A Stoicheiometric Conversion of CO_2 + CH_4 into 2 CO + 2 H_2 by Microwave Discharge

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Microwave discharge caused a mixture of CO_2 and CH_4 to undergo a stoicheiometric conversion into a mixture of CO and H_2, while discharge of CH_4 alone gave C_2H_2 and discharge of CH_4 in Xe yielded solid carbonaceous materials.

A plasma stimulated by a radio frequency discharge is an interesting phase in which thermodynamically unfavourable reactions and reactions *via* unusual intermediates can occur. Resources of carbon are being depleted and we will have to develop recycling methods for carbon dioxide as well as for methane. Therefore the conversion of CO_2 and CH_4 into more valuable reagents is an important subject in chemistry.

In this brief paper, we report a novel endothermic process ($\Delta H^{\ominus}_{0}$ = +247.27 kJ mol^{-1}), $CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2$, caused by a plasma discharge. The reaction was performed in a closed circulation system (332 ml), where a plasma discharge was stimulated in a 10 mm diameter Pyrex tube using microwave radiation at 2450 MHz. A stable discharge was obtained with a discharge zone of 3.1 ml at a pressure of *ca.* 5 Torr with 80 W incident power. The products were analysed by gas chromatography with thermal-conductivity (TC) and flame-ionisation detectors as well as by a Q-pole mass spectrometer. The microwave discharge of methane has been reported to give acetylene as the main product[1] and we obtained the same result (Table 1). The carbon balance in the gas phase was strictly in the form of C_1—C_4 hydrocarbons; no appreciable deposition of carbon was caused by the discharge.

In contrast, if the discharge was applied to a mixture of CH_4 and rare gases such as Ar, Kr, and Xe, methane disappeared rapidly from the gas phase and was efficiently converted into solid carbonaceous materials. A typical result is shown in Table 1 where the discharge was applied for 60 s to Xe (5 Torr) containing *ca.* 6.3% of CH_4.

The carbon material balance in the gas phase corresponded to only 4% of the initial CH_4, although the conversion of CH_4 computed by $1-[CH_4]/[CH_4]_{t=0}$ was as high as 96.3%, indicating that 96% of the initial CH_4 was converted into solid carbonaceous materials. In fact, after the discharge of CH_4 and Xe mixture, when the gas phase was evacuated and a mixture of Xe and H_2 (*ca.* 20% of H_2) was discharged for 120 s, *ca.* 91.5% of the deposited carbon was recovered in the form of hydrocarbons, as shown in Table 1.

When CO_2 was added to CH_4, however, an entirely different

Table 1. Plasma discharge of CH_4 and a mixture of CH_4 + Xe.

Discharge phase	CH_4 or H_2 in Xe (%)	Time /s	Conversion (%)	%							Carbon balance (%)
				CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	
CH_4	100	60	38.8	—	24	10	58	3.9	3.3	0.5	100
Xe + CH_4	6.3	60	96.3	—	13	6	81	0	0	0	4.0
H_2	20	120		31	4.8	1.9	59	2.7	1.1	0	91.5[a]

[a] Value indicates percentage of recovered carbon from the deposition.

Table 2. Plasma discharge of a mixture of CH_4 and CO_2 (48.9 : 51.1).

Discharge phase	Time /min	Conversion (%)	%						Carbon[b] balance (%)
			H_2	CO	CO_2	H_2O	CH_4	HC[a]	
CH_4 + CO_2	4	96.5 (CH_4) 74.6 (CO_2)	40.4	46.1	7.0	3.4	0.9	2.2	107.8

[a] HC = C_2H_6 + C_2H_4 + C_2H_2 + C_3H_8 + C_3H_6. [b] Computed using a TC detector for CO_2, CO, and CH_4, a flame-ionisation detector for the hydrocarbons, and a mass spectrometer for H_2, CO, CO_2, and O_2.

reaction was brought about by the discharge. As shown in Table 2, the discharge of a 1:1 mixture of CO_2 and CH_4 yielded small amounts of hydrocarbons and carbonaceous deposits but gave CO and H_2 in stoicheiometric ratio as the main products. The carbon balance exceeds 100%, and is related to inaccuracy in the analysis; the composition was computed by combining the gas chromatographic analyses with TC and flame-ionisation detectors, and a Q-pole type mass spectrometric analysis. Considering the limitations on the accuracy from the combination of the three methods, the carbon balance in the gas phase is quite well established, and it can be concluded that during discharge in the presence of CO_2 there was no deposit of carbonaceous materials.

This unique stoicheiometric reaction may be caused by reaction of CH_4 fragments or ions with an oxygen atom or ion from CO_2 in the plasma which may prohibit the deposition of carbonaceous materials as well as the formation of hydrocarbons, and lead to CO and a small amount of water, equations (1), (2), and (3).

$$CH_4 \rightsquigarrow \text{Hydrocarbons, mainly } C_2H_2 \quad (1)$$

$$Xe + CH_4 \rightsquigarrow \text{Solid carbonaceous deposit} \rightsquigarrow \text{Hydrocarbons} \quad (2)$$

$$CO_2 + CH_4 \rightsquigarrow 2\,CO + 2\,H_2 \quad (3)$$

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