*Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Styrene by Cyanine Dyes. III**

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(Received December 3, 1958)

As reported in the previous papers[1,2], the photopolymerization of styrene occurs when the mixture of styrene and butanol (15 : 1 in volume) involving various cyanine dyes is irradiated by the visible light. The dye, at the same time, is bleached and it was concluded that both these reactions are initiated by a direct interaction between the excited dye molecule and the styrene. Generally speaking, however, the initial processes for the two reactions are not identical, since, for example, the number of kinetic chains for one decomposed dye molecule is a function of temperature. The participation of halogen ion in the reaction is highly plausible because of a marked difference between the rates for pinacyanol-iodide and -chloride. In order to elucidate the photochemical processes in these reactions, it would be desirable to compare the kinetic features of bleaching and polymerization, but only studies on the latter will be reported in this paper. Activation energies for the chain initiation were determined for various dyes and the influence of halogen species was examined. In addition, the following two facts which had been tentatively described in the previous paper[2] were reconfirmed: 1) light promotes only the initiation process of polymerization; 2) the concentration of dye

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* Presented before the Ninth Annual Meeting of the Chemical Society of Japan, held at Kyoto, April 1956 and the Tenth Meeting at Tokyo, April 1957.

[1] A. Watanabe and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **5C**, 114 (1956); M. Koizumi and A. Watanabe, This Bulletin, **28**, 136 (1955).

[2] A. Watanabe and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **5C**, 124 (1956); A. Watanabe and M. Koizumi, This Bulletin, **28**, 141 (1955).

does not affect the rate in the region of $6.3\times10^{-6}\sim19\times10^{-6}$ mol./l.

Experimental

Material.—Styrene and *n*-butanol were purified in the same way as in the previous paper[1]. Isocyanine iodide, pinacyanol iodide and kryptocyanine iodide were granted by the late Dr. T. Ogata of the Institute of Physical and Chemical Research, Tokyo. All the other dyes except the above three were kindly supplied by the Japanese Research Institute for Photosensitizing Dyes, Co., Ltd. in Okayama.

Apparatus and Experimental Procedure.—The apparatus employed and the experimental procedure are mostly identical with the previous ones[1], but the dilatometric technique was adopted to follow the course of polymerization. The type of dilatometer was almost the same as used by Nakatsuka[3] except that a drum-type reaction cell of about 5 cc. in capacity was made of quartz and connected to a tube of hard glass. The reaction cell was arranged so as to let the parallel light beam illuminate the whole plane surface of the drum. Matsuda color filters were used; V-O 2 for pinacyanol, kryptocyanine and isocyanine, and V-Y 1 for trimethinthiocyanine.

One volume of *n*-butanol solution of dye was mixed with 15 volumes of styrene and the mixture was extensively evacuated. The concentration of the dye is always 1.2×10^{-5} mol./l. unless otherwise cited.

The extent to which the polymerization proceeded was calculated from the volume contraction, as performed by Burnett[4] employing the data of density for monomer and polymer reported by Patnode and Scheiber[5]. The average degree of polymerization was determined as in the previous paper[1].

Experimental Results

The Characteristics of the Bleaching Reaction.—The absorption spectra of various dyes employed are shown in Figs. 1 and 2. To avoid the overlapping of curves, the plot of $\log I_0/I$ is suitably displaced for some dyes, the magnitude of displacement being given by X. It is evident from these figures that in the butanol solution the position of absorption maximum is not affected by the kind of halogen, but in the styrene-butanol solution the maximum is more or less displaced to the longer wavelengths, the magnitude of shift being slightly different according to the species of dye and halogen.

