

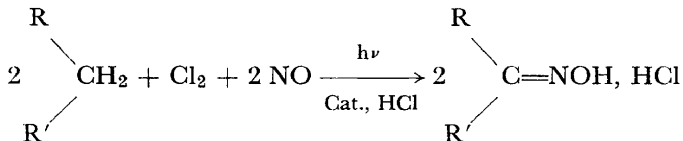
MECHANISM OF THE TÜBINGEN PHOTOOXIMATION REACTION

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INTRODUCTION

Towards the end of the second World War we attempted the preparation of cyclohexanone-oxime (an important intermediate in the synthesis of Perlon) starting from cyclohexane—that means benzene as the basis, by avoiding the then scarce phenol basis. We remembered the experiments of E. V. Lynn who as early as 1919 had obtained a mixture of various n-heptanone-oximes in small yields when he exposed n-heptane together with nitrosyl chloride to sunlight. Furthermore, we wanted to avoid the separate preparation of the offensive nitrosyl chloride. After overcoming the troubles of the postwar period, we were able to develop a special photooximation technique in 1952, and onwards. This photooximation reaction uses the gases nitric oxide and chlorine. By the addition of hydrogen chloride in the presence of a catalyst and a mercury high pressure lamp we were able to obtain the desired cyclohexanone-oxime directly from cyclohexane¹⁻⁴.



In order to facilitate the discussion of the reaction mechanism (discussed later) let me explain first the nature and scope of the photooximation reaction.

NATURE AND SCOPE OF PHOTOOXIMATION

Cycloalkanes

Let us begin with the cycloalkanes. The oxime yields with respect to the chlorine added are given in *Figure 1*. In order to get equivalent conditions in these cases the photooximation was carried out in carbon tetrachloride. Compared to the photooximation of pure cyclanes this results in a decrease in the yield by 3-5 per cent, apparently a solvent effect. Cyclopropane does not react at all, whereas cyclobutane and cyclopentane give very satisfactory yields. Cyclohexane provides the important cyclohexanone-oxime in a yield of about 90 per cent. Every further cyclane homologue can be easily photooximated; we proved this up to cyclododecane.

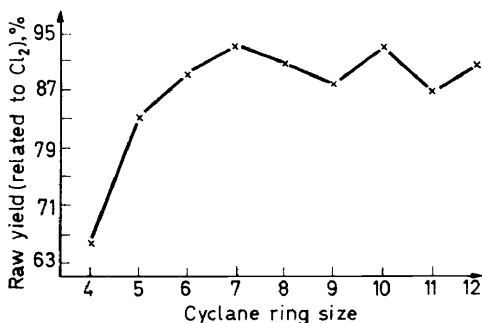


Figure 1. Photooxidation of cycloparaffins (30 per cent in carbon tetrachloride)

Substituted cycloalkanes

The photooxidation of substituted cycloalkanes depends on the nature and number of the substituents. When *alkyl* groups are introduced the oxime yield depends mainly on their size, number, and relative positions. This is shown in Table 1. A methyl group lowers the oxime yield by about 20 per cent as compared to the unsubstituted cyclohexane. As is indicated by the

Table 1. Photooxidation of alkylcyclohexanes

Alkylcyclohexane	Oxime	Raw yield related to Cl ₂ (%)	Isomer distribution		
			<i>o</i>	<i>m</i>	<i>p</i>
		79	1:3	2	1
		50	not determined		
		20	—	—	—
		45	1	2	1
		5	—	—	—

isomer distribution the methyl group particularly influences the *ortho* methylene groups. The same effect occurs with the vicinal cyclohexanes and the symmetrical trimethyl-cyclohexanes; understandably it is strongest with *t*-butyl-cyclohexane.




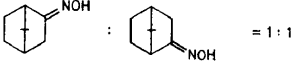

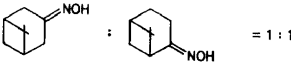

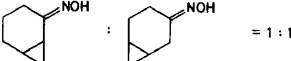

In our runs we found that a methyl group is virtually not attacked, a fact

that will be of special importance for the reaction mechanism. When methyl-cyclohexane is photooximated a trace of cyclohexane carboxylic acid is formed which cannot be isolated but merely betrays itself by its strong disagreeable smell.

