220-221°. The structure was confirmed by uv (found, $\lambda_{\max} = 300 \text{ m}\mu$, $\epsilon = 1.67 \times 10^4$; reported by Nagai, $\lambda_{\max} = 301 \text{ m}\mu$, $\epsilon = 1.87 \times 10^4$).

trans-4,4'-Dimethoxy- α,α' -dimethylstilbene

The procedure of Nagai (1961) was employed. Into a 200-ml round-bottomed flask fitted with a reflux condenser were placed 45 g (0.3 mole) of 4-methoxyacetophenone, 45 g (0.9 mole) of hydrazine hydrate, and 80 ml of absolute ethanol. The solution was refluxed for one hour on a water bath and cooled on an ice bath. The crude colorless crystals were isolated and twice recrystallized from absolute ethanol, yielding 39 g (0.238 mole, 79%) of 4-methoxyacetophenone hydrazone, mp 117.5-122°. Nagai reported the mp as 118.5-121°.

Into a 2-liter round-bottomed three-necked flask fitted with a dropping funnel, mechanical stirrer, and gas dispersion tube were placed 39 g of 4-methoxyacetophenone hydrazone, 400 g of lead dioxide, and 1.2 liters of benzene. The mixture was stirred vigorously for five hours. The solid material was filtered and sulfur dioxide was rapidly introduced at room temperature to the solution of 1-(4-methoxyphenyl)-diazethane (reddish) for thirty minutes. The resulting yellowish reaction mixture was distilled almost to dryness. The residue was dissolved in petroleum ether and purified by alumina column chromatography. The stilbene came off with petroleum ether. Isolation and recrystallization yielded 1.65 g (0.006 mole, 2%) of the colorless stilbene crystals, mp 129.0-130.5° (reported by Nagai, 129.5-132.0°).

The structure was confirmed by uv (found $\lambda_{\max} = 248 \text{ m}\mu$, $\epsilon = 1.91 \times 10^4$; reported by Nagai, $\lambda_{\max} = 249 \text{ m}\mu$, $\epsilon = 1.81 \times 10^4$).

trans-4,4', α,α' -Tetramethylstilbene

The procedure of Nagai (1961) was employed. Into a 250-ml round-bottomed flask fitted with a reflux condenser were placed 46 g (0.34 mole) of 4-methylacetophenone, 30 g (0.60 mole) of hydrazine hydrate, and 80 ml of absolute ethanol. The solution was refluxed one hour on a water bath. The solvent was removed at room temperature under reduced pressure yielding an oily substance. The 4-methylacetophenone hydrazone was extracted by shaking the oily substance with ca. 600 ml of petroleum ether. The petroleum ether extract was then dried and filtered.

Into a 2-liter round-bottomed three-necked flask fitted with a dropping funnel, mechanical stirrer, and gas dispersion tube were placed 350 g of lead dioxide, and the 600-ml petroleum ether extract. The mixture was stirred vigorously for two hours. The solid material was filtered and sulfur dioxide was rapidly introduced at room temperature to the solution of 1-(4-methylphenyl)-diazaoethane (reddish) for thirty minutes. The resulting yellowish reaction mixture was distilled almost to dryness. The residue was dissolved in petroleum ether and purified by alumina column chromatography. The stilbene came off with petroleum ether. Isolation and recrystallization yielded 4.05 g (0.017 mole, 5%) of the colorless stilbene crystals, mp 107.5-109.5° (reported by Nagai, 109.5-110.5°). The structure was confirmed by uv (found,

$\lambda_{\max} = 245 \text{ m}\mu$, $\epsilon = 1.51 \times 10^4$; reported by Nagai, $\lambda_{\max} = 245 \text{ m}\mu$, $\epsilon = 1.45 \times 10^4$).

trans- α, α' -Dimethylstilbene

The procedure of Nagai (1961) was employed. Into a 250-ml round-bottomed flask fitted with a reflux condenser were placed 46 g (0.38 mole) of acetophenone, 30 g (0.60 mole) of hydrazine hydrate, and 80 ml of absolute ethanol. The solution was refluxed one hour on a water bath. The solvent was removed at room temperature under reduced pressure yielding an oily substance. The acetophenone hydrazone was extracted by shaking the oily substance with ca. 600 ml of petroleum ether. The petroleum ether extract was then dried and filtered.