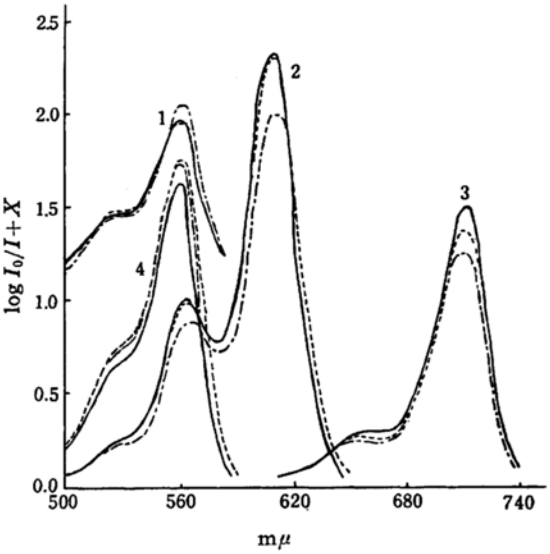

Fig. 1. Absorption spectra of cyanine dyes in *n*-butanol. Thickness of the cell, 1 cm.; 1.2×10^{-5} mol./l. (1, 2 and 4), 6.3×10^{-6} mol./l. (3). 1, isocyanine (X=1); 2, pinacyanol (X=0); 3, kryptocyanine (X=0); 4, trimethinthiocyanine (X=0). ——, iodide; ------, bromide; —·—, chloride.

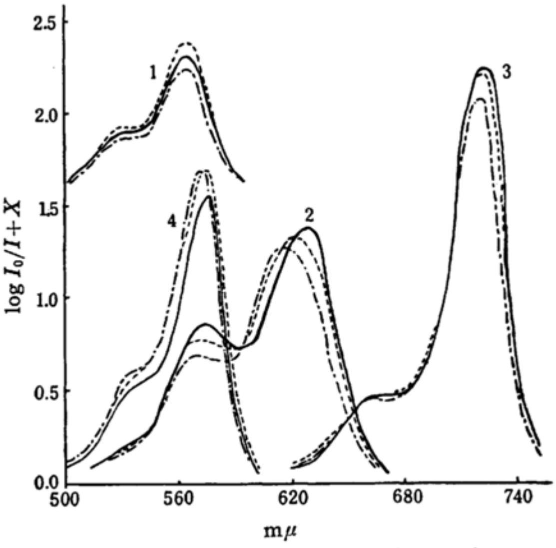

Fig. 2. Absorption spectra of cyanine dyes in styrene and *n*-butanol (15:1 in vol.). Thickness of the cell, 1 cm.; 1.2×10^{-5} mol./l. 1, isocyanine (X=1.5); 2, pinacyanol (X=0); 3, kryptocyanine (X=0); 4, trimethinthiocyanine (X=0). ——, iodide; ------, bromide; —·—, chloride.

The butanol solution of each dye does not bleach practically at 60°C even after illumination by the visible light for 6 hr. In the styrene-butanol solution, bleaching does not take place in the dark

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[3] K. Nakatsuka, S. Wada and M. Koizumi, *Chem. High Polymers* (*Kōbunshi Kagaku*), **14**, 609 (1957).

[4] G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950).

[5] W. Patnode and W. J. Scheifer, *J. Am. Chem. Soc.*, **61**, 3449 (1939).

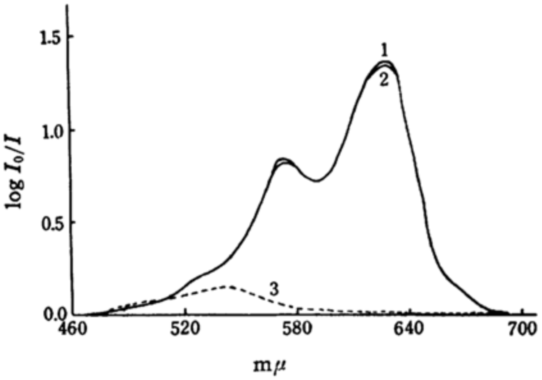

Fig. 3. Absorption spectra of pinacyanol iodide. 1, original sample; 2, after the reaction in dark for 2.5 hr. at 60°C; 3, after the reaction in light for 2.5 hr. at 60°C.

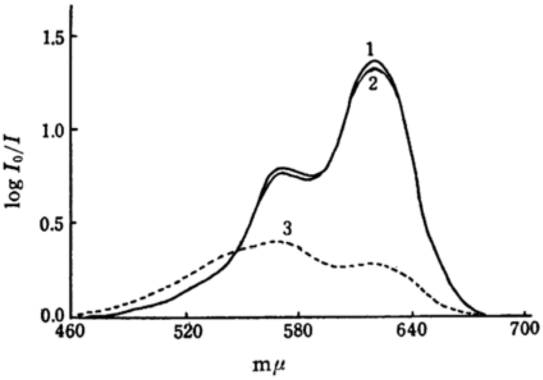

Fig. 4. Absorption spectra of pinacyanol bromide. 1, original sample, 2, after the reaction in dark for 5 hr. at 60°C; 3, after the reaction in light for 5 hr. at 60°C.

