Square-wave Amperometric Monitoring of Reaction Rates

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The application of square-wave amperometry, an analytical technique involving the use of two indicator electrodes polarized by a square wave, in the determination of reaction rates is described. Kinetic measurements have been made on the bromination of anisole in aqueous solution. Square-wave amperometry in conjunction with a stopped-flow apparatus equipped with Pt electrodes in the observation tube was used to monitor the disappearance of bromine in dilute solutions. Reaction rates with half-lives down to *ca*. 5 ms can be measured using relatively high-frequency square waves (*ca*. 800–1000 Hz). The results are in good agreement with values measured spectrophotometrically at higher bromine concentrations. The rate of dissociation of Ag⁺ from its macrobicyclic cryptand 211 complex was also measured, using a pair of silver indicator electrodes. Free Ag⁺ may be monitored selectively in the presence of its cryptate complex by using a low-amplitude square wave (± 150 mV). The advantages and limitations of the amperometric technique for kinetic measurements are discussed.

Square-wave amperometry is potentially a very useful technique for conventional analytical applications and for monitoring reactions over a wide range of reaction rates.¹

The principle of the method is illustrated in fig. 1. When an alternating potential [fig. 1(a)] is applied to a pair of identical polarizing electrodes immersed in a solution containing a suitable reversible redox couple (e.g. Br_2/Br^-) the resulting current is the sum of the faradaic current and the capacitance or charging current [fig. 1(b)]. The capacitance current depends upon the rate of change of potential, dE/dt, and with a square-wave potential a large capacitance current is observed immediately following the change in sign of the polarizing potential. This current decays rapidly during the time of constant polarizing potential. The faradaic current requires the presence of both (or all) species involved in the electrode reaction and depends upon the concentration of the limiting reagent governing the electrode reactions, e.g. Br₂ in the presence of excess Br^- (anode: $Br^- \rightarrow \frac{1}{2}Br_2 + e$; cathode: $\frac{1}{2}Br_2 + e \rightarrow Br^-$). The faradaic current also decays with time, owing to the depletion of depolarizer (Br_2 in the above example) in the vicinity of the electrode, but more slowly than the capacitance current [fig. 1(b)]. It remains at a significant level prior to change in sign of E, and if the current is sampled at the end of each square-wave period [fig. 1(c)] the measured value will be predominantly equal to the faradaic current. Both the capacitance and faradaic current depend upon the amplitude of the applied alternating potential. Full details of the technique have been discussed earlier.¹

A major advantage of the square-wave method over conventional d.c. amperometric methods is that when the square-wave potential is symmetrical (*i.e.* no d.c. bias is present) the measured current is independent of stirring. This is essential for use in



Fig. 1. (a) Square-wave signal, generator output; (b) square-wave signal, cell output: (----) total current, $(\ldots \ldots)$ capacitance current; (c) delay (t_d) and sampling time (t_s) of measuring circuit.

conjunction with techniques which require measurements on still solutions. For example, in the stopped-flow technique measurements are made on virtually still solutions, generated by stopping rapidly flowing solutions just after mixing. The use of high-frequency square waves should, in principle, allow very fast reactions to be monitored. In practice, however, the usable frequency range will be limited by the decay of the capacitance current, because of an increasingly high background level relative to the faradiac current as the frequency increases. It is also possible that the establishment of a steady current proportional to the depolarizer concentration will take a finite time and hence influence the observed kinetic behaviour.

The present paper describes a study of the use of the square-wave amperometric method to monitor the bromination of anisole in aqueous solution with an all-glass stopped-flow apparatus containing a pair of Pt electrodes in the observation tube. Reactions with half-lives down to *ca.* 5 ms could be followed using square-wave frequencies of up to 800 Hz. This is very close to the lower limit (1-3 ms) possible from rapid-mixing techniques, the application of which has until now been limited almost exclusively to reactions that may be followed using optical or conductimetric detection.

