The Photochemical Decomposition of α, α-Diphenyl-β-picrylhydrazyl (DPPH) in Solution. I. A Kinetic Study of the Reaction

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α, α - Diphenyl - β - picrylhydrazyl (DPPH), which was first prepared by Goldschmidt and Renn(1), has been well known to be a stable radical both in the crystalline state and in solution, and it has been submitted to many studies of electron spin resonance. The chemical behavior of this compound, which was studied first by Goldschmidt and Renn, has recently been of interest because the compound serves as a scavenger of the reactive free radicals. Since there is a noticeable color change from violet to light yellow upon the reaction with other free radicals, the rate of the free radical formation can be followed colorimetrically. On the basis of this principle, Bawn and Mellish(2) measured the rate of the thermal decomposition of benzoyl peroxide and 2, 2-azobisisobutyronitrile in several solvents. In these measurements there was a tacit assumption that DPPH reacts quantitatively with a radical to produce stable products.

However, Hammond(3) and most recently Verdin(4) have observed that the reaction of DPPH with the radicals produced in the thermal decomposition of azobisisobutyronitrile is non-stoichiometric and is sensitive to oxygen.

Although as yet the stability of DPPH itself has scarcely come into quesion, some doubt about its stability has been aroused in the present authors, because they have observed that the solution of DPPH fades gradually on standing in diffused light at room temperature, indicating the photochemical decomposition of DPPH.

In order to investigate the mechanism of this phenomenon, an experiment has been undertaken by the present authors. The experiment is divided into two parts, the first being a kinetic investigation of the reaction, and the second consisting of the identification of the products, the determination of the ratio of the amount of the products, and the structure investigation of an unknown reaction product.

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1) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

2) C. H. E. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

3) G. S. Hammond, J. M. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **72**, 3244 (1955).

4) D. Verdin, *Trans. Faraday Soc.*, **56**, 823 (1960).

The first part of the experiment will be described in the present paper, while the second will be treated in a succeeding paper.

Results

Influence of the Wavelength of the Irradiating Light.—As is shown in Fig. 1, DPPH has two absorption maxima, at 520 and 330 mμ. The rates of reaction obtained with different filters are shown in Fig. 2.

Characteristic curves of transmission of the filters used are shown in Fig. 3. As the intensities of the light in the three runs with different filters are not the same, the absolute rates of decomposition cannot be compared with one another; however, since it is observed that the reaction proceeds fairly fast when a Corning (Cd)-filter, which completely cuts the light below 460 mμ, is used, it may be concluded that the decomposition of DPPH can proceed in the light at the first absorption band of DPPH ($\lambda_{\max}=520$ mμ, $\varepsilon=1.23\times10^4$ mol^{-1}cm^{-1}l.). The rest of the kinetic experiments were carried out using a Corning (Cd)-filter.

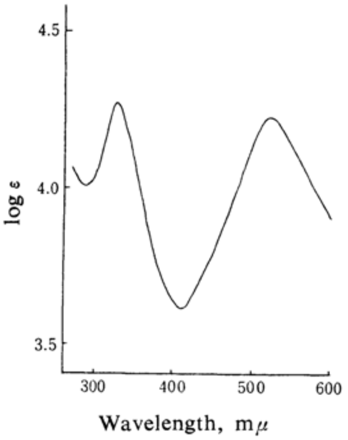

Fig. 1. Absorption spectra of DPPH in carbon tetrachloride.

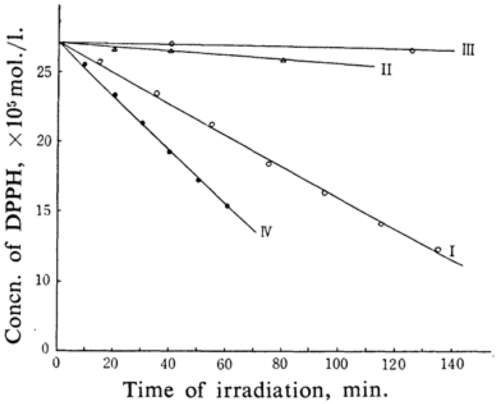

Fig. 2. Rate of decomposition of DPPH at 10°C in carbon tetrachloride with various kinds of filters.
I: Corning (Cd), II: Madzuda VB2, III: Madzuda VG1, IV: without filter. Concentration of DPPH was calculated from the optical density at 520 mμ using $\varepsilon=1.23\times10^4$ l./mol., and assuming $\varepsilon=0$ for the decomposition products.

