Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Acrylonitrile by Stannous Chloride and Acriflavine. I*

By Ai WATANABE and Masao KOIZUMI

(Received January 17, 1961)

The photochemical polymerization of vinyl compounds in the presence of a dye and a suitable reducing agent has been found by Oster(1), and it has been proposed that the initiation step is due to a certain kind of radical produced by the action of the oxygen upon leuco dye, which has been formed by the reduction of the original dye. It seems that most of the reactions can be well interpreted by this scheme, and yet there are only a few cases in which detailed kinetic studies have established the above scheme.

For example, the photopolymerization of acrylonitrile in the presence of a dye and a metallic ion such as Sn^{2+}, has not yet fully investigated, though it has been established by Oster that such systems are excellent for the preparatory purpose(2).

In the course of the preliminary investigations upon such systems which include more than twenty dyes and various reducing agents such as potassium thiocyanate, thiourea (TU), ascorbic acid (AA), sodium thiosulfate, stannous chloride etc., it was felt that a different scheme may occur in certain cases, especially in cases

---

* Partly presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

1) G. Oster, *Nature*, 173, 300 (1954).

2) G. Oster, *Chem. Abstr.*, 53, 12747 (1959).

TABLE I. SOME RESULTS OF THE PRELIMINARY EXPERIMENTS
[D] = 1.2×10^{-4} M, [reducing agent] = 0.12 M

		KSCN	TU	AA	$SnCl_2$**	$Na_2S_2O_3$	None
Thionine	P	+	+	−	+	−	−
	B	++	++	(+)	+++		
Methylene blue	P	+	+	−	++	−	−
	B	+	++	(+)	+++	++	
Uranine	P	−	±	−	±	−	−
	B		+	(+)	+		
Eosine	P	++	++	−	−	+	−
	B	+	+	+	++		
Erythrosine*	P	++	++	++	±	+	−
	B	++	+	++	++		
Acridine yellow	P	−	+	±	+++	−	−
	B					++	
Acriflavine	P	−	−	±	+++	−	−
	B						

* Concentration is less than 10^{-4} M.
** ca. 2.9×10^{-2} N HCl solution
P: Polymerization, B: Bleaching
+ and − represent respectively the occurrence and non-occurrence of the reaction. The number of + signs roughly gives the magnitude of the reaction. (+) shows that the bleaching takes place completely or nearly completely when mixed.

where stannous chloride is used as a reducing agent. Hence using acriflavine which was found to be most efficient in combination with stannous chloride, we have examined kinetically the effect of various factors upon the rate of photopolymerization. This paper pertains to the results obtained when the system containing dimethylformamide (DMF), water, acrylonitrile (AN), acriflavine (Af or D) and stannous chloride was irradiated in the presence of oxygen.

Preliminary Experiment

More than twenty dyes were tested preliminarily for examining their efficiency in promoting the polymerization, when they were added to the mixture of AN, water, methanol (2 : 1 : 1.2 in volume) containing potassium thiosulfate, TU, AA, sodium thiosulfate or stannous chloride as reducing agents. The samples in test tubes were irradiated by a 100 V.-500 W projection lamp (used at 80 V.) placed 10 cm. apart from the tubes for 1 hr. The magnitude of polymerization was visually judged from the quantity of the precipitate produced. The purpose of the experiments was to find extremely prominent cases, and the exact comparison of the result is of course impossible on account of crudeness in procedure, observation etc. In Table I are given the results obtained for the three types of dyes, about which the oxidative and reductive behavior have been examined to some extent. It is evident from the above table that there exists no parallelism between the magnitude of polymerization and the easiness in bleaching and recovery of color. For example, thiazine dyes which are easily reduced as well as rapidly reoxidized by oxygen, have rather a small power of initiating the polymerization. It is ture that the excess of oxygen will inhibit the polymerization since it has been confirmed by the suppression of polymerization by bubbling the air through the solution. But it is expected that the consumption of oxygen during the reoxidation of leuco dye will soon realize the situation in which the polymerization may take place rather smoothly. The above results in thiazine dyes contradict this expectation altogether. On the other hand xanthene dyes, of which the leuco form shows a great resistance against reoxidation by oxygen, can have some power of inducing polymerization when coupled with proper reducing agents. Acridine dyes, which lie between the above two classes as judged from our unpublished results which demonstrate that these dyes make reversible bleaching in the aqueous solution containing Sn^{2+} whether oxygen exists or not, show a very pronounced efficiency for promoting polymerization when used with stannous chloride.