Bridged saturated cycles

Let us continue with the saturated cyclic compounds and consider the results of the photooximation of bridged cycles. Strained bicyclanes having little sterical hindrance such as norbornane or norcarane, react relatively well, sterically hindered and strained systems like bornane, pinane, and above all carane on the other hand react weakly. Strainless bridged systems, even




Table 2. Photooximation of bicyclanes

Bicyclane	Oxime yield with respect to Cl ₂ (%)	Isomer distribution
	80	
	40	 = 1 : 1
	37	 = 1 : 1
	51	 = 1 : 1
	24	

adamantane, however, react well and give good yields. Occasionally, as with carane-oxime and very distinctly with adamantane-oxime a faint bluish colouring of the reaction liquid is observed which is caused by the formation of a small quantity of the 1-chloro-1-nitroso-compound. In the case of adamantane the influence of the solvent, which is also otherwise observed, shows up very clearly. The oxime yield in benzene solution decreases to less than half of what it is in carbon tetrachloride solution.

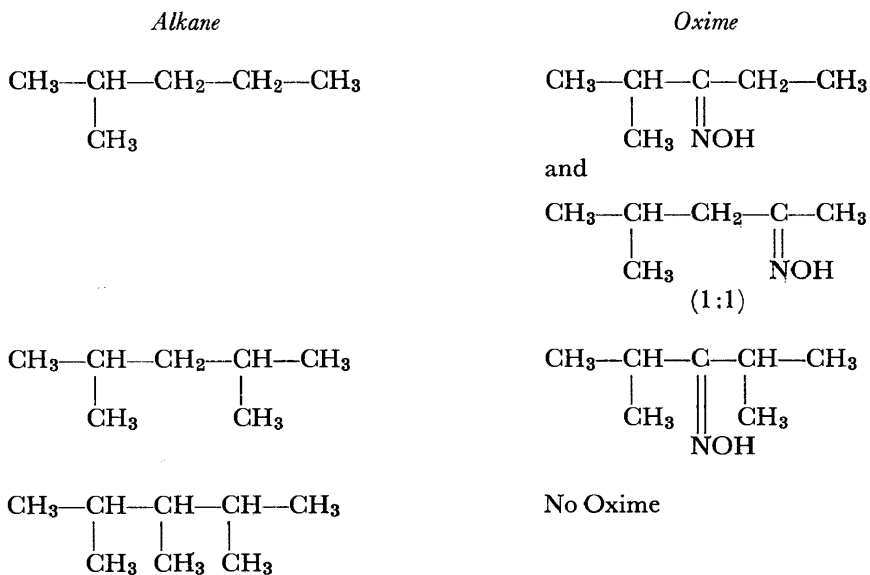
Let us now proceed to discuss the linear saturated hydrocarbons. In the series of n-hydrocarbons from n-butane to n-octane, n-decane, and n-dodecane experiments carried out by P. Baumgartner and A. Deschamps⁵ as well as by ourselves show that the primary carbon atoms, viz. the methyl groups, again do not react. The CH₂-groups, however, do react well and in some cases almost theoretical yields have been obtained.

Table 3. Photooxygenation of bicyclanes

Bicyclane	Oxime yield with respect to Cl ₂ (%)
	70
	60 a:b = 2:1
	63 in CCl ₄ , 27 in C ₆ H ₆

Branched saturated hydrocarbons

When the behaviour of branched saturated hydrocarbons is investigated with respect to photooxygenation, as was done by Baumgartner and Deschamps, the following features can be outlined:



Photooxygenation of branched hydrocarbons (Baumgartner and Deschamps)

Again only those oximes are isolated which are formed by the attack of CH₂-groups. 2,3,4-Trimethylpentane that does not have any CH₂-group reacts very slowly with the nitrosation agent and takes on a faint blue colour. No *tertiary* nitroso-compound can be found. Accordingly there results an almost

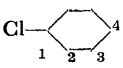
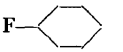
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exclusive reaction specificity of the CH_2 -groups. This reaction specificity may consequently be regarded as an anomaly of photooximation.

