

琉球大学学術リポジトリ

Kinetic Studies of Photochemical Addition of Iodine to Cyclohexene

メタデータ	言語: 出版者: 琉球大学理工学部 公開日: 2012-02-28 キーワード (Ja): キーワード (En): 作成者: Kinjo, Akio, Uchihara, Toshio, Toma, Shitoku, Kinjo, Yoshiaki, 金城, 昭夫, 宇地原, 敏夫, 当間, 嗣徳, 金城, 嘉昭 メールアドレス: 所属:
URL	http://hdl.handle.net/20.500.12000/23508

Kinetic Studies of Photochemical Addition of Iodine to Cyclohexene

Akio KINJO*, Toshio UCHIHARA*,
Shitoku TOMA**, and Yoshiaki KINJO***

Summary

Several mechanisms have been proposed for the addition of iodine to double bond. We have studied kinetics of the addition of iodine to cyclohexene under the irradiation of the sample solution at the iodine absorption band in visible region and at the charge transfer band in ultraviolet region of the electron donor acceptor complex between iodine and cyclohexene. The apparent order of the reaction was $3/2$ and 0.64 with respect to iodine and cyclohexene, respectively, when the sample solution was illuminated with visible light. We observed an evidence to suggest that the complex participates in the reaction from the study of temperature effect on the kinetics. However, kinetic data could not be fully explained by the complex participation mechanism alone. The experimental results seem to be explained by co-occurrence of radical chain mechanism and complex participation mechanism in parallel.

In case of the illumination of the solution with 315 nm light, the apparent order of the reaction was 2 and 0.64 with respect to iodine and cyclohexene, respectively. The electron donor acceptor complex may produce radicals upon the charge transfer absorption, and the subsequent reaction seems to proceed in the same way as illuminated with visible light because the apparent reaction order with respect to cyclohexene is same.

1. Introduction

Iodine does not add to alkene in nonpolar solvent at dark place^{1, 2)}, but the reaction takes place when the solution is illuminated with visible light which causes dissociation of iodine molecule into atomic iodine³⁾. Mechanistic studies have been done for the reaction. Skell and Pavlis⁴⁾ proposed a radical chain mechanism, proceeding via a bridged radical intermediate on the basis of their study of the addition-elimination cycle of iodine to *cis*- and *trans*-2-butenes. Benson, et al.⁵⁾, suggested the iodine atom catalyzed single step addition of iodine molecule to double bond from their study of the iodine atom catalyzed elimination of iodine molecule from vicinal diiodides.

Received April 30, 1974.

* Dept. of Chem., Sci. and Eng. Div., Univ. of the Ryukyus

** General Education Div., Univ. of the Ryukyus

*** Education Div., Univ. of the Ryukyus

Recently, Ayres, et al.⁶⁾, made kinetic studies of the addition of iodine to several pentene isomers in carbon tetrachloride at 25°C under the ordinary room illumination by means of the activity measurement of tagged iodine. On the basis of their experimental results of the reaction order and the positive correlation between the rate constants and the complexing abilities of the pentene isomers, they proposed a mechanism in which the electron donor acceptor complex (EDA complex) of iodine and pentene participates in the rate determining step. However, their observed correlation between the rate constant and the equilibrium constant of the EDA complex may not be a direct evidence for the actual participation of the complex in the rate determining step if the reactivities and the complexing abilities of these pentene isomers are proportional.

So far, the reaction has been studied by illuminating the solution with light in the region of absorption of iodine (visible light). No informations are available for the reaction when the solution was irradiated at the charge transfer band (CT band) in ultraviolet region.

We have made kinetic studies for the iodine-cyclohexene system under the various conditions such as different temperatures and solvents to obtain more informations about the reaction by exposing the solution to visible and ultraviolet light.

2. Experimentals

(1) Materials

Commercial iodine of reagent grade was sublimed first with calcium oxide and potassium iodide, and sublimed again under nitrogen atmosphere for purification following the method in a literature.⁷⁾ It was kept in a desicator until use. Cyclohexane, n-hexane, n-heptane and carbon tetrachloride of reagent grade were used as solvents after purifying by the method described elsewhere.^{8, 9)} Cyclohexene employed in this study was reagent grade material of Ishizu Pharmaceutical Co.. It was used without further purification.