The application of the method to monitoring free Ag^+ in rapid equilibrium with its complex (cryptate) with the macrobicyclic cryptand 211 ligand (cryp) (I) has also been studied using two Ag electrodes:

$$Ag^+ + cryp \stackrel{k_l}{\underset{k_d}{\Rightarrow}} Ag(cryp)^+.$$
 (1)

It was found that Ag^+ may be measured selectively in the presence of its cryptate complex, and this has been used to monitor the rate of dissociation of Ag^+ from $Ag(cryp)^+$ on the addition of excess acid:

$$Ag(cryp)^{+} \xrightarrow[H_{2}O]{}^{H^{+}} Ag^{+} + (cryp)H_{2}^{2+}.$$
 (2)

Rates were measured at total Ag⁺ concentrations down to 10^{-6} mol dm⁻³.

(I)

EXPERIMENTAL AND RESULTS

MATERIALS

Anisole was treated with $FeSO_4$, washed with aqueous sodium hydroxide, dried over calcium sulphate and fractionally distilled under reduced pressure.² No impurities were detectable in the n.m.r. and i.r. spectra. Cryptand 211 (Merck) was used without further purification. All inorganic chemicals were high-purity commercial grades.

APPARATUS

Square-wave signals were provided by a Farnell LFM4 Sine-Square generator, and the cell signal was measured using a sample-and-hold integrated circuit triggered by a delayed signal from the generator, as previously described.¹ The stopped-flow system was an all-glass apparatus, originally constructed for conductimetric detection,³ containing a pair of Pt electrodes *ca.* 0.2 cm² in area. The signal amplitude from the generator was normally ± 250 mV for bromine detection and ± 150 mV for Ag⁺ detection, at a frequency in the range 50–800 Hz. Measured rate constants were independent of the generator frequency. It is clear from fig. 1(*c*) that the sampling frequency is determined by the frequency output of the generator, and thus ideally the frequency should be high relative to the rate constant to be measured. Rate constants up to *ca.* 100 s⁻¹ were measured ($t_1 \approx 7$ ms) and on this time-scale signals recorded at 800 Hz (1.25 ms per sample) the output appears as an exponentially decaying step function. This, together with the increasingly high background capacitance current sets a lower limit of *ca.* 5 ms on the half-life of reactions that can be conveniently followed using the present electronic circuit.¹

Bromination reactions were also followed by observing the decrease in absorbance at 350 nm due to Br_2/Br_3^- using a Durrum Gibson stopped-flow apparatus. This equipment, when fitted with the temperature-jump cell containing a pair of stainlesssteel electrodes, could also be used for current measurements on the Br_2/Br^- system. However, it was difficult to avoid small leaks from the drive and stop syringes providing an independent connection between the reaction solution and earth, which led to severe distortion of the kinetic traces.

Output signals from the sample-and-hold circuit (current measurements) or the photomultiplier (optical measurements) were fed into a Commodore 3016 microcomputer *via* a Data Lab DL 901 transient recorder. The data were analysed by standard methods to yield the required first-order rate constants (see below).

Silver-ion concentrations were monitored using a pair of silver wire electrodes sealed through soda glass (electrode area ca. 0.3 cm^2) dipping into a glass, jacketed cell. Reactions were sufficiently slow ($t_{\frac{1}{2}} \approx 20 \text{ s}$) to be recorded with a conventional chart recorder.





Fig. 2. Rate of bromination of anisole in water at 25 °C: initial $[Br_2] \approx 7 \times 10^{-5} \text{ mol dm}^{-3}$, $[Br^-] = 0.1 \text{ mol dm}^{-3}$.

All kinetic measurements were carried out at 25.0 ± 0.2 °C (± 0.5 °C for the Durum Gibson stopped-flow apparatus).