All these facts suggest that the photopolymerization induced by dyes would some in cases go via a different scheme from Oster's, especially in case of acriflavine and stannous chloride.

From such a viewpoint the quantitative investigation upon the system acriflavine-stannous chloride was undertaken.

Experimental

Materials.—Acrylonitrile from American Cyanamide Co. was distilled after dehydrating with calcium chloride, b. p. 76.5°C. Dimethylformamide

(DMF) from Du Pont was dehydrated by potassium carbonate and then distilled, b. p. 151～151.5°C. $SnCl_2\cdot 2H_2O$ (G. R) and $SnCl_4\cdot 3H_2O$ (G. R) were used without further purification. Acriflavine from Merck was also used without purification.

Procedure.—As a light source a projection lamp 100 V.-500 W was used at 80 V. The distance between the light source and a reaction cell placed in a thermostat is 33 cm. Mazda Color Filter V-Y3C which cuts off $\lambda <$ ca. 420 mμ is set in front of the reaction cell. In the experiments for studying the effect of light intensity, neutral filters were used. A reaction cell is made of terex glass 1×1×4.5 cm. and it is connected with a capillary utilized as a dilatometer. The drop of meniscus in the capillary due to polymerization was followed by use of a travelling microscope. All the experiments were done at 35°C except otherwise described.

To prepare the sample for reaction, (1) acrylonitrile, (2) the aqueous solution of dye and (3) DMF dissolving stannous chloride were mixed in a proper ratio. The concentration of dye and stannous chloride in the latter two solutions are adjusted to get a desired composition of the ultimate sample. In studying the effect of [AN], the ratio of 1 and 3 was changed keeping the quantity of 2 as constant, while for investigating the effect of $[H_2O]$ the ratio of 2 and 3 was changed keeping the quantity of 1 as constant. It is to be noted that DMF solution of stannous chloride must be prepared prior to the experiment in order to get a good reproducibility.

In order to separate the polymer the sample, after the reaction, was poured into a large quantity of methanol and the precipitate was washed with methanol containing hydrochloric acid (concentrated hydrochloric acid : methanol=0.0015 : 1 in volume) and after washing once more with methanol was dried at 40°C in vacuo. The molecular weight of the polymer thus obtained was determined by measuring the viscosity of the solution of DMF containing about 0.1% of polymer at 25°C. To calculate the intrinsic viscosity Schulz and Sing's formula[3] was employed.

$$[\eta]=\frac{\eta_{sp}/c}{1+0.28\eta_{sp}}$$

The average molecular weight was evaluated from the following relation[4].

$$[\eta]=3.92\times10^{-4}\overline{M}^{0.75}$$

Results

When the sample containing stannous chloride and acriflavine is irradiated, the polymerization usually commences at once, but when the sample contains only either of the two the polymerization does not occur in fact. There is no dark reaction perceived even when a large quantity of stannous chloride and acriflavine are added. In Fig. 1, curve 1 represents the rate for the sample, AN : H_2O : DMF=4 : 3 : 4.2 (in volume), $[SnCl_2]=2.73\times10^{-2}$ M, [Acriflavine] $=2.73\times10^{-4}$ M. Accompanied with the polymerization, the solution becomes turbid due to the precipitation of the polymer. When the concentration of stannous chloride is small a certain period of induction appears and after that the curve becomes linear (curve 2). As regards curve 3 mention will be made later. In case of a small concentration of dye the rate begins to decrease earlier than in other cases. In all cases the rate was evaluated from the initial linear portion of the curve. It is to be noted that when the same cell was used for a long period of time, the cell walls gradually became opaque and it had to be renewed occasionally. Therefore, it is not always possible to compare and to correlate the data of a different series of experiments described below.