(2) Apparatus

When the kinetic experiments were performed by illuminating the solution with visible light, an ordinary 100-watt tungsten bulb was used as the light source. A filter of one cm glass cell containing 0.01 mol/l ethanol solution of 8-hydroxyquinoline was placed between the light source and the reaction vessel to remove ultraviolet light completely. The effectiveness of the filter was certified. For this test, the filter and the light source were placed in front of input slit of Hitachi EPS-3T recording spectrophotometer, and the energy was measured as a function of wavelength. The stability and reproducibility of the light source was also confirmed for several switching on-off actions. The reaction vessel was a glass cell with a thickness of 0.2 cm, which was placed in a constant temperature bath with glass wall for the regulation of the reaction temperature.

A thermostated high pressure mercury lamp of Riko Kagaku Sangyo Co., was

used as a light source when the reaction was studied by exposing the solution to light in the CT region. A combination of filters consisting of 2.5 cm thick aqueous cobaltous sulfate solution (60 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml water) and 0.5 cm thick aqueous potassium chromate solution (0.4 g $\text{K}_2\text{CrO}_4/1$) was employed to isolate 315 nm light. The effectiveness of the filter, the stability and reproducibility of the light source were also checked. The intensity of light of 315 nm gradually increased when the lamp was turned on, but became stable and reproducible after eight minutes elapsed. Therefore, the kinetic experiments were carried out by starting to illuminate the sample solution ten minutes after the lamp was turned on. The reaction vessel for the CT band irradiation was a quartz cell of 0.5 cm path length with a glass stopper. The cell was placed in a dark box with a shutter. The box had also a device to keep the inside temperature at a desired value by the circulation of the thermostated water.

In both cases the apparatus were kept at fixed positions to make experimental conditions same throughout all experiments.

(3) Kinetic Experiments

All the solutions were prepared under a red lamp of an ordinary dark room, which was confirmed not to cause the reaction in our previous study.²⁾ An aliquot of the sample solution was placed in the reaction cell and exposed to the light for a desired length of time. Then the sample was taken for assay. The reaction was followed by measuring the absorbance of iodine. The measurement of the absorbance was made at 25°C throughout the experiments. The concentration of the total iodine (complexed and uncomplexed iodine) was read from the calibration curve. The experimental data were treated using the total iodine concentration. The identification of the final product was not pursued when the reaction was initiated with visible light because it was already confirmed as the addition product by the other investigators.⁶⁾

In our preliminary experiment it was found that the reaction was faster when oxygen was removed from the solution with nitrogen than otherwise, but the order of the reaction was same in both cases. So all experiments were run without removing oxygen.

3. Results and Discussion

(1) Reaction with Visible Light

Several kinetic runs were made for the addition of iodine to cyclohexene with cyclohexene in excess. The velocity of the reaction was followed only in early stage of the reaction since the velocity became gradually leveling off later. This phenomena are supposed due to the reverse reaction.¹⁰⁾ From the slope of a double logarithmic plot of velocity vs. the concentration of I_2 , the reaction was found to be 3/2 order with respect to I_2 as mentioned by Ayres, et al..