Hydrocarbons containing fluorine and chlorine

Besides the steric effects, inductive effects may also be ascertained. When chlorine atoms are introduced into linear or cyclic paraffins the oximation takes place preferentially in the CH_2 group farthest from the chlorine atom (cf. Table 4). The strong electro-negative inductive effect

Table 4. Photooximation of halogenated hydrocarbons

Hydrocarbon	Reaction product	Isomer distribution	
		Exptl.	Theoret.
$\text{Cl}-\underset{1}{\text{CH}_2}-\underset{2}{\text{CH}_2}-\underset{3}{\text{CH}_2}-\underset{4}{\text{CH}_3}$	3-oxime	100	50
$\text{Cl}-\underset{1}{\text{CH}_2}-\underset{2}{\text{CH}_2}-\underset{3}{\text{CH}_2}-\underset{4}{\text{CH}_2}-\underset{5}{\text{CH}_2}-\underset{6}{\text{CH}_3}$	5-oxime	83	25
	4-oxime	16.5	25
	3- and 4-oxime	(35)	} total yield
	3- and 4-oxime	(20)	


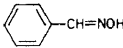
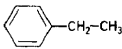

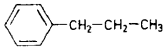
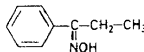
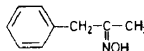
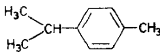
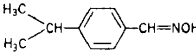
of the halogen atom lowers the electron density of the neighbouring C—H bonds and renders the attack of an electrophilic reagent in the neighbouring positions more difficult. Similar but by no means so marked effects can be noticed in the photochlorination of corresponding hydrocarbons. These results indicate that the attacking reagent of photooximation is particularly selective.

Phenylated saturated hydrocarbons

The introduction of a phenyl core into saturated hydrocarbons involves some changes in the reactivity of the substituted open or cyclic paraffin chain. Lynn has stated earlier that toluene can be transformed into benzaldoxime by nitrosyl chloride. Some examples investigated by Baumgartner-Deschamps and ourselves clearly show the strong directing effect of the phenyl core on the α -position (cf. Table 5). CH_2 -groups in β -positions as in propyl benzene are attacked less, as are primary CH_3 -groups as in ethyl benzene. Tertiary CH-groups as in *p*-cymene do not seem to react either. Baumgartner and Deschamps found only the benzaldoxime derivative. The explanation is evident as the benzyl position is always attacked preferentially. The reaction inertia of tertiary hydrogen atoms can here be interpreted as steric hindrance of the oximation reaction. In no case hitherto could any secondary oximation be observed. The reason is very probably to be found in the low solubility of the oxime hydrochlorides being formed which in this way escapes a further attack of the oximating reagent.

By summarizing the results of all experiments hitherto carried out in the photooximation of various hydrocarbons, it can be established that in

Table 5. Photooxidation of phenylated hydrocarbons (Baumgartner and Deschamps)

Phenylated hydrocarbon	Reaction product	Isomer distribution (%)
		
		100 α -position
	 +	57 α -position 43 β -position
		
		

this reaction CH_2 -groups are attacked predominantly. Steric effects are of particular importance, but inductive and mesomeric effects as well as the characteristic influence of solvents can also be clearly ascertained.

INFLUENCE OF WAVELENGTH ON THE DETERMINATION OF QUANTUM YIELD

For a discussion of the influence of wavelength on determining quantum yield a knowledge of the absorption of the nitrosyl chloride is of special interest.

Spectrum of NOCl

Of all the possible reaction partners only nitrosyl chloride absorbs in the range of the lamps used emitting from 300 to 600 nm (cyclohexanone oxime: $\lambda_{\text{max}} = 216$ nm, $\log \epsilon = 3.39$). The spectrum of NOCl, first measured carefully by S. Katz was verified in its main features in solution by us and is shown in Figure 2. At about 600 nm there are bands of low intensity ($\log \epsilon \sim 0$), followed by two bands at 475–440 nm ($\log \epsilon \sim 0.8$) lying close together and finally a broad band at 335 nm ($\log \epsilon \sim 1.5$). Katz attributes the bands at long wavelengths (~ 600 nm) to vibration terms of an excited state whereas the bands at shorter wavelengths are believed to belong to the dissociation of NOCl into NO and Cl radicals. The experiments mentioned above were all run with a mercury high pressure lamp (Q81 of the Hanauer Quarzlampen Gesellschaft mbH). The maximum of emission is located at about 360–450 nm, but between 300 and 580 nm several other wavelengths are also emitted.