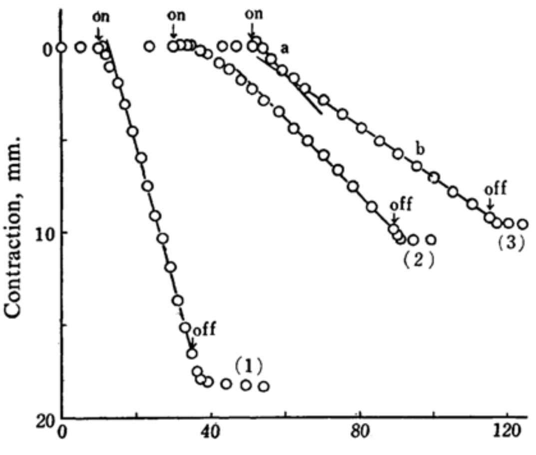

Fig. 1. The contraction-time curves.

	[D] 10^{-4} M	$[SnCl_2]$ 10^{-3} M	AN : H_2O : DMF (in volume)
(1)	2.73	27.3	4 : 3 : 4.2
(2)	2.73	1.71	4 : 3 : 4.2
(3)	3.00	11.0	3.6 : 0.51 : 5.89

1. The Effect of Evacuation. — The relative rates of the cautiously degassed samples were 1.02, 1.16 as compared with 1.49, 1.52, 1.46 of the aerated ones ([Acriflavine] $=1.0\times10^{-4}$ M, $[SnCl_2]=1.25\times10^{-2}$ M, AN : H_2O : DMF=3.3 : 2.0 : 4.7 (in volume)). It is evident that the polymerization does take place in the evacuated sample though the rate is somewhat smaller than the aerated solution. The ratio of the rates in two cases being about 1 : 1.4, it seems rather plausible to consider that the effect of oxygen is of the secondary importance (see Discussion). Tentatively assuming the above viewpoint and to orient the investigation, the effect of various factors upon the rate was examined in the first place using aerated solution. Another reason for this was to avoid

---

[3] G. V. Schulz and G. Sing, *J. Prakt. Chem.*, **161**, 161 (1942).

[4] P. F. Onyon, *J. Polymer Sci.*, **22**, 13 (1956).

the troublesome procedure for repeated evacuation. The results given below concern only with such aerated samples.

2. The Effect of Dye Concentration. — The variation of the rate when the concentration of acriflavine is changed from zero to 1.4×10^{-4} M is shown in Fig. 2. It is apparent from the figure that in the region of $\sim10^{-6}$ M of dye, the rate linearly increases with the dye concentration. This was further confirmed by log (rate)$\sim$log [AF] curve, which gave the slop of 0.9. When the concentration of dye exceeds ca. 3.5×10^{-5} M, the rate remains constant. From the above results it is concluded that, at a small concentration of dye, the rate is proportional to the dye concentration and it appears to be proportional also to the absorbed light but it will be shown below that it is not the fact (see Sect. 7).

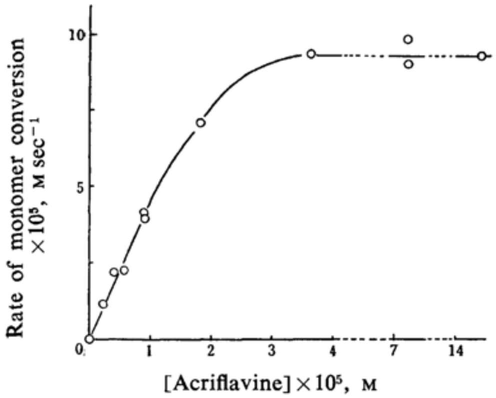

Fig. 2. Dependence of rate on acriflavine concentration.
$[SnCl_2]=1.8\times10^{-2}$ M ; AN : H_2O : DMF= 4 : 3 : 4.2 (in volume)

3. The Effect of the Concentration of Stannous Chloride.—The effect of the concentration of stannous chloride on the rate is shown in Fig. 3. Although there exists some scattering of the experimental points, it is still evident that in the low concentration region (< ca. 3.5×10^{-3} M) the linearity holds between the rate and $[SnCl_2]$, and this fact was also confirmed by the slope of 0.9 for log (rate)$\sim$log $[SnCl_2]$ plot. Above ca. 10^{-2} M of stannous chloride the rate remains constant. It is to be added that in the case of a high concentration of $[SnCl_2]$ the polymer deposits throughout the entire cell while in case of low concentration, the polymer adheres to the lower half of the front wall of the vessel.