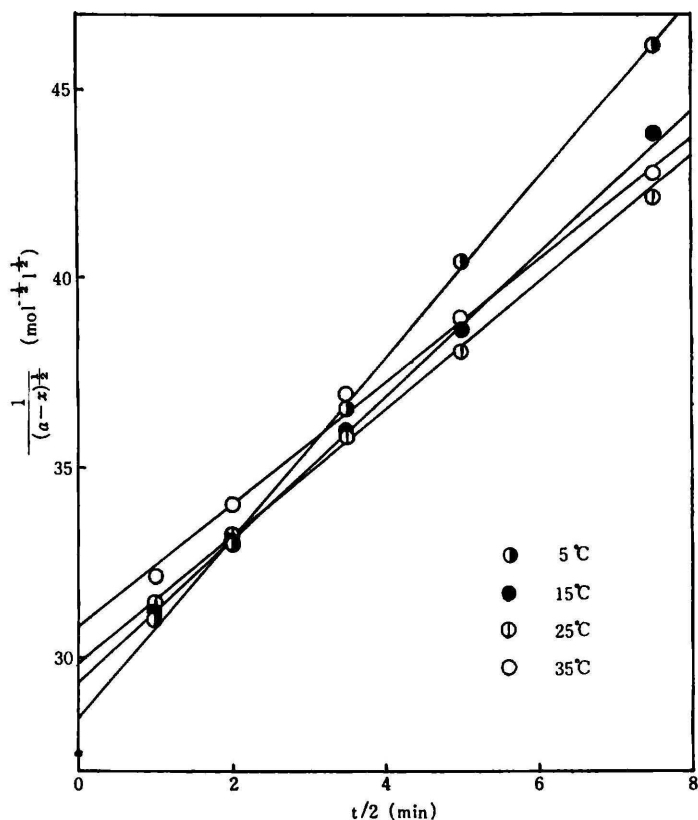


Fig. 1. Plot of the 3/2 order rate equation for the addition of iodine to cyclohexene in n-hexane with visible light

Since excess cyclohexene was used in the experiments, the rate of disappearance of iodine with respect to the concentration of iodine at time t can be expressed by equation (1) according to Ayres, et al..

$$-d(I_2)/dt = k(I_2)^{3/2} \quad (1)$$

Integration of equation (1) yields the following expression

$$1/(a-x)^{1/2} = kt/2 + 1/a^{1/2} \quad (2)$$

where a is the concentration of iodine at zero time and $(a-x)$ the concentration of iodine at time t . The rate constant k is determined from the slope of the straight line obtained by plotting the values of $1/(a-x)^{1/2}$ vs. $t/2$.

Table 1. Temperature effect on rate constant k for the addition of iodine to cyclohexene with visible light and equilibrium constant K_c for EDA complex in n-hexane

Temp °C	(cyclohexene) mol/l	(I ₂) mol/l	k mol ^{-3/2} l ^{1/2} min ⁻¹	K_c^* mol ⁻¹ l
5	0.107	1.16×10^{-3}	2.31	1.89
15	0.107	1.16×10^{-3}	1.88	1.73
25	0.107	1.16×10^{-3}	1.69	1.53
35	0.107	1.16×10^{-3}	1.61	1.35

* Taken from ref. 2)

First, the effect of temperature on the reaction was studied. Kinetic runs were made for the addition of iodine to cyclohexene in n-hexane at various temperatures with keeping the concentrations of cyclohexene and iodine at constant values. A plot of $1/(a-x)^{1/2}$ vs. $t/2$ for the data obtained is shown in Fig. 1. The rate constants obtained from the slopes are presented in Table 1 together with the equilibrium constants of the EDA complex between iodine and cyclohexene in n-hexane at respective temperatures for comparison.

Next, kinetic experiments were carried out for the addition of iodine to cyclohexene at 25°C with changing solvent to see the effect of solvent on the reaction kinetics. The data were plotted for the 3/2 order rate equation as before. Straight lines were obtained in all solvents used. From the slopes the 3/2 order rate constants were determined as usual. The resultant rate constants are given in Table 2. The table also includes the equilibrium constants of the EDA complex in respective solvent.

Finally, studies were made to obtain informations on the order of the reaction with respect to cyclohexene. Kinetic runs were made for iodine-cyclohexene system in n-hexane solvent at 25°C with changing the concentration of cyclohexene. The concentration of cyclohexene was in excess also in this study. The resultant rate constants are presented in Table 3.

If the order of the reaction with respect to cyclohexene is simple, the rate constant obtained in the previous paragraph can be expressed by

$$k = k' (\text{cyclohexene})^n \quad (3)$$

Taking logarithm of equation (3) yields the following expression

$$\log k = \log k' + n \log (\text{cyclohexene}) \quad (4)$$

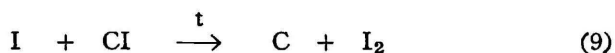
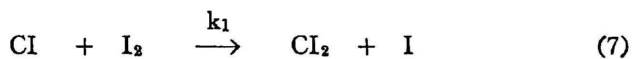
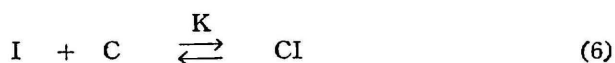
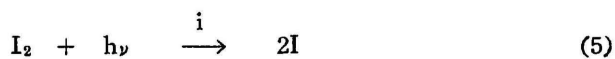
where (cyclohexene) refers to the concentration of cyclohexene, n order of the reaction with respect to cyclohexene and k' the rate constant in the complete form of the rate equation. A plot of $\log k$ vs. $\log (\text{cyclohexene})$ should give a straight line, the slope being the order of the reaction with respect to cyclohexene. The data of Table 3 were plotted in Fig. 2, giving a straight line. From the slope the apparent order of the reaction was determined to be 0.64 which suggests the reaction being complicated.

