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Direct conversion of methane to methanol, chloromethane and dichloromethane at room temperature

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As methane is extremely inert, its conversion into a form suitable for chemical use has been achieved by an indirect process in which methane is first converted to synthesis gas and then to methanol and to ethylene glycol¹. One disadvantage of this route of conversion is that it requires conditions of high temperature and pressure². Here we report the direct conversion of methane to methanol, chloromethane and dichloromethane at the three-phase interface (gas/solution/electrode) on illumination at room temperature. The key steps in this process are: (1) electrochemical oxidation of the chloride ion; (2) generation of the chlorine radical under illumination; and (3) formation of the methyl radical by the reaction of methane with the chlorine radical.

In the present study, we attempted the combined photochemical and electrochemical oxidation of methane at room temperature. A conventional two-compartment glass electrolysis cell was used, with the anode compartment separated from the cathode compartment by a fritted-glass partition. A water-sealed stopcock and a Luggin capillary provided contact between the anode and the reference electrode. The anode compartment incorporated a flat quartz window through which we illuminated the cell, using as a light source a 4-W low-pressure mercury lamp (Hamamatsu TV, L937-04). The wavelength of the illumination was 254 nm. The anode comprised a platinum plate partially immersed in the anolyte, and methane was introduced above the level of the solution. Only the surface of the platinum exposed to the gas phase was illuminated. To collect volatile products, the effluent gas was passed through a trap (25 cm³) containing 20% KOH by weight. Both the electrolytic solution and the trap were kept at 25 ± 1 °C. Various strengths of KCl solution were used as electrolytes; the results presented here are for a 0.6 M KCl solution of pH 11.0.

We determined the oxidation products present in both the electrolyte and residues in the trap by steam chromatography using an Ohkura Model SSC-1 which uses steam as the carrier gas and incorporates a flame ionization detector (FID) and a Poropak R column. This equipment is capable of detecting directly organic substances dissolved in an aqueous solution, without any pretreatment³.

The steam chromatograms of the solution after electrolysis at potentials more positive than +1.3 V (compared with the standard calomel electrode, SCE) showed four peaks at 2.0, 3.3, 10.0 and 26.1 min corresponding to chloromethane, methanol, dichloromethane and trichloromethane, respectively. However, the peak due to trichloromethane was very small compared with the other three peaks. No such peaks were observed for the solution electrolysed in the dark.

Table 1 shows the amounts of CH₃Cl, CH₃OH, CH₂Cl₂ and CHCl₃ produced in the 0.6 M KCl solution at pH 11.0 for various anodizing potentials. At potentials more negative than +1.0 V, there was no oxidation of methane. Conversion to CHCl₃ and

Table 1 Yield of chloromethane, methanol, dichloromethane and trichloromethane in a 0.6 M KCl solution at pH 11.0

| V _e (V) | CH ₃ Cl | CH ₃ OH | CH ₂ Cl ₂ | CHCl ₃ |
|--------------------|--------------------|--------------------|---------------------------------|-------------------|
| 1.1 | 0.4 | 0.2 | 0.0 | 0.0 |
| 1.2 | 15.3 | 0.8 | 0.0 | 0.0 |
| 1.3 | 24.9 | 6.1 | 9.6 | 0.3 |
| 1.4 | 164.3 | 6.3 | 16.7 | 0.3 |
| 1.5 | 239.9 | 10.5 | 17.9 | 0.9 |
| 1.6 | 18.1 | 1.1 | 0.2 | 0.0 |
| 1.7 | 29.3 | 1.9 | 0.4 | 0.0 |
| 1.8 | 59.6 | 2.9 | 1.6 | 0.1 |
| 1.9 | 95.1 | 6.6 | 6.4 | 0.3 |
| 2.0 | 95.8 | 7.4 | 8.6 | 0.7 |

V_e, electrolysis potential compared with the saturated calomel electrode. Values shown are the quantities (in μmol) of electrolysis products. Electrolysis time was 3 h; volume of electrolyte 20 cm³; the anode comprised a platinum plate of area 6 cm².

CH₃OH commenced at +1.1 V, and further conversion to CH₂Cl₂ and CHCl₃ began at +1.3 V. At +1.5 V, the formation of these compounds was at a maximum, the current efficiencies being 12.8% (CH₃Cl), 0.38% (CH₃OH) and 2.05% (CH₂Cl₂) where the electric charge passed was 361.7 C. Chemical and gas-chromatographic analyses were done to detect other species such as HCHO or CO₂; however, the results were negative.

The results presented here indicate that the electrochemical evolution of the chlorine molecule and the formation of its radical on illumination are prerequisites for triggering the activation of methane. The photochemical chlorination of methane is well understood. Mixtures of methane and chlorine react rapidly in the presence of light. However, for this reaction to occur, the two gases must be mixed at an appropriate ratio, and the reaction is difficult to control as hydrogen atoms are replaced by chlorine atoms almost at random. In the combined photochemical/electrochemical method described here, the chlorination can be stopped after the initial stage because the formation of the products is a function of the electrode potential. Another feature of this method is that methane is converted directly to methanol. The formation of methanol may be explained in two ways. First, by the further oxidation of the methyl radical by electrolytic catalysis:



where MOH is the intermediate species in the electrochemical evolution of oxygen⁴. The second explanation involves hydrolysis of CH₃Cl:



Reaction (1) is endoergic, and reaction (3) seems to predominate. In fact, the formation of methanol was more favourable at higher pH. However, reactions (1) and (2) must occur because methanol was produced even in strongly acidic solution (pH 1). We are presently studying the mechanism in detail. The rather complicated effect of the anodizing potential on the formation of the electrolytic products may be related to the evolution of oxygen—that is, an oxygen or hydroxyl radical generated during anodization could act as a scavenger for chlorine and methyl radicals. That the most important step in this conversion process is the radical reaction in the gas phase is demonstrated by the very small amounts of the products yielded when a methane-saturated solution was used, but the electrode was completely immersed (the light then passing through the solution).

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