

Laser-induced Partial Oxidation of Cyclohexane in Liquid Phase

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A laser-induced partial oxidation of cyclohexane was studied in the liquid phase. With KrF excimer laser (248 nm) irradiation to neat liquid cyclohexane in which O₂ was dissolved, cyclohexanol and cyclohexanone were obtained with very high selectivities, together with cyclohexene as a minor product. Radical recombination reactions to produce dicyclohexyl ether and bicyclohexyl also took place, while these products were not observed in the gas phase reaction. These experimental results were considered to be due not only to higher concentration of cyclohexane but to the cage effect in the liquid phase oxidation. To clarify the reaction progress including the photoabsorption process, the effects of laser intensity and O₂ pressure on product distribution were studied.

Keywords : Excimer laser, partial oxidation, cyclohexane, cyclohexanol

1. INTRODUCTION

Recently, several attempts have been made to use lasers in order to control chemical reactions, especially in the field of isotope separation and CVD process. In synthetic chemistry also, lasers with high power and high monochromaticity, which can produce a large concentration of specifically excited species, have a great advantage in the control of radical reactions. However, only a few works have so far been reported. Limited examples are the synthesis of vinyl chloride^[1], vinylidene chloride^[2], high pressure

polymerization of ethylene^[3], and the partial oxidation of hydrocarbons^{[4]-[7]}.

Partial oxidation of cyclohexane for synthesizing cyclohexanol and cyclohexanone is regarded as a very important chemical reaction, and is carried out on an industrial scale by way of autoxidation in the liquid phase using oxygen and metal ions as the catalyst. In this case, however, there still remains a problem of side reactions and secondary reactions because of the relatively high temperature, as well as a problem of the cost for the separation of catalysts from aimed products. Recently, the reaction of cycloalkanes with oxygen atoms has been investigated. Zadok and Mazur reported^[8] that the reaction of oxygen atoms, produced by CO₂ microwave discharge, with cycloalkanes leads to their hydroxy, keto, and epoxy derivatives. Rudich *et al.* specifically investigated^[9] the effect of cluster formation on the reactivity of cyclohexane with O(³P).

Laser-induced partial oxidation of cyclohexane in the gas phase has been reported^[7], in which it was found that the product distributions of oxygen-containing compounds, as well as those of hydrocarbons, varied significantly depending on the progress of the chain propagation steps subsequent to the laser photolysis of the initiator species, such as N₂O or O₃. In the gas phase reaction, however, the concentration of the substrate was so small that the rate of the abstraction reaction of H atom from cyclohexane by radicals was limited, and high yields for the aimed products could not be obtained.

The objective of this work is to clarify the effect of reaction conditions on the product distribution in the laser-induced partial oxidation of cyclohexane in the liquid phase. From the experimental results, the plausible reaction scheme is discussed.

2. EXPERIMENTAL

The reaction apparatus, as shown in Fig. 1, consisted of a pulsed excimer laser, a reaction cell, and a gas chromatography. The cylindrical reaction cell was made of pyrex equipped with quartz windows at both ends. Liquid cyclohexane (40 cm³), used as received, was pressurized by oxygen up to 1.4 - 2.6 x 10⁵ Pa with

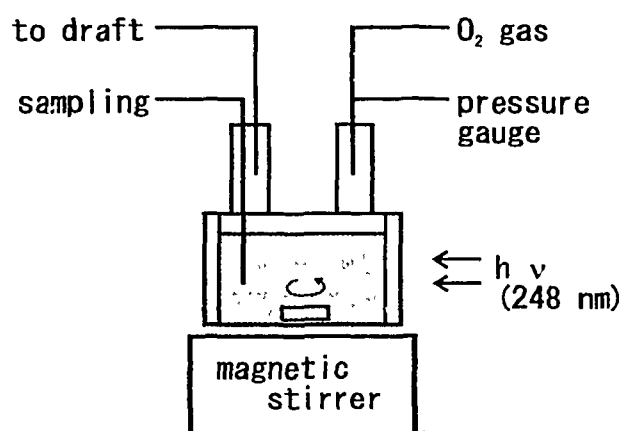


Fig.1 Experimental apparatus

stirring, and irradiated by short ultraviolet laser pulses from the KrF excimer laser (λ -Physik, 248 nm) at 10 Hz for 5 - 60 minutes. The products were analyzed by gas chromatography (FID, Shimadzu GC-14A with capillary column).

