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The mechanism of ketene photolysis

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THE MECHANISM OF KETENE PHOTOLYSIS

A Thesis Submitted to
LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY

by

Donald. E. Thornton, B. Tech.

Supervisor, Dr. A. N. Strachan.

In Partial Fulfilment of the Requirements for
the Degree of Doctor of Philosophy.

September 1967.

SUMMARY

Ketene has been photolysed both alone and in the presence of inert gases at 3660 and 3130 Å, at various temperatures. The mechanism for the photolysis at shorter wavelengths, around 2700 Å, is fairly straight forward because each ketene molecule that absorbs a quantum decomposes and the carbon monoxide quantum yield, equal to two, is independent of temperature and pressure. At 3130 Å and 3660 Å, however, deactivation processes play an important part in the photolysis and the mechanisms are more complicated at these wavelengths. At 3660 Å collisional deactivation has been found to be one-step process, but at 3130 Å this deactivation process becomes two-step, in certain circumstances. Mechanisms are proposed for ketene photolysis at both these wavelengths.

A simpler mechanism used by previous workers is shown to be invalid by its failure to reconcile the experimentally determined rate constants for decomposition, assuming this mechanism, with those calculated from unimolecular reaction theory.

The new mechanisms proposed include intersystem crossing, whereby excited singlet state molecules cross over to the triplet manifold. Decomposition of both excited singlet state and triplet state ketene molecules occurs, resulting in the production of both singlet and triplet methylene. These two methylenes react differently with hydrocarbons. Recent determinations, with ketene - olefin mixtures, of the proportions of singlet and triplet methylene formed are reviewed.

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The lack of agreement between different workers and the uncertainties of the methods are discussed. An alternative method using ketene-cyclopropane mixtures is described. From the results obtained by this method the proportions of triplet methylene, at 57°C , and 2700 and $3130\text{ \AA}$ are estimated to be 16 and 14% respectively.

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CONTENTS

	<u>Page</u>
SUMMARY	1
ACKNOWLEDGEMENT	3
INTRODUCTION	6
EXPERIMENTAL	17
RESULTS	28
DISCUSSION	Part I 46 Part II 63
BIBLIOGRAPHY	76

ILLUSTRATIONS

<u>Figure</u>	<u>Facing Page</u>
1E	21
2E	19
3E	25
1D	47
2D } 3D }	48
4D } 5D } 6D }	54
7D	50
8D	62
9D	73
10D	52
11D	61

INTRODUCTION

First Studies

The first studies of the action of ultraviolet light on ketene were made by Norrish, Crone and Saltmarsh.¹ They postulated that the light energy absorbed by the carbonyl group was transferred to the ~~methylene~~ ethylene group with consequent rupture of the bond.

This was followed by the attack of methylene on ketene,

These workers found that the decomposition led to the formation of two volumes of carbon monoxide to one of ethylene. Ross and Kistiakowsky² found the quantum yield of decomposition to be approximately unity at 3130 Å. They rejected the secondary reaction of Norrish and his co-workers because, if this occurred, the decomposition quantum yield should be two, and not unity as found. They suggested that methylene radicals formed in the primary process reacted with each other to form ethylene.

At 3660 Å they found that the decomposition quantum yield appeared to be less than unity.

Norrish and his co-workers³ did not agree that the observed quantum yields necessarily excluded the occurrence of their secondary reaction, since in polyatomic molecules, such as acetone, the quantum yield of the primary process may be less than unity, throughout a considerable portion of the region of continuous absorption.

Thus the carbon monoxide quantum yields of less than two in ketene photolysis could be explained by an inefficient primary process, where only a fraction of the excited molecules decomposed, the rest being deactivated. The fraction decomposing would be expected to be less at longer wavelengths (lower energy) and more at shorter wavelengths (higher energy). Norrish and his co-workers cited Ross and Kistiakowsky's value of 0.3, for the decomposition quantum yield at 3660 Å, in support of this explanation.

Later Kistiakowsky and Rosenberg⁴ admitted that the secondary reaction proposed by Norrish et al. was probably correct. They photolysed ketene in the presence of ethylene and found that the ratio of the rates of the formation of ethylene to propylene remained unchanged when the incident light intensity was varied by a factor of four. Propylene is almost certainly formed by the reaction,

Now if the ethylene forming step is reaction (2)

$$\begin{aligned} \frac{R_{\text{C}_2\text{H}_4}}{R_{\text{C}_3\text{H}_6}} &= \frac{k_2(\text{CH}_2)(\text{CH}_2\text{CO})}{k_4(\text{CH}_2)(\text{C}_2\text{H}_4)} \\ &= \frac{k_2(\text{CH}_2\text{CO})}{k_4(\text{C}_2\text{H}_4)}, \text{ and then the ratio is} \end{aligned}$$

independent of methylene radical concentration, and hence of the intensity of the incident light. If ethylene is formed by the recombination of methylene radicals (reaction (3)) then

$$\begin{aligned} \frac{R_{\text{C}_2\text{H}_4}}{R_{\text{C}_3\text{H}_6}} &= \frac{k_3(\text{CH}_2)(\text{CH}_2)}{k_4(\text{CH}_2)(\text{C}_2\text{H}_4)} \\ &= \frac{k_3(\text{CH}_2)}{k_4(\text{C}_2\text{H}_4)} \text{ and the ratio will} \end{aligned}$$

be dependent on the light intensity.

Strachan and Noyes⁶ found carbon monoxide quantum yields of two at 2700 Å and this is added confirmation that Norrish's secondary reaction is correct.

Postulated Mechanisms.

If the two reactions proposed by Norrish et al were all that happened in the photolysis, then the carbon monoxide/ethylene ratio should always equal two. The results of previous investigations(1,4,5,6.) have indicated that this ratio is always greater than two. Strachan and Noyes⁶ found the ratio to be 2.20 ± 0.06 , in excellent agreement with the value of 2.19 ± 0.02 found by Kistiakowsky and Rosenberg.⁴ This value appears to be constant over a wide range of temperature, pressure and wavelength.⁷ Strachan and Noyes came to the conclusion that this ratio was always greater than two, because some methylene formed in the reaction results in polymer, either by association or further reaction with ketene. It was suggested⁷ that 90% of the methylenes formed at 2700 Å reacted with ketene to give carbon monoxide and ethylene. The remaining 10% reacted to form carbon monoxide and polymer. The reciprocal of the carbon monoxide quantum yield was found to be independent of temperature and pressure at 2700 Å and the following mechanism was proposed.⁶

At 3660 Å Strachan and Noyes found that the plots of the reciprocal of the carbon monoxide quantum yield against ketene concentration were linear, with positive slopes and intercepts.

The slopes decreased with increase in temperature, as did the intercepts. The intercepts decreased from 13.0 at 26°C to 3.9 at 154°C. The low carbon monoxide quantum yields suggested that a deactivation process was taking place and the following mechanism was postulated for this wavelength:-

With steady state assumptions the above mechanism leads to the following expression for the reciprocal carbon monoxide quantum yield.

$$\frac{1}{\phi_{\text{CO}}} = \frac{1}{2} + \frac{k_{11}}{2k_9} + \frac{k_{10}}{2k_9} (\text{CH}_2\text{CO})$$

This, being a linear expression with positive slope and intercept, accounts for the experimental results. Although no phosphorescence or fluorescence has been observed from ketene, the inclusion of reaction (11) is necessary to account for the intercepts not being equal to $\frac{1}{2}$, which would be expected if k_{11} were zero. The decrease in the slopes and intercepts with increase of temperature is explained if (9) has a small activation energy.

The mechanisms proposed by Strachan and Noyes⁶ for 2700 Å and 3660 Å formed the basis for mechanism used in later work, by Porter and his co-workers.^{8,10,13.}

Porter and Connolly⁸ photolysed ketene at 3130 Å and 3340 Å. Previously Kistiakowsky and Mahan⁹ had found that the primary quantum yield at 3130 Å was independent of pressure, and had suggested a value of unity. This work was done at low pressures over a narrow range. Porter and Connolly investigated the photolysis at 3130 Å and 3340 Å at pressures up to one atmosphere. When the reciprocal of the primary quantum yield was plotted against ketene concentration, lines with positive slopes and intercepts were obtained. Porter and Connolly deduced from the positive slopes of such plots that collisional deactivation not only occurred at 3660 Å but at these wavelengths too. The intercepts of these plots appeared to be unity at 3130 Å but greater than unity at 3340 Å. The intercepts at 3340 Å decreased with increase in temperature. The authors did not rule out the possibility of the internal conversion reaction (11) at 3130 Å because of the possibility of experimental error.

Cascade Deactivation.

Porter and Connolly¹⁰ considered a mechanism involving a number of stages in the deactivation of excited ketene molecules. In this mechanism both singlet and triplet excited states of ketene were included, but for simplicity the authors omitted the triplet state in their detailed calculations concerning the number of stages in the collisional deactivation. The effect of the number of collisions required for deactivation, on the plots of the reciprocal of the primary quantum yield, ϕ , against ketene concentration was determined. With one-step deactivation the plots were linear but departure from linearity and increase in the quantum yield occurred as the number of stages in the collisional deactivation increased.

When thermal dissociation of the triplet state was included in the mechanism, such plots became S-shaped. The authors then compared the proposed mechanism with experimental results. In the case of cascade deactivation they found difficulty in comparing experiment with theory, because of the extra parameter involving the number of collisions. The authors concluded that more precise experimental data was required to see whether the $1/\phi$ v. (ketene) plot extrapolates to a value of less than unity, at 3130 Å. A further investigation by Porter and Taylor¹³ in 1962 examined ketene photolysis, again at 3130 Å and 3340 Å, at various temperatures. Once more, plots of the reciprocal of the primary quantum yield against ketene concentration were found to be linear, and the intercepts were always greater than or equal to unity. From previous theory¹⁰, any multistage deactivation in the photolysis would make these plots concave upwards at low ketene concentrations, and the intercepts would be less than unity. Porter and Taylor therefore favoured a strong collision mechanism and suggested that no more than three collisions were necessary to degrade an excited ketene molecule at 3130 Å. In order to simplify their calculations, the authors assumed that a single collision was effective in degrading the molecule.

k_9 v Energy

If reactions (8) to (11) represent the mechanism of the photolysis at all wavelengths, with (10) a one-step process,

$$1/\phi = 1 + \frac{k_{11}}{k_9} + \frac{k_{10}}{k_9} (\text{CH}_2\text{CO}) ,$$

where ϕ is the primary quantum yield.