Table 2. Solvent effect on rate constant k for the addition of iodine to cyclohexene with visible light and equilibrium constant K_c for EDA complex at 25°C

Solvent	(cyclohexene) mol/l	(I ₂) mol/l	k mol ^{-1/2} l ^{1/2} min ⁻¹	K_c mol ⁻¹ l
Cyclohexane	0.107	9.25×10^{-4}	1.55	3.09
Carbon tetrachloride	0.107	9.73×10^{-4}	1.57	1.60
n-Hexane	0.107	1.16×10^{-3}	1.68	1.53*
n-Heptane	0.107	1.21×10^{-3}	1.59	1.79

* Taken from ref. 2). Other K_c values were determined, in this study, by the method described in ref. 2).

According to the radical chain mechanism of Skell and Pavlis, the reaction may be expressed in a series of the following reactions



where i and t refer to the initiation and termination step, C cyclohexene, CI bridged radical intermediate and CI_2 the final addition product. Reaction (7) is also expressed as the reversible one like (6) in their mechanism. However, if reaction (7) is rate determining step, it may be expressed by one directional arrow in the early stage of the reaction investigated in the present study. If reaction (6) is rate determining step, the order of the reaction with respect to iodine should be 1/2 order, being different

from the experimental result. In order to be 3/2 order with respect to iodine, the rate determining step must be reaction (7). And further, the equilibrium of reaction (5) is supposed to be established instantaneously because iodine atom is produced immediately when the sample solution is illuminated. Then the rate of appearance of the product is expressed by

$$d(\text{Cl}_2)/dt = k_1(\text{Cl})(\text{I}_2) \quad (10)$$

Since the concentration of iodine was low and the reaction cell was thin in the present study, $(\text{I}) = k_0(\text{I}_2)^{1/2}$ holds⁶⁾ where k_0 is a constant including quantum yield of dissociation of iodine molecule, rate constant for the recombination of iodine atoms and etc.. Using this relation for reaction (6), the concentration of the radical intermediate is given by the following expression

$$(\text{Cl}) = Kk_0(\text{C})(\text{I}_2)^{1/2} \quad (11)$$

Substitution of (Cl) from equation (11) for that of equation (10) yields the following rate expression

$$d(\text{Cl}_2)/dt = k'(\text{C})(\text{I}_2)^{3/2} \quad (12)$$

where $k' = k_1Kk_0$. Therefore, this mechanism should give the first order with respect to cyclohexene, but our result is 0.64 far from unity. The mechanism of iodine atom catalyzed single step addition should also give the first order with respect to cyclohexene.

Table 3. The 3/2 order rate constant for the addition of iodine to cyclohexene in n-hexane at 25°C with visible light

Run	(cyclohexene) mol/l	(I ₂) mol/l	k mol ^{-1/2} l ^{1/2} min ⁻¹
1	4.05 × 10 ⁻²	1.11 × 10 ⁻³	1.15
2	6.02 × 10 ⁻²	1.11 × 10 ⁻³	1.39
3	8.10 × 10 ⁻²	1.11 × 10 ⁻³	1.65
4	1.21 × 10 ⁻¹	1.11 × 10 ⁻³	2.14
5	1.62 × 10 ⁻¹	1.11 × 10 ⁻³	2.58
6	2.41 × 10 ⁻¹	1.11 × 10 ⁻³	3.44
7	3.21 × 10 ⁻¹	1.11 × 10 ⁻³	4.03

