Plasma Reduction of CO_2 with H_2O for the Formation of Organic Compounds

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Synopsis. The reduction of CO_2 with H_2O was carried out by means of a microwave plasma reaction in order to obtain organic compounds. The main products obtained in a cold trap were determined to be oxalic acid and H_2O_2 by an analysis of reversed-phase chromatography using UV and conductivity detectors.

Cold plasma is known to be a technique for thin-layer formation (CVD) and etching. It is also useful for gas-phase chemical reactions which have high activation energies, because a very high energy can be supplied to the plasma. Although it is not easy to control the chemical reactions in the plasma, because of its wide energy distribution, the plasma may have a great chance to reveal new chemical reactions which have never proceeded before.

In our work, we tried to produce the opposite reaction of combustion possible: that is, the reduction of CO_2 with H_2O. One of the reasons that we chose CO_2 and H_2O was that the system is simple enough to investigate the plasma reaction mechanism.

As far as the reduction of CO_2 is concerned, many methods have been developed to create useful organic compounds.[1—6] Among them, the reduction of CO_2 with H_2 or CH_4 in the presence of catalysts is effective and seems to be a prominent method, so far.

Experimental

The apparatus used in the plasma reaction of CO_2 and H_2O was a quartz tubular reactor, in which a plasma was created at 2.45 GHz (microwave region), as shown in Fig. 1. A mixture of distilled and degassed H_2O and CO_2 (99.9% purity) was introduced from one end of the tubular reactor into the plasma zone. The other end was connected to a vacuum pump via a cold trap. The flow rate of CO_2 was controlled by a mass-flow controller at a fixed flow rate of 40 cm^3 (STP) min^{-1}, while that of H_2O was fixed at 40 cm^3 (STP) min^{-1} by a metering valve (unless otherwise specified). For preventing the condensation of water, the stainless-steel tubing between the water container and the reactor was heated at about 40 °C.

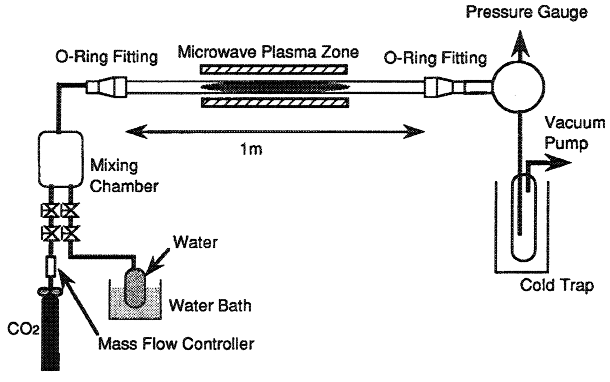

Fig. 1. Microwave plasma apparatus for the reaction of CO_2 and H_2O.

The microwave plasma reaction was carried out for 60 min, and the products were collected in the cold trap (dry ice-methanol) as an aqueous solution. The products were analyzed by reversed-phase chromatography with UV and conductivity detectors using water as an elutant.

Results and Discussion

At the beginning, H_2O plasma without CO_2 was generated and the recovery of water in the cold trap (R_{H_2O}) during the plasma reaction was determined. The results are shown in Fig. 2 as a function of the plasma energy density. The plasma energy density is an energy input against the unit mass of a gas, which is expressed in J kg^{-1}, obtained from a composite parameter of W/FM,[7] where W and FM represent the discharge wattage and mass flow (F: volume flow rate; M: molecular weight of a gas), respectively. The flow rates of H_2O in this experiment were 40 and 80 cm^3 (STP) min^{-1}.

R_{H_2O} was very high when W/FM was very low, indicating that reactions hardly proceeded in the plasma

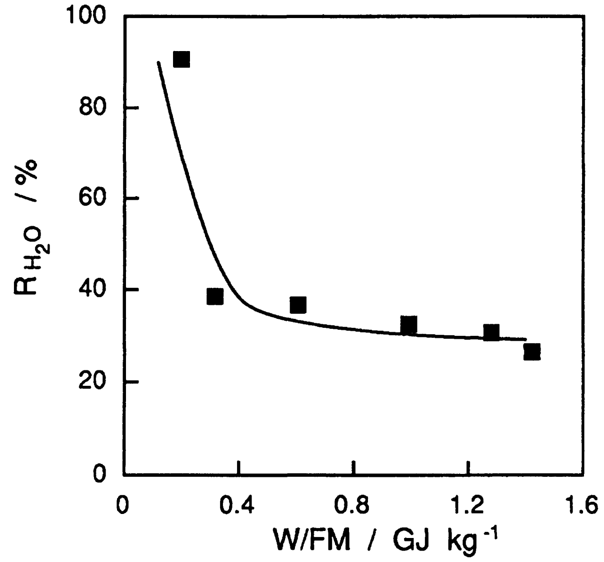

Fig. 2. Relation between the water recovery (R_{H_2O}) and the plasma energy density (W/FM) when the H_2O vapor plasma was excited without CO_2 at a flow rate of 40 cm^3 (STP) min^{-1} for 1 h.

at that energy level. (Without plasma generation, of course, 100% of the water was recovered.) When *W*/*FM* was 0.3 GJ kg^{-1} or greater, R_{H_2O} was almost constant at around 30%. The unrecovered water is believed to be converted into such substances as H_2 and O_2, which are unable to be trapped at he temperature of the cold trap.