Into a 2-liter round-bottomed three-necked flask fitted with a dropping funnel, mechanical stirrer, and gas dispersion tube were placed 400 g of lead dioxide and the 600-ml petroleum ether extract. The mixture was stirred vigorously for two hours. The solid material was filtered and sulfur dioxide was rapidly introduced at room temperature to the solution of 1-(phenyl)-diazaoethane (reddish) for thirty minutes. The resulting yellowish reaction mixture was distilled almost to dryness. The residue was dissolved in petroleum ether and purified with alumina column chromatography. The stilbene came off with petroleum ether. Isolation and recrystallization yielded 0.8 g (0.0038 mole, 1%) of the colorless stilbene crystals, mp 102.5-104.5° (reported by Ramart-Lucas and Salmon-Legaguer n.d., 104-105°). The structure was confirmed by uv (found $\lambda_{\max} = 243 \text{ m}\mu$, $\epsilon = 1.22 \times 10^4$; reported by Nagai, $\lambda_{\max} = 243.5 \text{ m}\mu$, $\epsilon = 1.23 \times 10^4$).

Standard Iodine Solution

The method outlined by Skoog and West (1963) was employed. Approximately 12 g of iodate-free potassium iodide crystals and about 6.5 g of resublimed iodine were dissolved in 10 ml of distilled water. The iodine solution was transferred to a glass-stopped bottle and diluted to approximately 500 ml.

Three portions of about 0.2 g of primary-standard-grade arsenious oxide (dried for one hour at 110°) were weighed accurately and transferred to 250-ml conical flasks. The samples were dissolved with 10-15 ml of 1 N NaOH (slight heating was necessary). The flask was cooled in tap water and the solutions neutralized with 1 N HCl after adding two drops of methyl red indicator. The solutions were buffered by adding about 5 g of powdered sodium bicarbonate. The solutions were diluted to 100 ml, then titrated with the iodine solution to the appearance of a deep blue color after adding 3 ml of starch indicator. The normality of the iodine solution was then computed.

Standard Sodium Thiosulfate

The 0.132 N sodium thiosulfate solution used throughout these experiments was prepared and standardized by the method outlined in Skoog and West (1963). To 1 liter of distilled water (boiled and allowed to cool) were added 25 g of reagent-grade sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and 2-3 g of borax crystals (preservative). The solution was transferred to a 1-liter glass-stoppered bottle. Three 25-ml portions of the thiosulfate solution were measured out with a calibrated pipette and 1-ml aliquots of starch indicator were added. Each

was titrated with the standard iodine solution to the appearance of a deep blue color. The normality of the thiosulfate solution was then computed.

Photooxygenation Procedure

Into a 250-ml Erlenmeyer flask were added 0.001 mole of 4,4'-disubstituted- α,α' -dimethylstilbene, 120 ml of A.R. methanol, and 50 mg of rose bengal sensitizer (found empirically to be the amount necessary over the reaction time interval). The solution was stirred until the rose bengal and stilbene were completely dissolved. The photooxygenation reactor was then prepared by turning on all cooling jackets, flushing the entire system several times with O_2 to remove any air, and isolating O_2 in the burette by closing stopcock III. The solution was added to the reaction cell via stopcock II with rubber stopper B removed, and stopcock I open to the O_2 tank (this prevented the backing up of the solution into the Tygon tubing). Once all of the solution was added, rubber stopper A was carefully lifted in order to bring the solution level to the top of the spout. The gas-circulation pump was started, stopcock I was closed to the tank, stopcock II was closed, rubber stopper B was replaced, and stopcock III was opened to the entire system. A cardboard shield was placed between the reaction cell and the Hg lamp until the maximum intensity was reached (approximately two minutes). The water levels in the bulb and the burette were equilibrated, the shield removed, and the O_2 uptake was recorded in 5-minute intervals. When the reaction was completed, the Hg lamp was turned off, and the solution was removed via stopcock IV with stopcock

