8-1-1972

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Recommended Citation

Niu, Chien-hua, "The Photodecomposition and Photooxidation of Aliphatic Amines" (1972). *Theses and Dissertations*. 3628.
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THE PHOTODECOMPOSITION AND PHOTOOXIDATION OF ALIPHATIC AMINES

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A Dissertation

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Grand Forks, North Dakota

August
1972

This dissertation submitted by Chien-hua Niu in partial fulfillment of the requirements for the Degree of Doctor of Philosophy from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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ACKNOWLEDGEMENTS

The author wishes to extend his sincere gratitude to Dr. V. I. Stenberg and Dr. N. Kulevsky for suggestion of the problem, stimulating guidance, and a well-rounded chemical education obtained throughout the investigation. He would also like to thank Dr. R. G. Severson, Dr. L. E. Cook, and Dr. F. A. Jacobs for serving on the advisory committee.

The author is indebted to Dr. R. G. Severson for providing the opportunity to pursue a graduate career.

The author wishes to express his appreciation to Dr. Cook for discussion of gas chromatography problems.

This investigation was supported by an NSF Grant No. 4392 and in part by NIH Grant No. 1-ROI-A108136.

The author wishes to dedicate this dissertation to his parents and his wife, Susie, without whose encouragement and understanding this work would not have been possible.

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ABSTRACT

The ultraviolet irradiation of ammonia-saturated liquid cyclohexane produces two products, cyclohexylamine in a photostationary state and cyclohexylcyclohexane. It is assumed that ammonia is responsible for the initial light absorption which leads to the observed reaction products.

The products and rates of product formation have been determined for the ultraviolet irradiation of cyclohexylamine, cyclopentylamine, and _n_-hexylamine in saturated hydrocarbon solvents. The results demonstrate that (1) imines are produced during the irradiation, (2) ammonia is isolated and identified, (3) both carbon-nitrogen and nitrogen-hydrogen bonds cleave to varying degrees during the irradiation, and (4) the cleavage pattern is dependent on the stability of the alkyl radicals produced.

Direct ultraviolet irradiation of the secondary amines, _i.e._, di-_n_-hexylamine, dicyclohexylamine, and _n_-hexylcyclohexylamine in cyclohexane liquid solution, produces the corresponding imine in preparative yields (89-91%).

The primary process of the photooxidation of cyclohexylamine is determined as charge-transfer excitation by the light absorption dependence of the reaction. The primary products are cyclohexanone oxime, N-cyclohexylidenecyclohexylamine, ammonia, and water. Synthesis and studies of 1-hydroperoxycyclohexylamine show that it is probably the

precursor for N-cyclohexylidenecyclohexylamine. Cyclohexanone oxime is presumably generated from the thermal or photodecomposition of N-hydroperoxycyclohexylamine. Hydrogen peroxide is probably present in the photomixture of cyclohexylamine. When ionization potentials of aliphatic amines are plotted versus the frequency of charge-transfer bands, a linear relationship is obtained.

The relative rates of oxygen uptake during the photooxidation of cyclic hydrocarbons show that the carbon-hydrogen rather than carbon-carbon bond is the donor in the contact charge-transfer process between oxygen and the hydrocarbon.

LITERATURE SURVEY

Photolysis of Ammonia

The probable primary processes in ammonia photolysis are as follows:

$$
\begin{aligned}
NH_3 + hv \longrightarrow\; & NH_2\cdot + H\cdot\,(^2S_{1/2}) && (1)\\
& NH\cdot\,(^3\Sigma^-) + 2H\cdot\,(^2S_{1/2}) && (2)\\
& NH\cdot\,(^1\pi) + H_2 && (3)
\end{aligned}
$$

At wavelengths between 217-168 nm, reaction 1 is the only primary process. There is abundant evidence that the hydrogen atoms are produced at all wavelengths in ammonia photolysis.[1-9] The NH_2 radical has been observed in ammonia photolysis and characterized by absorption spectrocopy,[3] and electron spin resonance (esr) spectroscopy.[10]

Indirect evidence as to the primary photodissociation products of ammonia at wavelengths 168-217 nm has been obtained from the ammonia photolysis in the presence of added gas. When oxygen was added to the ammonia photolysis, water, nitrite and nitrate were formed and hydrogen formation was suppressed.[1] Gesser[5] and Groth, et al.,[11] studied the photolysis of ammonia in the presence of propane. The products were hydrogen, nitrogen, 1-propene, 2-aminopropane, and 2,3-dimethylbutane. Irradiation of ammonia in the presence of NO yielded nitrogen, water, nitrous oxide, and a small amount of hydrogen. Further work was performed by Srinivasan[9] using $^{15}NH_3$. The isotopic composition of nitrogen produced was mainly $^{14}N^{15}N$. He concluded that reaction 4 is responsible for the production of nitrogen.

$$^{15}NH_2\cdot + {}^{14}NO \longrightarrow {}^{14}N^{15}N + H_2O \qquad (4)$$

In addition to amino radical formation, the NH radical has been identified in the photolysis of ammonia at shorter wavelengths; in photolysis below 155 nm, the $^3\Sigma^-$ state of NH was found,[8, 12, 13] while at 116.5, 123.6 and 129.5 nm,there was emission from the $^1\Pi$ state.[14]

The photolysis of ammonia was carried out both alone and with added C_2D_4 at 123.6 and 184.9 nm.[2] The production of H_2 in the presence of C_2D_4 indicates that molecular hydrogen is formed since hydrogen atoms are efficiently scavenged by C_2D_4. It was found that, at 184.9 nm, ammonia decomposes almost entirely to $NH_2\cdot + H\cdot$ as described in reaction 1, whereas at 123.6 nm, molecular hydrogen formed in reaction 3 accounted for about 14% of the total. Thus, the energetics are favorable for reactions 2 and 3 at wavelengths shorter than 142 and 136 nm, respectively.

Photolysis of Primary Aliphatic Amines

The direct and mercury sensitized photolysis of ethylamine in the gas phase produced H_2 as the main product.[15] Later it was found that both H_2 and ammonia were formed in the photolysis of methylamine and ethylamine.[16] However, Wetmore and Taylor[17] found that the photolysis of methylamine produced a high boiling liquid besides hydrogen and ammonia. The composition of this high boiling product was uncertain. It might have been either $CH_2{=}N{-}CH_3$ or C_2H_3N or a polymer of either of these substances. A high boiling product was also observed at the bottom of the reaction container when n-butylamine and n-amylamine were directly irradiated in the gas phase.[18] When an n-hexane solution of n-hexylamine was irradiated for a prolonged period of time, a brown polymer was also produced.[19] On treating the high boiling compound with dilute acid and neutralizing with base, the characteristic pink color of the carbonyl group was developed when Schiff's reagent was added.[18] Other workers have reported that the polymer formed from the photolysis of methylamine was hydrolysed by dilute HCl, and a yellow precipitate formed indicating the presence of formaldehyde when 2, 4-dinitrophenylhydrazine was added.[17] However, Watson and Darwent[20] reported that a trimer of $CH_2=N-CH_3$ was isolated and identified from the heavy liquid obtained from the photolysis of methylamine.

Photolysis of methylamine and ethylamine in the presence of oxygen produced little hydrogen, but yielded amounts of ammonia which were only slightly less than that obtained in the direct photolysis.[16, 17, 21] When propylene was introduced, the photolysis of methylamine[17, 21] n-butylamine, and n-amylamine[18] produced propane and hexane in the reaction mixture. Therefore, the primary step of photolysis of primary amines in gas phase is proposed to be:

$$RNH_2 \xrightarrow{h\nu} RNH_2^* \longrightarrow RNH\cdot + H\cdot \qquad (5)$$

Esr studies on the reaction mixtures of ultraviolet irradiated methylamine at 77°K also lead to the conclusion that the primary decomposition of primary amine can be described by reaction 5.[22] Furthermore, when propylene was irradiated with CD_3NH_2, 2, 3-dimethylbutane was the main product, while with CH_3ND_2, 70% of the dimethylbutane formed was 1,4-dideuterio-2, 3-dimethylbutane indicating that approximately 87% of CH_3ND decomposed by reaction 5.[21]

The route for formation of ammonia from the photolysis of primary amines is still a controversial one. In order to account for the formation of ammonia several authors have suggested that ammonia produced in the photolysis of primary amines must arise from two amino radicals as in reaction 6.[16, 18, 21]

$$2RNH\cdot \longrightarrow NH_3 + RN{=}CHR' \qquad (6)$$

Such a reaction between two radicals must be of rare occurrence unless reaction 6 is merely to be taken as an over-all reaction. That is, a two step reaction as illustrated in reactions 7 and 8.

$$RNH\cdot + RNH\cdot \longrightarrow R'CH{=}NH + RNH_2 \qquad (7)$$

$$R'CH{=}NH + RNH_2 \longrightarrow R'CH{=}NR + NH_3 \qquad (8)$$

If the formation of the imine involved reaction 7 and 8, the regenerated RNH_2 from reaction 7 should become CD_3NHD in the photolysis of CD_3NH_2. However, the data indicated that CD_3NDH was not observed in the recovered CD_3NH_2.[21] Therefore, Wetmore and Taylor[17] suggested a mechanism for the production of the imine and ammonia by reactions 9 and 10.

$$CH_3NH\cdot \longrightarrow CH_2{=}NH + H\cdot \qquad (9)$$

$$CH_2{=}NH + CH_3NH_2 \longrightarrow CH_3N{=}CH_2 + NH_3 \qquad (10)$$

However, in view of the data on the stability of a rather similar radical CH_2OH,[23] Watson and Darwent[20] concluded that reaction 9 appeared improbable.

As small amounts of methane and ethane were produced in the photolysis of methylamine[16, 17, 24] reaction 11 was postulated.

$$CH_3NH_2 \xrightarrow{h\nu} (CH_3NH_2^*) \longrightarrow CH_3\cdot + NH\cdot_2 \quad (11)$$

Since the amount of methane and ethane formed in the photolysis of methylamine is always small compared to that of hydrogen, reaction 11 probably plays a minor role in the irradiation of primary amines. However, reaction 11 becomes more important in the photodecomposition of methylamine at 147 nm.[25]

The effect of solvent on the photolysis of primary amine solutions has been studied. When n-hexane solutions of n-hexylamine are irradiated, unsaturated compounds and hydrogen gas are produced. However, no ammonia is observed.[19] In n-hexane, the bond affected by the ultraviolet light is nitrogen-hydrogen bond as in the gas phase, while in water the carbon-nitrogen bond is affected.[26] The prolonged irradiation of solutions of various other amines in n-hexane with ultraviolet light in 200-230 nm region produced hydrogen and hexene. The yield of hydrogen increases with increasing concentration of amine in the initial solution. The quantum yield of hydrogen had a positive temperature coefficient over the temperature range 15-30°. The quantum yield of hydrogen decreased regularly with increasing the chain length.[27]

Photolysis of Secondary Aliphatic Amines

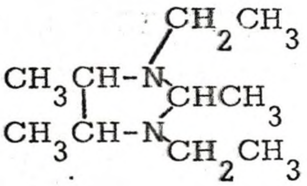
Dimethylamine on photolysis produced hydrogen, polymer, and small amounts of methane and ethane.[18] When ethylmethylamine was irradiated in an n-hexane solution,[19] hydrogen, methane, and a brown polymer were observed, however, no ethane could be found. Upon prolonged irradiation of pure diethylamine, Allan and Swan demonstrated that diethylamine provided four products, I-IV.[28]

$CH_3CH{=}CH\cdot CH{=}NCH_2CH_3$

(I)

$CH_3CH(NHCH_2CH_3)CH(NHCH_2CH_3)CH_3$

(II)



(III)

$(CH_3CH_2)_2\ N\ N\ (CH_2CH_3)_2$

(IV)

When propylene was introduced into the photolysis of dimethylamine, propane and isomers of hexane were isolated.[18] The formation of propane and hexane can only be accounted for by the attack of hydrogen atoms on propylene molecules, producing propyl or isopropyl radicals, which may either combine with each other to form the mixture of hexanes or be hydrogenated to propane by further combination with hydrogen atoms. Therefore, the primary act in the photolysis of secondary amines is as described in reaction 12.

$$RR'NH \xrightarrow{h\nu} RR'NH^{*} \longrightarrow RR'N\cdot + H\cdot \qquad (12)$$

Evidence obtained from esr studies of irradiated dimethylamine at 77° K demonstrates that reaction 12 is indeed the primary process.[22] Furthermore, the reaction of methyl radical with dimethylamine was studied. In radical attack abstraction of the H attached to N is much more favored than abstraction of the H attached to C.[29]

The polymer obtained from the photolysis of dimethylamine was soluble in dilute acid, and had a marked base reaction with the empirical formula, $(C_2H_5N)_x$. Bamford[18] originally suggested that the polymer was derived from $CH_2=N-CH_3$ and later it was isolated and shown to be the trimer of $CH_2=N-CH_3$.[20]

Thermal Oxidation and Photo-oxygenation of Amines

The thermal oxidation of primary, secondary, and tertiary aliphatic amines in the gas phase has also been studied extensively.[30-36] The major products in the oxidation of primary amines are aldehydes and ammonia[32] while those of secondary amines are aldehydes and primary amines.[33] However, major products of triethylamine are ethylamine and acetaldehyde plus a small amount of diethylamine.[34] Dimethylamine and formaldehyde are the major products from the oxidation of trimethylamine.[35] From the nature of these products, Jolley[30] suggested that the initial process was probably the formation of a complex $(RNH_2)\cdot O_2$ whose structure was unknown. The oxygen, then, somehow attacked a point on the hydrocarbon chain rather than at the nitrogen group of aliphatic amines to form hydroperoxides. These hydroperoxides had been detected in the oxidation of primary and secondary amines.[32,33] The hydroperoxide was believed to be the intermediate for the formation of further products.[32-36]

The structural influences on the oxidation of primary and secondary amines has also been investigated. In the primary amines, a rapid rise in oxidation rate with increasing length of the unbranched carbon chain was attributed to the inductive effect.[32] The accelerating effect of an NHR group was found to be much larger than that of an NH_2, as shown by comparison of the compounds $R'NH_2$ and R'NHR (R'NHR'), where R' is an alkyl group which is oxidized in preference to R. This acceleration of the oxidation is by virtue of the inductive effect. The ease of oxidation of secondary amine is markedly altered by changes in R' while being little affected by the nature of R.[33]

There are two distinct processes taking place during the oxidation of triethylamine.[34] The first process, established on the basis of steric arguements, involves unimolecular decomposition of intermediate peroxy-radicals. In this process, ethylamine and acetaldehyde are the two major products in the thermal oxidation of triethylamine. The second process proceeds via the formation of the corresponding hydroperoxide. The decomposition of the hydroperoxide of triethylamine gives rise to diethylamine and acetaldehyde. However, in the thermal oxidation of the trimethylamine,[35] the major products are formaldehyde and dimethylamine. Thus, only the second process takes place in oxidation of trimethylamine.

With primary amines, the development of the reaction is, to some extent, autocatalytic.[32] In the oxidation of secondary amines, the autocatalytic character appears to be less marked than with primary amines, and the accelaration observed towards the end of the reaction is almost certainly a reflection of further oxidation of intermediate products rather than of consumption of initial reactants.[33] With tertiary amines,[34, 35, 36] there is, generally speaking, no evidence of autocatalysis in the early stages of reaction except at comparatively high temperatures where intermediate products are rapidly further oxidized and thus unable to accumulate in the system.

The small influence of the surface of the reaction vessel and of added inert gases strongly suggests that the chain-breaking processes do not depend to any appreciable extent on the walls and it must be assumed therefore that the reactive chain-carriers are destroyed mainly by chemical reaction in the gas phase. There is evidence that, in the oxidation of hydrocarbons, aldehydes are the species whose further oxidation is responsible for chain-branching.[37] However, amines and ammonia are powerful inhibitors of aldehyde oxidation. Thus, the initial products of the oxidation of primary, secondary and tertiary amines, namely, the next lower nitrogen bases, will prevent chain-branching by destroying chain-carriers which would otherwise attach new reactant molecules. Now, since the order of decreasing inhibiting power is secondary amines > primary amines > ammonia, it is found that some autocatalytic character is present in the oxidation of secondary and primary amines. However, all the autocatalytic character has more or less disappeared in the combustion of tertiary amines. This is due to the powerful inhibition of acetaldehyde oxidation by the partially formed secondary amines whose presence, together with that of unchanged tertiary amines, evidently completely prevents chain-branching. Thus, with amines, many chains are broken due to the inhibiting effect of certain products. Chain-propagation is less effective and re-initiation of chains consequently becomes more important.

There have been several reports of dye-sensitized oxygenation of amines. The earliest was that of Gaffron,[38] who found that erythrosin photosensitized the oxygenation of n-propylamine, and that chlorophyll photosensitized the oxygenation of isoamylamine. More recently Schenck[39] reported that the dye-sensitized photooxygenation of primary, secondary, and tertairy amines resulted in the uptake of one, two, or three molecules of oxygen, respectively, indicating that the number of α-CH groups determines the stoichiometry. The products of these reactions were α-amine hydroperoxides. Others have reported that a variety of reactions occur when amines are irradiated in presence photosensitizing dyes and oxygen: α-oxidation,[40-44] dehydrogenation,[45, 46] dealkylation.[45] Kinetic studies on the oxygen-uptake in the photosensitized oxidation of triethylamine have also been reported.[47]

These reactions may take place by either or both of two well-recognized mechanisms.[48] In the type I photosensitized oxygenations (also known as the D-R mechanism),[49] the excited sensitizer interacts with the substrate to give a substrate radical. This radical may react with oxygen to give a substrate peroxy radical or undergo other reactions. Singlet oxygen is not involved in Type I photooxygenation. In type II photooxygenations (also known as the D-O mechanism)[50] the substrate interacts with oxygen to give what is now generally accepted to be singlet oxygen. This in turn may react with the substrate. The balance between these two mechanisms will be determined by (1) the relative reactivity of the sensitizer triplet toward the substrate and oxygen, and (2) relative concentration of the substrate and oxygen.

Photooxidation of Aliphatic Amines

The photooxidation of gaseous methylamine[16, 21] has been studied. The major noncondensable gas present after irradiation was ammonia. A large part of the product appeared as an uncharacterized white crystalline solid. Its composition was presumed to be a mixture of condensation products of formaldehyde with ammonia and methylamine. The reaction was carried out at wavelengths as short as 205 nm which have sufficient energy to cause the $n \longrightarrow \sigma^*$ transition of amines.

The results of Henbest[51] showed that tri-n-butylamine produced dibutylamine and n-butyric acid when an oxygen-saturated n-hexane solution was irradiated in the liquid phase with 253.7 nm radiation. Incomplete evidence was presented concerning the presence of tri-n-butylamine oxide and N, N-di-n-butylformamide. An uncharacterized polar oil separated during the irradiation. The relative rates of photochemical oxygenation are tri-n-propylamine > tri-n-butylamine> triethylamine >trimethylamine.

Charge-Transfer Theory

The thermal oxidation and photosensitized oxidation of aliphatic amines have been studied extensively.[30-35, 38-50] However, irradiation of the charge-transfer band of oxygen-amine has not been examined. In order to determine the mechanism involved in the direct irradiation of amine-oxygen solutions, it is necessary to understand the background of charge-transfer theory.

It is a familiar fact that iodine forms violet-colored solutions in certain solvents, brown in others. In benzene, it forms a solution of intermediate color. This phenomenon was known for quite a long time. However, it was not understood until Benesi and Hildebrand[52, 53] explained that the altered color resulted from formation of molecular complex between benzene and iodine. A comprehensive and extensive theory of charge-transfer complexes was put forth by Mulliken in his consecutive series of paper in the past two decades, now summarized in a recently published book.[54]

A molecular complex between two molecules, as defined by Mulliken, is an association somewhat stronger than ordinary van der Waals association and of a definite stoichiometry. The partners very often already contain a closed-shell (saturated valence) electronic structure. In loose complexes, the identities of the original molecules are more or less preserved. The tendency to form complexes occurs when one partner is an electron acceptor (A), and other is an electron donor (D).

Complexes are classified as strong or weak depending on whether the energy of formation and equilibrium constant K are large or small:

$$D + A \overset{K}{\rightleftharpoons} D, A \ (\longleftarrow D^{+}, A^{-}) \tag{13}$$

Increasingly strong donors and/or acceptors form increasingly stable complexes.

The ground state of any molecular complexes containing one donor molecule associated with one acceptor molecule can be represented in terms of the wave function.

$$\psi_N = a\phi_0 \ (D, A) + b\phi_1 \ (D^+, A^-) \qquad [I]$$

The wave function ϕ_0 (D, A) represents a no-bond function and corresponds to a structure in which bonding results from dipole-dipole, dipole-induced-dipole interactions, and London dispersion forces. The wave function ϕ_1 (D^+, A^-) has been termed the dative function. This corresponds to a structure where one electron has been completely transferred from the donor to the acceptor. In the case where A and D are neutral, this will involve covalent binding between the odd electron in A^- and D^+. A relatively weakly bonded molecular complex $(a^2 >> b^2)$, is regarded as a resonance hybrid having a major contribution from the no-bond form and minor contribution from the dative form.

If ψ_N represents the ground state (N) of molecular complex, there must exist an excited state represented by the following wave function:

$$\psi_E = a^*\phi_1 \ (D^+, A^-) - b^*\phi_0 \ (D, A) \qquad [II]$$

In the excited state, a molecular complex $(a^* >> b^*)$ is regarded as a resonance hybrid having a major contribution from the dative form and minor contribution from the no-bond form. The excited state, which presumably can be attained by the absorption of either visible or ultraviolet light is largely dative in character. The transition N ⟶ E which accompanies the absorption of light of appropriate wavelength corresponds to the transfer an electron from the donor to the acceptor.

$$D, A\ (\leftrightarrow D^{+}, A^{-}) \xrightarrow{h\nu} D^{+}, A^{-} (\leftrightarrow D, A) \tag{14}$$

Evans[55] reported that oxygen dissolved in aromatic substances gives rise to absorption at wavelengths longer than for the aromatic compounds alone. Also, Munck and Scott[56] found that saturated hydrocarbons, aliphatic alcohols, and ethers show absorption in the near ultraviolet when oxygen is dissolved in them. This property was found to disappear when the solutions were flushed with nitrogen, indicating that the extra absorption was not due to oxidation products.

Tsubomura and Mulliken[57] have also studied this phenomenon. From the effects of dilution with _n_-heptane and the variation of temperature on the spectra of triethylamine with oxygen, they concluded that the association constants and heats of association of the so-called oxygen complexes were nearly zero. In other words, there was no formation of a definite complex in these cases even though intense extra absorption was observed. Tsubomura and Mulliken[57] named the absorption a contact charge-transfer absorption, because no evidence had been found for the formation of a true complex between oxygen and triethylamine. The extra absorption was attributed to charge-transfer interaction from a contact pair (oxygen and organic molecule) in random orientations.

Murrell[58] pointed out that the major part of the intensity of these charge-transfer bands in saturated hydrocarbon solutions of iodine could be caused by interaction of charge-transfer states and donor excited states. In other words, the contact charge-transfer band, more or less, borrows its intensity from the strongly allowed transition between the donor ground state and the donor singlet excited state. This explanation was accepted by Tsubomura and Mulliken[54] to account for the oxygen-donor charge-transfer absorption.

