

Reaction of Methylene with Methanol

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Ketene has been photolyzed at 40° in the presence of methanol vapor by mixed light of about 3200 Å.

Ethanol and dimethylether have been found as main products together with some ethane, ethylene, *etc.* Based on an assumed reaction scheme, ratio of rate constants has been obtained, but whether the formation of ethanol and dimethylether has resulted from the insertion of CH₂ or the radical combinations with CH₃, is difficult to discuss from the results obtained.

INTRODUCTION

Several papers have appeared recently which suggest the insertion of CH₂ radical in the C-H bond of hydrocarbons in the photolysis of mixtures with ketene or diazomethane¹⁻⁶). When the substrate is methanol, we may expect to obtain ethanol and if the insertion can take place in the O-H, methylether should be produced. Preliminary investigation has been undertaken to find out these expected products in the photolysis of methanol-ketene mixture and also the variation of each with methanol/ketene ratio. Research is on the way at present, and the result is rather qualitative and evidences to discuss the mechanism are not sufficient. However, it appears significant to present the facts observed and some discussion at this stage.

EXPERIMENTAL

A cylindrical glass reactor (No. 1, 43mm×31.5mmφ, 33.5cc for pressure change measurements; No. 2, 45mmφ×170mm, 270cc for product analysis runs) furnished with a quartz window at one base was mounted in an electric furnace. The reactor had two capillary openings which were connected through silicone-greased cocks with the devices such as evacuation, reactant reservoirs, Töpler pump and manometers. The pressures in the reactor as well as the small change during the run were measured by a membrane type manometer, which consisted of a thin glass plate (thickness 0.1mm, 35mmφ) separating the reaction system and the counterbalancing pressure system and a strain gauge pasted on the rear surface of the membrane as shown in Fig. 1. The deflection of the membrane caused by pressure unbalance is converted into the change of electric resistance of strain gauge consisting an arm of a Wheatston's bridge, then the unbalance potential is multiplied by three-stage a. c. amplifier and the output is introduced into a 2 mV automatic balancing recorder. The precision of this instrument was 0.02mm Hg and the linearity between pressure and output was satisfactory within the pressure change experimented.

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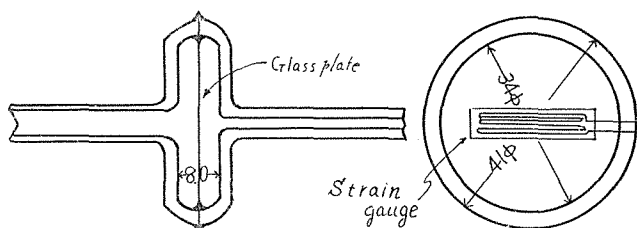


Fig. 1. Glass membrane manometer.

A high pressure mercury lamp (SHLD-500 watt) was operated by d.c. 5.0 ± 0.2 A and the light beam from the fire spot (6.5mm) was made roughly parallel by a quartz lens and adjusted by a stop to the size just to cover the window and projected axially into the reactor through a filter UV-27 (transparency 2600Å 25%, 3130Å 80%, >3650 Å 95%) and a layer of water (thickness 17 mm, cooled by running water). The mutual positions in the optical system were kept the same as careful as possible throughout this study.

Referring to the intensity distribution of the lamp (approximate relative intensity: 4358 Å 100, 4078 Å 14, 3650 Å 79, 3341 Å 16, 3132 Å 17, 3022 Å 10, 2968 Å 7, backgrounds are *ca.* 2), the absorption coefficient of ketene vapor⁽¹²⁾ and the experimented pressure range we may say the most effective wave lengths must be 3130 Å and 3341 Å; this may partly be supported by the results of the experiments with the filter UV-D 1 (<2900 Å 0%, 3600 Å 50%, >4000 Å 0%) in which the reaction rate was reduced to about 1/5 of that with UV-27.