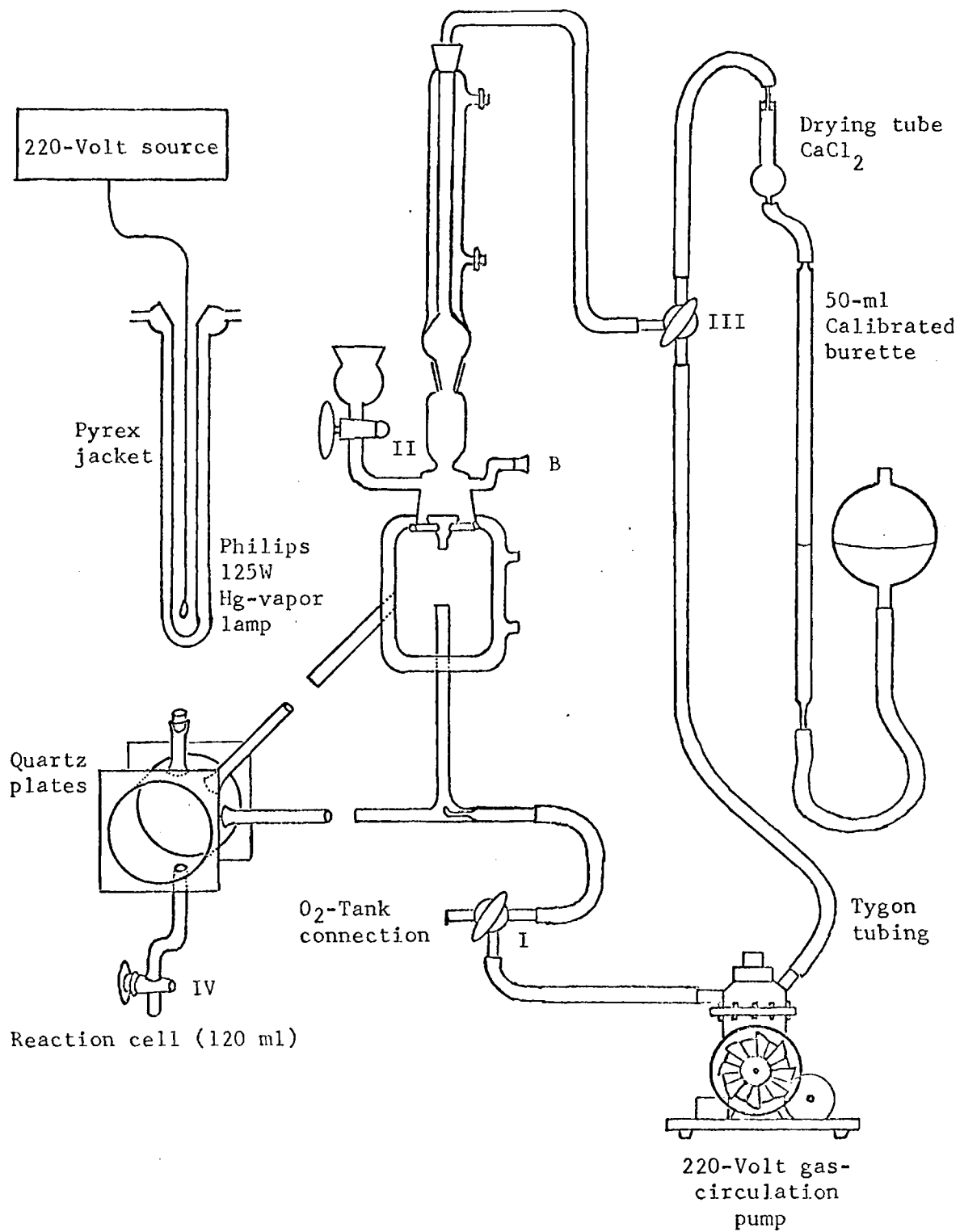


Figure 2. Photooxygenation Reactor.

II open (see Figure 2). The formed hydroperoxide was then set aside for product studies.

Reaction Conditions

The room temperature and the atmospheric pressure were recorded and used in calculating the volume (ml) occupied by 0.001 mole of O_2 . It was found that the variation in volume between runs due to temperature and pressure changes was negligible under experimental conditions.

Product Studies

The photooxygenation reaction was allowed to run at room temperature and atmospheric pressure until the reaction was more than 50% complete. The solution was drained from the photooxygenation reactor, and the methanol removed under reduced pressure leaving a residue of the hydroperoxide and the unreacted stilbene. The method of Fordham and Williams (1949) was employed to determine the amount of hydroperoxide present. The residue was dissolved in 100 ml of 99% isopropanol and placed in a glass-stoppered Erlenmeyer. Approximately 10 ml of glacial acetic acid and 1 ml of saturated potassium iodide were added, and the mixture was refluxed gently (to avoid loss of iodine) for 3 to 4 minutes. The condenser was washed with 10 ml of isopropanol, 25 ml of water was added, and the flask stoppered. When the resulting solution had cooled somewhat, the liberated iodine was titrated with the 0.132 N thiosulfate solution (previously prepared) to the disappearance of the yellow color.

