

Electrochemical impedance study of the reaction mechanism for electro-oxidation of isosorbide*

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Electrochemical impedance measurements in the anodic range were made in 0.1 and 1 M solutions of sodium bromide using a rotating platinum disc electrode. It has been shown that bromide is oxidized in a rapid transfer reaction accompanied by diffusion of a bromine intermediate species, which was thought to be bromine itself. At 1 M, a further reaction was observed involving formation of the tribromide ion Br_3^- in the vicinity of the electrode. In a second set of experiments, impedance was measured in the presence of isosorbide. The overall shape of the diagrams was unchanged, indicating that oxidation of isosorbide takes place essentially in the bulk of the solution and not on the electrode.

1. Introduction

In a previous study [1], it was shown that isosorbide (hydroxylated derivatives from biomass) in aqueous solution was oxidized to its monoketone under mild reaction conditions in the presence of sodium bromide. Maximal rates of conversion of around 85% showed the interest of this procedure. Favorable conditions for oxidation of isosorbide were obtained at a pH between 6 and 7, and at sodium bromide concentrations between 0.1 and 1 M. The highest rates of conversion were obtained at the highest sodium bromide concentration (1 M).

The present study was designed to further understanding of the mechanism of this reaction, and to find out in which reaction zone the oxidation was taking place. Electrochemical impedance spectroscopy was used to investigate processes taking place at the electrode/solution interface. The influence of such parameters as speed of rotation of the electrode, anodic overpotential and concentration of sodium bromide was studied. Impedances were also measured in the presence of isosorbide.

2. Experimental details

The electrochemical measurements were made with a rotating platinum disc (0.1 cm^2). Before each experiment, the surface of the disc was polished with alumina ($3 \mu\text{m}$), cleaned in ethanol in an ultrasonic bath and then dried in pulsed warm air. The counter-electrode was a platinum grid. A saturated calomel electrode (SCE) was used as reference.

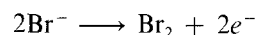
The electrolytic medium consisted of a 0.1 or 1 M solution of sodium bromide (Fluka; > 99% pure) in contact with air. Temperature was maintained at

$25 \pm 0.1^\circ\text{C}$. Water was deionized using an ion-exchange resin. Isosorbide was supplied by Société Roquette Frères. Electrochemical impedance was measured on a Solartron-Schlumberger 1174 frequency response analyzer (frequencies from 63 kHz to several mHz) and a Solartron-Schlumberger potentiostat. The experimental set-up is described elsewhere [2]. Impedance diagrams were traced in Nyquist coordinates with five points per decade.

3. Results

3.1. Anodic curves

The current rose rapidly during the oxidation of bromide.



The ohmic drop iR_e due to the finite conductivity of the electrolyte thus became a critical factor. The relative change in observed voltage V_{obs} was higher than that of the effective voltage V_{eff} :

$$V_{\text{obs}} = V_{\text{eff}} + iR_e$$

The resistance of the electrolyte R_e during the experiments was determined from the high frequency limit on the impedance diagram. The resistance of a 1 M solution of sodium bromide was found to be $14.7 \pm 0.3 \Omega$, and $112 \pm 1 \Omega$ for the 0.1 M solution. The curves were corrected for this ohmic drop.

The elementary anodic curve for a 1 M solution of sodium bromide at a rotation speed of 400 r.p.m. is represented on Fig. 1, without (○) and with (●) ohmic

* This paper is dedicated to the memory of Michel Duprat.

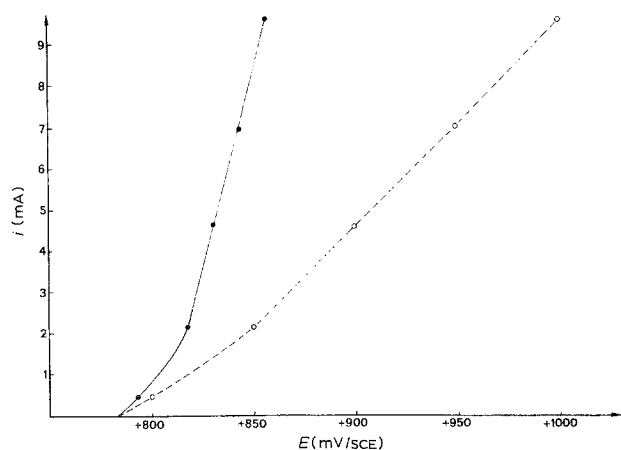


Fig. 1. Anodic current potential curves of a platinum electrode in a 1 M NaBr solution. $\Omega = 400$ r.p.m. (O) without ohmic drop and (●) with ohmic drop compensation ($R_c = 14.7 \Omega$).

drop correction. In the latter case, it can be seen that there was a rapid activation with increasing potential.