BROMINATION OF ANISOLE

Initial measurements using amperometric detection were carried out with $5 \times 10^{-4} \leq [anisole]/mol dm^{-3} \leq 4 \times 10^{-2}$, $[Br^{-}] = 0.1 \text{ mol } dm^{-3}$, ionic strength = 0.2 mol dm⁻³ (NaClO₄) and $[Br_2] \approx 5 \times 10^{-5} - 1 \times 10^{-4} \text{ mol } dm^{-3}$. Under these conditions, pseudo-first-order kinetics were observed:

$$-d[Br_{2}]^{*}/dt = k_{e}[Br_{2}]^{*}$$
(3)

where $[Br_2]^* = [Br_2] + [Br_2]$ represents the total bromine concentration. The observed first-order rate constant, k_e , was directly proportional to the anisole concentration:

$$k_{\rm e} = k_2[\text{anisole}] \tag{4}$$

as shown in fig. 2. The initial bromination products are much less reactive towards bromine than the original substrate,^{4, 5} so that no correction is necessary for further bromination. Product analysis was not attempted, but there is good evidence⁴⁻⁶ that bromination takes place predominantly (> 90%) in the *para* position.

Rate constants were then measured at varying concentrations of Br^- over the range $0.02 \leq [Br^-]/mol dm^{-3} \leq 0.3$. Provided that Br_2 is much more reactive towards anisole than $Br_3^{-,4}$ the observed second-order rate constant, k_2 , should be represented by

$$k_2 = k_{\rm Br_{\bullet}} / (1 + K[\rm Br^{-}]) \tag{5}$$

where k_{Br_2} is the second-order rate constant for reaction of anisole with Br_2 and K is the equilibrium constant $[\text{Br}_3^-]/[\text{Br}_2][\text{Br}^-]$. Values of k_2 measured at various bromide concentrations are listed in table 1, together with k_{Br_2} values obtained from eqn (5), using $K = 16 \text{ dm}^3 \text{ mol}^{-1.7}$ The k_{Br_2} values show no systematic trend with [Br⁻], in

[NaBr] /mol dm ⁻³	k ₂ /10 ⁴ dm ³ mol ⁻¹ s ⁻¹	$k_2(1 + K[Br^-])$ /10 ⁴ dm ³ mol ⁻¹ s ⁻¹	$k'_2(1 + K[Br^-])$ /10 ⁴ dm ³ mol ⁻¹ s ^{-1b}		
0.02	2.24	2.95			
0.05	1.69	3.05	3.55		
0.10	1.11	2.87	2.90		
0.15	0.851	2.91	3.02		
0.20	0.681	2.87	3.08		
0.30 ^c	0.524	3.04	3.15		

Table 1. Rate of bromination of anisole in water at 25 $^{\circ}C^{a}$

^{*a*} Ionic strength, I = 0.20 (NaClO₄). ^{*b*} k'_2 is the rate constant measured spectrophotometrically. ^{*c*} I = 0.3.

agreement with the assumption that Br_3^- is much less reactive towards anisole than Br_2 . The average value $[k_{Br_2} = (2.95 \pm 0.07) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$ is in good agreement with earlier reported values: $k_{Br_2} \approx 2.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (measured using ring–disc electrodes); $k_{Br_2} \approx 2.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (electrochemical generation of Br_2 at low anisole concentrations); $k_{Br_2} \approx 4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (approximate extrapolation from results obtained at 0 °C using cell-potential measurements at anisole concentrations of ca. $10^{-5} \text{ mol} \text{ dm}^{-3}$).⁴ The reactions were also checked using optical measurements as described above and the results are included in table 1 for comparison. The agreement between the two sets of data is satisfactory.

At low bromide concentrations, $\leq 0.05 \text{ mol dm}^{-3}$, it was very difficult to observe the reaction optically because of the low concentrations of the more highly absorbing Br₃⁻ species present. However, note that difficulty was also experienced with amperometric measurements at low bromide concentrations ($\leq 0.02 \text{ mol dm}^{-3}$). Separate measurements suggest that at these low bromide levels linear response to bromine concentration is limited to bromine concentrations $\leq 5 \times 10^{-5} \text{ mol dm}^{-3}$ (cf. linear response to [Br₂] $\geq 10^{-3} \text{ mol dm}^{-3}$ at [Br⁻] = 0.1 mol dm⁻³).¹

