Photopolymerization of Vinyl Chloride by Mercury Sensitization

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A. Introduction

In the course of the study of photopolymerization of vinyl compounds, we have found that the polymerization of vinyl chloride (in the vapor phase) initiated by the light of a low pressure mercury lamp, is mainly a photosensitized reaction by mercury vapor and that the effective light is 1850 Å and not 2537 Å. The present paper will report the main features of the reaction and some kinetic studies about it.

B. Apparatus and Procedure

The main part of the apparatus ordinarily used is shown in Fig. 1. It is somewhat similar to the one used by H. W. Melville[1]. B is the reaction vessel of about 20cc. (quartz) and A is a mercury-cut through which the sample is led into the reaction vessel, which is also utilized as a manometer to trace the reaction. The temperature was usually controlled by streaming water. The mercury lamp is a simple D. C. type of about 20 cm. long (300 W).

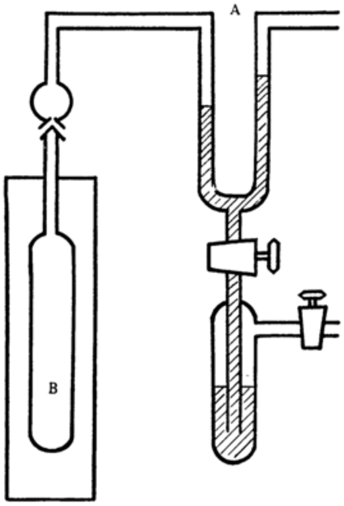

Fig. 1 The main part of the apparatus

C. Some Features of the Reaction

1. When the illumination is commenced, the pressure begins to decrease and a white polymer is deposited on the surface of the vessel. The deposition is observed only on the front part, and when the vessel is covered by Al foil partly, the back side of the covered part is completely free from the deposit, the boundary being as sharp as the foil itself. There is no sign of any side reactions.

2. When the illumination is cut off, the reaction stops at once, showing that there is no active material surviving such as observed by Melville in the case of methyl metacrylate[1]

3. When the wall of the vessel is lined with the material transparent down to 2000Å such as NaCl or paraffin, the reaction is affected remarkably. When pieces of metal such as steel or bronz are previously thrown into the vessel, the rate is slightly increased while pieces of quartz rods of the same origin as that of the vessel slightly retards the rate.

4. When only the light 2537 Å is employed, the reaction scarcely goes on. This fact was particularly confirmed by the following experiment. Using the reaction vessel with two parallel plates, it was ascertained that the intensity of light 2537 Å which had passed through the reaction vessel was quite strong and yet there was observed no pressure decrease nor the white deposit on the wall of the vessel. On the other hand, when the light of mercury lamp was filtered by a thick layer of water, the reaction was often suppressed remarkably. These facts strongly suggest that the effective light is the one of such short wave length that is liable to be absorbed by a trace of impurity in water.

5. When mercury vapor is cautiously eliminated, the reaction is reduced to a very small quantity. This fact was confirmed by the apparatus particularly designed, the pressure decrease being measured with a membrane manometer.

All the above facts strongly support the view that the present photopolymerization is initiated by 1850 Å line of Hg lamp, the intensity of which is so weak that it is almost completely absorbed in the region near the front part of the vessel and that the reaction is heterogeneous taking place on the wall of the vessel at least in some steps of the overall reaction. In addition, the mercury vapor supposedly acts as photosensitizer.

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[1] H. W. Melville, *Proc. Roy. Soc.*, **A163**, 511 (1938); *Proc. Roy. Soc.*, **A167**, 99 (1937).

D. Some Kinetic Studies

1. The Effect of the Pressure of Vinyl Chloride—In the present experimental condition, the pressure decrease is very small compared with the initial pressure of vinyl chloride, and it goes on linearly against time.

The pressure decrease during initial 60 minutes is completely proportional to the initial pressure of vinyl chloride showing that the reaction is of the first order with regards vinyl chloride. (See Fig. 2)

2. The Effect of Light Intensity—The reaction rate is proportional to the intensity of light as shown in the following table.

