Electrochemical reduction of dichloromethane to higher hydrocarbons

A. KOTSINARIS[‡], G. KYRIACOU[*,‡], CH. LAMBROU[§]

Laboratory of Inorganic Chemistry[‡] and Laboratory of Physical Chemistry[§], Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece

The electroreduction of CH_2Cl_2 at Ni, Cu, Pt and Ag electrodes in acetonitrile and $(C_4H_9)_4NI$ 0.1 M as supporting electrolyte was studied. The half-wave potential was found to be in the range −2.2 to −2.5 V vs SCE at room temperature. From the analysis of the gaseous products it was found that methane, ethylene, chloromethane, propene and butene isomers were the main products, while at silver and platinum cathodes methane was mainly produced. The effect of the potential on the current efficiency of the gaseous products was also studied. The current efficiency of the products increases at concentration levels of CH_2Cl_2 up to 0.2 M, whereas at higher values its CE is not significantly influenced. The application of the Schultz–Flory distribution analysis to the experimental data showed that the hydrocarbons are mainly formed via polymerization of methylene radicals on the surface of Ni and Cu electrodes. At Ag and Pt electrodes the mechanism appears to be different.

Keywords: *dichloromethane, electroreduction, reduction*

1. Introduction

The direct utilization of methane as a cheap starting material for synthesis of valuable substances is difficult because of the high stability of this molecule [1]. Many efforts have been made to produce synthesis gas, ethylene or electricity from methane. Pertinent references concerning catalytic [2, 3] or novel electrocatalytic processes [4, 5] with solid electrolytes are available in the literature. To extend the practical uses of methane beyond its primary utilization as a fuel, conversion of methane to more reactive substances capable of entering into technologically useful reactions would be a worthwhile endeavour.

Chloromethane and dichloromethane are promising derivatives in this regard. These materials are the main products of the reaction of methane with chlorine under the influence of light or heat [6]. Chloromethane and dichloromethane have also been formed in an electrochemical cell under illumination [7]. An electrochemical process for the conversion of methane to chloroderivatives and the simultaneous conversion of these to useful products would be desirable. The process would be nonpolluting since no chlorine would be emitted. The chloride ion liberated at the cathode would be oxidized to chlorine at the anode and this would react with methane to give the chloroderivatives, which are again reduced at the cathode and thus the catalytic cycle with the Cl^-/Cl_2 mediator would be repeated. Chloromethane conversion by chemical processes to other chemicals has

received most attention [8–10], while little interest has been shown in dichloromethane [11, 12].

Electrochemical processes for the conversion of the chloroderivatives of methane to higher hydrocarbons have not been reported. Polarographic and voltammetric studies with dichloromethane and other chloroderivatives have been performed without identification of the products [13–16]. The present study is mainly concerned with the detection and identification of the gaseous products of the cathodic reduction of dichloromethane at different electrodes in acetonitrile medium.

2. Experimental details

Electrolysis was performed in a three compartment glass cell equipped with a saturated calomel electrode (SCE) as reference. The cathodes were Ni (99.99%), Ag (99.9%), Pt (99.9%) and Cu (99.999%) in the form of foils with respective areas 39, 49, 31.5 and 45 mm². The first three were supplied by Aldrich Chemical, and the copper by Alpha Metal. Ni, Pt and Ag electrodes were polished with alumina with particle size down to 0.05 μm; they were then placed for 20 s in HNO_3 solution (5% w/v) and were washed many times with distilled water. Cu was electropolished in H_3PO_4 85% and washed with distilled water. The solvent was acetonitrile (Lab Scan) containing 0.1% water and 0.1 M $(C_4H_9)_4NI$ as supporting electrolyte. The CH_2Cl_2 concentration was 0.155 M, unless stated otherwise. The concentration change was never greater than 5% during each experiment.

The gaseous products were identified by gas chromatography by comparing their retention times

* Author to whom correspondence should be addressed.

with standards on different columns using an FID detector. The products were withdrawn from the cell by a flowing stream of nitrogen with a constant flow rate of $20 \, ml \, min^{-1}$. Estimation of the current efficiency of each of the products was made by dividing the measured concentration in the nitrogen stream by the theoretical concentration assuming all the current was used for the formation of this particular product. A similar method was used in a previous study for the estimation of CE of the gaseous products from CO_2 electroreduction [17].