The inverse slopes of plots of $1/\phi$ against ketene concentration are therefore equal to the decomposition rate constant k_g , divided by the collisional rate constant k_{10} . k_{10} was assumed by Porter and his co-workers^{8,10,13} to be independent of the exciting wavelength. Hence, by plotting the inverse slopes of the above plots against the energy of the exciting wavelength, the variation of the decomposition rate constant, k_g , with energy was demonstrated.⁸ In a later paper¹⁰, actual values of k_g were obtained from the inverse slopes by setting k_{10} equal to the collision number, with $4 \text{ \AA}$ chosen for the collision diameter of ketene. The values of the decomposition rate constant, k_g , so calculated from experimental data were compared with theoretical values obtained from the equation,

$$k_g = \nu \left(1 - \frac{E_0}{E}\right)^{s-1}$$

which is a consequence of the theories of Slater¹¹ and Kassel¹² for unimolecular reactions.

ν is a mean frequency of vibration of the molecule and should be $\sim 10^{13} \text{ sec}^{-1}$.

E_0 is the minimum energy required for decomposition, and E is the total vibrational energy of the molecule.

s is the number of degrees of freedom of the ketene molecule. ν , E_0 and the zero-zero energy of the ketene molecule are all unknown. Using experimental data at three wavelengths, Porter and Connolly¹⁰ found that direct calculation of these parameters gave values for them which were physically impossible. However, reasonable values of ν and E_{00} , the zero-zero energy, reproduced the experimental data within experimental error. But the authors stated that theory and experiment only agreed qualitatively. If the more complex case of cascade deactivation was considered, there was greater

difficulty in comparing experiment with theory because of the additional parameter related to the number of collisions required for deactivation.

Porter and Taylor¹³, in later work, found linear plots of $1/\beta$ v ketene concentration. They used the slopes of these plots to calculate values for k_d , the decomposition rate constant. Using these values the parameters in the equation:- $k_d = V \left(1 - \frac{E_0}{E}\right)^{a-1}$ were calculated for various values of a . These calculations placed the zero-zero band for ketene at approximately 4100 Å (24,390 cm^{-1}) which although it cannot be checked directly, does correspond to the long wavelength limit of ketene absorption. There are difficulties in comparing theoretical and experimental values of k_d , the decomposition rate constant, and only qualitative agreement has been achieved.

Intersystem Crossing

In earlier calculations showing the variation of k_d with energy, Porter and Connolly⁸ did not include triplet states in the postulated mechanism. The possibility of the contribution of triplet states to the dissociation process was mentioned by these authors. In their later work,¹⁰ these authors did include intersystem crossing in their detailed mechanism. In the theoretical plots of $1/\beta$ primary v. ketene concentration that were calculated, inclusion of the intersystem cross-over reaction led to S-shaped curves. Experimentally such plots were always found to be linear and hence the cross-over reaction was excluded.

Although linear plots rule out the possibility of intersystem crossing from the lowest vibrational levels of the excited singlet state, this reaction pathway could occur from the higher vibrational levels of the excited singlet state.

The significance of the intersystem cross-over reaction has been emphasized, by Noyes and Unger¹⁴, as one of the major pathways in photochemical reactions. These authors suggested that in ketene photolysis at 3660 Å many of the excited molecules cross over to the triplet state.

The authors suggest that the competing processes would be

Not enough is known to decide whether collisions would be rate determining in the cross over reactions or not. In conclusion the authors stated that the apparent effect of collisions in enhancing the number of triplet methylenes may be due to an effect in promoting cross over of singlet to triplet ketene, rather than in promoting crossover from singlet methylene to triplet methylene. It was suggested that in the wavelength region 3000 Å - 3700 Å, where dissociation is less rapid than at shorter wavelengths, excited singlet molecules, formed in the absorption act, mainly cross over to the triplet state.

Whether it is an excited precursor or methylene itself that undergoes singlet triplet transitions, collisions appear to play an important part in such transitions in other systems. Anet and his co-workers¹⁵ and Frey¹⁶ photolysed diazomethane in the presence of cisbutene-2 and an inert gas. Herzberg had shown previously that a high ratio of inert gas to diazomethane was necessary to produce triplet methylene¹⁷, and indeed Frey showed that the products due to the reactions of triplet methylene increased as the ratio of argon (the inert gas) to cisbutene-2 was increased. Frey pointed out that Anet et al did not work at sufficiently high pressures to prevent the geometrical isomerisation of the vibrationally excited cis 1.2. dimethyl cyclopropane, which was produced by the attack of methylene on the cis butene-2. It seems, therefore, that collisions play some part in the intersystem crossing reaction in this system but whether it is excited diazomethane molecules or methylenes themselves that undergo this reaction is uncertain.

Summary

Three main problems emerge from the studies of the photolysis of ketene. Firstly there is still some doubt as to whether deactivation, in the 3000-3700 Å region of the photolysis, is one-step or multi-step. Secondly comparisons between experimental data for the rate constants of decomposition and the rate constants calculated from unimolecular reaction theory of Kassel and Slater have not been too successful.

Thirdly, there is uncertainty as to the extent of the intersystem crossing reaction and the proportions of singlet and triplet methylenes produced in the photolysis.

The present studies were started with the object of trying to resolve some of these problems. Inert gases were used in the photolysis at both 3660 and 3130 Å. It was hoped that by comparison of their deactivation efficiencies with that of ketene, some more information on the deactivation processes in the photolysis would be obtained. The polymerisation of ketene accelerates as the pressure of ketene increases, and an alternate way of obtaining higher pressures in the system is to use a small constant amount of ketene with increasing amounts of inert gas.

At 3660 Å, ketene was photolysed at temperatures up to 300°C in order to obtain more information on the rapid change of k_g , with temperature, at this wavelength.

Discrepancies in the value of k_g at 3130 Å, in previous work,^{10,13} and some doubt as to the variation of the reciprocal primary quantum yields^{8,9} at low pressures, prompted the measurement of quantum yields at 3130 Å.

It is believed that only singlet methylene undergoes the insertion reaction with C - H bonds, and therefore by photolysing ketene in the presence of excess cyclopropane, it was hoped that singlet methylene would all react with the hydrocarbon, whilst the triplet would react with ketene to give ethylene and carbon monoxide. From the carbon monoxide/ethylene ratios an estimate of the proportions of singlet and triplet methylene in the photolysis could be made.

EXPERIMENTAL

Materials

Ketene was prepared on a vacuum line by pyrolyzing acetic anhydride.¹⁸ Acetic anhydride was allowed to pass through a furnace, maintained at 500°C, and the products from the pyrolysis were condensed in three cold traps. The first and second traps, of dry ice and acetone, at -78°C, condensed acetic acid and any undecomposed acetic anhydride. The third trap of liquid nitrogen, at -196°C, condensed the ketene. Trap to trap distillations were performed on the freshly prepared ketene to remove any uncondensables. The ketene was then frozen down into a detachable bulb, which was kept under liquid nitrogen at all times, to prevent polymerization.

Octafluoro Cyclobutane (Freon-C-318) was the product of the Matheson Company and was stated to be 99.99% pure. The gas was always thoroughly degassed, at the temperature of liquid nitrogen, prior to each run.

Sulphur Hexafluoride was the product of the Matheson Company and stated to be 98% pure. Prior to each run it was degassed in the same way as the octafluorocyclobutane.

Cyclopropane and Propylene were both products of the Matheson Company, and stated to be of 99% purity. These gases were degassed thoroughly before each run.

Carbon Monoxide, Ethylene, Methane, and Ethane were all obtained from the National Chemical Laboratory, Teddington, Middlesex. The gases were in 500ml. bulbs, at atmospheric pressure, which were sealed under vacuum.

The purities of the gases were stated to be as follows:-

CO	99.96%
C ₂ H ₄	99.92%
CH ₄	99.61%
C ₂ H ₆	99.90%

These gases were attached to the vacuum line, and used as standards for the chromatographic work.

Diethyl Ketone was a product of British Drug Houses, Poole, England. It was stated that 95% of the ketone boiled between 99°C and 104°C. The ketone was distilled on a Todd column, and a middle fraction, boiling at a constant 102.5°C was collected. This was stored temporarily over anhydrous copper sulphate. The sulphate did not indicate the presence of water. A portion of the ketone was thoroughly degassed on the vacuum line and subjected to several trap to trap distillations, the middle third being collected in a detachable bulb, where it was stored under liquid nitrogen.

Light Source and Filters

For the work at 3660 Å, the light source was a Phillips black glass mercury vapour lamp (H.P.W. 125 Watts).

For 3130 Å and shorter wavelengths, a Hanovia high pressure mercury arc lamp (Type U.V.S. 220) was used. A ten centimetre focal length quartz lens, and an aperture in the lamp housing, were sufficient to produce a fairly uniform and parallel light beam. Neutral density filters (Barr and Stroud Ltd., Glasgow N.3), were used to vary the intensity.

The filter combinations used to isolate different wavelength regions are listed in Table 1, and their transmission properties are shown in Figure 2E. Measurements were made with either a Hilger Watts Uvispec or a Unicam S.P. 700 recording spectrophotometer.

TABLE I

Filter combinations used:-

1. Corning Glass 9863 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (cn)iodide
(Red Purple Corax A)
Thickness 3mm. 30g/100ml 20mg/100ml
Transmits 2300 Å - 4200 Å
2700 Å % Transmission = 70 5cm. pathlength. 2cm. pathlength.
3130 Å % Transmission = 87
3660 Å % Transmission = 82
2. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ K_2CrO_4 $\text{KHC}_8\text{H}_4\text{O}_4$
4.231g/100ml. 0.0121g/100ml. 0.23g/100ml
5cm. pathlength. 2cm. pathlength 2cm. pathlength
+ Corning Glass 9863

3. Chance Pilkington Filters

O.V.I. (Purple) and O.X.I. (Ultraviolet)

Nickel Sulphate hexahydrate, nickel chloride

hexahydrate and potassium chromate were all obtained from

Hopkins and Williams Ltd., Chadwell Heath, Essex, as Analar grades.

Potassium hydrogen phthalate was obtained from

Hopkins and Williams Ltd., and stated to be 99.5% pure.