Ketene was produced by pyrolysis of freshly fractionated diketene at 550°. The crude product was, after bulb-to-bulb distillation under vacuum, shaken with some amount of tetraline in order to remove allene which was found to be the sole impurity (cyclopropane and propylene were not detected), and then vaporized at -20° before each run (vapor pressure of tetralne = 2.0×10^{-3} mm at -20°). The purity was ascertained as more than 99% (the rest was N₂ used for purge) by g.l. chromatography.

Methanol of c. p. grade was dehydrated with Mg methylate and fractionated; absence of ethanol, acetone, form- and acetaldehyde was confirmed. The reaction products mixture was withdrawn by a Töppler pump through a trap of -40°, and the non-condensable gas was separated from the liquid.

The analysis was made mainly by gas chromatography as described below: for the separation of

CO, H ₂ , CH ₄ :	g. s. chromato., Active carbon 2m, carrier gas H ₂ (N ₂), 56°.
C ₂ H ₆ , C ₂ H ₄ , C ₃ H ₈ , C ₃ H ₆ :	g. s. c. Na-permutite 2m, H ₂ 40°.
CH ₂ CO, allene, CH ₃ OCH ₃ :	g. l. c. dibenzylether 2m, H ₂ 26°.
C ₂ H ₄ , C ₃ H ₆ , allene, cyclopropane:	g. l. c. silicone oil 4m, H ₂ 25°.
CH ₃ COOCH ₃ , CH ₃ COOC ₂ H ₅ , CH ₃ OH, C ₂ H ₅ OH:	g. l. c. polyethylene glycol 4m, H ₂ , 58°.

Formaldehyde was estimated colorimetrically in acid condition with Schiff's reagent by means of spectrophotometer at 5630 Å.

RESULTS

Two dark reactions were observed, *i. e.*, the dimerization of ketene vapor and methyl acetate formation between ketene and methanol in vapor phase, both of these result in pressure decrease. Concerning the pressure change measurement of photoreaction, the extent of the former reaction was only minute to disturb the observation when the pressure of ketene was low, *e. g.*, 8mm, but the latter made the precise measurement somewhat difficult since the dark reaction pressure change was comparable to that of photoreaction and, moreover, the plot of this pressure change against time deviated from linearity, when the ratio of methanol to ketene (denoted by γ hereafter) is more than 3, appreciably in few minutes of the reaction which was necessary to evaluate the rate.

The figures reported here are the differences between the mean rate of the pressure change of photoreaction and the average of the mean dark reaction pressure changes before and after the photolysis, each in 3 minutes. In Fig. 2 the rates of the pressure change in photolysis are given, which were obtained under a fixed condition, *i. e.*, reactor No. 1, 40°, lamp current 5.0 ± 0.2 A, CH_2CO initial pressure 8.0mm, CH_3OH 0–57.0mm, $\gamma=0-7.13$ (at this condition the absorption of light is calculated as 2.9% of the incident at 3130 Å). Scattering of the points is rather large, but we may be able to say that the rate of pressure drop is reduced in the presence of methanol and approaches asymptotically to a constant value at higher γ .

Results on product analysis are given in Fig. 3, the condition being as follows:

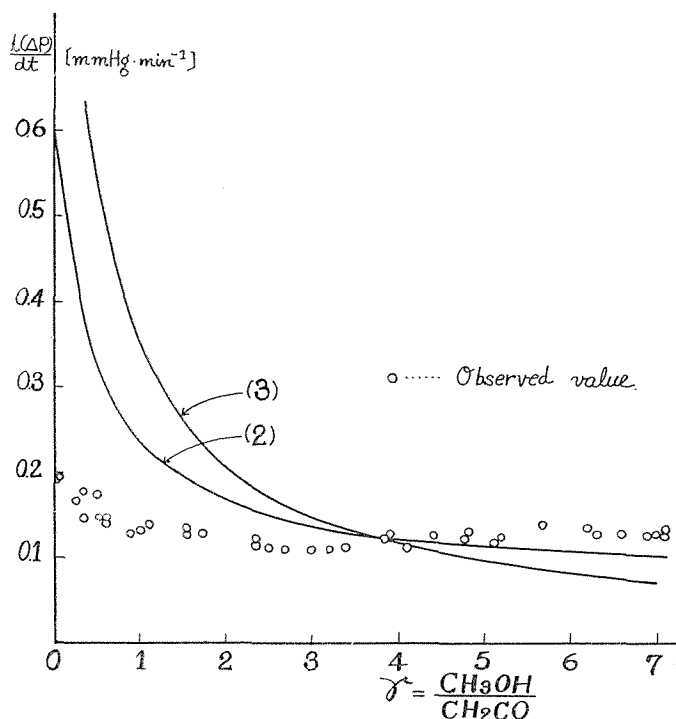


Fig. 2. Rate change with $\text{CH}_3\text{OH}/\text{CH}_2\text{CO}$ ratio
Lines (2) and (3): Calculated; see the text.

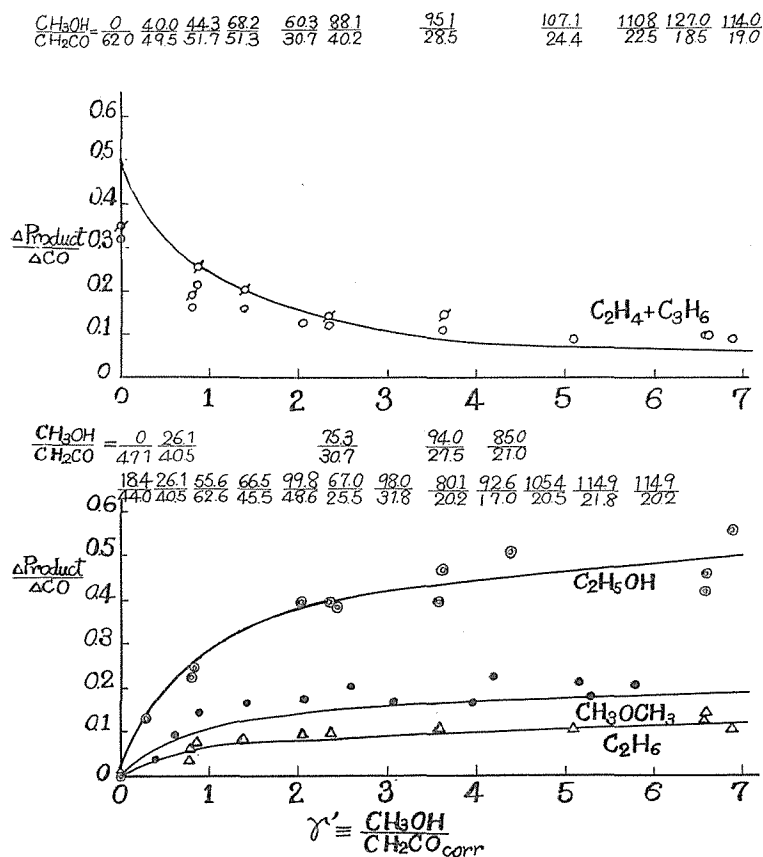


Fig. 3. Reaction products. (solid lines : calculated)

reactor No. 2, irradiation period 30 min, reaction temp. $42 \pm 1^\circ$, initial pressure of ketene 18.5–77.6mm, that of methanol 0–127.0mm (combinations of each pressure are given in Fig. 3), γ' 0–5.8, where γ' is the ratio of the mean pressures of reactants between the beginning and the end of the photolysis, *i. e.*, corrected one for the disappearance of reactants due to the ester formation during the photolysis, the extent of which can be measured from ester analysis.