DISSOCIATION OF Ag(cryp)⁺

In the presence of an excess of acid, metal cations may be displaced quantitatively from cryptate complexes [reaction (1)].^{10, 11} It can be readily shown that for a reaction scheme represented by

$$Ag(cryp)^{+} \underset{k_{t}}{\overset{k_{d}}{\rightleftharpoons}} Ag^{+} + cryp$$
(6)

$$\operatorname{cryp} + \mathrm{H}^{+} \xrightarrow{k} (\operatorname{cryp})\mathrm{H}^{+}$$
(7)

i.e. the acid is acting as a scavenger for free cryptand in equilibrium with $Ag(cryp)^+$, the observed rate law is given by

$$-d[Ag(cryp)^{+}]/dt = k_{e}[Ag(cryp)^{+}]$$
(8)

$$k_{\rm e} = k_{\rm d} \, k[{\rm H}^+] / (k_{\rm f}[{\rm Ag}^+] + k[{\rm H}^+]). \tag{9}$$

Provided $k[H^+] \gg k_f[Ag^+]$ eqn (9) simplifies to

$$k_{\rm e} = k_{\rm d} \tag{10}$$





	$k_{\rm e}/10^{-2}~{ m s}^{-1}$							
$[NaNO_3]/mol dm^{-3} \dots$	0.008	0.028	0.1	0.3	1.0	0.1		
initial [Ag(cryp) ⁺]/mol dm ⁻³		2.0	2.0		2.0			
9.0×10^{-5} 3.2×10^{-5}	4.6° 3.15	3.50° 3.14	3.34° 3.18	2.99	2.80	3.30		
1.0×10^{-5} 3.6×10^{-6}	3.12	3.19	3.17 3.19	2.90	3.15	3.17		

Table 2. Dissociation of $Ag(cryp)^+$ in water at 25 °C^a

^a Generator amplitude ± 150 mV, frequency 200 Hz; silver electrode area 0.3 cm². ^b Nonlinear response of measured signal with concentration.

i.e. the dissociation of the cryptate complex is the rate-determining step in the overall reaction.

The stability of Ag(cryp)⁺ in water is relatively high, log $K_s = 8.5$ ¹² [corresponding to a difference in standard reduction potentials of free Ag⁺ and Ag(cryp)⁺ of 500 mV], and the kinetic characteristics of the reduction of Ag⁺ and Ag(cryp)⁺ are presumably rather different. By applying a low potential difference across two silver electrodes (*e.g.* ± 150 mV) a current controlled by the electrode reactions

Ag (anode) \rightarrow Ag⁺+e

$$Ag^+$$
 (cathode) + e $\rightarrow Ag$

may be used to monitor Ag^+ selectively in the presence of $Ag(cryp)^+$.

Reactions were initiated by adding a small aliquot of a concentrated solution of $Ag(cryp)^+$ to an aqueous $HClO_4$ solution (normally 2×10^{-3} mol dm⁻³) at varying ionic strengths (NaClO₄). Fig. 3 shows a typical reaction trace. The increase in signal

corresponds to the increase in [Ag⁺] as Ag⁺ is displaced from Ag(cryp)⁺ by H⁺. Rates were measured for a variety of Ag(cryp)⁺ concentrations down to 3×10^{-6} mol dm⁻³ and several different ionic strengths. The observed rate constant, k_e , was independent of acid concentration, the ionic strength and the initial concentration of Ag(cryp)⁺ [table 2, cf. eqn (10)]. The value obtained, $k_e = (3.1 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$, may be identified with the dissociation rate constant, k_d , for Ag(cryp)⁺ and compares favourably with an independent determination of this rate at low ionic strength with conductimetric detection, which gives $(2.9 \pm 0.1) \times 10^{-2} \text{ s}^{-1.18}$ When combined with K_s (= k_f/k_d) this gives a value of $k_f = 1.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

It is expected that the use of silver-plated Pt electrodes in the stopped-flow apparatus will enable much faster reactions involving Ag^+ to be monitored.