(cn) iodide (2,7 - dimethyl - 3, 6 - diazocyclohept - 1,6 - diene iodide). The preparation of the corresponding perchlorate (Cation X) is described by Scharsenbach and Lutz¹⁹. The iodide can be prepared by the same method using hydriodic acid in place of perchloric, if the quantity of water added in the final stage is reduced.⁷ The properties of most of these filters are described in detail by Kasha.²⁰ Filter combination 2 has been described by Hunt and Davis.²¹

All the filters used were found to be stable to prolonged exposure to ultraviolet light, except for potassium hydrogen phthalate. After one or two weeks of use, a mould started growing in this solution. Therefore when light in the 3130 Å⁰ region was used, this solution was changed every week.

The ultraviolet spectrum of ketene is shown in Figure 1E. A 10cm. gas cell was filled with ketene to a pressure of 20cm. The spectrum was recorded on the Unicam S.P. 700 spectrophotometer.

Apparatus

The apparatus was of conventional high vacuum design. A good vacuum was obtained using a mercury diffusion pump backed by a rotary high vacuum pump (Edwards Speedivac). The reaction vessel was a cylindrical quartz cell, 20cm. in length and 3.0cm. in diameter. Its volume was 141.4mls. The cell was encased in an aluminium jacket and heated electrically through a variac control. It was well insulated with asbestos paper and good temperature control ($\pm 0.5^{\circ}\text{C}$) was obtained from 37°C to 300°C . At the lowest temperature used, (37°C), better temperature control was obtained by incorporating a 10 M.P.D. condenser in the variac circuit.

A small finger, at the far end of the reaction cell, immersed in liquid nitrogen, was the means of transferring gases into the cell. For the low pressure runs of ketene and ketene with inert gases, the contents of the cell were thoroughly mixed by means of a 250ml. bulb, filled with mercury, and attached to the tube leading into the cell.

By raising and lowering the mercury in this bulb, the gases in the cell were alternately compressed and expanded. Ten or so expansions gave good mixing. The mercury was then raised, and a mercury float valve sealed the cell and its contents. In high pressure runs with inert gases and in all runs with cyclopropane and propylene, the gases were mixed by rapid evaporation from -196°C and allowing the cell contents to stand for 15-20 minutes before the start of each run.

The first series of runs consisted of photolysing ketene alone and ketene with inert gases, cyclo- C_4F_8 and SF_6 . For these runs the only product measured was carbon monoxide. This was done on a combined McLeod gauge - Toepler pump.⁶

In the second series of runs, in which ketene was photolysed in the presence of cyclopropane or propylene, both carbon monoxide and ethylene were measured. Carbon monoxide analysis consisted of pumping the gas into the McLeod gauge - Toepler pump and measuring it quantitatively. Then the gas was put through a chromatograph. Ethylene was only measured chromatographically. The instrument used for chromatographic analyses was a Shandon K.G.2. Thermocell Chromatograph. This was run at a temperature of 31°C . Argon was the carrier gas and the flow rate was 6.0ml./min. Nylon tubing ($\frac{3}{16}$ " outside diameter) was used for the column and also for the connections from the instrument to the vacuum line. The column packing material was Perkin Elmer Part No. DE. 124. The liquid phase was bis-2-methoxyethyl adipate + di-2- ethylhexyl sebacate. The support was Chromasorb P (mesh size 60-80). Amounts of these constituents were $13\frac{1}{2} : 6\frac{1}{2} : 80$ wt./wt., respectively. The column was 25 feet in length and was capable of separating ethylene from cyclopropane (or propylene) and from any ketene present.

This column would not separate carbon-monoxide from methane or ethylene from ethane. However a few runs were done using a silver nitrate/ethylene glycol column. This column would not effect a complete separation of methane from carbon monoxide or ethane from ethylene. However distinctive shoulders, due to methane and ethane, did show on the carbon monoxide and ethylene peaks, when small amounts of CH_4 and C_2H_6 were injected with slugs of CO and C_2H_4 respectively. Analysing a run at 3130 Å, small shoulders were seen on the CO and C_2H_4 peaks but it was estimated that the CH_4 and C_2H_6 constituted approximately 5-10% of the main products, CO and C_2H_4 . In all later runs, using the ester column, only CO and C_2H_4 were measured.

Experimental Procedure

Experimental procedure can be conveniently divided into two parts:

- (1). Runs with ketene alone and ketene with inert gases, and
- (2). Runs with ketene alone and ketene with hydrocarbons.

- (1). Ketene alone and ketene with inert gases.

For each run, a small quantity of ketene was removed from the storage bulb and degassed three times at the temperature of liquid nitrogen. A known pressure was allowed to fill the cell. In low pressure runs the pressure of the cell contents could be measured directly using the mercury-filled mixing bulb, attached to the cell. At higher pressures, the quantities of ketene were measured in a known volume of the vacuum line, by means of an on-line mercury manometer.

The gas was then condensed into the cell and the pressure in the cell was calculated. For runs in which an inert gas was used, the quantity of inert gas was measured in a similar way, and then condensed into the cell. Sulphur hexafluoride and octafluorocyclobutane were kept in two litre storage bulbs, attached directly to the vacuum line. At the end of each run, the gases in the cell were allowed to pass through two cold traps. The first was at -196°C and the second at -210°C . The -210°C trap was achieved by pumping on freshly prepared liquid nitrogen for at least twenty minutes. The temperature of this trap could be measured by a copper-constantan thermocouple connected to a Pye thermocouple testset. These traps condensed all products and reactants except carbon monoxide. This gas was pumped into the combined McLeod gauge - Toepler pump and measured quantitatively. Conversions were kept $< 2\%$.

(2). Ketene alone and ketene with hydrocarbons

For all runs, quantities of ketene and hydrocarbon were measured in a known line volume by the mercury manometer, and then condensed into the reaction cell. The hydrocarbons were taken directly from their cylinders and thoroughly degassed by several trap to trap distillations before each run. At the end of each run a small fraction of the reaction cell's contents was isolated. This was achieved by having a small, known, volume next to the reaction cell. By opening the cell, allowing the cell contents to fill this small volume and waiting until equilibrium was established, a known percentage of the total reaction mixture was isolated.

In calculating the percentage this represented, account was taken of the difference in temperature between the cell and this small volume. The reasons for this procedure were twofold:- Firstly it allowed duplicate analyses of each run to be performed. Secondly, only small slugs of the ethylene fraction could be injected into the chromatograph because of the low carrier gas flow rate. If the pressure of the gases to be injected became equal to or exceeded the carrier gas pressure, then the slug would not be injected cleanly. This could cause back pressure, resulting in long drawn out, mis-shapen, peaks. When the small fraction of the cell contents had been isolated, it was condensed over soda - asbestos (Hopkins and Williams Ltd., M.A.R.). This removed most of the undecomposed ketene. Stopcock A (see Figure 3.E.) was closed and the gases were then allowed to pass through traps at -196°C and -210°C . These traps removed all reactants and products except carbon monoxide and any methane. The carbon monoxide fraction was pumped into the McLeod gauge - Toepler pump and its pressure and volume measured. After this the carbon monoxide fraction was transferred to the injection loop for chromatographic analysis. The procedure for doing this was as follows:-

The mercury in the McLeod gauge - Toepler pump was lowered to just below point F. (see Figure 3.E.). Stopcock B was closed and the loop, which had been evacuated through D, C and the high vacuum line, was opened through D and C to Toepler II. The mercury in Toepler II was lowered and the mercury float valves at G and H were freed. This allowed free passage of the carbon monoxide fraction from I, through II, to the loop.

This gas fraction was then transferred quantitatively from I to II by raising and lowering the mercury in II a few times. The mercury in II was then raised to H and the CO fraction filled the loop and the small dead - space between D, B and H. Stopcock D was turned off. B was opened and the gas in the dead-space was pumped back into I, and its volume and pressure measured. This was between 30 and 40% of the total gas first measured. During this sequence of operations the carrier gas was flowing into E, along the by-pass and back to the chromatograph. The carbon monoxide fraction was injected by turning E and D simultaneously, so that the carrier gas swept the contents of the loop into the chromatograph.

The next stage in the procedure was the introduction of the ethylene fraction, which contained ethylene, cyclopropane, a small amount of ketene, and any ethane, into the chromatograph. The cold traps were removed and the condensed gases evaporated into the closed line (A closed). The gases were condensed into the injection loop through B, C and D, by placing a flask of liquid nitrogen around the loop. When all the gases were condensed into the loop, D was turned off and the liquid nitrogen removed from the loop. When the gases had reached room temperature, injection of this ethylene fraction was performed in the same way as for the carbon monoxide fraction. Duplicate analyses were performed in this second series of runs.

Quantum yield determinations.

Quantum yields were determined in two wavelength regions
centred around 3660 Å and 3130 Å.

Light intensities were measured before, during and after each run by means of a vacuum photocell (Type Q.V.A.39). The photocell was connected in series with a 120 volt high tension battery (Ever Ready Winner) and a D.C. microammeter (Pye Scalamp). The ammeter was very sensitive and any current from 0.05 mA. to 1000mA. could be read accurately. Light intensities measured this way, before and after each run were averaged to give I_0 values.

Light intensities measured during a run gave I_t values. $I_0 - I_t = I_a$ (the intensity absorbed). At 3660 Å relative quantum yields only were measured. The absolute magnitudes of the reciprocal quantum yields at 3660 Å were based on the values obtained at this wavelength by Porter and Taylor¹³, at 25°C, using a ferrioxalate actinometer. For a plot of the reciprocal of the primary quantum yield against ketene concentration they found an inverse slope of 4.029×10^{-5} mole litre⁻¹. Using this value, and assuming the inverse slope increases with temperature with an activation energy of 4.5 kcal. mole⁻¹,⁶ the inverse slope at 37°C was calculated to be 5.697×10^{-5} mole litre⁻¹. This was then compared to the inverse slope measured in this work at 37°C, in terms of a microammeter reading. Hence $2/\phi_{CO}(\text{measured}) \times F = 2/\phi_{CO}(\text{absolute})$ and F was found to be 30.09×10^{-6} . All the $2/\phi_{CO}$ values which were measured at 3660 Å were multiplied by F to obtain absolute values.

For quantum yield determinations at 3130 Å diethyl ketone was used as an internal actinometer. Actinometer runs were made at 100°C and ketone pressures employed were around 2.0cm. The carbon monoxide quantum yield, under these conditions has been shown to be unity.²²

Standardisation of the Chromatograph.