Figure 2 shows the anodic curve for 0.1 M sodium bromide at a rotation speed of 1000 r.p.m. It should be noted that the speed of rotation had little influence on the anodic curves.

3.2. A.C. impedance

The first set of experiments were carried out in the absence of isosorbide.

3.2.1. Influence of rotation speed. The electrochemical impedance diagrams were plotted at a potential of 800 mV/SCE, and for different speeds of rotation of the electrode. We also investigated the effects of sodium bromide concentration and anodic overpotential.

Figure 3 shows the electrochemical impedance diagrams for 0.1 M sodium bromide at three different rotation speeds. The diagrams were characterized by two well-separated capacitive loops:

(i) a high frequency loop defined by a characteristic frequency f_c and diameter R_T . In view of the high values of frequency (≈ 200 Hz), this loop was attributed

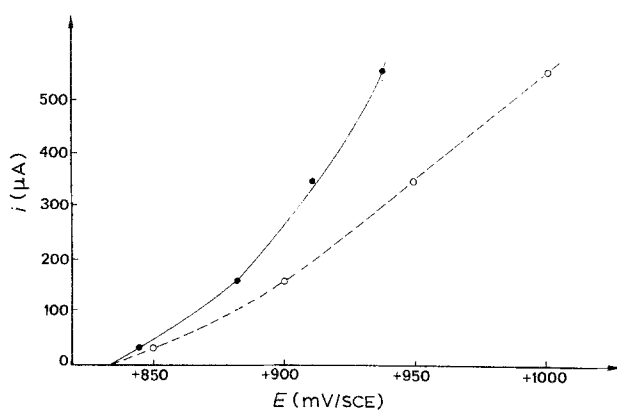


Fig. 2. Anodic current potential curves in a 0.1 M NaBr solution. $\Omega = 1000$ r.p.m. (O) without ohmic drop and (●) with ohmic drop compensation ($R_c = 112 \Omega$).

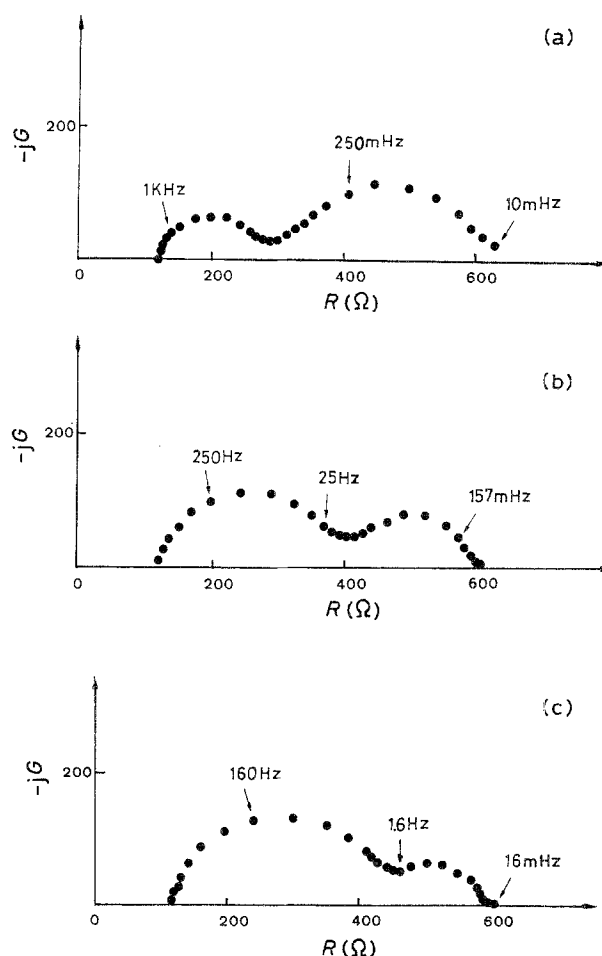


Fig. 3. Electrochemical impedance diagrams in 0.1 M NaBr recorded in potentiostatic mode at different rotation speeds: (a) 100, (b) 400 (c) 1000 r.p.m. $E = +850$ mV/SCE.

to charge transfer. The capacity of the double layer C_d was calculated from the relationship

$$C_d = 1/2\pi f_c R_T$$

The value of $4 \mu\text{F}$ ($40 \mu\text{F cm}^{-2}$) obtained is of the right order of magnitude for a double layer capacity. It should be noted that this value was also obtained in sodium sulphate, which indicated that little adsorption took place.

(ii) a low frequency loop defined by a characteristic frequency f'_c and diameter R_D .