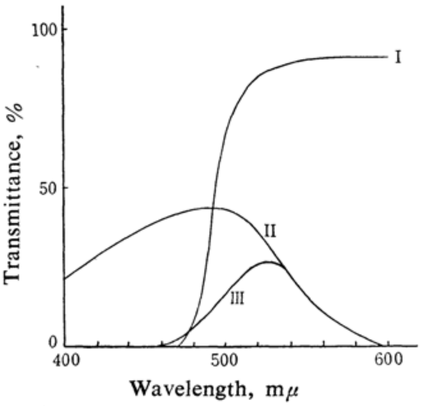

Fig. 3. Characteristic absorption curves of filters.
I: Corning (Cd), II: Madzuda VB2, III: Madzuda VG1.

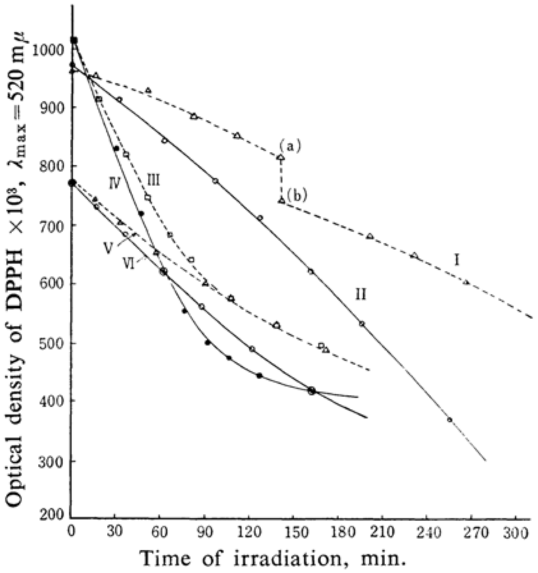

Fig. 4. Rate of decomposition of DPPH at 25°C in various solvents in the absence or in the presence of air.
I: in the absence of air in *n*-heptane, II: in the presence of air in *n*-heptane, (a)—(b) without irradiation for 12 hr. in the dark, showing after effect, III: in the absence of air in benzene, IV: in the presence of air in benzene, V: in the absence of air in carbon tetrachloride, VI: in the presence of air in carbon tetrachloride.

Influence of the Solvent and of Oxygen on the Reaction Rate. — The kinetic features of the decomposition in carbon tetrachloride and in benzene are almost identical, but in *n*-heptane it is different, as is shown in Fig. 4. A remarkable after-effect was observed in *n*-heptane, indicating the interaction of DPPH with the solvent. No further experiment in *n*-heptane was, however, undertaken in the present work. Oxygen slightly accelerates the decomposition, both in carbon tetrachloride and in benzene, but it does not seem to change the main features of the kinetics or of the reaction products, and the nature of its effect is not clear at present.

The Reaction Products. — The recation products were separated and identified by the paper chromatographic method. α, α-Diphenyl-β-picrylhydrazine, α-phenyl-α-(p-nitrophenyl)-β-picrylhydrazine and the third, unknown compound were separated on a paper chromatograph.

The details of the separation of these compounds, the determination of their molar ratio after different periods of reaction time, and the discussion of the structure of the third component will be given in the succeeding paper.

Influence of Light Intensity on the Decomposition Rate. — The experiment was carried out using the carbon tetrachloride solution of DPPH, changing the light intensity with copper nets. The plots of the optical densities of DPPH against the time of irradiation at various intensities of irradiating light are shown in Fig. 5.

The decompsition rate for each run was calculated from the slope of the initial part of the decomposition.