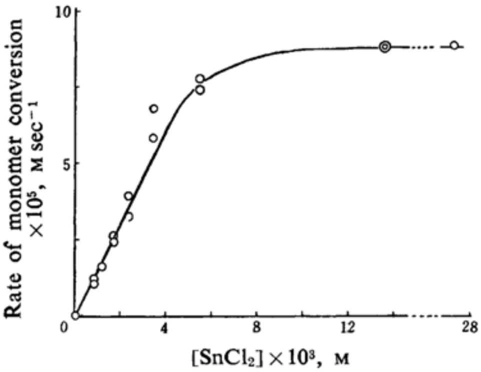

Fig. 3. Dependence of rate on stannous chloride concentration.
$[D]=2.73\times10^{-4}$ M ; AN : H_2O : DMF=4 : 3 : 4.2 (in volume)

4. The Effect of Monomer Concentration.—In Fig. 4, the rate is plotted against the square of the monomer concentration. It is apparent that the rate $\propto[AN]^2$. Another series of experiments gave a similar result. log(rate)$\sim$log[AN] plot gave a straight line of slope 1.9$\sim$2.05.

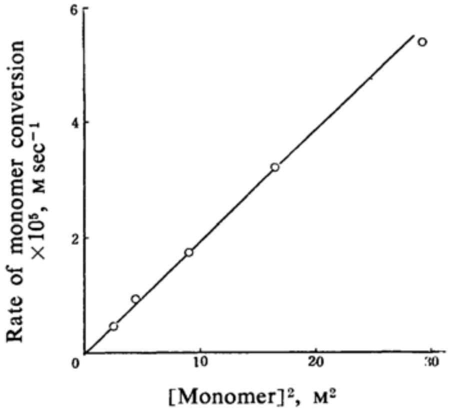

Fig. 4. Dependence of rate on acrylonitrile concentration.
$[D]=3.00\times10^{-4}$ M ; $[SnCl_2]=1.37\times10^{-2}$ M ; $[H_2O]=14.9$ M

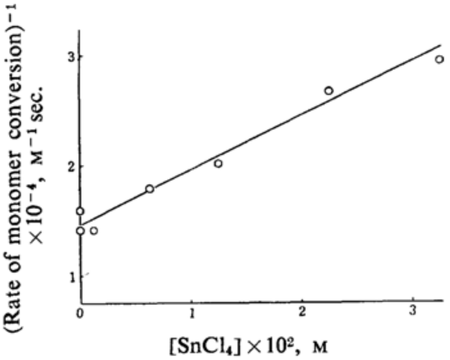

Fig. 5. Dependence of rate on stannic chloride concentration.
$[D]=2.00\times10^{-4}$ M ; $[SnCl_2]=1.25\times10^{-2}$ M ; AN : H_2O : DMF=3.6 : 2.5 : 4.0 (in volume)

5. The Effect of the Concentration of Stannic Chloride. — When $SnCl_4$ is added, the rate is decreased. As shown in Fig. 5, there exists an approximate linearity between the reciprocal of the rate and the concentration of stannic chloride.

6. The Effect of Water Content. — It was found that the polymerization can occur without any water being added, and the effect of water content on the rate was investigated in some detail. Time plots in the case of a large quantity of water were simple as shown in Fig. 1 (1), but they were curved as shown in Fig. 1 (3) when the content of water was low. Corresponding to this anomaly the polymer did not appear at first; the above phenomenon may perhaps be connected with the precipitation of the polymer. In Fig. 6 the rate is plotted against $[H_2O]/[DMF]$; × and ○ represent respectively the rates evaluated from parts a and b of the curve. It is apparent from the figure that the addition of water up to about $[H_2O]/[DMF]=1$ scarcely affects the rate but a larger quantity causes an increase to some extent. It is known that 1 : 1 complex is formed between DMF and water[5], and the above result might be correlated with this phenomenon.