A small amount of carbon monoxide was taken from the sample bulb attached to the vacuum line, and pumped into the McLeod gauge - Toepler pump (I. Figure 3.B). Its pressure and volume were measured. The mercury in I was then lowered and the mercury thread broken at F, trapping the carbon monoxide in the McLeod gauge. A small quantity of ethylene was then pumped from the sample bulb into the McLeod gauge with the carbon monoxide. The total pressure and volume were then measured. From these measurements the numbers of moles of carbon monoxide and ethylene in the mixture were calculated. The mixture was then transferred via Toepler II to the loop. The gases were allowed to equilibrate in the loop and the deadspace D, B and H. Stopcock D was turned off and the mixture remaining in the deadspace was pumped back to McLeod I and remeasured. The slug, of known amounts of carbon monoxide and ethylene, was then injected and the areas of the carbon monoxide and ethylene peaks measured. The area/mole for both gases was worked out, and also the ratio $\left(\frac{\text{ethylene area/mole}}{\text{carbon monoxide area/mole}} \right)$, which gave the relative sensitivity of the instrument to these two gases. This procedure was done a few times and reproducible results for the relative sensitivity, at various chromatograph sensitivities, were obtained. The average of these results was calculated to be 1.868, and in the second series of runs, ketene with hydrocarbons, the $\left(\frac{\text{area carbon monoxide}}{\text{area ethylene}} \right)$ ratio was multiplied by this factor to get true carbon monoxide/ethylene ratios.

RESULTS

Tables A - L show values of $2/\beta_{CO}^0$ at various ketene and inert gas concentrations at 3660 Å, 3130 Å and various temperatures. At certain ketene concentrations in Tables A, C, E, G, I and K, optical density values have been included, and these will be used later to construct Beers Law plots.

TABLE A

3660 Å ⁰ 57° C

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\rho_{CO}$
3.16	0.180	59.6
5.39	0.330	103.6
5.90	0.336	118.1
8.18	0.481	141.9
9.96	0.578	180.4
3.62	0.216	76.4
15.03	0.875	304.7
20.31		386.3
2.67	0.165	72.8
2.17		73.2
1.76		62.0
1.38		54.1
0.52		33.4
1.16		48.1
1.35		45.8

(K) is ketene concentration.

TABLE B
°
3660 A 37° C

MEIENH + H

(K) = 2.59 moles/litre x 10³

(H) MOLES/LITRE x 10³

2/p_{CO}

21.78	519.2
11.61	326.6
15.60	464.4
5.69	201.8
5.67	171.1
2.20	94.4
8.51	268.0
13.35	431.4

11.23	261.3
17.59	398.0
14.43	334.5
21.34	470.0
4.81	167.8
3.03	142.5
13.43	318.7

(K) is ketone concentration.

(H) is inert gas concentration.

TABLE C

3660 Å [°] 150°C

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\delta_{CO}$
2.01	0.128	9.0
4.21	0.407	18.5
7.60	0.684	29.1
11.49	0.994	40.4
14.85	1.222	48.7
0.91	0.079	7.3

(K) is ketene concentration.

TABIE D

3660 Å⁰ 150°C

RETENE + M

(K) = 1.90 moles/litre x 10³

(M) MOLES/LITRE x 10 ³		2/p _{CO}
	M = C ₄ P ₈	
15.03		55.5
11.03		43.3
7.20		34.3
3.39		20.5
1.25		17.7
	M = SP ₆	
10.84		41.1
16.30		57.1
4.87		27.3
7.58		34.4
2.24		20.1

TABLE E

$3660 \overset{\circ}{\text{A}}$ 225°C

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\beta_{\text{CO}}$
1.06	0.118	4.45
2.20	0.230	5.74
5.75	0.686	10.28
10.79	1.281	15.21
13.72		18.98

TABLE F

$3660 \overset{\circ}{\text{A}}$ 225°C

KETENE + C_4F_8

(K) = 1.61 Moles/litre $\times 10^3$

C_4F_8 MOLES/LITRE $\times 10^3$	$2/\beta_{\text{CO}}$
6.84	10.34
10.15	11.11
3.32	7.75
1.77	6.58
9.81	10.91

TABLE G

$\overset{\circ}{3660 \text{ A}}$ $\overset{\circ}{300 \text{ C}}$

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\rho_{CO}$
0.99	0.108	1.87
2.03	0.304	2.87
4.45	0.709	4.26
7.33		9.26
9.12		8.96

TABLE H

$\overset{\circ}{3660 \text{ A}}$ $\overset{\circ}{300 \text{ C}}$

KETENE + C_4F_8

(K) = 1.40 moles/litre $\times 10^3$

C_4F_8 MOLES/LITRE $\times 10^3$	$2/\rho_{CO}$
6.19	3.81
3.02	3.75
8.38	4.56
1.36	3.26

TABLE I
O
5150 Å 37°C

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\beta_{CO}$
2.56	0.580	1.01
6.24	1.288	0.99
0.85	0.171	1.03
10.61		0.97
21.48		1.20
15.52		0.98
19.66		1.07
24.16		1.14
0.83	0.182	1.00
23.70		1.22
37.84		1.37
42.33		1.46
28.25		1.17
32.62		1.23

(K) is ketene concentration

TABLE J

3130 Å 37°C

KETENE + M

(K) = 2.59 moles/litre $\times 10^3$

(M) MOLES/LITRE $\times 10^3$

$2/p_{CO}$

21.52	1.53
14.22	1.32
3.36	1.06
16.92	1.38
7.14	1.12
10.56	1.20
1.32	0.97
40.21	1.77
80.26	2.64
61.76	1.91
98.11	3.00

20.02	1.40
14.23	1.27
10.76	1.25
3.67	1.07
1.73	1.00
7.71	1.12

TABLE K

3130 Å [°] 100°C

KETENE ALONE

(K) MOLES/LITRE $\times 10^3$	OPTICAL DENSITY	$2/\rho_{CO}$
2.28	0.553	0.98
10.83		0.98
0.60	0.143	0.97
6.71	1.603	0.99
19.90		1.08
16.38		1.07
13.48		1.02

(K) is ketene concentration.

TABLE I

3130 Å ⁰ 100°C

KETENE + M

(K) = 2.15 moles/litre x 10³

(M) MOLES/LITRE x 10 ³		2/p _{CO}
	M = C ₄ F ₈	
31.21		1.50
61.60		2.06
48.90		1.64
81.10		2.43
15.64		1.15
	M = SF ₆	
13.35		1.17
10.28		1.13
4.50		1.00
6.45		1.04
2.88		1.00
2.24		0.98
1.08		0.97
0.77		0.99
2.54		0.97

Experimental values of k_d , the decomposition rate constant were calculated from the slopes of the plots of twice the reciprocal of the carbon monoxide quantum yield against ketene concentration, at 3660 Å and various temperatures. These slopes are equal to the ratio of the rate constant for deactivation to the rate constant for decomposition.

The deactivation rate constants were calculated from collision theory, assuming a collision diameter for ketene of 4 Å, and found to be equal to $9.614 \times 10^9 \sqrt{T}$, where T = temperature in degrees absolute. Hence k_d , the rate constants for decomposition were calculated.

The energy corresponding to these rate constants was calculated as follows:-

The rotational and vibrational energy of the excited ketene molecules is equal to the difference between the energy of the exciting wavelength ($h\nu$) and the zero-zero energy (E_{00}), plus the rotational (E_r) and the vibrational (E_v) energy of the ground state. Thus,

$$E = h\nu - E_{00} + E_r + E_v$$

Therefore

$$E - E_{00} = h\nu + E_r + E_v$$

The quantities on the right hand side can be calculated.

$$\text{Energy of exciting light} = \frac{N \times h \times c}{\lambda \times 4.184 \times 10^7} \quad \text{cals.,}$$

where N = Avogadro's number.

h = Planck's constant.

c = Velocity of light

λ = Wavelength of the light in cms.

1 calorie = 4.184 joules.

E_r , the rotational energy of the ground state = $\frac{3}{2} RT$.

E_v values were obtained directly from the tables of Taylor and Glasstone.²³

Their values $\frac{E - E_0}{T}$ were equivalent to $\left\{ \frac{E_v - E_0}{T} \right\} \gamma_i$ where

$(E_v - E_0)_{\gamma_i}$ is the contribution to E_v of the i th vibrational

frequency. Vibrational frequencies for ketene were obtained

from Bradley Moore and Pimentel.²⁴ Therefore for each

temperature the nine contributions from the fundamental vibration

frequencies were added together and then multiplied by T to give

the vibrational energy E_v .

Addition of $h\nu$, E_r , and E_v gave values of $E + E_{00}$

at all the temperatures used. These values, with the

experimental values for $\log_{10} k_g$ are shown in Table N, together with some data from other workers.

The values for the theoretical rate of decomposition and energy were obtained as follows. The theories of Kassel¹² and Slater¹¹ for unimolecular reaction lead to an equation of the following form.

$$k_g = \gamma \left(\frac{E - E_0}{E} \right)^{s-1}$$

Values for $\log_{10} k_g$ were calculated, using $s = 12$ and

$\gamma = 4 \times 10^{10}$, for values of n from 1.175 to 5.0. E_{00} was

assumed to be 70,000cals, and E_0 5,000cals. These calculations

are shown in Table N.

TABLE II

EXPERIMENTAL VALUES OF $\log_{10} k_g$ AND $B + E_{00}$

$T^{\circ}C$	$\log_{10} k_g$	$B + E_{00} \text{ cal.}$	Reference
23	6.8235	79,391	13
26	6.8591	79,425	6
37	6.9814	79,508	This work
71	7.3284	79,778	6
107	7.5478	80,098	6
150	7.8122	80,485	This work
154	7.9571	80,526	6
225	8.2788	81,249	This work
300	8.3766	82,082	This work
23	8.9489	86,881	13
23	9.4014	92,621	13

TABLE N.