Fortran Program for the Calculation of k_1 's

Input. The first data card had the maximum oxygen consumption (MAXCON, ml/minute) in columns 1-4 (i.e., the volume occupied by 0.001 mole of O_2 at atmospheric conditions). The remaining data cards had the total oxygen consumption (SINCON, ml) at each time interval in columns 1-4, and the time elapsed (TIME, minutes) in columns 5 and 6.

Fortran Program.

```

PROGRAM FRANK (INPUT, OUTPUT, TAPE 1 = INPUT)
COMMON TT (25), K11(25)
REAL MAXCON, LSTILB, K11
6 READ 1, MAXCON
1 FORMAT (F4.1)
  IF (EOF, 1) 40,30
30 I = 1
  PRINT 10, MAXCON
10 FORMAT (1H1, *MAXIMUM OXYGEN CONSUMPTION = *, F4.1,/)
  3 READ 2, SINCON, TIME, ISTOP
  2 FORMAT (F 4.1, F2.0, 73X, I1)
  IF (ISTOP.GT.0) GO TO 5
  PRINT 20, SINCON, TIME
20 FORMAT (1X, * SINGLET OXYGEN CONSUMPTION = *, F4.1, * TIME
  = *, F2.0, 1/)
  DIFFCON = MAXCON-SINCON
  PCON = DIFFCON/MAXCON
  CSTILB = PCON * 0.00833

```

```
LSTILB = ALOG (0.00833/CSTILB)
TT (I) = TIME
K11 (I) = LSTILB
PRINT 50, CSTILB
50 FORMAT (1X, * CONCENTRATION OF STILBENE = *, F6.5)
I = I + 1
GO TO 3
5 CALL LEAST SQ (I)
GO TO 6
40 STOP
END
SUBROUTINE LEAST SQ (I)
COMMON TT (25), K11 (25)
REAL K11
N = I-1
SUM X = 0.0
SUM Y = 0.0
SUM XY = 0.0
SUM X2 = 0.0
SUM Y2 = 0.0
DO 4 I = 1,N
SUM X = SUM X + TT(I)
SUM Y = SUM Y + K11 (I)
SUM X2 = SUM X2 + TT (I) **2
SUM Y2 = SUM Y2 + K11(I) **2
```



```

SUM XY = SUM XY + TT(I)*K11(I)
4 CONTINUE
DENOM = N*SUM X2-SUM X**2
SLOPE = (N*SUM XY-SUM X*SUM Y)/DENOM
B = (SUM XY-SLOPE *SUM X2)/SUM X
PRINT 5, SLOPE, B
5 FORMAT (1H0,* THE SLOPE IS *, F10.8, * THE INTERCEPT
IS *, F10.8)
RETURN
END

```

Output. The printed output included MAXCON, TIME, SINCON, and the concentration of stilbene (CSTILB), moles/liter) at each time interval. The intercept and the slope (k_1 found via least squares method) of the plot of $\ln ([A]_0/[A])$ vs. TIME (where A_0 equals initial stilbene concentration and A equals concentration of stilbene at each time interval) were calculated and reported in the output.

Fortran Program for the Calculation of β 's

Input. The first data card had the rate of the O_2 uptake of 2,5-dimethylfuran (ADMF, moles/liter-sec) at atmospheric conditions in columns 1-4. The remaining data cards had time elapsed (TIME, minutes) in columns 1 and 2, the k_1 for the stilbene (KSTILB, sec^{-1}) in columns 3-8, and the concentration of the stilbene (CSTILB, moles/liter) at each time interval in columns 9-14.