As seen from Table 1, a good correlation was observed between the apparent rate constant k and the equilibrium constant K_c of the EDA complex in our study of the effect of the temperature on the reaction kinetics in *n*-hexane solvent. As the temperature becomes lower, both rate constant and equilibrium constant become larger. The rate constant k is affected by the steady concentration of iodine atom which is, in turn, influenced by the solvent viscosity because the disappearance of iodine atom due to the recombination of two iodine atoms is diffusion controlled process.¹¹⁾ So it appears at first glance that the larger rate constant at lower temperature may be due to the larger concentration of iodine atom because the recombination reaction is slower at lower temperature. However, the steady concentration of iodine atom is not determined only by the velocity of recombination of iodine atoms. According to Rosman and Noyes¹²⁾, the steady concentration of iodine atom is expressed by

$$(I) = (q\phi/k_r)^{1/2} \quad (13)$$

where q is the rate of absorption of light, ϕ quantum yield for producing iodine atoms ($I_2 + h\nu \rightarrow 2I$) and k_r rate constant for the recombination reaction of iodine atoms ($2I \rightarrow I_2$). They observed that both k_r and ϕ increase with temperature and the ratio ϕ/k_r also increases slightly with temperature in *n*-hexane. It means that the steady

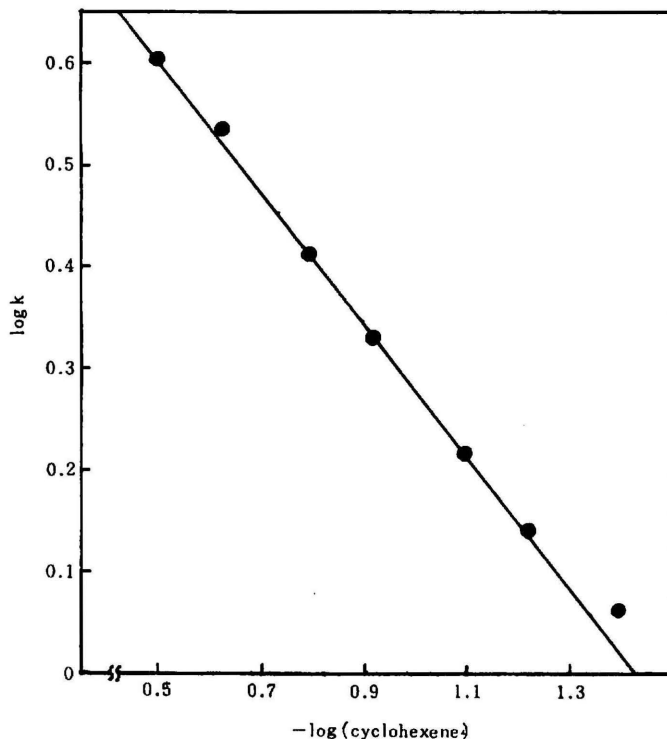


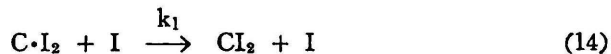
Fig. 2. Double logarithmic plot of $\log k$ vs. $-\log (\text{cyclohexene})$ for the addition of iodine to cyclohexene in *n*-hexane at 25°C with visible light

concentration of iodine atom slightly increases with temperature in our experiments since the light source was kept constant. Then, if the concentration of iodine atom alone is taken into account, the rate constant for the addition of iodine to cyclohexene would increase with temperature, but our observation was contrary.

Further, in our preliminary experiment we observed that the velocity of the reaction became faster when oxygen was expelled from the solution by nitrogen as mentioned previously. Oxygen dissolves into n-hexane more at lower temperature. It is supposed that if oxygen is removed from the solution, the addition reaction becomes even faster at lower temperature. As a conclusion, the observed correlation between the rate constant and the equilibrium constant strongly suggests that the EDA complex participates in the rate determining step.

In our study of the solvent effect on the reaction kinetics (Table 2), we could not obtain the useful informations for the relation between the rate constant and the equilibrium constant. It is supposed due to the facts that dissociation and recombination velocities of iodine change from solvent to solvent and so the steady concentration of iodine atom.

According to the EDA complex participation mechanism proposed by Ayres, et al., the rate determining step of the reaction is the one containing the EDA complex,



where $C \cdot I_2$ is the EDA complex and CI_2 the addition product. They derived, for the 3/2 order rate constant k , the following expression

$$(C)/k = 1/k_1 K_c + (C)/k_1 \quad (15)$$

where k_1 is the rate constant for the rate determining step (14), K_c equilibrium constant for the iodine-cyclohexene EDA complex and (C) concentration of cyclohexene. According to equation (15) a plot of $(C)/k$ vs. (C) would give a straight line. Our data of Table 3 were used for the plot and the result is presented in Fig. 3. We did not obtain a straight line.

