Potentiostatic Study of Heterogeneous Chemical Reactions. The ClO_2^-–ClO_2–Cl^- System on Platinized Platinum

F. Pergola, R. Guidelli, and G. Raspi

Contribution from the Istituto di Chimica Analitica ed Elettrochimica of the University of Pisa, and the Istituto di Chimica Analitica of the University of Firenze, Italy. *Received July 14, 1969*

Abstract: The voltammetric behavior of chlorite ion on platinized platinum has been studied in a pH range from 1 to 14 by making use of an electrode with periodical renewal of the diffusion layer. In neutral and alkaline media ClO_2^- yields a reversible oxidation wave to ClO_2 and an irreversible reduction wave to Cl^-. The reduction process proceeds through an initial rate-determining step involving one electron and one proton. For pH values lower than 5.5 an increase in the acidity of the solution causes the anodic reversible wave to become composite, thus exhibiting a cathodic portion which grows at the expense of the cathodic irreversible wave. At pH 1 the cathodic portion of the composite wave becomes higher than the anodic by a factor of 4 and the irreversible wave vanishes. The examination both of the current–potential characteristic and of the potentiostatic current–time curves of $HClO_2$ in 1 *M* $HClO_4$ on platinized platinum leads to the conclusion that the electroreduction of $HClO_2$ to Cl^- under these conditions proceeds through the heterogeneous decomposition of $HClO_2$ into ClO_2 and Cl^- and the simultaneous reduction of the ClO_2 so formed to $HClO_2$.

It is well known that chlorine dioxide is stable in acid, neutral, and weakly alkaline media, whereas in strongly alkaline media it tends to decompose according to the homogeneous disproportionation reaction

$$2ClO_2 + 2OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O$$

In practice the amount of ClO_2 decomposing in 1 min at 20° for a solution $10^{-3}M$ in ClO_2 and 10^{-10} *M* in H^+ is about 0.01%.[1,2] On the contrary chlorite ion is stable in neutral and alkaline media, whereas in acid media it disproportionates giving rise to Cl^-, ClO_2, and ClO_3^-. Kieffer and Gordon[3] interpreted the stoichiometry and kinetics of the disproportionation reaction of chlorous acid by assuming that this reaction follows two parallel paths. The first path, uncatalyzed, is characterized by the rate-determining step

$$HClO_2 + HClO_2 \longrightarrow HOCl + H^+ + ClO_3^-$$

and by the stoichiometry

$$4HClO_2 \longrightarrow 2ClO_2 + ClO_3^- + Cl^- + H_2O + 2H^+$$

The second step, catalyzed by chloride ion, is

$$HClO_2 + Cl^- \rightleftharpoons HCl_2O_2^-$$

$$HCl_2O_2^- + Cl^- \longrightarrow \text{products} \qquad \text{rate determining}$$

thus first order with respect to $HClO_2$, and is characterized by the stoichiometry

$$5HClO_2 \longrightarrow 4ClO_2 + 2H_2O + H^+ + Cl^-$$

A voltammetric study of the system ClO_2^-–ClO_2–Cl^- on platinized platinum was carried out by two of us for analytical purposes.[4] The present work deals with the kinetic aspects of the problem and is part of a wider potentiostatic study of heterogeneous chemical reactions coupled with charge-transfer processes.[5,6] The technique employed both in ref 4 and in the present work is based on the use of an electrode with periodical renewal of the diffusion layer (dlpre), described by Cozzi and coworkers.[7] In the cell of the dlpre a Teflon-finned piston containing an iron nucleus is moved at regular intervals of time by a magnetic coil, causing a rapid laminar flow of the solution around a hemispherical microelectrode. The period of time during which the flowing solution reduces the diffusion layer thickness around the electrode almost to zero (washing period) is about 30 msec. The washing period, t_p, is followed by a much longer period of time, t_1 (3–9 sec), during which the solution around the electrode is perfectly still and the depolarizer reaches the electrode by simple diffusion. Owing to the periodical renewal of the diffusion layer, the current–potential characteristic recorded when the cell of the dlpre is connected with a polarograph is analogous to a polarographic wave. The only difference is represented by the fact that in the present case the average recorded current expresses the mean value over t_1 of an instantaneous potentiostatic current at a stationary spherical electrode rather than at a growing drop.

The quantitative examination both of the instantaneous potentiostatic currents and of the current–potential characteristics obtained from solutions of sodium chlorite at different acidities has led to the conclusion that the electroreduction of $HClO_2$ to Cl^- on platinized platinum in acid media proceeds through the heterogeneous decomposition of $HClO_2$ into ClO_2 and Cl^- and the simultaneous reduction of the ClO_2 so formed to $HClO_2$ according to the depolarization scheme

$$5HClO_2 \longrightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \qquad (1)$$

$$4(ClO_2 + H^+ + e^- \rightleftharpoons HClO_2) \qquad (2)$$

$$HClO_2 + 3H^+ + 4e^- \longrightarrow Cl^- + 2H_2O \qquad (3)$$

The heterogeneous disproportionation reaction (1) is first order with respect to chlorous acid and its rate increases with increasing hydrogen ion concentration, reaching a maximum for pH values less than 1. The charge-transfer process (2) is polarographically reversible on platinized platinum.

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(1) W. C. Bray, *Z. Anorg. Allg. Chem.*, **48**, 217 (1906).

(2) H. Taube and H. Dodgen, *J. Amer. Chem. Soc.*, 71, 3330 (1949).

(3) R. G. Kieffer and G. Gordon, *Inorg. Chem.*, 7, 235 (1968).

(4) G. Raspi and F. Pergola, *J. Electroanal. Chem.*, 20, 419 (1969).

(5) R. Guidelli, L. Nucci, and G. Raspi, *Trans. Faraday Soc.*, **64**, 3321 (1968).

(6) R. Guidelli, *J. Phys. Chem.*, 72, 3535 (1968).

(7) D. Cozzi, G. Raspi, and L. Nucci, *J. Electroanal. Chem.*, 12, 36 (1966).

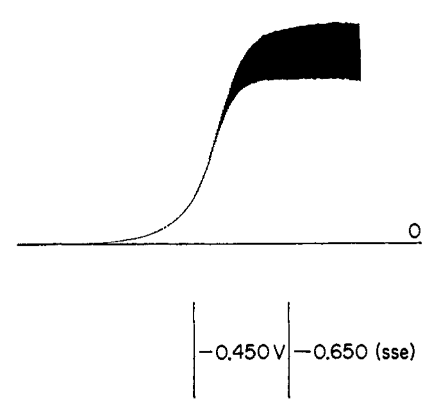

Figure 1. Reduction wave of 1 × 10^{-3} *M* sodium chlorite in a borax–NaOH buffer, pH 9.95.