THEORETICAL VALUES OF $\log_{10} k_9$

$s = 12, \quad \gamma = 4 \times 10^{10} \text{ sec}^{-1}, \quad E_{00} = 70,000 \text{ cal.},$
 $E_0 = 5,000 \text{ cal.}$

$n = \frac{E}{E_0}$	$E + E_{00} \text{ cal.}$	$\log_{10} k_9$
1.175	78,750	6.5541
2.0	80,000	7.2911
2.5	82,500	8.1623
3.0	85,000	8.6661
4.0	90,000	9.2282
5.0	95,000	9.5362

As outlined in the experimental section the chromatograph was calibrated by injecting known samples of carbon monoxide and ethylene, and measuring the areas of the resultant peaks. Area/mole for each gas was worked out and then the relative sensitivity of the instrument to these gases was calculated. The results are shown in Table O.

TABLE O.

(The results are reduced to sensitivity values of 100 on the instrument in all cases).

Run	CO(area/mole)	C ₂ H ₄ (area/mole)	$\frac{\text{C}_2\text{H}_4 \text{ area/mole}}{\text{CO area/mole}}$
1	2.38	4.18	1.76
2	1.32	2.66	2.02
3	1.897	3.20	1.69
4	3.66	7.18	1.96
5	1.56	3.02	1.94
6	1.95	3.81	1.954
7	2.304	4.034	1.75

Mean relative sensitivity = 1.868

The CO/C₂H₄ ratios measured were all multiplied by this factor to give true values.

CO/C₂H₄ ratios were measured at 3130 Å and 2700 Å at 37°C. These ratios, together with the cyclopropane/ketone ratios at which they were measured, are shown in Tables P and Q.

TABLE P.

3130 Å [°] 37°C

Cyclopropane/ketene	Carbon monoxide/ethylene
13.1	6.2
16.2	6.0
19.5	7.3
19.9	7.8
25.2	8.1
41.1	7.7
31.8	8.0
78.4	8.45
7.85	5.0

Three runs of ketene alone were done and the CO/C₂H₄ ratio measured at this wavelength and temperature:

Ketene pressure(cm.)	Carbon monoxide/ethylene
3.0	2.2
3.0	2.3
3.08	2.2

TABLE Q

2700 Å [°] 37°C

Cyclopropane/ketene	Carbon monoxide/ethylene
20.5	7.5
28.0	7.3
23.6	7.1
9.9	4.4

Ketene was photolysed alone at 2700 Å [°] and 37°C. The carbon monoxide/ethylene ratio was found to be 2.3.

Results of two runs in which ketene was photolysed with excess of propylene at $3130 \text{ \AA}$, and $2700 \text{ \AA}$, and at 37°C , are not tabulated. No ethylene was detected in these runs.

DISCUSSION

Part I.

THE PHOTOLYSIS OF KETENE

Ketene Absorption.

The optical densities observed at different wavelengths and temperatures are listed in Tables A, C, E, G, I and K, and are plotted against ketene concentration in Figure 1D. It will be seen that Beer's Law is obeyed at both wavelengths and all temperatures, indicating that the light transmitted by the filters used, was reasonably monochromatic. From the slopes of the lines in Figure 1D, the extinction coefficients at 37°C were calculated. These can be compared with values calculated from the absorption spectrum of ketene (Figure 1E.), and with the values of Porter and Taylor.¹³

TABLE R.

T°C	λ Å	Extinction Coefficient (litre mole ⁻¹ cm ⁻¹)	Reference.
37	3130	10.70	Figure 1D
	3660	2.90	
21	3130	11.70	Figure 1E
	3660	4.20	
23	3130	9.00	Porter and Taylor ¹³
	3660	2.99

The extinction coefficients calculated from the Beer's Law data are in reasonable agreement with those obtained from the absorption spectrum of ketene. Some error is caused in the latter by the uncertainty of the position of the base line, when the spectrum was recorded. This leads to errors in the optical density values obtained from the spectrum. The values for the extinction coefficients from the work of Porter and Taylor¹³ have been corrected in Table R. The Beer's Law plots, in the paper by these authors, appear to be correct, but the values quoted for the extinction coefficients, in the text, are too large by a factor of ten. Interference filters were used to isolate the various wavelengths. The Beer's Law plots are linear up to optical density values of 0.4, but then deviate from the straight lines, indicating that light of a different wavelength was present. This would account for the slightly lower value which these authors find for the extinction coefficient at 3130 Å.

The Mechanism of the Photolysis.

The results obtained with ketene alone, and ketene - inert gas mixtures are best explained in terms of the reactions and transitions shown in Figure 7D (facing page 50).

Spectroscopic evidence and theoretical calculations place the triplet state and the first excited singlet state of ketene 61 and 74 kcal mole⁻¹, respectively, above the ground state.²⁵

3660 Å

On the above basis, absorption at 3660 Å will result in the formation of excited singlet state molecules with approximately 4 kcal. mole⁻¹ of vibrational energy.

These may then undergo the three alternative processes seen in Figure 7D as [2], [3] and [4]. [2] is decomposition into singlet methylene ($^1\text{CH}_2$) and carbon monoxide. There is evidence that some singlet methylenes are formed at 3660 Å, although estimates of the percentage of the total methylenes which are singlet at this wavelength vary.^{26,41} [3] is intersystem crossing to the triplet state. Other workers²⁶ now agree that this is an intramolecular process and is not collision induced. The triplet state formed by [3] is assumed to live long enough to reach thermal equilibrium. Then it can undergo decomposition into triplet methylene ($^3\text{CH}_2$) and carbon monoxide, [5], or intersystem crossing to the ground state [6]. The fate of singlet and triplet methylene is assumed to be reaction with ketene to form ethylene and carbon monoxide.

Competing with [2] and [3] is collisional deactivation [4]. Since the average vibrational energy transferred per collision to polyatomic deactivators in other systems has been found²⁷ to be approximately 10 kcal mole⁻¹ it is probable that a single collision with either ketene, or one of the two gases added, is sufficient to deactivate the excited singlet state molecule to its lowest vibrational level. Figures 2D and 3D confirm the findings of previous workers^{6,13} that there is no tendency for the carbon monoxide quantum yield to reach a limiting value at high concentrations. Such a phenomena, which is observed in some other systems⁵², would be expected if either decomposition or intersystem crossing were occurring from the lowest vibrational level of the excited singlet state.

Intereystem crossing from this level of the singlet state has been included in previous mechanisms postulated for ketone photolysis^{10,42} but the evidence does not support the occurrence of such a step. It appears that from this level, internal conversion is considerably faster than either decomposition or intereystem crossing, and takes place to the exclusion of both. A fast internal conversion process [7] would also explain why no fluorescence from ketene has ever been observed, despite several attempts to find it. The above processes may be written

where K represents a ground state molecule of ketone, H a molecule of added gas, 1K_m a molecule of ketene in the m^{th} vibrational level of the excited singlet state, and 3K_n a molecule of ketene in the n^{th} vibrational level of the triplet state.

Application of the usual steady state assumption leads to:-

$$\frac{2}{\beta_{CO}} = \frac{k_2 + k_3}{k_2 + k_3 k_5 / (k_5 + k_6)} + \frac{k_{4a} (K)}{k_2 + k_3 k_5 / (k_5 + k_6)} + \frac{k_{4b} (H)}{k_2 + k_3 k_5 / (k_5 + k_6)} \quad (A)$$

$$\text{and} \quad \alpha = \frac{k_2}{k_2 + k_3 k_5 / (k_5 + k_6)} \quad (B)$$

where β_{CO} is the quantum yield of carbon monoxide and α is the fraction of methylenes formed which are singlet.

Figures 2D, 3D and 4D show how, at all temperatures, in agreement with (A), $2/\beta_{CO}$ increases linearly with (K) in the absence of added gas, and linearly with (H), at constant concentration of ketene. Furthermore, at the two lower temperatures the slopes for the three different gases (see Table S. below) are all of similar magnitude, a result which would be expected if [4a] and [4b] occur on every collision.

TABLE S.

3660 Å

<u>KETENE ALONE</u>		
T°C	Slope (moles ⁻¹ litre)	Intercept $k_2 + k_3$ (sec ⁻¹)
37	17,680.0	20.05 1.91×10^8
150	3,050.0	4.63 3.00×10^8
225	1,131.0	3.35 6.36×10^8
300	966.0	0.84 2.01×10^8

KETENE + C₂F₄

T°C	Slope (moles ⁻¹ litre)
37	23,350.0
150	2,810.0
225	530.0
300	158.0

Cont'd.

TABLE 3 (Continued)

$T^{\circ}\text{C}$	<u>KETENE + SF₆</u>	Slope (moles ⁻¹ litre)
37		17,950.0
150		2,580.0

Appreciable thermal polymerisation of ketene occurs at the higher temperatures. The experimental results at 225°C and 300°C (Figure 4D) are therefore less reliable than those at 37°C and 150°C. Nevertheless the differences between the slopes for ketene and those for C₄F₈ (Figure 4D and Table 3) are too large to be accounted for by experimental error. In Figure 10D the logarithms of the reciprocal slopes from Figures 2D, 3D and 4D are plotted against the reciprocal of the absolute temperature. Some similar data by Strachan and Noyes⁶ is included for comparison. It will be seen that the ketene points at 225 and 300°C are in line with the points at the lower temperatures, and the line, drawn through those points, has a similar slope to that fitting the data of Strachan and Noyes. But the C₄F₈ points at 225 and 300°C are quite clearly out of line.

As the temperature is raised, C₄F₈ appears to remove energy from the excited singlet state increasingly less efficiently than ketene. One possible explanation is that some of the collisions at the higher temperatures result in energy transfer to, rather than from, the excited singlet state.

If, because of the greater number of its vibrational modes, the average energy transferred from C_4F_8 were larger than from ketene, a fraction of the excited singlet state molecules could, on collision, be acquiring sufficient energy from C_4F_8 to decompose, but insufficient to do so from ketene. In this way C_4F_8 would become less effective at lowering the carbon monoxide quantum yield than ketene, as observed.

Without a knowledge of α , it is not possible to calculate or assign values for all the individual rate constants. But some calculations and assignments can be made and conclusions drawn. Assuming a collision diameter for ketene of 4 Å and that $[4\alpha]$ occurs on every collision, the value of $k_{4\alpha}$ is calculated to be $9.61 \times 10^9 \sqrt{T} \text{ mole}^{-1} \text{ litre sec}^{-1}$. Multiplication of $k_{4\alpha}$ by the intercepts divided by the slopes of the $2/\phi_{CO}$ v. (K) plots gives $k_2 + k_3$, whose values are listed in Table S. $k_2 + k_3$ appears to increase slightly with temperature. (The value at 300°C is unreliable as the intercept would be expected to be greater than unity). The absence of fluorescence, and the lack of evidence for decomposition or intersystem crossing occurring from the lowest vibrational level of the excited singlet state suggests that k_7 has a value greater than 10^9 sec^{-1} . The decrease in the slopes of $2/\phi_{CO}$ v. (K) or (M) plots with temperature (Table S), indicates that (5) has a small activation energy. If α is zero at this wavelength, this activation energy will be around $3500 \text{ cal/mole}^{28}$. If α is not zero, the value will be greater.

