Use of the rotating ring disc electrode for electrochemically-induced redox initiation of aqueous polymerization

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(Received 12 July 1978)

The redox polymerizations of acrylic acid, acrylamide, methacrylic acid and acrylonitrile were conducted in aqueous solution on a micro scale with the rotating ring disc electrode. The redox couple was Cu(I)/$S_2O_8^{2-}$, and the Cu(I) was generated at the disc of the electrode system, whereas the ring current reflected the Cu(I) which reached the ring. In essence the Cu(I) and monomer compete for the $SO_4^{\overline{\cdot}}$ radical ion, and the relative rates and rate constants of these steps are deduced from the electrochemical measurements. The relative reactivities of the monomers towards the $SO_4^{\overline{\cdot}}$ were thus determined and are indicative of the initiation step in the respective polymerizations.

The primary process in many electrochemically-initiated polymerizations is the formation of a chemically active species by electron transfer. This may be viewed as the electrochemical formation of a catalyst. A familiar model system is the Fenton reagent for the formation of OH• radicals by the interaction of Fe(II) with H_2O_2. If the Fe(II) is formed from Fe(III) *in situ* at the electrode, the rate of OH• formation and of polymerization is controlled by the passage of current.

These redox systems are remarkably complex in their detailed overall chemistry. The elementary steps of electrochemical reduction, radical formation and monomer initiation are intertwined. Furthermore the metal ions may act as terminators as well as initiators of the polymerization[1,2]. We considered it desirable to study and quantify the individual processes separately. The system chosen is the $S_2O_8^{2-}$/Cu(I) activated redox couple. The system was investigated with the rotating ring disc electrode (*RRDE*).

The rotating ring disc electrode developed by Frumkin[3] provides a powerful and revealing technique for the study of chemical and electrochemical reactions. The reactions of short-lived transient species can be investigated quantitatively and pertinent rate constants of competitive reactions obtained.

The electrode consists of two separate electroactive surfaces, the inner disc and, separated from it by an insulated band, an outer ring electrode. The addition of this second electrode to the conventional disc electrode makes possible the virtually simultaneous detection at the ring of substances generated at the disc.

The technique permits precisely defined mass transport conditions to be set, and a quantitative treatment of hydrodynamic and diffusion behaviour can be made[4,5].

In essence, an ion reduced at the disc is collected at the ring electrode. The ratio of ring to disc currents is termed the collection efficiency, N_0, and is a constant defined by the geometry of the electrode. If an intervening chemical reaction occurs in the transit time between disc and ring, the collection efficiency will be altered. The variation of collection efficiency with concentration of an added reagent may be employed to determine the kinetic parameters of competing reactions.

The technique has been used previously to examine the polymerization of various monomers by electrochemically generated persistent stable cations[6]. In the present studies, the *RRDE* was employed to study the electrochemically induced redox initiation of aqueous polymerization. Two parameters (i) the rate of formation of radicals and (ii) the efficiency of capture of these radicals by monomer were investigated.

We had previously determined[7] that the redox system Cu(I)/$S_2O_8^{2-}$ produced radicals very rapidly. The rate of formation of $SO_4^{\overline{\cdot}}$ was determined to be 6300 l/mol/sec. Polymerization induced by this redox pair has not been investigated previously. In this paper we report the polymerization kinetics of several water-soluble monomers initiated by this system.

The reaction between cuprous ion and peroxydisulphate is complex. Adopting the mechanism proposed by Kolthoff[8] we can write:

$$Cu^+ + S_2O_8^{2-} \xrightarrow{k_1} Cu^{2+} + SO_4^{\overline{\cdot}} + SO_4^{2-} \quad (1)$$

$$Cu^+ + SO_4^{\overline{\cdot}} \xrightarrow{k_2} Cu^{2+} + SO_4^{2-} \quad (2)$$

$$M + SO_4^{\overline{\cdot}} \xrightarrow{k_3} \cdot MSO_4^- \quad (3)$$

in which reaction (1) is the rate determining step.