In neutral and alkaline media the reduction of chlorite ion on platinized platinum proceeds through the initial slow electrochemical step

$$ClO_2^- + H^+ + e^- \longrightarrow ClO + OH^- \qquad (4)$$

or alternatively

$$ClO_2^- + H^+ + e^- \longrightarrow ClO^- + OH \qquad (4')$$

Experimental Section

The polarographic currents were recorded with a three-electrode system using a Polarecord E261 Metrohm, modified to allow a slow change of the applied potential (0.47 mV/sec) and connected with an IR compensator, Type E446 Metrohm. The potentiostatic current–time curves were measured on the screen of a Tektronix Type 502 dual-beam oscilloscope by making use of a 68-TS-1 Wenking potentiostat for the control of the applied potential. The platinum microelectrode was platinized by cathodizing it for 4 sec at a current density of 1.2 A cm^{-2} in a 3% solution of chloroplatinic acid containing 0.025% of lead acetate. Both the reference and the auxiliary electrodes were saturated mercurous sulfate electrodes, joined to the polarographic cell by bridges consisting of a solid mixture of silica gel and Na_2SO_4 (3:2). All potentials reported in the present work are referred to the above electrode. The supporting electrolytes consisted of mixtures of H_3PO_4-NaH_2PO_4 (1.8 < pH < 3.5), CH_3COOH-CH_3COONa (3.5 < pH < 5.5), NaH_2PO_4-Na_2HPO_4 (6.0 < pH < 8.0), $Na_2B_4O_7$-NaOH (9.3 < pH < 10.8), and Na_2HPO_4-Na_3PO_4 (11.0 < pH < 12.0). The ionic strength was kept equal to 1 by adding $NaNO_3$, whenever necessary. The pH values were measured with a Metrohm E388 potentiometer using a glass electrode, except for the 1 *M* and 0.1 *M* NaOH solutions. In these cases the pH was taken as 14.0 and 13.0, respectively. The sodium chlorite solutions were prepared according to Foerster and Dolch[8] and the chlorine dioxide solutions were prepared by the method suggested by Bray.[9]

The Neutral and Alkaline Media

In the pH range from 5.5 to 9.5 chlorite ion yields an anodic wave on platinized platinum, characterized by the transfer of 1 faraday per gram-ion, as shown by coulometric measurements carried out at potentials corresponding to the limiting current. The familiar *E* *vs.* log $i/(i_d - i)$ plot yields a straight line with a slope near 60 mV. Hence the above anodic wave, having an half-wave potential of +0.305 V, corresponds to the reversible charge-transfer process

$$ClO_2^- \rightleftharpoons ClO_2 + e^-$$

Analogous conclusions can be drawn on examining the cathodic wave obtained within the same potential range from a solution of chlorine dioxide or also the cath-anodic wave given by a mixture of ClO_2 and ClO_2^-.

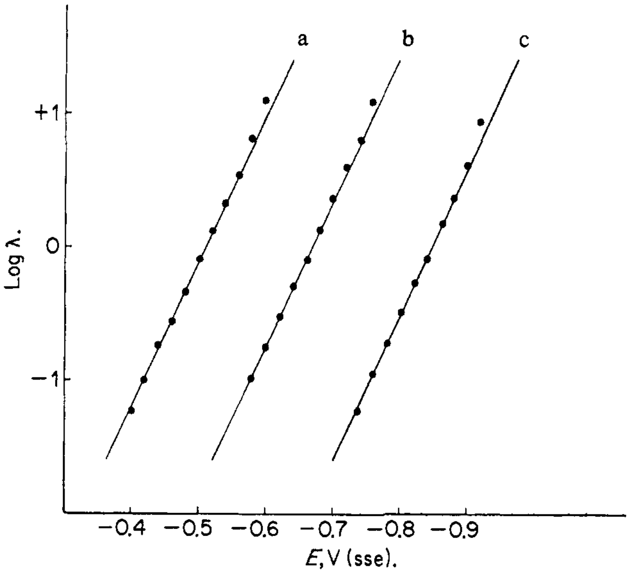

Figure 2. Plots of log λ *vs.* *E* along the rising portion of the cathodic wave of chlorite ion. Curves a and b were derived from the voltammograms of 5 × 10^{-4} *M* $NaClO_2$ in buffered solutions, pH 9.95 and 11.84, respectively. Curve c refers to a 5 × 10^{-4} *M* $NaClO_2$ solution in 1 *M* NaOH of which the pH value was assumed equal to 14.

Besides yielding the oxidation wave to ClO_2 previously described, a solution of chlorite ion in the pH range from 5.5 to 14 gives a cathodic wave higher than the anodic one by a factor of 4. The reduction wave corresponds to the overall electrode process

$$ClO_2^- + 2H_2O + 4e^- \longrightarrow Cl^- + 4OH^- \qquad (5)$$

Figure 1 shows a cathodic wave obtained by polarographing 10^{-3} *M* $NaClO_2$ in a buffer solution consisting of borax and NaOH, pH 9.95. The cathodic wave is irreversible and its half-wave potential shifts gradually toward more positive values with decreasing pH. The cathodic limiting current is diffusion controlled. In order to obtain reproducible cathodic waves of ClO_2^- at the various acidities, all the waves were recorded toward more negative potentials after having preelectrolyzed the solution for 2 min at a potential about 0.5 V more positive than the half-wave potential of the wave under study. This procedure is justified by the fact that within the potential range corresponding to the rising portion of the cathodic wave of ClO_2^- at the various acidities explored, the electrode is firmly covered with a surface layer of platinum oxides. Thus a current peak due to the electroreduction of this layer is superimposed on the cathodic limiting current in the proximity of the rising portion of the wave, provided the recording of the voltammogram is performed at a relatively high sweep rate (2.8 mV/sec). Consequently preelectrolysis and recording toward more negative potentials warrant that the electroreduction of ClO_2^- always takes place on an oxidized platinum electrode.

The investigation of the reduction wave of ClO_2^- to Cl^- allowed the rate constant, k_f, for the charge-transfer process (5) to be determined as a function of the applied potential by following a procedure described in a previous paper.[10] Thus from the values for the mean current at different potentials along the rising portion of

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(8) F. Foerster and P. Dolch, *Z. Elektrochem.*, **23**, 138 (1917).