3130 Å

Absorption at 3130 Å leads to the formation of excited singlet state molecules with approximately 17 kcal of vibrational energy.

Table I, and Figure 5D, show that the carbon monoxide quantum yield is constant and, within experimental error, equal to 2.0 at low pressures, and only begins to decrease at pressures greater than 200mm. This is in reasonable agreement with the findings of Kistiakowsky and Mahan⁹, and Porter and Connolly.⁸ In both cases filter solutions were used to isolate the 3130 Å region, as in this work. Taylor and Porter¹³, using interference filters, found quantum yields considerably lower than those reported either here or by the authors mentioned above. This lack of agreement makes it probable that Taylor and Porter did not isolate 3130 Å efficiently, and that the interference filters were transmitting some light of longer wavelength.

A carbon monoxide quantum yield having the value 2.0 at low pressures, indicates that every molecule absorbing a quantum under these conditions ultimately decomposes. There is evidence, from other work,^{26,29} that not all the methylenes formed on decomposition are singlet. This can be explained if intersystem crossing [3a], followed by decomposition from a high vibrational level of the triplet state, is competing with direct decomposition, [2a] (Figure 7D).

The most likely explanation of the departure from linearity of the $2/\beta_{CO}$ v. (K) plot, shown in Figure 5D, is that collisional deactivation is multistage,¹⁰ and that only part of the 17 kcal of vibrational energy of the excited singlet state molecule is lost as a result of its first collision with ketene. After this first collision, the excited molecule still retains sufficient vibrational energy to decompose [2b] or undergo intersystem crossing to the triplet state [3b], from which it then decomposes.

Only after additional collisions does the excited singlet state molecule lose all its excess vibrational energy. The data are not sufficiently accurate to allow any of the methods for determining the number of deactivation stages¹⁰, to be applied. But a two-stage process seems the most likely and, as will be shown later, will adequately account for the data.

Figure 5D shows that when inert gases cyclo-C₄F₈ and SF₆ are used at this wavelength and 37°C, with small constant amounts of ketene, the plots of $2/\beta_{CO}$ v. (M) are linear with unit intercept, and the primary quantum yield $\beta_{CO}/2$ is reduced below unity by the smallest quantities of inert gas used. Both C₄F₈ and SF₆ have more vibrational modes than ketene and might be expected to absorb greater amounts of vibrational energy than ketene on collision with the excited singlet state molecule. Thus while the latter requires at least two collisions for deactivation by ketene, it would still be deactivated in a single collision by C₄F₈ and SF₆. Such single stage deactivation by C₄F₈ and SF₆ would account for small additions of either gas lowering the primary quantum yield, and for $2/\beta_{CO}$ increasing linearly with pressure of inert gas. Such an explanation means that the major part of the 17 kcal of vibrational energy possessed by the excited molecule is lost on its first collision with either of the inert gases. This is not unreasonable in the light of the observations of other workers on the amounts of energy transferred per collision during the deactivation of vibrationally excited molecules.²⁷

As the temperature is raised, more vibrational modes of C_4F_8 and SF_6 become active and the capacity of the two gases for absorbing vibrational energy on collision is correspondingly reduced. There is a likelihood of single stage deactivation giving way to a two-stage process at higher temperatures. Evidence of this change is to be found in the data at $100^\circ C$ (Table L and Figure 6D). In contrast to $37^\circ C$, at least 100mm. of C_4F_8 or SF_6 have to be added before the carbon monoxide quantum yield is reduced significantly, and the difference between the deactivation behaviour of the two gases and that of ketene is less marked than at $37^\circ C$. This would be explained if deactivation by C_4F_8 and SF_6 becomes similar to that by ketene, namely two-stage, at $100^\circ C$. The slightly greater deactivation efficiency of C_4F_8 and SF_6 is understandable if on the first collision, the excited singlet state molecule still loses more energy to either of the inert gases than to ketene. It will then be reduced to a lower vibrational level after an inert gas collision than after a collision with ketene. Decomposition and interystem crossing from this lower level will be slower than from the higher level, reached after an encounter with ketene, and thus the two inert gases will remain slightly more efficient deactivators than ketene.

The processes occurring at the lower temperature at 3130 Å may be written:-

Continued.../

The processes occurring at the lower temperature at 3130 Å may be written:- (Continued).

Application of the steady state assumption leads to,

$$\frac{2}{P_{CO}} = \frac{k_{2a} + k_{3a} + k_{4a}(K) + k_{4b}(M)}{k_{2a} + k_{3a} + \frac{(k_{2b} + k_{3b}) \cdot k_{4a}(K)}{k_{2b} + k_{3b} + k_{4a}(K) + k_{4b}(M)}} \quad (C)$$

and when $M=0$,

$$\alpha = \frac{k_{2a} + \frac{k_{2b} \cdot k_{4a}(K)}{k_{2b} + k_{3b} + k_{4a}(K)}}{k_{2a} + k_{3a} + \frac{(k_{2b} + k_{3b}) \cdot k_{4a}(K)}{k_{2b} + k_{3b} + k_{4a}(K)}} \quad (D)$$

From (C),

$$\frac{2}{P_{CO}} = \frac{X + k_{4a}(K) + k_{4b}(M)}{X + Y \frac{k_{4a}(K)}{Y + k_{4a}(K) + k_{4b}(M)}}$$

where $X = k_{2a} + k_{3a}$

and $Y = k_{2b} + k_{3b}$

When M is large $2/\beta_{CO}$ will become linear with M , with a slope equal to k_{4b}/X . Figure 5D shows that this is observed when M is C_4F_8 , the limiting slope having the value $19.6 \text{ (moles/litre)}^{-1}$. Hence $k_{4b} = 19.6X \text{ (moles/litre)}^{-1} \text{ sec}^{-1}$. At $3660 \text{ \AA}$ $k_{4a}/k_{4b} = 17,680/23,330$ and therefore

$$k_{4a} = 19.6X \times (17,680/23,330) \text{ (moles/litre)}^{-1} \text{ sec}^{-1}$$

$$k_{4a} = 14.9X \text{ (moles/litre)}^{-1} \text{ sec}^{-1}$$

Decomposition from the q^{th} level of the excited singlet and from the w^{th} level of the triplet state, should be slower than from the r^{th} and v^{th} levels, respectively. Thus, Y should be less than X . If we assume $Y = X/4$, and using $k_{4a} = 14.9X$, and $k_{4b} = 19.6X$, we find,

$$\frac{2}{\beta_{CO}} = \frac{X + 14.9X(K) + 19.6X(M)}{X + \frac{X}{4} \frac{14.9X(K)}{X + 14.9X(K) + 19.6X(M)}}$$

and

$$\frac{2}{\beta_{CO}} = \frac{1 + 14.9(K) + 19.6(M)}{1 + \frac{14.9(K)}{1 + 59.6(K) + 78.4(M)}}$$

when $(M) = 0$,

$$\frac{2}{\beta_{CO}} = \frac{1 + 14.9(K)}{1 + \frac{14.9(K)}{1 + 59.6(K)}} \quad (E)$$

and when $(K) = 0.00259$,

$$\frac{2}{\beta_{CO}} = \frac{1.0386 + 19.6(M)}{1 + \frac{0.0386}{1.1544 + 78.4(M)}} \quad (F)$$

Equation (E), and the values of (K) used experimentally, were employed to calculate values of $2/\beta_{CO}$. These are shown in Table T, together with the experimental values.

Equation (F), and the values of (M), used at constant (K), were employed to calculate values of $2/\beta_{CO}$. These are shown in Table U, together with the experimental values.

TABLE T.

(K) mole/litre	$2/\beta_{CO}$ calculated	$2/\beta_{CO}$ experimental
0.00256	1.01	1.01
0.00624	1.02	0.99
0.00085	1.00	1.03
0.01061	1.06	0.97
0.02148	1.16	1.20
0.01552	1.10	0.98
0.01966	1.14	1.07
0.02416	1.19	1.14
0.00083	1.00	1.00
0.02370	1.18	1.22
0.03784	1.33	1.37
0.04233	1.38	1.46
0.02825	1.23	1.17
0.03262	1.28	1.23

$$(M) = 0$$

TABLE U.

(K) = 0.00259 mole/litre

(M) mole/litre	$2/\rho_{CO}$ calculated.	$2/\rho_{CO}$ experimental
$M = C_4F_8$		
0.02152	1.44	1.53
0.01422	1.30	1.32
0.00336	1.08	1.06
0.01692	1.35	1.38
0.00714	1.15	1.12
0.01056	1.22	1.20
0.00132	1.03	0.97
0.04021	1.81	1.77
0.08026	2.60	2.64
0.06176	2.24	1.91
0.09811	2.95	3.00
$M = SF_6$		
0.02002	1.41	1.40
0.01423	1.30	1.27
0.01076	1.23	1.25
*0.00338	1.08	1.18
*0.00794	1.17	1.05
*0.00367	1.08	1.07
*0.00173	1.04	1.00
0.00771	1.16	1.12

*These points are not plotted in Figure 11D, to avoid confusion with C_4F_8 points.

The results of these calculations are plotted in Figure 11D. The solid lines are the calculated values of $2/\beta_{CO}$ and the points are the experimentally determined values. The good agreement between the calculated and experimental values shows that the proposed mechanism, with its two stage deactivation by ketene, and single stage deactivation by inert gases, adequately accounts for the experimental data at 37°C . The data at 100°C have not been treated in the same way as those at 37°C because the situation at the higher temperature is more complicated. Although C_4F_8 or SF_6 still deactivate the excited singlet state molecules more effectively than ketene at 100°C , decomposition or intersystem crossing can still occur after one collision with these gases.

The Variation of k_2 with Energy.