All the graphically-estimated parameters are listed in Table 1. It can be seen from Fig. 3 and the data listed in Table 1 that:

1. the characteristic frequency f_c fell with increasing speed of rotation, indicative of a fall in rate of reaction. The increase in resistance R_T may also be indicative of a fall in effective area of the electrode.

2. the resistance R_D fell with increasing speed of rotation. The characteristic frequency f'_c was directly proportional to the speed of rotation, showing that this loop represents a liquid phase diffusional process. From the following relationship [3]:

$$D^{1/3} = (1.61)^2 / 2.53 \omega_{\max} v^{1/3} \Omega^{-1}$$

where D = coefficient of diffusion, ω_{\max} = maximum

Table 1. Parameters deduced from the impedance diagrams for different rotation speeds. 0.1 M NaBr. $E = +850 \text{ mV/SCE}$.

Ω (r.p.m.)	i (μA)	R_T (Ω)	f_c (Hz)	C_d (μF)	R_D (Ω)	f'_c (Hz)
100	25	160	250	3.9	300	0.15
400	31	280	140	4.1	200	0.6
1000	35	350	120	3.7	180	1.5

Table 2. Parameters deduced from the impedance diagrams for different anodic mean potentials. 0.1 M NaBr. $\omega = 1000 \text{ r.p.m.}$

E (mV/SCE)	i (μA)	R_T (Ω)	f_c (Hz)	C_d (μF)	R_D (Ω)	f'_c (Hz)
850	35	350	120	3.7	180	1.45
900	160	140	350	3.2	20	1.2
950	350	100	510	3.1	10	2.0
1000	560	80	610	3.2	-	-

cycle frequency (in Hz), ν = viscosity of the medium ($0.01 \text{ cm}^2 \text{ s}^{-1}$) and Ω = speed of rotation of electrode (rad s^{-1}). An order of magnitude of the diffusion coefficient was estimated. Thus,

$$D = (0.65 \pm 0.13) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Values reported by other workers for the diffusion coefficient of bromide are $1.58 \pm 0.06 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [4], and $1.2 \pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for bromine [5].

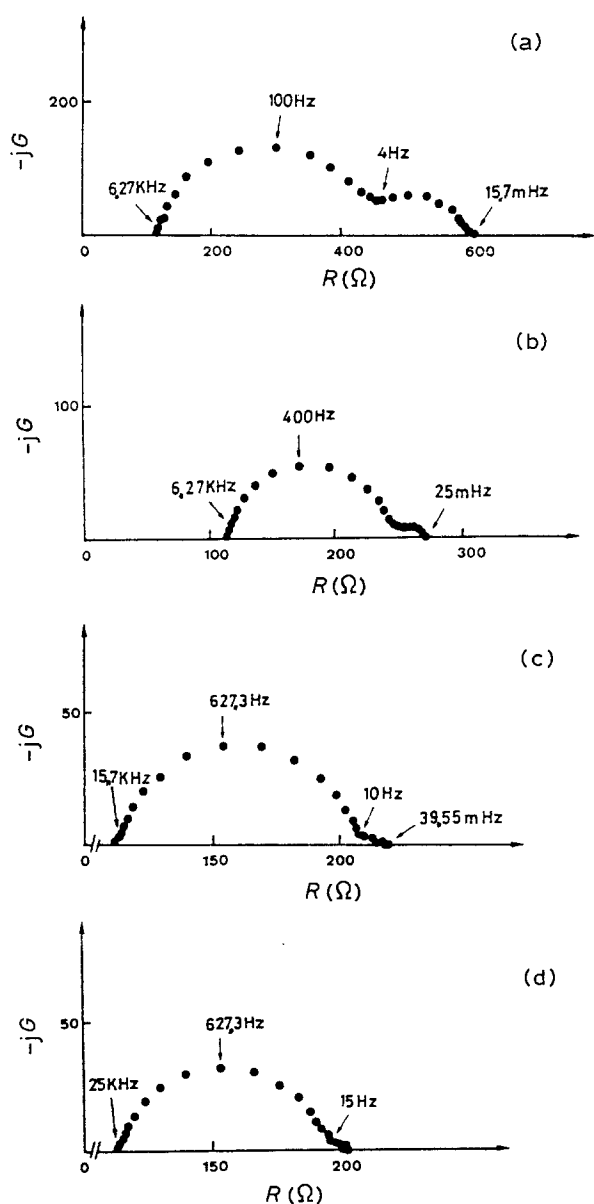


Fig. 4. Electrochemical impedance diagrams recorded in potentiostatic mode at different anodic mean potentials \bar{E} : (a) +850 mV ($i = 35 \mu\text{A}$); (b) +900 mV ($i = 160 \mu\text{A}$); (c) +950 mV ($i = 350 \mu\text{A}$); and (d) 1000 mV ($i = 560 \mu\text{A}$). 0.1 M NaBr. $\Omega = 1000 \text{ r.p.m.}$

It would thus appear that the diffusing species was bromine.