(9) W. C. Bray, *Z. Phys. Chem.*, **54**, 569 (1906).

(10) R. Guidelli and G. Piccardi, *Electrochim. Acta*, **13**, 99 (1968).

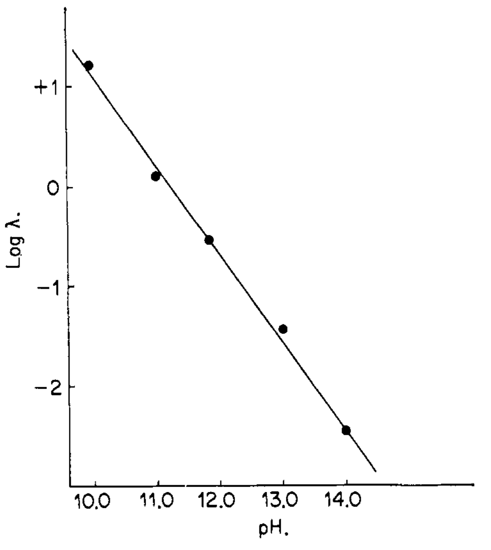

Figure 3. Values of log λ at $E = -0.620$ V against pH.

the cathodic wave it was possible to deduce the corresponding values for the dimensionless parameter $\lambda = k_f t_l^{1/2}/D^{1/2}$, where t_l is the period of electrolysis and D the diffusion coefficient of the depolarizer. Figure 2 shows log $k_f t_l^{1/2}/D^{1/2}$ against the applied potential, E, for pH values respectively equal to 9.95, 11.84, and 14.0. The linear plots in Figure 2 show that the electrode process (5) proceeds through a single rate-determining step. The value 10.8 V^{-1} for the slope of the straight lines log $k_f t_l^{1/2}/D^{1/2}$ *vs.* E in Figure 2 equals $(n_0/\nu_l + \alpha n_l)F/2.3RT$, where n_0 is the number of electrons preceding the rate-determining stage, calculated with reference to the stoichiometric equation of the electrode process; n_l is the number of electrons involved in the rate-determining step; ν_l is the stoichiometric number of this step; and α is the transfer coefficient.[11] Taking into account that the most probable value for α is 0.5, the experimental value 0.64 for $n_0/\nu_l + \alpha n_l$ strongly suggests that in the case under study $n_0 = 0$ and $n_l = 1$.

The dependence of the rate constant, k_f, upon the hydrogen ion concentration is shown in Figure 3 where some experimental values of log λ at $E = -0.620$ V are plotted against pH. These values were obtained by extrapolating, whenever necessary, the linear log λ *vs.* E plots. The slope −0.9 of the straight line log λ *vs.* pH reveals that the rate constant, k_f, for the charge-transfer process (5) at a given potential is proportional to the hydrogen ion concentration. This constant can therefore be written in the form $k_f = k_0[H^+] \exp[-\alpha F(E - E_0)/RT]$, where $\alpha = 0.64$ and k_0 is the rate constant at the reference potential E_0 for a unitary hydrogen ion concentration. The experimental results indicate stage 4, or alternatively stage 4′, as the rate-determining step of the overall electrode reaction (5).

Recently Schwarzer and Landsberg[12] have shown that the electroreduction of hypochlorite ion to Cl^- on platinum in neutral and alkaline media proceeds through the mechanism

$$ClO^- + e^- + H^+ \longrightarrow Cl + OH^-$$

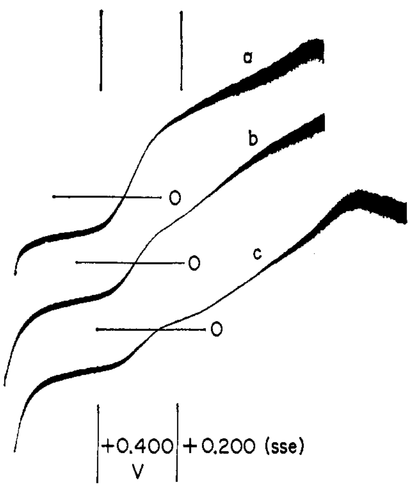

Figure 4. Voltammograms of 5×10^{-4} *M* $NaClO_4$ in buffered solutions: pH 2.8 (a), 4.0 (b), and 5.0 (c).

Taking into account that at any given acidity the reduction wave of hypochlorite ion on platinized platinum occurs at more positive potentials than the reduction wave of chlorite ion, a plausible complete mechanism for the electroreduction of ClO_2^- to Cl^- is the following

$$ClO_2^- + H^+ + e^- \longrightarrow ClO + OH^-$$
$$ClO + e^- \longrightarrow ClO^-$$

or

$$ClO_2^- + H^+ + e^- \longrightarrow ClO^- + OH$$
$$OH + e^- \longrightarrow OH^-$$

$$ClO^- + H^+ + e^- \longrightarrow Cl + OH^-$$
$$Cl + e^- \longrightarrow Cl^-$$

or

$$ClO^- + H^+ + e^- \longrightarrow Cl^- + OH$$
$$OH + e^- \longrightarrow OH^-$$

where hypochlorite ion appears as an intermediate product.

The Acid Media

For pH values higher than 5.5 chlorite ion gives both a reversible anodic wave and an irreversible cathodic wave, the one well distinct from the other. With increasing acidity the anodic wave tends to become composite, exhibiting a cathodic portion which progressively grows at the expense of the irreversible cathodic wave (see Figure 4). Thus at pH 4 the cathodic portion of the composite wave reaches a height which is equal to that of the anodic portion. It must be noted that the value for the anodic limiting current, which corresponds to the oxidation of chlorous acid to chlorine dioxide, remains constant with changing acidity. In practice at pH 1 the composite wave exhibits a cathodic portion higher than the anodic one by a factor of 4, with the consequent disappearance of the irreversible cathodic wave.

The rate of the homogeneous disproportionation of chlorous acid, which reaches a maximum at pH values less than 3, does not alter the bulk concentration of the acid during the recording of a single voltammogram. Thus the anodic limiting current of 10^{-3} *M* $HClO_2$ in 1 *M* $HClO_4$ decreases by no more than 5% within 30 min, in agreement with Kieffer and Gordon.[3]

Curve a in Figure 5 is the composite wave of 5×10^{-4} *M* $HClO_2$ in 1 *M* $HClO_4$ for an electrolysis period

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[11] R. Parsons, private communication. See also H. Mauser, *Z. Elektrochem.*, **62**, 419 (1958).