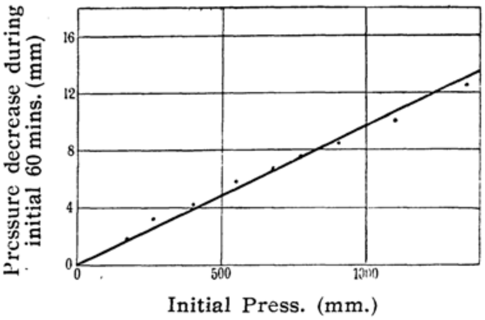

Fig. 2. Dependence of the rate upon the pressure of vinyl chloride

THE EFFECT OF INTENSITY OF LIGHT UPON THE RATE

	P (Press. of $CH_2=CHCl$)	I (Relative intensity)	ΔP (Press. decrease per hr.)	k' ($\Delta P/P$)	k'/I
1	760.5 mm	1	9.5 mm	0.0125	0.0125
2	763.0	½	5.2	0.0068	0.0136
3	768.0	1/3	3.4	0.0044	0.0132
4	761.2	¼	2.4	0.0032	0.0128

In this experiment the intensity of light was varied with the use of blackened copper nets or black perforated celluloid plates.

3. The Effect of Temperature—The reaction rate was measured at three temperatures 10°C, 41°C and 95°C. At all temperatures, the pressure decrease is linear against time, and the reaction rate calculated from the slope of each line is proportional to the pressure of vinyl chloride.

Under the present experimental condition, the rates at various temperatures are expressed by the following formulas.

10°C $v=0.00017\ P_{C_2H_3Cl}$ (mm./min.)
41°C $v=0.000025\ P_{C_2H_3Cl}$
95°C $v=0.00001\ P_{C_2H_3Cl}$

The measurement at 95°C is somewhat unreliable but it is evident that the rate decreases with the rise of temperature. The activation energy is calculated to be about −6 Kcal.

4. The Effect of the Pressure of Mercury Vapor—The effect of the pressure of mercury vapor was examined by comparing the results of the two series of experiment at elevated temperatures of which the one was performed in the presence of a mercury drop at the bottom of the vessel while the other was done in the ordinary condition. The result is that the rate increases monotonously with the rise of the pressure of mercury vapor as shown in the following table (mean value of several experiments).

Temp.	Mercury pressure	Rate of pressure decrease
	mm.	mm./min.
41 °C	0.0005	0.000025
	0.0065	0.00025
95 °C	0.0005	0.000007
	0.21	0.0014

The rate may be regarded as approximately proportional to the mercury pressure in its low pressure region.

To sum up the above results, the reaction rate can be expressed as follows.

$$v=k\ [CH_2=CHCl]\ [Hg]\ I \qquad (1)$$

where I is the intensity of the incident light, which is absorbed completely.

E. Discrimination of the Function of Mercury Vapour on the Basis of the Photopolymerization by Al Spark

In section C, it was shown that the existence of mercury vapor is essential for the reaction.

To decide whether the function of mercury is sensitization or catalysis, the investigation of photopolymerization induced by the light of different wave length other than 1850 Å is expected to be much helpful. Thus if the polymerization takes place by another light and the accelerating action of mercury vapor is still perceived, then the function of mercury vapour in the case of mercury lamp would perhaps be catalytic in nature, while on other hand, if no effect of mercury vapour is existent in the case of another light, the action of mercury in the case of mercury lamp ought to be a sensitizing one.

From such a viewpoint, we examined the photopolymerization by Al· spark and particularly the effect of mercury vapour on the reaction rate. The conditions of Al spark employed are as follows: spark gap 0.5 cm., voltage 10000 V; condenser inserted; capacity, 0.02 μF. By taking the emission spectrum, three strong lines near 1850 Å were confirmed to exist in this condition. We were much indebted to Dr. T. Kuzirai of Kyoto University for taking the spectrum.

1. The polymerization occurs in the ordinary condition (mercury vapour is existent) just in the same order of magnitude as in the case of mercury lamp.
2. The polymer deposited is quite different in appearance from that obtained in the case of mercury lamp. It is transparent and looks like liquid. Even when mercury vapour is excluded as cautiously as possible, the reaction rate is not influenced beyond the experimental error. It seems rather to be accelerated to some extent.

The above results lead us to the conclusion that the polymerization by Al spark is quite a different reaction from that by mercury lamp, and that in the former case it is a simple photochemical one, while in the latter it is a photosensitized reaction by mercury vapor.

F. Discussion of the Mechanism on the Basis of Kinetic Formula

In Section D. the kinetic formula (1) was derived from the experimental results.

The reaction mechanism must be such as conforms to the above relation, and this condition gives us the criterion to decide the probable mechanism.

The problem is therefore to tabulate all the mechanisms conceivable and to give for each of them an appropriate reaction formula.

Let us therefore classify, at first, the types of reaction in the following way.