Here the light absorption is 20.6% and 61.5% at 3130 Å, respectively for 18.5mm and 77.6mm ketene. The decomposed fraction of ketene was 15–20% as calculated from the ratio of CO produced to the original ketene, thus, this value involves not only the decomposition due to the primary photochemical process but also those due to the secondary reactions of CH_2 if we take the following scheme as described later :



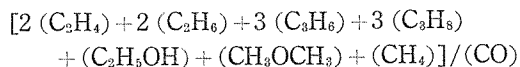
The main products were CO, C_2H_6 , C_2H_4 , CH_3OCH_3 and C_2H_5OH , numerical values of the last given in the figure being the sum of C_2H_5OH and $CH_3COOC_2H_5$ appeared in g.l. chromatography.

As minor products which are not shown in Fig. 3, we detected H_2 , CH_4 , C_3H_6 and HCHO ($H_2/CO=0.3\%$, $CH_4/CO=1\%$, $C_3H_6/CO=3\%$ for $\gamma' < 3$, = 0 for $\gamma' > 3$, HCHO/

Reaction of Methylene with Methanol

CO=4%, each at 15% decomposition of the mixture of $\gamma' \approx 1$ except for C₃H₆), but no detailed study was made on the variation with γ' . C₃H₆, cyclopropane and dimethyl peroxide could not be found. Presence of methylether and ethanol should be noted. Furthermore, in the photolysis of pure ketene we observed thin deposit of faint brown color having some order which did not dissolve in ether or acetone.

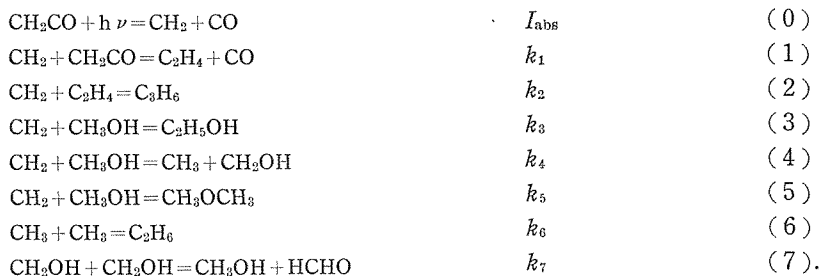
The material balance given by



was 0.74 for pure ketene photolysis and 1.01-1.16 between $\gamma' = 0.9$ and 6.9; to this balance we will return in the next section.

DISCUSSION

As one of the probable scheme to account for the observed products, we assume the following set of elementary steps:



Of course many alternative steps are conceivable which lead to the similar overall rate equation explicable as well the facts here obtained. Some of them will be referred to later, but discrimination of each step cannot be the first aim of the present study, the only trial intended at the present stage is to get the ratio of rate constants of the steps which appear probable.

Concerning the ethylene formation survey of recent papers seems to favor the step (1) than the dimerization of methylene; we are to choose (1) without discussion.

Also, about the electronic state, and vibrational and kinetic excitation of methylene produced by photolysis there has been proposed a variety of opinions; here we are to treat the methylene produced by the light of mixed wave lengths as a whole using a single notation.

No back reaction $\text{CO} + \text{CH}_2 \rightarrow \text{CH}_2\text{CO}^{(9)}$ is considered since we are interested in the case of high γ . Step (2) is the one which has been frequently proposed hitherto. Steps (3) and (5) are the insertion of CH₂ in the bonds C-H, C-O or C-C (the last two may be ruled out as suggested by Doering¹³), and O-H, respectively, many examples of the former can be seen in recent papers on the reaction with hydrocarbons, but the formation of ether seems not to have been reported except in one liquid phase photoreaction of diazomethane with isopropanol¹⁰; we assume (5) analogously to (3).

Ethane formation must be due to the dimerization of CH₃, other course seems hardly conceivable in the present condition although the steps



have been suggested⁹, then it would be most probable that the methyl is produced by the abstraction of H of methanol with methylene when γ is large. The point of attack of CH_2 , *viz.*, C-H or O-H splitting, is a problem to be studied in future since the reactivity of CH_2 is supposed to be quite different from CH_3 which is known to attack C-H predominantly. The low methane yield observed here suggests that at about room temperature methyl will preferentially recombine rather to form methane in accord with the results of similar experiments conducted at room temperature. Step (7) will be discussed later.