3. RESULTS AND DISCUSSION

3.1 Product distribution

The dependence of product distribution on reaction temperature is shown in Table 1. Only the products observed in the liquid phase are listed in this table, because the total amount of products in the gas phase, such as CO, CO₂, ethylene and acetylene, are negligible compared to that in the liquid phase. Cyclohexanol and cyclohexanone are obtained with high selectivities, together with cyclohexene, cyclohexyl ether, bicyclohexyl as minor products. The conversion of cyclohexane as well as the selectivity for cyclohexanol increases with increasing the reaction temperature.

In addition to these products, a minor unknown peak has always appeared on the chromatogram with a retention time which is not coincident to any of those of the stable compounds likely to form in this system. This peak has been identified as

Table 1 Effect of reaction temperature on cyclohexane conversion and product distribution

Temperature (K)	300	340
Cyclohexane conversion (%)	0.12	0.23
Selectivity (C-base,%)		
Cyclohexanol	52.0	66.7
Cyclohexanone	23.4	18.9
Cyclohexyl ether	7.9	4.8
CHPO	6.5	4.3
Bicyclohexyl	1.2	0.7
Cyclohexene	9.1	4.6

O₂ pressure : 2.5 x 10⁵ Pa, Pulse energy : 20 mJ /pulse, Reaction time : 15 min.

Table 2 Effect of O₂ pressure on cyclohexane conversion and product distribution

O ₂ Pressure (/10 ⁵ Pa)	1.5	2.5
Cyclohexane conversion (%)	0.31	0.47
Selectivity (C-base,%)		
Cyclohexanol	61.9	60.1
Cyclohexanone	19.7	21.4
Cyclohexyl ether	7.0	6.9
CHPO	0.4	1.0
Bicyclohexyl	0.9	0.6
Cyclohexene	10.1	10.3

Temperature : 300 K, Pulse energy : 100 mJ /pulse, Reaction time : 15 min.

Table 3 Effect of pulse energy on cyclohexane conversion and product distribution

Pulse energy (mJ/pulse)	20	60	100	125
Cyclohexane conversion (%)	0.12	0.31	0.47	0.49
Selectivity (C-base,%)				
Cyclohexanol	52.0	57.7	60.1	59.7
Cyclohexanone	23.4	22.5	21.4	21.5
Cyclohexyl ether	7.9	7.6	6.9	7.0
CHPO	6.5	2.3	1.0	0.7
Bicyclohexyl	1.2	0.7	0.6	0.7
Cyclohexene	9.1	9.3	10.1	10.3

Temperature : 300 K, O₂ pressure : 2.5 x 10⁵ Pa, Reaction time : 15 min.

cyclohexylhydroperoxide (CHPO) by GC-MS analysis and iodometric analysis. The following two results support the identification: 1) In the thermal oxidation of cyclohexane in the liquid phase, the formation of CHPO was reported to be enhanced in the presence of nitriles^[10]. In the present case, the increase of the area of the peak has been observed when acetonitrile was added to neat cyclohexane. 2) The selectivity for this product has decreased with increasing the reaction temperature, which suggests that this compound should be chemically unstable.

Table 2 shows the effect of O₂ pressure on cyclohexane conversion and product distribution. The product distribution is almost independent of the O₂ pressure, while the conversion increases with increasing the O₂ pressure, which implies that only the initiation reaction is affected by the dissolved O₂.

The dependence of the product distribution on pulse energy is shown in Table 3. With increasing the pulse energy, the selectivity for cyclohexanol increases and those for cyclohexanone and CHPO decrease.

3.2 Reaction mechanism

Since no product was obtained in the absence of O₂ and the conversion of cyclohexane increased with increasing O₂ pressure, the initiation step of the reaction is considered to be photoabsorption by the dissolved O₂. The absorption of the KrF excimer laser light by O₂ does not lead to the O-O bond cleavage but generate O₂^{*} (excited oxygen molecule in Herzberg states). The threshold energy of the bond dissociation is 242 nm. Chemical

reactivity of O_2^* is not yet extensively studied. Thus we tentatively consider that the reaction product of O_2^* with cyclohexane is cyclohexyl radical by H atom abstraction by O_2^* from cyclohexane. Once cyclohexyl radical is produced, it reacts with O_2 rapidly to produce cyclohexylperoxy radical, which then form CHPO via H atom abstraction from the substrate. As the O-O bond dissociation of CHPO requires a certain activation energy, the unimolecular decomposition of CHPO into cyclohexoxy radical and OH radical is accelerated under high temperatures. The formation of the main products, cyclohexanol and cyclohexanone, can be explained by the reactions of cyclohexoxy radical; H abstraction from cyclohexane for the former, and unimolecular decomposition for the latter, respectively. Cyclohexyl ether and bicyclohexyl can be regarded as radical recombination products, taking the high radical concentration induced by laser irradiation into consideration. The relevant reaction network is shown in Fig. 2.