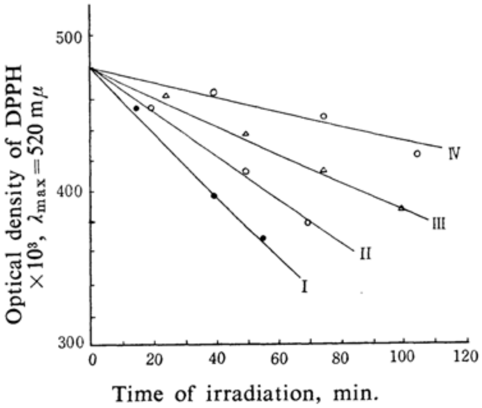

Fig. 5. Plot of the optical density of DPPH solution in carbon tetrachloride against time under the irradiations of various light intensities ranging 100 to 27% at 10°C.
I: 100%, II: 70%, III: 47%, IV: 27%. The initial concentration of DPPH is 3.10×10^{-5} mol./l.

The experiments described here were carried out at a lower concentration (3.5×10^{-5} mol./l.) for convenience in determining the concentration of DPPH in the course of the reaction by photometry in vacuo without dilution*. In such a low concentration of DPPH, the amount of light absorbed could not be approximated as I_0, but it is expressed as $I_0(1-10^{-\epsilon xl})$. However, since the initial concentrations of DPPH in these four runs are identical, the initial rate of the disappearance of DPPH is plotted against the relative intensities of the incident light instead of against the amount of light absorbed in Fig. 6, but this method is considered an approximation sufficient for obtaining a linear relationship between the rate and the amount of light.

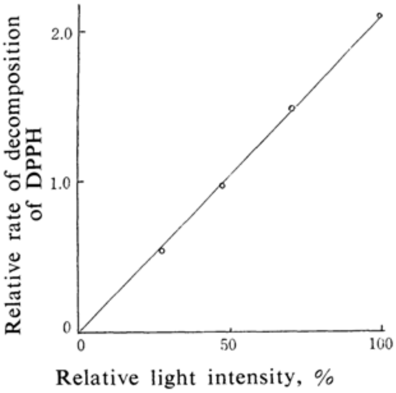

Fig. 6. Relationship between the relative intensity of the irradiating light and the relative rate of the decomposition of DPPH at 10°C.

The extrapolation of the correlation line passes through the origin; this is consistent with the fact that DPPH does not decompose in the dark.

Kinetic Expression of the Experimental Results.—As is shown in Fig. 7, a plot of the concentration against the time hardly shows any departure from linearity in the early stage of the reaction in any run of the experiments in a carbon tetrachloride solution, and the slope might be used as a measure of the observed zero-order rate constant.

This apparent zero-order rate constans was, however, found to be dependent upon the initial concentration of DPPH, and further

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* The experiments of photolysis, except for the four runs shown in Fig. 5, were carried out at relatively high concentrations of DPPH (more than 10^{-4} mol./l. in order to keep the absorption of light close to one hundred per cent throughut course of the reaction except in the very late stage.

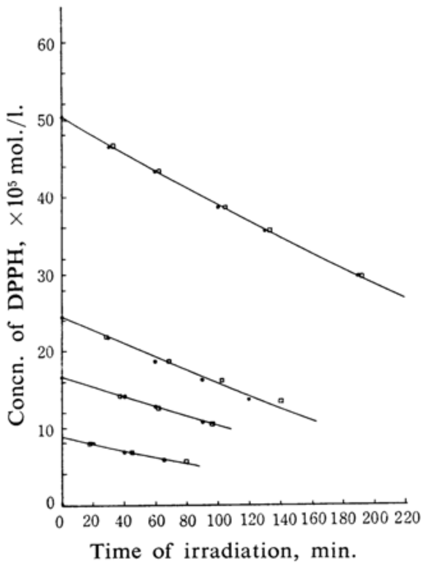

Fig. 7. Rate of decomposition of DPPH at various initial concentrations in carbon tetrachloride at 25°C. Marks of square □ show the calculated values from Eq. 3.

careful inspection of the plots of the concentration of DPPH against the time revealed their slight deviation from linearity, showing that more complicated processes are involved. The initial rate increases with the initial concentration of DPPH up to a limiting value at a higher concentration of 5.0×10^{-4} mol./l. of DPPH.

