THE PHOTOLYSIS OF NITROSYL CHLORIDE AND THE STORAGE OF SOLAR ENERGY

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Nitrosyl chloride, dissolved in carbon tetrachloride, is photochemically decomposed by light below 6400 Å. into nitric oxide and chlorine. The quantum yield is reduced by the reverse reaction and values of 0.75 or less up to approximately 1.0 are obtained. Experiments using sunlight with a flowing system are described. The nitric oxide is insoluble and can be stored and later recombined with chlorine in carbon tetrachloride to give the original nitrosyl chloride and release some of the solar energy consumed in the photolysis.

Photochemical reactions are needed which will absorb energy and store the energy of incident sunlight, the products recombining later under controlled conditions with the release of some of the energy. Suitable reactions of this type are dif-ficult to find. The photolysis of nitrosyl chloride is such a reaction. In the gas phase, nitrosyl chloride absorbs most of the visible sunlight up to 6400 Å. and in the absence of oxygen, gives nitric oxide and chlorine according to a first-order reaction. It was thought that nitrosyl chloride dissolved in carbon tetrachloride would undergo similar photodecomposition and that the chlorine would remain dissolved but that the nitric oxide, which is relatively insoluble in carbon tetrachloride, would escape and thus permit separation and storage. The nitric oxide could then be recombined with the chlorine in carbon tetrachloride to give back the original nitrosyl chloride solution with the evolution of heat.

The reaction has been studied in the gaseous phase by Kiss,¹ Bowen and Sharp² and Kistia-kowsky.³ The scheme shown in (1) and (2) has been proposed³

$$NOCl + h\nu \longrightarrow NO + Cl$$
(1)

$$NOCl + Cl \longrightarrow NO + Cl_2$$
(2)

where the light absorbing step is followed by the very fast reaction 2. This reaction scheme has been confirmed by some recent investigations,⁴ where it was found that chlorine atoms catalyze the reaction by accelerating step 2.

Experimental Results

The photodecomposition was followed at constant temperature by measuring as a function of time the pressure of nitric oxide produced photochemically and released into the gas space.

gas space. The apparatus consisted of a 500-watt tungsten projection lamp, a large glass lens, a shutter and a filter. The circular reaction vessel of Pyrex glass, 1 cm. in thickness, is placed in a Pyrex thermostat, kept at a constant temperature to $\pm 0.2^{\circ}$. From the top of the reaction vessel a connection leads to a mercury manometer. Thorough stirring was carried out during the whole experiment by means of a magnetic stirrer.

The energy of the incoming light was measured with a sensitive bolometer, previously standardized by a carbon filament lamp provided by the U.S. Bureau of Standards. This bolometer was placed in a Wheatstone bridge with a multiflex galvanometer. The energy absorbed by the nitrosyl chloride was obtained from the difference in transmission of pure carbon tetrachloride and the carbon tetrachloride solution of NOCl.

Figure 1 gives the decomposition curves, which show the pressure of nitric oxide released (in mm.) as a function of the time of irradiation. The different curves give the results with different light intensities. As in the gas phase experiments, a steady state is reached when the products, nitric oxide and chlorine, accumulate to such an extent that the reverse reaction is equal to the forward photochemical reaction. The sharp decrease in pressure shown in the curves occurs when the light is turned off. Figure 2 gives the volume of NO liberated in another set of experiments.

reverse reaction is equal to the forward photochemical reaction. The sharp decrease in pressure shown in the curves occurs when the light is turned off. Figure 2 gives the volume of NO liberated in another set of experiments. The determination of quantum yields for the photodecomposition and separation is only approximate. The light used extended continuously over the whole visible spectrum in order to simulate the conditions of a practical reaction operating with sunlight. The quantum yield in the gaseous phase is 2. In solution

The quantum yield in the gaseous phase is 2. In solution Atwood and Rollefson⁵ determined the quantum yield of the photo-oxidation of a similar reaction (nitrosyl chloride + O_2 to give NO₂ + Cl₂) and found it to be between 0.47 and 0.72.