According to this reaction scheme the material balance given in the preceding section should be unity; the observed values nearly meet the requirement though a little higher.

Now, applying the steady state method we have

$$(\text{CH}_2) = I_{\text{abs}} / \{k_1(\text{K}) + k_2(\text{C}_2\text{H}_4) + (k_3 + k_4 + k_5)(\text{M})\} \equiv I_{\text{abs}}/A,$$

where K and M stand for ketene and methanol respectively, and

$$\begin{aligned} d(\text{CO})/dt &= I_{\text{abs}} \cdot \{1 + k_1(\text{K})/A\} \\ d(\text{C}_2\text{H}_4)/dt &= I_{\text{abs}} \cdot \{k_1(\text{K}) + k_2(\text{E})/A\} \\ d(\text{C}_2\text{H}_6)/dt &= I_{\text{abs}} \cdot k_4(\text{M})/2A \\ d(\text{C}_2\text{H}_5\text{OH})/dt &= I_{\text{abs}} \cdot k_3(\text{M})/A \\ d(\text{CH}_3\text{OCH}_3)/dt &= I_{\text{abs}} \cdot k_5(\text{M})/A \\ d(\text{C}_3\text{H}_6)/dt &= I_{\text{abs}} \cdot k_2(\text{C}_2\text{H}_4)/A \\ d(\text{HCHO})/dt &= I_{\text{abs}} \cdot k_4(\text{M})/2A. \end{aligned}$$

In order to eliminate the absolute amount of light absorption rate which changes somewhat during one run and also in different runs we express the rates of product formation relative to that of CO in each run, and take the total amount of product as a measure of rate (this may be permissible as a first approximation, since $(\text{M}) = \text{const.}$ and variation of (K) is averaged using γ' in single run). Furthermore, we know the propylene formation is quite small, especially so for high γ' , hence dropping $k_2(\text{E})$ from A and introducing γ' we get

$$\begin{aligned} \Delta \text{C}_2\text{H}_4 / \Delta \text{CO} &= k_1 / \{2k_1 + (k_3 + k_4 + k_5)\gamma'\} \equiv k_1/B, \\ \Delta \text{C}_2\text{H}_5\text{OH} / \Delta \text{CO} &= k_3\gamma'/B, \\ \Delta \text{CH}_3\text{OCH}_3 / \Delta \text{CO} &= k_5\gamma'/B, \\ \Delta \text{HCHO} / \Delta \text{CO} &= \Delta \text{C}_2\text{H}_6 / \Delta \text{CO} = k_4\gamma'/2B, \end{aligned}$$

where Δ denotes the total amount of product at the end of each run.

Introduction of the observed numerical values at $\gamma' = 4$ in these equations gives the ratio of constants,

$$k_1 : k_3 : k_4 : k_5 = 1 : 1.23 : 0.55 : 0.48 \text{ at } 42^\circ,$$

and finally we get the rate equation for each product;

$$\begin{aligned} \Delta (\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6) / \Delta \text{CO} &= 1 / (2 + 2.26\gamma'), \\ \Delta \text{C}_2\text{H}_5\text{OH} / \Delta \text{CO} &= 1.23\gamma' / (2 + 2.26\gamma'), \\ \Delta \text{CH}_3\text{OCH}_3 / \Delta \text{CO} &= 0.48\gamma' / (2 + 2.26\gamma'), \\ \Delta \text{C}_2\text{H}_6 / \Delta \text{CO} &= 0.28\gamma' / (2 + 2.26\gamma'). \end{aligned}$$

The calculated values are given in Fig. 3 by solid lines.