Fortran Program.

```
PROGRAM FRANK (INPUT, OUTPUT, TAPE 1 = INPUT)

COMMON TT (25), K11 (25)

REAL K11, ICSTILB, KSTILB

6  READ 1, ADMF

1  FORMAT (F 7.6)

   IF (EOF, 1) 40,30

30  I = 1

   PRINT 10, ADMF

10  FORMAT(1H1, *A FROM 2,5-DIMETHYLFURAN = *, F7.6,/)

3  READ 2, TIME, KSTILB, CSTILB, ISTOP

2  FORMAT (F2.0, F7.6, F6.5, 64S, I1)

   IF (ISTOP. GT.0) GO TO 5

   PRINT 20, TIME, KSTILB, CSTILB

20  FORMAT (1X, * TIME = *,F2.0, * KSTILB = *, F7.6, * CSTILB =
*, F6.5)

   SRATE = KSTILB*CSTILB

   ARATE = ADMF 1SRATE

   I CSTILB = 1.0/CSTILB

   TT(I) = ICSTILB

   K11(I) = ARATE

   PRINT 50, ARATE, ICSTILB

50  FORMAT (1X, * ARATE = *,F7.2,* ICSTILB = *,F7.2,/)

   I = I + 1

   GO TO 3
```

```

5  CALL LEASTSQ(I)
    GO TO 6
40 STOP
    END

```

(REPEAT Subroutine LEAST SQ(I) previously outlined, see p. 24).

Output. The printed output included ADMF, TIME, KSTILB, CSTILB, 1/CSTILB(ICSTILB, liter/moles) and ADMF/(KSTILBXCSTILB) (which is ARATE) at each time interval. The intercept and the slope (B, found via least squares method) of the plot of ADMF/(KSTILBXCSTILB) vs. ICSTILB were calculated and recorded in the output.

Calculations

The rate α (slope) of the O_2 uptake (or AO_2 formation) of 2,5-dimethylfuran was calculated directly from a plot of ml of O_2 uptake vs. time elapsed (sec), as it is a zero-order reaction under existing experimental conditions (Gollnick and Schenck 1964). This value of α (ml/sec) was then converted to appropriate dimensions (mole/l \cdot sec, since ml of uptake represent moles of product formation).

In the case of 4,4'-disubstituted- α,α' -dimethylstilbenes,

$$\text{rate}_{O_2\text{-uptake}} = \text{rate}_{AO_2} = k_1' [A]$$

where $[A] = [A]_0 - [AO_2]$ in moles/liter. The rate constant k_1' (slope, sec⁻¹) was calculated from a plot of the $\ln([A]_0/[A])$ vs. the time elapsed (Gould 1959).¹

1. A Fortran program using the least squares method to obtain the best k_1' 's and β 's is included in the Experimental section.

It has been shown that

$$\phi_{AO_2} = \phi_{1O_2} \frac{[A]}{[A] + \beta}$$

is a general equation for the photosensitized oxygenations of the olefins herein investigated (Gollnick 1968a). This equation is equivalent to

$$\text{rate}_{AO_2} = \text{rate}_{1O_2} \frac{[A]}{[A] + \beta}$$

which is a more convenient form for experimental calculations. The $\text{rate}_{AO_2} = \text{rate}_{1O_2}$ (or α) for 2,5-DMF, since $[A] \gg \beta$; consequently,

$$\text{rate}_{AO_2} = \alpha \frac{[A]}{[A] + \beta}$$

where α is calculated from 2,5-DMF. Upon rearrangement, the above equation becomes

$$\frac{\alpha}{\text{rate}_{AO_2}} = \frac{\beta}{[A]} + 1$$

A plot of $\alpha/\text{rate}_{AO_2}$ vs. $1/[A]$ yields β (slope, moles/liter).

The determination of ρ (slope), which is a measure of the sensitivity of this type of reaction series to ring substitution (Hammett 1940), was accomplished by plotting the $\log \beta_H/\beta_X$ vs. known σ values for the substituents (Jaffee 1953). The σ values giving the best ρ (i.e., the best straight line) were a combination of σ^+ and σ . The ratio β_H/β_X is a reflection of the rate of hydroperoxide formation

($k_9, A + O_2 \longrightarrow AO_2$) for α, α' -dimethylstilbene compared to that for 4,4'-disubstituted- α, α' -dimethylstilbenes (Gollnick 1968a)

A proportionality constant K, defined by

$$K = \frac{k_1', X \text{ (in acetonitrile)}}{k_1', X \text{ (in methanol)}}$$

was calculated for the rate enhancement due to solvent change for each substrate. The rate enhancement was found to be linear; consequently, a K avg (17.6 ± 0.8) was calculated and used to determine the k_1' of 4,4'-dinitro- α, α' -dimethylstilbene in methanol (n.b., this substrate could not be dissolved at the required concentration in methanol).