If the mechanism proposed above is correct, the slopes of $2/\beta_{CO}$ v. (K) plots at $3660 \text{ \AA}$ are, from equation (A) given by,

$$\frac{k_{4a}}{k_2 + \frac{k_3 k_5}{k_5} + k_6}$$

The limiting slopes of similar plots at $3130 \text{ \AA}$, at high concentrations of ketene, are from equation (C) equal to

$$\frac{k_{4a}}{k_{2a} + k_{3a} + k_{2b} + k_{3b}}$$

Therefore the slopes at the two wavelengths are given by different expressions of rate constants. Previous workers^{8,10,13}, and more recently Bowers⁵¹ have assumed that the slopes at the different wavelengths are directly comparable.

They have assumed the simpler mechanism,

which leads to

$$\frac{2}{p_{\text{CO}}} = 1 + \frac{k_{11}}{k_9} + \frac{k_{10}}{k_9} (\text{CH}_2\text{CO}).$$

The slopes are then all equal to k_{10}/k_9 and their variation with wavelength and temperature has been assumed to reflect the variation of k_9 with energy. That this assumption is invalid, and the mechanism used too simple, is shown when the apparent values of k_9 are compared with one another and with theory. The collision deactivation rate constant, in this case k_{10} , has been calculated previously, assuming a collision diameter for ketone of 4 Å. The apparent values of k_9 were then calculated from the slopes obtained in this work at 3660 Å. These are listed, together with values of other workers, in Table II (page 41). Plots of $\log_{10} k_9$ (the theoretical decomposition rate constant) against $E + E_{00}$ were drawn for values of E_{00} from 70.6 to 68.6 kcal mole⁻¹ and for E_0 values from 5.7 to 3.4 kcal mole⁻¹. The best fit between the experimental and theoretical values was achieved when $E_{00} = 70$ kcal mole⁻¹ and $E_0 = 5.0$ kcal mole⁻¹. These values were then used to obtain $\log_{10} k_9$ at various $E + E_{00}$ values, as listed in Table B (page 42), and plotted as the dotted line in Figure 8D. Also on this plot are experimental values, shown as the solid line.

The experimental line deviates from the smooth theoretical curve and exhibits a sudden change of slope between $E + E_{00}$ values of 79.5 and 87 kcal mole⁻¹. Such a near discontinuity cannot be explained on the basis of reactions(8) - (11) and provides evidence in favour of the more complex mechanism, in which the slopes at the different wavelengths are not directly comparable.

If the more complex mechanism proposed in this work is correct, it should still be possible to investigate the variation of the rate constants for decomposition of the excited singlet state (k_2 , k_{2a} and k_{2b}) with energy, if α , the proportion of total methylenes formed which are singlet, were known. The slopes at 3660 Å, and the limiting slopes at high concentrations of ketene at 3130 Å, divided by α would give

$\frac{k_{4a}}{k_2}$ and $\frac{k_{4a}}{k_{2a} + k_{2b}}$ respectively. The determination

of α is the subject of Part II.

PART II

THE PROPORTIONS OF SINGLET AND TRIPLET

METHYLENE

Differences in the Reactivities of Singlet and Triplet Methylene

Before considering the determination of the proportions of singlet and triplet methylene, it is necessary to review the evidence for differences in the reactivities of the states of methylene.

1. Addition to Carbon - Carbon Double Bonds.

Skell and Woodward³² and Doering and LaFlamme³³ observed that methylene (formed by the photolysis of diazomethane dissolved in hydrocarbon) added cis stereospecifically to the double bond of cis or trans butene - 2. The stereospecificity coupled with the rapidity of the reaction pointed to the methylene so formed being in the singlet state.^{31,32} It is now generally accepted that the addition of singlet methylene to the carbon - carbon double bond is stereospecific, and occurs via the formation of an excited cyclopropane which isomerizes to other products, if not stabilized by collisions.⁴⁷

Following Hersberg's detection of the spectrum of triplet methylene, when diazomethane was flash photolysed in the presence of an excess of inert gas,¹⁷ Frey photolysed diazomethane in the presence of both argon and cis butene-2.³⁷ The total pressures ranged from 210 to 320cm, and the argon to cis butene-2 ratio varied from 7.6/1 to 1600/1. He found that as the ratio increased the stereospecificity of the addition reaction was lost. This was taken as evidence that triplet methylene adds to carbon - carbon double bonds non-stereospecifically.

Addition of a small amount of oxygen greatly decreased the products favoured by dilution with argon. Since oxygen, being a triplet species itself, would be expected to react readily with triplet methylene or its addition products, this seemed to confirm the presence of triplet methylene in this system.

Benson and DeMore³⁸ pointed out that dilution of the reaction mixture with argon, while maintaining a constant total pressure, leads to decreased deactivation efficiency. Hence the loss of stereospecificity may result from geometric isomerisation of the initial excited adducts rather than from a different mechanism of reaction of triplet methylene.

However, Frey's contention that triplet methylene reactions were being observed is supported by the work of Duncan and Cvetanovic.³⁹ These authors avoided the disadvantages of working with gas mixtures of such high dilution, to produce triplet methylene, by using the mercury - photosensitized decomposition of ketene. In this system with cis butene - 2 as added olefin, they found that the product ratios became constant at pressures greater than 500mm and that the values of these ratios were very similar to those observed by Frey³⁷ at his highest inert gas to olefin ratio.

Thus despite Benson and DeMore's doubts, the evidence does point to the formation of triplet methylene in these systems and to its adding to carbon - carbon double bonds non-stereospecifically. Such non-stereospecific addition is explained if it takes place via the formation of a diradical in which rotation about the former double bond occurs before subsequent cyclization or isomerisation.

2. Insertion into Carbon - Hydrogen Bonds.

There is considerable evidence that singlet methylene inserts into carbon - hydrogen bonds. The work of Doering and Prinsbach³⁴ helped to establish this. They used the reaction of methylene with isobutene, labelled with carbon - 14 in the 1 - position. A number of products were formed in this reaction but the one of interest was 2 methyl butene - 1. Frey³⁵ had shown that, in this system, the yield of 2 methyl butene - 1 was independent of the total pressure of the system. This indicated that the means of formation of this product was by insertion into one of the C - H bonds of the methyl groups. If it were the result of the isomerisation of the initially formed 1, 1, dimethylcyclopropane, then its yield would be pressure dependent. However a radical reaction scheme could be responsible for the formation of 2 methyl butene - 1, but this would lead to scrambling in the C - 14 labelled isobutene system. If the reaction to give 2 methyl butene - 1 were direct insertion, then all the C - 14 should appear in the 1 - position of the product. Doering and Prinsbach found no scrambling in the liquid phase, and in the gas phase, only 8% of the C - 14 appeared in the 3 - position. This showed that direct insertion was the major reaction pathway.

Furthermore, additional evidence indicates that it is only singlet methylene which reacts in this way and that triplet methylene does not insert into carbon - hydrogen bonds. In Frey's experiments with the methylene - cis butene - 2 system,³⁷ the yield of the insertion product 2 - methyl butene - 2 declined from 12.9% to 4% as the inert gas to cis butene - 2 ratio was increased.

A similar low yield of 2 methyl butene - 2 was found by Duncan and Cvetanovic³⁹ when triplet methylene, from the mercury photosensitized decomposition of ketene, was reacted with cis butene - 2. The residual yield of this product can be accounted for by the isomerisation of the diradical formed when triplet methylene adds to the olefin.

Further evidence that triplet methylene does not undergo the insertion reaction is to be found in the comparison of the high pressure yields of the products formed when singlet methylene (from the photolysis of diazomethane) and triplet methylene (from the mercury photosensitized decomposition of ketene) react with isobutene (Table V).

TABLE V.

Methylene + Isobutene

	$^1\text{CH}_2$ 35	$^3\text{CH}_2$ 39
1,1, dimethylcyclopropane	57%	91%
2-methyl butene - 1	34%	6.5%
2-methyl butene - 2	8%	2.3%
3 methyl butene - 1	0%	0.5%

The increased yield of the addition product 1,1, dimethylcyclopropane, and decreased yields of the insertion products, 2 methyl butene - 1 and 2 methyl butene - 2, in the triplet methylene system as compared with the singlet methylene system, indicate the absence of insertion into carbon-hydrogen bonds by triplet methylene.

The small yields of the three methyl butenes in the triplet methylene system is again accounted for by the isomerisation of the diradical formed when the methylene triplet adds to the olefin.

Thus the differences in the reactivities of singlet and triplet methylene may be said to be fairly well established. Singlet methylene adds stereospecifically to carbon - carbon double bonds, whereas triplet methylene adds non-stereospecifically. Singlet methylene inserts into carbon - hydrogen bonds but triplet methylene does not.

Determination of the Proportions of Singlet and Triplet Methylene.

Until quite recently it was generally assumed that in the photolysis of diazomethane and in that of ketene, at normal pressures, only singlet methylene was formed. But over the past few years evidence has been accumulating that some triplet methylene is also generated. Frey³⁰ has pointed out that the postulation of triplet states in these, and analogous systems, helps in the simplification and interpretation of many experimental results. One relevant example is in the observations of Strachan and Noyes⁶ on the effect of oxygen on the quantum yield for the formation of ethylene in the photolysis of ketene. The effect can be explained by postulating the formation of $\cdot\text{CH}_2\text{COCH}_2\cdot$ with a relatively long lifetime.³¹ The reaction of this radical with oxygen, and its long lifetime are both consistent with it being formed by the reaction of triplet methylene with ketene.³⁰

The determination of the proportions of singlet and triplet methylene formed in the photolysis of these two compounds has been the subject of several recent publications.

The differences in the reactivities of the two methylenes with respect to the carbon - carbon double bond and the carbon - hydrogen bonds of olefins have formed the basis of all the determinations so far published.

Simons and Rabinovitch²⁹ estimated that there was 29% triplet methylene formed at high pressures in the system ketene - cis butene - 2 d_0 , or cis butene - 2 d_0 at 3200 Å and 25°C. The proportion of triplet appeared to be pressure dependent, increasing from a small or zero value at low pressures to a constant level at high pressures. A similar amount of triplet methylene and a similar pressure dependence was found by Rabinovitch and Dorer⁴⁰ with the ketene - butene - 1 system at the same wavelength and temperature.