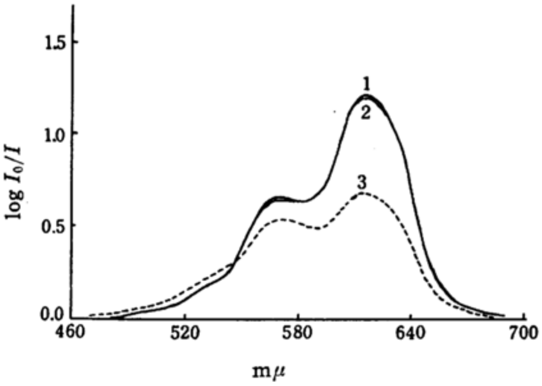

Fig. 5. Absorption spectra of pinacyanol chloride. 1, original sample; 2, after the reaction in dark for 5 hr. at 60°C; 3, after the reaction in light for 5 hr. at 60°C.

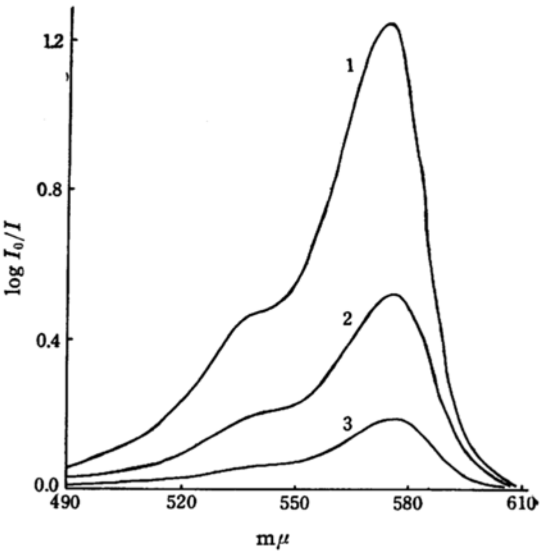

Fig. 6. Absorption spectra of illuminated trimethinthiocyanine. 1, chloride (60°C, 5 hr.); 2, bromide (60°C, 5 hr.); 3, iodide (60°C, 1 hr.).

(or does very slightly perhaps because of the dissolved oxygen or some impurities), but when illuminated, the bleaching occurs and at the same time the polymerization is promoted. The only curious exception is kryptocyanine bromide which is photobleached without inducing the polymerization, but retarding it very slightly at 60°C. Some of the absorption curves after the reaction for several hours are shown in Figs. 3, 4, 5 and 6. In case of pinacyanol, a new small absorption band appears in the visible region. So does it with isocyanine. In case of trimethinthiocyanine or kryptocyanine, the absorption curves merely decline over the whole visible region.

Effect of the Concentration of Dye.— Though it is a natural expectation that the rate of photochemical initiation is proportional to the intensity of light absorbed, there is some doubt about it under the present experimetal condition, since the dye of about 10^{-5} mol./l. in concentration absorbs nearly all the light and the distribution of the excited molecule in the system is not uniform. Hence it is desirable to check whether such a state of affairs does influence the rate or not. In the previous report it was perceived that the rate of polymerization is independent of the concentration of pinacyanol iodide in the range of $6\sim20\times10^{-6}$ mol./l. at 60°C, but this was not necessarily conclusive since the styrene then used was not so carefully purified. Therefore the analogous experiment was repeated with more caution at 40°C. The results are tabulated in Table I. It is quite certain from Table I that the rate is completely independent of the dye concentration. In view of the absorbance of the dye the effective light is almost completely absorbed and the rate is not influenced by the dye concentration under the light intensity employed, but is determined by the quantity of excited dye produced in the whole system in a unit time.

TABLE I. EFFECT OF PINACYANOL IODIDE CONCENTRATION AT 40°C

Expt. no.	Dye concn. (10^{-6} mol./l.)	Relative rate (mm./hr.)
1	6.3	1.60
2	6.3	1.70
3	6.3	1.50
4	12	1.65
5	12	1.70
6	12	1.65
7	19	1.55
8	19	1.60

