Chemical Behaviors of the Intermediates Produced during the Reductive Photobleaching of Eosin in the Evacuated Alcoholic Solution

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One of the present authors (Koizumi) and Imamura[1] investigated kinetically the photobleaching of eosin in the deaerated ethanol solution and concluded that the reaction proceeds via the following primary processes:

$$D \xrightarrow{h\nu} D^* \quad \text{(i)}$$

$$D^* \rightarrow D^t \quad \text{(ii)}$$

$$D^t + RH \rightarrow DH\cdot + R\cdot \quad \text{(iii)}$$

$$(DH\cdot \rightarrow \text{final products})$$

Where D: dye ion; D*: singlet excited state of dye (S*); D^t: triplet state of dye (T); RH: ethanol; DH·: semiquinone of eosine; R·; radical produced from ethanol.

Now, in order to make clear the details of these elementary reactions, it is essential to study about the chemical behaviors of the intermediates, D^t and DH·. Experiments by the flash technique have already been commenced in the authors' laboratory. However, the ordinary kinetic studies, for example, the investigation about the effect of added substances on the reaction rate are expected to be useful for this purpose to some extent. In the present research, isopentane, *n*-hexane, benzene, cyclohexene, *n*-hexene and cyclooctatetraene (COT) were added to the reaction system and the variation of the rate of photobleaching was examined.

Experimental

Materials.—*Eosine.* — Grübler's product was used. Stock solution 1×10^{-4} M was kept in the dark and this was diluted to 1×10^{-5} M for each experiment. Isopentane, *n*-hexane and benzene were purified by the usual methods. COT prepared kindly by Dr. N. Hagiwara of Osaka University, was further distilled under vacuum three times and was stored in an evacuated ampule.

n-Hexene-2 and cyclohexene of Tokyo Kasei were distilled two or three times and were reserved in vacuo.

Ethanol, after being treated with concentrated sulfuric acid, was made free from aldehyde by the addition of silver oxide and dehydrated by calcium oxide.

Apparatus and Procedures.—A tungsten projection lamp (75 V. 500 W.) was used as a light source. The voltage was fixed at 45.0±0.5 V. and the intensity was checked by measuring the bleaching rate of the aqueous eosine solution (not deaerated) throughout all the experiments[1]. A yellow glass filter cutting off < 450 mμ and a reaction cell was attached to the metallic case surrounding a glass tube, 6 cm. in diameter, in which the lamp was placed. Degassing of the sample was performed carefully by repeating the vacuum distillation. A Terrex cell for measuring the absorption spectra was used as a reaction vessel, the upper part of which was fused to a tube of hard glass for the cell to be attached to the

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[1] M. Koizumi and M. Imamura, This Bulletin, **28**, 117 (1955); **29**, 899 (1956); M. Imamura, ibid., **30**, 249 (1957).

above distillation set. After the deaerated sample was poured into the cell it was fused off at a suitable position. The sample was irradiated in a thermostat usually at 25°C and at suitable time intervals the absorption spectra were measured by a Hitachi spectrophotometer (EPU-2A). The measurement of fluorescence spectra was done by the fluorescence attachment of the spectrophotometer.

Results

Rate Formula.—Throughout all the experiments, the absorption spectra of the irradiated solution gradually declined keeping the same shape and particularly with the maximum at the same position as in the original solution. The situations are exactly the same as in the case of the pure alcoholic solution of eosine[1]. One example is shown in Fig. 1.

The rate of bleaching can be expressed by the same formula presented by Koizumi and Imamura[1],

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=\frac{k}{d}I_0(1-e^{-\alpha cd})\times 10^3 \qquad (1)$$

where c is the concentration of dye in mol./l., I_0 the intensity of illuminating light (mol. cm^{-2} sec^{-1}), α the average or effective molar absorption coefficient and d the thickness of the solution in cm.