[12] O. Schwarzer and R. Landsberg, *J. Electroanal. Chem.*, **19**, 391 (1968).

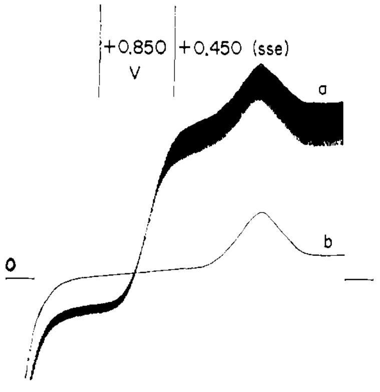

Figure 5. Composite wave of 5×10^{-4} M $HClO_2$ in 1 M $HClO_4$ (a) and voltammogram of 1 M $HClO_4$ alone (b).

t_1 = 5 sec. The potential, $E(0)$, at which the mean current equals zero, has a value of +0.511 V. The current peak superimposed on the cathodic limiting current at about +0.16 V is due to the electroreduction of the film of platinum oxides covering the electrode along the rising portion of the composite wave. This peak is also encountered in the voltammetric curve of 1 M perchloric acid alone (curve b in Figure 5).

An increase in the acidity of the solution, besides causing an increase in the cathodic portion of the composite wave, produces a shift of this wave toward more positive potentials which is higher than would be expected for the reversible oxidation wave of ClO_2^- to ClO_2. In this connection let us denote by $E_{1/2}$ the half-wave potential which would characterize the reversible anodic wave of ClO_2^- if the kinetic complications giving rise to the composite wave did not take place. Taking into account the reversibility of the ClO_2/ClO_2^- couple on platinized platinum and assuming for simplicity that the species ClO_2, ClO_2^-, and $HClO_2$ have equal diffusion coefficients, the surface concentrations $[\overline{ClO_2}]$, $[\overline{ClO_2^-}]$, and $[\overline{HClO_2}]$ are related to the applied potential, E, according to the equation

$$E = E_{1/2} + \frac{RT}{F} \ln \frac{[\overline{ClO_2}]}{[\overline{ClO_2^-}] + [\overline{HClO_2}]} =$$

$$E_{1/2} + \frac{RT}{F} \ln \frac{[\overline{ClO_2}]}{[\overline{ClO_2^-}]} - \frac{RT}{F} \ln \left(1 + \frac{[H^+]}{K}\right) \quad (6)$$

where K is the dissociation constant $[H^+][ClO_2^-]/[HClO_2]$ of chlorous acid. In neutral and alkaline media, where no kinetic complications arise and the percentage of undissociated chlorous acid is wholly negligible, the half-wave potential for the reversible wave $ClO_2^- \rightleftharpoons ClO_2 + e^-$ equals +0.305 V, as previously stated. In view of eq 6, we therefore have, for any pH value

$$E_{1/2} = +0.305 \text{ V} + \frac{RT}{F} \ln \left(1 + \frac{[H^+]}{K}\right)$$

The value for the dissociation constant, K, of chlorous acid is about 10^{-2} mol/l.,[13,14] so that the calculated value of $E_{1/2}$ in 1 M $HClO_4$ is about 0.423 V. In order to obtain the correct value for the difference $E(0) - E_{1/2}$ in this medium we must also take into account the appreciable liquid junction potential which is established at the boundary between the polarographic solution and the salt bridge separating it from the reference electrode when passing from hydrogen ion concentrations lower than 0.1 M to the 1 M concentration.

In order to estimate the magnitude of the liquid junction potential it has been found convenient to record the reversible oxidation wave of 10^{-3} M I^- to I_2 on smooth platinum at various acidities, employing the same supporting electrolytes as well as the same salt bridge used with chlorous acid. The half-wave potential of the anodic wave of iodide ion remains constant with respect to the reference electrode for hydrogen ion concentrations lower than 0.1 M, but it shifts toward more negative values by about 42 mV when $[H^+]$ is made equal to 1 M. Since the reversible system I^-/I_2 is not affected by a change in the acidity for pH values lower than 7, the above shift must be attributed to the appearance of an appreciable liquid junction potential due to the high mobility of hydrogen ions. Therefore the difference $E(0) - E_{1/2}$ relative to a solution of chlorous acid in 1 M $HClO_4$, after correction for the liquid junction potential, amounts to about 130 mV.

The composite waves of $HClO_2$ in acid media exhibit distinct oscillations when the mean current, $\bar{\imath}$, equals zero. This fact is confirmed by the oscillographic investigation of the instantaneous potentiostatic current at the potential $E(0)$ corresponding to $\bar{\imath} = 0$. This current passes from negative to positive values when the time of electrolysis, t, increases, which explains the slight experimental change of $E(0)$ with t_1.

The voltammetric behavior of chlorous acid previously described could be qualitatively explained by assuming that the protonation reaction

$$ClO_2^- + H^+ \underset{k_b = Kk_f}{\overset{k_f}{\rightleftharpoons}} HClO_2 \quad (7)$$

is slow and that $HClO_2$ is more easily electroreduced than ClO_2^-. With these assumptions the cathodic limiting current of the composite waves in Figure 4 could be attributed to the electroreduction of $HClO_2$ to Cl^-, limited by the rate of the antecedent protonation of ClO_2^-. Since the composite waves do not show inflections at zero current, we must further assume that the direct electroreduction of $HClO_2$ occurs at more positive potentials than those at which the electrooxidation of ClO_2^- to ClO_2 starts to take place. Apart from the fact that this latter assumption seems rather odd, we must also note that the value of the rate constant k_f for the protonation reaction (7), as calculated from the ratio of the mean cathodic limiting current $\bar{\imath}_{c,l}$ of the composite waves in Figure 4 to the corresponding diffusion limiting current $\bar{\imath}_d$, is exceedingly small. Thus the value of the ratio $\bar{\imath}_{c,l}/\bar{\imath}_d$ for curve b in Figure 4 is about 1/4, leading to a value of $\lambda \equiv [H^+] \sqrt{k_f t_1/K}$ equal to 0.32 (see eq 20 of ref 10 for an expression of $\bar{\imath}_{c,l}/\bar{\imath}_d$ as a function of k_f). Since the period of electrolysis t_1 equals 5 sec, $[H^+] = 10^{-4}$ g-ion $l.^{-1}$, and the dissociation constant K of $HClO_2$ amounts to 10^{-2} mol $l.^{-1}$, it immediately follows that $k_f \cong 2 \times 10^4$ l. mol^{-1} sec^{-1}. As a matter of fact, protonation reactions relative to inorganic acids are usually diffusion-controlled ($k_f = 10^{11}$ l. mol^{-1} sec^{-1}) or, anyway, they are characterized by k_f values higher than 10^{10} l. mol^{-1} sec^{-1}.[15] Therefore the interpreta-

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(13) G. F. Davidson, *J. Chem. Soc.*, 1649 (1954).

