

Photochemical Transformation of CO in Cyclohexane

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As industrial society has been developed, fossil fuels such as coal, oil, natural gas, as energy source have been increasingly used. During the combustion, nitrogen oxides, sulfur oxides and carbon oxides are produced. These gases are the main source of air pollution. Especially, carbon monoxide is very toxic compound and cause significant environmental problems, which are oxidized in the atmosphere to give carbon dioxide, which causes green house effect or destroys ozone layer. On the other hand, it is industrially important compound because it could be used as a raw material for chemical syntheses. Consequently, the development of the techniques has been keenly needed to remove CO as well as to use it. One of these is to use photochemical reaction which can be treated simply. Earlier investigation showed that carbon monoxide could be removed by photocatalytic oxidation.¹⁻⁴ But it is not entirely satisfactory method because of CO₂ formation.

After Holian *et al.*⁵ showed that CO reacts with hydrogen atom to give CHO radical and Marz *et al.*⁶ proved the presence of this radical by ESR spectroscopy, Arai *et al.*⁷⁻⁹ and Getoff *et al.*¹⁰⁻¹⁴ have also studied the radiation induced reduction CO in gas state and in liquid state, respectively. A problem for the reaction is, however, to use the special γ -ray device required various safety equipment. To circumvent this difficulty, we have employed photochemical method using UV light at 184.9 nm and reported the result along with the reaction mechanism for the chemical reaction of aqueous carbon monoxide.¹⁵ We also reported that the reactivity of CHO radical formed in the reduction is higher than in hydrated state, and that the carbonylation production can be also occurred in the presence of other substances.¹⁶ Despite a great intensive research on the photochemical transformation of carbon monoxide in polar solvents, little attention has been paid to that in nonpolar solvents.

In the present study, cyclohexane was selected as a model substance for a nonpolar solvent and it was irradiated with vacuum UV light of 184.9 nm in the absence and presence of CO. The purpose of this study is to investigate the possibility of photochemical transformation of carbon monoxide in a nonpolar solvent.

Experimental

Lightsource and Actinometry. A low pressure mercury lamp (Osram HNS 12/oz) was used as the light source of UV light with 184.9 nm. The lamp was mounted in a quartz tube which was surrounded by the solution to be irradiated. The intensity (I_0) of the 184.9 nm light was determined by ethanol actinometer. The yield of hydrogen produced after irradiation of air-free aqueous ethanol (5 mol·dm⁻³)

was measured by gas chromatography. The lamp intensity was found to be 3.97×10^{17} hv·ml⁻¹·min⁻¹ at 20 °C from the known quantum yield, $Q(\text{H}_2) = 0.40$ ^{17,18}. It corresponds to about 30% of the number of quanta at 253.7 nm. No change in intensity of the lamp over the period of the experiments.

Reagents and General. Cyclohexane (99.9%) purchased from Junsei Co., Japan was purified by fractional distillation after adding molecular sieve (4A). Such cyclohexane contained no significant impurities detectable by gas chromatography with a flame-ionization detector. Cylinder carbon monoxide (state to be 99% pure) was purified by passing through an alkaline pyrogallol solution followed by an alkaline sodium hydrosulphite solution sensitized by the addition of sodium anthraquinone β sulphonate.¹⁹ A 150 ml of pure cyclohexane in the irradiation vessel was purged for about 60 min. either with high purity argon in order to remove contained oxygen or with carbon monoxide. The solution was then irradiated with vacuum UV light. During the irradiation procedure, the temperature was kept at 20±0.1 °C. The UV spectrum of cyclohexane in methanol-water mixture (1:4 v/v) was recorded on a Hitachi Model 557 UV-spectrophotometer. The molar extinction coefficient (ϵ) of cyclohexane at 184.9 nm was obtained 1.375 L mol⁻¹cm⁻¹ by extrapolation. Cyclohexane did not absorb the simultaneously emitted light at 253.7 nm.

Analysis. Mass spectra of the products were obtained on a Varian saturn GC-MASS system (stabilwas DA capillary column 50 m×0.25 μ m, EI method) [product; m/z (rel. intensity), cyclohexene; 41 (25), 54 (30), 67 (100), 68 (50), 81 (85), Dicyclohexyl; 42 (53), 55 (80), 67 (100), 82 (95), 165 (13), cyclohexanol; 39 (55), 57 (100), 67 (70), 83 (75), 99 (10), cyclohexanone; 38 (70), 43 (80), 55 (100), 69(30), 98 (60), cyclohexanecarboxaldehyde, 55 (100), 68 (25), 83 (40), 112 (5)]. Identifications and determinations were made by comparison with fragmentation patterns of known amounts of the pure substances. Gas chromatographic analysis was performed by the Varian Model 3700 gas chromatography. The separated GC peaks were reconfirmed by comparison with retention time of the identified products from the Mass spectra. Qualitative analysis was carried out by estimation with area ratio of the products and 1-pentanol as a internal substance.

Result and Discussion

The photolysis at 184.9 nm of air-free cyclohexane (saturated with argon) yields cyclohexene and dicyclohexyl as main products. In the presence of carbon monoxide, cyclohexanecarboxaldehyde, cyclohexanol and cyclohexanone in addition to above two products were produced mainly. No organic products are observed in both experimental conditions when irradiation is done only 253.7 nm. The products yield as a function of the number of quanta are represented in Figure 1 and 2. As shown in Figures, the products yield is not increased linear with the number of quanta. One should note that a back reaction occurred in the system during the irradiation; the obtained product was decomposed by direct photolysis of product or by an attack of the radicals which were formed during the photochemical reaction. It is therefore determined the initial quantum yields (Q_i) and they are summarized in Table 1. The results given in Table 1 show that

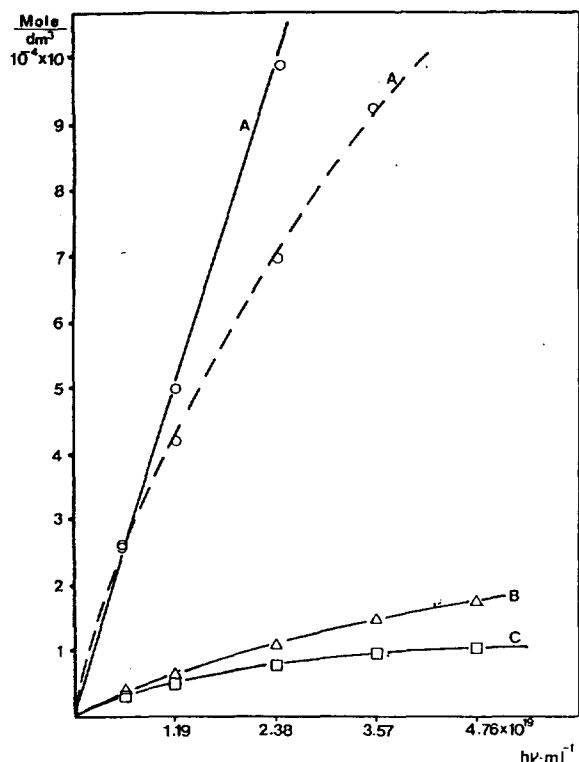


Figure 1. Formation of products (A; cyclohexene, B; cyclohexanol, C; cyclohexanone) after irradiation of cyclohexane in the absence (a dotted line) and presence of CO (a solid line) as a function of the number of quanta.

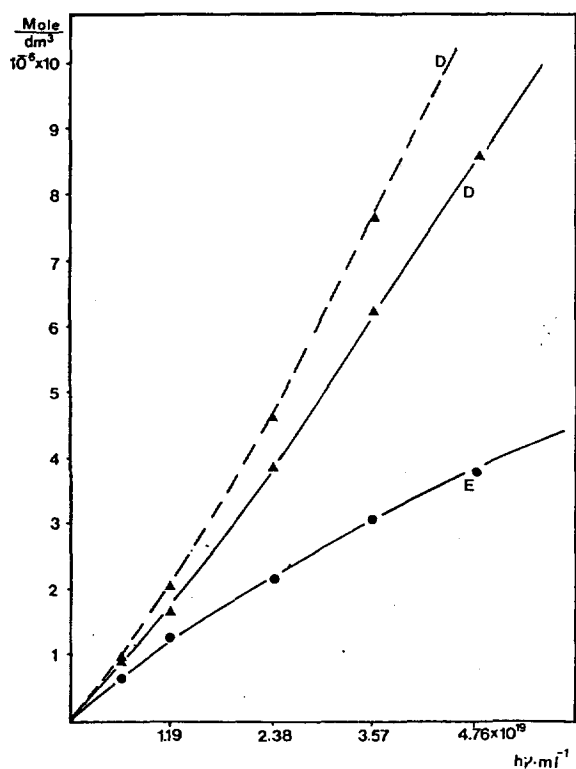


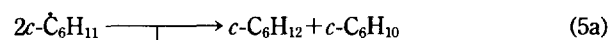
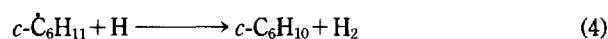
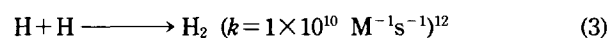
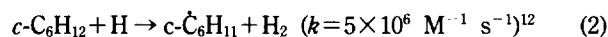
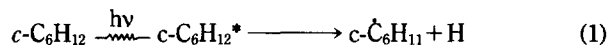
Figure 2. Formation of products (D; dicyclohexyl, B; cyclohexanecarboxaldehyde) after irradiation of cyclohexane in the absence (a dotted line) and presence of CO (a solid line) as a function of the number of quanta.

Table 1. Initial quantum yield (Q_i) of the products by irradiation ($\lambda = 184.9$ nm) of cyclohexane in the absence and presence of CO

Products	Ar	CO
Cyclohexene	2.60×10^{-2}	2.53×10^{-2}
Dicyclohexyl	1.01×10^{-2}	0.86×10^{-2}
Cyclohexanol	—	3.42×10^{-4}
Cyclohexanone	—	2.99×10^{-4}
Cyclohexanecarboxaldehyde	—	0.63×10^{-4}

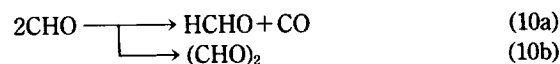
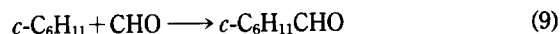
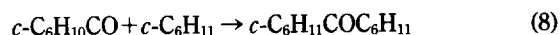
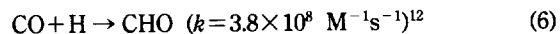
cyclohexene and dicyclohexyl were formed as major products by the irradiation of air-free (saturated with argon) cyclohexane at 184.9 nm, although the initial quantum yields of the products are relatively small. This behavior is because cyclohexane has a low molar extinction coefficient at 184.9 nm ($\epsilon = 1.375 \text{ L mol}^{-1} \text{ cm}^{-1}$) and the fraction of absorbed quanta by cyclohexane is small.

In the photolysis of the gas-phase cyclohexane at 123.6 nm (ca. 10.03 eV) and 147.0 nm (ca. 8.44 eV), it was reported that ethane, propane, 1-butene and methylcyclohexane were produced mainly with small amount of butane and cyclohexene.²⁰⁻²² The formation of these products can be interpreted that methyl, ethyl, allyl and cyclohexyl radicals were produced as the major radical intermediates during the irradiation of those lights whose photon energy are relatively large. On the other hand, the light of 184.9 nm has relatively small photon energy (ca. 6.70 eV). It is therefore inferred on the basis of the products that the electronically excited cyclohexane is splitted mainly into H and cyclohexyl radicals. The formed hydrogen atom can attack to cyclohexane and thereby much more cyclohexyl radicals are produced. Although the hydrogen atom can be reacted with each other in order to produce hydrogen molecules, the formation of cyclohexyl radicals according to reaction (2) is superior because the reaction probability of the reaction is greater than that of reaction (3). Cyclohexene and dicyclohexyl are produced by disproportionation process or dimerization process of cyclohexyl radicals according to reaction (5). Cyclohexene can be formed also by the reaction (4). But the yield of the products through this reaction is negligible because only a small amount of hydrogen atom can be reacted with cyclohexyl radicals to give cyclohexene.



As shown in Table 1, the initial quantum yield of cyclohexene is much greater than that of dicyclohexyl. From the results, one should note that the rate for the disproportionation process is faster than that for dimerization in the case of cyclohexyl radicals.

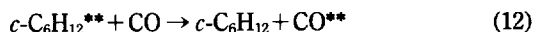
In the presence of carbon monoxide, the reaction should be initiated by the photolytic dissociation of cyclohexane molecules into H and cyclohexyl radicals, and the reduction of carbon monoxide starts with an attack by a hydrogen atom, since carbon monoxide does not absorb at 184.9 nm.²³ Hence, the following reactions are expected to take place in this case.



The formation of cyclohexanecarboxaldehyde could be explained by the reaction (9). But the initial quantum yield of the product is very small. Especially, the other carbonylation products such as formaldehyde, glyoxal and dicyclohexyl ketone were not detected. This behavior is quite different in the case of polar solvents. In aqueous solution, those products were formed with relatively large initial quantum yield. The formation of carbonylation products results from the CHO radical and its yield depends on the concentration of carbon monoxide in cyclohexane. Although the solubility of carbon monoxide in cyclohexane could not find, it might be deduced that the solubility of carbon monoxide is probably more soluble in cyclohexane than in aqueous solution from the fact that the solubility of carbon monoxide in non polar solvents such as benzene, heptane is about ten times better than that in aqueous solution.²⁴ It means that the reaction probability for the formation of CHO radical is larger and more carbonylation products can be produced. Nevertheless, it is surprising that formaldehyde, glyoxal and dicyclohexyl ketone could not be detectable. Furthermore, unexpected products such as cyclohexanol and cyclohexanone were also formed with relatively high initial quantum yield under this condition. These results indicate that carbon monoxide is rather dissociated into carbon and oxygen atom than combined with hydrogen atom in the system during the irradiation. The following primary events therefore should be considered, for the reaction.



$c\text{-C}_6\text{H}_{12}^{**}$ represents a superexcited molecule and its energy can be transferred to carbon monoxide.

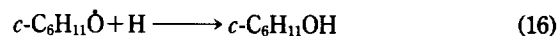
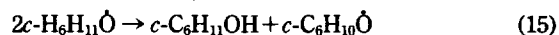


The electronically superexcited carbon monoxide, CO^{**} can be dissociated as follows.



The formed oxygen atom is combined with cyclohexyl radical and then cyclohexanol and cyclohexanone are produced by disproportionation process of $c\text{-C}_6\text{H}_{11}\text{O}$ radicals according to reaction (15). But the initial quantum yields of cyclohexanol and cyclohexanone are not same as shown in Table 1. This

difference comes from that a small amount of cyclohexanol could be formed also by the reaction (16).



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References

- Steinbach, F. *Nature* **1952**, *215*, 152.
- Schwab, G.; Noller, H.; Steinbach, F.; Venugopalan, M. *Nature* **1962**, *193*, 774.
- Nagarjunan, T. S.; Calvert, J. G. *J. Phys. Chem.* **1964**, *68*, 17.
- Amigues, D.; Teichner, S. J. *Discuss. Faraday Soc.* **1966**, *41*, 362.
- Holian, J.; Scholes, G.; Weiss, J. J. *Nature* **1961**, *193*, 1386.
- Marz, R.; Chachaty, C. *J. Chem. Phys.* **1961**, *58*, 527.
- Arai, H.; Nagai, S.; Hatada, M. *Z. für Phys. Chem.* **1981**, *126*, 187.
- Zecchina, A.; Spoto, G.; Garrone, E.; Boiss, A. *J. Phys. Chem.* **1984**, *88*, 2582-2587, 2587-2591, 2575-2581.
- Charles, F.; Hanrahan, R. J. *Radiat. Phys. Chem.* **1985**, *24*, No. 5, 475-479, 511-516.
- Seitner, D.; Getoff, N. *Z. für Phys. Chem.* **1969**, (NF), *66*, 22.
- Getoff, N.; Lehmann, H. P. *Radiat. Phys. Chem.* **1970**, *2*, 91.
- Park, H. R.; Lugovoi, Y. M.; Getoff, N. *Radiat. Phys. Chem.* **1989**, *33*, No. 6, 473.
- Park, H. R.; Lugovoi, Y. M.; Nikiforov, A.; Getoff, N. *Radiat. Phys. Chem.* **1991**, *37*, No. 3, 469.
- Park, H. R.; Getoff, N. *Z. für Naturforschung* **1992**, *47a*, 985.
- Park, H. R.; Getoff, N. *Z. für Naturforschung* **1988**, *43a*, 430.
- Park, H. R.; Getoff, N. *J. Photochem.* **1988**, *43*, 155.
- Getoff, N.; Schenck, G. O. *Photochem. Photobiol.* **1968**, *8*, 167.
- Getoff, N. *Monatsheft chemie.* **1968**, *99*, 136.
- Raef, Y.; Swallow, A. J. *Trans Faraday Soc.* **1963**, *59*, 1631.
- Hentz, R. H.; Rzed, S. J. *J. Phys. Chem.* **1967**, *71*, No. 12, 4096.
- Auslos, P.; Rebbert, R. E.; Lias, S. G. *J. Phys. Chem.* **1968**, *72*, No. 11, 3904.
- Sevilla, M. D.; Holroyd, R. A. *J. Phys. Chem.* **1970**, *74*, No. 12, 2459.
- Myer, J. A.; Samson, J. A. R. *J. Chem. Phys.* **1970**, *52*, 266.
- D'ans, J.; Boettcher, S.; Freund, H. E.; Kaufmann, E.; Koch, K. J.; Kruis, A.; Kubaschewski, O.; May, A.; Mosebach, R.; Woelk, N. H.; Zimmer, H.; Landolt-Börnstein, II Band, 2 Teil, Bandteil b, **1962**, S. 1-89, Springer Verlag, Berlin, Gottingen, Heidelberg.