Integrating Eq. 1, one obtains

$$\ln(e^{\alpha c_0 d}-1)-\ln(e^{\alpha cd}-1)=10^3 kI_0\alpha t \qquad (2)$$

By using the properly determined value of α, one can obtain k from the inclination of the linear plot of $\ln(e^{\alpha cd}-1)$ against t.

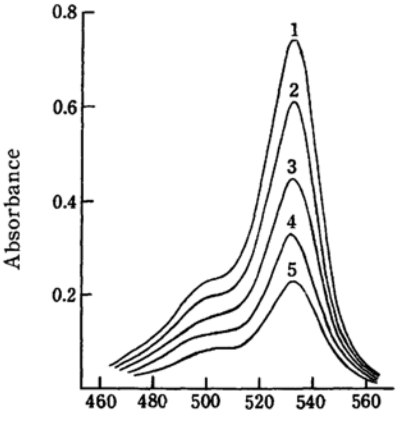

Fig. 1. The absorption spectrum of the irradiated solution of eosin in ethanol with 25% isopentane.

1. initial
2. 10 min.-irradiation
3. 20 min.-irradiation
4. 30 min.-irradiation
5. 40 min.-irradiation

The Effect of the Added Substance.—*a) Isopentane, n-hexane, benzene and COT.* — The addition of these substances does not affect appreciably the absorption spectra of eosin in the visible region nor the fluorescence spectra. In the case of high concentration there is a slight decrease

TABLE I

Isopentane		*n-Hexane*	
Mole fraction	$k\times10^4$	Mole fraction	$k\times10^4$
0.334	1.18	0.309	2.55
0.143	2.53	0.130	2.87
0.100	2.74*	0.0731	3.84
0.0814	4.86	0.0472	4.36
0.0529	4.94	0.0230	3.82
〃	3.80*	0	4.30**
0.0254	5.66		
0	5.82**		

Benzene		*Cyclooctatetraene*	
Mole fraction	$k\times10^4$	Mole fraction $\times10^8$	$k\times10^4$
0.220	1.23	650	0
0.141	1.27	65	0.532
0.0681	1.38	32.2	0.841
0.0334	1.41	8.07	1.22
0.0167	1.67	5.26	1.93
0.00269	2.10	0	1.97
0	1.85		

* Isopentane purified with utmost caution.

** In these two runs, *k*-value in the pure alcoholic solution is markedly different from that of the other runs (including those in Table II). The cause for this is unknown though it may perhaps be due to the pretreatment of alcohol employed. The effect of the added substance will certainly not be affected seriously by this, since it is essentially related with a relative quantity to the reference alcohol.

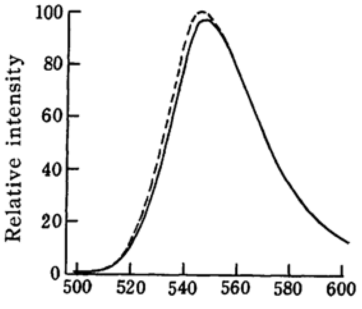

Fig. 2. The effect of addition of isopentane on the fluorescence of eosin.
—— 25% isopentane
------ without isopentane

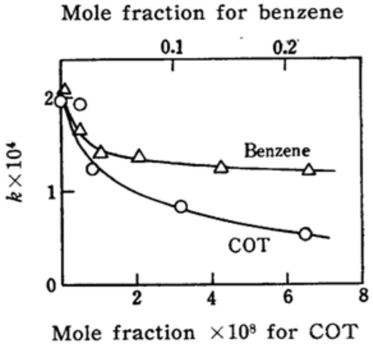

Fig. 3. Plot of k against the concentration of COT and benzene.