Theoretically, the frequency of the charge-transfer band is given approximately by $hv = I^D - E^A - W$, where I^D is the lowest ionization potential of donor, E^A is the electron affinity of the acceptor, and W is the electrostatic and other interaction energy between the molecules in the charge-transfer state. If W is assumed to be relatively constant for various donors, a linear relationship is expected between v and I^D. It also is expected that the smaller the ionization potential of the organic donor is, the longer the wavelength of the observed oxygen-induced band will be.

Part of this dissertation is devoted to proving by experimental work that contact charge-transfer complexes do indeed initiate the photooxidation of aliphatic amines.

STATEMENT OF THE PROBLEM

This dissertation involves several subjects. In order to place these subjects in proper perspective for the reader, the dissertation is divided as follows:

(1) Photolysis of ammonia in cyclohexane solution.

(2) Photodecomposition of primary and secondary aliphatic amines.

(3) Photooxidation involving in the charge-transfer complex of oxygen-amine.

(4) Oxygen uptake of hydrocarbons in the photochemical oxidation.

In the primary process in ammonia photolysis at wavelengths between 217-168 nm, reaction 1 is believed to be the only primary process.[1-11]

$$NH_3 + hv \longrightarrow NH_2\cdot + H\cdot \qquad (1)$$

Gesser[5] and Groth, et al.[11] studied the photolysis of ammonia in the presence of propane in the gas phase. The products were hydrogen, nitrogen, 1-propene, 2-aminopropane, and 2,3-dimethylbutane. However, ammonia-saturated hydrocarbon solutions have never been examined. In order to determine whether the nature of the primary products and the same primary process is operating in the liquid phase as in the gas phase, the photolysis of ammonia-saturated cyclohexane was undertaken.

Studies of the vapor phase photochemistry of primary aliphatic amines have been reported on numerous occasions,[15-18, 20, 21, 23, 24] and the primary step in the reaction has been proposed to be that of reaction 5 using 253.7 nm. The main products from the irradiation of primary amines in gas phase were hydrogen gas, ammonia, and a high boiling liquid. Small amounts of methane and ethane were isolated from the photolysis of methylamine.[16, 21] When n-hexane solutions of primary aliphatic amines were irradiated with 253.7 nm light, unsaturated compounds and hydrogen gas were produced, however, no ammonia was formed.[19, 26, 27]

$$RNH_2 \longrightarrow (RNH_2)^* \longrightarrow RNH\cdot + H\cdot \qquad (5)$$

The explanation of the liquid phase photodecomposition process of primary amines, as put forth by Booth and Norrish,[19] and Pouyet[26,27] is open to question. Two cleavages are possible, i.e., carbon-nitrogen and nitrogen-hydrogen, and the extent of each is thought to be dependent upon the nature of the alkyl group. To test this hypothesis, n-hexylamine, cyclohexylamine, and cyclopentylamine were chosen for irradiation under a nitrogen atmosphere because of the stability of their radicals which can be attributed to differences in bond hybridization. The products were isolated and identified in order to understand the nature of the mechanism of the photolysis of primary amines.

Prolonged irradiation of diethylamine has been reported to provide four major compounds.[28] However, the primary products have not been isolated. In order to determine the nature of the primary products and to gain an understanding of the reaction mechanism of secondary aliphatic amines photolysis, efforts were directed toward studying the reaction at shorter times and lower temperatures.

The thermal oxidation and photooxygenation of aliphatic amines have been extensively studied.[16, 21, 30-47, 51] It is also known that in the liquid phase, tri-n-butylamine produced di-n-butylamine and n-butyric acid when an oxygen-saturated hexane solution was irradiated with 253.7 nm light.[51]

Molecular association of oxygen with aliphatic amines, as demonstrated by Tsubomura and Mulliken,[57] seems to be of prime importance for the understanding of their photooxidation. Thus, Mulliken interpreted the ultraviolet light absorption observed in n-butylamine and triethylamine and other basic organic solvents as charge-transfer bands of oxygen-solvent complexes.[57]

Evans[55] suggested that oxygen complexes would provide a plausible initial stage in photooxidations. In recent years, our laboratory has determined the role of the charge-transfer absorption in the photochemical oxidation of oxygen-ether[59-61] and oxygen-saturated hydrocarbon solutions.[62-64] It is considered a probability that aliphatic amines can be oxidized in a similar fashion. Part of the present work is an attempt to determine the part which oxygen-amine charge-transfer complexes may play in the photooxidation of amines.

Attention was focused on the oxidation of cyclohexylamine. This compound was chosen because of the simplicity of product formation and because of a known procedure for the synthesis of the hydroperoxide of cyclohexylamine.

The principal goal in studying photooxidation of cyclohexylamine is to determine the overall mechanism, not only the mode of initiation but also intermediates and the products formed.

The fact that oxygen-saturated hydrocarbons[54-56, 62-64] form charge-transfer complexes is quite well accepted. It is also known that these complexes play an initial role in the photooxidation of saturated hydrocarbons.[62-64] A problem connected with this is, which bond, carbon-carbon or carbon-hydrogen is the electron donor of these complexes. To answer this, the relative rates of oxygen uptake during the photooxidation of cyclic hydrocarbons, *i.e.*, cyclohexane and cyclopentane, as a function of ring-size was investigated.

EXPERIMENTAL SECTION

Instruments

Infrared (ir) spectra were determined on a Beckman Model IR-12 or IR-33 Spectrophotometer. The ultraviolet spectra were obtained with a Cary recording Spectrophotometer, Model-14. The nuclear magnetic resonance (nmr) spectra were determined on a Varian A-60 Spectrometer. Gas chromatographs used were Wilkens Aerograph Autoprep Model A-700 equipped with a thermal conductivity detector, and a Beckman GC-5 equipped with a dual flame ionization detector. All irradiations were performed with a 450-W Hanovia medium-pressure quartz mercury-vapor arc lamp. The spectral energy distribution of the radiated mercury lines of the lamp is given in Table I.

Purification of Amines

The general procedure for purification of the aliphatic primary amines was as follows: amines were dried over potassium hydroxide overnight, and then fractionally distilled over dry potassium hydroxide and freshly extended sodium wire under a nitrogen atmosphere, using a silvered vacuum-jacketed column. Finally, the amines were fractionally distilled once more under a nitrogen atmosphere. The purity of the amines was checked by ultraviolet spectroscopy and gas chromatography, and no detectable amount of impurity was present. The high boiling-point

TABLE 1

SPECTRAL ENERGY DISTRIBUTION OF RADIATED MERCURY LINES IN HANOVIA HIGH-PRESSURE QUARTZ MERCURY-VAPOR LAMPS

Lamp code	L	A
Lamp cat. no	679A	633A
Lamp watts	450	550
Lamp volts	135	145
Current, amps	3.6	4.4
Arc-length (inch)	4.5	4.5
Mercury Lines (Angstroms) Radiated Energy in Watts		
13673	2.6	4.6
11287	3.3	3.8
10140	10.5	12.2
5780 (yellow)	20.0	23.0
5461 (green)	24.5	28.2
4358 (blue)	20.2	23.3
4045 (violet)	11.0	12.7
3660 (U-V.)	25.6	30.1
3341	2.4	2.8
3130	13.2	15.0
3025	7.2	8.2
2967	4.3	5.0
2894	1.6	1.8
2804	2.4	2.8
2753	0.7	0.8
2700	1.0	1.2
2652	4.0	4.6
2571	1.5	1.8
2537 (reversed)	5.8	5.0
2482	2.3	2.6
2400	1.9	2.2
2380	2.3	2.6
2360	2.3	1.8
2320	1.5	2.4
2224	3.7	4.2
Total Watts	175.8	202.7

Data from Hanovia Lamp Division, Engelhard Industries, Inc., Newark, New Jersey.

secondary aliphatic amines were purified and collected by preparative gas chromatography using a 10 ft x 1/4 in., 5% KOH-20% Carbowax-Chromosorb W column.[65]

Preparation of Imines

The general procedure for the preparation of imines was the same as the method of Campbell *et al*.[66] The only difference was that a stream of nitrogen was bubbled into the reaction mixture during the reaction.

TABLE 2

PHYSICAL CONSTANTS OF IMINES

Compound	B.P.	n_d^{20}
N-1-(Hexylidene) cyclohexylamine	96-97° (10mm)	1.4592
N-1-(Hexylidene)-*n*-hexylamine	89-90° (4mm)	1.4357
N-Cyclopentylidenecyclopentylamine	110-112° (10mm)	
N-Cyclohexylidenecyclohexylamine	118-110° (9mm)	1.4964
N-(Cyclohexylidene)-*n*-hexylamine	105-106° (5.5mm)	1.4680

General Procedure for the Synthesis of Secondary Aliphatic Amines

The imine solution, 0.2 moles, was dissolved in 50 ml of absolute ethanol and 0.8 g of 10% palladium on carbon (Pd/C) was then added to the solution. The mixture was shaken with hydrogen at an initial pressure of 50 lb/in.^{2} until no more hydrogen was taken up. The ethanol was distilled off after filtration of the mixture. The remaining material was vacuum distilled and stored over potassium hydroxide.

TABLE 3

PHENYLTHIOUREA DERIVATIVES OF SECONDARY ALIPHATIC AMINES

Compound	M.P.
Dicyclohexylamine	94- 95°
Dicyclopentylamine	104-105°
_n_-Hexylcyclohexylamine	91- 92° (lit.[67] 91.5°)

Procedure for Amination of Cyclohexane with Ammonia

Into a quartz tube with a ground glass joint were placed 50 ml of purified cyclohexane. Ammonia, dried by passing through a carbon tetrachloride-dry ice (-22°) trap and potassium hydroxide tower, was passed into the solution _via_ a bubbler for 30 minutes prior to irradiation. The sample tube and the water-cooled, quartz, double-walled imersion well containing the lamp (450-W) were placed in a water bath (13.4 ± 0.1°). Aluminum foil was placed around the upper part of the sample tube to avoid irradiating the vapor. The distance between the quartz tube and the edge of immersion well was held constant at 3.5 cm.

Identification of Products from the Photolysis of Ammonia with Cyclohexane

The reaction mixture (150 ml) from the photolysis of ammonia in cyclohexane solution was concentrated to 40 ml by distillation using a spinning band column. Phenylisothiocyanate (1 ml) was added to the solution which was stirred for about 10 minutes. The mixture was taken to dryness with a vacuum pump and then n-hexane was added to the residue. The n-hexane solution was heated for several minutes, and the solvent evaporated with a rotary evaporator. The product was recrystallized several times from n-pentane. The melting point of the phenylisothiourea derivative of cyclohexylamine was 146-148° (lit.[68] 148°).

Cyclohexlcyclohexane was identified as follows: 150 ml of the reaction mixture from the photolysis of ammonia with cyclohexane was washed with 2N HCl, and the organic layer then washed with water, and dried over magnesium sulfate. This solution was then concentrated to 10 ml with a rotary evaporator. Cyclohexylcyclohexane was obtained by preparative gas chromatography using a 10 ft x 1/4 in., 5% KOH-20% Carbowax-Chromosorb W column. The product was identified by gas-liquid phase chromatography (glpc) retention times and by comparing nmr and ir spectra with an authentic sample.

General procedure for Identification of Products from the Photolysis of Primary Aliphatic Amines

The quartz immersion well with lamp (450-W) was placed in a reaction vessel with a ground glass joint. The vessel had two sidearms to allow introduction and exit of gases. The reaction vessel contained ca. 1.5 g of sample in 300 ml of puried solvent. The solutions were irradiated for 4 hours with nitrogen bubbling through, then concentrated and the products separated by preparative glpc using a 10 ft x 1/4 in., 5% KOH-20% Carbowax-Chromosorb W column. The products, except for the air-oxidizable, cyclopentylidenecyclopentylamine, were identified by glpc retention times and by comparing nmr and ir spectra with those of an authentic sample. The imine could be removed from the reaction solution by a 2N HCl wash or by hydrogenation to dicyclopentylamine with excess 10% Pd/C in ethanol. The latter compound was identified in the usual manner. Ammonia was trapped from the cyclohexylamine and n-hexylamine irradiation solution by passing the effluent gas stream first through a NaCl-ice trap and subsequently through a dry-ice acetone trap. Ammonia was identified by its characteristic ir spectrum.[69]

General Procedure for Product Accumulation Studies of the Primary Aliphatic Amines

The irradiations were done using the 450-W lamp in a quartz immersion well. A quartz tube with a ground glass joint containing 50 ml samples was utilized. Nitrogen gas free of oxygen was passed into the solutions via a bubbler for 30 minutes prior to irradiation. The sample tube and the immersion well containing the lamp were placed in a water bath (13.4 ± 0.1°). Aluminum foil was placed around the upper part of the sample tube to avoid irradiating the vapors. The distance between the quartz tube and the edge of the immersion well was held constant at

3.5 cm. The reactions were monitored by use of a Beckman Chromatograph and recorder equipped with a Disc integrator, and two 20 ft x 1/8 in., 5% KOH-20% Carbowax-Chromosorb W columns. The cyclohexylamine was analyzed using two 20 ft x 1/8 in., 18% THEED-Chromosorb P columns.

General Procedure for Identification of the Products of the Photolysis of Secondary Aliphatic Amines

The procedure used was the same as that for the photolysis of primary aliphatic amines except for one modification. A 3-g sample in 300 ml of purified cyclohexane was irradiated. The imines and cyclohexylcyclohexane were isolated by preparative glpc using a 10 ft x 1/4 in., 5% KOH-20% Carbowax-Chromosorb W column. The imines and cyclohexylcyclohexane were identified by glpc retention times and by comparing nmr and ir spectra with those of authentic samples. The other products were identified by glpc retention times.

The Optimum Yield Time for the Photolysis of Secondary Alphatic Amines

The procedure used was the same as that for the product accumulation studies for the primary aliphatic amines except the temperature of the water-bath was maintained at $18 \pm 0.1^{\circ}$ in order to obtain the optimum yield of the imine. A known concentration of N-n-hexylcyclohexylamine was irradiated for various times, i.e., 6, 8, 12 hours. The optimum yield of the imines, N-1-(hexylidene) cyclohexylamine and N-cyclohexylidene-n-hexylamine, was obtained after 6 hours of irradiation.

Charge-Transfer Spectra

The procedure used to measure the ultraviolet absorption spectra of oxygen-saturated aliphatic amines was as follows: The purified aliphatic amine was placed in a 1-cm quartz spectrophotometric cell fitted with ground glass stopper, nitrogen was bubbled through for at lease one and one-half minutes, the stopper immediately put on, and the absorption spectrum recorded using a matched empty cell as a reference. The reference cell was then filled with purified amine and nitrogen bubbled through as described above. A spectrum was again taken to obtain the base line. Oxygen was then bubbled into the amine in the sample cell for at least one and one-half minutes, the stopper was placed on cell, and the spectrum again recorded. Afterward, nitrogen was bubbled into the sample, and the absorption spectrum once more recorded. Absorption caused by oxygen-saturated aliphatic amines was completely removed by latter procedure. This was evidence that the extra absorption bands found when oxygen was present were not due to oxidation products. The spectra of all the aliphatic amines studied are shown in Figures 10 through 17.

Irradiation of Oxygen-Saturated Aliphatic Amine Solutions, Product Identification

A 450-W lamp was placed in a Pyrex immersion well. The well was then inserted into a 300 ml sample container with a ground glass joint. This container had two sidearms on it which allowed a means of introduction and escape of oxygen. A piece of thin glass tubing long enough to reach to the bottom of the sample container was inserted into one of the sidearms and was used to bubble in oxygen. The other sidearm was connected to a NaCl-ice trap and subsequently to a dry-ice actone trap in order to trap the lower boiling products. Oxygen gas was passed into the solution for 30 minutes prior to irradiation and the solution was stirred with a magnetic stirring bar. The cyclohexylamine solution was irradiated for about 3 hours. An aliquot of the reaction mixture was injected into a Beckman GC-5 chromatograph equipped with two 20 ft x 1/8 in., 5% KOH-20% Carbowax-Chromosorb columns, and a number of peaks were obtained. The reaction mixture was concentrated to about 40 ml by vacuum distillation. The concentrated solution was divided into two parts. One part was dissolved in a solution of ethanol and hydrogenated with an excess of 10% Pd/C. The ethanol was distilled after filtration of mixture. Gas chromatography of the hydrogenated mixture showed a new peak not present in the original reaction mixture. By comparison of glpc retention time with a known sample and using spiking techniques, the new peak corresponded to dicyclohexylamine. The second part of the concentrated solution from the photooxidation of cyclohexylamine was transferred into a 2N HCl solution and extracted with 20 ml n-pentane several times. The n-pentane solution was washed with 10% potassium carbonate and water and finally dried over magnesium sulfate. This solution was concentrated to about 10 ml by rotatary evaporator. Then by preparative glpc using 10 ft x 1/4 in., 5% KOH-20% Carbowax-Chromosorb W column, two products, cyclohexanone and cyclohexanone oxime, were collected and identified by comparing their nmr and ir spectra with those of authentic samples.

The photomixture of cyclohexylamine was introduced into one matched ir cell. The reference cell was filled with cyclohexylamine. The infrared spectrum was recorded, and showed a peak at 1660 cm^{-1} which was identical to the C=N value of an authentic sample of N-cyclohexylidenecyclohexylamine.

Since peroxides cannot be be detected by gas chromatography, the identification of peroxides was done with 0.05 M cobalt(II) acetate.[70] When the reaction mixture from the photooxidation of cyclohexylamine was introduced into a 0.05 M cobalt(II) acetate solution, the pink color of cobalt(II) ion turned to a black precipitate just as hydrogen peroxide had done in cyclohexylamine. A control was also prepared by bubbling oxygen into cyclohexylamine for 3 hours in the absence of ultraviolet light. The cobalt(II) acetate solution was introduced into the control and pink color turned to greenish brown. The quantity of peroxides in the irradiated oxygen-saturated cyclohexylamine was determined by the method of Vogel.[71]

Anhydrous copper sulfate turned blue in contact with the oxygen-saturated, irradiated cyclohexylamine solution. By comparison of glpc retention times and spiking procedures using a 8 ft x 1/4 in. Porapak column, water was identified in the reaction mixture.

Ammonia, trapped from the photooxidation of cyclohexylamine, was identified by its characteristic ir spectrum[69] and its glpc retention time using a Porapak column.

Irradiation of Oxygen-Saturated Cyclohexylamine Solution, Filter Studies

A 1-cm quartz spectrophotometric cell was placed in a holder kept at a distance of 2.5 cm from the outside surface of the Pyrex immersion well. A 450-W lamp was placed in the Pyrex well. Cyclohexylamine (3.0 ml) was transferred into the cell flushed with oxygen, and irradiated for 3 hours. After this time, the concentration of N-cyclohexylidenecyclohexylamine and cyclohexanone oxime were 3.81×10^{-2} M and 1.12×10^{-2} M, respectively, as determined by gas chromatography. Upon repeating the procedure in the Rayonet Reactor with 350 nm lamps, the amounts of products were reduced to one-third of the amount of that obtained with Pyrex well. With a 100-W tungsten lamp, no products were obtained. Upon repeating the procedure with Pyrex, no products were observed when cyclohexylamine was irradiated under a nitrogen atmosphere.

Reaction of Irradiated Oxygen-Saturated Cyclohexylamine Solution with Triphenylphosphine

It was known that alkylhydroperoxides would react with triphenylphosphine to form alkyl alcohols and triphenyl phosphine oxide at room temperatures.[72] It was possible that 1-hydroperoxyalkylamine reacted with triphenylphosphine in cyclohexylamine solution to form an alkyl ketone which could then react with with cyclohexylamine to generate the corresponding imine.

To test this idea, triphenylphosphine (0.5 g) was added to 0.05 M 1-hydroperoxycyclohexylamine in cyclohexylamine, and the solution was stirred under a nitrogen atmoshpere at room temperature. An aliquot was removed and analyzed by gas chromatography. The amount of the imine decreased to half the amount formed when this procedure had been followed without using triphenylphosphine. No peroxide could be detected after adding triphenylphosphine to a 1-hydroperoxycyclohexylamine solution.

Triphenylphosphine (0.5g) was added to 20 ml of cyclohexylamine photooxidation solution, and the solution was stirred under a nitrogen atmosphere at room temperature. Aliquots were removed at 30 minutes and 5 hours, and analyzed by gas chromatography. The amount of the imine decreased slightly after the addition of triphenylphosphine. The reaction was complete after 30 minutes, and no change in the amount of the imine could be detected during the last 4.5 hours of the triphenylphosphine reaction. Neither new products nor peroxide were detected after adding triphenylphosphine to the photooxidation reaction mixture.

Preparation of 1-Hydroperoxycyclohexylamine

Hydrogen peroxide (30%, 35 ml) was added to a stirred, cooled mixture of cyclohexanone (25 g), methanol (20 ml), ammonia (d 0.880, 85 ml), and ethylenediamine tetraacetate (EDTA-disodium salt, 0.25 g) and the temperature was maintained at 0° for one hour. The solid was washed with ice water and *n*-pentane and the solvent removed with a vacuum pump. The dried solid, recrystalized from acetone, gave a needle crystals, m. p. 56.5° (decomposed) (lit.[73] 57-58°).

The Thermal Decomposition of 1-Hydroperoxycyclohexylamine in Cyclohexane

When 1-hydroperoxycyclohexylamine in cyclohexane was stirred under a nitrogen atmosphere, two major products were found, namely, cyclohexanone and ammonia. By comparison of the glpc retention time with that of an authentic sample and spiking techniques, cyclohexanone was identified. Ammonia was trapped and then identified by its characteristic ir spectrum. Cyclohexanone oxime and cyclohexylhydroxylamine were not observed in the reaction mixture.

The Thermal and Photochemical Decomposition of 1-Hydroperoxycyclohexylamine in Cyclohexylamine

The Pyrex immersion well containing a 450-W lamp was placed in a water bath set at 10 ± 0.2°. A 21.5 mm diameter quartz tube was used as the sample cell and kept at a distance of 2.5 cm from the edge of the well. To the sample cell containing about 0.10 g peroxide was added 25 ml of cyclohexylamine and a fine stream of nitrogen was supplied by means of a glass bubbler connected to a microvalve. Aluminum foil was placed between the container and the well in order to prevent light from reaching the reaction vessel while the lamp was attaining full intensity. Aluminum foil also placed around the upper part of the container to avoid irradiating the vapor. Before the irradiation, the solution was pre-saturated with carbon dioxide-free nitrogen for 15 minutes. A sample was withdrawn after one-hour of irradiation and analyzed for the peroxide. A 10 ml aliquot of the irradiated sample was titrated for peroxides with 0.01095 N

$Na_2S_2O_3$. The thermal reaction at 10° was carried out using the same procedure but without irradiating. The same procedures were used for studying the thermal and photochemical decompositions of the peroxide at $35 \pm 0.2^\circ$. Cyclohexanone oxime was not observed in the reaction mixture.

Preparation of N-Cyclohexyl-1-hydroperoxycyclohexylamine

Cyclohexanone (16.7 g) was added to a cooled hydrogen peroxide (30%, 19 ml) solution. The stirred mixture was cooled to 10° with CCl_4-dry ice immediately, and then cyclohexylamine (20 g) was introduced gradually. Within a few minutes, a white solid appeared. The solid was filtered off, washed with water, and dried with a vacuum pump. The dried solid was then washed with ether, and finally dried with a vacuum pump. The melting point of N-cyclohexyl-1-hydroperoxycyclohexylamine was $89\text{-}90^\circ$ (lit.[74] $88\text{-}89^\circ$).