3. Results

3.1. *Influence of the cathode*

Cyclic voltammetry showed that the reduction of CH_2Cl_2 on Ni, Cu, Pt and Ag began at -1.8 V vs SCE and the half wave potentials were between -2.2 and -2.5 V vs SCE, while reduction of the electrolysis medium occurred at potentials below -3.0 V. This is in general agreement with observations of previous workers at Hg, Pb [14, 18] and Ag, Pt [19, 20] cathodes. The form of repeated voltammograms change, probably because of electrode deactivation. This change made it difficult to obtain reliable voltammograms. Preparative electrolyses were carried out at -2.6 V vs SCE, close to the voltammetric half wave potentials.

3.1.1. *Nickel electrode.* The main gaseous products using a solution containing 0.155 M CH_2Cl_2, were methane, ethylene, propylene, isomeric butenes, chloromethane and small amounts of C_5 and C_6 hydrocarbons. Analysis of the catholyte by GCMS showed the presence of propanonitrile, butanonitrile and 1,2 dichloromethane. Other products were not identified. Analysis of the catholyte after the passage of 288.9 C charge by ion chromatography showed the presence of Cl^-. The expected amount based on the electrical charge was 0.106 g, while the determined amount was 0.088 g. The electrolysis solution initially became yellowish and gradually turned reddish. Similar behaviour was observed by other workers [18, 20], who studied the electroreduction of halogenated compounds in acetonitrile. The amount of main products, as shown in Fig. 1, is an almost linear function of the passed charge for all products.

The reproducibility of the experiments at nickel was about 15%.

Dichloromethane was converted to unsaturated hydrocarbons with average CE 12% for $CH_2=CH_2$ and 7.2% for isomeric butenes. Propene, not shown in the figure, was less than 1%. About 18.5% of the charge was consumed for the formation of CH_3Cl. The remainder of the charge was consumed for the formation of methane (24%) and for various liquid catholyte products. Figure 2(a) shows that the current increased during the first 10 min, gradually levelled off and finally stabilized at 36 mA corresponding to a current density $92.7 \, mA \, cm^{-2}$. Apparently, at the
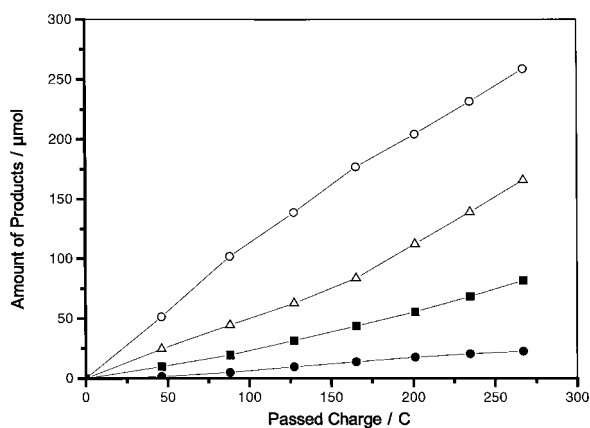

Fig. 1. Dependence of the amount of main products of CH_2Cl_2 reduction on the passed charge at a nickel electrode at -2.6 V vs SCE ($\triangle$) methane, ($\blacksquare$) ethylene, ($\bigcirc$) chloromethane and ($\bullet$) isomeric butenes.

high electrode potentials, used, electrode deactivation does not occur to the extent as in the cyclic voltammetric runs.

3.1.2. *Copper electrode.* Results at copper were qualitatively similar to those at nickel. The CE for methane was about 40% and for ethylene about 8%. Chloromethane with an approximate CE of 5% and traces of isomeric butenes were also detected. Figure 3 shows the dependence of the amounts of chloromethane, methane, ethylene and propene on the charge passed. The ratio of the products against charge passed was constant, although the current gradually decreased from 32 to 12 mA after 1.5 h, as depicted in Fig. 2(b).

It should be noted that the interruption of electrolysis for five minutes reestablished the initial current. The decrease in current may be attributed to the slow diffusion of products from the electrode surface.