Dependence of photooxidation on wavelength

Cyclohexane—In the oxidation of cyclohexane the light source was varied by replacing the mercury high pressure burner by several luminescence

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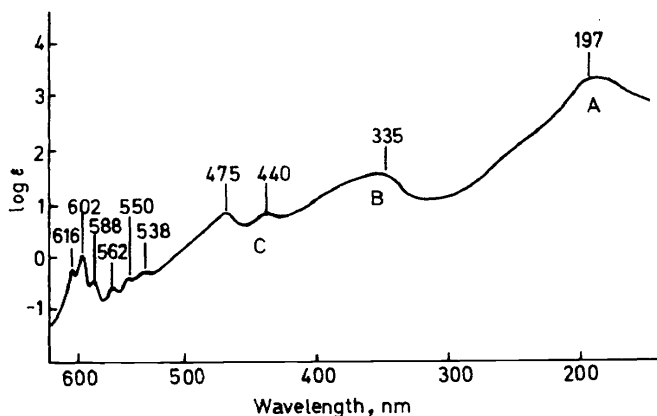


Figure 2. Spectrum of NOCl according to S. Katz

tubes as well as by the thallium lamp and the sodium vapour lamp. Even with the sodium vapour lamp (589 nm) photooxidation can be carried out well. Still higher yields (95 per cent cyclohexanone-oxime) are obtained when the thallium lamp is combined with a filter solution of 3 per cent sodium nitrite that cuts off all wavelengths below 400 nm. Thus besides the line at 546 nm practically only the lines at 535 nm are effective.

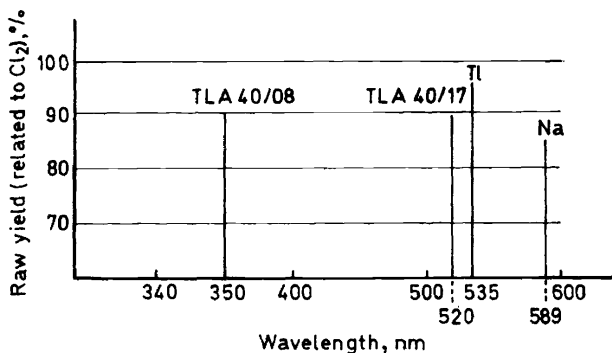


Figure 3. Dependence of photooxidation on wavelength (Tübingen technique)

From the data presented in *Figure 3* an essential fact, however, is not evident which has been of great importance for the industrial development of the photooxidation process. The purity of the oximes increases considerably with the increasing wavelength of the irradiation. The oxime obtained by the thallium lamp has a degree of purity of 97 per cent, the oxime obtained with the sodium vapour lamp of 99 per cent. Because of this reason the purification procedure of such a photo-oxime, that would otherwise be required, might be markedly reduced.

In principle, all wavelengths shorter than 600 nm may be used for photooxidation. However, with regard to the purity of the eventually obtained

plastic materials (Perlon) it is better to cut off the short wavelengths and adopt as far as possible the longer wavelengths.

Methylpentanes—Baumgartner and Deschamps investigated the dependence on wavelength of the photooxidation of 2-methyl- and 2,2-dimethylpentane (Table 6). Shorter wavelengths exhibit a statistical distribution over the

Table 6. Dependence of wavelength on photooxidation (selectivity)

Hydrocarbon	λ (nm)	Isomer distribution	
		3-oxime	4-oxime
$ \begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \\ 1 & & 2 & & 3 & & 4 & & 5 \end{array} $	254 450 589	49 46 42	51 54 58
$ \begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_3 & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & & & & \\ & & \text{CH}_3 & & & & \end{array} $	254 450 589	50 42 39	50 58 61

secondary CH₂-groups whilst the D-line of sodium that lies at longer wavelengths directs more selectively into positions of least steric hindrance. That the selectivity and purity of the formed oximes increase along with increasing wavelength of irradiation is an important clue for establishing the reaction mechanism.

Quantum yield

It is difficult to determine the quantum yield of photooxidation. Because of their low solubility the originating oxime hydrochlorides drop out immediately and make the solution turbid. Thus considerable fabrication of optical measurements can be involved. Therefore, it is not surprising that contradictory data are found in the literature (cf. Table 7).

Table 7. Dependence on wavelength of the quantum yields of cyclohexane

λ (nm)	ϕ (mole/Einstein)	Investigators
365-560	0.6 - 0.76	F. P. 1 348 005 (1963) Toyo Rayon Co.
420	0.87 \pm 0.05	P. Baumgartner and A. Deschamps
450	0.85 \pm 0.05	P. Baumgartner and A. Deschamps
589	0.68 \pm 0.05	P. Baumgartner and A. Deschamps
405	0.85 \pm 0.05	E. Müller, J. Heiß and G. Fiedler ^{5a}
366	0.65 \pm 0.05	E. Müller, J. Heiß and G. Fiedler

A Japanese patent gives ϕ values of 0.6 to 0.7 for the wavelengths from 365 to 560 nm. Baumgartner gave $\phi = 1.3$ to 1.5 for cyclohexane but recently revised this value. Our own not very precise preliminary experiments gave a ϕ value of 0.7 for a wavelength of 589 nm. Recent investigations on cyclohexane by Baumgartner and Deschamps gave quantum yields that indicate

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a slight dependence on the applied wavelengths. Furthermore, when working with benzene as the solvent Baumgartner and Deschamps found a sharper decrease of the quantum yield on diluting than when carbon tetrachloride was used as the solvent; this difference is more marked at shorter wavelengths than at the longer ones.