Reaction of N-Cyclohexyl-1-hydroperoxycyclohexylamine with Triphenylphosphine in Cyclohexane

Triphenylphosphine (1.0 g) was added to 0.19 M N-cyclohexyl-1-hydroperoxycyclohexylamine in cyclohexane, and the solution was stirred under a nitrogen atmosphere at room temperature for 2 hours. An aliquot of cyclohexane solution was removed and analyzed by gas chromatography. By comparison of the glpc retention time with that of an authentic sample and using spiking techniques, cyclohexanone, cyclohexylamine, and N-cyclohexylidenecyclohexylamine were identified.

Decomposition of N-Cyclohexyl-1-hydroperoxycyclohexylamine in Cyclohexylamine

N-Cyclohexyl-1-hydroperoxycyclohexylamine (1.0 g) was added to 15 ml cyclohexylamine, and the solution was stirred under a nitrogen atmosphere for one hour. An aliquot of cyclohexylamine solution was removed and analyzed by gas chromatography. N-Cyclohexylidenecyclohexylamine was obtained by a preparative gas chromatography. The product was identified by glpc retention times and by comparing its ir spectrum with that of an authentic sample.

Preparation of N-Cyclohexylhydroxylamine

N-Cyclohexylhydroxylamine was synthesized by the method of Borch *et al.*[75] The melting point of cyclohexylhydroxylamine was 140-141° (lit.[75] 138-139°).

Oxidation of N-Cyclohexylhydroxylamine with Hydrogen Peroxide in Ethanol

Hydrogen peroxide (30%, 50 ml) was gradually added to a stirred solution of 0.08 M N-cyclohexylhydroxylamine in ethanol. After being stirred under a nitrogen atmosphere at room temperature for 3 hours, the solution was then saturated with NaCl and extracted with four 15 ml portions of chloroform. The mixture was dried over magnesium sulfate and filtered off. The filtrate was then concentrated by rotary evaporation. The concentrated solution was poured into a small amount of water, and a white solid appeared. Upon repeating the same extraction procedure as above, a solid appeared on a watch glass after the solvent was evaporated. The crystals were then recrystalized from light petroleum ether. The compound was identified as cyclohexanone oxime by its melting point, 85-86° (lit.[76] 89-90°) and by comparing its ir spectrum with that of an authentic sample.

Photolysis of Hydrogen Peroxide in Cyclohexylamine

A 1-cm quartz spectrophotometric cell was placed in a holder kept at a distance of 2.5 cm from the edge of the Pyrex immersion well. A 450-W lamp was used as the light source. Cyclohexylamine (3 ml) was placed in the sample cell and 50 ul of 30% hydrogen peroxide (0.162 mmoles) was added to the cyclohexylamine. Nitrogen was passed into the solution *via* a long needle for 15 minutes prior to irradiation. After two and one-half hours of irradiation, 0.165 mmole of N-cyclohexylidenecyclohexylamine was formed as determined by gas chromatography.

The Thermal and Photochemical Reaction of Cyclohexanone Oxime in Cyclohexylamine

Four grams of cyclohexanone oxime were dissolved in 25 ml of cyclohexylamine and 3 ml of this solution were transferred to a 1-cm spectrophotometric cell. This was irradiated with a 450-W lamp under a nitrogen atmosphere for 3 hours. The distance between the Pyrex well and the cell was 2.5 cm. No detectable amount of N-cyclohexylidenecyclohexylamine was observed by gas chromatography. The remaining 22 ml solution of cyclohexanone oxime in cyclohexylamine was heated at 45° under a nitrogen atmosphere at 45 for 8 hours. No detectable amount of N-cyclohexylidenecyclohexylamine was observed by glpc.

The Thermal Effect on the Photooxidation of Cyclohexylamine

The procedure was the same as that used for the thermal and photochemical decomposition of 1-hydroperoxycyclohexylamine. The reaction was carried out in a water bath at $10 \pm 0.2^{\circ}$ and $35 \pm 0.2^{\circ}$. A 25 ml cyclohexylamine solution saturated with oxygen was irradiated for 3 hours. A sample was withdrawn and analyzed for products. Two 10 ml aliquots from the irradiated sample were titrated for peroxides. The remaining 5 ml were analyzed for cyclohexylidenecyclohexylamine and cyclohexanone oxime by gas chromatography. Known concentrations of N-cyclohexylidenecyclohexylamine in cyclohexylamine and cyclohexanone oxime in cyclohexane were used as standards in the glpc analysis. The results are shown in Table 4.

Identification of Triethylamine Oxide from the Photoxidation of Triethylamine

Oxygen gas was passed through 50 ml of triethylamine in a quartz container for 30 minutes prior to irradiation while the solution was stirred with a magnetic stirring bar. The triethylamine solution was irradiated with the 350 nm Rayonet lamps for 2 hours. The reaction mixture was concentrated to about 10 ml, and a cold, saturated solution of picric acid was added. Yellow crystals were collected and dried. The compound was recrystalized from cold water. The melting point of the derivative was 163-164.5°(lit.[77] 164°).

TABLE 4

THE THERMAL EFFECT ON THE PHOTOOXIDATION OF CYCLOHEXYLAMINE

Time (hr)	Temp (°C)	Oxime ($\times 10^2$ M)	Imine ($\times 10^2$ M)	Peroxide ($\times 10^2$ M)
3	10	0.75	1.31	2.01
3	35	1.12	3.82	4.52

Charge-Transfer Spectra of Cyclohexane and Cyclopentane

Cyclohexane and cyclopentane was purified by known procedures.[63] The procedure for recording the charge-transfer spectra was the same as that for the aliphatic amines.

Product Identification from Photooxidation of Cyclopentane

The procedure used for the product identification was the same as that described by Sneeringer[78] except for one modification. The water bath was kept at 8.4 ± 0.1°. By comparing retention times with known compounds and using spiking techniques, cyclopentanone and cyclopentanol were identified in the reaction mixture. The irradiated cyclopentane solution was concentrated by spinning band distillation. Products were collected by a preparative gas chromatography using 10 ft x 1/4 in., 20% Carbowax-Chromosorb W column, and identified by comparing nmr and ir spectra with those of authentic samples. The peroxide was titrated by the method dead-stop.[79] The peroxide concentration was 6.76 x 10^{-4} M after one-hour of irradiation.

Irridation of Oxgyen-Saturated Hydrocarbons, Rates of Oxygen Uptake

The rate of oxygen uptake was studied by essentially the same procedure described by Wang,[80] with the following modifications. A Krebs manometer was used instead of a mercury manometer, and the entire pressure-measuring apparatus was placed in a large insulated wooden box in order to keep the temperature constant at $25.6 \pm 0.2^{\circ}$. The reaction vessel was placed in a constant temperature water bath at $8.4 \pm 0.1^{\circ}$.

Solubilities of Oxygen in Hydrocarbons

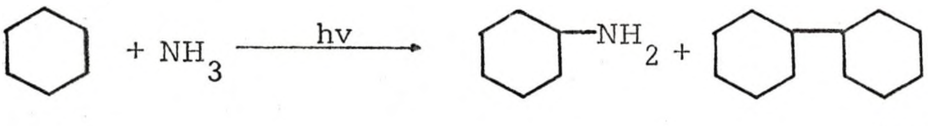
The solubility of oxygen in saturated cyclic hydrocarbons was followed by the method of Petrocelli and Lichtenfels.[81] The solubility of oxygen in cyclopentane is 1.20×10^{-2} mole 1^{-1} atm $^{-1}$ and in cyclohexane is 0.99×10^{-2} mole 1^{-1} atm^{-1} at 8.4°.

RESULTS AND DISCUSSION

The Photolysis of Ammonia in Cyclohexane

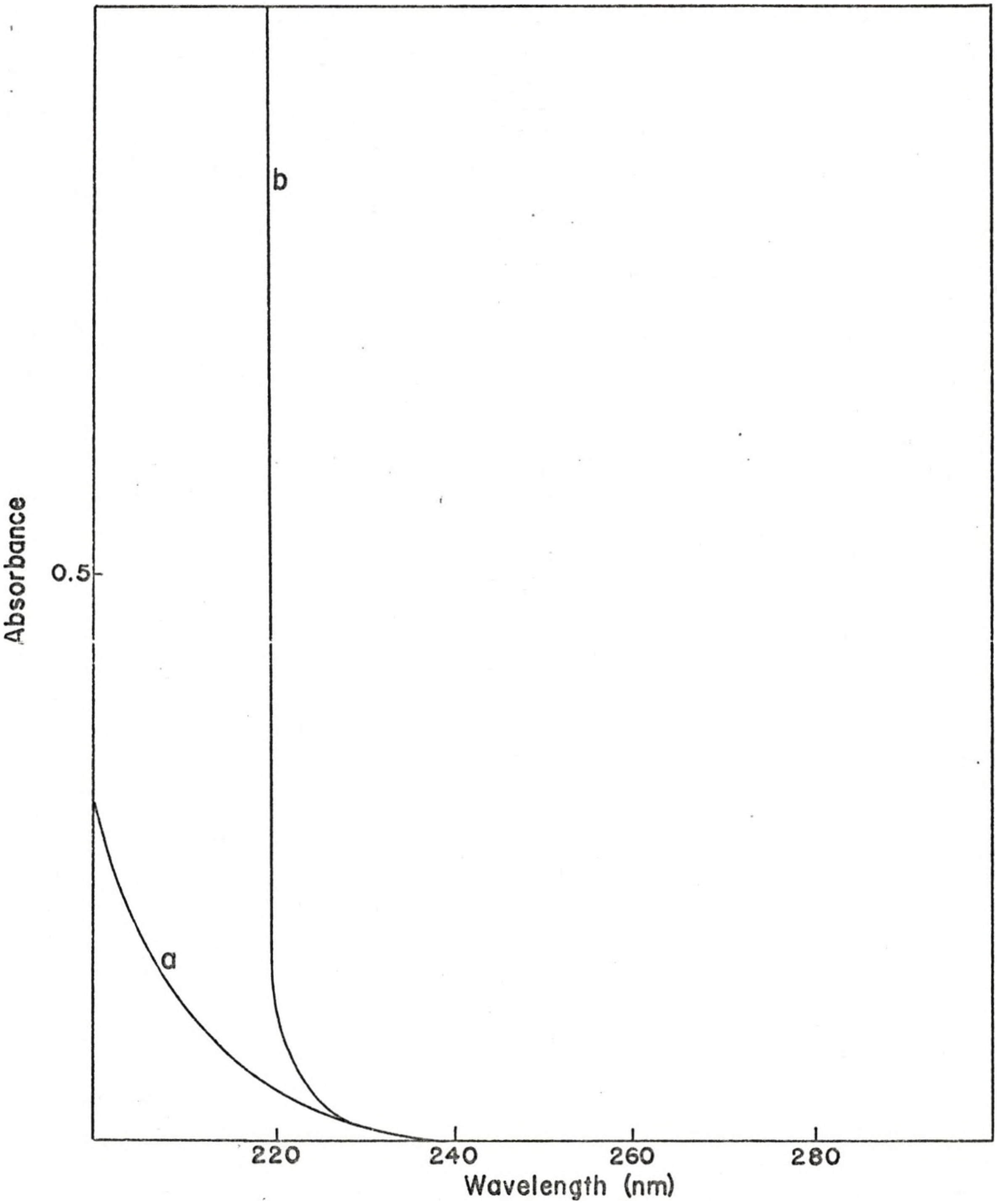
Photochemistry cannot be divorced from spectroscopy, particularly when the primary reaction is considered. The absorption spectra of high-purity cyclohexane into which nitrogen had been passed is transparent in the ultraviolet up to the far ultraviolet. The spectra of an ammonia-saturated cyclohexane solution with an identical nitrogen-saturated cyclohexane as a reference, is illustrated in Figure 1. It is known that ammonia has an absorption band in the region of 165-220 nm.[82] Therefore, this ultraviolet absorbance can be attributed to the absorption bands of ammonia.

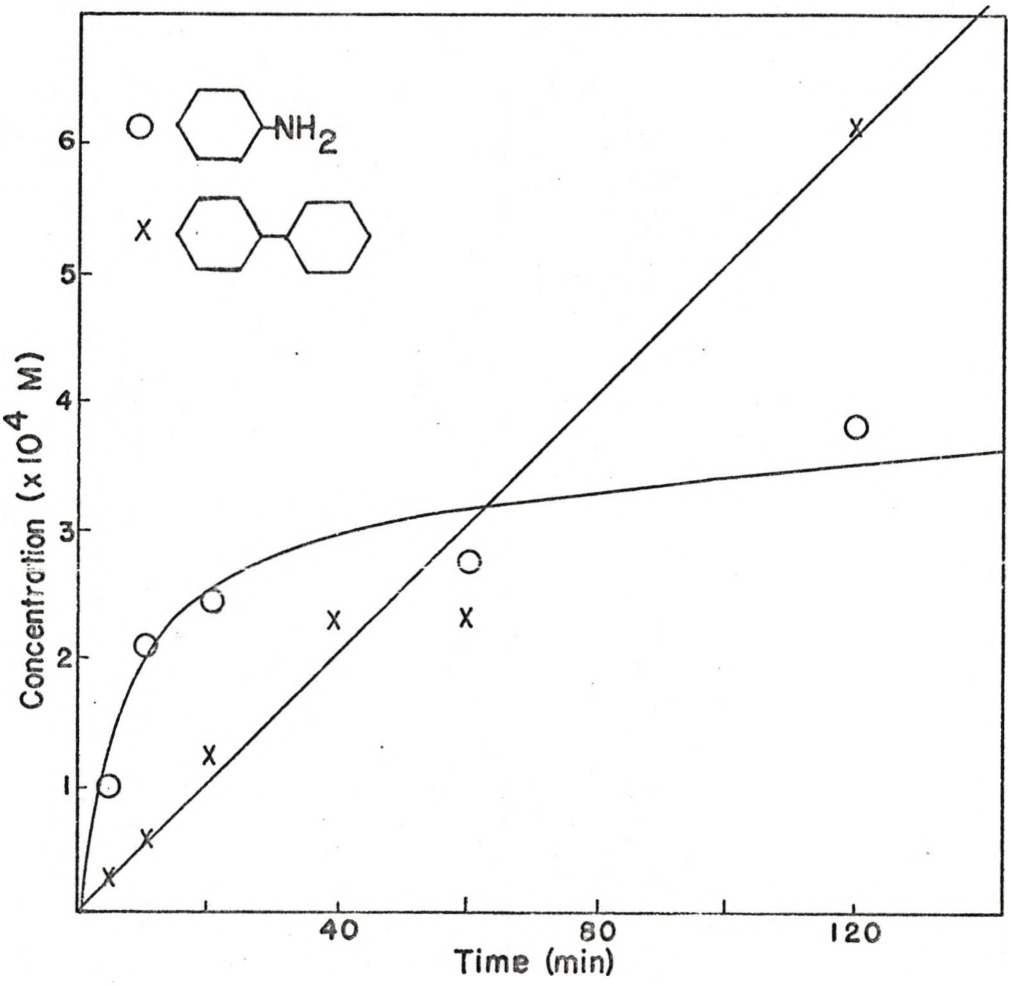
When a 450-W arc lamp is used as the light source, it is assumed that ammonia is responsible for the initial light absorption which leads to the observed reaction products, cyclohexylamine in a photostationary state and cyclohexylcyclohexane, cf. reaction 15.



(15)

From the rates of product accumulation illustrated in Figure 2, it is apparent that both cyclohexylamine and cyclohexylcyclohexane are


Absorbance
0.5
b
a
220
240
260
280
Wavelength (nm)


Concentration (x 10^4 M)
1
2
3
4
5
6
Time (min)
40
80
120
○
NH$_2$
X

formed in the initial stages of the reaction; and thus, can be properly classified as primary photoproducts. These curves summarize the activity in the solution up to 0.005% conversion of cyclohexane.

It is evident from Figure 2 that cyclohexylamine reaches a photostationary state whereas cyclohexylcyclohexane does not. The known photochemical reactivity of alkylamines accounts for this behavior but does not elaborate on the nature of the products formed.[19, 26, 27] As a consequence, cyclohexylamine was irradiated, and it was found to be quantitatively converted to cyclohexylcyclohexane as illustrated in Figure 3.

The above observations are consistent with the following mechanistic scheme.

$$\mathrm{NH_3} \xrightarrow{\mathrm{hv}} \mathrm{NH_3}^{*} \longrightarrow \mathrm{NH_2}\cdot + \mathrm{H}\cdot \tag{16}$$

$$\mathrm{NH_2}\cdot + \mathrm{C_6H_{12}} \longrightarrow \mathrm{C_6H_{11}}\cdot + \mathrm{NH_3} \tag{17}$$

$$\mathrm{H}\cdot + \mathrm{C_6H_{12}} \longrightarrow \mathrm{C_6H_{11}}\cdot + \mathrm{H_2} \tag{18}$$

$$\mathrm{C_6H_{11}}\cdot + \mathrm{NH_2}\cdot \longrightarrow \mathrm{C_6H_{11}NH_2} \tag{19}$$

$$\mathrm{C_6H_{11}}\cdot + \mathrm{H}\cdot \longrightarrow \mathrm{C_6H_{12}} \tag{20}$$

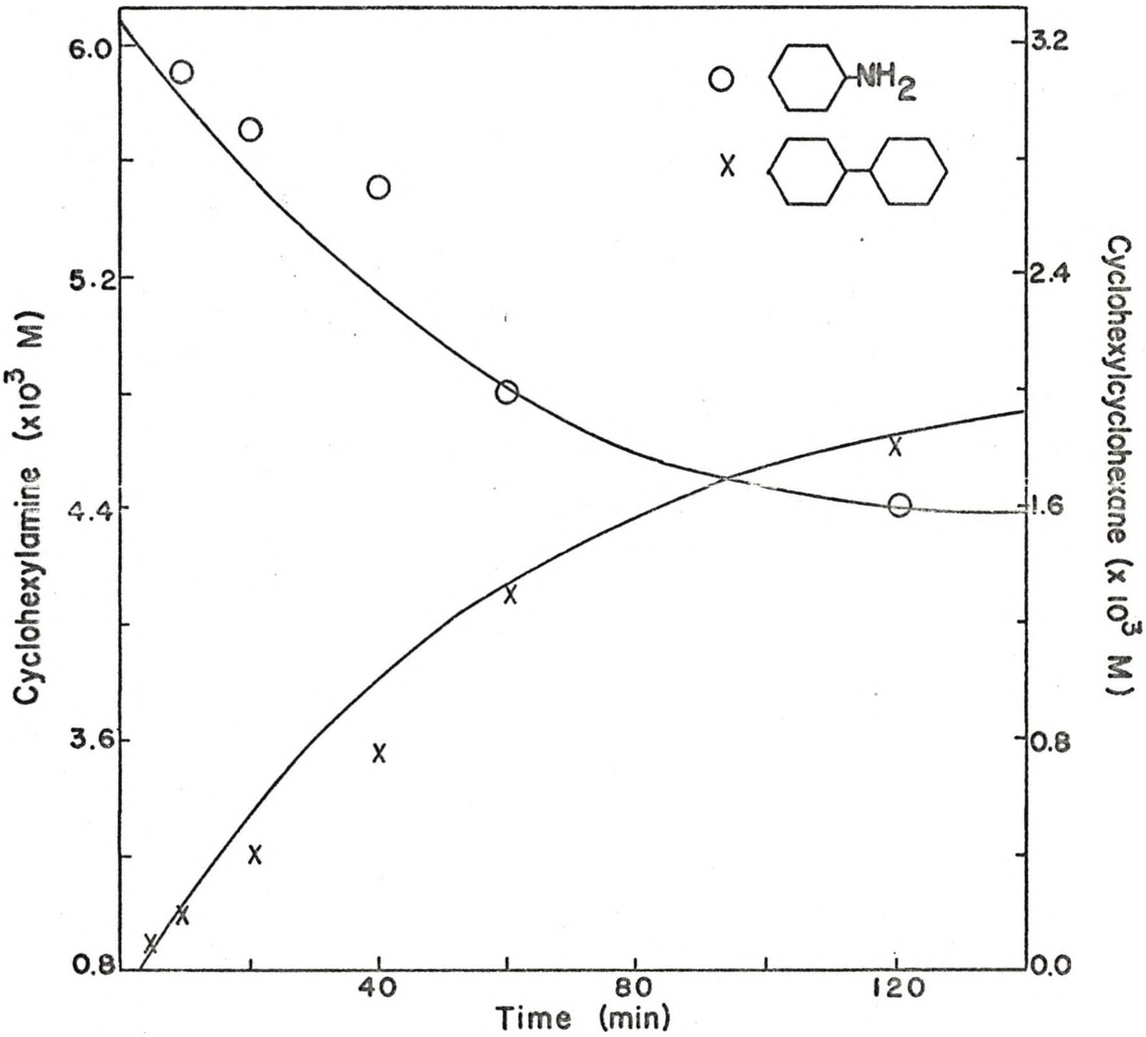
$$2\mathrm{NH_2}\cdot \underset{\longrightarrow}{\xleftarrow{\mathrm{hv}}} \mathrm{N_2H_4} \tag{21}$$

$$\mathrm{C_6H_{11}NH_2} \xrightarrow{\mathrm{hv}} \mathrm{C_6H_{11}NH_2}^{*} \longrightarrow \mathrm{C_6H_{11}}\cdot + \mathrm{NH_2}\cdot \tag{22}$$

$$2\mathrm{C_6H_{11}}\cdot \xrightarrow{k_R} \mathrm{C_{12}H_{22}} \tag{23a}$$

$$2\mathrm{C_6H_{11}}\cdot \xrightarrow{k_R} \mathrm{C_6H_{12}} + \mathrm{C_6H_{10}} \tag{23b}$$

In support of this mechanism, hydrogen gas and n-propylamine have been observed as products during the gas phase photolysis of

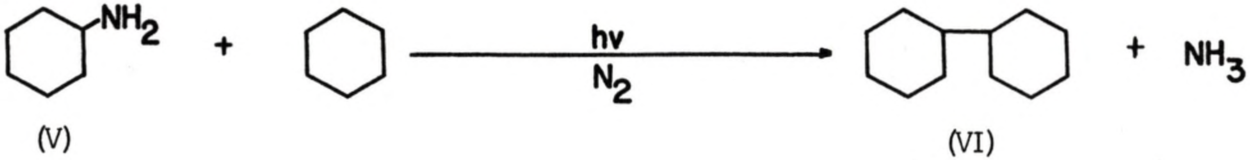

6.0
5.2
4.4
3.6
0.8
Cyclohexylamine (x10^3 M)
3.2
2.4
1.6
0.8
0.0
Cyclohexylcyclohexane (x 10^3 M)
40
80
120
Time (min)
○
NH$_2$
X

ammonia and propane.[5] The initial step of the photolysis of ammonia, reaction 16, in the region 168-217 is well accepted.[1, 83] Reaction 17 and 18 are energetically favorable.[84] It has been shown that amino radicals combine to form hydrazine in a flow system during the photolysis of gaseous ammonia (reaction 21).[85, 86] However, in the liquid phase where the amino radicals generated are surrounded by cyclohexane molecules these will react according to the energetically favorable reaction 17.[84] The hydrazine formed would in part be dissociated to amino radicals in the presence of ultraviolet light.[87]