3.1.3. *Silver and platinum electrodes.* At silver and platinum the main gaseous product was methane with current efficiencies about 90% and 17%, respectively. Unsaturated hydrocarbons were detectable only in traces.
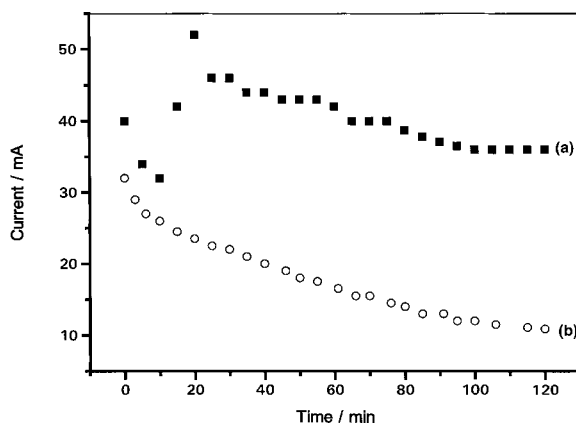

Fig. 2. Current against time for the reduction of CH_2Cl_2 at -2.6 V vs SCE (a) at a nickel and (b) at a copper electrode.
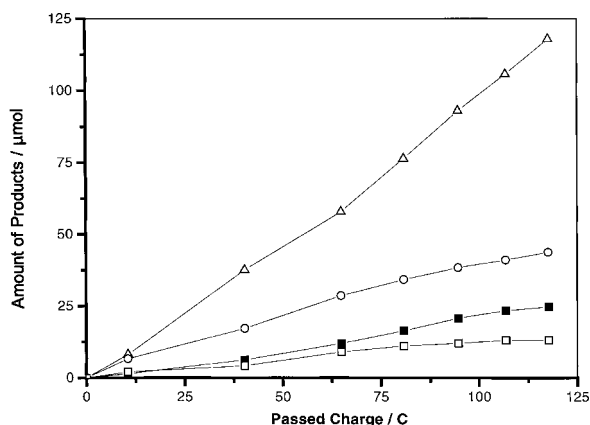
Fig. 3. Dependence of the amount of main products of CH_2Cl_2 reduction on the passed charge at a copper electrode at $-2.6\,V$ vs SCE ($\triangle$) methane, ($\blacksquare$) ethylene, ($\bigcirc$) chloromethane and ($\square$) propene.

Fig. 5. Current efficiency against concentration of CH_2Cl_2 at a copper electrode at $-2.6\,V$ vs SCE ($\triangle$) methane, ($\blacksquare$) ethylene.

3.2. Influence of applied cathodic potential

The influence of the applied potential on the average CE of the main products was studied at a copper cathode and for an electrolysis time of 120 min. Figure 4 shows experimental results for methane, ethylene and chloromethane. The CEs vary with potential and tend to stabilize beyond $-2.4\,V$. The change in CE is greatest for methane and reaches a minimum at about $-2.2\,V$ and then increases until it stabilizes at about $-2.4\,V$.

3.3. Effect of the concentration of CH_2Cl_2 on the reduction products

The average CE for methane and ethylene as a function of CH_2Cl_2 concentration at a copper electrode at a $-2.5\,V$ vs SCE is shown in Fig. 5. It appears that above about 0.2 M CH_2Cl_2 the CE does not change significantly, but below 0.2 M it decreases with corresponding decrease in the total current.

4. Discussion

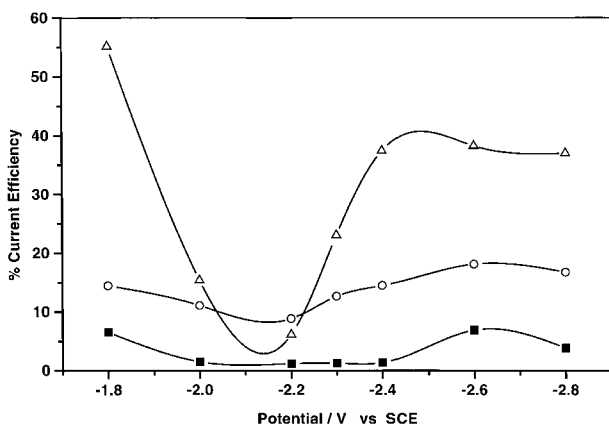It is suggested [16, 18] that the electrochemical reduction of dichloromethane proceeds as follows:

$$CH_2Cl_2 + 2e^- \longrightarrow CH_2Cl^- + Cl^- \qquad (1)$$

$$CH_2Cl^- \rightleftharpoons :CH_2 + Cl^- \qquad (2)$$

The results indicated that the reduction products are influenced significantly by the nature of the working electrode. To clarify the mechanism of hydrocarbon formation the Schultz–Flory distribution analysis as proposed by Kudo et al. [21] for electrochemical reactions was applied to the results depicted in Figs 1 and 3. The distribution is expressed by the following equation:

$$\ln(m_p/P) = \ln(\ln^2 \alpha) + P \ln \alpha \qquad (3)$$

where m_p is the weight per cent of the hydrocarbon whose carbon number is P and α represents the probability of chain growth.

Figure 6 shows the Schultz–Flory distribution for the copper and nickel electrodes. The correlation coefficients were found to be 0.978 and 0.957, respectively, which shows that the linearity between P and $\ln(m_p/P)$ was satisfactory. The probability, α, determined from the slope of the lines by the least squares method was found to be 0.247 and 0.485, respectively. This indicates that the higher hydrocarbons are possibly formed via polymerization of the :CH_2 radicals, adsorbed on the electrode surface. This

Fig. 4. Current efficiency against potential for the main products of the reduction of CH_2Cl_2 at a copper electrode ($\triangle$) methane, ($\blacksquare$) ethylene and ($\bigcirc$) chloromethane.
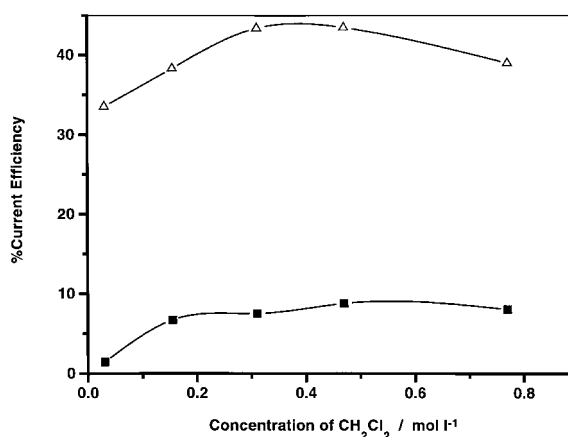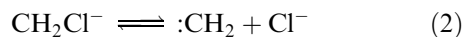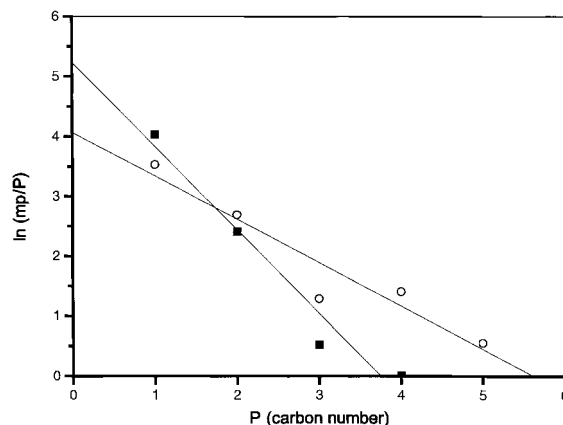

Fig. 6. Shultz–Flory plots of hydrocarbons formed on Ni ($\bigcirc$) and ($\blacksquare$) Cu electrodes by electrochemical reduction of CH_2Cl_2.

mechanism is similar to that of the Fischer–Tropsch reaction [22]. It is worth noting that the value of possibility, α, at nickel is similar to that found during the electrochemical reduction of CO_2 ($\alpha = 0.36$) [21]. The value of α for Ni was greater than that for Cu, which is in agreement with the fact that Ni is a better Fischer–Tropsch catalyst than Cu [23]. According to the literature [24], the decomposition of the supporting electrolyte through the reaction with methylene radicals leads to the formation of C_4 hydrocarbons with parallel formation of tributylamine. In our case tributylamine was not detected and this fact leads to the conclusion that this is not the main reaction path for the formation of C_4 hydrocarbons.