Ho, Unger and Noyes⁴¹ photolysed ketene in the presence of cis butene - 2 in two wavelength regions. From the product composition they estimated that in the region 2650 - 2950 Å, 98% of the methylenes formed were singlet. In the longer wavelength region, 3460 - 3820 Å the proportion of singlet was well below 50%. Rabinovitch, Watkins and Ring⁴² photolysed both ketene and diazomethane in the presence of cis butene - 2, (and in one experiment ethylene), over a pressure range which went up to several atmospheres. A maximum appeared to occur in the proportion of triplet methylene in both systems at around one atmosphere. The temperature effect reported in this work was distinctly odd. The proportion of triplet methylene was found to increase as the temperature was raised in the diazomethane system, but to decrease as the temperature was raised in the ketene system.

Kistiakowsky and Carr²⁶ photolysed ketene in the presence of trans butene - 2 and calculated the percentages of triplet methylene formed at 2800, 3130, 3340 and 3660 Å. In experiments with added oxygen, products which were a result of triplet methylene reactions were eliminated. Ethane and methane were entirely eliminated by oxygen. Comparison of runs with and without oxygen enabled the authors to calculate the amount of products formed by triplet methylene, and to estimate the quantities of "triplet type" products that were formed by isomerisation of the singlet methylene - trans butene - 2 'hot' adducts. The variations in methane and ethane production with the wavelength of the incident light were the same as those of cis 1,2, dimethylcyclopropane and 3 methyl butene - 1. The authors therefore concluded that methane and ethane were formed as a result of triplet methylene abstraction reactions. Taking this into account they estimated the proportions of triplet methylene as 15% at 2800 and 3130 Å, 30% at 3340 Å and 40% at 3660 Å.

McKnight, Lee and Rowlands⁴³ very recently reported 29% of methylene - t in the system CH₃C = O - ethylene, photolysed at 3130 Å.

It can be seen that agreement between the findings of the different authors, discussed above, is not good.³ In all cases ketene or diazomethane was photolysed in the presence of an olefin. The reliability of this method was questioned by Cundall and Davis⁴⁴, who suggested that the added olefin might quench excited state triplet, hence altering the distribution of methylene between its singlet and triplet states.

The results obtained by these workers were not reproducible and later work showed that the isomerisation of *cis* butene - 2, in the ketene - *cis* butene-2-system at 3130 Å and 46⁰ C, was very slight.⁴⁶

Although the quenching of triplet ketene by the olefin is thus ruled out, there are other reasons for questioning the reliability of using added olefin to determine the relative amounts of singlet and triplet methylene present. Uncertainties exist in such systems as to how much of a given product is formed from singlet methylene and how much from triplet methylene. The triplet addition product may also be formed by the isomerisation of the 'hot' singlet methylene - olefin adduct. The singlet methylene insertion products may also be formed by the isomerisation of the triplet methylene - olefin diradical. Furthermore, to avoid isomerisation of 'hot' molecules, high pressures have to be used which promote the conversion of singlet methylene to triplet methylene^{37,48} and thereby alter the proportions of the two species present. These uncertainties may account for the lack of agreement between the results, discussed above, of the different workers using this method. They make it desirable to find alternative methods to olefin addition for determining the proportions of the two methylenes present.

One alternative method which has been suggested by Kistiakowsky and DeGraff⁴⁵ is the use of carbon monoxide. They found that triplet methylene reacted more readily with carbon monoxide than did singlet, and therefore triplet methylene could be removed, and the reactions of singlet methylene studied. They gave no estimate, however, in their note of the relative proportions of the two methylenes formed in the photolysis of ketene.

A second alternative method is to add cyclopropane. The possibilities of this method, and the results obtained using it will now be discussed.

Photolysis of Ketene - Cyclopropane Mixtures

The insertion reactions of methylene occur only with the singlet state. In the photolysis of ketene - cyclopropane mixtures, at high cyclopropane/ketene ratios, it was expected that all the singlet methylene would react with the hydrocarbon, whilst the triplet would react with ketene. Triplet methylene could, however, react with the cyclopropane, abstracting a hydrogen atom to form methyl, and leading to methane and ethane as by products. Previous work indicated that the contribution from this reaction was slight, and that the amounts of methane and ethane formed were small.⁴⁹ The main reactions occurring at high cyclopropane/ketene ratios were therefore expected to be:-

Where ${}^1\text{CH}_2$ and ${}^3\text{CH}_2$ denote singlet and triplet methylene respectively.

$$(\text{Total CO}) - \text{C}_2\text{H}_4 \quad \equiv \quad \text{CO from} \quad [1]$$

$$\quad \equiv \quad {}^1\text{CH}_2 + {}^3\text{CH}_2$$

$$\text{and } {}^3\text{CH}_2 \quad \equiv \quad \text{C}_2\text{H}_4 \text{ from} \quad [3]$$

Hence

Hence (Cont'd)

$$\frac{{}^1\text{CH}_2 + {}^3\text{CH}_2}{{}^3\text{CH}_2} \equiv \frac{\text{Total CO} - \text{C}_2\text{H}_4}{\text{C}_2\text{H}_4}$$

$$\frac{{}^1\text{CH}_2}{{}^3\text{CH}_2} \equiv \frac{\text{Total CO}}{\text{C}_2\text{H}_4} - 2$$

Also

$$\frac{{}^1\text{CH}_2}{{}^3\text{CH}_2} \equiv \frac{\text{C}_4\text{H}_8}{\text{C}_2\text{H}_4}$$

Experimentally, in agreement with this mechanism carbon monoxide, ethylene and C_4 hydrocarbons were the only major products formed. Traces of methane and ethane were detected but their yields were very small in comparison with those of the other products (see page 22). Methane and ethane are by products in the photolysis of ketene - n - butane⁴⁹ and ketene - butene - 2²⁶ mixtures. Their absence as significant by products in the cyclopropane - ketene mixtures must indicate that the rate of hydrogen abstraction by triplet methylene from cyclopropane is considerably slower than from either n - butane or butene - 2. This is to be expected if the reactivity of ${}^3\text{CH}_2$ is similar to that of CH_3 , whose relative rates of hydrogen abstraction, at 37°C, from cyclopropane, n - butane and butene - 2 are 1: 28 : 103 respectively.⁵⁰

It was difficult to obtain columns and conditions which would separate carbon monoxide, ethylene, excess cyclopropane and the insertion products from each other, and from the impurities in the cyclopropane. The peaks of the insertion products occurred on the tail of the cyclopropane peak, as did some impurities in the hydrocarbon.

It was therefore decided to measure only carbon monoxide and ethylene.

Figure 9D shows the $\left[\frac{\text{carbon monoxide}}{\text{ethylene}} \right]$ ratio as a function of cyclopropane/ketene ratio at 37°C . Both at 3130 Å and 2700 Å the carbon monoxide/ethylene ratio becomes constant when the cyclopropane/ketene ratio exceeds 20 : 1. Further results, not shown in Figure 9D, indicate that this constancy is maintained up to cyclopropane/ketene ratios of 80/1. The limiting values of the carbon monoxide/ethylene ratio are 8.0 and 7.2 at 3130 and 2700 Å, respectively. The corresponding proportions of triplet methylene at the two wavelengths are therefore 14 and 16% respectively. These values are in excellent agreement with those of Kistiakowsky and Carr²⁶ obtained at similar wavelengths. Runs were done at each wavelength with propylene in place of cyclopropane. As expected, no ethylene was detected in these experiments.

It appears that at 3130 Å, not all of the methylenes formed are singlet. Some 14% are triplet. This is further evidence in support of the mechanism outlined on page 55, in which intersystem crossing occurs from the higher vibrational levels of the excited singlet state of ketene to form vibrationally excited triplet ketene which decomposes to yield triplet methylene.

The value of α at 3130 Å and 37°C can be used to calculate $k_{2a} + k_{2b}$, the rate constants for decomposition from the singlet state. The limiting slope of the $2/\phi_{\text{CO}} v$ (K) plot is equal to 14.9 (mole/litre)⁻¹ and this divided by α furnishes $k_{4a}/k_{2a} + k_{2b}$. k_{4a} has been calculated previously, (page 52) and hence

$$k_{2a} + k_{2b} = 9.77 \times 10^9 \text{ sec}^{-1}.$$

Knowing the value of $k_{2a} + k_{2b}$, α can be used to calculate $k_{3a} + k_{3b}$, the sum of the rate constants for intersystem crossing to the triplet state. This was found to be $1.59 \times 10^9 \text{ sec}^{-1}$.

When α is determined at $3660 \text{ \AA}$, and at various temperatures at $3660 \text{ \AA}$ and $3130 \text{ \AA}$, it will be possible to compare the rate constants for decomposition, at both wavelengths and all temperatures, with the rate constants calculated from unimolecular reaction theory. Attempts to measure α at $3660 \text{ \AA}$ in this work were frustrated by the small quantities of products formed in the photolysis of ketene - cyclopropane mixtures. A reaction cell surrounded by the ultraviolet lamp⁹ would increase the amount of products, and this together with a more sensitive chromatograph would enable α to be determined at $3660 \text{ \AA}$.

It would be advantageous to know the rate of hydrogen abstraction by triplet methylene compared to its rate of reaction with ketene. The method of producing triplet methylene as used by Duncan and Cvetanovic³⁹ might be suitable for this purpose.

In the ketene-cyclopropane system, singlet methylene can react with the C = C bond in ketene or with the C - H bonds of cyclopropane. The relative rates of double bond addition and C - H bond insertion have been measured in methylene-olefin systems, and the ratio of addition: insertion is 10-30:1⁴⁷. Aliphatic carbon-hydrogen bonds are attacked by methylene, 6-17 times slower than carbon - carbon double bonds³⁶. In the ketene- cyclopropane system the carbon monoxide/ethylene ratio became constant at a cyclopropane/ketene ratio of 20/1. This indicated that virtually all the singlet methylene, formed in the photolysis at this ratio, was reacting with cyclopropane, and it can be estimated from this that singlet methylene reacts with ketene about twice as fast as

with cyclopropane, or about twelve times as fast as with one of the C - H bonds of cyclopropane. Thus the ratio of addition: insertion observed in this system is within the range found by other workers.

The singlet/triplet ratio of methylene could be determined by measuring the insertion products from the reaction of singlet methylene with cyclopropane. As indicated above,

$$\frac{{}^1\text{CH}_2}{{}^3\text{CH}_2} = \frac{\text{C}_4\text{H}_8}{\text{C}_2\text{H}_4}, \text{ so that if methylcyclopropane}$$

and butenes were measured, as well as ethylene, a second determination of the singlet/triplet ratio could be obtained.

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