(14) D. Leonesi and G. Piantoni, *Ann. Chim.* (Rome), 55, 668 (1965).

(15) R. P. Bell, *Quart. Rev.*, 13, 169 (1959).

tion of the features of the composite wave of chlorous acid based on the assumption of a slow protonation of ClO_2^- must be ruled out as unsound. Conversely, all the features of the composite wave of chlorous acid can be quantitatively accounted for if we assume that the reduction of $HClO_2$ to Cl^- proceeds through the mechanism 1–3 involving the heterogeneous chemical decomposition of $HClO_2$ on the electrode surface. An analogous mechanism was proposed by two of us[5] for the interpretation of the composite wave of hydrogen peroxide on platinized platinum.

In order to prove the strong catalytic effect of platinized platinum upon the disproportionation of chlorous acid, we measured the decrease in the mean diffusion-limiting current of $HClO_2$ to ClO_2 in 0.1 M $HClO_4$ at a platinized platinum dlpre, area 0.055 cm^2, after having immersed a platinized platinum coil, area 8.5 cm^2, in the solution contained in the electrolysis cell. The renewal of the solution, depleted in $HClO_2$, around the platinum coil was produced by the same piston renewing the diffusion layer around the dlpre. In a typical experience the cell contained 25 cm^3 of 10^{-3} M $NaClO_2$ in 0.1 M $HClO_4$ and the period of electrolysis t_1 was adjusted at 3 sec. Under these conditions the mean limiting current $\bar{\imath}_{a,l}$ of $HClO_2$ to ClO_2, which measures the bulk concentration of $HClO_2$, decreased exponentially with the time τ elapsed after immersion of the platinum coil into the solution, reducing to $^1/_{100}$th of its original value after 25 min. The plot of the common logarithm of the bulk concentration $[HClO_2]^*$ of $HClO_2$ against τ yielded a perfectly straight line from $[HClO_2]^* = 10^{-3}\ M$ to $[HClO_2]^* = 10^{-5}\ M$.

Incidentally it must be noted that the linearity of the plot is not indicative of a decomposition reaction first order with respect to $HClO_2$. In fact, owing to the high rate of the chemical disproportionation proper at the surface of the catalyst, the rate of the overall decomposition process is exclusively controlled by the diffusion[16] of $HClO_2$ toward the platinized platinum coil. This is confirmed by the strong dependence of the slope of the log $[HClO_2]^*$ *vs.* τ plot upon the rate of stirring of the solution as measured by the frequency $1/t_1$ of the piston strokes.

After having decomposed $^{99}/_{100}$th of the amount of $HClO_2$ initially present in the cell (τ = 25 min), the platinum coil was extracted from the solution and this latter was polarographed from +0.8 to +0.2 V, *i.e.*, in the potential range corresponding to the composite wave of $HClO_2$. In this connection it must be noted that both ClO_3^- and Cl^- are electroinactive within this potential range (Cl^- is electrooxidized at about +0.86 V). The voltammetric curve thus obtained was exclusively cathodic, corresponding to the reduction to Cl^- of the ClO_2 produced in the disproportionation of $HClO_2$. The value of the reduction limiting current of ClO_2 to Cl^- was equal to that of the cathodic limiting current of the composite wave yielded by the initial solution of $HClO_2$. Hence the number of moles of ClO_2 produced in the almost complete heterogeneous decomposition of $HClO_2$ equals $^4/_5$th of the number of moles of $HClO_2$ originally present in the solution; *i.e.*, the stoichiometry of the heterogeneous disproportionation reaction of $HClO_2$ is expressed by eq 1. Since eq 1 is also the stoichiometric equation of the homogeneous decomposition reaction catalyzed by Cl^-, it is probable that the heterogeneous decomposition of $HClO_2$ takes place under the influence of a stationary monolayer of chloride ions adsorbed on platinized platinum. Obviously the experiments previously described do not allow the detailed mechanism of the heterogeneous disproportionation of $HClO_2$ to be disclosed through the consideration of unstable intermediate radicals eventually participating in the overall reaction (1). The mechanism 1–3 must therefore be regarded as consisting of the overall purely chemical heterogeneous decomposition reaction (1) coupled with the polarographically reversible charge-transfer process (2).

If we assume the validity of the above mechanism and designate by ϑ the ratio

$$\vartheta = \frac{[\overline{ClO_2}]}{[\overline{ClO_2^-}] + [\overline{HClO_2}]} = \exp\left[\frac{F}{RT}(E - E_{1/2})\right]$$

then, for sufficiently positive potentials, corresponding to the anodic diffusion-limiting current, the overall concentration of chlorous acid at the electrode surface is practically zero and consequently its heterogeneous disproportionation does not take place. With decreasing potential the surface concentration $\{[\overline{ClO_2^-}] + [\overline{HClO_2}]\}$ begins to become appreciable and the same must be said for the rate of the heterogeneous reaction (1). For a given value of the applied potential, and therefore of ϑ, the disproportionation reaction tends to increase ϑ both through an increase in $[\overline{ClO_2}]$ and a decrease in $[\overline{ClO_2^-}] + [\overline{HClO_2}]$. Owing to the reversibility of the system ClO_2/ClO_2^-, a cathodic "kinetic" contribution to the current is originated which instantaneously restores the ϑ value corresponding to the applied potential through the electroreduction of ClO_2 to chlorous acid. It follows that the anodic current decreases with respect to its limiting value at potentials more positive than those which would be expected in the absence of the heterogeneous reaction (1). With decreasing potential the rate of chlorous acid decomposition becomes so high that, provided pH is sufficiently low (≤ 1), the effect of the kinetic current is identical with that of the direct electroreduction of $HClO_2$ to Cl^- under limiting conditions.