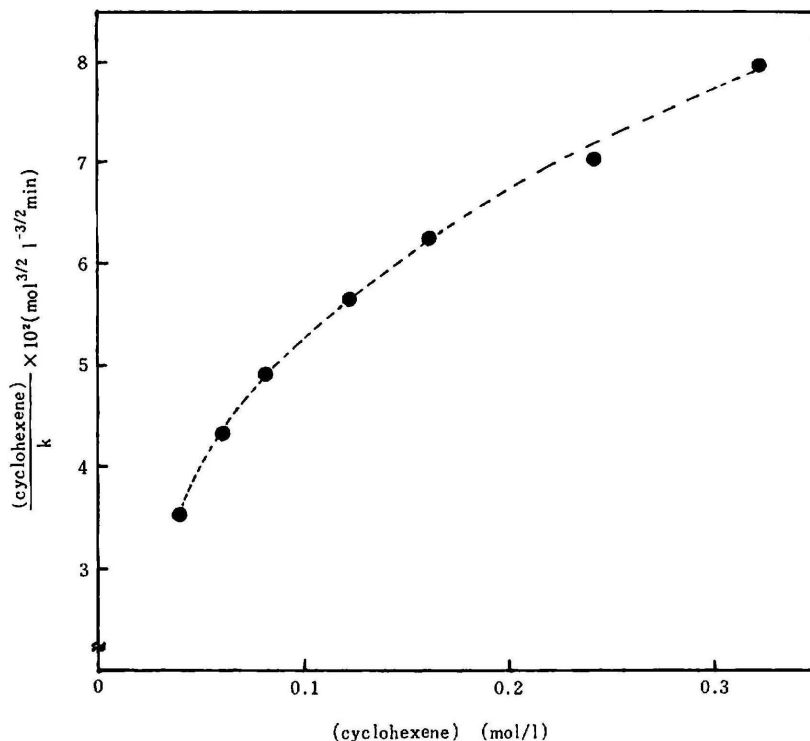


Fig. 3. Plot of (cyclohexene)/k vs. (cyclohexene)

In our temperature effect on the reaction kinetics we obtained an evidence to suggest that the EDA complex participates in the reaction. However, as seen from Fig. 3, our kinetic data could not be fully explained by the EDA complex participation mechanism proposed by Ayres, et al.. As a conclusion, it seems that photochemical addition of iodine to cyclohexene proceeds via both radical chain and EDA complex participation mechanisms in parallel.

(2) Reaction with the 315 nm Light

The absorption spectra of the n-hexane solution of iodine and cyclohexene are shown in Fig. 4 together with energy spectra of the light source for the reaction. The band in ultraviolet region is the charge transfer band of the EDA complex between iodine and cyclohexene and the band in visible region is absorption of iodine. A dotted curve refers to energy spectra of the 315 nm light used to illuminate the sample solution and given in the figure to show its relative position to the CT band. Neither iodine nor cyclohexene has absorption in the vicinity of 315 nm.

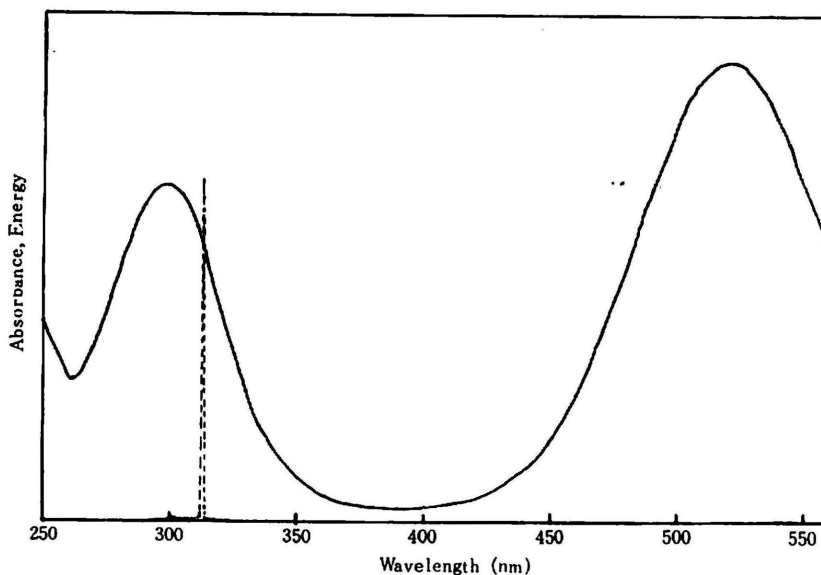


Fig. 4. Absorption spectra of n-hexane solution of iodine and cyclohexene (solid curve) and energy spectra of light source (dotted curve)