At platinum and silver electrodes the only hydrocarbon detected was methane, with a CE approaching 90%. It is possible that the products are formed at these electrodes by a free radical mechanism [14, 24].

$$:CH_2 + 2CH_3CN + 2e^- \longrightarrow CH_4 + 2[CH_3CN^-]$$
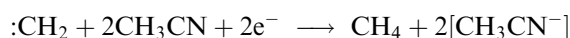
It is possible that 1,2 dichloroethane and chloromethane which were found in the products are formed through the following reactions [25]:

$$CH_2Cl^- + CH_2Cl_2 \longrightarrow ClCH_2CH_2Cl + Cl^-$$

$$CH_2Cl^- + CH_3CN \longrightarrow CH_3Cl + CH_2CN^-$$
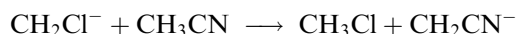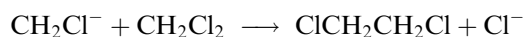
On the basis of the products detected at nickel and copper electrodes it is clear that the above mentioned reactions also play an important role.

References

[1] E. E. Wolf, 'Methane Conversion by Oxidative Processes', Van Norstrand Reinhold, New York (1992).
[2] C. N. Satterfield, 'Heterogeneous Catalysis in Industrial Practice', 3rd edn, McGraw-Hill, New York (1991).
[3] M. Goula, A. Lemonidou, A. Efstathiou, *J. Catal.* **161** (1996) 626.
[4] M. Stoukides, *J. Appl. Electrochem.* **25** (1995) 899.
[5] J. Anderson, *Appl. Cat.* **47** (1989) 177.
[6] Kirk-Othmer, 'Encyclopedia of Chemical Technology', 3rd edn, J. Wiley & Sons, Vol. 5, New York (1978), pp. 668–93.
[7] K. Ogura and K. Takamagari, *Nature* **319** (1986) 308.
[8] P. Lersch and F. Bandermann, *Appl. Catal.* **75** (1991) 133.
[9] M. White, L. Douglas, J. Hackett and R. Anderson, *Energy & Fuels* **6** (1992) 76.
[10] Y. Soong, A. Blackwell, R. Scehehl and R. Noceti, *Fuel Sci. Technol. Int.* **11** (1993) 937.
[11] J. Tavakoli and J. Doney, *Chem. Engng Commun.* **119** (1993) 135.
[12] J. Tavakoli, M. Chiang, J. Bozzelli, *Combust. Sci. Technol.* **101** (1994) 13.
[13] I. Kolthoff, T. Lee, D. Stoceva and E. Parry, *Anal. Chem.* **22** (1950) 521.
[14] G. Girina, V. A. Kokorekina, Zh. I. Krinets, V. A. Petrosyan and L. G. Feoktistor, *Elektrokhimiya* **26** (1990) 1102.
[15] J. Hine and S. Ehrenson, *J. Am. Chem. Soc.* **22** (1958) 824.
[16] S. Wawzonek and R. Duty, *J. Electrochem. Soc.* **108** (1961) 1135.
[17] Y. Hori, A. Murata and R. Takahashi, *J. Chem. Soc., Faraday Trans. I* **85** (1989) 2309.
[18] H. Fritz and W. Kornrumpf, *Liebigs Ann. Chem.* (1978) 1416.
[19] G. Horanyi and K. Torkos, *J. Electroanal. Chem.* **140** (1982) 329.
[20] D. Coutagne, *Bull. Soc. Chim. Fr.* **38** (1971) 1940.
[21] A. Kudo, S. Nakagawa, A. Tsuneto and T. Sakata *J. Electrochem. Soc.* **140** (1993) 1541.
[22] P. Maitlis, H. C. Long, R. Quyoum, M. L. Turner and Z. Q. Wang, *Chem. Commun.* (1996) 1.
[23] R. B. Anderson, 'The Fischer–Tropsch Synthesis', Academic Press, Orlando (1984).
[24] S. Wawzonek, R. Duty and J. Wagenknecht, *J. Electrochem. Soc.* **111** (1964) 74.
[25] J. Nedelec, H. Moluloud, J. Folest and J. Perichon, *J. Org. Chem.* **53** (1988) 4720.