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Oxidation of Cycloalkanes in a Radiofrequency Plasma

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Synopsis. Cyclopentane, cyclohexane, cycloheptane, and cyclooctane were reacted in a radiofrequency plasma containing oxygen to give mixtures of the corresponding cycloalkanones and cycloalkanols. Tetralin was also oxidized to 1-tetralone and 1-tetralol. Based on the effects of reaction variables on the oxidation rate, the reaction scheme involving the autoxidation of cycloalkyl radicals was proposed.

In the recent decades, much interest of organic chemists has been devoted to nonequilibrium plasma as a novel synthetic tool, since there are molecules activated by energetic electron bombardment to yield a diversity of reactive species which might not be readily generated by conventional chemical methods. Of late, a microwave or radiofrequency (rf) plasma was utilized for the purpose of partial oxidation of hydrocarbons. In this case, the effluents from the plasma containing atomic oxygen were passed over the organic substrates either dissolved in nonvolatile solvents[1,2] or adsorbed on solid supports.[3] Separately, we have also exerted ourselves to exploit a versatile oxidation process using plasma and reported that aromatic hydrocarbons could be effectively hydroxylated when the vaporized substrates flowed together with oxygen gas through an rf plasma.[4]

In this paper, we describe the oxidation of cycloalkanes in the plasma. For the mechanistic study, cycloalkanes were supposed to be suitable as starting materials, because they would yield less complicated products than other saturated hydrocarbons. It seems of not only scientific but also practical significance to establish the fundamental knowledge about the direct partial oxidation of saturated hydrocarbons.

Results and Discussion

The reactions of cyclopentane, cyclohexane, cycloheptane, cyclooctane, and tetralin with oxygen in an rf plasma were investigated. As major organic liquid products, the corresponding cycloalkanone(**1**) and cycloalkanol(**2**) were produced in comparable amounts. Their formation was favored under the con ditions giving the conversions below ca. 20%. Typical results are listed in Table 1. The higher conversion was, on the whole, unfavorable, since it tended to induce the formation of tars. However, the ratio of products(**1**/**2**) was mostly unchanged regardless of kind of cycloalkanes and their conversion. The compounds which should be preferably formed in the plasma reactions without oxygen, for example, bicyclohexyl or cyclohexene from cyclohexane were not detected when oxygen was fed sufficiently. As for tetralin, the oxidation took place exclusively on the carbons of 1-position. In addition, the formation of considerable amounts of carbon dioxide and water was observed in each run.

In order to get mechanistic insight into the reaction of cycloalkanes in the plasma containing oxygen, effects of reaction variables, i.e., an rf power, and flow rates of the starting materials and oxygen in the oxidation of cyclohexane were examined in detail. With increasing power, the conversion of cyclohexane rose almost linearly (Fig. 1), while it diminished exponentially as the flow rate of cyclohexane was enhanced (Fig. 2). In practice, such a dependence of the conversion on the power and flow rate is so general in organic plasma chemistry,[5] and has been reasonably interpreted on the basis of a theorem that the

Table 1. Oxidation of Cycloalkanes in an rf Plsma[a)]

Substrate	Conversion/%	Product yield[b)]/%	
		1	**2**
Cyclopentane	16	12	9
Cyclohexane	19	13	14
Cycloheptane	12	20	15
Cyclooctane	22	26	19
Tetralin	26	9	13

a) Radiofrequency power: 20 W; oxygen flow rate: 5 mmol min^{-1}; substrate flow rate: 0.5—1.5 mmol min^{-1}. b) Based on moles of substrate reacted.