3.2.2. *Influence of overpotential.* The influence of charge transfer and mass transport on the kinetics can be altered by a change in potential applied to the electrode. Figure 4 represents the impedance diagrams obtained for different values of overpotential at a constant speed of rotation ($\Omega = 1000 \text{ r.p.m.}$). Table 2 lists the characteristic parameters. It can be seen that there was a fall in values of R_T and R_D with increasing overpotential. The low frequency loop disappeared at overpotentials above 950 mV/SCE. This shows that the diffusing species is formed during oxidation of bromide, and is probably bromine. The bromide ion is not the diffusing species since anodic polarization would lead to the opposite effect (increase in R_D).

3.2.3. Influence of sodium bromide concentration.

(a) *Influence of rotation speed.* Impedance diagrams were plotted at an anodic overpotential of 800 mV/SCE for different speeds of rotation in 1 M sodium bromide (Fig. 5). The diagrams have a similar shape to those represented in Fig. 3. However, the resistances R_T were much lower than those at 0.1 M sodium bromide, and reflect the much higher values of current (Fig. 1).

In addition, the values of C_d were lower than in 0.1 M sodium bromide ($30 \mu\text{F cm}^{-2}$ against $40 \mu\text{F cm}^{-2}$). This may have been due to adsorption.

The adsorption of bromide ion on platinum has been observed by Breiter [6]. Johnson and Bruckenstein [4] have also reported the strong adsorption of bromide on platinum except on an oxide-coated surface. Adsorbed bromide is thought to be less reactive to oxidation than the ions in solutions [7]. The amount of bromide adsorbed has been estimated [8]. The adsorption isotherms show an abrupt increase in adsorbed Br^- with increasing anodic potential. A Raman spectroscopic study by Loo and Lee [9, 10] showed the presence of Br_2 and Br_3^- coadsorbed on the electrode.

The present results suggest that there is adsorption of a bromine species in 1 M sodium bromide, but relatively little absorption at 0.1 M (undetectable by electrochemical impedance). Now bromide should adsorb equally easily in 1 M as in 0.1 M sodium bromide, and the adsorbed species was more likely to have been Br_2 and/or Br_3^- . The surface preparation of electrodes may in fact have hindered adsorption of bromide ions.