The disc current i_d is determined by the electrode reaction

$$Cu^{2+} + e \rightarrow Cu^+ \quad (4)$$

and the ring current i_r is determined by

$$Cu^+ \rightarrow Cu^{2+} + e \quad (5)$$

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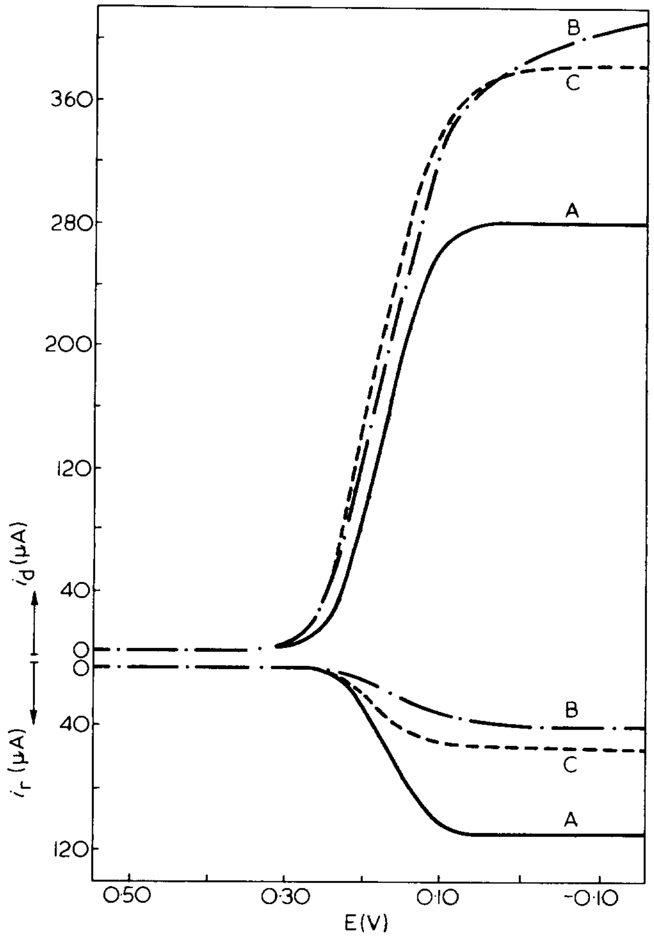

Figure 1 Disc and ring currents: A, 2 mM Cu(II); B, A with 2 mM $S_2O_8^{2-}$; C, B with 0.286 M AN; ω = 694 rpm; supporting electrolyte, 0.5 M KCl; temperature = 25°C

In the presence of peroxydisulphate, Cu(I) formed at the disc reacts very rapidly with $S_2O_8^{2-}$ and $SO_4^{\overline{\cdot}}$ regenerating Cu(II) which is again reduced at the disc in an electrocatalytic reaction. There will thus be a limiting increase and decrease in i_d and i_r respectively. When monomer is present in the system, reactions (2) and (3) are competitive for $SO_4^{\overline{\cdot}}$ and the amount of Cu(I) reaching the ring electrode (or Cu(II) detected at the disc electrode) will depend upon the concentration of monomer and the relative rates of reactions (2) and (3).

EXPERIMENTAL

The apparatus and techniques have been described previously[6].

Materials

Acrylic acid, methacrylic acid and acrylonitrile were distilled on a spinning band column prior to use. Acrylamide was recrystallized from chloroform and washed with benzene then dried under vacuum at room temperature for 24 hours.

Water was doubly distilled, then purified by percolation through an ion-exchange demineralization. Inorganic salts were analytical grade and were not purified further.

The solutions were deaerated and thermostatted at 25° ± 0.1°C for electrical measurements. All potentials were measured with respect to the *SCE*.

RESULTS AND DISCUSSION

Typical sweeps showing reduction and oxidation are presented in *Figure 1*. The solid curve A is obtained with Cu(II) only. When $S_2O_8^{2-}$ is added the disc current increases and curve B is obtained. On addition of monomer the competition for $SO_4^{\overline{\cdot}}$ reduces the electrocatalytic effect and curve C is obtained. Corresponding behaviour is evident from the plots of ring current.