The back reaction between chlorine and nitric oxide has been investigated by Trautz and co-workers⁶. It is a thirdorder reaction with an exothermic heat of reaction of 9000 cal. per mole of NOCl formed. The two gases react slowly at room temperature and the reaction is complete over charcoal at slightly increased temperatures.⁷ It was found in the present investigation that the reaction is quite rapid in carbon tetrachloride even at room temperature.

In order to store the energy absorbed in the photochemical reaction, the reaction products must be separated and then recombined at a later date. This separation can be performed (a) in the gas phase by removing one of the products by adsorption or absorption, (b) in a solution by dissolving one but not both of the products of photolysis. The first method is difficult because the products recom-

The first method is difficult because the products recombine before diffusing to the surface of the adsorbent or absorbent, or at the catalytic surface of an adsorbent.

In the present work the second method was chosen using carbon tetrachloride as the solvent for nitrosyl chloride. Chlorine also is soluble to a large extent, whereas the nitric oxide formed is practically insoluble and escapes into the gas space above the solution. Nitrosyl chloride in carbon tetrachloride shows continuous optical absorption and the shape of the absorption curve is the same as that given in the literature for nitrosyl chloride in the gas phase.⁸

It is likely that the quantum yield is lower in carbon tetrachloride solution than in the gas phase because of the Franck-Rabinowitch cage effect of solvent molecules, which increases the rate of recombination of the nitric oxide and chlorine. The bolometer circuit measures only the amount of incoming and transmitted energy. To obtain the number of quanta absorbed over the whole range it is necessary to calculate a mean value from the energy distribution in the different wave lengths for a 500-watt tungsten projector lamp and the number of quanta per erg for each wave length. A

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Fig. 1.--Pressure of nitric oxide in a stationary system exposed to light.



Fig. 2.---Volume of nitric oxide released by exposure to light in a stationary system.

further small correction is needed to allow for the fact that the per cent. of light transmitted and measured by the bolometer is less at the shorter wave lengths where nitrosyl chloride absorbs more strongly.

The calculated quantum yields of decomposition and separation are shown for different concentrations in Table I.

These quantum yields are calculated for the initial reac-tion corresponding to the first steep part of the decom-position curves shown in Fig. 1. The quantum yields decrease as the reaction proceeds due to the increasing con-contraction of the specific products which excellents the centration of the reaction products which accelerate the back reaction. After long exposures with the light intensity used in these experiments a steady state is reached, where the quantum yields drop to values from 0.05 to 0.1. Flow System.—The previous experiments were carried

out in a stationary system in which the photo products,



Fig. 3.—Pressure of nitric oxide in a flowing system exposed to light.



Fig. 4.-Volume of nitric oxide released by exposure to light in a flowing system.

TABLE I

QUANTUM YIELDS FOR THE PHOTOLYSIS OF NOCL IN CCL Solutions

Concn. NOCl, moles/l.	I	II	III	IV		Av.
0.246	0.68	0.77	0.80	1.0		0.83
.371	0.53	0.67	0.67	0.87		0.74
.511	0.75	0.81	0.91	0.94	1.00	0.94
.646	0.95	1.01	1.14			1.08

chlorine and nitric oxide, accumulate. For storage of the converted light energy it is necessary to minimize this back reaction and prevent the decomposition products from re-combining. Two different types of back reactions occur: (1) The recombination in the liquid carbon tetrachloride phase, whereby the products in solution react to form nitrosyl chloride at a rate which depends on their concentration in solution. (2) The back reaction between the chlorine in solution and the nitric oxide in the overlying gas space. The nitric oxide in the gas space reacts at the surface of the carbon tetrachloride solution with the dissolved chlorine. This type of reaction can be seen in the curves of Fig. 1, where after turning off the light the pressure decreases rapidly as the nitric oxide molecules react with the solution. The velocity of this recombination is limited by the diffusion of chlorine molecules to the surface and the decrease in pressure is faster when the solution is stirred.