The Relation between the Average Degree of Polymerization and the Overall Rate.—In the previous report[2)], a test was made to see whether the irradiation only induces the chain initiation or also affects other steps such as propagation or termination. Using many data for several cyanine dyestuffs under various experimental conditions, the reciprocal of $\bar{P}_L$ (the average degree of polymerization for the polymer produced in the irradiated region of the reaction cell) was plotted against the overall rate V (the quantity of polymer produced in the irradiated region in a unit time). An approximately linear relationship was obtained supporting the view that the light only promotes the initiation process. But the points of data were not so satisfactory showing some scattering and it seemed desirable to repeat it again. In the present experiments, the solution of pinacyanol iodide of 1.2×10^{-5} mol./l. in concentration was used at 60°C and the intensity of light was varied by means of gauze wires. The results obtained by a similar treatment as in the previous paper are shown in Fig. 7. In this figure $\bar{P}_D$ is the average degree of polymerization in the dark part. The data are still distributed with some randomness, but in view of the fact that the value of $\bar{P}_D$ employed for the evaluation of $\bar{P}_L$ was a mean of many data in the dark, and further taking into account the poor reproducibility of the experiment the linearity can be regarded to hold.

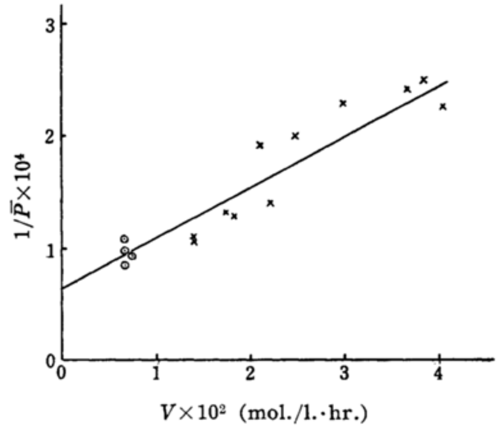

Fig. 7. Variation of the average degree of polymerization with the overall rate. ⊙, in dark; ×, in light.

Activation Energy. — The energy of activation was determined from rate measurements between 20° and 60°C under illumination and between 40° and 60°C in the dark using the dye solution of 1.2×10^{-5} mol./l. in concentration. The rate of photochemical reaction V_p was determined from the expression $V_p=\sqrt{V_l^2-V_d^2}$, where V_d is the rate of thermal reaction in the illuminated space and V_l is the total rate under illumination. The relation between $\log V_p$ and $1/T$ for various dyes is shown in Figs. 8, 9 and 10, where V_p are represented in per cent per hour. In case of pinacyanol iodide, V_p shows an abnormally high value at 50° and 60°C, but these are excluded from the calculation of

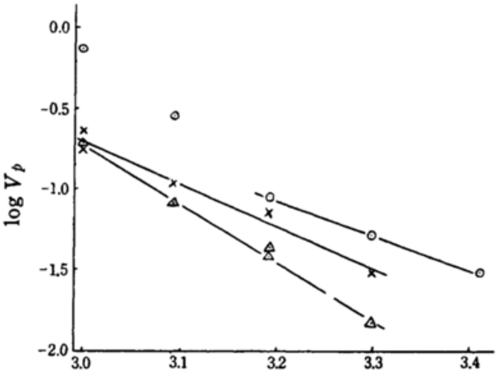

Fig. 8. Arrhenius plot for photopolymerization. ⊙, pinacyanol iodide; ×, pinacyanol bromide; △, pinacyanol chloride.

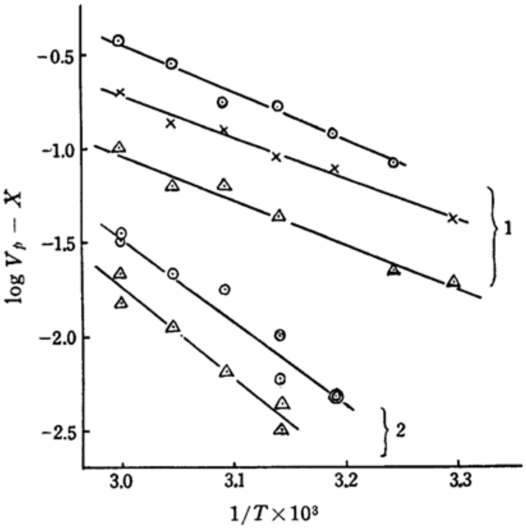

Fig. 9. Arrhenius plot for photopolymerization. 1, isocyanine (⊙, iodide (X=0); ×, bromide (X=0); △, chloride (X=0.4)); 2, kryptocyanine (⊙, iodide (X=1); △, chloride (X=1)).