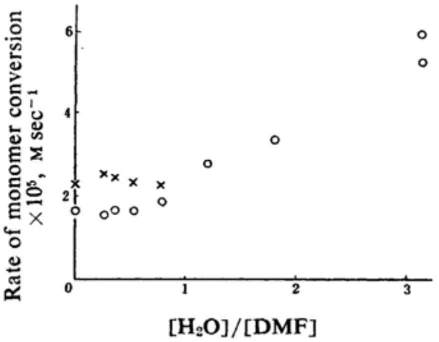

Fig. 6. Dependence of rate on $[H_2O]/[DMF]$. $[AN]=5.4$ M; $[D]=3.0\times10^{-4}$ M; $[SnCl_2]=1.1\times10^{-2}$ M

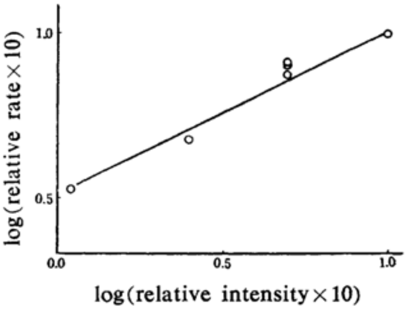

Fig. 7. The intensity exponent. $[D]=2.00\times10^{-4}$ M; $[SnCl_2]=1.25\times10^{-2}$ M; $AN : H_2O : DMF=3.6 : 2.5 : 4.0$ (in volume)

7. The Effect of Light Intensity. — The intensity of the exciting light was changed to 50, 25 and 11% of the standard light by use of neutral filters. As seen from Fig. 7 the rate is nearly proportional to the root of light intensity. Although these experiments were done only for the samples containing such a large quantity of dye as to absorb almost all the effective light, there is scarcely any doubt that this relation also holds for the case of a small concentration of dye.

8. Average Degree of Polymerization.—The effect of the monomer concentration on the degree of polymerization was examined. As shown in Fig. 8, linear relation holds approximately between $\bar{P}$ and [AN]. The effect of the addition of stannic chloride on $\bar{P}$ was also

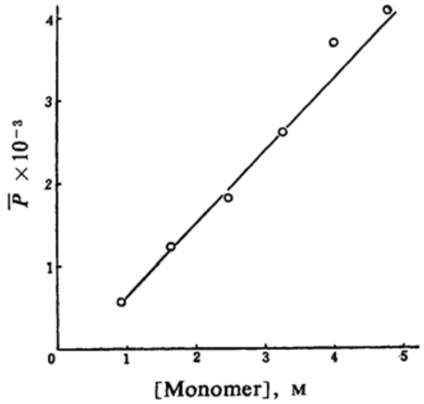

Fig. 8. Dependence of average degree of polymerization on acrylonitrile concentration. $[D]=2.00\times10^{-4}$ M; $[SnCl_2]=1.25\times10^{-2}$ M; $[H_2O]=13.9$ M

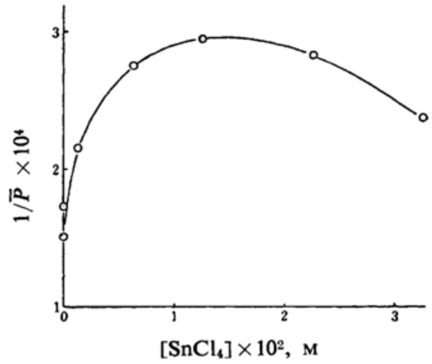

Fig. 9. Dependence of average degree of polymerization on stannic chloride concentration. $[D]=2.00\times10^{-4}$ M; $[SnCl_2]=1.25\times10^{-2}$ M; $AN : H_2O : DMF=3.6 : 2.5 : 3.9$ (in volume)

---

[5] A. D. Jenkins and R. Johnston, ibid., 39, 81 (1959).

examined. The result is shown in Fig. 9. If stannic chloride only takes part in the termination or chain transfer process, $1/\overline{P}$ should increase monotonously with $[SnCl_4]$, so that it is certain that stannic chloride interferes with other processes, particularly with the initiation step.