α) Complete homogeneous gaseous reaction

β) Heterogeneous reaction

β) is further classified into seven types according to the circumstances that each step of the overall reaction, that is initiation, propagation, and termination, be a gaseous or a wall reaction. They are

	β							α
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
Init.	W	W	W	W	G	G	G	G
Prop.	W	W	G	G	W	W	G	G
Term.	W	G	W	G	W	G	W	G

In the above list, G and W means a gaseous or wall reaction, respectively. All these types must be further classified according to the detailed scheme of initiation, propagation and termination.

Case (α) Let us first consider case (α). To derive an overall kinetic formula, one must give the rate expression for each step.

I) *Initiation*

$Hg+h\nu\rightarrow Hg^{*}$ $Hg^{*}+M\rightarrow M^{*}+Hg$

The velocity of initiation is given by the following equation.

$$v_i=k_i\,I\frac{\alpha_{Hg}[Hg]}{\alpha_M[M]+\alpha_{Hg}[Hg]}\,[M]$$

where I is the intensity of light to be absorbed, α_{Hg} and α_M are the molecular extinction coefficients of mercury and vinyl chloride vapour respectively. The above equation is derived on the assumption that the spontaneous deactivation of excited mercury atoms is not important.

The magnitude of α_{Hg} and α_M are unknown but there is no doubt that the vapor of vinyl chloride absorbs the light in the region of 1850 Å not so little. Besides $[M]\gg[Hg]$. Therefore, it may safely be assumed that $\alpha_M[M]\gg\alpha_{Hg}[Hg]$. This relation may also be supported to some extent by the experimental result. Thus if $\alpha_M[M]\approx\alpha_{Hg}[Hg]$ the reaction formula can not be so simple as (1). Again, if $\alpha_{Hg}[Hg]\gg\alpha_M[M]$, v_i ought to be independent of [Hg] and the overall reaction rate cannot be proportional to [Hg] irrespective of any scheme of the two succeeding steps, if the gaseous initiation really holds at all.

For these reasons, the above formula can be put as follows

$$v_i=k_iI\,\frac{\alpha_{Hg}[Hg]}{\alpha_M}\qquad(2)$$

II) *Propagation*

$M^{*}+M\rightarrow M_2^{*}$ $M_2^{*}+M\rightarrow M_3^{*}$

There may be no question as to the propagation process,

$$v=k_p\,[M]\,[R]$$

where R is an active radical.

III) *Termination*

Types of termination conceivable are as follows.

a) $R+R \rightarrow P$
b) $R+Hg \rightarrow P$
c) $R+M \rightarrow P$

Now the velocity of the overall reaction is given by v, that of the propagation process, and the application of the stationary state method easily leads to the following kinetic formulas for each case.

$$\text{a)}\quad v=k_p\sqrt{\frac{k_i}{k_t}}\,\frac{I}{\alpha_{\text{M}}}\,\alpha_{\text{Hg}}[\text{Hg}][\text{M}]$$

$$\text{b)}\quad v=k_p\frac{k_i}{k_t}\,\frac{I}{\alpha_{\text{M}}}\,\alpha_{\text{Hg}}[\text{M}]$$

$$\text{c)}\quad v=k_p\frac{k_i}{k_t}\,I\,\frac{\alpha_{\text{Hg}}}{\alpha_{\text{M}}}[\text{Hg}]$$

All the above formulas contradict the experimental result. Thus the conclusion that the reaction is not homogeneous, can be derived merely from the kinetic formula.

Case (β) The analogous deduction can be made for case (β). The details of the discussion will be given eleswhere and only essential points will be described here briefly.

I) *Initiation* when the initiation takes place in the gaseous phase, the result is just the same as in the case α.

When the initiation takes place on the wall, v_i will be given by the following equation

$$v_i=k_i\,I\,\frac{\alpha_{\text{Hg}}[\text{Hg}][[\text{M}]]}{[\text{M}]} \qquad (3)$$

where [[M]] represents the surface concentration of vinyl chloride monomer.

This relation can be derived as follows.

Excited mercury atoms which can arrive at the wall during its life are those which exist in the extremely close neighbourhood of the surface. If the mean distance through which activated atoms can reach the wall be put as Δd, v_i may be put as follows:

$$v_i=k_i\,I\,\alpha_{\text{Hg}}[\text{Hg}]\,\Delta d\,[[\text{M}]]$$

Δd depends on various factors, but in the present case it is essential how it is influenced by the pressure of vinyl chloride. Taking account of the fact that the experimental relation (1) is very simple, it may be most probable to put Δd as inversely proportional to the latter, since it is theoretically expected to decrease as the pressure of vinyl chloride increases. Thus the equation 3) is obtained*.