In order to obtain the appropriate kinetic expression for these experimental results, a plot of $1/(\mathrm{d}x/\mathrm{d}t)$ against $1/x$ is given in Fig. 8, which shows a fairly good linear relationship. Taking this result into consideration, the following empirical rate equation is introduced;

$$-\mathrm{d}x/\mathrm{d}t=KI_{\mathrm{a}}x/(x+\alpha) \qquad (1)$$

or

$$-1/(\mathrm{d}x/\mathrm{d}t)=1/KI_{\mathrm{a}}+(\alpha/KI_{\mathrm{a}})/x \qquad (1')$$

where K and α are constants. I_{a}, the average rate of light absorption is kept constant through the each series of experiments, though there is some variation between the different series of experiments. The determination of the amount of light absorbed has not been carried out, so that the quantum yield of this experiment is not known at present. As is shown in Fig. 7, the initial concentration of DPPH ranged from 10^{-4} to 5×10^{-4} mol./l., insuring a nearly complete absorption of light. In Table I, the values of α/KI_{a} and $1/KI_{\mathrm{a}}$ as slope and as its intercept in the ordinate axis, calculated by the least square method from each run of I, II, III, IV in Fig. 7, are given. In addition the values of the slope and the intercept obtained by plotting $1/(\mathrm{d}x/\mathrm{d}t)_{t=0}$ against $1/x$ in the four runs in Fig. 7 are given in the last column.

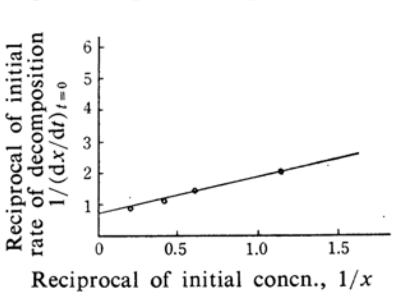

Fig. 8. Relationship between the reciprocal of initial concentration $(1/x)$ and that of the initial rate of decomposition $(1/(\mathrm{d}x/\mathrm{d}t)_{t=0})$ obtained from Fig. 7.

TABLE I

	I	II	III	IV	
$\alpha/KI_a\times10^{-2}$	1.63	0.19	0.69	0.61	1.41
$1/KI_a\times10^{-5}$	4.88	10.21	10.10	14.05	5.65

The values of α and KI_{a} calculated from the figures in the last column are 1.8×10^{-4} mol./l. and 2.5×10^{-6} mol./l. min. respectively*.

As may be seen, the variations in the values of the slope and of the intercept in four runs seem to be fairly large, but the following procedure of the recalculation of x at the various intervals of the reaction time, using the values in the last column, shows that these values are actually within the range of experimental error.

Integrating Eq. 1, Eq. 2 is obtained,

$$(x_0-x)+2.303\ \alpha\log(x_0/x)=KI_{\mathrm{a}}t \qquad (2)$$

where x_0 is the initial concentration of DPPH. Using $\alpha=1.8\times10^{-4}$ mol./l. and $KI_{\mathrm{a}}=2.5\times10^{-6}$ mol./l. min., a relation between x and t was obtained. The calculated values of x from Eq. 2 at various time intervals are plotted in Fig. 7, with a square mark showing that the agreement between observed and calculated values is satisfactory.

The Influence of Temperature on the Decomposition Rate.—The rate of the decomposition of DPPH in carbon tetrachloride was measured at 10, 30 and 50°C. The results are shown in Fig. 9.

The increase in the reaction rate with the temperature indicates that some temperature-dependent processes are involved in the reaction. The plots of $1/(\mathrm{d}x/\mathrm{d}t)$ against $1/x$ for the curves in Fig. 9 are shown in Fig. 10; KI_{a} and α in Eq. 1′ at 10, 30 and 50°C were determined from each line. From the values of the

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* The probable ranges of KI_{a} and α with 95% reliability are $3.7\times10^{-6}>KI_{\mathrm{a}}>1.2\times10^{-6}$ and $6.8\times10^{-4}>\alpha>1.2\times10^{-4}$ respectively.

usual Arrhenius plot, the activation energy and frequency factor were evaluated. The results are listed in Table II.