9. Activation Energy.—The temperature dependence of the rate was measured in the region from 16.5 to 40°C. The Arrhenius plot is shown in Fig. 10. The rate is almost independent of temperature between 25 and 40°C. But below about 25°C, the rate decreases with the fall of temperature. The apparent activation energy is evaluated to be 7±2 kcal./mol.

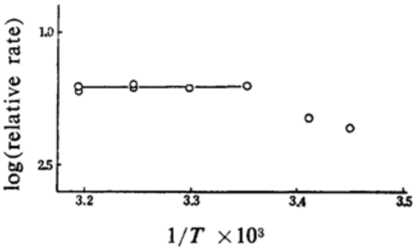

Fig. 10. Arrhenius plot.
$[D]=2.00\times10^{-4}$ M; $[SnCl_2]=1.25\times10^{-2}$ M; AN : H_2O : DMF = 3.6 : 2.5 : 4.0 (in volume)

Discussion

From the result that the polymerization takes place in the degassed solution and with the same order of rate as that of the aerated one, it is certain that the existence of oxygen is not of primary importance for the reaction to occur. Hence it is tentatively assumed that oxygen is not involved in the essential steps of the reaction, particularly in the early stages of the initiation. Then the molecular species which participate in the initiation step would be stannous chloride, acriflavine and AN, since both water and stannic chloride do not affect the rate so much. Thus the addition of stannic chloride as much as 3×10^{-2} M only decrease the rate to about a half and 15 M of water increases the rate only 3~4 times, a small amount scarcely affecting the rate. It may be certain that stannous chloride employed contains a small amount of stannic chloride, but its effect may be neglected from the experimental results. Hence attention will be paid only on the dependence of the rate upon $[SnCl_2]$, $[D]$, $[AN]$ and intensity of light I_0.

Now the overall rate of polymerization is in general expressed by the following equation if the condition of steady state is satisfied.

$$v=k_p[R][M] \tag{I}$$

where [R] and [M] are the concentrations of growing polymer and monomer. [R] can be expressed by II or III according as the termination process is the first order or the second order in regard to [R].

$$[R]=v_i/k_t \tag{II}$$

$$[R]=(v_i/k_t)^{1/2} \tag{III}$$

The experimental rate formula satisfies the following condition

$$v \propto [D]\,[SnCl_2]\,[M]^2$$

and $$v \propto I_0^{1/2}$$

when [D] and $[SnCl_2]$ are small.

Hence v_i in this case must be expressed as follows:

$$\text{case II,}\quad v_i \propto [D]^{1/2}[D^*]^{1/2}[SnCl_2]\,[M]$$

$$\text{case III,}\quad v_i \propto [D]\,[D^*]\,[SnCl_2]^2[M]^2$$

where D* is the excited dye. Case III however can be rejected since it was found experimentally that the following relation holds,

$$\overline{P} \propto [M]$$

and in general $\overline{P}$ may be equated to v/v_i at least approximately (unless the rate of chain transfer is quite appreciable). Thus the initiation processes must be those that satisfy the following relations.

When [D] and $[SnCl_2]$ are small

$$v_i \propto [D]^{1/2}[D^*]^{1/2}[SnCl_2]\,[M] \tag{IV}$$

When both [D] and $[SnCl_2]$ are large

$$v_i \propto [M]\,I_0^{1/2} \tag{V}$$

The equations IV and V look rather unusual and these suggest the peculiar character of the reaction scheme.

Here we propose the following two schemes as plausible ones.

$$\begin{tikzcd}
\text{A.}\ D \arrow[r, "h\nu", "(1)"'] & D^* \arrow[r, "D", "(3)"'] \arrow[d, "(2)"] & D^t \arrow[r, "Sn^{2+}", "(5)"'] \arrow[d, "(4)"] & (D^- \cdots\cdots \arrow[d, "(6')"] & Sn^{3+}) \arrow[d, "(6)"] \\
 & D & D & D+Sn^{2+} & \text{Leuco}+Sn^{4+}
\end{tikzcd}$$

$$\xrightarrow[(7)]{Sn^{2+}} D + Sn^+ + Sn^{3+} \xrightarrow[(8)]{} D + 2Sn^{2+}$$

