The rate data obtained from the experiments are given in Table II. The initial partial pressures of the reactants are given to show the variations in the initial pressures used. The pressures were assumed to be reliable to ± 0.2 mm. and the temperatures to ± 0.05°. The rate constants, in dimensions of $(\text{mm.}^{-1})(\text{hr.}^{-1})$, were computed from the slopes of lines drawn through the plotted data.

In experiment 7, the surface area of the reaction vessel was increased by a factor of about five by placing nickel wire mesh in it. The volume change was negligible. In experiments 3, 5 and 9, another reaction vessel of approximately twice the original volume was used. The fact that variations in the surface and volume had no effect on the rate indicates homogeneous behavior of the reaction.

The activation energy for the reaction was determined by plotting the logarithm of the rate constant against the reciprocal absolute temperature as shown in Fig. 1. The activation energy calculated from the slope of the line is 14 kcal. per mole. This activation energy is a reasonable value for a homogeneous bimolecular reaction. The linear nature of this plot is in accord with a reaction of this type.

Acknowledgment.—The authors wish to thank Mr. William Lechnick for his assistance in performing the experimental determinations.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolysis of Ketene at 3650 Å. in the Presence of Oxygen[1]

BY GERALD B. PORTER[2]

RECEIVED DECEMBER 21, 1956

The photolysis of ketene at 3650 Å. was investigated in the presence of oxygen. Even at low concentrations, oxygen virtually eliminates the dissociation of ketene into carbon monoxide and methylene radicals at room temperature. There is a direct reaction of oxygen with excited ketene molecules which leads to carbon monoxide and carbon dioxide among the products, but which gives very little ethylene. Within experimental error, the quantum yield of formation of carbon monoxide is equal to that of oxygen consumption. All quantum yields are small and the principal reaction of oxygen is deactivation of excited ketene molecules. At low oxygen concentrations, the quantum yields, with the exception of that of ethylene, show maxima at about 5×10^{-6} mole of oxygen/liter (about 0.1 mm. pressure). At 160°, there is an intensity dependent chain reaction with oxygen.

The photochemistry and photoöxidation of ketene have been studied extensively at wave lengths near 2700 A.[3,4] At these wave lengths, dissociation into methylene radicals and carbon monoxide occurs with a quantum yield of unity. At 3650 Å., near the long wave length limit of absorption, the quantum yields are small and are functions of pressure. This effect has been interpreted to mean that electronically excited ketene molecules are formed. The excited ketene molecules may in turn dissociate, internally convert or suffer collisional deactivations.[3,5,6]

In the presence of oxygen at 2700 Å., the products include carbon monoxide, carbon dioxide, formaldehyde and ethylene.[3,4] The ethylene quantum yield is reduced somewhat by the addition of oxygen, but does not fall below 0.67.

At about 1 mm. of oxygen, the products are formed in different ratios at 3650 Å. compared with those formed at 2700 Å.[3] Since the photolysis of ketene at 3650 Å. almost certainly involves the formation of electronically excited molecules, the difference in the ratios of products at these two wave lengths may be interpreted as reaction of oxygen with excited molecules at the longer wave length, rather than with radicals as at the shorter wave length.[7]

The photoöxidation at 3650 Å. has now been studied in some detail. Only two other examples of oxygen-excited molecule reaction have appeared in the literature.[8,9] One of these[8] is somewhat ambiguous. This study may aid in interpretation of the photochemical decomposition of pure ketene and of the various electronic states that are formed.

Experimental

The experimental procedure and apparatus have been described.[3,4] The 3650 Å. lines from a British Thomson-Houston Hg lamp ME/D 250 watt were isolated on the short wave length side by a Corning filter #7380 and on the long wave length side by the rapid decrease in absorption coefficient of ketene. A cylindrical quartz cell with a volume of 78 ml. was enclosed in an electrically heated brass block and was connected to a magnetically driven centrifugal stirrer to circulate the gases in the cell. In the work at low oxygen concentrations, a 1-liter bulb was included in the cell-stirrer system and oxygen was dosed into the cell at frequent intervals to avoid serious oxygen depletion.