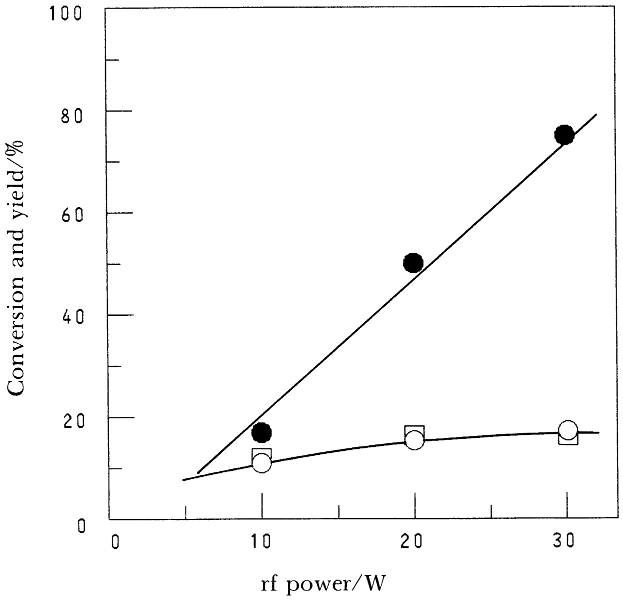

Fig. 1. Oxidation of cyclohexane in an rf plasma. Oxygen flow rate: 5 mmol min^{-1}; cyclohexane flow rate: 0.7 mmol min^{-1}; ●: cyclohexane conversion; O: cyclohexanone yield; □: cyclohexanol yield.

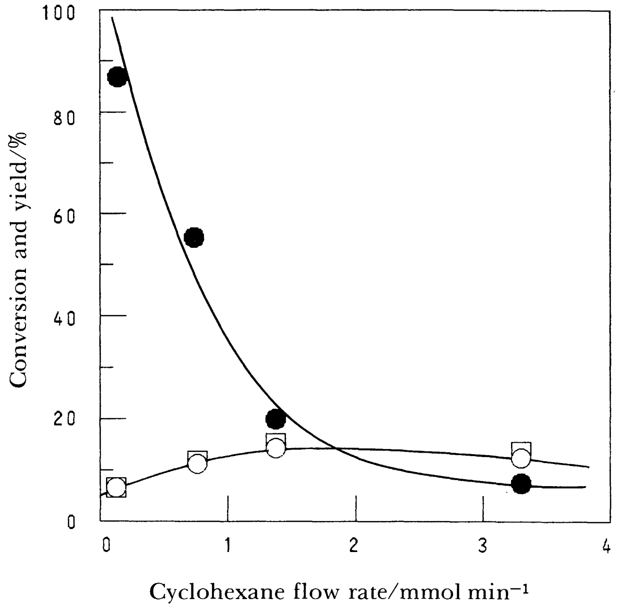

Fig. 2. Oxidation of cyclohexane in an rf plasma. Oxygen flow rate: 5 mmol min^{-1}; rf power: 20 W; ●: cyclohexane conversion; ○: cyclohexanone yield; □: cyclohexanol yield.

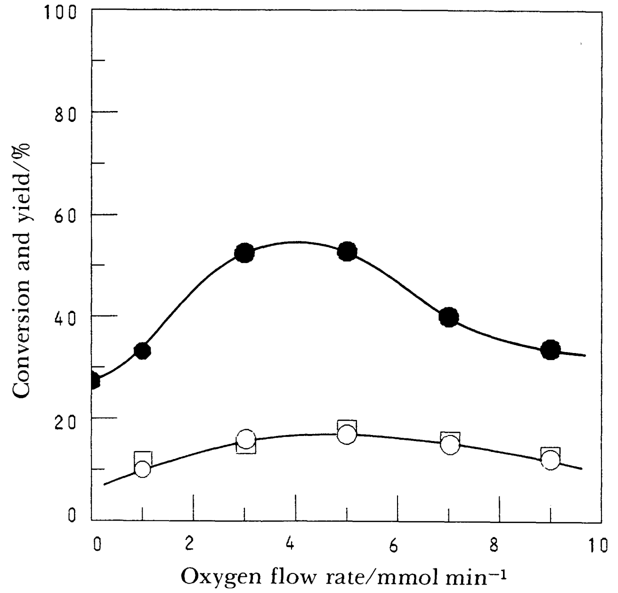

Fig. 3. Oxidation of cyclohexane in an rf plasma. Cyclohexane flow rate: 0.7—1.1 mmol min^{-1}; rf power: 20 W; ●: cyclohexane conversion; ○: cyclohexanone yield; □: cyclohexanol yield.

density and average energy of free electrons which should be most responsible for initiating chemical changes in nonequilibrium plasmas can be primarily controlled by these variables.[6] Thus, one might conclude that the rate-determining step still involves the collision of energetic electron onto molecules even in the presence of oxygen.