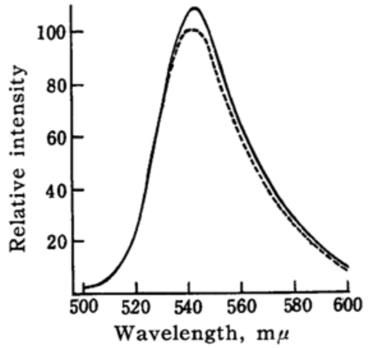

Fig. 4. The effect of addition of cyclohexene on the fluorescence of eosin.
—— 5% cyclohexene
------ pure alcohol

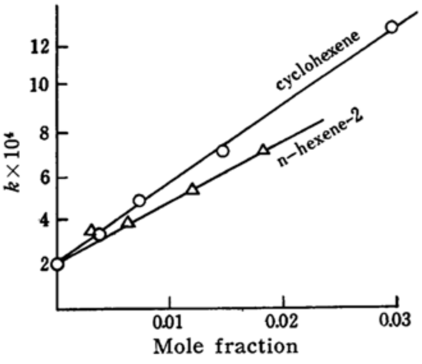

Fig. 5. Plot of k against the concentration of the added substances.

TABLE II

Cyclohexene		*n-Hexene*	
Mole fraction	$k\times10^4$	Mole fraction	$k\times10^4$
0.0295	12.8	0.0181	7.25
0.0146	7.07	0.0119	5.39
0.00726	4.87	0.00593	3.98
0.00362	3.42	0.00296	3.48
0	1.97	0	2.18

in the fluorescence intensity. As an example, the influence of the addition of isopentane upon the fluorescence spectra is shown in Fig. 2. Other substances show more or less similar effects. In Fig. 3 rate constants k's are plotted against the concentration and the data are given in Table I. It is apparent that the above four substances have a retarding effect and among them, COT is by far the most significant inhibitor for the bleaching reaction.

b) *n-Hexene and cyclohexene.* — Neither absorption spectra nor the fluorescence intensity is affected essentially. At higher concentration, the intensity of fluorescence increases slightly as shown in Fig. 4. The values of k are plotted against mole fraction in Fig. 5, which shows that k linearly increases with the concentration of the added substance. The data are given in Table II.

Discussion

The primary processes were already described in the introduction. The fate of DH· and R· is not yet quite certain but the effect of the added substance on the rate is expected to be due to their interference with one of the above three steps i—iii. Since the mechanism would naturally be different for two groups, the retarding substances (isopentane, *n*-hexane, benzene and COT) and the promoting substances (*n*-hexene and cyclohexene), they will be considered separately.

The Retarding Effect.—Since either the absorption spectrum or the intensity of fluorescence is scarcely affected by the addition of the retarding substances, the first two processes in these systems have a rate almost equal to what they have when they are not added. Hence the remaining process iii ought to be eventually retarded by the interference of the added substance. There are two possibilities to be considered for this; the one is the deactivation of D^t and the other is the recovery of D by the removal of hydrogen from DH·. But the latter possibility may safely be ignored from the fact that the above retarders have no tendency to be hydrogenated or scarcely any. Hence the conclusion is that the triplet state of eosin is deprived of its excess energy by the added substance, resulting in the decrease of the bleaching rate. Thus the only process which must be taken into account is the following one which competes with process iii,

$$D^t + Q \rightarrow D + Q \qquad k_Q[Q] \qquad \text{(iv)}$$

where Q represents an added retarder.

Assuming the steady-state concentration for D^* and D^t one can write for k the following:

$$k = \varphi_{S\rightarrow T} \frac{k_a[RH]}{k_a^S[RH] + k_Q[Q]} \tag{3}$$

where $\varphi_{S\rightarrow T}$ gives the fraction of the singlet state going to the excited triplet, k_a is the rate constant for the effective hydrogenating reaction iii, k_a^S, the sum of the rate constants for the genuine reaction and the deactivation of D^t by alcohol. From Fq. 3

$$\frac{1}{k} = \frac{1}{\varphi_{S\rightarrow T}} \frac{k_a^S}{k_a} + \frac{1}{\varphi_{S\rightarrow T}} \frac{k_Q[Q]}{k_a[RH]} \tag{4}$$

Thus, the plot of $1/k$ against $[Q]/[RH]$ gives a straight line as shown in Fig. 6. From the inclination $k_Q/\varphi_{S\rightarrow T}k_a$ and the intersect with the ordinate $\left(\frac{1}{\varphi_{S\rightarrow T}} \frac{k_a^S}{k_a}\right)$, one can easily evaluate a value of k_Q/k_a^S, which gives a measure for the efficiency of the added substances in deactivating D^t. The results are shown in Table III.