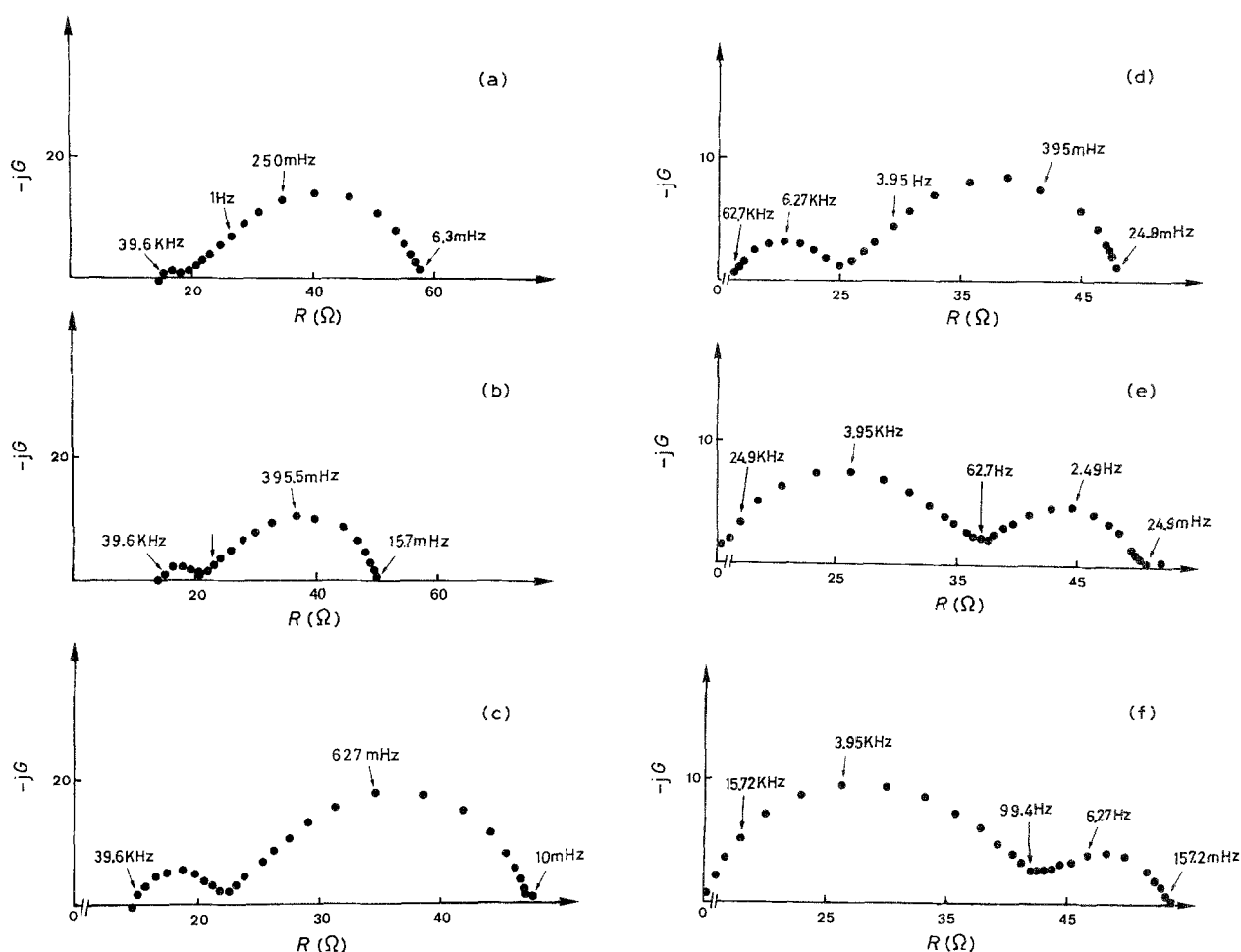


Fig. 5. Electrochemical impedance diagrams in a 1 M NaBr solution recorded in potentiostatic mode at different rotation speeds, Ω : (a) 100, (b) 250, (c) 400, (d) 560, (e) 2240 and (f) 4000 r.p.m. $E = +800$ mV/SCE.

The increase in speed of rotation of the electrode led to an increase in R_T and a fall in R_D (Table 3). This was identical behaviour to that observed in 0.1 M sodium bromide. However, in this case, the diffusional process was characterized by a linear part in the frequency domain between 250 and 2.5 Hz. This is characteristic of a Warburg type impedance and indicates a relaxation of concentration. It can be seen that the characteristic frequencies of the low frequency loop (*cf.* Table 3) were directly proportional to the speed of rotation. The same frequencies were obtained to those observed in 0.1 M sodium bromide. These results show that the same diffusing species was involved in the oxidation of bromide.

Table 3. Parameters deduced from the impedance diagrams for different rotation speeds. 1 M NaBr. $E = +800$ mV/SCE.

Ω (r.p.m.)	i (μ A)	R_T (Ω)	f_c (kHz)	C_d (μ F)	R_D (Ω)	f'_c (Hz)
100	300	4.0	10	4	33	0.16
250	380	6.0	10	2.7	26	0.40
400	425	7.4	7.5	2.9	23	0.55
560	410	9.0	6.3	2.8	20.6	0.63
2240	460	21.3	4	1.9	13	3.30
4000	445	27.0	3.2	1.8	11	4.20

(b) *Influence of overpotential.* Figure 6 shows the impedance diagrams for different values of anodic overpotential ($\Omega = 400$ r.p.m.) in 1 M sodium bromide. As in the 0.1 M solution, there was a fall in the values of R_T and R_D with increase in overpotential (*cf.* Table 4). On the other hand, the value of C_d increased with increasing overpotential, which was thought to reflect desorption of the adsorbed species such as Br_2 and Br_3^- .

Moreover, in contrast to that observed in 0.1 M sodium bromide, the low frequency capacitive loop did not disappear with increasing overpotential, and f'_c remained constant. This could be accounted for by a linked chemical reaction such as the formation of a

Table 4. Parameters deduced from the impedance diagrams for different anodic mean potentials. 1 M NaBr. $\omega = 400$ r.p.m.