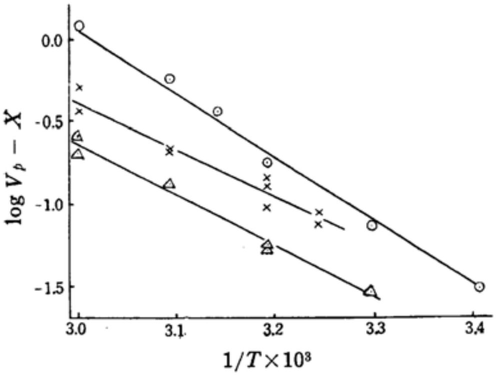

Fig. 10. Arrhenius plot for photopolymerization. Trimethinthiocyanine; ⊙, iodide (X=0); ×, bromide (X=0); △, chloride (X=0.3).

activation energy for the following reason. In the course of decomposition, this dye is transformed into a stable intermediate with a new visible absorption band, which is further decomposed by light absorption at 60°C accompanied with the induced polymerization. The above mentioned decomposition of the intermediate is far more rapid for iodide than for bromide or chloride as is evident from the Figs. 3, 4 and 5. Hence the polymerization induced by the decomposition of the intermediate is remarkable only for pinacyanol iodide at higher temperatures, while for bromide and chloride, in which similar intermediates are also produced, this secondarily induced polymerization is negligible at least in the initial stage of reaction due to their much lower rates of decomposition**. In case of isocyanine a new small peak also appears in the shorter wavelength region but the filter V-O 2 in this case does not transmit the light corresponding to the absorption of the intermediate, hence the polymerization due to its destruction will not take place. In case of kryptocyanine or trimethinthiocyanine the absorption declines monotonously in the whole visible region and the above considerations need not be taken into account. The values of the activation energy for the overall reaction thus evaluated are tabulated in Table II. By making use of Bamford's values[6] of activation energies for chain growth and chain termination (E_p=6.5 kcal./mol., E_t=2.8 kcal./mol.), the activation energy for initiation E_i can be calculated from the relation $E_i=2E-2E_p+E_t$. They are also included in Table II. Although the errors of these values are rather large owing to the poor reproducibility of experiments, some features can be seen and semiquantitative discussions will be given below on the basis of these data.

TABLE II. ACTIVATION ENERGY (kcal./mol.)

Dye	Dark-reaction		Photo-reaction	
	E	E_i	E	E_i
No dye	22.9	35.6		
Pinacyanol iodide	—	—	10.4	10.6
Pinacyanol bromide	21.6	33.0	12.1	14.0
Pinacyanol chloride	22.6	35.0	16.9	23.6
Kryptocyanine iodide	22.6	35.0	20.6	31.0
Kryptocyanine chloride	22.0	33.8	22.4	34.6
Isocyanine iodide	18.3	26.4	11.7	13.2
Isocyanine bromide	—	—	10.5	10.8
Isocyanine chloride	15.8	21.4	11.0	11.8
Trimethinthiocyanine iodide	—	—	17.4	24.6
Trimethinthiocyanine bromide	—	—	12.8	15.4
Trimethinthiocyanine chloride	22.0	33.8	14.2	18.2

Discussion

If the irradiation only promotes the

** Filter V-O 2 transmits the light including the absorption maximum of the intermediate as well as the two absorption peaks of the original dye.

[6] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, **A192**, 309 (1948).

chain initiation, then the following linearity between the reciprocal of $\bar{P}_L$ and V must hold as derived in a previous paper[2].

$$1/\bar{P}_L = k_t V/2\,k_p^2\,[M]^2 + (R_{tr\cdot M}[M] + k_{tr\cdot S}[S])/k_p[M] \qquad (1)$$