The best way to reduce the amount of back reaction due to the increasing concentration of the reaction products is to use a dynamic system in which the carbon tetrachloride solution of nitrosyl chloride is removed continuously from the photo reaction vessel. The photochemical reaction then proceeds with a high quantum yield as indicated by the first, steep part of the curves of Fig. 1. The streaming velocity of the solution through the photocell is kept at a rate which does not allow an accumulation of chlorine molecules during the time that the solution is in contact with the nitric oxide gas phase. Another advantage of this dynamic method is that the chlorine does not accumulate and provide an inner optical filter which absorbs some of the light and prevents it from reaching the NOC1.

A few experiments with the dynamic system were made in direct sunlight which was focussed onto a 500-ml. round bottom flask containing the carbon tetrachloride solution of nitrosyl chloride and placed between two 5-liter storage containers. The carbon tetrachloride solution of nitrosyl chloride flowed through the photochemical reaction chamber of 500 ml. at a rate of about 30 ml. per minute.

From the top of the reaction vessel a connection led to a container for storing the nitric oxide gas. Figure 3 gives

the pressures of nitric oxide produced in the photolysis, by focussed sunlight, of the flowing solution of NOCl in carbon tetrachloride. It is evident that the curves retain their steep slope much longer than the curves shown in Fig. 1, obtained with the stationary system, because the reverse reaction, the recombination of nitric oxide and dissolved chlorine, is suppressed.

In Fig. 4 the evolution of nitric oxide produced by the photolysis in focussed sunlight of nitrosyl chloride is shown as measured in the flowing system. The amount of nitric oxide formed photochemically increases continuously with irradiation time, showing that the reverse reaction is small.

Conclusions

These experiments show that it is possible to bring about an endothermic reaction with sunlight, to separate and store the products and to get back as heat part of the absorbed sunlight, when desired. The photochemical reaction has a reasonably high quantum yield approaching 1, and it absorbs most of the sunlight in the visible range of the spectrum. It is of the general type to be sought after for the utilization of solar energy but the energy storage per gram of material is low and it is hoped that much better photochemical reactions making use of these general principles will be found and tested.

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KINETIC COMPLICATIONS ASSOCIATED WITH PHOTOCHEMICAL STORAGE OF ENERGY

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If energy is to be stored in a photochemical process, the initial act of absorption of a photon must be followed rapidly by additional reactions. These can be classified according to whether or not a non-absorbing species must react either with the excited absorber or with a fragment formed from its dissociation. Because of the compressed time scale in which many of these additional reactions must occur, the kinetic treatment requires consideration of the special problems associated with very fast reactions.

Introduction

The principle of microscopic reversibility requires that if the ground electronic state of a chemical species absorbs radiation efficiently, then the rate constant must be large for re-emission by the excited state first produced. Therefore, if a system is to store photochemical energy, the primary act of absorption must be followed very rapidly by secondary processes that make it improbable the initial excited species will be regenerated.

Three types of secondary processes can be considered. First, some of the energy of the original quantum may be dissipated in thermal motions leaving the absorbing molecule in a metastable triplet state. If selection rules forbid conversion to the ground state with emission of radiation, and if a considerable energy barrier opposes regeneration of the initial excited state, the metastable state may live for some time and thus store a large fraction of the energy of the original quantum.

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Second, the energy of the excited absorber may be transferred by electronic excitation or chemical reaction with another molecule that does not absorb or emit radiation. Entropy restrictions then help to prevent regeneration of the excited state formed in the primary absorption.

Third, the absorbing molecule may be dissociated into fragments during or soon after the primary absorption. If these fragments are then separated by diffusion, entropy restrictions can again oppose regeneration of the initial excited state.

Because the secondary processes must frequently take place in times of the order of 10^{-9} second if reemission is to be prevented, the kinetics may exhibit features that are not important when molecules are allowed longer times in which to react.

In this paper, we shall classify secondary processes according to whether or not there is dissociation of the original absorber and whether or not a large fraction of the energy of the original