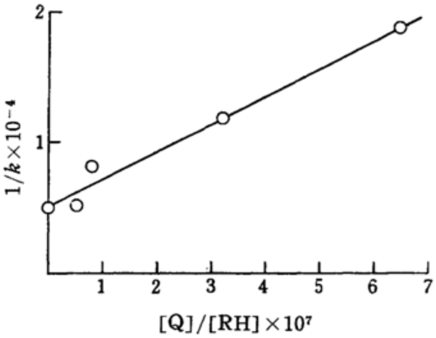

Fig. 6. Plot of $1/k$ against $[Q]/[RH]$ where Q is cyclooctatetraene.

TABLE III. THE KINETIC DATA FOR THE RETARDING SUBSTANCES

Retarder	$k_Q/\varphi_{S\rightarrow T}\cdot k_a$	$k_a^S/\varphi_{S\rightarrow T}\cdot k_a$	k_Q/k_a^S
Isopentane	5.0×10^3	1.7×10^3	2.9
n-Hexane	4.4×10^3	2.4×10^3	1.9
Benzene	3.4×10^4	5.4×10^3	6.3
COT	2.0×10^{10}	5.5×10^3	3.7×10^6
Water			0.053[1]

It is interesting that saturated hydrocarbons which are chemically inactive are rather better deactivators than water. The value for COT is enormously large, the result being consistent with that of Schenck[2]. It may be that the electronic excess energy can effectively be transferred to the vibrational energy of COT which has various modes of bending and torsion due to the nonplanarity of its structure.

The Promoting Effect. — Cyclohexene and *n*-hexene which promote the bleaching rate have a single double bond. These two substances also give scarcely any influence on the absorption spectrum and fluorescence intensity of eosine, so that they do not have much effect upon the rate of processes i and ii. Furthermore in view of their promoting effect, their action on the T-state of the dye is not thought to be an essentially deactivating one. At first sight, the promoting action might be attributed to the same kind of reaction between D and the added substance (P) as that between D^t and alcohol represented by iii. But if so, it is very curious that COT, which is exceedingly unsaturated, shows a quite opposite effect. Moreover, since much of the deactivating process would certainly occur along with the genuine reaction (dehydrogenation of P), the overall rate constant k should be represented as follows:

$$k = \varphi_{S\rightarrow T} \frac{k_a[RH] + k_P[P]}{k_a^S[RH] + k_P^S[P]} \tag{5}$$

where $k_P[P]$ refers to the rate of reaction leading to bleaching and $k_P^S[P]$ is the sum of $k_P[P]$ and that for the deactivating process. Eq. 5 never gives linearity between k and $[P]$ since $k_P^S[P]$ most certainly can not be neglected in view of the rather large value of $k_P[P]$.

Thus, it seems that a plausible interpretation can never be given on the basis of the reaction scheme presented by Koizumi and Imamura[1].

Now, according to the unpublished results for the bleaching reaction of eosine in alcohol by the flash-technique which have been obtained in the authors' laboratory[3], there are two intermediates spectroscopically observed, other than D^t, and these have different durations though in the same order of magnitude (few millisec.).

As another intermediate besides semiquinone, the most probable one would be a certain kind of intermolecular complex between D^t and RH, or alternatively, $(DH\cdot \ldots\ldots R\cdot)$ trapped in the same cage. In either case the introduction of another

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[2] G. O. Schenck and K. Kinkel, *Naturwissenschaften*, 38, 355 (1951).