Plots of i_d and i_r vs. $\omega^{1/2}$ are presented in *Figure 2* for various concentrations of acrylamide.

The experimental collection efficiency, N_0, is in good agreement with the calculated value of 0.399. Both i_d and i_r are linearly dependent on $\omega^{1/2}$. In the absence of perturbing reactions the plots pass through the origin as expected from the Levich equation[9,10].

$$i_L = 0.62\, n\, FAD^{2/3}\, \upsilon^{-1/6}\, \omega^{1/2} C^b \qquad (6)$$

where i_L = limiting current; n = no. of electrons transferred; F = Faraday constant; A = area of the electrode; D = diffusion coefficient; υ = kinematic viscosity; C^b = bulk concentration of electroactive species; ω = radial velocity of rotation.

It can be seen that the currents are significantly affected by the addition of $S_2O_8^{2-}$. i_d and i_r reach their maximum and

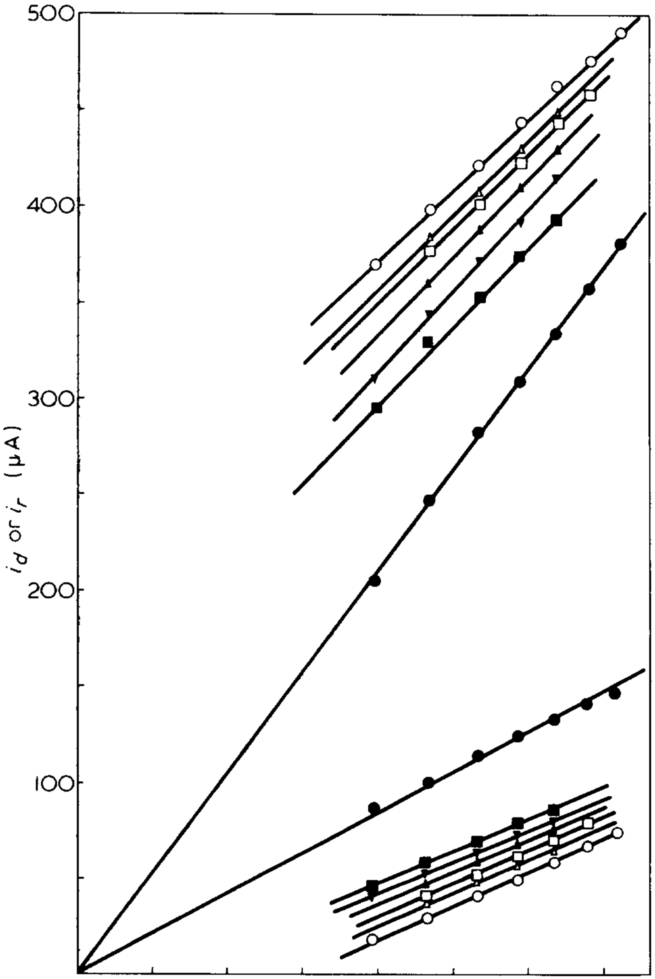

Figure 2 Ring and disc currents vs $\omega^{1/2}$ for various concentrations of acrylamide. All solutions: 2 mM Cu(II)/2 mM $S_2O_8^{2-}$/0.5 MKCl/ 25°C, except Cu(II) blank run. Monomer concentrations: △, 0.022M; □, 0.044M; ▲, 0.088M; ▲, 0.132M; ■, 0.176M; ○, 0.0M