There are three essential differences to be noticed between the product distributions in the liquid phase oxidation and that in the gas phase, those are; 1) the formation of the radical recombination products only in the liquid phase, 2) the formation of CHPO in the liquid phase, and 3) the higher cyclohexanol/cyclohexanone ratio in the liquid phase. (The selectivity for cyclohexanone was higher than that for cyclohexanol under any reaction conditions in the gas phase^[71].)

The first may be explained by the cage effect. The recombination reaction of radicals is considered to be an exothermic reaction, and the solvent which is surrounding the

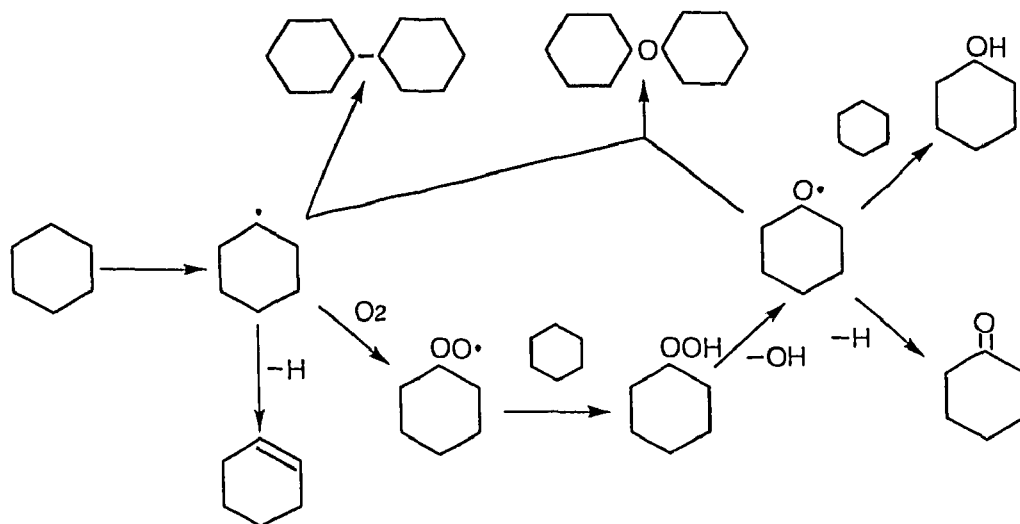


Fig. 2 Reaction network

radicals would play a role as a quencher of the excess energy.

The second and the third ones arise from the difference in the substrate concentration between two phases. In the gas phase reaction, the concentration of cyclohexane is so low, compared to the liquid phase, that the H atom abstraction from cyclohexane by cyclohexyl radical to form cyclohexanol is unfavorable to take place. The concentration of the substrate also affects the reaction path of cyclohexylperoxy radical. In the liquid phase, CHPO is produced by H abstraction of cyclohexylperoxy radical. The disproportionation reaction between cyclohexylperoxy radical and cyclohexyl radical to produce two cyclohexoxy radicals, in contrast, would be kinetically favorable in the gas phase reaction because of the low cyclohexane concentration and the high radical concentration.

3.3 Kinetic analysis

The dependence of the cyclohexane conversion on reaction time is shown in Fig.3. The conversion of cyclohexane increases almost linearly to the reaction time, though it seems to decline slightly at longer reaction time.

From these experimental results, a kinetic analysis is made to calculate the apparent overall rate constant of the laser-induced oxidation of cyclohexane. In this treatment, the reaction of cyclohexane is considered to be first order on the concentration of O_2 dissolved, based on the assumption that the conversion of cyclohexane is proportional to the total amount of the photons absorbed by O_2 . Then the differential equation for this reaction can be written as eq. (1),