Comparison can be made with the relative rate between $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$ k_4'' (4'') and (1) under similar conditions reported by Gesser and Steacie¹¹⁾, according to them $k_4''/k_1 = 0.40$ and 0.52 , at 26° and 99° respectively. The abstraction of H from methanol by methylene is of comparable magnitude with that from hydrogen. According to this scheme the rate of insertion in C-H (considered as probable) of methanol is 2.5 times faster than in O-H, and the specific rate for single C-H becomes about the same as that for O-H.

Occurrence of (7) has been frequently proposed, but we have to consider the competition with $2\text{CH}_2\text{OH} \rightarrow (\text{CH}_2\text{OH})_2$, k_8 (8). The discrimination cannot be achieved from the calculation of pressure change in this experiment because of the roughness of observation.

From the scheme given above we get

$$\frac{d(\Delta p)}{dt} = k_1(\text{CH}_2)(\text{K}) + \frac{1}{2}k_4(\text{CH}_2)(\text{M}) = I_{\text{abs}} \cdot \left\{ \frac{k_1 + \frac{1}{2}k_4\gamma}{k_1 + (k_3 + k_4 + k_5)\gamma} \right\},$$

and introduction of ratio of k 's yields

$$\frac{d(\Delta p)}{dt} = I_{\text{abs}} \left\{ \frac{1 + 0.28\gamma}{1 + 2.2\gamma} \right\}.$$

The observation $d(\Delta p)/dt = 0.12\text{mm}/\text{min}$ at $\gamma = 4$ leads to $I_{\text{abs}} = 0.55\text{mm}/\text{min}$.

The calculated $d(\Delta p)/dt$ is given in Fig. 2 (curve 2), the large discrepancy at low γ is not unexpected since no high polymer formation is taken into consideration, but even at high γ the calculated curve shows a tendency to deviate from the rather broad band of points. Such being so, the ratio of k 's obtained above should be regarded as only an approximate one.

Next, if we replace (7) with (8) and assume that the produced glycol does not condense (approximate calculation of the maximum amount of glycol shows that this assumption is valid under the present condition), we get

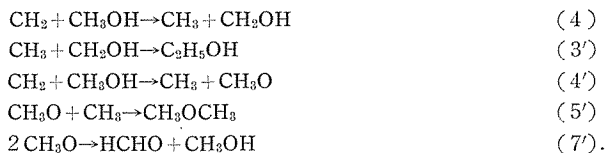
$$d(\Delta p)/dt = I_{\text{abs}}/(1 + 2.26\gamma).$$

The discrepancy in the trend of the calculated curve is enhanced further (Fig. 2, curve 3).

In the scheme assumed above, $\Delta\text{C}_2\text{H}_6$ should be equal to $\Delta(\text{CH}_2\text{OH})_2 + \text{HCHO}$, so the difference between the observed $\Delta\text{C}_2\text{H}_6$ and ΔHCHO may account for the extent of (8).

Further photo- or radical decomposition of formaldehyde may take place; the absence of hydrogen would not be an evidence for the non-occurrence, since H atom, if produced at these wave lengths, is reported to react with ketene to produce CH_3 and $\text{CO}^{12)}$ although the competition with CH_3OH should be considered, and the attack of CH_2 or CH_3 on formaldehyde will not produce H_2 . At any rate, however, the amount of initial formaldehyde formation is minute. Likewise, we have neglected all the subsequent reactions of main products with CH_2 or CH_3 at high γ .

Finally we have to consider the formation of ethanol and ether by other elementary steps, *e. g.*,



Replacement of (3) by (3'), or (4) and (5) by (4') and (5') gives the same overall rate equations as before. Absence of dimethyl peroxide may suggest the absence of (4'), but by no means compelling and since CH_2 is known to be much more reactive than methyl, the extent of (4') should be decided by separate experiment, *e. g.*, using CH_3OD .

Thus, we have no reason at present to exclude the reaction (3') or (4') in the system where CH_3 radical formation is observed which must be due to the abstraction of H from the substrate by CH_2 ; so until we obtain clear-cut argument against these we would confine ourselves only to cite the possibility of insertion in O-H.

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