where k_p, $k_{tr\cdot M}$, $k_{tr\cdot S}$ and k_t are the rate constants for propagation, monomer transfer, solvent transfer and termination, respectively, and $[M]$ and $[S]$ denote the concentrations of the monomer and the solvent, respectively. Under the present experimental conditions $k_{tr\cdot S}[S]$ can be neglected against $k_{tr\cdot M}[M]$, hence from the intercept and the inclination of the straight line in Fig. 7, $k_{tr\cdot M}/k_p$ and k_t/k_p^2 can be evaluated, to be 6×10^{-5} and 2.1×10^3 mol. l^{-1} sec., respectively. The value of $k_{tr\cdot M}/k_p$ obtained above shows an excellent coincidence with that reported by Mayo et al.[7] As for the value of k_t/k_p^2, Bamford's data[6], $k_t=4.6\times10^6$ l. mol^{-1} sec^{-1} and $k_p=60$ l. mol^{-1} sec^{-1} at 60°C, give $k_t/k_p^2=1.28\times10^3$ mol. l^{-1} sec., while Matheson's values[8], $k_t=7.2\times10^7$ l. mol^{-1} sec^{-1} and $k_p=176$ l. mol^{-1} sec^{-1}, give $k_t/k_p^2=2.32\times10^3$ mol. l^{-1} sec. and the present value is about the same as the Matheson's one. From the agreement of these constants it is certain that the irradiation only induces the chain initiation process and does not affect either the propagation nor the termination process. Thus there is no doubt that the mechanism of the photochemical initial process may be discussed on the basis of the values of E_i tabulated in Table II.

Table II indicates that mere interchange of the halogen often results in a marked change in E_i-value and it can be concluded that the halogen ion plays an essential rôle in the primary photoprocess. Next, broadly speaking, a tendency is noted that the larger the frequency of absorbed light, the smaller is the value of E_i. In the following, some considerations will be given about these results more closely.

From the fact that bleaching does not occur in the absence of monomer, there is no doubt that the photochemical process takes place between the excited dye and the monomer. Further the chain initiation of polymerization is considered to be induced by a radical, since the quantitative aspects of polymerization such as the values of k_t/k_p^2 and $k_{tr\cdot M}/k_p$ coincide with the data for the well-established radical polymerization. Of course, a detailed description of the photochemical primary process is beyond the scope of the present stage of investigation, but some consideration about it will be helpful for further investigation.

As regards the formation of the radical, it seems natural to suppose that in the course of attack of a styrene molecule on dye, an electron-transfer occurs, the electron of a halogen anion being transferred to a dye cation. Then, the styrene molecule may seize a halogen atom and the two radicals produced may sometimes both induce the chain-initiation, or otherwise the dye-radical produced may decompose of itself.

It will be described in the following how the above idea is materialized and how it can explain the present results. Firstly, according to the above idea, the photochemical primary process may be pictured as follows:

$$\underset{\text{Initial state}}{D^{+*}\cdots X^{-}+M}\rightarrow\underset{\text{Activated state}}{D\cdots X\cdots M}\rightarrow\underset{\text{Final state}}{D\cdot+MX\cdot}$$

where D^+ and X^- are a dye cation and a halogen anion, respectively. The activated state would have a configuration in which an electron is transferred from X^- to D^+ and a bond is partially formed between X and M, these two processes chiefly determining the energy of the activated state.

In case of a common D, a) the ease of electron transfer would be in the order, I > Br > Cl, while b) the energy decrease due to X−M partial bond formation would be in the reversed order Cl > Br > I. If a styrene molecule is separated from D···X in the activated state, then a) would be a chief factor in determining the activation energy. On the contrary, when a styrene molecule is in close proximity to X, the activation energy would depend largely on b). Such would be the reason why the influence of halogen on activation energy is different in each dye.

In case of different D, the maximum of absorption differs and at the same time the tendency of electron transfer would also do so. Roughly speaking, these two factors would commonly act in the same direction for the following reason. The longer the wavelength of the absorption maximum which in many cases is caused by the longer chain of conjugation, the higher the highest occupied level

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[7] F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

[8] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, ibid., **73**, 1700 (1951).

(or the lowest vacant level) lies and an electron is expected to transfer from X^- to D^+ with more difficulty. Thus it is expected that activation energy becomes greater as the absorption band is situated in the longer wavelength. This expectation is in accord with a general trend of the results.