In order to verify the validity of the preceding mechanism from a quantitative point of view, the diffusional problem relative to the depolarization scheme 1–3 has been solved. Let us designate the sum $[ClO_2^-] + [HClO_2]$ of the concentrations of the dissociated and undissociated forms of chlorous acid by a and the concentration $[ClO_2]$ of chlorine dioxide by b. The instantaneous potentiostatic current on a stationary spherical electrode for the case under examination can be obtained by solving the system of differential equations

$$\frac{\partial a}{\partial t} = D\left(\frac{\partial^2 a}{\partial r^2} + \frac{2}{r}\frac{\partial a}{\partial r}\right) \tag{8}$$

$$\frac{\partial b}{\partial t} = D\left(\frac{\partial^2 b}{\partial r^2} + \frac{2}{r}\frac{\partial b}{\partial r}\right) \tag{9}$$

with the initial and boundary conditions

$$\begin{array}{l} a = a^* \text{ for } r \geqslant r_0,\ t = 0 \\ b = 0 \quad \text{for } r \longrightarrow \infty,\ t > 0 \end{array} \tag{10}$$

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[16] E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1947, pp 367–370.

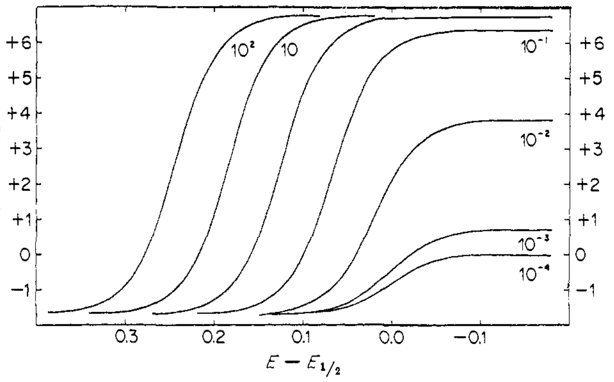

Figure 6. Theoretical current–potential characteristics as obtained from eq 18 for the following data: 25°, $D = 10^{-5}$ cm^2/sec, $r_0 = 10^{-1}$ cm, $t_1 = 5$ sec. The number on each curve is the value of σ in cm/sec.

$$\frac{b(r_0,t)}{a(r_0,t)} = \vartheta = \exp\left[\frac{F}{RT}(E - E_{1/2})\right] \qquad \text{for } r = r_0,\ t > 0 \tag{11}$$

$$D\left(\frac{\partial a}{\partial r}\right)_{r_0} = -D\left(\frac{\partial b}{\partial r}\right)_{r_0} - D\left(\frac{\partial[\mathrm{Cl^-}]}{\partial r}\right)_{r_0} = -D\left(\frac{\partial b}{\partial r}\right)_{r_0} + \frac{\sigma}{5}a(r_0,t) \tag{12}$$

Here r_0 is the radius of the spherical electrode, r the distance from its center, t the electrolysis time, a^* the overall concentration of chlorous acid in the bulk of the solution, and D the diffusion coefficient common to the species ClO_2, ClO_2^-, and $HClO_2$. The boundary condition 12 expresses the fact that the flux of chlorous acid toward the electrode $[D(\partial a/\partial r)_{r_0}]$ equals the flux of chlorine dioxide $[-D(\partial b/\partial r)_{r_0}]$ and chloride ion $[-D(\partial[\mathrm{Cl^-}]/\partial r)_{r_0}]$ away from the electrode. The flux of chloride ion leaving the electrode is in turn set equal to the quantity $d[\mathrm{Cl^-}]/dt$ of Cl^- produced per unit area of the electrode per unit time, which amounts to one-fifth of the quantity $\sigma a(r_0,t)$ of chlorous acid decomposing on the unit surface in the same unit time.

$$-D\left(\frac{\partial[\mathrm{Cl^-}]}{\partial r}\right)_{r_0} = \frac{d[\mathrm{Cl^-}]}{dt} = \frac{\sigma}{5}a(r_0,t)$$

σ is the rate constant for the heterogeneous reaction (1), which we have considered to be first order with respect to chlorous acid. This assumption is based on the theoretical consideration that, in the case of higher order kinetics with respect to chlorous acid, an increase in a^* is expected to cause a shift of the composite wave towards more positive potentials. This behavior, which is qualitatively analogous to that produced by an increment in the rate constant, σ, of a first-order heterogeneous reaction, has not been observed. On the contrary an increase in a^* at constant hydrogen ion concentration produces a shift of the $E(0)$ potential of the composite wave toward more negative values, for $a^* > 10^{-3}$ mol/l. This shift is accompanied by a slight drawing-out of the wave and can be attributed to the adsorption of depolarizer and depolarization product on the electrode.[17] The instantaneous current is expressed by the equation

$$i = -FA\left[D\left(\frac{\partial a}{\partial r}\right)_{r_0} - \sigma a(r_0,t)\right] \tag{13}$$

according to which the current density is proportional to the flux of chlorous acid toward the electrode minus the amount of chlorous acid decomposing per unit time per unit area of the electrode.

The diffusional problem 8–12 has been solved through the use of Laplace transformations and the expression for the concentration, $a = a(r,t)$, so derived, has been replaced in eq 13. The resulting equation for the potentiostatic current is

$$\frac{i}{FAa^*} = -\frac{\vartheta}{1+\vartheta}\frac{D^{1/2}}{\pi^{1/2}t^{1/2}} + \frac{5D\sigma}{\sigma r_0 + 5D(1+\vartheta)} - \alpha\frac{D}{r_0} + \frac{4+5\vartheta}{5(1+\vartheta)^2}\frac{\sigma^2 r_0}{\sigma r_0 + 5D(1+\vartheta)} \times \exp(\beta^2 t)\,\mathrm{erfc}(\beta t^{1/2}) \tag{14}$$

where

$$\alpha = \frac{5D\vartheta + \sigma r_0}{5D(1+\vartheta) + \sigma r_0}$$

and

$$\beta = \frac{D^{1/2}}{r_0} + \frac{\sigma}{5D^{1/2}(1+\vartheta)}$$

Equation 14 shows that two limiting currents are to be expected when chlorous acid is present in the solution. Thus, when $\vartheta \rightarrow \infty$ eq 14 yields the anodic limiting current, $i_{a,l}$

$$i_{a,l} = \lim_{\vartheta\rightarrow\infty} i = -FAa^*\left(\frac{D^{1/2}}{\pi^{1/2}t^{1/2}} + \frac{D}{r_0}\right) \tag{15}$$

which has the form of the usual diffusion limiting current at a spherical electrode. Conversely, if we let ϑ tend to zero in eq 14, we obtain the cathodic limiting current, $i_{c,l}$

$$i_{c,l} = \lim_{\vartheta\rightarrow 0} i = FAa^*\left[\frac{4D\sigma}{\sigma r_0 + 5D} + \frac{4}{5}\frac{\sigma^2 r_0}{(\sigma r_0 + 5D)}\exp(\gamma^2 t)\,\mathrm{erfc}(\gamma t^{1/2})\right] \tag{16}$$

where

$$\gamma = \frac{D^{1/2}}{r_0} + \frac{\sigma}{5D^{1/2}}$$

The current $i_{c,l}$ is simultaneously controlled by diffusion and by the rate of the heterogeneous reaction (1). If the value for the rate constant, σ, is so high that $\sigma \gg 5D/r_0$ and $\gamma t^{1/2} > 7$, eq 16 takes the simplified form

$$\lim_{\sigma\rightarrow\infty} i_{c,l} = 4FAa^*\left[\frac{D^{1/2}}{\pi^{1/2}t^{1/2}} + \frac{D}{r_0}\right] \tag{17}$$

