Electrolytic Behaviour of 1,2-Dichloroethane–Ethylene Mixtures Towards Aluminium Anodes

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Ethylene dissolved under medium pressure in an electrolytic solution containing 1,2-dichloroethane and tetrabutylammonium chloride is polymerized to partly unsaturated oils, by means of anodic dissolution of pure aluminium anodes. At low current densities the rate of conversion is determined by the current, and a kinetic relation is experimentally drawn.

VARIOUS electrochemical methods of producing metal complexes which can act as catalysts for polymerization of olefinic compounds have been reported.[1-3] In particular formation of high-molecular-weight polyethylene, by means of anodic dissolution of aluminium with a small amount of a transition metal in an electrolytic solution containing 1,2-dichloroethane, ethylene, and tetrabutylammonium chloride, has been described.[4] However aluminium alone, if anodically dissolved in the same electrolytic solution, causes formation of branched-chain oily polymers of ethylene. The extent of this reaction can be controlled by means of suitable choice of current and anodic-current density at temperatures *ca.* 0 °C or lower, so that, if the aim is production of polyethylene, the quantity of oils obtained as by-product can be limited to a few percent of converted ethylene. Otherwise, only oily polymers are obtained, under the same conditions which allow synthesis of polyethylene, if the presence in the solution of transition metals such as chromium, vanadium, or titanium is carefully avoided, particularly by use of very pure aluminium anodes.

EXPERIMENTAL

A pressure-resistant cell (capacity 250 cm^3), analogous to those already described,[5,6] was employed in all experiments. As a relatively thin layer of solution between the electrodes was desirable in order to limit ohmic dissipation and allow temperature control, stirring of the layer and its mixing with the bulk of solution were effected by use of an aluminium-net cathode, and of a magnetically driven stirrer (Figure 1). The cell was dipped in a water–ethylene glycol thermostat bath. Blank experiments showed that heat exchange through the wall of the cell was sufficient to maintain the temperature increase within 1 °C, with an internal dissipation ranging from 0 to 0·5 W.

Conversion of ethylene with time was evaluated by plotting equilibrium pressure against amount of ethylene present in the cell, with a given amount of 1,2-dichloroethane (36 g), and checked with the weight of oils obtained. Oils were recovered by hydrolysis of the effluent with aqueous HCl, extraction and washing with H_2O, and stripping of the solvent and other volatile products at 50 °C, *in vacuo*.

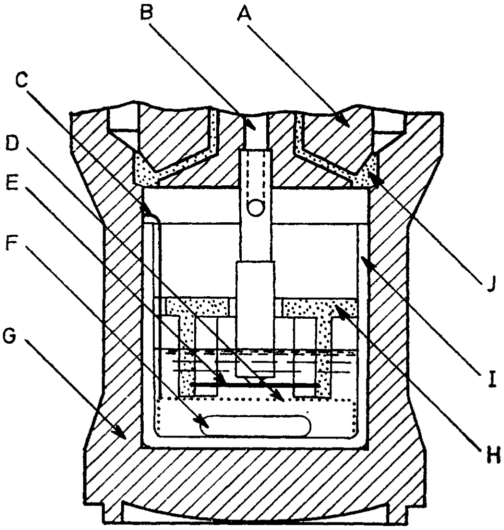

FIGURE 1 Electrode assembly for electrolytic polymerization of ethylene: A, cell head; B, gas duct; C, cathode electrical connection; D, aluminium-net cathode; E, aluminium-disk anode; F, magnetic stirrer; G, cell body; H, Teflon anode holder; I, glass beaker; J, insulating gasket

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Polymerization of ethylene on electrolysis

Expt.	Dissolved Al (g)	Mean oxidation state	Electrical charge (C)	Current (mA)	Reaction time after electrolysis (h)	C_4H_2 Pressure (atm) Initial	Final	Oils (g)	Polyethylene (g)
(1)	0·156	1·8	1 000	25	50	20·2	17·2	1·3	
(2)	0·213	1·57	1 200	25	50	20·6	15·5	2·5	
(3)	0·394	1·53	2 160	25	50	22·6	0·5	10·0	
(4)	0·396	1·53	2 160	50		23·3	7·1	6·3	
(5)	0·380	1·59	2 160	25		23·0	9·2	5·5	
(6)	0·386	1·56	2 160	50 *		22·4	6·4	6·4	
(7)	0·108	1·68	650	2		27·9	26·0	0·92	0·53
(8)	0·179	1·53	980	2		28·0	21·3	2·4	3·45
(9)	0·269	1·51	1 450	2		30·0	15·9	2·6	8·5
(10)	0·125	1·57	700	2	240	32·9	19·3	2·4	13·0

Solvent, 1,2-dichloroethane (36 g); electrolyte Bu_4NCl (0·3 g); 0 °C. Expts. (1)—(6), Al anode (99·99%, 10 cm^2); (7)—(10) Al anode (99·5%, 10 cm^2); aluminium-net cathode. Constant current maintained in each electrolysis. Voltage in the range 30—2·5 V.

* Square pulses, 50 mA peak, 0·01 Hz.

RESULTS

Ethylene was converted to oily polymers having a mean molecular weight of *ca.* 500 (by cryoscopy in benzene), $\nu_{max.}$ at 2 900, 1 460, and 1 380 cm^{-1}, ratio of methyl C–H bonds to others 3 : 2, 20% unsaturated C–C bonds, relative to the mean-molecular-weight hydrocarbon. This product was obtained by anodic dissolution of aluminium in 1,2-dichloroethane containing tetrabutylammonium chloride as electrolyte, and filling of the cell with ethylene after interruption of electrolysis [expts. (1)—(3), Table]. The rate of conversion increased sharply with initial concentration of aluminium in solution [Figure 2, plots (1)—(3)].