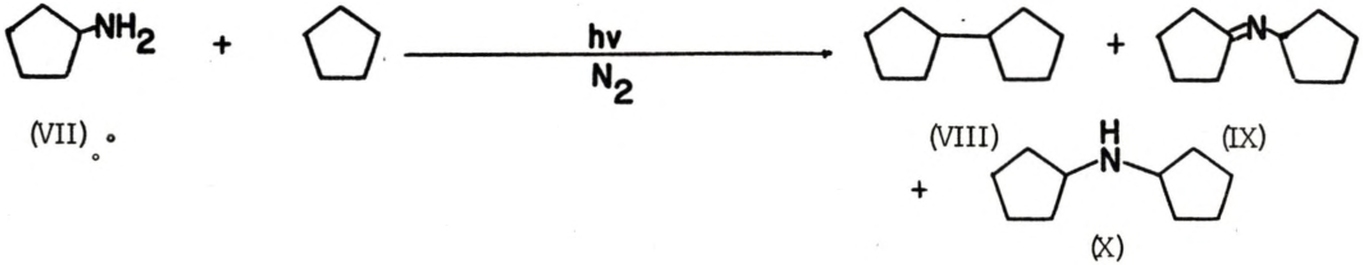
Concerning reaction 23, there are two possible processes which the cyclohexyl radical may undergo, recombination and disproportionation. However, as only cyclohexylcyclohexane was observed as a major product in the photolysis of both ammonia and cyclohexylamine each in cyclohexane solutions, and cyclohexene was not found in the photomixture, reaction 23a is the process chosen. These results are in agreement with those reported for the n-pentyl radical. The ratio of disproportionation to radical recombination for n-pentyl radical at 25° was estimated to be 0.14.[88]

Photodecomposition of Primary Aliphatic Amines

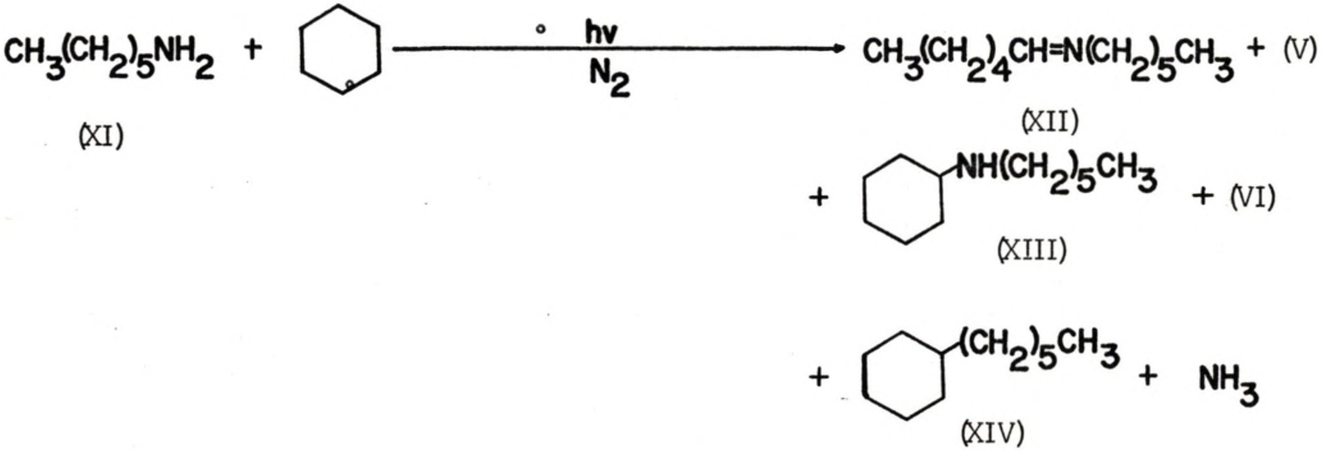
The products isolated and identified from the irradiation of cyclohexylamine, n-hexylamine and cyclopentylamine are shown in reactions 24-26. The data regarding product accumulation during the irradiations are given in Table 5, 6 and 7.


NH2
+
hv
N2
+ NH3
(V)
(VI)

(24)


NH2
+
hv
N2
+
N
(VII)
(VIII)
(IX)
H
N
+
(X)

(25)


CH3(CH2)5NH2 +
hv
N2
CH3(CH2)4CH=N(CH2)5CH3 + (V)
(XI)
(XII)
+
NH(CH2)5CH3
+ (VI)
(XIII)
+
(CH2)5CH3
+ NH3
(XIV)

(26)

TABLE 5

THE PHOTOCHEMISTRY OF CYCLOHEXYLAMINE IN CYCLOHEXANE

Time (min)	V (x 10^5 M)	VI (x 10^5 M)	ΔV (x 10^5 M)	VI/ΔV
0	611	. .	. .	. .
10	590	18	21	0.85
20	573	39	38	1.03
40	554	75	57	1.31
60	480	132	121	1.09
120	438	182	173	1.05
180	295	193	316	0.61

TABLE 6

THE PHOTOCHEMISTRY OF CYCLOPENTYLAMINE IN CYCLOPENTANE

Time (min)	VII ($\times 10^5$ M)	VIII ($\times 10^5$ M)	IX ($\times 10^5$ M)	X ($\times 10^5$ M)
0	570	. .	. .	. .
5	546	13	8	7
10	538	19	9	9
20	515	32	21	9
40	445	54	35	10
60	385	77	59	10
120	273	119	115	11

TABLE 7

THE PHOTOCHEMISTRY OF *n*-HEXYLAMINE IN CYCLOHEXANE

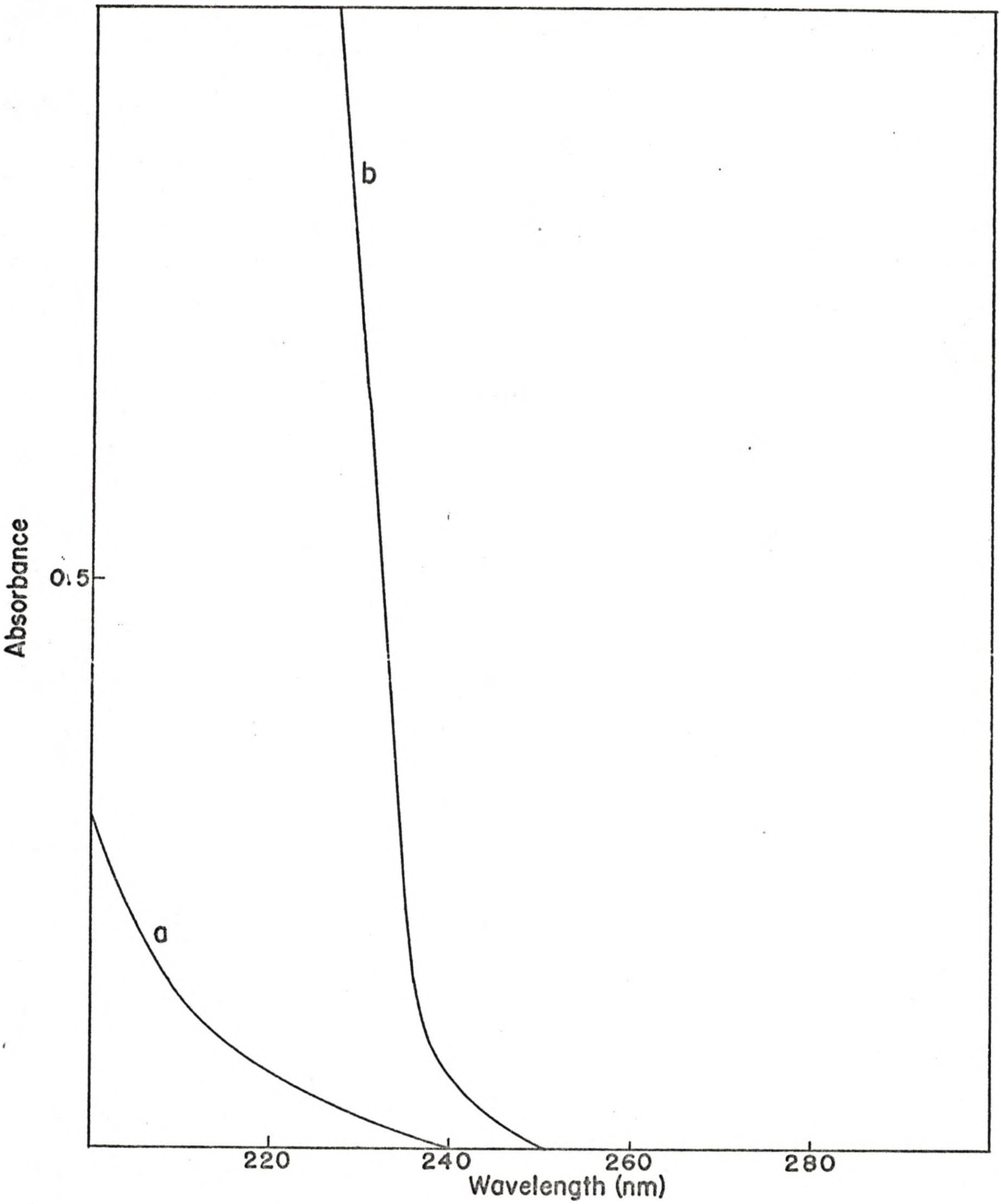
Time (min)	XI (x 10^5 M)	XII (x 10^5 M)	VI (x 10^5 M)	XIII (x 10^5 M)	V (x 10^5 M)	XIV (x 10^5 M)
0	611	. .	. .	. .	. .	. .
5	573	16	6	7	3	1
10	528	34	8	. .	3	1
20	491	65	17	8	4	1
40	325	92	31	. .	11	2
60	309	116	47	14	15	5
120	244	181	77	14	12	10

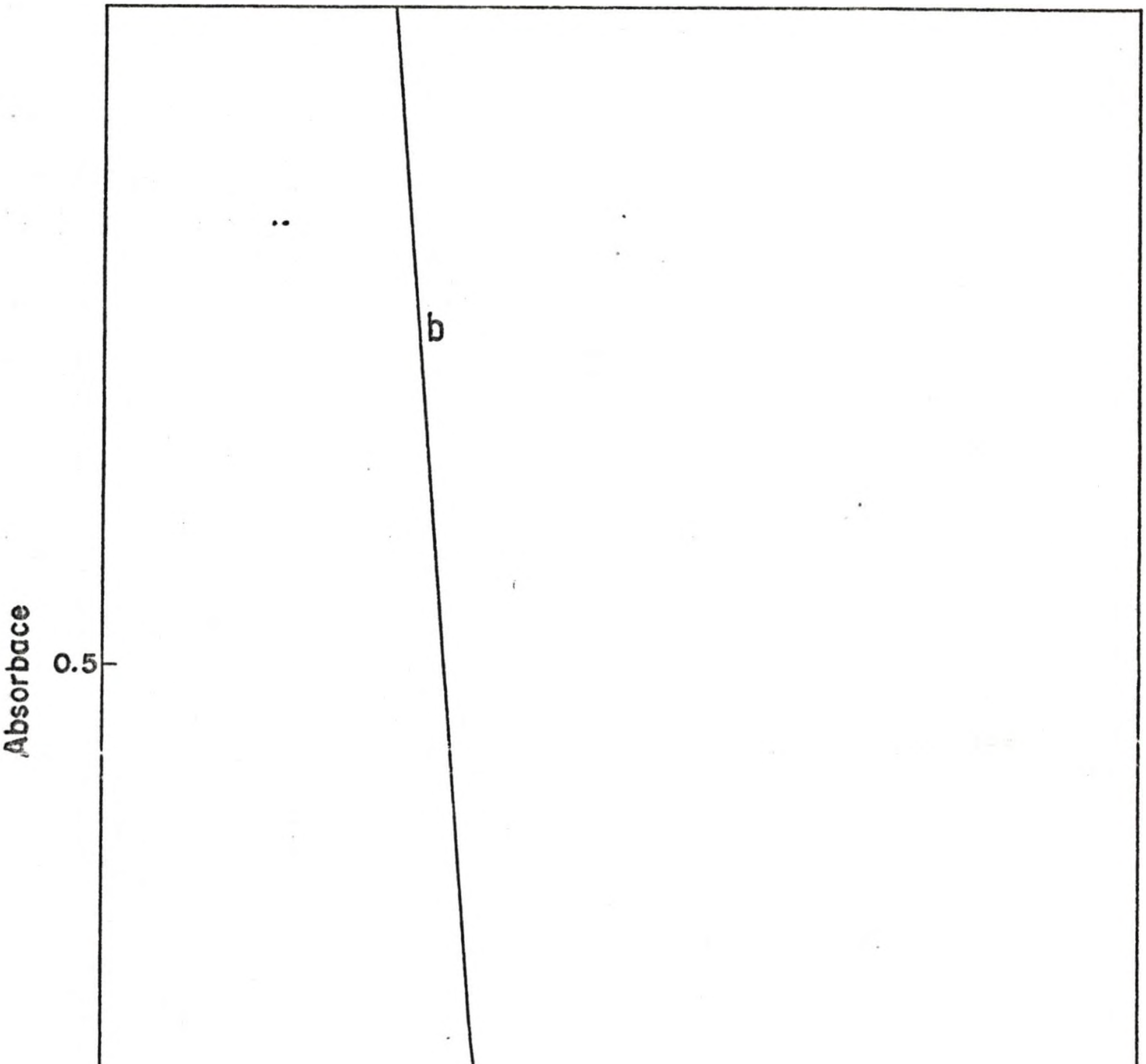
All the amines in this study have absorption only at the far end of near ultraviolet range of the spectrum. The absorbance of pure amine in cyclohexane or cyclopentane, which is virtually an ultraviolet transparent liquid, reached 1 at 230 nm with tailing to about 250 nm when the spectra were measured in 1-cm cell (illustrated in Figures 4-6). These absorbances are presumably $n \longrightarrow \sigma^*$ transitions.

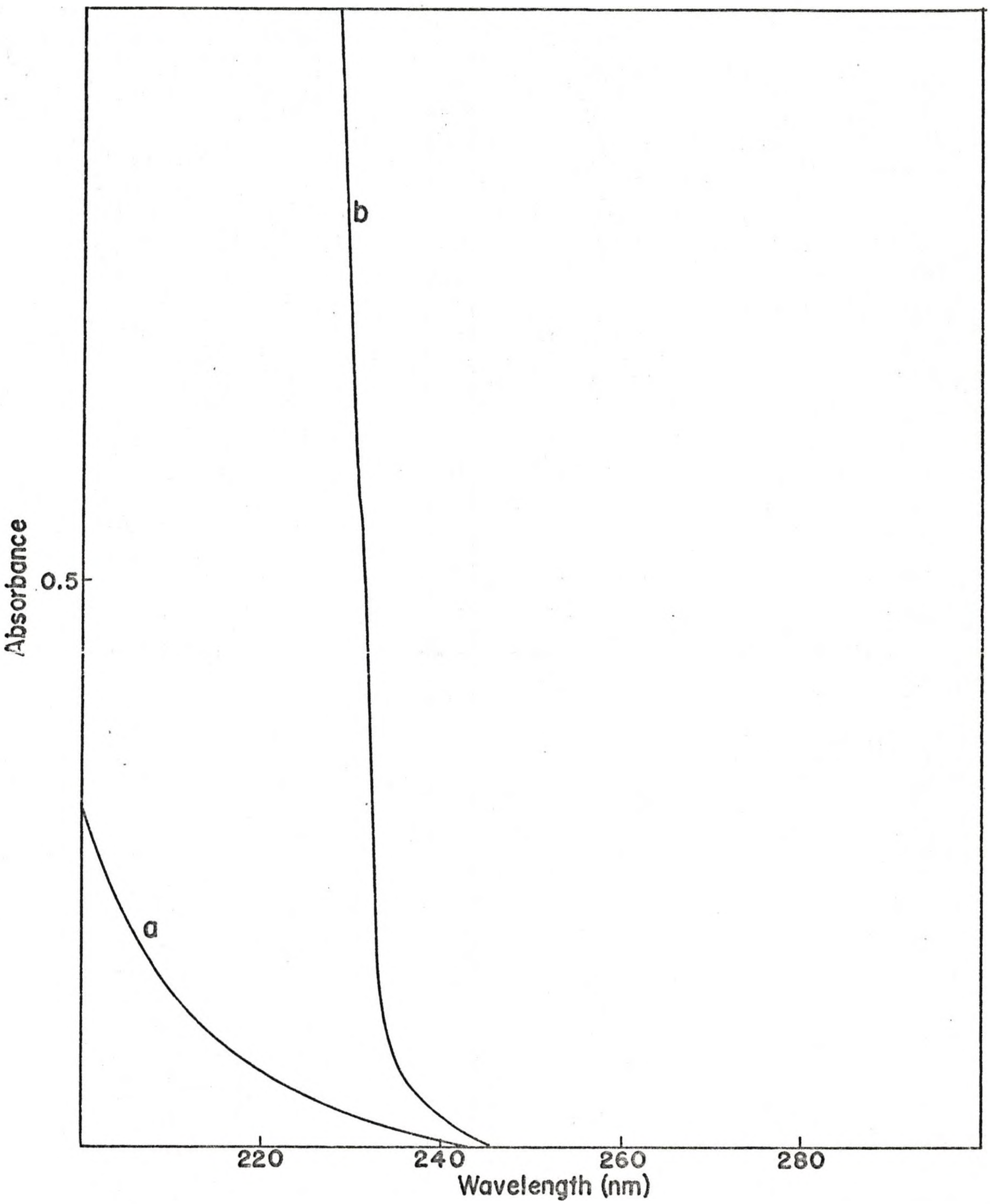
The four postulated cleavage patterns resulting from the irradiation of primary amines in the vapor phase are represented in equation 27a-d.[21] Pathway 27a is well known, however, 27b is presently relegated to a minor role. There is some but not definitive evidence for 27c and 27d.

$$\begin{array}{lllll} RR'CHNH_2 \xrightarrow{h\nu} RR'CHNH_2^{*} & \xrightarrow{a} & RR'CHNH\cdot & + H\cdot & \\ & \xrightarrow{b} & RR'CH\cdot & + NH_2: & \\ & \xrightarrow{c} & RR'\dot{C}NH_2 & + H\cdot & (27) \\ & \xrightarrow{d} & RR'C{=}NH & + H_2 & \end{array}$$

If pathway 27b is functioning, then the relative importance of this reaction for different compounds are influenced by the stability of the alkyl radical RR'CH·. The alkyl radicals of the amines selected have the following order of stability $C_6H_{11} > C_5H_9 > C_6H_{13}$. The primary radical is less stable than the two secondary ones, and bond hybridization accounts for the relative stability of the cyclohexyl and cyclopentyl radicals.[89,90] If the alkyl radical stability determines the relative importance of 27b, cyclohexylamine irradiation solutions should contain more products resulting from carbon-nitrogen cleavage than that of n-hexylamine with cyclopentylamine giving an intermediate amount.


b
a
Absorbance
0.5
220
240
260
280
Wavelength (nm)


b
a
Absorbace
0.5
220
240
260
280
Wavelength (nm)


Absorbance
0.5
b
a
220
240
260
280
Wavelength (nm)

In cyclohexylamine, the carbon-nitrogen bond cleavage, 27b, is the dominant reaction since the sole product is cyclohexylcyclohexane (VI). Further, the number of moles of cyclohexylcyclohexane produced with experiment error equals the amount of amine decomposed, *cf.* Table 5. Though Booth and Norrish[19] were unsuccessful in finding ammonia during the irradiation of *n*-hexylamine in hexane, it has been found as a product in gas phase methylamine irradiations,[16, 21] ammonia was successfully trapped from the irradiated solution of cyclohexylamine and *n*-hexylamine. Thus equations 27b, 28, and 29 adequately summarize the latter reaction.

$$NH_2\cdot + C_6H_{12} \longrightarrow C_6H_{11}\cdot + NH_3 \qquad (28)$$

$$2C_6H_{11}\cdot \longrightarrow C_{12}H_{22} \qquad (29)$$

In contrast to the cyclohexylamine reaction, the irradiation of cyclopentylamine in cyclopentane produces a considerably different set of products, *cf.* reaction 25. Though cyclopentylcyclopentane (VIII) is the major product, nitrogen-containing products such as N-cyclopentylidenecyclopentylamine (IX) and dicyclopentylamine (X) are also formed in good yields. The imine (IX) is not reduced in the reaction solution to the amine (X); however, the reverse reaction can and does occur. Consequently, dicyclopentylamine achieves a photostationary state in the reaction solution, *cf.* Table 6. Although the irradiation of dicyclohexylamine produces a high yield of N-cyclohexylidenecyclohexylamine,[91] it is not the principal source of the imine because of the immediate formation of IX.

The appearance of dicyclopentylamine in the cyclopentylamine reaction solution implies that reaction 27a is functioning during the irradiation. It is unlikely that reaction 30 following reaction 27c is an alternative to 27a because in the cyclohexylamine irradiation 27c did not operate and the reaction 30 is expected to be slow since the carbon-hydrogen and nitrogen-hydrogen bond dissociation energies are nearly the same.[92]

(30)

The irradiation of *n*-hexylamine (XI) in cyclohexane provides the imine, N-1-(hexylidene)-*n*-hexylamine (XII), as the major product, *i.e.*, 50% yield at all times measured, *cf*. reaction 26 and Table 7. Both alkyl groups of the imine are derived from *n*-hexylamine in accordance with the well-accepted reaction 31. The remaining question of whether

$$CH_3(CH_2)_5NH_2 + CH_3(CH_2)_4\,CH{=}NH \longrightarrow XII \qquad (31)$$

the imine, $CH_3(CH_2)_4$ CH=NH, is formed by a two step process involving reaction 27a or a one step one utilizing 27d can be readily decided by comparing the *n*-hexylamine and the cyclohexylamine reaction. Reaction 27d is expected to occur more readily during the irradiation of cyclohexylamine than with *n*-hexylamine whether one considers the relative bond dissociation energies of the carbon-hydrogen bonds or the stability of the resulting imine double bonds. Yet imine formation does not occur with cyclohexylamine. Consequently it appears that the reaction of *n*-hexylamine occurs *via* reaction 27a.

It is now possible to conclude that nitrogen-hydrogen bond rupture is the dominant primary reaction of the excited state n-hexylamine whereas carbon-nitrogen bond rupture is most important for the excited state of cyclohexylamine. Though less clear, it appears cyclopentylamine occupies an intermediate reactivity position as expected.

Photodecomposition of Secondary Aliphatic Amines

The results of the three dialkylamine irradiations are illustrated in Table 8. The absorption spectra of nitrogen-saturated dialkylamine solution are shown in Figures 7-9. At the wavelength of 238 nm, an absorption was observed for each dialkylamine which is attributed to the absorption of amine $n \longrightarrow \sigma^*$ transition.