The dosing technique is somewhat different than that previously employed[3,4] in that a sample of oxygen was measured into the Toepler–McLeod gage,[3] then part of this was pumped into the cell. This amount and the amount of further additions during a run were determined by measuring the remaining oxygen in the Toepler–McLeod gage. Thus the oxygen concentration during a run could be calculated after the rate of oxygen consumption had been measured. The rate of addition of oxygen was determined by trial and error.

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[1] This work was supported in part by contract with the Office of Naval Research, United States Navy, and the Chemistry Division, Air Force Office of Scientific Research, United States Air Force. The material in this article may be reproduced or used in any way by the United States Government.

[2] Postdoctoral fellow 1954–1956 under a grant from the Shell Fellowship Committee. Department of Chemistry, University of British Columbia, Vancouver, Canada.

[3] A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 2358 (1954). This reference cites earlier work.

[4] R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **79**, 4831 (1957).

[5] W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956).

[6] G. B. Porter, THIS JOURNAL, **79**, 827 (1957).

[7] G. B. Kistiakowsky and K. Sauer, *ibid.*, **78**, 5699 (1956).

[8] F. E. Blacet and D. H. Volman, *ibid.*, **61**, 582 (1939).

[9] R. Livingston and K. E. Owens, *ibid.*, **78**, 3301 (1956).

The quantum yields were determined by comparison of the rates of product formation in the oxidation with the rate of formation of carbon monoxide in the photolysis of pure ketene, for which the quantum yields are known.[3] The radiation was also monitored with an RCA #935 phototube.

Results

The quantum yields at room temperature are shown in Fig. 1 as a function of oxygen concentration. The quantum yields of carbon dioxide are not shown because of the excessive scatter of the points. After correction for carbon dioxide in the ketene supply, the data indicate that the quantum yield of carbon dioxide is about half that of carbon monoxide. All of the quantum yields are small but are essentially constant at concentrations of oxygen above about 2 × 10^{-5} mole/liter. The ethylene yield is quite small, but does not go to zero at high oxygen concentrations. The quantum yields of carbon monoxide and of oxygen pass through a maximum at about 5 × 10^{-6} mole/liter of oxygen.

At 160°, all quantum yields are higher, as is the quantum yield of carbon monoxide in the absence of oxygen. There is definite evidence for an intensity dependent chain reaction as shown in Table I. A chain reaction is also found at 160° at 2700 Å. wave length.[4]

TABLE I

QUANTUM YIELDS IN THE PHOTO OXIDATION OF KETENE AT 160° AND AT 3650 Å.

(K) × 10^{+8} moles/l.	(O_2) × 10^{+5} moles/l.	Ia × 10^{10} Einsteins/sec.	Φ_{CO}	Φ_{O_2}	$\Phi_{C_2H_4}$
1.87	3.94	179	0.51	0.62	0.017
1.88	4.45	54	.62	.74	.036
1.87	4.11	2.2	.99	.99	.056

Discussion

It is apparent from the data at room temperature that dissociation of excited ketene molecules is suppressed by oxygen. At 2700 Å. where dissociation does occur in the presence of oxygen, ethylene is always a product with a quantum yield of at least 0.67. Since the ethylene quantum yields are smaller in these experiments by a factor of 15 than those in the photolysis of pure ketene at 3650 Å. and since all of the quantum yields are essentially constant above an oxygen concentration of 2 × 10^{-5} mole/l., it can be assumed that the only reactions occurring at high oxygen concentrations are

$$K + h\nu = K' \qquad (1)$$

$$K' + O_2 = \text{Products} \qquad (2)$$

$$K' + O_2 = K + O_2 \qquad (3)$$

The small amount of ethylene formed at high oxygen concentrations may either be a product of reaction 2 or represent some dissociation which arises from short wave length radiation transmitted by the filter. Since the effect of wave length on dissociation is unknown except at 2700 and 3650 Å., the distinction between these possible sources of ethylene cannot be made at the present time.