TABLE II. KI_a AND α AT 10, 30 AND 50°C, AND THE CALCULATED ACTIVATION ENERGY (E) AND FREQUENCY FACTORS (A)

	10°C	30°C	50°C	ΔE	A
KI_a	1.27×10^{-6} a)	2.00×10^{-6}	2.93×10^{-6}	3.8×10^{3} c)	1.2×10^{-3}
α	0.34×10^{-4} b)	0.58×10^{-4}	0.84×10^{-4}	4.1×10^{3}	5.2×10^{-2}

a) mol./l. min.
b) mol./l.
c) cal.

In addition to these experiments, the induction period and the after effect were investigated, but neither of them was noticeable in the carbon tetrachloride solution, as is shown in Fig. 9.

Discussion of the Reaction Mechanism

The kinetic data obtained above are not enough to establish a unique and overall reaction mechanism, but some possible mechanisms will be discussed. As in most photochemical reactions, the process of this reaction may consist of excitation, quenching (deactivation), and chemical reaction. No fluorescence of DPPH in solution is observed. The deactivation of excited DPPH may proceed by solvent or by another DPPH. As the primary process of chemical reaction, the three different mechanisms, (I) the spontaneous decomposition of excited DPPH, (II) the bimolecular decomposition of the excited DPPH with normal DPPH, and (II′) the complex formation of excited DPPH with other molecules of DPPH and the successive decomposition of the complex, are considered, and the expression of the rate of disappearance of DPPH in terms of the concentration of DPPH is derived from each mechanism. The succeeding process of the reaction seems to be complicated, but it may be reasonably assumed that it does not modify the main character of the kinetic expression of the rate of disappearance of DPPH, because the relative ratio of the products is almost constant throughout the course of the reaction, as the succeeding paper will show.

Mechanism I

$$\begin{array}{lll}
\mathrm{D}+h\nu & \longrightarrow \mathrm{D}^* & I_a \\
\mathrm{D}^*(+\text{Solvent}) & \longrightarrow \mathrm{D} & k_1 \ \text{(I–1)} \\
\mathrm{D}^*+\mathrm{D} & \longrightarrow 2\mathrm{D} & k_2 \ \text{(I–2)} \\
\mathrm{D}^* & \longrightarrow \mathrm{A}+\mathrm{B} & k_3 \ \text{(I–3)}
\end{array}$$

$$-\mathrm{d}x/\mathrm{d}t=I_a k_3/(k_1+k_3+xk_2) \tag{3}$$

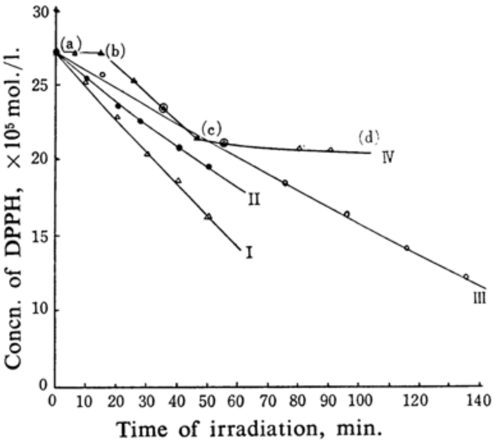

Fig. 9. Influence of temperature on the decomposition rate of DPPH in carbon tetrachloride measured at 520 mμ.
I, IV: 50°C, II: 30°C, III: 10°C, (a)—(b): in the dark, (b)—(c): light on, (c)—(d): light off.

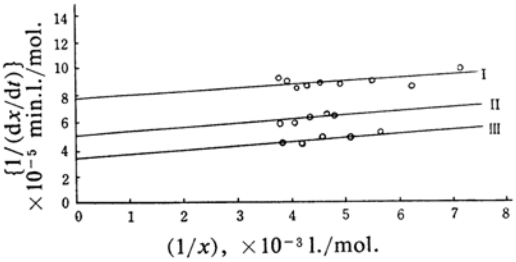

Fig. 10. Plot of $1/(\mathrm{d}x/\mathrm{d}t)$ against $1/x$ in Eq. 1′.
I: 10°C, II: 30°C and III: 50°C