However, the recovered water was found not to be pure. There was a plasma product found in it. The UV spectrum of the recovered water showed absorption at about 210 nm, which was assigned to be H_2O_2. The absorbance of the product (recovered water) at 210 nm was also found to be dependent of *W*/*FM*. The maximum of the absorbance was found at a *W*/*FM* of 0.60 GJ kg^{-1}, which seems to be the most appropriate energy level for H_2O_2 formation. At a lower plasma-energy density than that, the supplied energy may not be high enough to form H_2O_2, while at a higher *W*/*FM*, too much energy probably decomposes H_2O_2 to H_2 and O_2. Interestingly, exactly the same results were obtained when H_2 and O_2 (in the ratio of 2 : 1) were used as plasma gases instead of H_2O. In that case, about 30% of them reacted to form H_2O and H_2O_2.

Next, plasma reaction of a mixture of CO_2 and H_2O was carried out at three different discharge power levels: high (680 W), medium (520 W), and low (300 W). The plasma energy density for these discharge power levels correspond to 0.37, 0.29, and 0.16 GJ kg^{-1}, respectively. Figure 3 shows the relationship between the recovered amount in the cold trap ($R_{(CO_2+H_2O)}$) and the plasma energy density. In the calculation of the plasma energy density, the mean value of their molecular weight (31) was used in this case. Contrary to the case for the H_2O plasma, $R_{(CO_2+H_2O)}$ increased with the plasma energy density in the range between 0.16 and 0.37 GJ kg^{-1}. In the H_2O plasma, H_2 and O_2 are stable products which are excluded from the system. On the other hand, in the H_2O plasma with the addition of carbon (CO_2), relatively stable organic products seem to be formed and saved in the cold trap.

In order to identify the plasma products of the CO_2 and H_2O mixture, an analysis by means of reversed-phase chromatography with UV and conductivity detectors was carried out using water as an elutant. Figure 4 shows the results of the plasma products obtained at three different discharge power levels. In this figure, the chromatograms obtained by the UV detector (abbreviated as UV chromatogram) are shown upward from the bottom; those obtained by the conductivity detector (abbreviated as conductivity chromatogram) are shown downward from the top. The elution time passes from left to right.

The UV chromatogram of the products shows two peaks in all cases. The first peak (at the left), which has another absorption at its shoulder, has a corresponding peak in the conductivity chromatogram. The second peak in the UV chromatogram (at the right) has no corresponding peak in the conductivity chromatogram.

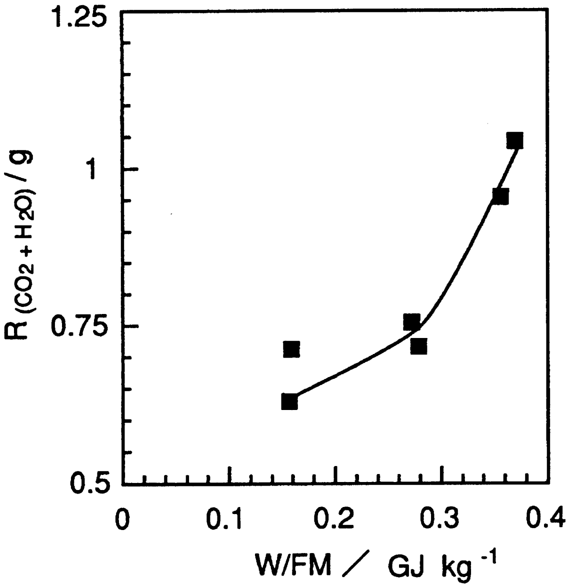

Fig. 3. Relation between the recovered amount in cold trap ($R_{(CO_2+H_2O)}$) and the plasma energy density (*W*/*FM*) when the H_2O vapor and CO_2 gas mixture plasma was excited at a flow rate ratio of 40 : 40 (cm^3 (STP) min^{-1}) for 1 h.

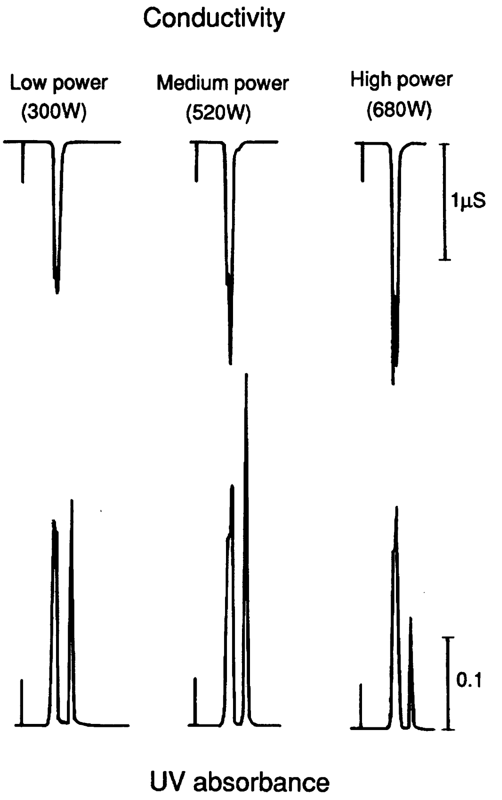

Fig. 4. LC of plasma products obtained at different powers, detected by UV and conductivity.