If reaction 2 is assumed to be the only reaction which consumes oxygen or produces carbon monoxide at high oxygen concentrations, then

$$-\Phi_{O_2} = \frac{k_2}{k_2 + k_3} \qquad (4)$$

and $k_2/k_3 = 0.025$. The principal reaction of excited ketene molecules with oxygen is deactivation.

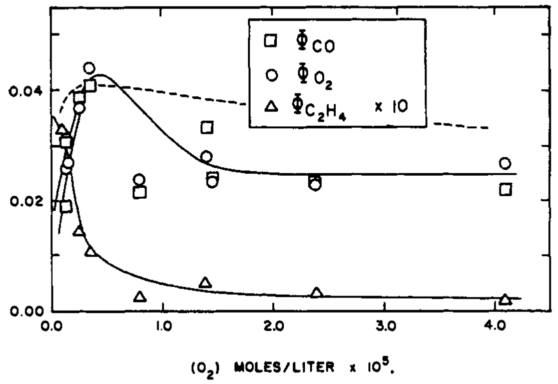

Fig. 1.—Quantum yields in the photochemical oxidation of ketene at 3650 Å.: ketene concentration, 5.5 × 10^{-3} moles/l.

This result is in contrast with data obtained with biacetyl and oxygen[10] which indicate that oxygen reacts with, rather than deactivates, excited biacetyl molecules. The reaction almost certainly involves only the triplet state of biacetyl. Tentatively, these results indicate that a triplet state is not formed to any great extent in the photolysis of ketene or that, if a triplet state is formed, it is not reactive with oxygen. However, fluorescence has not been observed from ketene and little is known about the electronic states formed.

All quantum yields except that of ethylene pass through maxima at an oxygen concentration of about 5 × 10^{-6} mole/l. Above this concentration, the data show a rapid decrease of the quantum yields as the oxygen concentration is increased, until at and above about 2 × 10^{-5} mole/l., all quantum yields are constant. Since it is unlikely that we are dealing with a chain reaction at room temperature, there must be a deactivation reaction involving the oxygen concentration to a higher power than that leading to reaction to explain the maxima. Such a reaction may involve the formation of an addition compound of oxygen and excited ketene molecules which may either dissociate to form products or be deactivated by further collisions with oxygen molecules. This mechanism reproduces the general shape of the curve, but the calculated curve, as shown by the dotted line in Fig. 1, decreases more slowly than the experimental curve at the higher concentrations.

A complete mechanism which leads to the products found cannot be written at the present time. The fact that the quantum yields of carbon monoxide formation and of oxygen consumption are equal (except at low oxygen concentrations, where it would be expected from the data at 2700 Å. that $\Phi_{CO} > \Phi_{O_2}$) may be fortuitous. However, if reaction 5 is written

$$K' + O_2 = CO + CH_2O_2 \qquad (5)$$

the radical CH_2O_2 would have to react to form CO_2 and other products such as acetaldehyde but not to form ethylene or carbon monoxide or use more oxygen. Unfortunately, an analysis was not made for acetaldehyde.

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[10] G. B. Porter, unpublished work.

There are insufficient data to draw many conclusions about the reaction at 160°. The strong dependence of the quantum yields on absorbed intensity shows that there must be a chain reaction. There is also a chain reaction at the same temperature at 2700 Å. which shows a similar dependence on absorbed intensity. The ethylene yield increases at 3650 Å. with decreasing intensity whereas it is constant at 2700 Å. This result would mean that ethylene is formed in the chain reaction at 3650 Å. and in a chain stopping reaction at 2700 Å. However, this conclusion cannot be verified at present.