$$\text{(or } D^- + Sn^{3+}\text{)} \qquad \text{(or } D + Sn^{2+}\text{)}$$

$$Sn^{3+} + M \xrightarrow[(9)]{k_1} R$$

$$\text{(or } Sn^+ + M \longrightarrow R\text{)}$$

$$\begin{tikzcd}
\text{B.}\ D + Sn^{2+} \arrow[r, shift left, "K_0"] & (DSn^{2+}) \arrow[l, shift left, "(0)"] \arrow[r, "h\nu", "(1)"'] & (D^*Sn^{2+}) \arrow[d, "(2)"] \\
 & & D
\end{tikzcd}$$

$$\begin{tikzcd}
\arrow[r, "D", "(3)"'] & (D^tSn^{2+}) \arrow[r, "(5)"'] \arrow[d, "(4)"] & (D^- \cdots\cdots \arrow[d, "(6')"] & Sn^{3+}) \arrow[d, "(6)"] \\
 & D & D+Sn^{2+} & \text{Leuco}+Sn^{4+}
\end{tikzcd}$$

$$\xrightarrow[(7)]{Sn^{2+}} \text{same as above}$$

In scheme A, Sn^{2+} participates in the steps 5 and 7 while in scheme B a complex is formed between Sn^{2+} and D and the corresponding scheme to 5 in A is lacking. In both schemes it is assumed that the transition from singlet excited state (D*) to triplet (D^t) is induced by the ground state dye molecule. Although this is plausible and in fact such a process has also been accepted by Oster for the case of acridine dyes⁶⁾, it is noteworthy that there is another possibility that the excimer⁷⁾ be formed between D and D*. The discrimination may however be impossible only from the rate formula. ($D^- \cdots\cdots Sn^{3+}$) is supposed to be a charge transfer complex or the like.

For both schemes A and B the essential point is that two kinds of molecular species of radical nature produced by process 7, react almost exclusively in such a way as to produce stable molecular species and only a small fraction of them react with monomer to produce an initiator of polymerization 9. Thus when D^- and Sn^{3+} are produced by 7 electron transfer should rapidly occur between them, recovering D and Sn^{2+}, while when D, Sn^+ and Sn^{3+} are produced, the analogous electron transfer should take place between Sn^+ and Sn^{3+} (8), Sn^+, Sn^{3+}, D^- (this is rather unplausible) or all of them may initiate the polymerization. In fact such schemes as above seem almost indispensable to interpret the following relations consistently.

$$v_i \propto I_0^{1/2}, \qquad v \propto [M]^2, \qquad \overline{P} \propto [M]$$

From the above schemes, the following rate formulas can be derived.

Case A

$$v_i = \left[\left\{\frac{k_1 I_0 k_3 [D]}{k_2 + k_3 [D]}\right\}\left\{\frac{k_5 [Sn^{2+}]}{k_4 + k_5 [Sn^{2+}]}\right\} \times \left\{\frac{k_7 [Sn^{2+}]}{k_6 + k_6' + k_7 [Sn^{2+}]}\right\}\right]^{1/2} \frac{k_9}{k_8^{1/2}} [M] \qquad \text{(VI)}$$

Case B

$$v_i = \left[\left\{\frac{I_0 k_1 K_0 [Sn^{2+}]}{1 + K_0 [Sn^{2+}]}\right\}\left\{\frac{k_3 [D]}{k_2 + k_3 [D]}\right\}\left\{\frac{k_5}{k_4 + k_5}\right\} \times \left\{\frac{k_7 [Sn^{2+}]}{k_6 + k_6' + k_7 [Sn^{2+}]}\right\}\right]^{1/2} \frac{k_9}{k_8^{1/2}} [M] \qquad \text{(VII)}$$

Both VI and VII can express the experimental results satisfactorily as in the following way.

i) Large [D]: v is independent of [D].

$$v \propto I_0^{1/2}$$

ii) Small [D]: $k_1 I_0$ may be put approximately proportional to [D]. Hence

$$v \propto [D]$$

iii) Large $[Sn^{2+}]$: v is independent of $[Sn^{2+}]$.

iv) small $[Sn^{2+}]$: $v \propto [Sn^{2+}]$

v) In all cases, $v \propto [M]^2$

As for the effect of water, both hydration of D and the formation of a certain ion pair from Sn^{2+} and OH^- would favor the reaction. For example the formation of $(SnOH)^+$ would promote processes 5 and 7 in both case A and case B; moreover the hydration of D would also be favorable for these process and in addition, for 3 and 0 (in case B). All these effects together should cause the rate to increase with the content of water. But these effects are of secondary importance in the reaction scheme and to not affect the rate very much.