Mechanism II

$$\begin{array}{lll}
\mathrm{D}+h\nu & \longrightarrow \mathrm{D}^* & I_a \\
\mathrm{D}^*(+\text{Solvent}) & \longrightarrow \mathrm{D} & k_1 \ \text{(II–1)} \\
\mathrm{D}^*+\mathrm{D} & \longrightarrow 2\mathrm{D} & k_3 \ \text{(II–3)} \\
\mathrm{D}^*+\mathrm{D} & \longrightarrow \mathrm{A}+\mathrm{B} & k_4 \ \text{(II–4)}
\end{array}$$

$$-\mathrm{d}x/\mathrm{d}t=2I_a k_4 x/\{k_1+(k_3+k_4)x\} \tag{4}$$

Mechanism II′

$$\begin{array}{lll}
\mathrm{D}+h\nu & \longrightarrow \mathrm{D}^* & I_a \\
\mathrm{D}^*(+\text{Solvent}) & \longrightarrow \mathrm{D} & k_{1'} \ \text{(II′–1)} \\
\mathrm{D}^*+\mathrm{D} & \longrightarrow \mathrm{D}^*\mathrm{D} & k_{2'} \ \text{(II′–2)} \\
\mathrm{D}^*\mathrm{D}(+\text{Solvent}) & \longrightarrow 2\mathrm{D} & k_{3'} \ \text{(II′–3)} \\
\mathrm{D}^*\mathrm{D} & \longrightarrow \mathrm{A}+\mathrm{B} & k_{4'} \ \text{(II′–4)}
\end{array}$$

$$-\mathrm{d}x/\mathrm{d}t =2I_a\{xk_{2'}/(xk_{2'}+k_{1'})\}\{k_{4'}/(k_{3'}+k_{4'})\} \tag{5}$$

where D is a molecule of DPPH, D* is an excited DPPH. The structures of A and B are not known, but it may be reasonably assumed that they are free radicals or reactive molecules, such as NO_2. Mechanism 1, which assumes the spontaneous decomposition of excited DPPH, does not agree with the experimental results, because the rate expression derived from this mechanism requires a decrease in the rate with a decrease in the concentration of DPPH. The second and third mechanisms have similar kinetic characteristics of rate expression; that is, the rate increases with the concentration. Both satisfy the requirement of kinetic expression (1)*, making it impossible to choose a mechanism on the basis of the present experimental results only. These two mechanisms differ in the point that the complex has some definable lifetime in the latter. The authors are slightly in favor of the latter mechanism, considering similar experimental evidence. Förster and Kasper5) presumed a complex formation of excited pyrene with normal pyrene from their observation of fluorescence. It is likely that excited DPPH forms a complex with normal DPPH, for many aromatic polynitro compounds tend to form a complex, even at the ground state. If the flash photolysis technique could be applied to the present case, it would be possible to determine whether or not a dimer complex of DPPH is present. According to the proposed reaction mechanisms II and II′, the experimental constants, KI_a, in Eq. 1 are related to the rate constants of Eqs. 4 and 5.

According to mechanism II,

$$K=2k_4/(k_3+k_4)$$

and $$\alpha=k_1/(k_3+k_4)$$

Considering the fact that K increases with the temperature, we might assume that $k_3\gg k_4$, since otherwise K would actually be independent of the reaction temperature. Assuming $k_3\gg k_4$, the relation

$$K\doteqdot 2k_4/k_3$$

would be derived; this also gives an interpretation of the experimental activation energy:

$$E_4-E_3\doteqdot E_K=3.8\ \text{kcal./mol.}$$

and $$2I_aA_4/A_3\doteqdot A_{KI_a}=1.2\times10^{-3}$$

It is reasonable that reaction 4 has a larger activation energy than reaction II-3, because the latter is a simple deactivation process.

A similar treatment may be applied to the temperature dependence of α. Assuming $k_3\gg k_4$, we might also derive the relation

$$\alpha\doteqdot k_1/k_3$$

$$E_1-E_3\doteqdot E_\alpha=4.1\ \text{kcal./mol.}$$

and $$A_1/A_3=A_\alpha=5.2\times10^{-2}\ \text{l./mol.*}$$

The finding that reaction II-1 has an appreciable amount of activation energy is not well understood, since the reaction is a simple deactivation process of an excited DPPH with a solvent.