E (mV/SCE)	i (mA)	R_T (Ω)	f_c (kHz)	C_d (μ F)	R_D (Ω)	f'_c (Hz)
800	0.43	7.4	7.5	2.9	23	0.55
850	2.15	2.6	15.7	3.9	4.2	0.58
900	4.65	1.4	17	6.7	2.2	0.60
950	7.05	1.1	17	8.5	1.4	0.60
1000	9.65	1.0	16	9.9	1.2	0.58

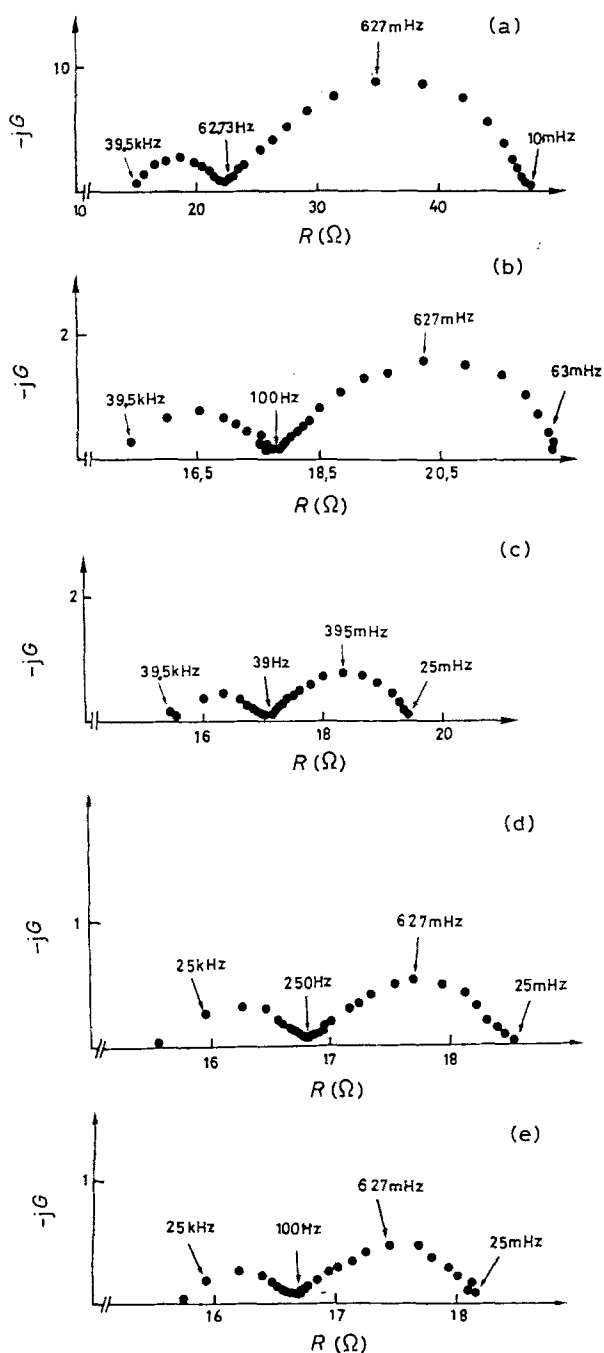
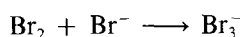
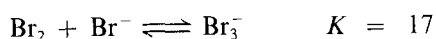


Fig. 6. Electrochemical impedance diagrams recorded in potentiostatic mode at different anodic mean potentials \bar{E} : (a) 800 mV ($i = 425 \mu\text{A}$), (b) 850 mV ($i = 2.15 \text{ mA}$), (c) 900 mV ($i = 4.65 \text{ mA}$), (d) 950 mV ($i = 7.05 \text{ mA}$), (e) 1000 mV ($i = 9.65 \text{ mA}$). 1 M NaBr. $\Omega = 400 \text{ r.p.m.}$

tribromide (or perbromide ion):



Lee and Loo [9, 10] using Raman spectroscopy under identical experimental conditions to ours showed that the simultaneous appearance of bands due to Br_2 and Br_3^- was due to rapid equilibrium between these species, which would be expected from the thermodynamics of the system:



In addition, more of this species was formed in the molar solution than in the 0.1 M solutions. A dis-