When the solution of iodine and cyclohexene in n-hexane was illuminated with the 315 nm light, the reaction proceeded smoothly. A new band appeared in the shorter wavelength region of the CT band as the reaction proceeded. Since absorption spectra of the reaction mixture was same as those of the reaction mixture obtained by illumination with visible light, we concluded that the final product was addition product. Further identifications of the product was not pursued. The tailing part of the absorption band of the product appeared at 315 nm, but the absorption of the light by the product during the reaction was neglected in the analysis of kinetic data because the kinetic experiments were carried out only in the early stage of the reaction.

Several kinetic runs were made for the addition of iodine to cyclohexene in n-hexane at 25°C by illuminating the sample solution with the 315 nm light with cyclohexene in excess to obtain the order of the reaction with respect to iodine. A double logarithmic plot of the velocity vs. the concentration of iodine yielded a straight line, the slope being equal to the order of the reaction with respect to iodine. The reaction was found to be 2 order with respect to iodine in this case, while the order was 3/2 when the sample solution was illuminated by visible light in the previous section.

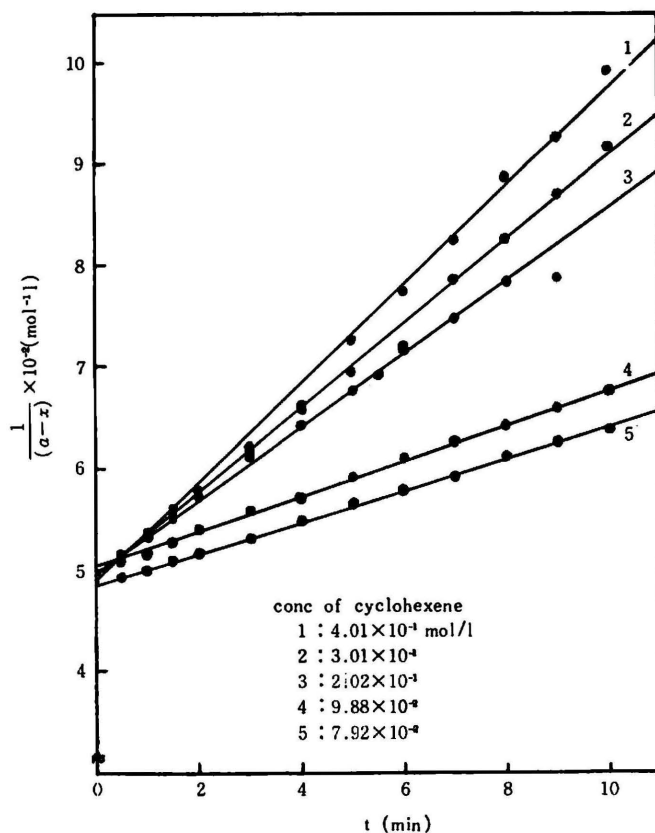


Fig. 5. Plot of the second order rate equation for the addition of iodine to cyclohexene in n-hexane at 25°C with 315 nm light for various conc. of cyclohexene

Since all kinetic runs were made with cyclohexene in excess, the rate of disappearance of iodine with respect to the concentration of iodine at time t is expressed by

$$-d(I_2)/dt = k(I_2)^2 \quad (16)$$

Integration of equation (16) yields the following expression

$$1/(a-x) = kt + 1/a \quad (17)$$

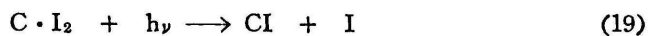
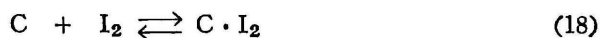
where a is the initial concentration of iodine at zero time, $(a-x)$ the concentration of iodine at time t , and t the time in minutes. The rate constant k were determined from the slope of the straight lines obtained by plotting the values of $1/(a-x)$ vs. t . A plot of the data for kinetic runs made with various concentration of cyclohexene in n-hexane at 25°C is shown in Fig. 5. The second order rate constants were obtained from the slope for each concentration of cyclohexene. The resultant k values are presented in Table 4.