[3] To be published in the near future.

intermediate of this kind modifies the reaction scheme in such a manner that process iii must now be divided into the following ones,

$$D^t + RH \rightarrow X \qquad (iii')$$

$$X \rightarrow D + RH \qquad (iii'')$$

$$X \rightarrow DH\cdot + R\cdot, \quad k_X \qquad (iii''')$$

where X represents either the complex between D^t and RH, or DH· and R· exisitng in the same cage.

In view of a small quantum yield of photobleaching, a large part of X would perhaps decompose into D and RH (process iii'') resulting only in the dissipation of excess energy of D^t, while a small fraction of X would complete the bleaching reaction by step iii'''. It is of course undecided whether X is some kind of molecular complex or a transient state in which DH· and R· exist in the same cage, but the two alternatives give exactly the same kinetics.

Now, if one modifies the reaction scheme as above, one can interpret quite rationally the promoting action of the added substance. Thus, if the added substance P attacks X in such a manner that it detaches the R-part from the latter, producing a more stable radical PR· and leaving behind a metastable DH·, then the rate of bleaching would be increased. This type of attack may perhaps be so specific that it would not be accompanied with much of the deactivating process. The process can formally be written as follows:

$$X + P \rightarrow DH\cdot + RP\cdot \qquad (v)$$

Taking into account iii', iii'', iii''' and v instead of iii, one can give the expression for k as follows:

$$k = \varphi_{S\rightarrow T}\varphi_{T\rightarrow X}\frac{k_X + k_P[P]}{k_X{}^S + k_P[P]} \qquad (6)$$

where $k_X{}^S$ is the sum of the rate constants for reaction iii'' and iii'''. If one assumes that the action of P on X consists mainly of reaction v and is not of such a nature as to promote reaction iii'' and moreover that $k_X{}^S \gg k_P$ holds as already discussed above, then Eq. 6 is approximately rewritten as

$$k = \varphi\frac{k_X + k_P[P]}{k_X{}^S} \qquad (\varphi = \varphi_{S\rightarrow T}\varphi_{T\rightarrow X}) \qquad (7)$$

which explains the linear relationship between k and [P] experimentally obtained. From the plot of k against [P], one can evaluate the values of k_X/k_P, which are shown in Table IV.

TABLE IV. THE KINETIC DATA FOR THE PROMOTING SUBSTANCES

Promotor	Inclination	Intersection	k_P/k_X
Cyclohexene	21.4×10^{-4}	2.15×10^{-4}	10.0
n-Hexene-2	15.3×10^{-4}	2.50×10^{-4}	6.1

It is to be added that the same relation as Eq. 7 would be obtained, if P attacks D^t in such a specific manner as to produce DH· far more rapidly than to dissipate the excess energy in vain. A relation similar to Eq. 4 would also be obtained for retarding substances if one assumes that X instead of D^t is selectively decomposed by Q into D and RH·. But the assumption is highly improbable that the retarding substances and the promoting substances attack the same one molecular species in a quite different and peculiar fashion. A more natural picture would be that the two groups of the added substances act on different molecular species in a different way as described above. Of course, in order to make the above remark more definitely, it is necessary to study further about the chemical behavior of D^t, X and DH· toward many other substances and especially to use the flash technique.

Summary

The effect of the addition of isopentane, *n*-hexane, benzene, cyclohexene, *n*-hexene and cyclooctatetraene was examined upon the rate of the reductive photobleaching of eosine in the evacuated alcoholic solution. It was found that the saturated hydrocarbons, benzene and COT retard the reaction more or less, COT being most prominent in its effect, while the hydrocarbons with a single double bond (cyclohexene and *n*-hexene) act, contrary to the authors' expectation, as the promotors of the bleaching. The retarding effect of the first group was interpreted to be due to the deactivation of the T-state of dye ion by the added substances, but the promoting action of the second group could not be accounted for rationally on the basis of the above scheme. To fit the present results, therefore, a modified scheme was newly proposed in which a certain kind of molecular complex between D^t and RH is formed prior to DH·.

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