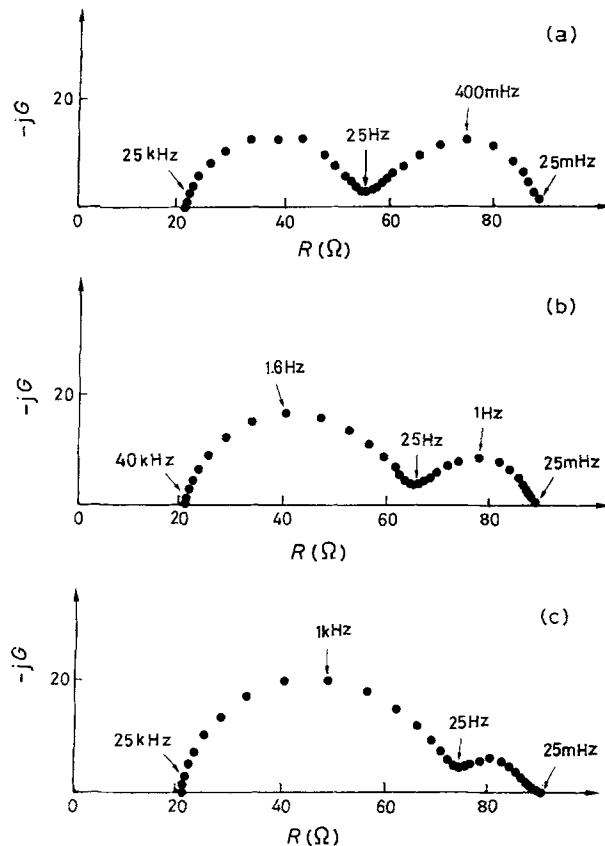


Fig. 7. Electrochemical impedance diagrams recorded at different rotation speeds: (a) 400, (b) 1000 and (c) 4000 r.p.m. 1 M NaBr + 1 M isosorbide. $E = +800 \text{ mV/ECS}$.

mutation of bromine to hypobromous acid could also take place:



As the bromide concentration increases, the hypobromous acid disappears at the expense of the perbromide ion Br_3^- .

3.2.4. *Electro-oxidation of isosorbide.* The overall appearance of the impedance diagrams was not affected by the presence of 1 M isosorbide (Fig. 7). However, the following differences were observed:

(i) The electrolyte resistance was increased ($R_e = 20.5 \Omega$). Viscosity was also increased ($\eta = 1.17 \times 10^{-3} \text{ pl}$ for 1 M sodium bromide against $1.41 \times 10^{-3} \text{ pl}$ for 1 M sodium bromide and 1 M isosorbide), which would account for the higher value of electrolytic resistance.

(ii) the value of R_T was higher in the presence of isosorbide (*cf.* Table 5) associated with a lower capaci-

Table 5. Parameters deduced from the impedance diagrams for different rotation speeds. 1 M NaBr + 1 M isosorbide. $E = +800 \text{ mV/ECS}$.

ω (r.p.m.)	i (μA)	R_T (Ω)	f_c (kHz)	C_d (μF)	R_D (Ω)	f'_c (Hz)
400	235	34	1.8	2.6	29	0.46
1000	260	42	1.45	2.6	22	1.1
4000	285	51	1.2	2.6	14	4

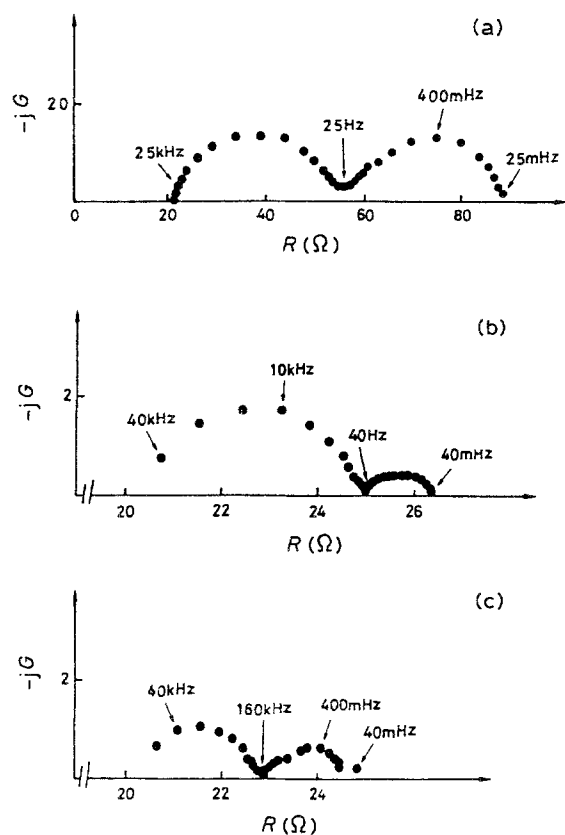


Fig. 8. Electrochemical impedance diagrams at different anodic mean potentials, \bar{E} : (a) 800 mV ($i = 235 \mu\text{A}$), (b) 1000 mV ($i = 6 \text{ mA}$), and (c) 1200 mV ($i = 14 \text{ mA}$). 1 M NaBr + 1 M isosorbide. $\Omega = 400 \text{ r.p.m.}$

tance $26 \mu\text{F cm}^{-2}$), but it was unaffected by change in speed of rotation. Taken together, these results indicated that isosorbide was adsorbed onto the surface of the platinum electrode.

(iii) the value of R_D was almost unaffected by the presence of isosorbide, and the characteristic frequency f_c' depended directly on the speed of rotation of the electrode. This suggested that the diffusional processes were not affected by the presence of isosorbide. Furthermore, there was a similar influence of anodic overpotential with (Fig. 8 and Table 6) and without isosorbide (*cf.* Fig. 6 and Table 4). Thus it appeared that no specific chemical reactions took place on the surface of the electrode, and that isosorbide was probably oxidized chemically in the bulk of the solution.