Table 4. The second order rate constant for the addition of iodine to cyclohexene in n-hexane at 25°C with 315 nm light

Run	(cyclohexene) mol/l	(I ₂) mol/l	k mol ⁻¹ l min ⁻¹
1	4.01 × 10 ⁻¹	2.05 × 10 ⁻³	48.5
2	3.01 × 10 ⁻¹	2.05 × 10 ⁻³	41.1
3	2.02 × 10 ⁻¹	2.01 × 10 ⁻³	35.9
4	9.88 × 10 ⁻²	2.01 × 10 ⁻³	17.2
5	7.92 × 10 ⁻²	2.05 × 10 ⁻³	15.6

In order to determine the apparent order of the reaction with respect to cyclohexene, a double logarithmic plot of $\log k$ vs. \log (cyclohexene) was made using the data of Table 4 as mentioned in the previous section. It gave a straight line. From the slope the apparent order of the reaction with respect to cyclohexene was determined to be 0.64 in accordance with the result when the reaction was initiated with the visible light.

Judging from the order of the reaction with respect to iodine and the fact that the only species absorbing in this region is the EDA complex, the initiation reaction must be the dissociation of the EDA complex into radicals.



where again C is cyclohexene and $C \cdot I_2$ the EDA complex between iodine and cyclohexene. When iodine molecule, as mentioned previously, is dissociated by the visible light, the concentration of iodine atom was proportional to square root of the concentration of iodine molecule, giving 3/2 order of the reaction with respect to iodine in the addition reaction. In the present case one iodine atom is produced from one iodine molecule via the EDA complex. Then the concentration of iodine atom would be proportional to the concentration of iodine molecule if we assume that most of the iodine atom is consumed by the addition reaction, giving negligibly small amount of recombination of two iodine atoms. This assumption is supposed to be reasonable because the concentration of iodine atom may be low since it is produced from the EDA complex. This one to one correspondence of the concentration of iodine atom and molecule seems to be the reason for giving the second order with respect to iodine in the addition reaction when the solution is illuminated with the 315 nm light.

Since the order of the reaction with respect to cyclohexene is 0.64 same as in the

case of the visible light irradiation, the subsequent reaction sequence following the initiation step appears to be same as the case when the reaction is initiated with the visible light.

Acknowledgement. The authors wish to express their appreciation to Messrs. Hiroshi Hirano and Tatsuo Chibana for their help in some part of the experiment.

References

- 1) T. S. Paterson and J. Robertson, *J. Chem. Soc.*, **125**, 1526 (1924); A. Fairtourne and D. W. Stevens, *ibid.*, 1973 (932); P. M. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 ('957); F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 ('958).
- 2) S. Toma, Y. Kinjo, and A. Kinjo, *Bull. of Science & Eng. Div., Univ. of the Ryukyus, Science ed.*, No. 15, 51 (972).
- 3) G. Sumrell, B. M. Wyman, R. G. Howell, and M. C. Harvey, *Can. J. Chem.*, **42**, 2710 (964).
- 4) P. S. Skell and R. R. Pavlis, *J. Am. Chem. Soc.*, **86**, 2956 (964).
- 5) S. W. Benson, D. M. Golden, and K. W. Egger, *J. Chem. Phys.*, **42**, 4265 ('965).
- 6) R. L. Ayres, C. J. Michejda, and E. P. Rack, *J. Am. Chem. Soc.*, **93**, 1389 (97).
- 7) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 ('960).
- 8) S. O. Morgan and H. H. Lowry, *J. Phys. Chem.*, **34**, 2385 ('930).
- 9) J. A. Riddick and E. E. Toops, Jr., "Organic Solvent", 2nd ed., Interscience, New York, 1967, p. 4'3.
- 10) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 ('960).
- 11) R. L. Strong, *ibid.*, **87**, 3563 ('965).
- 12) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).