DISCUSSION

The stopped-flow study of the bromination of anisole shows that the amperometric method utilizing a square-wave polarizing potential can be used to measure reaction rates close to the stopped-flow limit. In this case we have used without modification a stopped-flow apparatus designed for conductimetric detection. It is clear from the agreement between results obtained with optical and electrochemical detection that the establishment of a faradaic current proportional to concentration is rapid on the stopped-flow time scale. The rapid response time combined with the very high sensitivity of amperometric methods¹⁴ means that it should be possible to measure second-order rate constants covering a very wide range. The time range of the present technique is limited by the decay rate of the capacitance current, which typically had a time constant of the order of 1 ms in our system ($\tau = RC$, where R is the resistance between the electrodes and C is the capacitance of the double layer).

Experiments using pulsed potentials have reently been used to monitor reactions with half-lives approaching 10^{-6} s,¹⁵ further emphasising the rapid response times possible using amperometric detection. This has been achieved in pulse polarographic experiments using i.r. compensation or charge–injection techniques^{15, 16} to charge the double layer in $< 10^{-5}$ s, allowing delays between charging the double layer and measuring the faradaic current as low as 7 μ s. This technique is of course limited to measuring rates of systems at equilibrium, rather than the irreversible reactions that we have described. Equivalent double-layer charging rates may be very difficult to achieve during continuous monitoring of concentration levels.

Compared with conductimetric methods, a significant advantage of electrochemical detection is the ability to monitor selectively a given electroactive species in the presence of high concentrations of other ions. This is illustrated clearly in reaction (2), in which the concentration of Ag⁺ is measured in the presence of Ag(cryp)⁺, excess HClO₄ and NaClO₄. Because the electrode processes at the two electrodes are identical (Ag⁺ + e \Rightarrow Ag), square-wave potentials with very low amplitudes can be used, thus allowing great selectivity. A disadvantage is the requirement of reasonably high background electrolyte levels (10⁻² to 10⁻¹ mol dm⁻³) to ensure rapid decay of the capacitance current. In practice the background capacitance current is relatively insensitive to electrolyte concentration. This is because as the electrolyte concentration decreases the fraction of capacitance current remaining after a given time increases (τ increases) but the absolute level of the initial current decreases.

An important distinction may be made between the two reactions described here. In the dissociation of $Ag(cryp)^+$, the species monitored (Ag^+) is not a reactant and its concentration does not affect the reaction rate. On the other hand the bromination of anisole is first order in bromine concentration and alteration in concentration as

MONITORING OF REACTION RATES

a result of the electrode reactions will in principle influence the rate. For such a first-order reaction, however, the depletion of the species (Br_2 in this case) during one half cycle will be cancelled by the increase during the second half cycle. The cancellation will not be exact for a reaction which is, for example, second order with respect to a particular component, except in the limit of low potential (and hence low current). It can be readily shown that such effects should be small; *e.g.* variations by as much as a factor of two in the concentration of the monitored species in the vicinity of the electrode during one a.c. cycle result in an error of only 11% in the measured rate constant. It may also be noted that the stopped-flow technique is in general inconvenient for the determination of rates of reactions which are second order in the monitored component, irrespective of the analytical technique used.

The principle of the amperometric method described is identical to that used in the familiar dead-stop titration method based on a d.c. polarizing potential. However, analytical work involving d.c. polarizing potentials is hampered by the stirrer-dependent decay of the faradaic current. Quantitative measurements using rotating indicator electrodes^{8, 14, 17, 18} have been described, but these are often inconvenient and cannot be used in some situations, such as stopped-flow measurements of fast reactions. By contrast, when symmetrical alternating potentials with frequencies as low as a few Hz are used the measured currents are independent of stirring. Furthermore, the required faradaic current may be conveniently measured using a simple and inexpensive sample-and-hold circuit.¹ This should greatly enhance the applicability of amperimetric measurements to the measurement of reaction rates.

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