In connection with the above schemes, it may be worthy of adding here some discussions about the rate of dye bleaching in the absence of acrylonitrile. Provided that process 7 be neglected, the rate of bleaching of dye will be given as follows:

Case A

$$\frac{k_1 I_0 k_3 [D]}{k_2 + k_3 [D]} \cdot \frac{k_5 [Sn^{2+}]}{k_4 + k_5 [Sn^{2+}]} \cdot \frac{k_6}{k_6 + k_6'} \qquad \text{(VIII)}$$

Case B

$$\frac{k_1 I_0 K_0 [Sn^{2+}]}{1 + K_0 [Sn^{2+}]} \cdot \frac{k_3 [D]}{k_2 + k_3 [D]} \cdot \frac{k_5}{k_4 + k_5} \cdot \frac{k_6}{k_6 + k_6'} \qquad \text{(IX)}$$

Thus the similar relation in respect to [D] and $[Sn^{2+}]$ will hold for two cases. But when the process 7 participate in the reaction the rate would decrease when the concentration of Sn^{2+} exceeds a certain value. It may be possible to examine this effect experimentally.

If Oster's mechanism holds in the present case, which postulates the formation of leuco dye prior to the initiation process, the rate formula of initiation would be similar to VIII and IX which contradicts the experimental results altogether. Thus three relations $v \propto I_0^{1/2}$, $v \propto [M]^2$ and $\overline{P} \propto [M]$ can not be interpreted satisfactorily on this basis. Analogous discussion may be extended to the effect of oxygen on the rate, the increase amounting to about 40% of that of the evacuated solution. If this increase is due to the participation of the process $D + SnCl_2 \rightarrow \text{Leuco} + SnCl_4$, $\text{Leuco} + O_2 \rightarrow$ active radical, then the kinetic order in respect to $[SnCl_2]$ and [D] would be the average of the two simultaneous reactions and

---

6) F. Millich and G. Oster, *J. Am. Chem. Soc.*, **81**, 1357 (1959).

7) B. Stevens and E. Hutton, *Nature*, **186**, 1045 (1960).

would not be the whole number as experimentally obtained. Hence it seems more plausible that oxygen interferes with the intermediate ($D^{-}\cdots\cdots Sn^{3+}$) rather than its attack on leuco dye. The discrimination between cases A and B may perhaps be made by spectroscopic investigation. Further investigations are now under way to confirm the above schemes more definitely and to select case A or case B.

Summary

When the aerated solution of acrylonitrile, acriflavine and stannous chloride in the mixture of water and dimethylformamide is irradiated by the visible light, the polymerization of acrylonitrile immediately takes place. The presence of water and oxygen was found to be unnecessary for the reaction to occur. The dependence of rate on the concentration of each species and on the light intensity (I_0) can be summarized as follows.

Acriflavine	$<$ca. 1×10^{-5} M, 1st order; $>$ca. 3.5×10^{-5} M, const.
Stannous chloride	$<$ca. 3.5×10^{-3} M, 1st order; $>$ca. 1.2×10^{-2} M, const.
Acrylonitrile,	2nd order
I_0,	1/2th order

It was further found that the average degree of polymerization is proportional to the monomer concentration. The scheme involving the photoreduction of dye by stannous chloride and its recovery by the existent oxygen cannot explain the present result. It was proposed as a new mechanism that a transient metallic ion of tin with an odd valency is formed and this, interacting with acrylonitrile, initiates the polymerization.

The present research was mostly performed by Ai Watanabe at Osaka City University and was finished during her stay at Sendai as a visiting research fellow. The authors express their cordial thanks to Professor R. Fujishiro of Osaka City University for his interest and encouragement.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai