

ON THE PHOTOCHEMICAL EXPLOSIVE REACTIONS (1).

By JIRO OSUGI.

Physicochemical or kinetical investigations of photochemical chlorination reactions have been made down to date on simple substances i. e. hydrogen, carbonic oxide, and formaldehyde etc. chiefly by Rollefson and his co-workers,¹⁾ and never on esters.

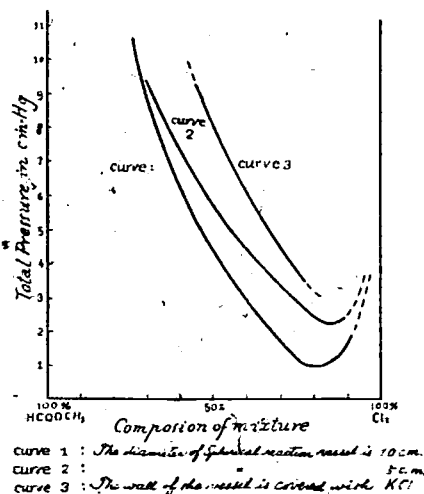
The present studies are concerned to the photochemical chlorination of methyl formate, and chiefly to its explosive reaction which is caused by the irradiation of light.

The photochemical explosion phenomena of this reaction were already found in 1887,²⁾ but not studied scientifically.

Experimental method.

A spherical glass reaction vessel is filled with purified chlorine and methyl formate. The Ultra-violet rays of mercury lamp illuminate the vessel. The pressure change depending on reaction velocity is recorded by a membrane manometer. The initial and final pressures are measured by a feder manometef.

Fig. 1. Explosion limit.



Experimental results.

(1) Explosion limits.

When a gaseous mixture of methyl formate and chlorine, in a definite composition is illuminated by a definite intensity of light (mercury lamp), the pressure change increases with the rise of its initial pressure. The ratio of the final pressure to the initial pressure varies from 1 to 2. When this ratio is equal to 1.3, we will call the initial pressure the explosion limit.

(Fig. 1) shows the curve of the explosion limit. The abscissa is the composition of

- 1) Rollefson and Burton, *photochemistry*, 320 (1939).
- 2) Hentschel, *J. pract. chem.*, 36, 99, 209, 305, 469 (1887).
 Greignard, Rivat et Urbain, *Ann. de chem.*, 9, 229 (1624).

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mixture and the ordinate is the total pressure of the explosion limit. This curve shows a tendency to explode easily in excess of chlorine similar to the chlorination of formaldehyde¹⁾ and formic acid.²⁾

The effects of the wall of the reaction vessel are shown by curve 2 (small reaction vessel) and curve 3 (the wall is covered with KCl).

(2) Effects of other gases.

Generally, oxygen remarkably retards photochemical chlorination reactions. In this reaction, a small quantity of oxygen added (6~18 mmHg) retards the explosion completely or lengthen the induction period.

Carbon dioxide added nearly twice the initial pressure, smooths out the pressure change curve, and extinguishes the ignited explosion. These facts indicate that the explosive reaction is retarded.

(3) Reaction temperature and decomposition quantities.

By the use of the glass water bath in which the reaction vessel is dipped, the reaction temperature is easily controlled. The initial pressure P' and the final pressure P of the reaction are measured.

Decomposition quantities ΔP equal to $(P - P')$. The results of the experiments whose conditions: composition, the initial pressure and light intensity are quite the same except the reaction temperature, are as follows:

$$\text{the reaction temperature } 68^\circ\text{C}, \frac{\Delta P}{P} = 0,97$$

$$\text{ " " " " " " } \frac{\Delta P}{P} = 0,78$$

The decomposition quantity increases when the reaction temperature becomes higher.

(4) Reactions and light intensity.

The relation between the decomposition quantity per unit time and light intensity I , indicates that the former is proportional to \sqrt{I} . The decomposition quantity per unit time is the reaction velocity, so

$$\text{the reaction velocity} = k\sqrt{I}, \quad k: \text{contant.}$$

(5) Explosion phenomena and composition.

The experiments, whose conditions are the definite intensity of light, the fixed

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- 1) Krauskopf and Rollefson, *J. Am. chem. soc.*, 56, 2542 (1934).
 - 2) West and Rollefson, *J. Am. chem. soc.*, 58, 2140 (1936).

partial pressure of chlorine (2 cmHg) and variable compositions of mixtures by the addition of methyl formate, show various explosion phenomena.

In Fig. 2, the ordinate and abscissa are $\frac{\Delta P}{P}$ and composition in curve I, and are $\frac{\Delta P}{P_e'}$, composition in curve II. (P_e' : partial pressure of methyl formate)

In curve I, \odot sign indicates the point where white powder is produced in the vessel after the reaction. \square sign indicates the ignited explosion and the producing of carbon powder after the reaction.

Thus the explosion phenomena differ according to the composition of a mixture.

It is shown that $\frac{\Delta P}{P_e'}$ increases step by step in curve II, i. e. it has the regions $\frac{\Delta P}{P_e'}=0$, $\frac{\Delta P}{P_e'}=2$, and $\frac{\Delta P}{P_e'}=4$. Further, the pressure-time curves which are recorded on film by means of a membrane manometer (Fig. 3) indicate the difference of the reaction processes.

From these experimental facts, the explosion phenomena can be classified typically as follows:

- (a) methyl formate below 20%, $\frac{\Delta P}{P_e'}=4$

Rapid decomposition occurs, no solid residuals being found after the reactions.

- (b) methyl formate 20%~45%, $\frac{\Delta P}{P_e'}=2$

Rapid decomposition, white powder remaining after the reactions.

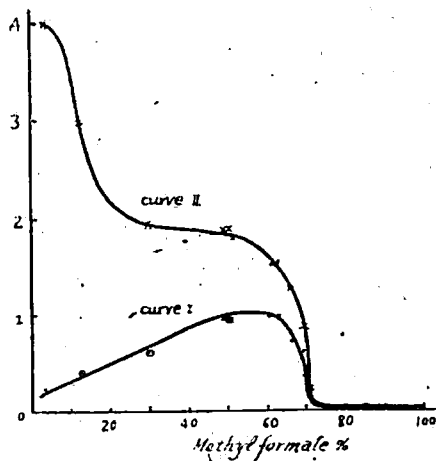


Fig. 2.

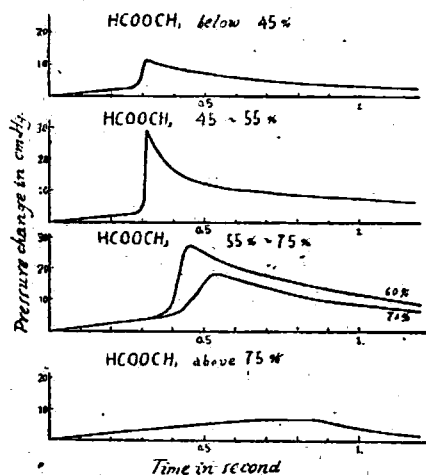


Fig. 3. Pressure-Time Curve.

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- (c) methyl formate 45% ~ 55%, $\frac{\Delta P}{P_e'} = 2$

Ignited explosion, carbon powder remaining after the reactions.

- (d) methyl formate 55% ~ 75%, $\frac{\Delta P}{P_e'} = 2$

rapid decomposition, with no solid residuals and no ignition.

- (e) methyl formate above 75%, $\frac{\Delta P}{P_e'} = 0$

Draper effect, without any decomposition.

There are, of course, the intermediate phenomena between each classified region.

Considerations.

(1) Reaction mechanism.

From the experimental result (4) i. e. the reaction velocity is proportional to the square root of light intensity, it is believed that this is kinetically a chain reaction in which atomic chlorine takes part.¹⁾ It is able to be understood from this reason, that the wall of the reaction vessel influences explosion limits and that the addition of O₂ and CO₂ retards explosions.

From the experimental result (3) i. e. decomposition quantities increase with the rise of the reaction temperature, it is clear that this reaction involves the primary photochemical reaction and the following secondary thermal reactions.

In the result (5), the experimental conditions are as follows: definite light intensity, 2 cmHg partial pressure of chlorine, and variable partial pressure of methyl formate.

Partial pressure of chlorine is definite, so by the absorption of light the gain of energy in the reaction system is constant. Therefore, the energy available per methyl formate molecule depends upon the partial pressure of methyl formate. Below the partial pressure, more energy is available to the molecule and more completely become the decompositions of methyl formate.

The obtainment of energy is homogeneous and the reaction finishes in a short time, so the reaction progresses in a simple mechanism which depends on the energy received in each region.

According to Rollefson's experiment on this reaction²⁾, this is a chain reaction which has a few thousand Quantum yields in the region with no decomposition.

1) cf. Bonhoeffer und Harteck, *Grundlagen der Photochemie* p. 227.

2) West and Rollefson, *J. Am. Chem. Soc.*, 58, 2140 (1936).

So the experimentally classified region (e): methyl formate above 75%, has a (straight) chain mechanism. The reaction is



$$\therefore \frac{\Delta P}{P_e} = 0.$$

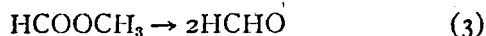
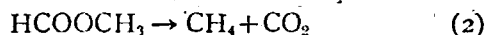
This has been also proved by the analysis of reaction products.

Below 75%, the decomposition occurs, so $\frac{\Delta P}{P_e} \neq 0$.

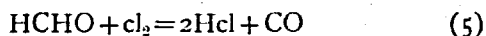
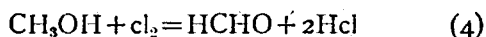
(2) On the decompositions of methyl formate.

The decomposition of methyl formate is able to be discussed from the experimental facts described above, considering thermal decompositions and photochemical chlorine sensitized reactions.

Mechanisms of the decomposition reactions of methyl formate is as follows:¹⁾



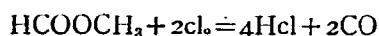
The reaction (3) is thermally difficult to occur and objections are presented.²⁾ It is reasonable that the reactions (1) and (2) can occur. Further, the sensitized reactions



follows.

When the experimental result (5) is compared with these reactions, it is believed that the mechanisms of photochemical decomposition reactions are as follows:

Class (a): violent decomposition occurs through reactions (1), (4) and (5).



$$\therefore \frac{\Delta P}{P_e} = 4$$

Class (b): decomposition is rather incomplete.

1) Steacie, *Proc. Roy. Soc.*, **A127**, 314 (1930).

Baird and Hinshelwood, *J. chem. Soc.*, 1147 (1933).

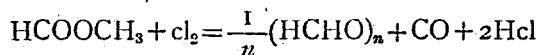
Müller and Peytral, *C. R.*, **179**, 831 (1924).

2) Paul and Rollefson, *J. Amer. chem. Soc.*, **58**, 1755 (1936).

Krauskopf and Rollefson, *J. Am. chem. Soc.*, **56**, 2542 (1934).

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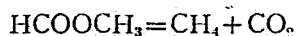
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$$\therefore \frac{\Delta P}{P_e'} = 2$$

Owing to rapid cooling and the illumination of ultra-violet rays, HCHO is polymerized and produces white solid powder.

Class (d): as the partial pressure of methyl formate becomes higher, it is probable that the energy accepted from chlorine is held in the internal energy of the molecule. According to Hinshelwood's view,¹⁾ the molecule which has much internal energy is decomposed by the transfer of hydrogen atom in a molecule as follows:



$$\therefore \frac{\Delta P}{P_e'} = 2$$

The gentle explosion pressure curve (Fig. 3) is due to the facts that the reaction energy is held in the internal energy and the reaction produces carbon dioxide.

Last, let us consider the ignited explosion in the narrow region (c). It was found by Bone, Newitt and Townend²⁾ that the violent oxidation explosion of methane produced carbon powder. So it is understood in this reaction, owing to the violence of explosion carbon powder is produced.

It is interesting to mention that such ignited explosion occurs in the region in which the accepted energy is most effective to reactions.

It is believed that such decomposition mechanisms as these can be cleared by the studies of photochemical explosions, because this method has essentially simplicity.

The author wishes to express his hearty appreciation to Prof. S. Horiba for continued guidance throughout this research.

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1) Hinshelwood, *J. chem. Soc.*, 1147 (1933).

Hinshelwood, *The Kinetics of chem. change in gaseous system* 3rd Ed. p. 226.

2) Bone, Newitt and Townend, *gaseous combustion at high pressures*.