Since the value of I_a is not known, no further discussion of the frequency term will be attempted at this stage.

In mechanism II′, a similar argument may be applied, giving the relations:

$$E_K=E_{4'}-E_{3'},\quad A_{KI_a}=2I_aA_{4'}/A_{3'}$$

and $$E_\alpha=E_{1'}-E_{2'},\quad A_\alpha=A_{1'}/A_{2'}$$

Experimental

Material.—DPPH was prepared by the method of Porier6), recrystallized from a chloroform-ether mixture (1 : 1 by volume), and dried in vacuo at 80°C for more than 10 hr.7) The solvents used were purified by ordinary methods8).

Procedure.—A solution of DPPH was irradiated in a thermostat with a light of a constant intensity, and after various periods of time the concentration of DPPH was determined with a spectrophotometer at its maximum absorption ($\lambda_{\max}=520\ \text{m}\mu$). The light source was a tungsten lamp (100 V. 150 W), and variations of the source voltage were compensated for by a manual setting of a transformer. The range of wavelengths of the irradiating light was varied by choosing a proper filter.

The light intensity was varied with copper nets of several different meshes, blackened with ammonium sulfide.

In order to study the effect of oxygen on the photolysis of DPPH, the experiments were carried out both in the presence of air and in the absence of air. The solution in the latter experiment was prepared by the following procedure, using the apparatus shown in Fig. 11.

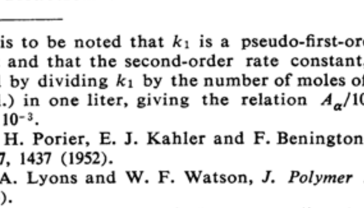

Fig. 11. Shematic diagram of the apparatus of preparing the sample in vacuo.
C: Reaction cell

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* For convenince in comparing reaction mechanisms II and II′, the rate constants are numbered k_1, k_3 and k_4 in the reaction II instead of k_1, k_2 and k_3. The following relation is easily derived by a comparison of the two mechanisms: $k_3=k_{2'}k_{3'}/(k_{3'}+k_{4'})$ and $k_4=k_{2'}k_{4'}/(k_{3'}+k_{4'})$.

5) T. Förster and K. Kasper, *Z. Elektrochem.*, **59**, 976 (1955).

* It is to be noted that k_1 is a pseudo-first-order rate constant and that the second-order rate constant, k_1^*, is obtained by dividing k_1 by the number of moles of solvent (10.2 mol.) in one liter, giving the relation $A_\alpha/10.2=A_1^*/A_3=5.1\times10^{-3}$.

6) R. H. Porier, E. J. Kahler and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952).

7) J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **18**, 141 (1955).

8) A. Weisberger and E. S. Proskauer, "Technique of Organic Chemistry", Vol. VII, Interscience Publishers, Inc., New York (1955).

DPPH was placed in B, and a purified solvent was distilled into B from A after degassing. Then A was sealed at (a), a part of the solution in B was poured into C, and B was sealed at (b). The rest of the solution in B was used for the comparative experiments in the presence of air. The solution in C was degassed on a high vacuum line with several repetitions of freezing in liquid nitrogen (−196°C) and melting to remove the residual gas. A reaction cell C was then sealed at (c), and the concentration of the solution was determined photometrically, without contact of the solution with air.

Summary

Studies of the photochemical decomposition of DPPH in solution have been made by the kinetic method.

1) The decomposition proceeds by means of the light in the region of the first absorption band of DPPH ($\lambda_{\max}=520\,\mathrm{m}\mu$), and the decomposition rate has a linear dependence on the amount of light absorbed.

2) A rate expression fitting the kinetic experiment has been obtained, and this expression has been compared with the rate expession derived on the basis of the possible reaction mechanism, which includes the process of the reaction of an excited DPPH with another, normal DPPH.

3) An increase in the rate with the reaction temperature has been observed in the temperature range 10∼50°C, and the two constants determined in the experiment have been related to the rate constants of the elementary processes in the proposed reaction mechanism.

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