Our own investigations of the quantum yield and its dependence on wavelength were carried out in a way different from that of Baumgartner and Deschamps. For the wavelengths 366 and 405 nm the quantum flows were measured directly by means of the iron oxalate actinometer. The determination of the oximes was best carried out by a colorimetric method. All these investigations indicate that no radical chain reaction is involved. The quantum yield is certainly less than 1, it is $\phi = 0.85$ at $\lambda = 405-450$ nm for the technically interesting cyclohexane. At shorter wavelengths (366 nm) we found a decrease down to 0.65, probably because side reactions became more significant.

REACTION MECHANISM

General considerations

Let us now discuss the reaction mechanism of photooximation. The reaction between the partners, i.e. between saturated hydrocarbon, nitrogen monoxide and chlorine on nitrosyl chloride and hydrogen chloride is intricate. The general reaction pattern is shown in *Figure 4*. Excess of

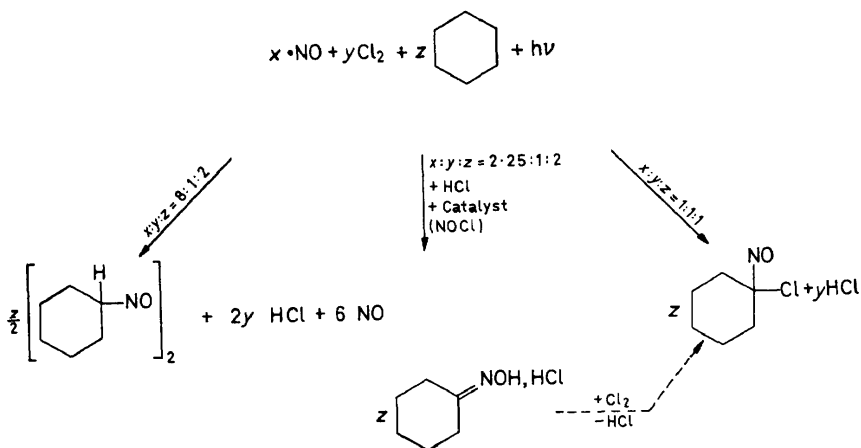


Figure 4. Photoreactions of nitric oxide and chlorine with cyclohexane

NO (on the left-hand side of *Figure 4*) involves the formation of bis-nitroso compounds whereas an excess of chlorine (on the right-hand side of *Figure 4*) produces the blue 1,1-chloro-nitroso compounds. The ratio $\text{NO}:\text{Cl}_2 = 2.25:1$, addition of HCl, and passing the gases over an appropriate catalyst that at once forms NOCl quantitatively give the best oxime yields. We will now deal more thoroughly with this part of the reaction.

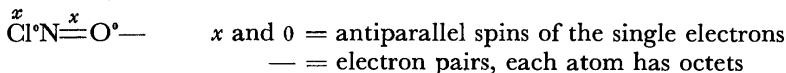
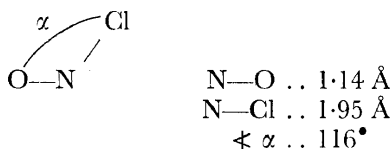
From the above pattern it follows that definite conditions must be observed if the oximation that stands between the formation of a nitroso- and a

chloro-nitroso compound is to take place. Let us remember the most important results that have been illustrated hitherto: (i) Almost exclusive attack of a CH_2 -group; (ii) strong influence of steric and inductive effects; (iii) influence of solvents (well in CCl_4 , badly in benzene); (iv) effective wavelengths, 360–600 nm; (v) quantum yield less than 1 (decreases with increasing wavelength but selectivity is enhanced).