The results do not contradict those of Allan and Swan[28] as described in the Introduction, because our results were obtained at an earlier stage of irradiation. The results are also in agreement with the accepted cleavage pattern of secondary amines (reaction 32).[18, 19] The products obtained herein give validity to the postulate of Allan and Swan that $CH_3CH{=}NCH_2CH_3$ was produced in the diethylamine irradiation. The low yield of cyclohexylcyclohexane in the reaction of di-n-hexylamine favors reaction 33 occurring predominantly after the initial radical formation rather than a combination of reaction 34 and 35. If the radical escaped the

$$R_2NH \xrightarrow{hv} R_2NH^* \longrightarrow R_2N\cdot + H\cdot \qquad (32)$$

$$(R_2N\cdot + H\cdot) \longrightarrow R'CH{=}NR + H_2 \qquad (33)$$

$$H\cdot + R_2NH \longrightarrow R_2N\cdot + H_2 \qquad (34)$$

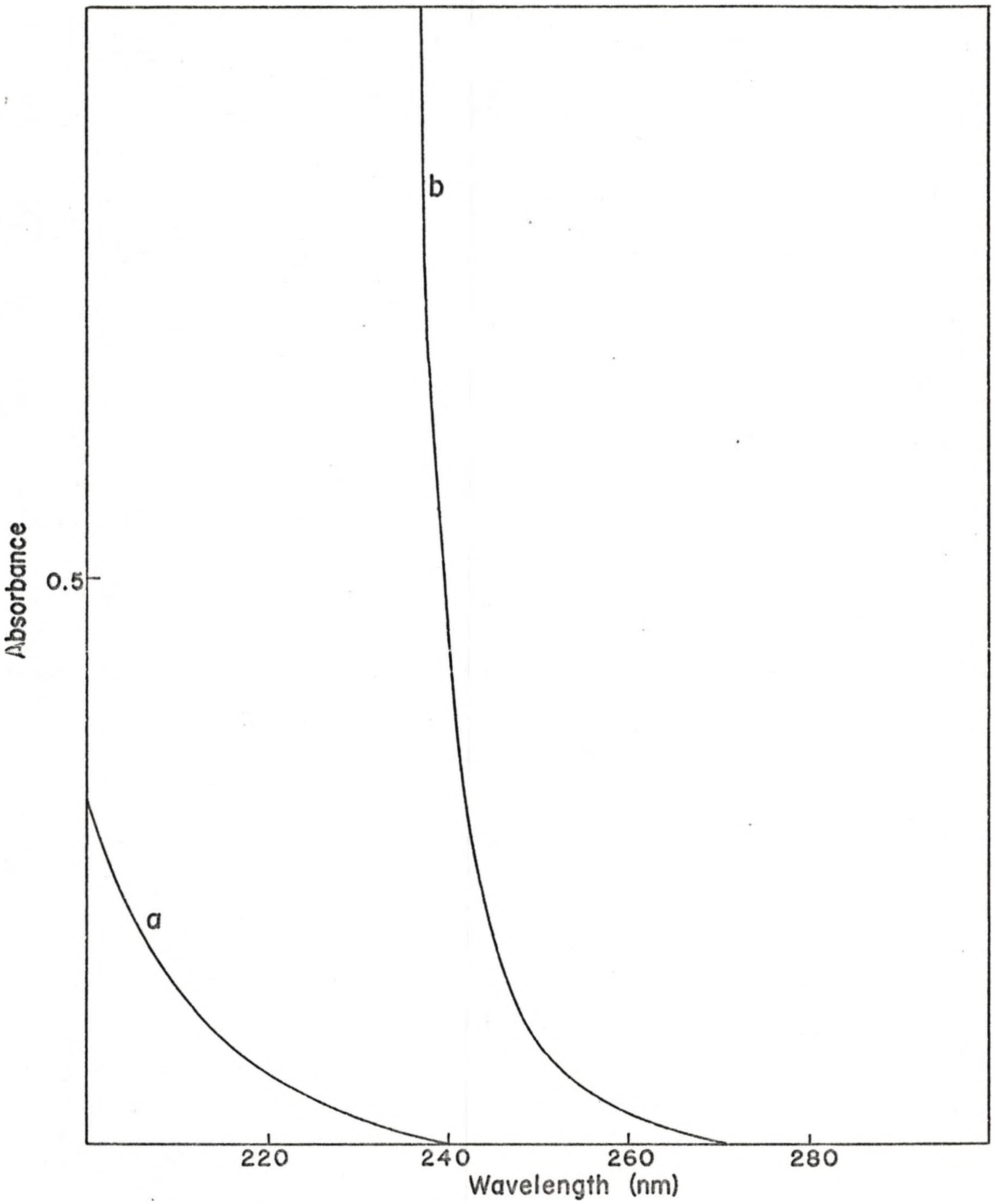
TABLE 8

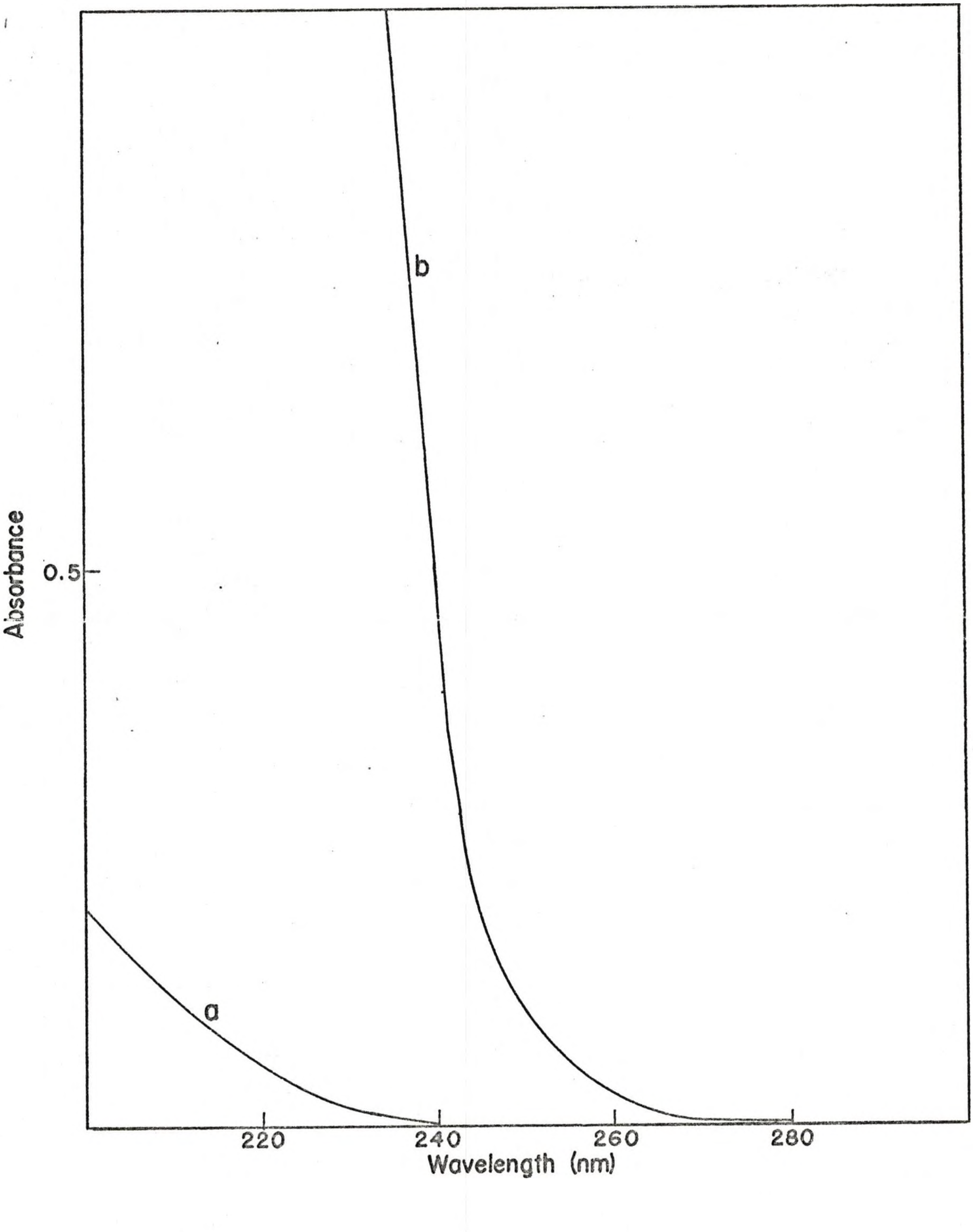
PRODUCTION DISTRIBUTION AND YIELDS FROM THE PHOTOLYSIS OF SECONDARY ALIPHATIC AMINES

Reactant	Product	Percent yield ± 5%	Irradiation time hour
Di-n-hexylamine (XV)	N-n-Hexylidene-n-hexylamine	89	6
	Cyclohexylcyclohexane	10	
	XV	2	
	n-Hexylamine[a]	11	
Dicyclohexylamine (XVI)	N-Cyclohexylidene-cyclohexylamine	89	6
	Cyclohexylcyclohexane	15	
	XVI	5	
	Cyclohexylamine[a]	4	
n-Hexylcyclohexylamine (XVII)	N-n-Hexylidene-cyclohexylamine	62	6[b]
	N-Cyclohexylidene-n-hexylamine	29	
	Cyclohexylcyclohexane	16	
	n-Hexylamine[a]	3	
	XVII	2	
	Cyclohexylamine[a]	4	
	n-Hexylcyclohexane[a]	2	

[a] Identified by retention time.

[b] Optimum yield time.


Absorbance
0.5
Wavelength (nm)
220
240
260
280
a
b


Absorbance
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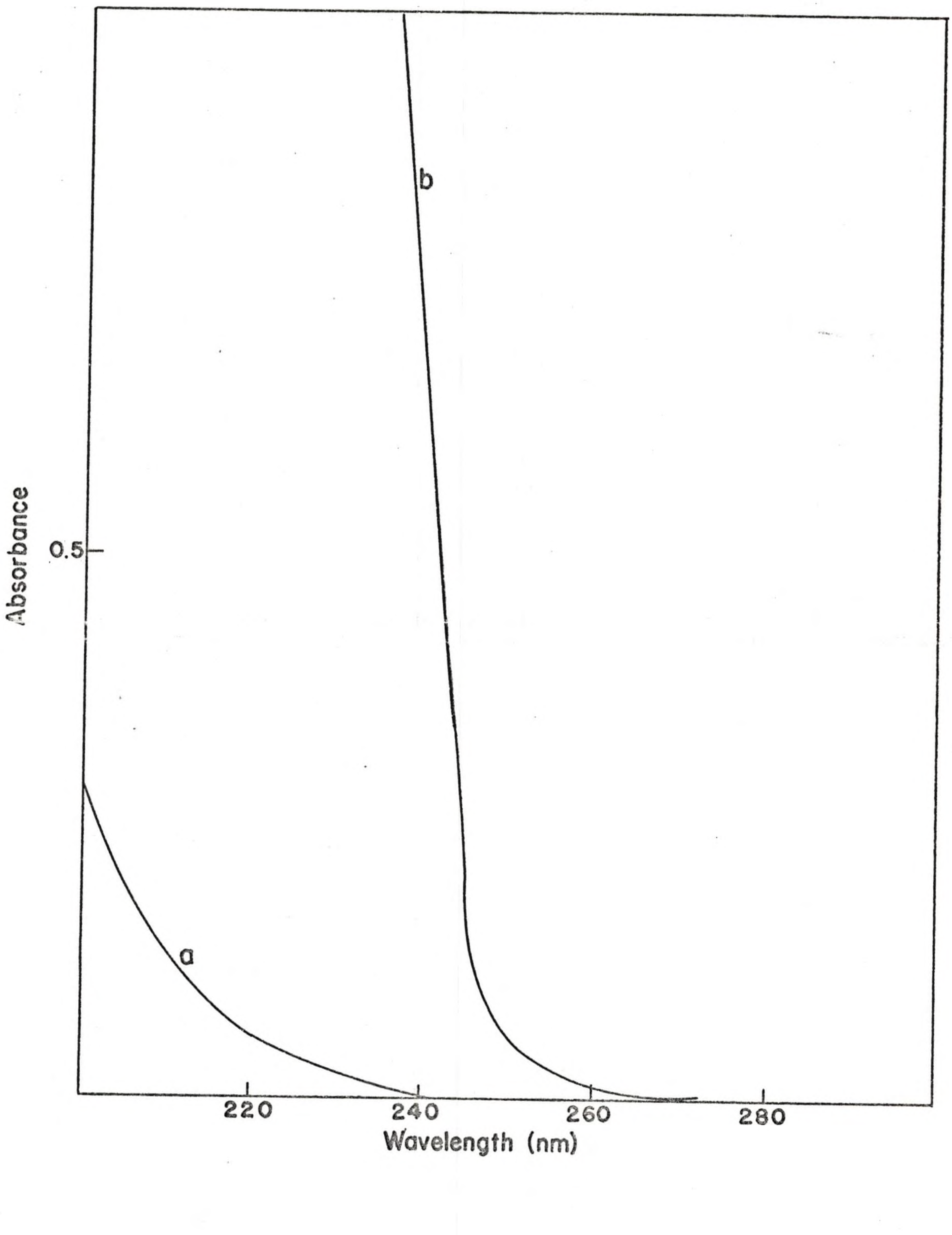
a
b
220
240
260
280
Wavelength (nm)


Absorbance
0.5
a
b
220
240
260
280
Wavelength (nm)

$$2R_2N\cdot \longrightarrow R'CH{=}NR + R_2NH \qquad (35)$$

solvent cage, more solvent radicals would be formed, with the consequence of enhanced cyclohexylcyclohexane yields. Secondary amines with a cyclohexyl group, _i.e._, dicyclohexylamine and _n_-hexylcyclohexylamine produce more cyclohexylcyclohexane because of more efficient carbon-nitrogen scission and the resulting cyclohexyl radicals can participate more directly in cyclohexylcyclohexane formation.

The hydrogen atom abstraction reaction 33 is governed by statistical considerations and attack on the least substituted center explains the 2:1 product distribution of the _n_-hexylcyclohexylamine reaction. This result is consistent with the photoreduction of benzophenone by isopropylethylamine.[93] The double bond of N-cyclohexylidene-_n_-hexylamine was isomerized in trace amounts of N-_n_-hexylidenecyclohexylamine under the reaction conditions.

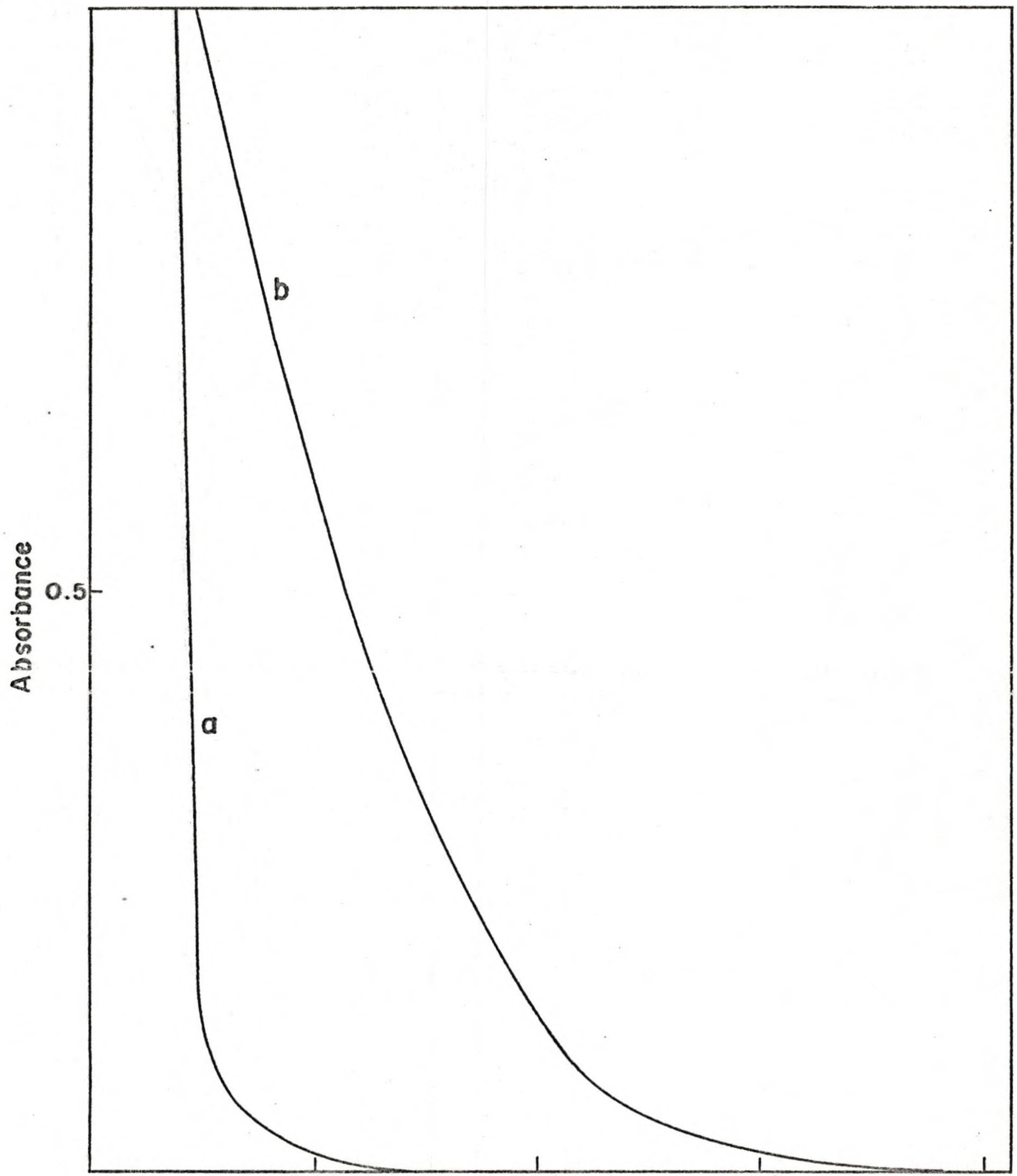
It is possible that two dialkylamino radicals might dimerize. However, this possibility is eliminated by the following reasoning. The nitrogen-nitrogen bond strength in hydrazine is about 72 kcal/mole.[94] If any hydrazine did form in the reaction, it could itself be photolyzed under the conditions of the irradiation. When tetraisopropyltetrazene was photolyzed at -70^{o}, the only detectable products were diisopropylamine and N-isopropylideneisopropylamine. Tetraisopropylhydrazine was not observed by the nmr.[95]

It is interesting to note that the nitrogen-hydrogen cleavage predominates during the irradiation of dicyclohexylamine whereas carbon-nitrogen scission is dominant for cyclohexylamine.[96] Presumably the stability of $(C_6H_{11})_2N\cdot$ is sufficiently greater than that of $C_6H_{11}NH\cdot$ because of inductive factors.

Charge-Transfer Spectra of Amine-Oxygen Complexes

The absorption spectra of high-purity amines into which nitrogen had been passed was transparent in the near ultraviolet where the tail-end absorption of amines ($n \longrightarrow \sigma^*$) begin. The spectra of oxygen-saturated amine solutions with an identical nitrogen-saturated amine solution as a reference, are illustrated in Figures 10-17.

The absorbance of oxygen-saturated amine solutions with an identical nitrogen-saturated amine solution as a reference vanishes when nitrogen is bubbled through the solution and can be reestablished by passing oxygen into the amine again. The reversible nature of the observed bands indicates that they are not due to formation of oxidation products. This enhanced ultraviolet absorbance can be attributed to the formation of a weak complex between oxygen and amine. The reversible character of the absorption band in the ultraviolet region for the amine-oxygen saturated solutions is in agreement with the previous reports by Munck and Scott[56] and by Tsubomura and Mulliken.[57] Because this complex has the general properties of a charge-transfer complex, *i.e.*, reversible formation and enhanced ultraviolet absorbance which is not observed with oxygen or the amines alone, it most probably is of this type with oxygen acting as the electron acceptor and the amine as the electron donor.


Absorbance
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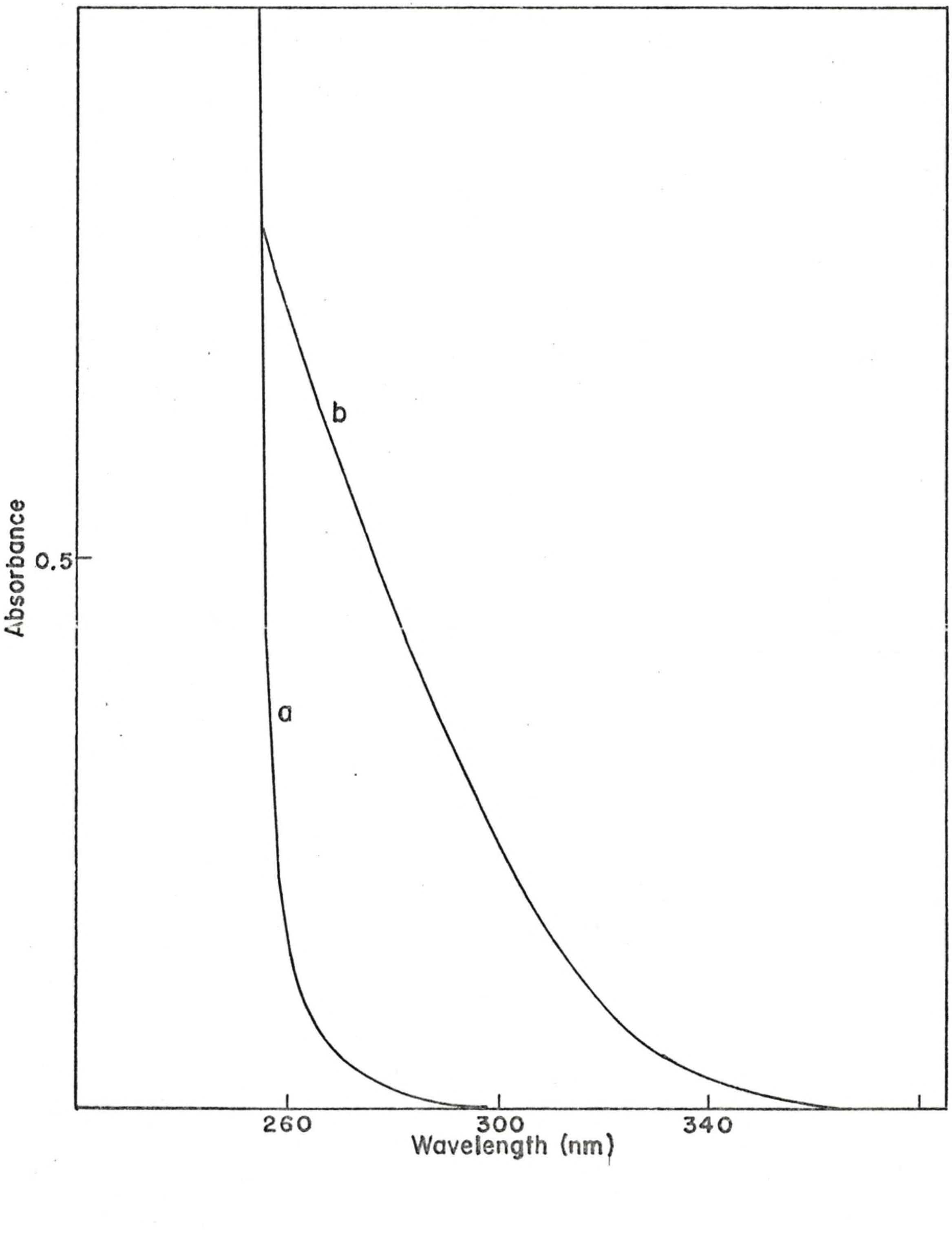
a
b
280
320
360
Wavelength (nm)