The above qualitative discussion can be stated in much clearer form for an ideal case in which only the electron transfer

$$(D^+X^-)^* \rightarrow D\cdot X\cdot$$

is essential. It would be convenient to discuss this problem in terms of potential energy curves drawn against the distance between D and X. In Fig. 11, 1 is a potential energy curve of a dye in the ground state which is chiefly determined by the coulombic attraction between the solvated ions. 2 is the one of the excited dye, and 3 is a curve for the system after the electron is transferred from a halogen anion to a dye cation. The relative positions of the three curves are arbitrarily chosen but this does not essentially affect the discussion. Now at a larger distance, the energy difference between 2 and 3, $\varDelta$, is given by the equation

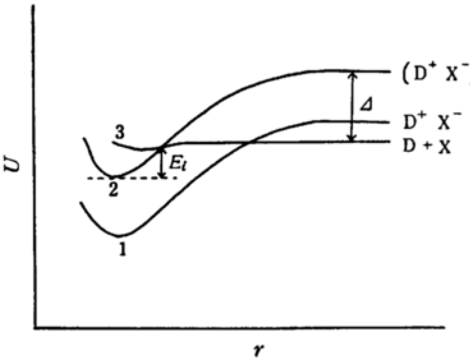

Fig. 11. Potential energy diagram.

$$\varDelta = I_D - A_X + h\nu - S \qquad (2)$$

where I_D is the ionization potential of a dye radical, A_X, the electron affinity of a halogen atom, $h\nu$, the energy of an absorbed quantum and S, a correction term related with the energy of solvation.

If the potential minimum in 1 and 2 is given by $e^2/\varepsilon r_X$ where r_X is the D–X distance in the minimum and ε is the effective dielectric constant, then the energy of activation is given by the following equation,

$$\begin{aligned} E_i &= e^2/\varepsilon r_X - \varDelta \\ &= e^2/\varepsilon r_X - I_D + A_X - h\nu + S \qquad (3) \end{aligned}$$

For a series of cyanine dyes with various halogens, E_i is determined by the value of

$$(e^2/\varepsilon r_X + A_X + S_X) = \delta_X$$

A_X for iodine, bromine and chlorine is respectively $72 < 81 < 87$ kcal./mol.[9] and S_X is most certainly in the same order. $e^2/\varepsilon r_X$ cannot always be determined by the size of a free ion, but may depend rather on the degree of solvation. In the former case it is in the order $Cl > Br > I$ while in the latter case it might be reversed. If the magnitude of δ_X is mainly determined by $A_X + S_X$ then the activation energy will be in the order $Cl > Br > I$. Such would be the case for pinacyanol. The fact that there is no great difference in the values of E_i for isocyanine and kryptocyanine might be due to the participation of X–M bond energy in the activated state or to the contribution of $e^2/\varepsilon r_X$ in the inverse order depending on the structure of dye. In this connection, it seems suggestive that for trimethinthiocyanine and pinacyanol for which halogen anion can be placed naturally in between two N atoms, the value of E_i is much dependent on X, while for isocyanine and kryptocyanine for which halogen ion has to be situated in the neighborhood of one N atom apart from the other, the value of E_i is scarecely dependent at all on X. But it is a problem for the future why in the former pair, trimethinthiocyanine and pinacyanol, the effect of halogen is roughly in the inverse order.

Eq. 3 can also give a plausible interpretation of the results for various dyes with common X. With larger ν, I_D perhaps will also become larger, especially in cases when ν is largely dependent on the length of the chain and this causes E_i to become smaller. This is a general tendeny already mentioned.

Although a conclusive statement must await further investigation, the general feature of scheme would be as pictured above.

Summary

Extensive studies on the photopolymerization of styrene by virtue of cyanine dyes were performed and it was reconfirmed

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[9] A. Eucken and Landolt-Börnstein, "Zahlenwerte und Funktionen", I. Band, 1. Teil, Springer-Verlag, Berlin (1950), p. 213.

that only the chain initiation is promoted by the direct interaction between the excited dye and the styrene molecule. Activation energies for the photochemical initiation process were experimentally determined for several dyes of iodide, bromide and chloride. In general the activation energy depends on the kind of halogen ion and from this result it was concluded that halogen ion plays an essential rôle in the reaction. A general tendency was observed that the activation energy diminishes as the wavelength of absorption maximum of dyes becomes shorter. A plausible scheme for the chain initiation process was given, in which an electron transfer from X^- to D^+ is involved in the process of activation.

The author expresses her cordial thanks to Professor M. Koizumi of Tohoku University for his helpful discussions and to Professor R. Fujishiro and Professor S. Kawaguchi for their encouragement. She is also grateful to Dr. M. Banno of the Japanese Research Institute for Photosensitizing Dyes, Co., Ltd. in Okayama and to the late Dr. T. Ogata of the Institute of Physical and Chemical Research in Tokyo for their kind favors with dye samples. The cost of the present research has been partly defrayed from the Scientific Research Grant from the Ministry of Education.

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