Figure 5 shows UV and conductivity chromatograms for H_2O_2 and a few carboxylic acids. In Fig. 6, the relative elution times for those compounds are compared

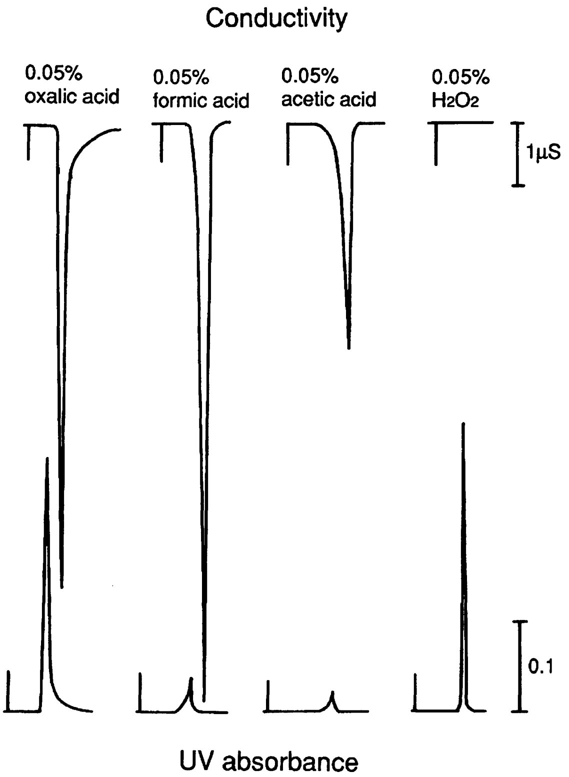

Fig. 5. LC of some chemicals detected by UV and conductivity.

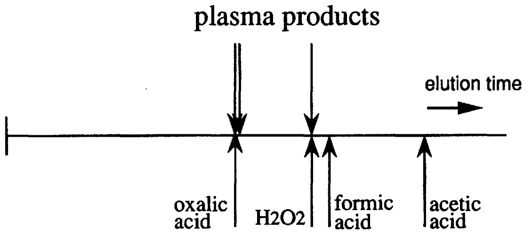

Fig. 6. LC elution time for the plasma products and some chemicals.

with those for the plasma products. As shown in Fig. 5, each of these three carboxylic acids has both UV absorption and conductivity, while H_2O_2 has only UV absorption. Although the elution time of the first and second peaks for the plasma products corresponds to that of oxalic acid and H_2O_2, respectively, but there are no corresponding compounds for the shoulder peak. The identification of the first peak as oxalic acid is also supported by the peak-strength ratio of the UV absorbance and conductivity. Looking into the peak strengths of the UV absorbance and the corresponding conductivity in Fig. 4, both peak strengths are well balanced. On the other hand, comparing the peak-strength balance among the three acids in Fig. 5, only oxalic acid has nearly balanced peaks, which matches the plasma product. Based on these results, the first and the second peaks could be assigned to oxalic acid and H_2O_2, respectively. As for the shoulder peak in the first peak, it is now under investigation.

Table 1. Yields (%) of H_2O_2 and Oxalic Acid[a)]

Discharge power (W)	300	520	680
(W/FM in GJ kg^{-1})	(0.16)	(0.29)	(0.37)
H_2O_2	14.7×10^{-3}	23.9×10^{-3}	8.3×10^{-3}
Oxalic acid	6.0×10^{-3}	6.4×10^{-3}	5.3×10^{-3}

a) During the experiment ($F_{CO_2} = F_{H_2O} = 40$ cm^3-(STP) min^{-1}), 4.71 g of CO_2 and 1.93 g of H_2O were supplied to the reactor.

The yields of the plasma products, oxalic acid and H_2O_2, at three different discharge power levels were calculated and are listed in Table 1. The highest yield was found at the medium discharge power for both oxalic acid and H_2O_2. The energy dependence is significant, especially for H_2O_2, for the same reason stated earlier concerning the H_2O plasma. The plasma products were found not only in the cold trap, but also on the inner wall of the quartz reactor. The product deposited on the wall was a transparent solid crystal film formed downstream of the outside of the plasma zone. The UV spectrum of this aqueous solution and UV and conductivity chromatograms of the reversed-phase chromatography were exactly identical to those of oxalic acid. These results imply that a great portion of the oxalic acid formed in the plasma was deposited on the inner wall of the reactor, and some reached the cold trap.

As a conclusion, we could not obtain a mixture of many organic compounds, but a lone organic compound, oxalic acid. Although the yield was very low and more useful compounds, such as alcohol, have not yet been found, control of the plasma reaction to some degree may be possible by a precise adjustment of the plasma conditions.

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