An interesting fact is revealed in Fig. 3; cyclohexane underwent the fragmentation or condensation principally in the plasma without oxygen and the conversion was around twenty percents under the conditions therein stated. As oxygen was added, the conversion gradually swelled and culminated around 4 mmol min^{-1} of oxygen flow rate. With a further addition of oxygen, it descended eventually close to the prime value. In contrast, as seen in Figs. 1, 2, and 3, the product yields were not substantially influenced by either of these variables. This can be understood by noting that the yield is based on the product against the starting material reacted. The final products such as **1** or **2** would be yielded through a complex of elementary chemical reactions following the initiation step caused by electron collision, and the relative importance of chemical processes is not supposed to be greatly affected by plasma parameters.

The formation of cyclohexanol and cyclohexanone in almost equimolar amounts strongly suggests that the oxidation involves the autoxidation of cyclohexyl radical as a key step. The cyclohexyl radical might be generated from cyclohexane through either C–H bond cleavage induced by electron bombardment or H abstraction by atomic oxygen. Although it is taken for granted that the latter process is most crucial in the oxidation of organic solids using oxygen plasmas, the former one seems rather superior in the system where organic substrates exist in the gas phase. Nevertheless, Fig. 3 demonstrates that the role of oxygen atom might not be neglected under the appropriate conditions, where the H abstraction should compete with the addition to O_2 giving ozone which is poorly reactive to saturated hydrocarbons. Consequently, the conversion of cyclohexane rose initially with increase in O_2 flow rate and then began to reverse in the presence of large excess O_2.

From the above discussion, the following reaction scheme could be proposed for the oxidation of cyclohexane in an rf plasma;

$$\begin{aligned} O_2 &\xrightarrow{\text{rf}} 2O\cdot \\ C_6H_{12} &\xrightarrow{\text{rf}} C_6H_{11}\cdot + H\cdot \\ C_6H_{12} + O\cdot &\longrightarrow C_6H_{11}\cdot + \cdot OH \\ O\cdot + O_2 &\longrightarrow O_3 \\ C_6H_{11}\cdot + O_2 &\longrightarrow \longrightarrow \mathbf{1} + \mathbf{2} \end{aligned}$$

It seems undoubted that the analogous reaction steps proceed also in the oxidation of other cycloalkanes, since the effects of reaction variables on the products and oxidation rate were essentially identical to those in the cyclohexane oxidation.

Experimental

All of organic substrates and oxygen were of reagent grade from commercial sources and used without further purification.

The assembly and equipment of reaction apparatus are quite similar to those stated in the literature.[7] A starting material and oxygen flowed simultaneously through a plasma zone in a 40 cm×4.5 cm i.d. Pyrex reactor tube at pressure below a few hundreds Pa. The flow rate of oxygen was controlled with a gas needle valve and monitored with a float-type flowmeter; the flow rate of substrate was controlled with a Teflon needle valve and determined from the quantity of material lost from a reactant reservoir and the elapsed time. Energy was supplied by an inductively coupled 13.56 MHz generator and in every run the impedance matching was conducted so that the reflected power was negligible. The products and recovered starting material were collected in cold traps on liquid nitrogen. The controlled variables were the applied power (10—30 W), the oxygen flow rate (1—8 mmol min^{-1}), and the flow rate of starting material (0.1—3 mmol min^{-1}).

Analysis of organic liquid products was carried out by means of GC(PEG 20 M). Identification of the products was achieved by coinjection of authentic samples with product mixtures and confirmed by GC-MS. For the quantitative analysis, toluene was used as an internal standard. Gaseous products and polymeric deposits on the reactor wall were not analyzed. The product yields were based on the starting material reacted.

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