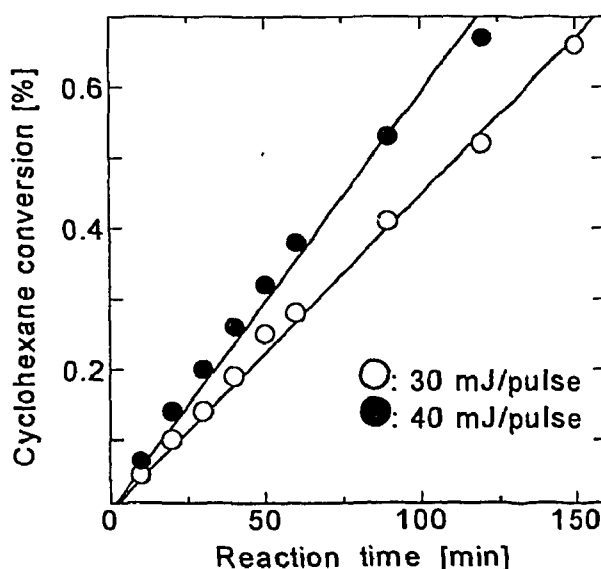


Fig. 3 Dependence of cyclohexane conversion on reaction time

$$\frac{d[O_2]}{dt} = k_s([O_2]_{sat} - [O_2]) - k_r[O_2] \quad (1)$$

$$= -(k_s + k_r)[O_2] + k_s[O_2]_{sat} \quad (2)$$

where k_s and k_r denote the rate constants of O_2 dissolution and reaction with cyclohexane, respectively, and $[O_2]_{sat}$ means the concentration of O_2 in the saturated solution. By solving this equation under the initial condition that $[O_2] = [O_2]_0$ at time $t=0$, $[O_2]$ can be determined by eq. (3).

$$\frac{[O_2] - \frac{k_s [O_2]_{sat}}{k_s + k_r}}{[O_2]_0 - \frac{k_s [O_2]_{sat}}{k_s + k_r}} = e^{-(k_s + k_r)t} \quad (3)$$

Integration of eq. (3) gives the total amount of O_2 consumption during the reaction course, as is shown in eq. (4),

$$\int_0^t k_r [O_2] dt = k_r \left\{ \frac{[O_2]_0 - \alpha [O_2]_{sat}}{k_s + k_r} (1 - e^{-(k_s + k_r)t}) + \alpha [O_2]_{sat} t \right\} \quad (4)$$

where α is $k_s/(k_s + k_r)$.

Provided that the stoichiometry of the reaction of cyclohexane with O_2 is 2:1, the conversion of cyclohexane can be written as eq. (5),

$$\begin{aligned} \frac{[RH]_0 - [RH]}{[RH]_0} &= \frac{2 \int_0^t k_r [O_2] dt}{[RH]_0} \\ &= \frac{2k_r}{[RH]_0} \left\{ \frac{[O_2]_0 - \alpha [O_2]_{sat}}{k_s + k_r} (1 - e^{-(k_s + k_r)t}) + \alpha [O_2]_{sat} t \right\} \quad (5) \end{aligned}$$

where $[RH]$ designates the concentration of cyclohexane. The experimental result that the conversion increases linearly with increasing the reaction time, suggests that α can be regarded as unity ($k_s \gg k_r$) and $[O_2]_0$ is nearly equal to $[O_2]_{sat}$ in eq. (5), that is, the rate of O_2 dissolving into cyclohexane is suggested to be much faster than the oxidation reaction. Then the conversion can be rewritten as eq. (6).

$$\frac{[RH]_0 - [RH]}{[RH]_0} = \frac{2k_r [O_2]_{sat}}{[RH]_0} t \quad (6)$$

Substituting $[O_2]_{\text{sat}}=3.1 \times 10^{-2}$ (mol/l) and $[RH]_0=9.3$ (mol/l) into eq.(6), the rate constant k_p can be calculated to be 1.1×10^{-2} and 1.5×10^{-2} (s^{-1}) at a pulse energy of 30 and 40 (mJ/pulse), respectively, which suggests that the rate constant increases linearly with increasing the pulse energy of laser. From these experimental value of k_p , the absorption cross section of O_2 in liquid cyclohexane is calculated to be 7.4×10^{-21} (cm^2), which is about 10^4 times larger than that in the gas phase (3.8×10^{-25} cm^2 by Shardanand⁽¹¹⁾). Thus the photoabsorption by O_2 would be really enhanced in the liquid phase, and/or this reaction would proceed via chain mechanism with a long chain length.

4. CONCLUSION

- 1) In laser-induced oxidation of cyclohexane in liquid phase, cyclohexanol and cyclohexanone were obtained with high selectivities, together with cyclohexene, CHPO, cyclohexyl ether and bicyclohexyl as minor products. From the experimental results, a plausible reaction scheme was proposed.
- 2) The product distribution in the liquid phase reaction was different from that in the gas phase reaction, due not only to higher concentration of cyclohexane but to the cage effect in the liquid phase oxidation.
- 3) From the kinetic analysis, it was suggested that O_2 dissolution is much faster than the reaction of cyclohexane with O_2 , and the rate constant was proportional to the laser pulse energy.

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