When the mechanism of the photooxygenation reaction is considered two different reactions must be distinguished: the primary light reaction and the subsequent dark reactions. The active agent of the Tübingen technique is nitrosyl chloride that in contrast to Lynn and other later investigators is prepared from the gases NO and Cl_2 immediately before it is introduced into the reaction vessel. Former attempts to work only with the pure gases NO , Cl_2 and HCl lead also to the desired oximes but, because of the low solubility of nitrogen monoxide in cycloalkanes compared to nitrosyl chloride, they give only poor yields and not very pure compounds.

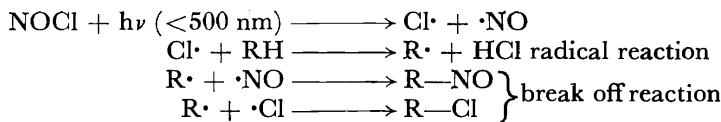
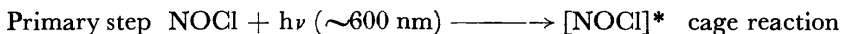
Primary light reaction

Therefore, let us consider first the nitrosyl chloride reaction. What occurs to the NOCl molecule when it is irradiated with light? To answer this question it is useful to recall the results of Linnet concerning the structure of NOCl .



Molecular structure of NOCl according to Linnet

According to these x-ray investigations NOCl has a peculiar arrangement of bonds. The N—Cl bond tends to a one electron bond and the NO -bond to a triple bond. Thus an eventual dissociation into $\text{Cl}\cdot$ atoms and $\cdot\text{NO}$ radicals is performed in the molecule itself.



Primary step: Cage respective radical reaction

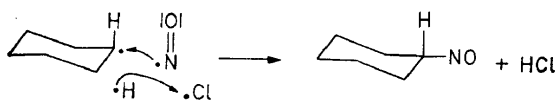
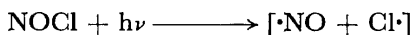
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It is, therefore, natural to assume the existence of a predissociated state of nitrosyl chloride when it is irradiated with longer waves that have less energy. As the energy of the Cl—NO bond is about 38 kcal, light of a wavelength shorter than 750 nm can be thoroughly effective. On the other hand, a dissociation of NOCl into a chlorine atom and an excited NO molecule has to be taken into consideration. Such an excited NO molecule was recently found by Basco and Norrish in the flash photolysis of pure nitrosyl chloride in the gas phase when they used wavelengths shorter than 260 nm. The dissociation into free radicals is then followed by a radical break off reaction by nitrogen monoxide shown in the reaction pattern on the slide.

As the photooximation is run in solution the gas phase results of NOCl cannot be directly compared with our experiments although the primary step of the photoreaction is very probably the same in both cases. In solution nitrosyl chloride molecules are very likely to exist in several excitation states up to full dissociation, the latter being more important at shorter wavelengths—a fact that corresponds to our experimental results. (Influence of solvent also in dependence on wavelength, quantum yield.)

If shorter wavelengths are used the excess energy of the nitrosyl chloride molecules is eventually transferred to the radical fragments thus enabling them to escape from the molecular sphere surrounding them. As the process continues secondary reactions will take place like the formation of mono- or dichloro-compounds, 1,1-chloro-nitroso compound, chlorooximes, unsaturated oximes, and so on, that lower the purity of the oximes obtained as well as their yields.

Cage effect—The experimental results, (e.g., the high yield of very pure oxime when longer waves are used) suggest that under such conditions the primary formation of activated NOCl molecules (predissociation) becomes predominant and controls the reaction mechanism. A predissociated nitrosyl chloride molecule will also be stabilized by the interaction with the solvent molecules that surround it as in a cage. Such a cage of solvent molecules is also suggested by the results of Artemev who detected a marked change in the absorption spectrum of nitrosyl chloride when it was measured in benzene solution. Such a change indicates an interaction with the solvating molecules. On the other hand nitrosyl chloride has a strong dipole moment ($\mu = 2.19$ D in the gas phase, 1.83 D in CCl_4).



4 centre reaction

Study of the reaction mechanism I

In photooxygenation with nitrosyl chloride at low excitation energies it may therefore be assumed that an excited nitrosyl chloride molecule appears which is kept in a cage and effects the nitrosation reaction in a four-centre reaction without any marked origination of free radicals. This hypothesis is practically identical with the assumption of a "narrow" radical pair reacting simultaneously. The postulated cage effect gives rise to further investigations.