Absorbance
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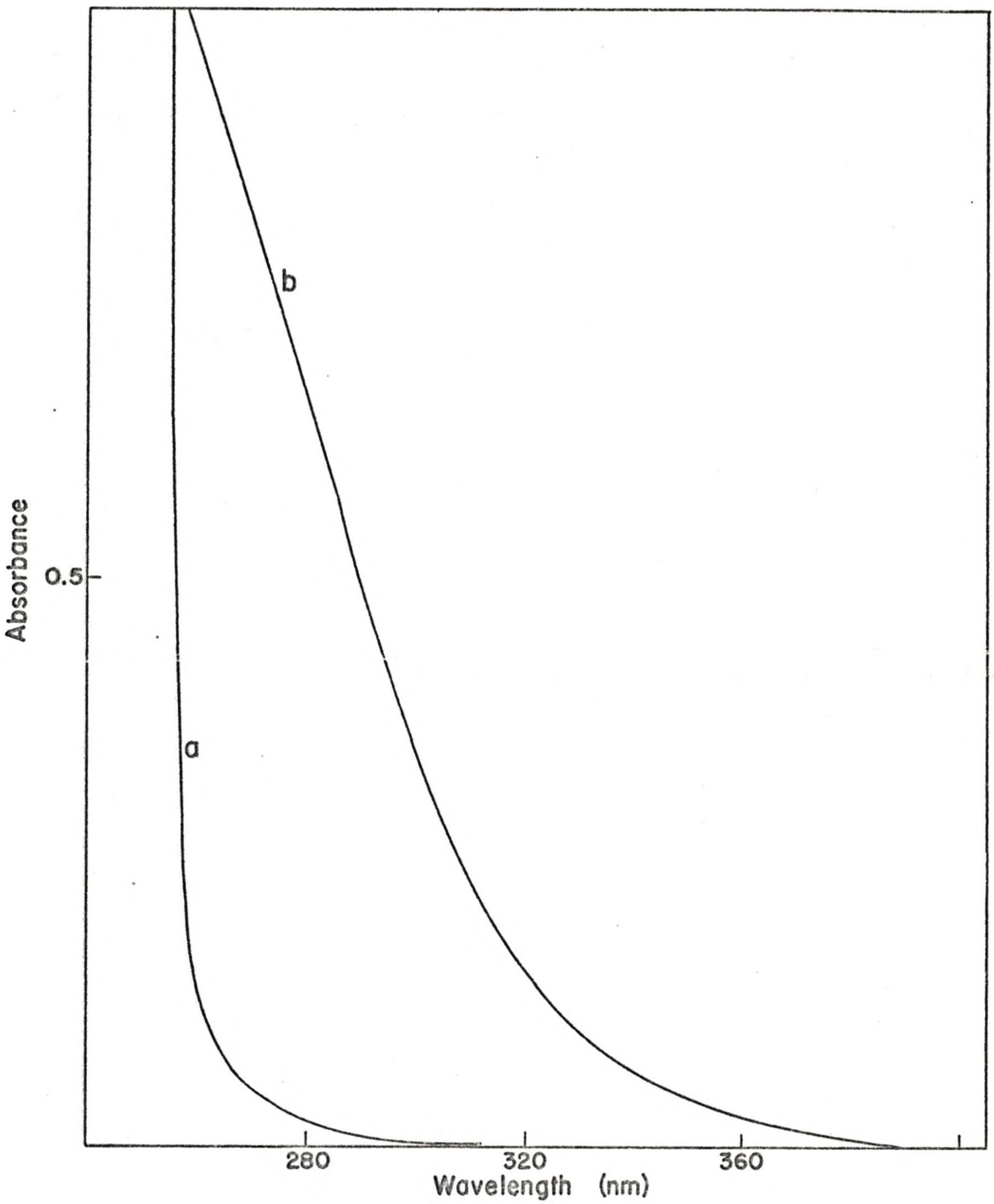
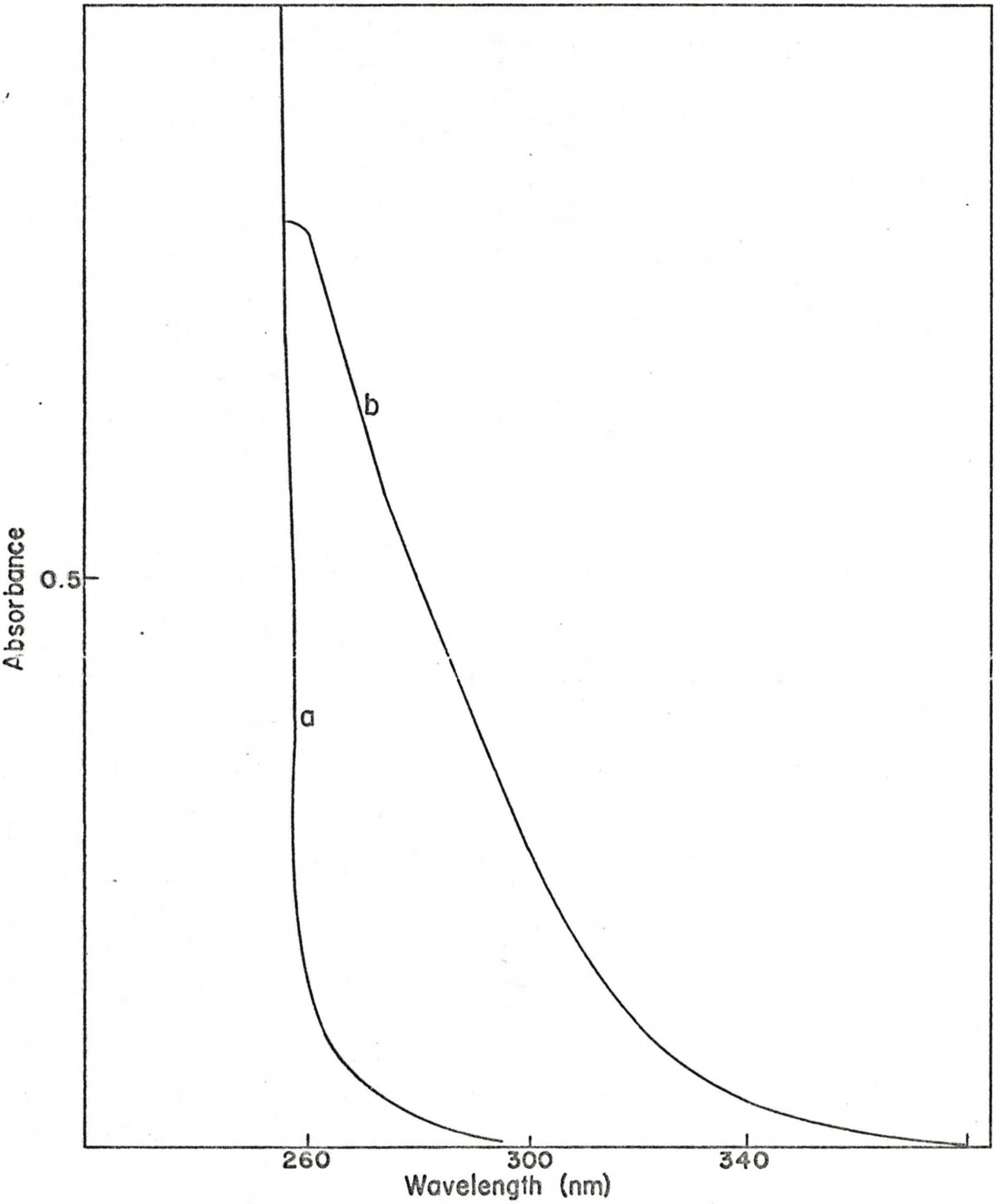
b
a
260
300
340
Wavelength (nm)


Absorbance
0.5
a
b
280
320
360
Wavelength (nm)


Absorbance
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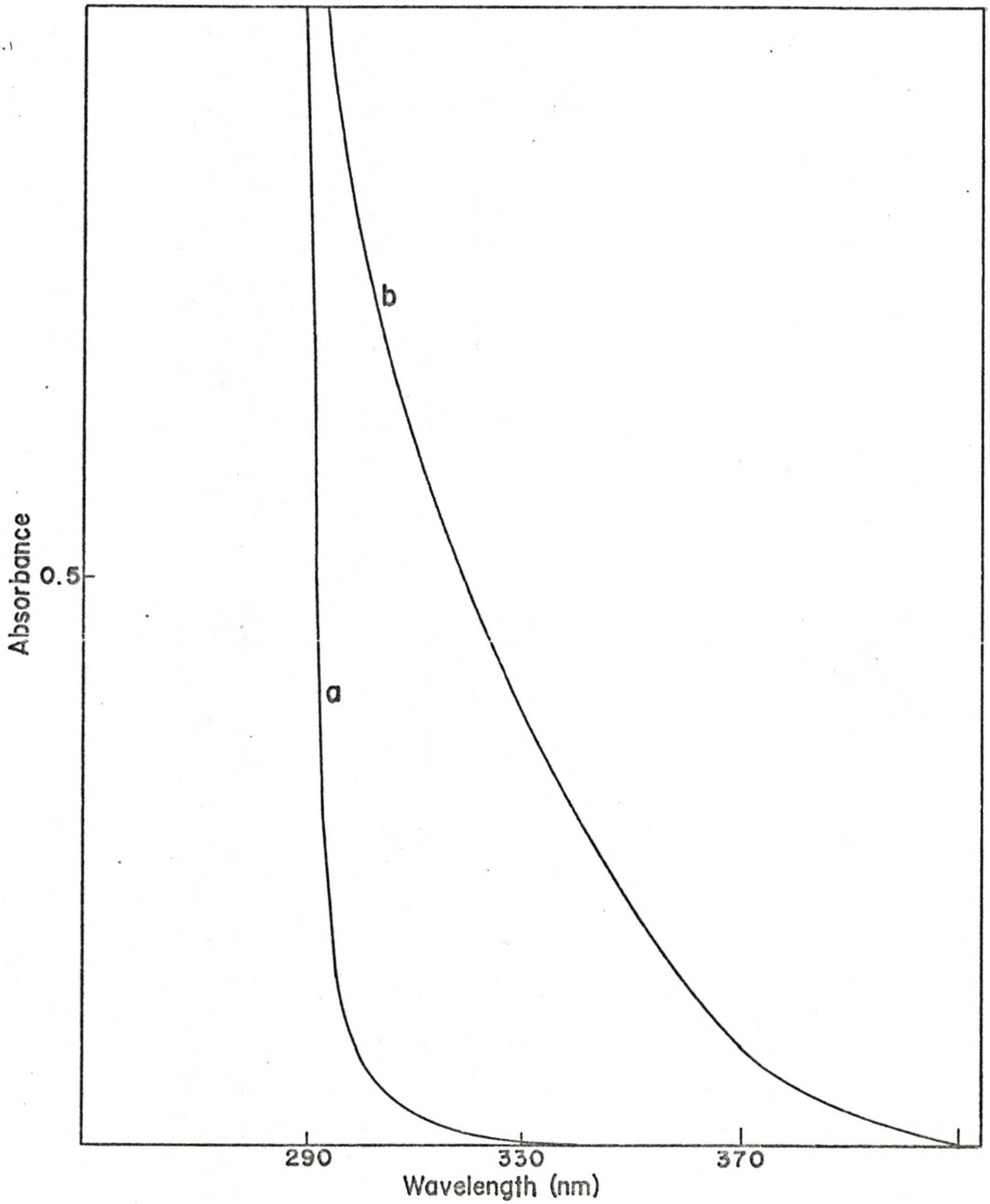
a
b
260
300
340
Wavelength (nm)


Absorbance
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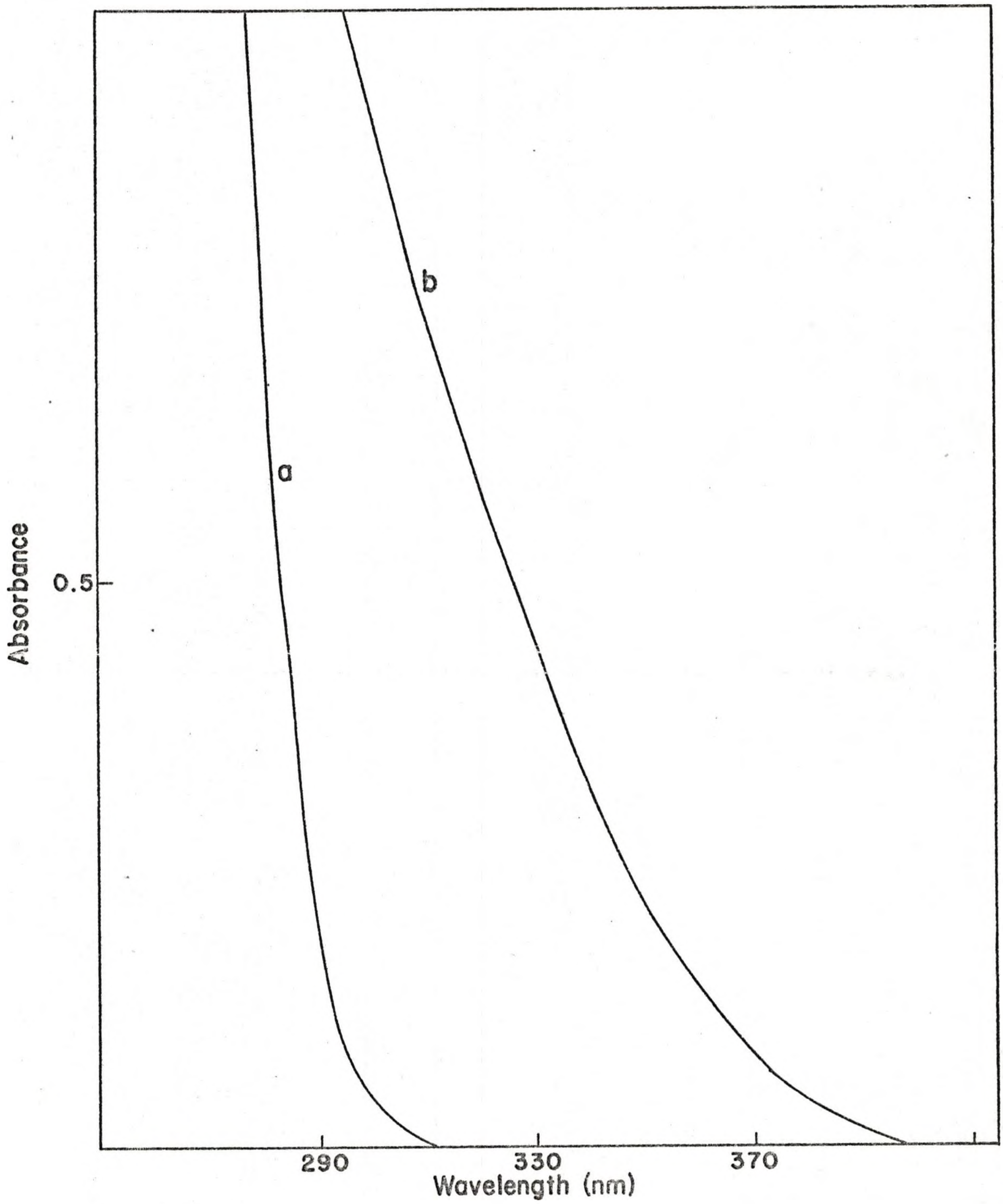
b
a
290
330
370
Wavelength (nm)


Absorbance
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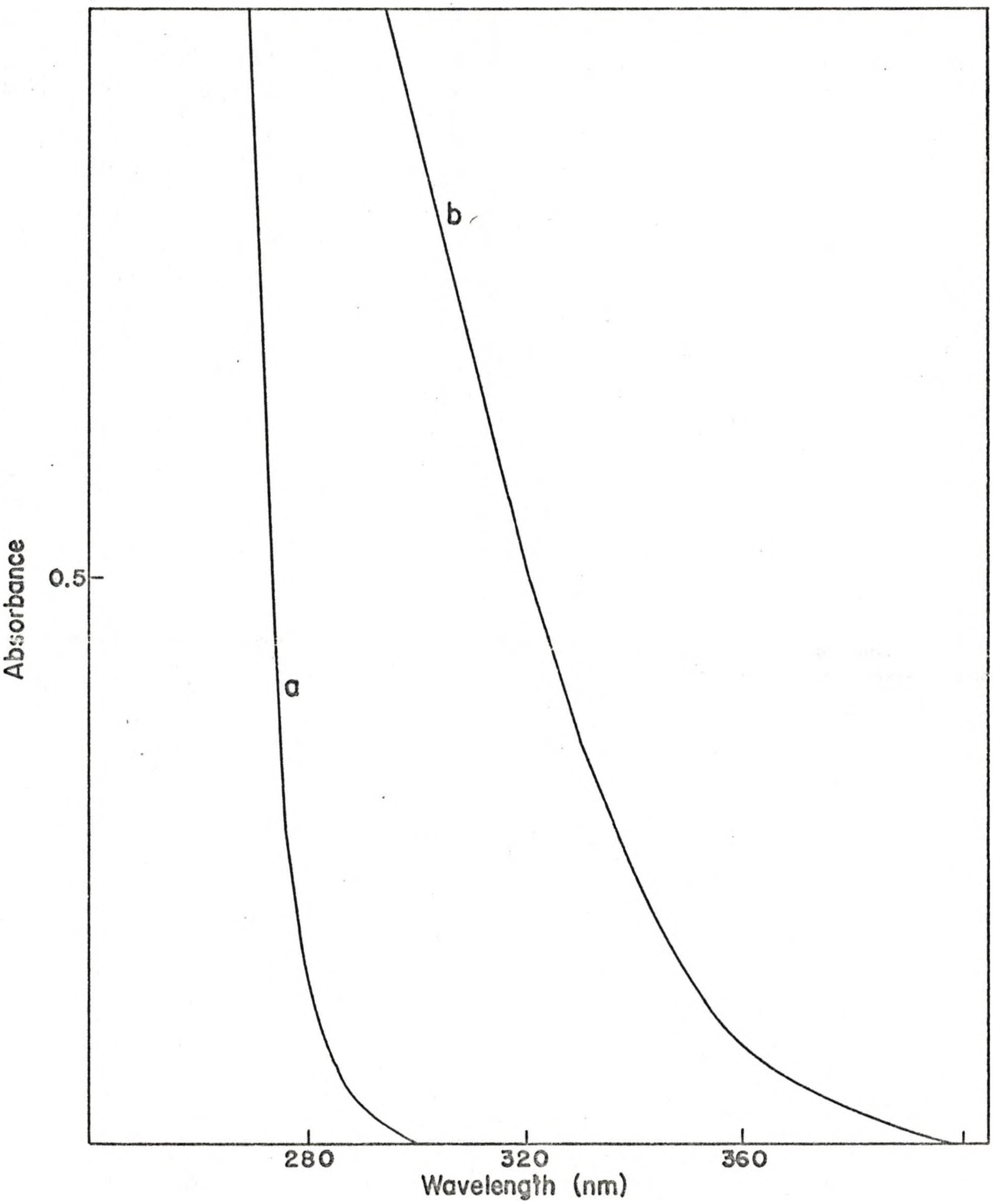
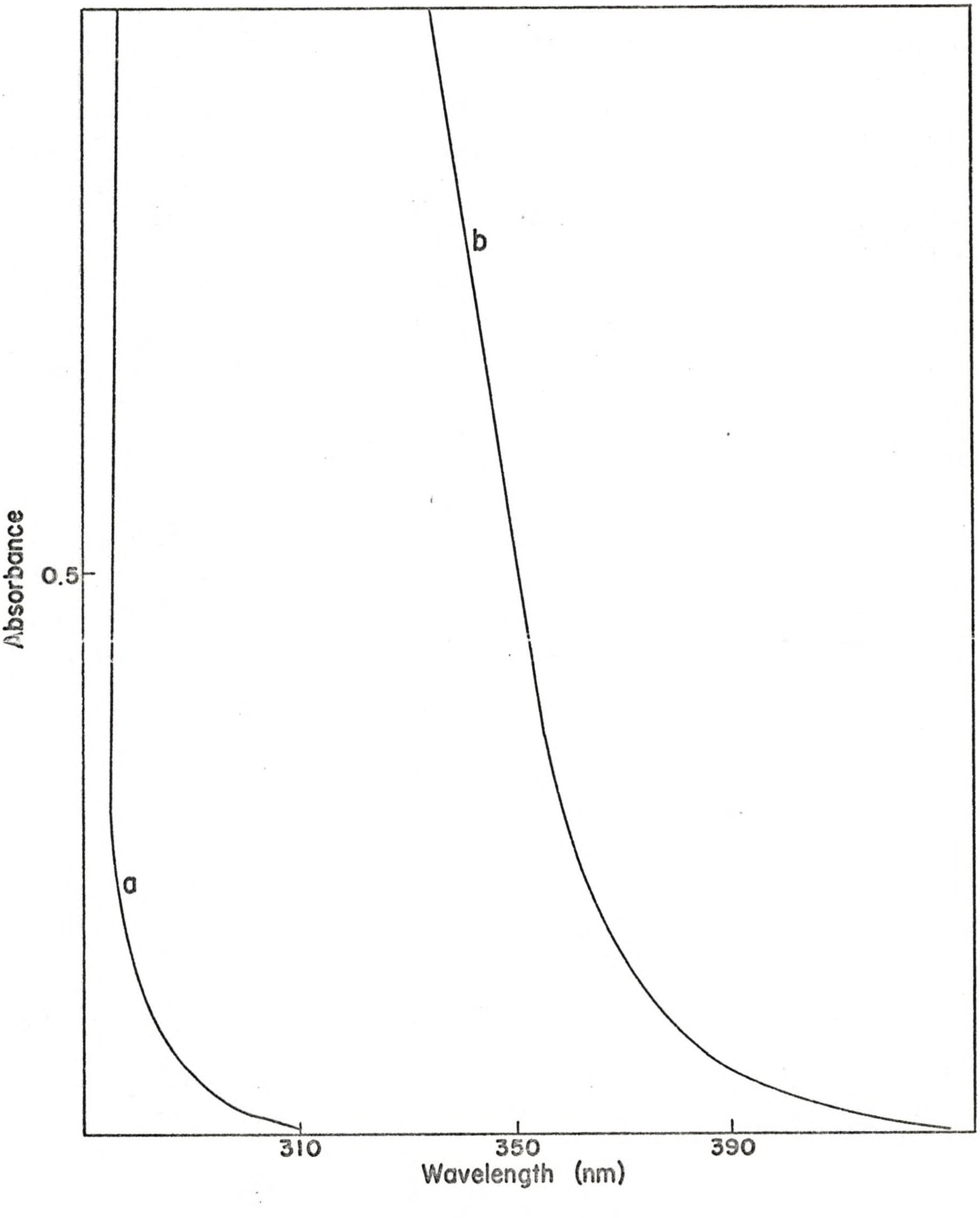
a
b
290
330
370
Wavelength (nm)


b
a
Absorbance
0.5
280
320
360
Wavelength (nm)


Absorbance
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a
b
310
350
390
Wavelength (nm)

The Relationship between Ionization Potential and Charge-Transfer Bands of Oxygen-Hydrocarbon, Oxygen-Ether, and Oxygen Amine

The energy of the charge-transfer (CT) transition for weak interactions can be related theoretically to the ionization potential of the donor (I^D) and the electron affinity of the acceptor (E^A). By simple perturbation theory:

$$E_{CT} = I^D - (E^A + G_1 - G_O) + \frac{B_O^2 + B_1^2}{I^D - (E^A + G_1 - G_O)} \qquad [III]$$

where B_O and B_1 are the matrix elements $(H_{01} - S_{01}W_0)$ and $(H_{01} - S_{01}W_1)$, respectively, G_0 is the energy of the "no bond" interaction and G_1 is the interaction of D^+ and A^- in the excited state. Where W_0 is the energy of the "no bond" state, W_1 is the energy of the dative state and S_{01} is the overlap integral for these two states, respectively.

If it is supposed that the terms $(G_0 - G_1)$ and $(B_0^2 + B_1^2)$ in equation III are constants for a series of complexes of different donors with same acceptor species, then this equation may be written:[97]

$$h\nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \qquad [IV]$$

where $C_1 = (E^A + G_1 - G_0)$ and $C_2 = (B_1^2 + B_0^2)$. McConnell, et al.[98] showed that there is an approximately linear relationship (equation V) between I^D and ν_{CT} for complexes of iodine with a wide range of relatively weak donors:

$$h\nu_{CT} = I^D - E^A - W \qquad [V]$$

where E^A is the electron affinity of the acceptor and W is the electrostatic and other interaction energy between the molecules in the charge-transfer state. If W is assumed to be relatively constant for various donors in weak complexes, a linear relationship is expected between the ionization potential of electron donors and the onset of absorption of the charge-transfer band arising with common acceptor.

$$h\nu_{CT} = aI^{D} + b \qquad [VI]$$

Yada, et al.,[99] have made an extensive study of amine complexes with iodine. When the ν_{CT} values for primary, secondary, and tertiary amines were combined and plotted against ionization potentials of donors, parabola was observed. Each series, i.e., primary, secondary, and tertiary amines, taken individually also showed parabola within the series. The explanation for this tendency is that the bulky alkyl group attached to nitrogen atom of the amine molecule probably causes an increase in the steric repulsions. This steric repulsion may conceivably bring about the increase in N-I distance of the complex, in the order of the primary < secondary < tertiary amine. This means that the S (overlap integral) and the B (exchange integral) values, and the magnitude of electrostatic attraction in dative (charge-transfer) structure decreased in the following order, primary > secondary > tertiary amine. Moreover, C_1 in equation IV is considered to be the sum of the electron affinity of the electron acceptor and the electrostatic attraction between component molecules in complexed state. Therefore, the values of C_1 turn out to decrease in the above order even if the electron affinity of iodine may be regarded as constant.

Because the frequency at which charge-transfer complexes absorb depends not only on the transition energy, but also on the solubility of oxygen in the liquids,[57] one should plot frequencies of charge-transfer complexes at equal absorption intensity, corrected for the solubility of oxygen in the liquids, against their respective ionization potentials. However, due to the lack of information about oxygen solubility in various organic compounds at room temperature, the frequencies of oxygen-amine, oxygen-ether, and oxygen-hydrocarbon charge-transfer complexes at which the absorbance reached the value of 0.7 (peaks are not used) and their respective known ionization potentials listed in Table 8 are used in the correlation. The frequencies plotted against the ionization potentials are illustrated in Figure 18. The regression coefficient of this straight line is 0.9465, and the confidence coefficient or "student" t is 8.2972. The confidence level is over 99.99%.

From Figure 18, a straight line was observed for all three classes of amines, i.e., primary, secondary, and tertiary, when oxygen is the acceptor for the charge-transfer complex. Presumably, the oxygen-amine complexes are much weaker than the amine-iodine complexes, and also the size of the oxygen molecule is considerably smaller than iodine. Therefore, the steric repulsion between amine and oxygen may be conceivably diminished. This means that S and B, and the magnitude of the electrostatic attraction of the dative structure may remain constant in the series of primary, secondary, and tertiary amines. In the case of the oxygen-amine complex, C_1 and C_2 in equation IV may be regarded as constant.

TABLE 9

FREQUENCIES OF THE OXYGEN-HYDROCARBON, OXYGEN-ETHER, OXYGEN-AMINE CHARGE-TRANSFER COMPLEXES AT A=0.7 AND THE IONIZATION POTENTIALS

Number	Compound	V_{CT} (x 10^{-3} cm^{-1})	I.P. (ev)
1.	Cyclopentane	47.62	10.53[b]
2.	n-Hexane	45.45	10.18[b]
3.	Cyclohexane	44.25	9.88[b]
4.	Ethyl ether	42.19[a]	9.35[b]
5.	n-Propyl ether	40.00[a]	9.28[c]
6.	n-Butyl ether	40.65[a]	9.18[c]
7.	Tetrahydropyran	39.22[a]	9.25[b]
8.	Tetrahydrofuran	39.06[a]	9.42[b]
9.	Cyclohexylamine	37.59	8.86[d]
10.	n-Butylamine	36.36	8.71[e]
11.	n-Hexylamine	36.50	. .
12.	Cyclopentylamine	35.97	. .
13.	Diethylamine	32.26	8.01[b]
14.	Piperidine	31.95	7.85[f]
15.	Pyrrolidene	32.05	. .
16.	Triethylamine	29.07	7.50[b]

[a] see Ref. 80.

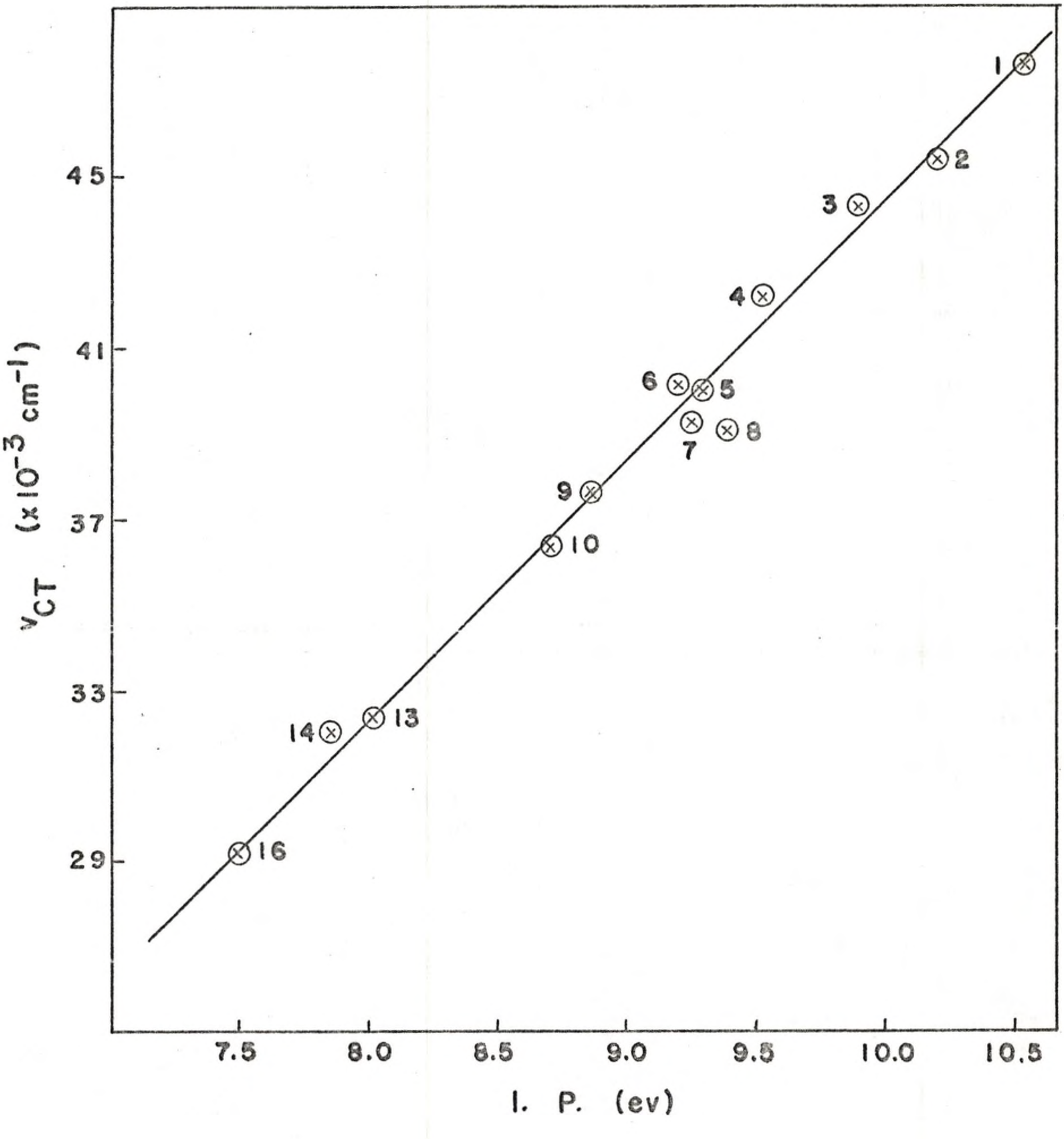
[b] see Ref. 54 .

[c] see Ref. 100.

[d] see Ref. 101.

[e] see Ref.. 102.

[f] see Ref. 103.



ν_{CT} (x10^{-3} cm^{-1})
45
41
37
33
29
7.5
8.0
8.5
9.0
9.5
10.0
10.5
I. P. (ev)
1
2
3
4
5
6
7
8
9
10
13
14
16

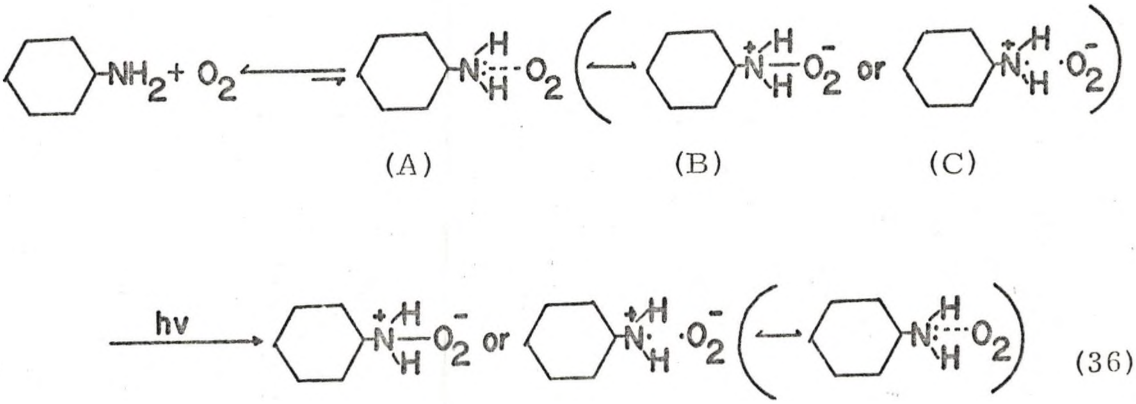
From the linear relationship of Figure 18, the ionization potentials of cyclopentylamine, n-hexylamine, and pyrrolidene can be predicted as 8.60, 8.71, and 7.98 ev, respectively. It seems reasonable that the ionization potential of the secondary amine, pyrrolidene, is lower than that of primary amines because of the inductive effect. Also, the ionization potential of pyrrolidene, 7.98 ev, obtained from Figure 18, is identical to the theoretically calculated value.[103]

Primary Process of the Photooxidation of Cyclohexylamine

The products found upon irradiation of the oxygen-saturated cyclohexylamine solutions are cyclohexanone oxime, cyclohexylidenecyclohexylamine, ammonia, and water. Besides products mentioned above, cobalt(II) acetate reaction and iodometric titration indicated that peroxides are also formed in the reaction mixture from the photooxidation of cyclohexylamine.

The tail-end absorption of cyclohexylamine $(n \longrightarrow \sigma^*)$ could conceivably have absorbed enough light and given rise to the reaction product, i.e., excited state amine could have entered into chemical reactions or dissociated into radical fragments. In exploring this possibility, the nitrogen-saturated cyclohexylamine solution was irradiated with light which had been passed through a Pyrex immersion well which excluded light of all wavelengths shorter than 280 nm. There was no product observed under this condition, hence the tail-end light absorption of cyclohexylamine was not essential to reaction. With the Pyrex well, irradiation of an oxygen-amine solution for 3 hours produced 1.12 x 10^{-2} M of cyclohexanone oxime and 3.81 x 10^{-2} M of N-cyclohexylidenecyclohexylamine. The oxygen-cyclohexylamine solution when irradiated with 350 nm light produced 1.27 x 10^{-2} M of N-cyclohexylidenecyclohexylamine and 0.37 x 10^{-2} M of cyclohexanone oxime. Using a 100-W tungsten lamp which excluded all ultraviolet light, no products were obtained. Therefore, the wavelength of light responsible for the photochemical reaction is between 280 nm and 375 nm. This is the region where the charge-transfer complex is the absorbing species for ultraviolet light and the excited species produced there from leads to a photochemical reaction.

With the light absorption assigned to the excitation of a charge-transfer complex, it is desirable to know the nature of the excited state charge-transfer complex and how it can give rise to the resulting photooxidation products. According to Mulliken's theory as described in the Introduction, charge-transfer complex is a hybrid of nonbonded (A) and dative bond (B) or charge-separated structure (C).

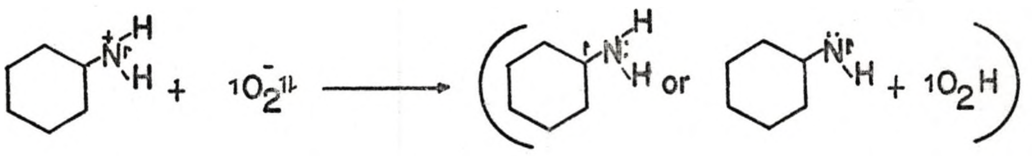


(36)

The ground state of the weak complex has the major contribution from (A) and the excited state from (B) and (C). It should be pointed out that there is a negligibly small stabilization by the donor-acceptor interaction between oxygen and organic molecules,[57, 104] *i.e.*, the electron donor and acceptor are randomly disposed in solution. When they contact each other, momentary charge-transfer takes place which gives rise to a "contact" charge-transfer absorption spectrum.[105]

The excitation process is considered to involve an electron transfer to give a diradical ion pair (C). None-the-less, no electron spin resonance (esr) spectrum of excited oxygen-amine complex has been done to prove this point. Recently, much evidence has been introduced on analogous cases for this purpose. When flash photolysis of N, N-dimethylaniline (DMA) and N, N-dimethyl-*p*-anisidine (DMAN) in highly polar solvent, *i.e.*, acetonitrile, water, and formamide, were studied in an oxygenated environment, absorption spectra showed that DMA and DMAN cations existed.[106] Miller and Wynne-Jones[107] studied complexes of the acceptor, 1, 3, 5-trinitrobenzene, with aliphatic and aromatic amines whether in solution in the amines or in acetone. They obtained an unresolved spectrum which was attributed to $C_6H_3(NO_2)_3^{\overline{\cdot}}$ because its g value (the position of resonance in the esr spectrum is defined as g values which is a function of the ratio of frequency to the applied magnetic field at resonance conditions) and line width corresponded to that for $C_6H_3(NO_2)_3$ dissolved with Na in 1, 2-dimethoxyethane. Both radical cation and anion esr spectra have been observed when complexes composed of p-phenylenediamine or N,N,N',N'-tetramethyl-p-phenylenediamine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were mixed in an oxygen-free flow system.[108]

Assuming that the excited state of the cyclohexylamine-oxygen complex dissociates into radicals, the formation of products can be rationalized on this basis. Both the N<u>H</u> protons and the α hydrogen atoms in the cyclohexylamine cation are loosened by both the presence of a positive charge on the nitrogen atom and the high electron affinity of nitrogen. Thus, they may be abstracted as protons by the oxygen molecule anion radical, giving either the α-aminoalkyl radical (D) or the alkylimino radical (E), and the hydroperoxo radical (F) as shown in reaction 37.

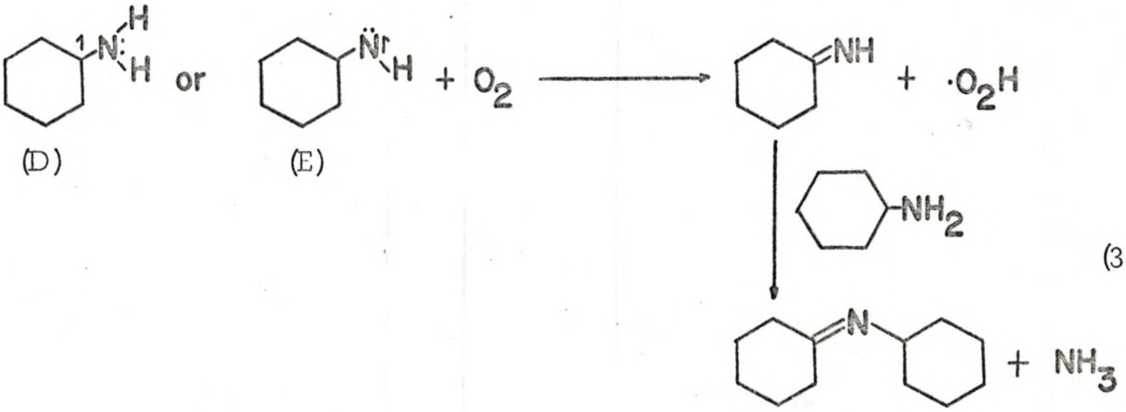


(37)

(D) (E) (F)

From data on the photosensitized oxidation amines,[38-47] the photoreduction of aromatic ketones by amines,[93, 109-112] the photooxidation of ethers,[59-61] and the stability of radical (D), the radical (D) may be more likely than the radical (E) to participate in the reaction. However, the radical (D) alone cannot account for the formation of all the products from the photooxidation of cyclohexylamine. Further evidence on this point will be presented later.

The radicals (D) or (E), and (F) formed in reaction 37 can combine in a solvent cage to give directly either N-hydroperoxycyclohexylamine (NHPCA) or 1-hydroperoxycyclohexylamine (HPCA). However, the spin of the electron on product (D) or (E) must be parallel to the electron on hydroperoxo radical (F). Thus, before hydroperoxides can be formed, the electron spin either on product (D) [or (E)] or (F) must be flipped. In the time required for equilibration to occur, products (D) or (E) have a chance to diffuse out the solvent cage, and probably to contact other molecules of oxygen to form the hydroperoxo radical and cyclohexylimine which then reacts with cyclohexylamine to form N-cyclohexylidenecyclohexylamine, as described in reaction 38. The spin inversion step is consistent with the work on the photooxidation of trans- and cis-decalin.[62] The



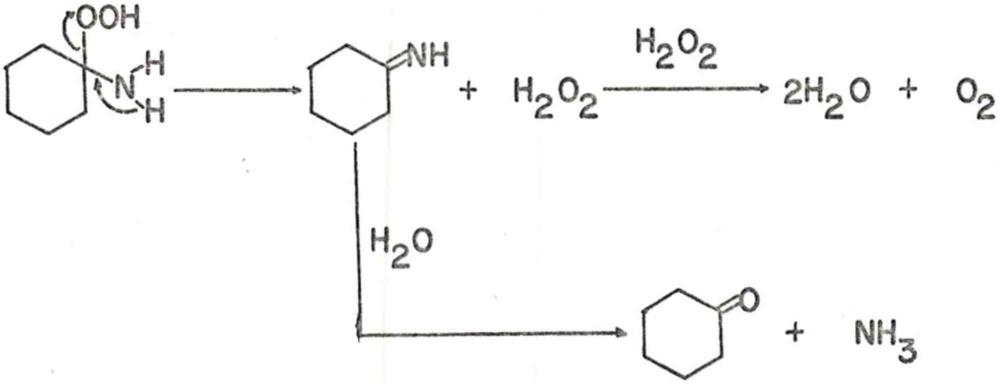
(38)

mechanism for the reaction between radical (D) [or (E)] and the oxygen molecule is in agreement with the results found for the photoreduction of aromatic ketones with amines.[93, 109-112]

Chemistry of Peroxides

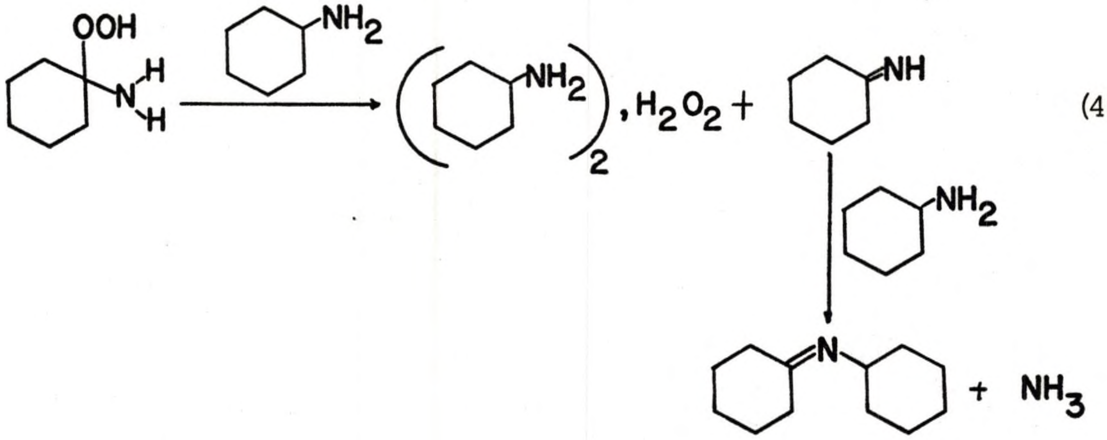
Peroxides were shown to be present in low concentration (4.58×10^{-2} M) in the cyclohexylamine reaction solution by (1) cobalt(II) acetate reaction and (2) iodiometric titration. The identity of the labile peroxides present in the cyclohexylamine reaction solution is difficult to establish because of their low concentrations. Nmr and ir data on the peroxides could not be obtained. The possible peroxides are 1-hydroperoxycyclohexylamine (HPCA), N-hydroperoxycyclohexylamine (NHPCA), and hydrogen peroxide. Although there is no direct evidence that HPCA may be formed in the photooxidation of cyclohexylamine, it has been isolated from the photosensitized oxidation of cyclohexylamine in hydrocarbon solvents.[46]

When a cyclohexane solution of synthesized HPCA[73] was stirred under a nitrogen atmosphere for 5 hours, cyclohexanone and ammonia were the major products. Cyclohexylcyclohexane, which usually forms when cyclohexyl radicals are present, was not observed among the products. These data indicate that HPCA is decomposed thermally according to reaction 39.