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ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

The Imine Radical[1]

BY FRANCIS OWEN RICE AND CHESTER GRELECKI

RECEIVED DECEMBER 3, 1956

We have made an over-all weight balance of the decomposition that occurs when hydrazoic acid is passed through a quartz furnace at about 1000° and 0.1 mm. pressure and the products brought in contact with a cold finger placed 1 to 2 cm. beyond the outlet end of the furnace. Under these conditions we find that only 5 to 10% of the hydrazoic acid entering the furnace can be recovered from the cold finger on warming to room temperature. No other gas comes off and the only other product is ammonium azide. Our experiments are in accord with the over-all equation $6HN_3 \rightarrow 7N_2 + H_2 + (NH)_4$. All experiments with the blue material should be done behind a safety glass screen. While we have had only one explosion out of several hundred experiments, it was extremely violent and completely demolished the apparatus. After this experience we used very small deposits on the cold finger and found that under these conditions the transition from blue to white occurs at about −150 instead of −125°. We also measured the absorption spectra of the blue material produced thermally, electrically and photochemically. All three show strong absorption in the ultraviolet characteristic of ammonium azide and all three show a broad absorption band with its center at about 6500 Å. The blue material that is produced electrically and photochemically shows a second absorption band with its center at about 3500 Å. Both bands disappear at the transition temperature.

Introduction

In two earlier papers[2] are described the conditions necessary for the preparation and stabilization of the intermediate formed during the thermal, electrical or photochemical decomposition of hydrazoic acid. Thus when hydrazoic acid vapors at low pressure are drawn through a hot tube at 1000°, a portion of the products may be frozen out as a blue solid on a surface cooled with liquid nitrogen. The blue solid may also be frozen out of the exit gases leaving the tube in which hydrazoic acid has been subject to an electrical discharge and may also be prepared by illuminating solid hydrazoic acid at −196° with the 2537 mercury line.

In our previous papers it was reported that the evidence available indicated that the composition of the blue solid is $(NH)_n$ so that it might be the imine radical or diimide or a mixture of both. Mador and Williams[3] have recently attributed the blue color to the presence of the NH_2 radical which in the vapor state has a broad absorption band near 6300 Å. We have been unable to confirm this, but rather are presenting new evidence which strongly suggests that the intermediates stabilized at low temperatures are NH and a higher polymer of NH.

The present investigation is concerned with the quantitative study of the thermal reaction and an evaluation of the absorption spectra of the blue solid prepared by three different methods.

Experimental

The Thermal Reaction.—Small quantities of hydrazoic acid were prepared immediately prior to each experiment by allowing concentrated sulfuric acid to react drop by drop with solid sodium azide *in vacuo*. The gas was then allowed to expand into an evacuated reservoir of known volume.

In a typical experiment about 0.5–1.0 g. of hydrazoic acid was passed through a quartz tube heated to 1000°. The rate of flow was adjusted so that the pressure at the inlet end of the furnace was about 0.1 mm. The products of the reaction which are condensable at −196° are frozen out onto the surface of a liquid nitrogen cooled tube which is located about 3 cm. from the exit end of the furnace. The noncondensable gases which were formed at this stage were removed from the reaction chamber by means of a high speed pumping system and passed into a gas measuring buret. Use then was made of the mass spectrometer as an analytical tool for the determination of the composition of these gaseous products. This fraction consisted mainly of nitrogen with some hydrogen.

Anal. N_2, 88.2, 87.4; H_2, 11.8, 12.6.

All other products were condensed on the surface cooled to −196°. After the flow of hydrazoic acid stopped, this section of the apparatus was isolated from the pumping system by means of a stopcock and the deposit was allowed to warm up to −125° at which temperature the blue solid undergoes a transition to a white solid. An important observation at this point is that there is no gas evolution during the transition. Warming to room temperature results in the evaporation of undecomposed hydrazoic acid; the amount was determined from pressure, volume and temperature measurements.

Finally the amount of white solid which remains at room temperature was determined by direct weighing. The results of the analysis of this white solid which prove that it is pure ammonium azide have been reported earlier.[2] Table I gives the complete mass balance obtained in duplicate experiments.

The Absorption Spectra.—In all experiments the same amount of hydrazoic acid was decomposed either thermally, photochemically or in an electrical discharge. In the cases of the thermal decomposition and the reaction in the electrical discharge the blue material was frozen out of the vapors leaving the exit end of the furnace and the discharge tube,

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(1) This work was supported in part by the United States Atomic Energy Commission, contract No. AT-(40-1)-1305.

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