Preliminary attempts to prove the origination of free radicals by e.s.r. have still not been successful. That such a reaction via free radicals can occur under totally different conditions is indicated, however, by our experiments using high energy radiation. In the absence of any other radical yielding partner, cyclohexanone-oxime was obtained from cyclohexane, nitrogen monoxide and hydrogen chloride by the impact of a 2 MeV electron beam ($G = 3.9$). Thus it is not unlikely that above a certain limit of excitation energy radicals may be formed when ultraviolet light is used for irradiation. This means that according to the reaction conditions photooxygenation might be directed via two different reaction paths: (i) cage—NOCl, and (ii) independent $\cdot\text{NO}$ and $\text{Cl}\cdot$ radicals. Because of practical reasons the first reaction path is preferable.

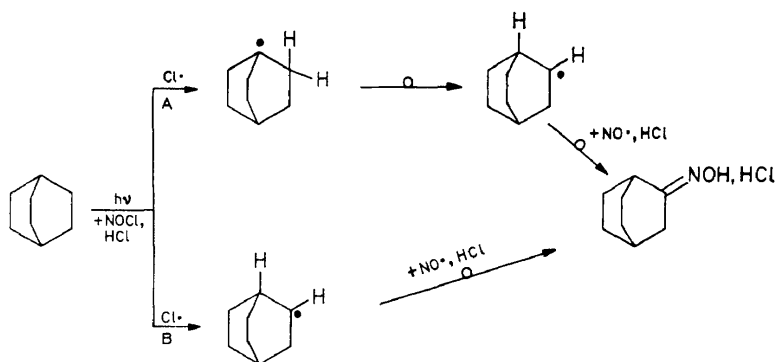
Connection between cage effect and experimental results—Do the experimental results correspond to the interpretation of the mechanism via a preferential cage four-centre reaction? The anomaly of photooxygenation, i.e. the exclusive attack of the CH_2 -group giving a secondary nitroso-compound, agrees with the assumption of a 4-centre-cage mechanism. Equally the great importance of steric effects can be understood since the nitrosyl chloride molecule as a whole or even as an associate with the solvent must have unhindered access to the reaction centre.

As to the effective wavelengths, it is understandable that because of the two competing reaction paths, firstly via a predissociated NOCl molecule and secondly via the decomposition of the NOCl molecule into the free radicals $\cdot\text{NO}$ and $\text{Cl}\cdot$, wavelengths over the whole range up to 600 nm are effective. The purity of the oximes, of course, increases with the increasing weight of the cage-4-centre mechanism and the decreasing weight of the reaction path via free radicals since in the former case no by-products are to be expected.

Experiments with deuterated compounds—In order to secure the 4-centre-cage mechanism we approached the problem in yet another way. We investigated the photooxygenation of bornanes, a bicyclooctane, and an adamantane, all deuterated in the bridge head.

Let it be assumed for the moment that besides the reaction of the predissociated nitrosyl chloride a genuine radical reaction plays an important part. Then in the photooxygenation of the bicyclooctane the attack of the chlorine atom should take place preferentially at the D-atom of the bridge head as is the case in photochlorination.

After the attack of the *tertiary* bridgehead CH a transformation to the secondary CH radical might occur by radicalotropy and eventually the oxime would be formed. The reactivity of the CH_2 group would be sham. That should make itself conspicuous in the deuterated hydrocarbons by a diminished content of deuterium. In the photochlorination of the



bicyclo-[2,2,2]octane the ratio of the reactivities of the *tertiary* bridgehead H-atom to the secondary H-atom of a CH_2 -group is 6:1. Here a similar effect may be expected if photochlorination and photooximation take the same reaction path via free radicals.

Taking into account the isotope effect (estimated according to the radical chlorination since not otherwise accessible) as well as the fact that only one bridgehead in the bicyclooctane compound is deuterated, a maximum loss of deuterium of about 15 per cent is calculated. Mass spectrometer measurements, however, show that the bridgehead deuterium is fully conserved⁶. Experiments, are at present being carried out with 1,3,5,7-tetra-deuterated adamantane. Also in this case all four bridgehead deuterium atoms are fully conserved in the corresponding oxime^{6a}. Corresponding to our previous experience these results also prove that the primary step of photooximation is not the same as in photochlorination.