Equation 17 has been derived from eq 16 upon neglecting $5D$ with respect to σr_0 and replacing $\mathrm{erfc}(\gamma t^{1/2})$ by the first term of its series expansion for high values of the argument, *i.e.*, $\exp(-\gamma^2 t)/(\pi^{1/2}\gamma t^{1/2})$. From eq 17 it is manifest that the cathodic limiting current approaches the value for the diffusion limiting current due to the direct reduction of $HClO_2$ to Cl^- when σ tends to ∞. The potentiostatic mean current, $\bar{i}$, is obtained by integrating the instantaneous current, i, given by eq 14, over the period of electrolysis, t_1

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[17] R. Guidelli, *J. Phys. Chem.*, 74, 95 (1970).

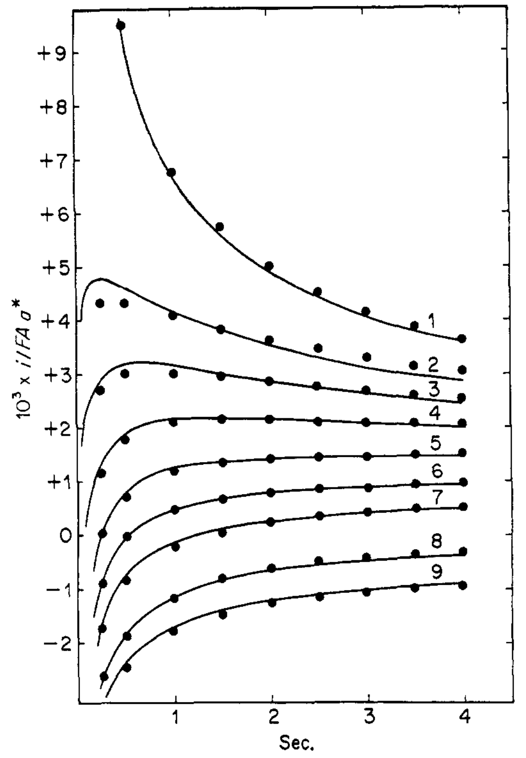

Figure 7. The solid curves express the theoretical current–time curves as obtained from eq 19 for the following data: 25°, $D = 0.8 \times 10^{-5}$ cm²/sec, $r_0 = 0.094$ cm. The curves refer to different values of $(RT/F)\ln(\vartheta/\sigma)$: (2) 0.110, (3) 0.120, (4) 0.130, (5) 0.140, (6) 0.150, (7) 0.160, (8) 0.190; (RT/F) in V, ϑ/σ in sec/cm. The circles represent experimental values for 5×10^{-4} M $HClO_2$ in 1 M $HClO_4$. The values of potential (V) against the saturated mercurous sulfate electrode for the various curves are as follows: (2) 0.461, (3) 0.471, (4) 0.481, (5) 0.491, (6) 0.501, (7) 0.511, (8) 0.541.

$$\frac{\bar{\imath}}{FAa^*} = \frac{1}{t_1}\int_0^{t_1} \frac{i}{FAa^*}\,\mathrm{d}t = -\frac{2\vartheta D^{1/2}}{(1+\vartheta)\pi^{1/2}t_1^{1/2}} + \frac{5D\sigma}{\sigma r_0 + 5D(1+\vartheta)} - \alpha\frac{D}{r_0} + \frac{4+5\vartheta}{5(1+\vartheta)^2} \times \frac{\sigma^2 r_0}{\sigma r_0 + 5D(1+\vartheta)}\frac{1}{\beta^2 t_1}\left[\exp(\beta^2 t_1)\operatorname{erfc}(\beta t_1^{1/2}) + \frac{2}{\pi^{1/2}}\beta t_1^{1/2} - 1\right] \quad (18)$$

Figure 6 shows a series of current–potential characteristics derived from eq 18 for $D = 10^{-5}$ cm²/sec, $t_1 = 5$ sec, $r_0 = 0.1$ cm, and for different values of σ. From Figure 6 it is manifest that for σ values $>10^{-1}$ cm/sec and $E(0) - E_{1/2}$ values >100 mV the cathodic limiting current reaches its maximum value corresponding to four times that for the anodic limiting current. At the same time the rising portion of the composite wave occurs at potentials for which $\vartheta \gg 1$. Under these conditions the expression for the instantaneous current can be strongly simplified. Thus, upon neglecting 1 with respect to ϑ, eq 14 becomes

$$\frac{i}{FAa^*} = -\frac{D^{1/2}}{\pi^{1/2}t^{1/2}} + \frac{5\zeta D}{\zeta r_0 + 5D} - \frac{D}{r_0} + \frac{\zeta^2 r_0}{\zeta r_0 + 5D}\exp(\beta'^2 t)\operatorname{erfc}(\beta' t^{1/2}) \quad (19)$$

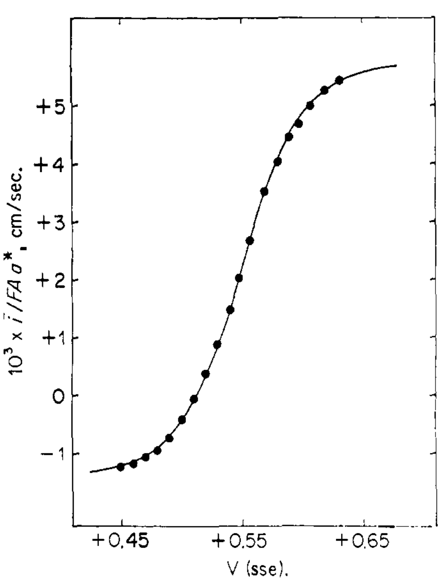

Figure 8. The solid curve expresses the theoretical current–potential characteristic obtained from eq 18 for $D = 0.8 \times 10^{-5}$ cm²/sec, $r_0 = 0.094$ cm, $t_1 = 5$ sec, $\log \sigma = -0.5$ (σ in cm/sec) and corrected for the "washing period," $t_p = 3 \times 10^{-2}$ sec. The circles represent experimental values for 5×10^{-4} M $HClO_2$ in 1 M $HClO_4$ at 25°.

where

$$\zeta = \frac{\sigma}{\vartheta} \qquad \beta' = \frac{D^{1/2}}{r_0} + \frac{\zeta}{5D^{1/2}}$$

Equation 19 shows that for $\vartheta \gg 1$ the instantaneous current, i, and consequently the mean current, $\bar{\imath}$, do not depend upon ϑ and σ separately, but rather upon the ratio between these parameters. It follows that an increase in the rate constant, σ, does not alter the shape of the current–potential characteristic but simply causes it to shift toward more positive potentials. Obviously the relation between the potential, $E(0)$, at which $\bar{\imath} = 0$, and the rate constant, σ, is of the type $E(0) - E_{1/2}$ = constant + $(RT/F)\ln\sigma$ (see Figure 6).

If $\vartheta \gg 1$, a given potentiostatic current–time curve preserves its shape with changing σ provided that it is attributed to a potential suitably changed in order to keep the ratio σ/ϑ constant. This circumstance, which is encountered along the whole rising portion of the composite wave of $HClO_2$ in 1 M $HClO_4$, is particularly advantageous since it allows the theoretical relation (19) to be tested without knowing the exact value for $E_{1/2}$. Figure 7 shows a series of theoretical current–time curves obtained from eq 19 together with the corresponding experimental curves represented by circles. The superimposition of the experimental curves on the theoretical ones has been accomplished by choosing, among the various experimental curves, that in best agreement with the theoretical curve 6 in Figure 7 and associating the remaining theoretical curves with the experimental curves corresponding to the same potential increments, $\pm\Delta E$, with respect to curve 6. Curves 1 and 9 represent the cathodic and anodic limiting currents, respectively. Since, as appears from Figure 5, the cathodic limiting current is disturbed by the current due to the reduction of platinum oxides, the experimental curve 1 in Figure 7 has been obtained by subtracting the current–time curve, given by 1 M

$HClO_4$ at $+0.50$ V, from the current–time curve given by 5×10^{-4} *M* $HClO_2$ in 1 *M* $HClO_4$ at the same potential. The agreement between experimental and theoretical curves is good. An analogous agreement is encountered in comparing the experimental current–potential characteristics with the corresponding theoretical characteristics as obtained from eq 18. In this connection a series of theoretical voltammograms was calculated for $D = 0.8 \times 10^{-5}$ cm^2/sec, $r_0 = 0.094$ cm, $t_1 = 5$ sec, and for several values of σ. These voltammograms were subsequently corrected for the "washing period," $t_p = 3 \times 10^{-2}$ sec, by following a procedure described in ref 7. The above values of D, r_0, t_1, and t_p correspond to the experimental conditions employed in the measurements. From the comparison between the theoretical voltammograms and the experimental curve of 5×10^{-4} *M* $HClO_2$ in 1 *M* $HClO_4$ it has been possible to attribute the value 0.3 to the rate constant σ in 1 *M* $HClO_4$. The theoretical current–potential characteristic corresponding to this value of σ is represented by the solid curve in Figure 8, whereas circles express the experimental voltammetric curve.

Unfortunately the uncertainty about the value for the dissociation constant, K, of $HClO_2$ as well as the error made in the evaluation of the liquid junction potential cause the experimental value for $E(0) - E_{1/2}$ to be inaccurate. It follows that the value of σ is also roughly approximate. Furthermore it must be noted that the value of σ depends upon the state of the surface of the platinized platinum electrode. Thus the voltammetric curves recorded on platinum electrodes platinized some days before recording are characterized by $E(0) - E_{1/2}$ values lower than that obtained with a freshly platinized electrode even by 30 mV, as a consequence of a decrease in σ due to the aging of the platinization.

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Electronic Spectra of the Dithioacetylacetone Complexes of Nickel(II), Palladium(II), and Platinum(II)[1]

Olavi Siimann and James Fresco

Contribution from the Chemistry Department, McGill University,
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Abstract: An extended Wolfsberg-Helmholz molecular orbital calculation has been performed for bis(dithioacetylacetonato)nickel(II). The energy level diagram produced permitted assignment of the electronic spectra of nickel(II), palladium(II), and platinum(II) dithioacetylacetonates recorded in coordinating and noncoordinating solvents. Bands in the electronic spectrum of cobalt(II) dithioacetylacetonate were also assigned. Values obtained for the splitting parameter, Δ_1, of the nickel(II) and palladium(II) complexes indicated that the dithioacetylacetonate anion assumes an intermediate position in a spectrochemical series of sulfur donors.

The electronic spectra of planar d^8 metal complexes containing sulfur donor atoms have been investigated to establish the properties of the molecular orbitals in planar metal complexes. Semiempirical molecular orbital calculations were performed for metal dithiolates,[2] dithiooxalates,[3] and dithienes.[4] The recent synthesis of metal complexes of dithioacetylacetone[5] in which the donor atoms exist in six-membered rather than five-membered rings has stimulated interest in their spectral properties.[5a]

The electronic properties of dithioacetylacetonates appear more similar to those of dithiolates than acetylacetonates. The profound influence of sulfur can be further noted in the electronic spectra of monothioacetylacetonates.[6] These spectra have a greater resemblance to the spectra of dithioacetylacetonates than acetylacetonates.

A molecular orbital calculation for the diamagnetic nickel(II) chelate of dithioacetylacetone has been performed to determine the energies of the molecular orbitals of the complex and to ascertain the donor properties of the dithioacetylacetone anion. Since the observed absorption bands of the complex could be reasonably assigned and agreement exists between observed and calculated frequencies, the Wolfsberg–Helmholz[7,8] molecular orbital calculation employed appears satisfactory. The results obtained will be reported here.

Experimental Section

The complexes studied were prepared by previously described methods.[5b] All spectra were recorded on a Perkin-Elmer 350 spectrophotometer. Matched pairs of quartz cells of 1.0- and 10.0-cm path lengths were used to examine solutions over the concentration range 0.001–0.00001 *M*. Spectrograde solvents were employed without further purifications.

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[1] A preliminary account of this work was presented at the 52nd Canadian Chemical Conference, Montreal, May 1969.

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