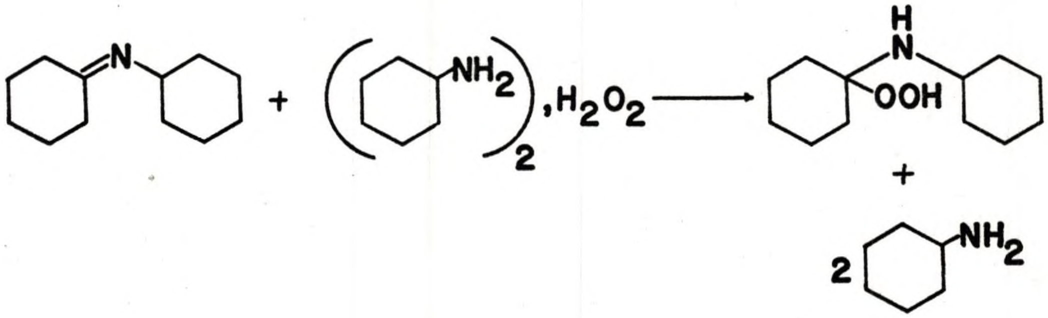


(39)

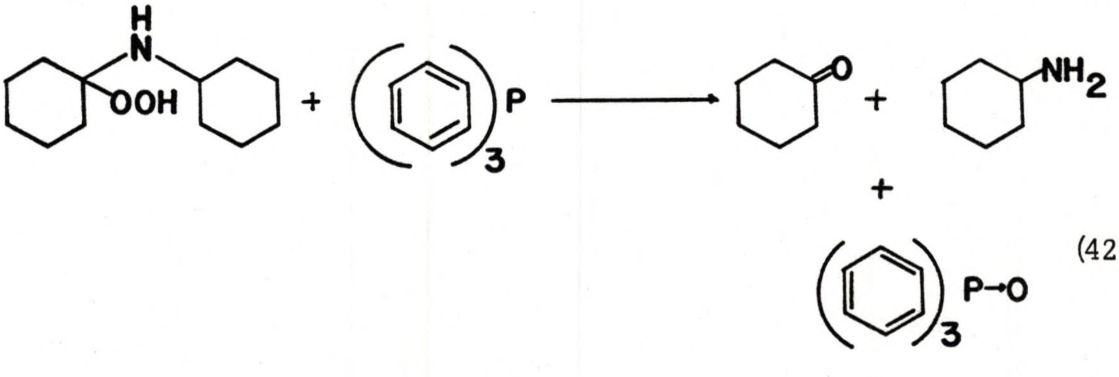
Since triphenylphosphine reacts with alkyl-hydroperoxides at room temperature to produce alkyl alcohols,[72] it was expected that HPCA will react with triphenylphosphine in cyclohexylamine solution to form an alkyl ketone which would then react with cyclohexylamine to generate the corresponding imine. Assuming that this reasoning is correct, the glpc-observed concentration of N-cyclohexylidenecyclohexylamine should increase after treatment of the cyclohexylamine reaction solution with triphenylphosphine. However, the concentration of N-cyclohexylidenecyclohexylamine, instead of increasing, slightly decreased. To explain the contradiction, the following experiments have been done. Injection of a 0.0394 M cyclohexylamine solution of HPCA into the gas chromatograph produced 0.0410 M of N-cyclohexylidenecyclohexylamine. However, injection of the same solution, pretreated with excess triphenylphosphine, produced cyclohexanone and N-cyclohexylidenecyclohexylamine. The amount of the imine present after treating the cyclohexylamine solution of HPCA with triphenylphosphine was only half as great as compared to that of untreated solution. Therefore, the existence of an intermediate which would react with triphenylphosphine to produce cyclohexanone appeared possible. To test this possibility, when cyclohexylamine solution of a synthesized N-cyclohexyl-1-hydroperoxycyclohexylamine (NCHPCA)[74] was injected into the gas chromatograph, cyclohexylidenecyclohexylamine was the only product. Nevertheless, when cyclohexane solution of NCHPCA was stirred with escess of triphenylphosphine under a nitrogen atmosphere for one hour, cyclohexanone, cyclohexylamine, and cyclohexylidenecyclohexylamine were the major products. Hence the decrease in amount of imine after treatment with triphenylphosphine of cyclohexylamine solution of HPCA can be rationalized by reactions 40 to 42.



(40)



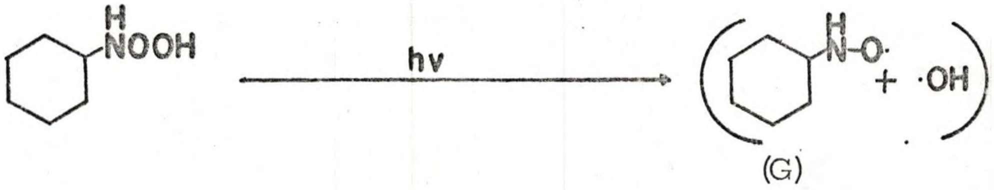
(41)



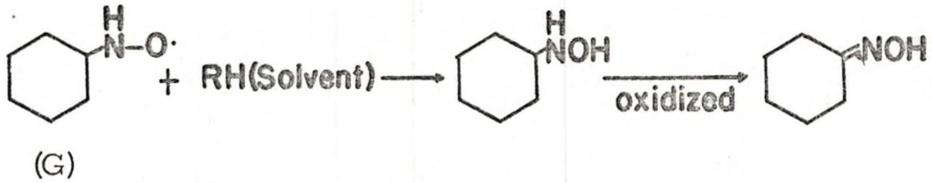
(42)

When the cyclohexylamine solution of HPCA was injected into the gas chromatograph, the amount of N-cyclohexylidenecyclohexylamine was equal to the imine formed from reaction 40 plus the imine produced from the thermal decomposition of NCHPCA obtained from reaction 41. However, when the cyclohexylamine solution of HPCA was first treated with triphenylphosphine to produce cyclohexanone and cyclohexylamine as shown in reaction 42. In the latter case, N-cyclohexylidenecyclohexylamine results from incomplete conversion according to reaction 41. Further proof for the rationalization was provided by the fact that NCHPCA was isolated and identified when HPCA and cyclohexylamine were stirred in dry benzene.[46] The above experiments also demonstrate that HPCA indeed decomposes very rapidly in the cyclohexylamine reaction solution and, if it were formed, would not exist in high concentrations at any given time.

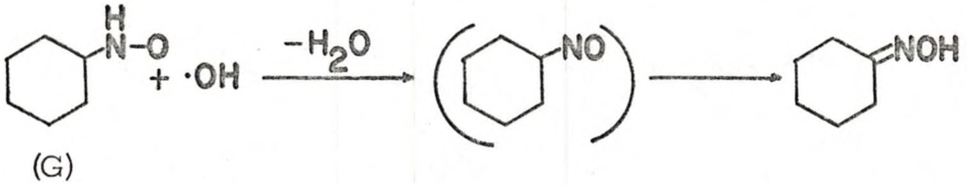
The precursor of cyclohexanone oxime in the cyclohexylamine reaction is more obscure. Irradiation of either HPCA or hydrogen peroxide in cyclohexylamine under a nitrogen atmosphere, showed no cyclohexanone oxime in the photo-mixture. Hence cyclohexanone oxime is probably generated from the other possible hydroperoxide, N-hydroperoxycyclohexylamine (NHPCA). N-Hydroperoxypiperidine has been found in the radiolysis and radiative oxidation of piperidine;[113] and N, N-diethylhydroxylamine was observed in the reaction mixture from the thermal oxidation of diethylamine.[33] Furthermore, when triethylamine, saturated with oxygen, was irradiated at 350 nm, triethylamine oxide was indeed one of the products. Therefore, it is reasonable to assume that NHPCA is present in the cyclohexylamine photooxidation solution. The possible sequence of reactions leading to cyclohexanone oxime is illustrated in reactions 43-45.



(43)



(44)



(45)

NHPCA can presumably be decomposed as described in reaction 43. There are two possible routes leading to the formation of cyclohexanone oxime. (1) The nitrosocyclohexane radical (G) probably will abstract one hydrogen atom from the solvent to form N-hydroxylcyclohexylamine which then is oxidized to produce cyclohexanone oxime[45, 114-116] as described in reaction 44. Indeed, when N-hydroxylcyclohexylamine was stirred with hydrogen peroxide in an ethanol solution under a nitrogen atmosphere, cyclohexanone oxime was isolated and identified. (2) The radical (G) will probably react with the hydroxide radical to form nitrosocyclohexane which then isomerizes to cyclohexanone oxime under the influence of light as described in the photosynthesis of cyclohexanone oxime from NOCl with cyclohexane[117] as shown in reaction 45.

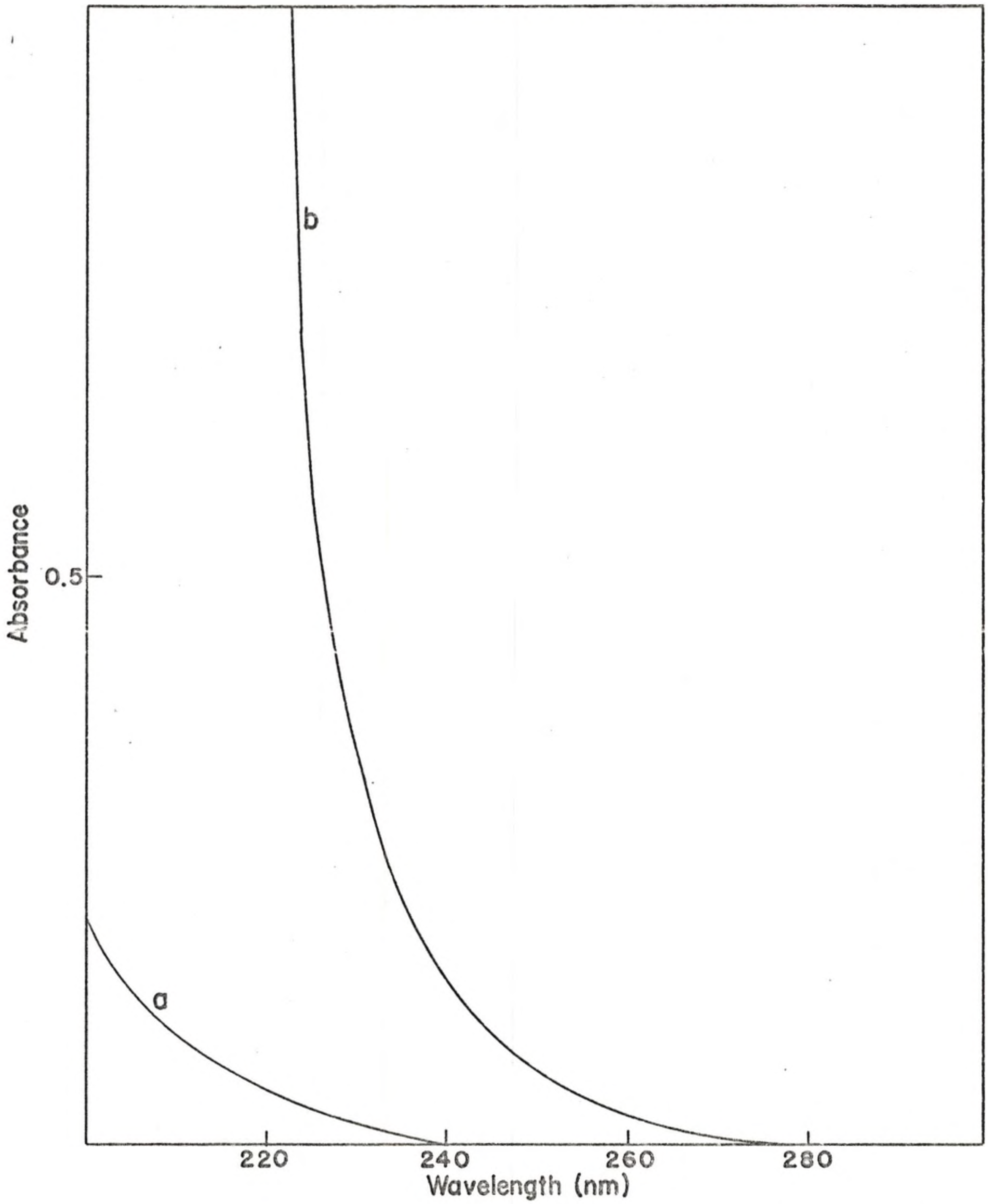
An additional source of N-cyclohexylidenecyclohexylamine during the photooxidation of cyclohexylamine is the photochemical reaction of the cyclohexylamine-hydrogen peroxide adduct. The photolysis of 0.162 mmoles of cyclohexylamine-hydrogen peroxide adduct under a nitrogen atmosphere produced 0.165 mmole of N-cyclohexylidenecyclohexylamine after two and one-half hours of irradiation.

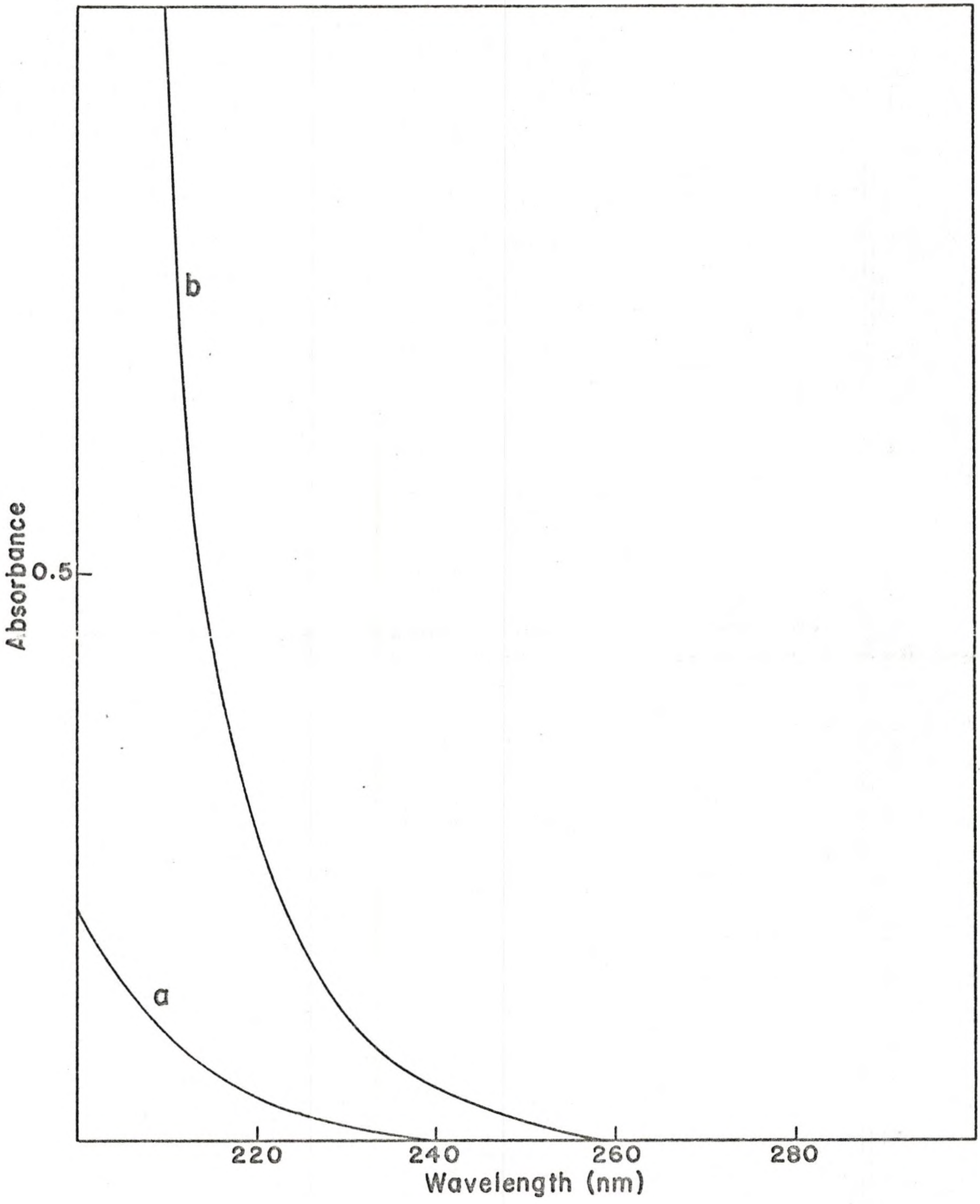
Since the cyclohexylamine-hydrogen peroxide adduct was isolated and identified when cyclohexylamine was oxidized by the method of photosensitized oxidation in a light petroleum,[46] it will be present in the cyclohexylamine reaction solution. Due to the photolysis of hydrogen peroxide at 77° K in the presence of methylamine and diethylamine gave only $CH_3NH\cdot$ and $(CH_3CH_2)_2N\cdot$ radicals as shown by esr spectra,[118] hydrogen peroxide is probably responsible for the free radical mechanism in the photooxidation of cyclohexylamine when the concentration of hydrogen peroxide reaches a certain amount.

Oxygen Uptake of Hydrocarbons

The absorption spectra of high-purity saturated cyclic hydrocarbon into which nitrogen had been passed was transparent to far ultraviolet where the tail-end absorption of hydrocarbon ($\sigma \longrightarrow \sigma^*$) begins. The spectra of oxygen-saturated cyclohexane and cyclopentane with identical nitrogen-saturated hydrocarbon solutions as references, are illustrated in Figures 19 and 20.

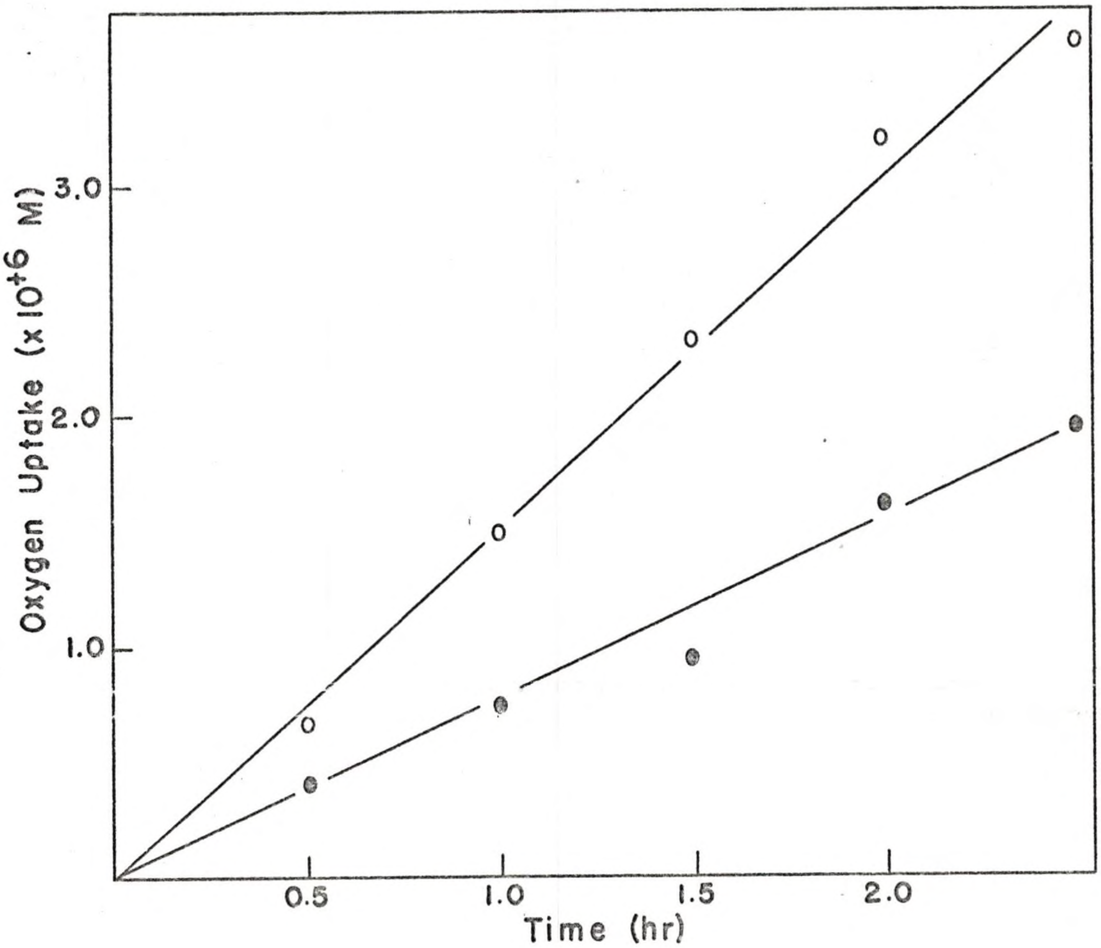
Before the results of the rate studies on cyclohexane and cyclopentane can be discussed, it is necessary to show that their reaction involved a common mechanism. The first item of importance regarding this point is that all of the hydrocarbons in this study when saturated with oxygen have ultraviolet spectra which cannot be accounted for by either of the components alone. These enhanced spectra which show absorption beginning at ca. 250 nm can be removed by bubbling nitrogen through the solutions. This indicates that each of compounds possesses a contact charge-transfer absorption spectrum with molecular oxygen.[57] Since irradiation of such a complex was shown to be the first step in the oxidation of cyclohexane,[63] it is reasonable to assume a similar process takes place with the other hydrocarbons. Furthermore, the same type of products, cyclopentanol and cyclopentanone, were formed in the photooxidation of cyclopentane as cyclohexanol and cyclohexanone were formed in the photooxidation of cyclohexane. Thus, the same mechanism must be operative in these reactions.


Absorbance
0.5
Wavelength (nm)
220
240
260
280
a
b


Absorbance
0.5
b
a
220
240
260
280
Wavelength (nm)

The rates of oxygen uptake for the two cyclic hydrocarbons in the liquid phase are plotted in Figure 21. Because there are differences in the solubility of oxygen in the two hydrocarbons, the solubility was determined, and the data corrected for oxygen concentration differences. It may be seen from Figure 21 that cyclohexane ($-dO_2/dt = 1.52 \times 10^{-6}$ M/hr) reacts more rapidly than cyclopentane ($-dO_2/dt = 0.64 \times 10^{-6}$ M/hr).

In order to rationalize the difference in the rate of oxygen uptake between cyclohexane and cyclopentane, it is necessary to understand the reason for comparing the rates of photooxidation of these hydrocarbons. If the excitation of a contact charge-transfer complex is the preliminary step in the reaction of both compounds, then the rates of reaction should correlate with the stability of the oxygen complexes. This is primarily because there rates depend upon the amount of complex present in the solution which in turn is related to the basicity of the hydrocarbons. In support of this contention, it was shown in the photooxidation of ethers, where a charge-transfer absorption also was the initial step in the reaction, that the relative rates of oxygen uptake correlate with the basicity of the donors.[60] For cyclic compounds, it is known that, as the ring size varies, there are changes in both the hybridization and angle of the carbon-hydrogen and carbon-carbon bonds.[119] As the ring becomes smaller, the "s character" of the carbon-hydrogen bond increases and its basicity decreases, while the basicity of carbon-carbon bond follows an opposite trend. Since the basicity trends of the two bond types as a function of ring size are opposed to each other the relative rates of oxygen



Oxygen Uptake (x 10+6 M)
1.0
2.0
3.0
0.5
1.0
1.5
2.0
Time (hr)

uptake for the photooxidation of the cyclohexane and cyclopentane should indicate which bond is acting as the donor. Conformational effects prevent an unambiguous conclusion.

The results illustrated in Figure 21 are in agreement with the concept that electron donation occurs from the carbon-hydrogen bond, since this bond would be the stronger base in the larger ring, *i.e.*, less "s character." To further substantiate this conclusion, no ring-opened products were observed as would be expected if the carbon-carbon bond were the donor. Also, the rate of product accumulation of *n*-hexane and 3-methylpentane during the induction period were shown to increase with the basicity of the carbon-hydrogen bond, *i.e.*, teritiary C-H > secondary C-H > primary C-H.[64]

Previously, Chien,[120] while studying similar reactions, indicated that there was an induction period where only the charge-transfer absorption takes place. The data on the rates of product formation of *n*-hexane and 3-methylpentane[64] indeed showed the induction period for both compounds. A comparison of the intensity of light used in the two types of studies, *i.e.*, the rate of oxygen uptake and the rate of product formation, demonstrates that in the former the induction period would last one hour. Thus, of the data in Figure 21, only that given for the first hour pertains exclusively to the reaction involving the charge-transfer absorption.

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