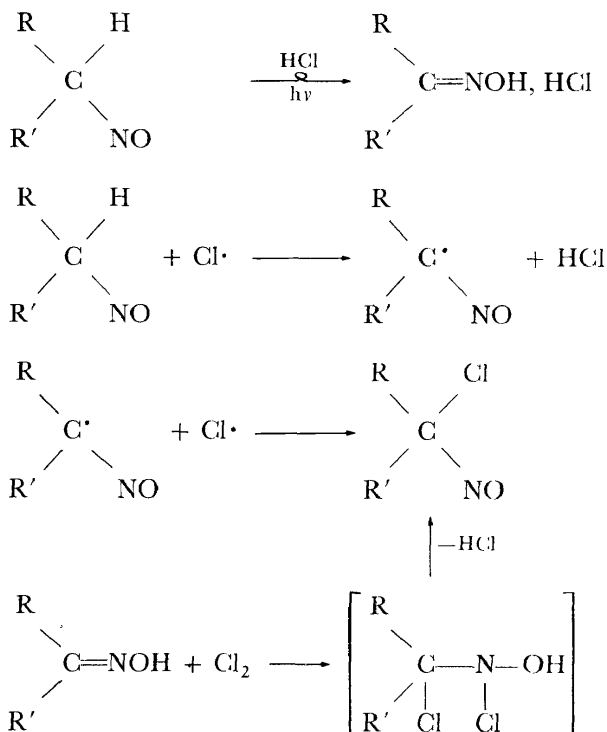
In conclusion we can make the following statement concerning the primary step of the light reaction: the hypothesis of an excited predissociated nitrosyl chloride molecule or of a narrow radical pair and its attack in the cage of the surrounding medium in a four-centre reaction corresponds excellently to every piece of experimental evidence. Further attempts to secure our interpretation of the photooximation reaction are being undertaken.

Secondary dark reactions

Following the primary light reaction leading to a secondary nitroso compound several dark reactions take place that may be directed by the experimental conditions.

In the presence of a high excess of hydrogen chloride the secondary nitroso compound immediately rearranges to the oxime. This rearrangement is catalyzed by the hydrogen chloride and possibly by light (cleavage of the bis-nitroso compound by $\lambda < 300 \text{ nm}$). Because of the low solubility of its hydrochloride the oxime escapes further reactions and falls out in oily drops or in solid colourless crystals.

Under conditions more favourable for the formation of independent



Secondary dark reactions of photooximation

radicals the mostly blue coloured monomeric 1-chloro-1-nitroso compounds originate. They also can be formed from the oximes when chlorine is in excess (last equation in the above scheme).

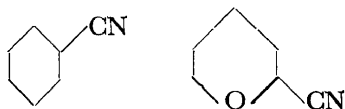
CONCLUSION

Let us finally summarize our results. The importance of photooximation covers not only the scientific but also the industrial field. Here we have the rare case that these two often antagonistic aspects unite. Under usual conditions photooximation is not a radical reaction, as is for example photochlorination, but a cage-4-centre reaction of an excited NOCl molecule. From the industrial point of view the experiments with light of longer wavelengths seem to be particularly with regard to the excellent purity of the oximes obtained although the quantum yields are lower and the apparative requirements higher.

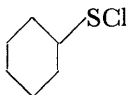
From the scientific point of view the success in photooximation has incited us to look for some other photoreactions with saturated hydrocarbons. We have detected the following cases.

MECHANISM OF THE TÜBINGEN PHOTOOXIMATION REACTION

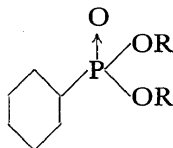
1. photocyanation⁷ with ClCN
(saturated hydrocarbons as well
as ethers), e.g.



2. photosulphochlorination⁸ with
 ClSCl (saturated hydrocarbons),
e.g.



3. photophosphonylation⁹ with
 ClP(OR)_2 (saturated hydro-
↓
O
carbons), e.g.



The mechanisms of these reactions are not known as yet. We are engaged in finding further photoreactions with saturated hydrocarbons. During the last ten years photooxidation has received attention from industrial countries all over the world. In Japan and in the German Federal Republic (by BASF) the process has been developed technically. It is the first photoreaction with "light as reaction partner" of technical importance! But also from the scientific aspect photooxidation offers several attractive problems some of which I had the honour of illustrating to you.

ACKNOWLEDGEMENT

I would like to thank very cordially the following workers for their untiring, and excellent co-operation in the development of the Tübingen photooxidation reaction: Drs. Horst Metzger, Dorla Metzger-Fries, Ulrich Heuschkel, Karsten Witte, Edmund Waidelich, Hans Huber, Eckart W. Schmidt, Hans Gerd Padeken, Manfred Salamon, Gerhard Fiedler, Jürgen Heiß, Martin Fischer, Gernot Baumeyer, and Dipl.-Chem. Ulrich Trense.

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