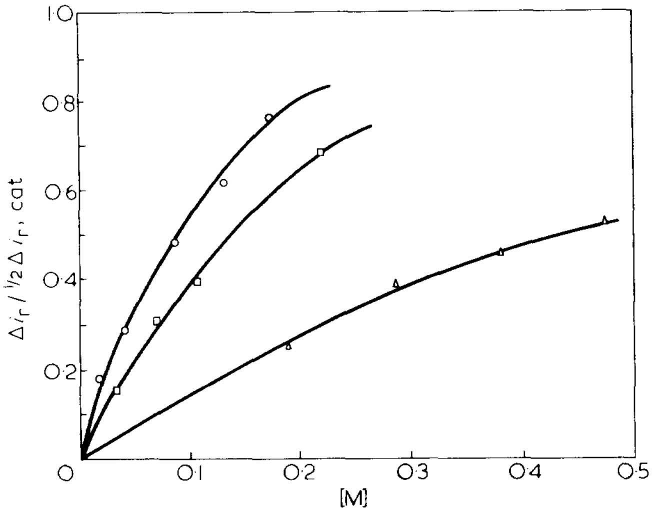

Figure 3 Fractional change in i_r with monomer concentration: ○, acrylamide; □, methacrylic acid; △, acrylonitrile

minimum values respectively as a result of the homogeneous reactions (2) and (3). Evidence was previously presented that $S_2O_8^{2-}$ was not electroreduced in the range of potential investigated. The rate of reaction (2) may be calculated directly from the kinetic collection efficiency N_K. When monomer is added, reaction (2) competes with reaction (3) and corresponding increases in i_r and decreases in i_d are observed. With excess monomer, reaction (2) will be suppressed completely and only reaction (1) will be effective. Under these conditions the changes in i_r and i_d will be one half of the catalytic effect due to $S_2O_8^{2-}$ alone, because the rate determining step, (1), is independent of monomer concentration.

At monomer concentrations intermediate between these two extremes the changes in i_r and i_d reflect the competitive effects of reactions (2) and (3).

Thus when the rates of (2) and (3) are equal catalytic current should be ½ of the maximum attainable change, i.e :

$$k_2[SO_4^{-}]\,[Cu(I)] = k_3[SO_4^{-}]\,[M] \qquad (7)$$

or

$$\frac{k_2}{k_3} = \frac{[M]}{[Cu(I)]} \qquad (8)$$

This expression is identical to that obtained by Baxendale[11] from the stationary state method. Orr and Williams[12] studied the Fe(II)/H_2O_2 and Fe(II)/$S_2O_8^{2-}$ systems and found:

$$\frac{R_1}{R_2} = \frac{k_2}{k_3}\,\frac{[Fe(II)]}{[M]} \qquad (9)$$

where R_1 and R_2 are the fractions of the total radicals produced which have reacted in steps (2) and (3) respectively. When $R_1 = R_2$ equations (8) and (9) are identical

The fractional change in ring current ($\Delta i_r/½\Delta i_r$ cat) with varying concentrations of acrylamide methacrylic acid and acrylonitrile are shown in *Figure 3.* The ratio k_2/k_3 for several monomers are shown in *Table 1.*

Table 1 Relative reactivities of monomers with $SO_4^{-\cdot}$

Monomer	k_2/k_3	k_3 relative
Acrylic acid	23	1 (standard)[7]
Acrylamide	44	0.52
Methacrylic acid	69	0.33
Acrylonitrile	205	0.11

Since acrylamide is a very efficient scavenger of OH· radicals one should consider the possibility of initiation by the following mechanism:

$$SO_4^{-} + H_2O \rightarrow HSO_4^{-} + OH\cdot \qquad (10)$$

$$M + OH\cdot \xrightarrow{k_{11}} M\cdot \qquad (11)$$

The value of k_{11} has been reported to be 1.1 x 10^{11} l/mol/min[13]. However, recent flash photolysis studies indicate that reaction (10) is not likely to be significant at pH below 8.5 [14]. Results by Riggs *et al.*[15] on the peroxydisulphate initiated polymerization of acrylamide support this view.

The relative reactivities listed in *Table 1* are indicative of the initiation step in the polymerization. The quantification of this effect in contradistinction to the effectiveness of the initiator has been reported for only a few systems. The *RRDE* technique is well suited to this probing of the mechanism. It allows the study to be performed without sensible change in the monomer concentration and avoids the build-up of ionic species which may alter the polymerization process and introduce further complexities into the reaction mechanism.

ACKNOWLEDGEMENT

This work was supported by a grant from the National Research Council of Canada.

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