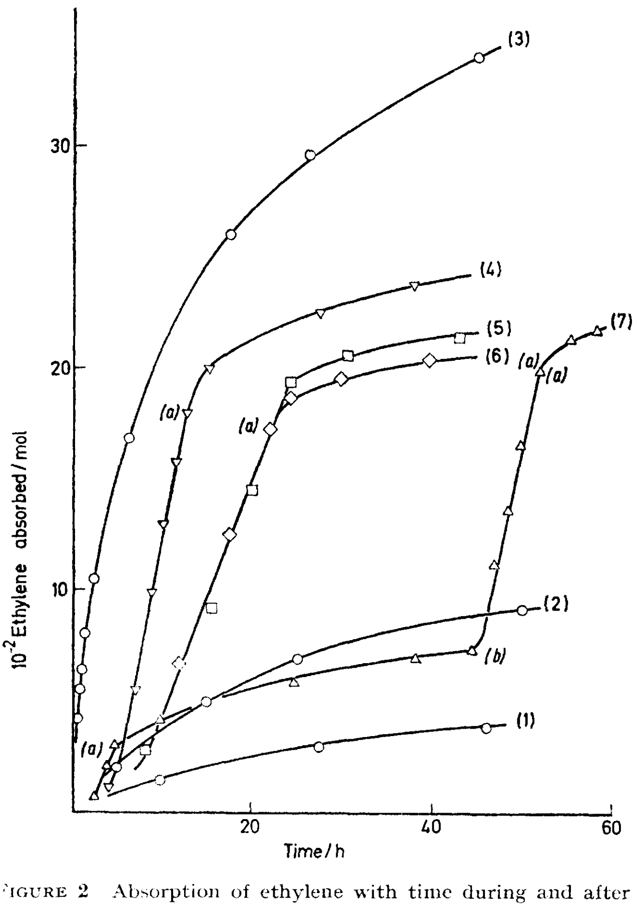

FIGURE 2 Absorption of ethylene with time during and after electrolysis: plots (1)—(6) correspond to expts. (1)—(6) in the Table

A set of experiments at constant current was carried out with ethylene present at commencement of electrolysis. Although the current density was not quite uniform on the surface of the electrodes, and its distribution probably not strictly constant in time, the results were consistent (if the current density did not exceed 4 mA cm^{-2} at 0 °C) with the rate of conversion of ethylene, except for an initial stage, being proportional to the current. Comparable values of ethylene conversion, of mean oxidation state of dissolved aluminium (*ca.* 1·5), and of mean molecular weight of oils, were obtained by using the same quantity of electricity at a steady current of 50 mA [expt. (4)], 25 mA [expt. (5)], or with periodic square-current pulses of 50 mA corresponding to a mean value of 25 mA [expt. (6)]. Figure 2 shows diagrams of absorbed ethylene as a function of time for these experiments [plots (4)—(6)]. In each case a stationary state was attained, where the gradient of the plot is proportional to the current. If electrolysis was interrupted [points (*a*)] absorption continued with decreasing rate; however the gradient of the plot at the previous steady state was reattained if electrolysis was restarted [plot (7), point (*b*)].

If technical-grade (99·5%) aluminium anodes were employed (Ti *ca.* 0·02%; other transition metals *ca.* 0·4%) polyethylene and branched polymers were obtained. The course of the overall conversion, and the weight ratio of the polymers during electrolysis, was examined by a set of slow-conversion experiments, of increasing length. After an initial induction stage, the yield of polyethylene, referred to overall conversion of ethylene, was proportional to time, at constant current [expts. (7)—(9)]. Moreover if the current was stopped during the course of reaction, absorption continued at almost constant rate and the main product of this spontaneous reaction was polyethylene [expts. (8) and (10)].

The mean oxidation state of the dissolved Al anode was always *ca.* 1·5 [except in the early stages of electrolyses, as shown in expt. (1)], and cathodic reaction was found to produce 1 g-ion Cl$^-$ for each electron equivalent; thus the overall balance of electrode reactions is consistent with the well known reaction (1)[7] (R = 2-chloroethyl). In fact

$$2Al + 3RCl \longrightarrow R_2AlCl + RAlCl_2 \qquad (1)$$

ethyl chloride was detected by gas chromatography in the hydrolysed effluent of blank electrolyses in the absence of ethylene.

DISCUSSION

The plots of adsorption of ethylene during electrolysis with pure aluminium anodes show that, at low currents, the electrode process becomes the rate-determining step in the polymerization. Relation (2) can be drawn

$$-\,\mathrm{d}n_{C_2H_4}/\mathrm{d}t = 1{\cdot}3 \times 10^{-4} I \qquad (2)$$

empirically at 0 °C, c.d. <4 mA cm^{-2}, and I, n, and t have the units A, mol, and s respectively. This stoicheiometric correspondence suggests, in contrast to spontaneous polymerization in pre-electrolysed systems, kinetic coupling between oligomerization and electrode process. However it is improbable that ethylene is directly involved in the electrode processes; the results are consistent with anodic polarization during electrolysis leading to a high concentration of initiating species at the electrode surface (indeed the limit layer of the anolyte appears to be the site of initiation during electrolysis). In this respect it may be recalled that ethylene has been reported to depolarize aluminium anodes in dichloromethane.[8]

When technical-grade aluminium anodes are employed, the dependence on current and time of the distribution products suggests that two distinct catalytic effects are present. One, rate-determined by the anodic process leads to branched oligomers, while the other, rate-determined by chain growth, leads to polyethylene.

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