APPENDIX

TABLES OF EXPERIMENTAL DATA

Table A-I. Photooxygenation of a 0.0083 M Solution of 4,4', α,α' -Tetramethylstilbene in Methanol (three runs).

Time, mins	ml of $^{1}O_2$ Consumed	Time, mins	ml of $^{1}O_2$ Consumed	Time, mins	ml of $^{1}O_2$ Consumed
10	1.1	5	1.4	10	1.2
15	2.2	10	2.6	15	2.5
20	3.3	15	4.0	20	3.9
25	4.8	20	5.4	25	5.0
30	6.0	25	8.2	30	6.4
35	7.2	30	9.7	35	8.0
40	8.9	35	11.0	40	8.5
45	9.9	40	12.8	45	9.2
50	10.6	45	13.2	50	9.7
		50	15.4	55	10.2
				60	10.8
				65	11.4

$$k_1' \text{ avg} = 2.20 \pm 0.46 \times 10^{-4} \text{ sec}^{-1}$$

Table A-II. Photooxygenation of a 0.00833 M Solution of 4,4'-Dimethoxy- α,α' -dimethylstilbene in Methanol (two runs).

Time, mins	ml of $^{1}O_2$ Consumed ²	Time, mins	ml of $^{1}O_2$ Consumed ²
10	2.4	10	2.8
15	4.6	15	5.7
20	7.8	20	11.0
25	10.8	25	13.4
30	12.8	30	15.1
35	14.1	35	16.5
40	15.6	40	17.8
45	16.8	45	19.2
50	17.9	50	20.7
55	18.9	55	21.9
60	19.8		
65	20.7		
70	21.6		

$$k_1' \text{ avg} = 5.03 \pm 0.74 \times 10^{-4} \text{ sec}^{-1}$$

Table A-III. Photooxygenation of a 0.00833 M Solution of α, α' -Dimethylstilbene in Methanol (two runs).

Time, mins	ml of $^{1}O_2$ Consumed	Time, mins	ml of $^{1}O_2$ Consumed
5	2.0	10	0.8
10	4.0	15	1.5
15	6.0	20	2.5
20	7.5	25	3.4
25	8.5	30	5.2
30	9.0	35	6.1
35	11.2	40	6.7
40	12.0	45	7.4
45	12.8	50	7.8
50	13.2	60	8.0
55	14.2	65	8.8
60	14.5	70	9.6
70	15.2		

$$k_1' \text{ avg} = 1.59 \pm 0.44 \times 10^{-4} \text{ sec}^{-1}$$

Table A-IV. Photooxygenation of a 0.00833 M Solution of 4,4'-Dinitro- α,α' -dimethylstilbene in Acetonitrile (two runs).

Time, mins	ml of 1O_2 Consumed	Time, mins	ml of 1O_2 Consumed
10	1.8	10	1.4
15	3.1	15	2.6
20	4.1	20	4.1
25	5.5	25	5.4
30	6.7	30	8.0
35	8.1	35	10.2
40	8.9	40	10.8
45	10.1	45	11.6
50	11.4	50	12.5
55	12.5	55	13.4
62	14.0	60	15.1
70	15.1	65	15.8
		70	16.5

k_1' avg = $2.38 \pm 0.21 \times 10^{-4} \text{ sec}^{-1}$

Table A-V. Photooxygenation of a 0.0083 M Solution of 4,4'-Dimethoxy- α,α' -dimethylstilbene in Acetonitrile (two runs).

Time, mins	ml of $^{1}O_2$ Consumed ²	Time, mins	ml of $^{1}O_2$ Consumed ²
1	4.6	1	4.3
2	9.5	2	9.4
3	14.2	3	14.2
4	18.0	4	18.4
5	21.9	5	22.1
6	25.5	6	24.5

k_1' avg = $8.44 \pm 0.71 \times 10^{-3} \text{ sec}^{-1}$

Table A-VI. Photooxygenation of a 0.00833 M Solution of 4,4', α,α' -Tetramethylstilbene in Acetonitrile (two runs).

Time, mins	ml of $^{1}O_2$ Consumed ²	Time, mins	ml of $^{1}O_2$ Consumed ²
2	5.1	2	5.5
4	11.1	4	12.2
6	15.8	6	17.1
8	18.9	8	21.5
10	21.4	10	24.3
12	23.3		
14	24.6		
16	25.6		

k_1' avg = $4.05 \pm 0.51 \times 10^{-3} \text{ sec}^{-1}$

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