Using 2) or 3) for initiation, the following possibilities were criticized for i), ii), iii), iv), v), vi), vii) of case (β).

I) *Initiation* Gas or wall

II) *Propagation* Radicals combine with monomer molecules (in the vapour phase) irrespective whether the reaction takes place in the gaseous phase or on the wall.

III) *Termination* Gas: Three possibilities similar to a), b), c) of (α)

Wall: d) $[R]+[R] \rightarrow [P]$
e) $[R]+R \rightarrow [P]$
f) $[R]+Hg \rightarrow [P]$
g) $[R]+M \rightarrow [P]$
h) $[R]+[S] \rightarrow [P]$
i) $[R]+[M] \rightarrow [P]$
j) $R+[M] \rightarrow [P]$
k) $R+[S] \rightarrow [P]$

where S means the wall of the vessel, and [ ] represents the molecular species in the adsorbed state.

The result of the critique is that five types of mechanisms conform the relation (1) and if one takes account of the fact that the addition of quartz rod decrease the rate to some extent, then the selected mechanisms are as follows.

	Init.	Prop.	Term.	Type of termination	kinetic formula
v)	G	W	W	h) $[R]+[S] \rightarrow P$	$v=\frac{k_pk_i}{k_t}I\frac{\alpha_{Hg}}{\alpha_M}[Hg][M]$
				i) $[R]+[M] \rightarrow P$	$v=\frac{k_pk_i}{k_t}I\frac{\alpha_{Hg}}{\alpha_M}\frac{[Hg][M]}{[[M]]}$
Vii)	G	G	W	k) $R+[S] \rightarrow P$	$v=\frac{k_pk_i}{k_t}I\frac{\alpha_{Hg}}{\alpha_M}[Hg][M]$
				j) $R+[M] \rightarrow P$	$v=\frac{k_pk_i}{k_t}I\frac{\alpha_{Hg}}{\alpha_M}\frac{[Hg][M]}{[[M]]}$

It is to be noted that the adsorption of vinyl chloride must be saturated in order that the scheme v) i) and vii) j) may be adopted.

The conclusion is that the mechanism of the principal polymerization reaction by mercury lamp is given as follows.

Initiation takes place in the gaseous phase

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* Any relations other than (3) can not lead to (1), how the succeeding steps may be ascumed.

Propagation proceed in the gaseous phase or on the wall. Termination takes place on the wall and the radical in the gaseous phase is stabilized either by its collision against the surface or by the interaction with adsorbed monomer molecules, while in the case that propagation proceeds on the wall, the radical is stabilized spontaneously or by the interaction with adsorbed monomer.

Thus the scheme of the reaction is given as follows.

$$
\begin{array}{ll}
\text{Init.} & \mathrm{Hg}+h\nu\rightarrow\mathrm{Hg}^* \\
 & \mathrm{Hg}^*+\mathrm{M}\rightarrow\mathrm{M}^* \\
\text{Prop} & \mathrm{M}^*+\mathrm{M}\rightarrow\mathrm{M}_2 \\
\text{or} & \left\{\begin{array}{l} \mathrm{M}^*\rightarrow[\mathrm{M}^*] \\ [\mathrm{M}^*]+\mathrm{M}\rightarrow[\mathrm{M}_2{}^*] \end{array}\right. \\
\text{Term.} & [\mathrm{R}]+[\mathrm{S}]\rightarrow\mathrm{P} \\
 & \text{or } [\mathrm{R}]+[\mathrm{M}]\rightarrow\mathrm{P} \\
 & \text{or } \mathrm{R}+[\mathrm{S}]\rightarrow\mathrm{P} \\
 & \text{or } \mathrm{R}+[\mathrm{M}]\rightarrow\mathrm{P}
\end{array}
$$

Summary

It was found that the photopolymerization of vinyl chloride in the presence of mercury vapor is mainly a sensitized reaction due to the latter. The effective light is 1850 Å and not 2537 Å.

As a result of some kinetic studies, it was confirmed that the initiation of the chain takes place in the gaseous phase, the propagation proceeds in the gaseous phase or on the wall, and lastly, the termination occurs only on the wall of the vessel.

Details of the experiment and full discussions will be published in Journ. Polytech. Osaka City University.

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