4. Discussion and conclusion

The results obtained in this study provide more information on the mechanism of oxidation of bromide. In addition, they show that indirect oxidation of iso-

Table 6. Parameters deduced from the impedance diagrams for different anodic mean potentials. 1 M NaBr + 1 M isosorbide. $\Omega = 400 \text{ r.p.m.}$

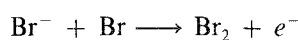
E (mV/SCE)	i (mA)	R_T (Ω)	f_c (Hz)	C_d (μF)	R_D (Ω)	f_c' (Hz)
800	0.24	34	1.8	2.6	29	0.46
1000	6.05	4.3	14	2.6	1.7	0.51
1200	14	2.4	25	2.6	1.5	0.51

sorbide via a bromine intermediate takes place essentially in solution.

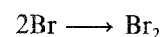
Various mechanisms for the oxidation of bromide have been described. Llopis and Vasquez [11] proposed the following scheme:



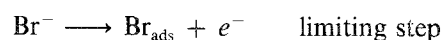
Cooper and Parsons [12] include the process of adsorption of bromide on platinum as follows:



or

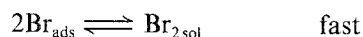
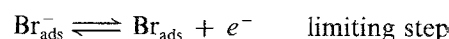
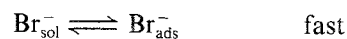


Other workers [5, 13] have cast doubt on the mechanism proposed by Llopis and Vasquez. Faïta *et al.* [13] propose the following two stage reaction, each stage contributing to the overall kinetics:



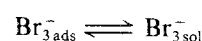
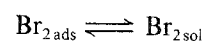
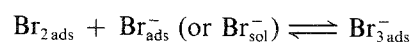
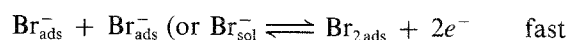
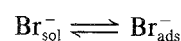
Rubinstein has pointed out [14] that these studies have determined the kinetics by extrapolation to infinite speed of rotation without correcting for ohmic drop. Moreover, the Br^-/Br_2 system is too fast to be measured using this technique.

The nature of the electrode surface should also be taken into consideration. It has been suggested that for a reduced electrode (the electrode is brought to an anodic potential from a highly cathodic potential before being introduced into the reaction cell) the mechanism should be:



Johnson and Bruckenstein [4] suggest that apart from production of BrOH at overpotentials above 1.25 V/SCE, bromine is formed from bromide by a diffusion-limited mechanism.

The Raman study by Lee and Loo [9, 10] demonstrated the presence of Br_2 and Br_3^- co-adsorbed on the electrode according to the following mechanism:



The following points emerge from the results of this study:

1. The high values of frequency observed indicate a rapid charge transfer reaction. The plot of the charge transfer resistance R_T against the anodic polarization gave an estimate of the resistance in the vicinity of the equilibrium potential. Once R_T is known in relationship:

$$R_T = RT/nF \times 1/i_0$$

where R is the perfect gas constant, T the temperature (K), n the number of electrons transferred ($= 2$), and F the Faraday constant, then the exchange current, i_0 can be determined for the two concentrations of NaBr used, viz. $i_0(\text{NaBr} = 1 \text{ M}) = 11 \text{ mA cm}^{-2}$ and $i_0(\text{NaBr} = 0.1 \text{ M}) = 0.3 \text{ mA cm}^{-2}$.

In addition, little evidence for adsorption of the bromide ion was found, probably due to the oxidation state of the electrode.

2. The impedance measurements in the anodic domain demonstrate the existence of a transport process, most probably of bromine. We also suspected formation of the tribromide ion. The presence of this species in 1 M solutions of sodium bromide is in line with the high yield of monoketone obtained from isosorbide, since electro-oxidation of isosorbide was thought to involve species such as Br_3^- or BrOH .

3. In the presence of isosorbide, there was little change in the overall shape of the impedance diagrams, indicating that oxidation of isosorbide took place essentially in solution. The results did, however, indicate that isosorbide was adsorbed onto the elec-

trode, which is in agreement with results from cyclic voltammetry [15]. The presence of isosorbide had no effect on the shape and characteristics of the voltammograms, especially the i_c/i_a ratio, and isosorbide appeared to be adsorbed onto the electrode thereby inhibiting the anodic reaction.

In conclusion, electro-oxidation of bromide via a bromine intermediate takes place in solution, which was confirmed by the purely chemical nature of the oxidation of isosorbide by oxidizing bromine species.

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