808. *The Polarography of Oximes.*

By H. J. Gardner and W. P. Georgans.

The polarographic behaviour of some alkyl aryl and diaryl ketoximes has been studied in buffered solutions. A wave is given by each compound in the pH range 2—*ca.* 10, and corresponds to the uptake of four electrons. The $E_{\frac{1}{2}}$–pH coefficient is *ca.* -70 mv per pH unit. Reduction of the oxime probably proceeds via the conjugate acid of the oxime, $(R_2C{:}N{\cdot}OH)H^+$, which is expected at the electrode interface as an intermediate. The wave height falls to zero at pH $>$ *ca.* 6, owing probably to the decreasing rate of formation of $(R_2C{:}N{\cdot}OH)H^+$. With some oximes in alkaline solutions there is a second wave which is not clearly differentiated from the solution decomposition current. The maximum wave height is nearly equal to that of the first wave. The $E_{\frac{1}{2}}$–pH coefficient is small. Reduction probably proceeds *via* the initial uptake of four electrons to the neutral oxime.

Oximes from alkyl aryl and diaryl ketones have been studied polarographically in buffered solutions by Langer,[1] Stone and Furman,[2] and Souchay and Ser.[3] The present work, which was begun before publication by Souchay and Ser,[3] confirms their findings for the the general behaviour of oximes but also suggests phenomena in both acidic and alkaline regions which may be typical of oximes generally.

The oximes studied were derived from benzophenone, phenyl *p*-tolyl ketone, methyl β-naphthyl ketone, acetophenone, methyl *p*-tolyl ketone, and benzoin.

Results

The current–voltage waves of benzophenone oxime in solutions of pH $>$ 2 were typical of the oximes generally (see Fig. 1). The decrease of the first wave height with pH is broadly

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[1] Langer, *Ind. Eng. Chem. Anal.*, 1942, **14**, 283.

[2] Stone and Furman, *J. Amer. Chem. Soc.*, 1948, **70**, 3062.

[3] Souchay and Ser, *J. Chim. phys.*, 1952, **49**, 172.

similar to that observed for pyruvic acid [4] but differs by the presence of a maximum and a minimum in the wave between pH 5 and 8. The maxima were not removed by the addition of small amounts of gelatine and the oximes were studied in the absence of a maximum suppressor. Fig. 2 shows plots of the maximum (limiting) currents against pH for the oximes studied.

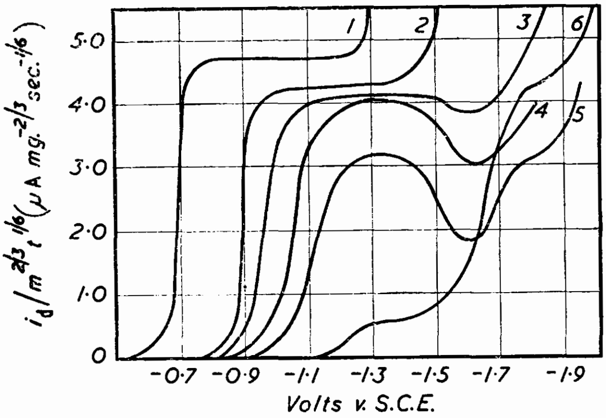

FIG. 1. *Benzophenone oxime*: 1·0mM *with buffer mixture A and* 25% (*vol.*) *ethanol, showing shape of waves at various* pH. *The* pH *values are*: 1, 2·29; 2, 4·56; 3, 5·62; 4, 6·57; 5, 7·65; 6, 9·5.

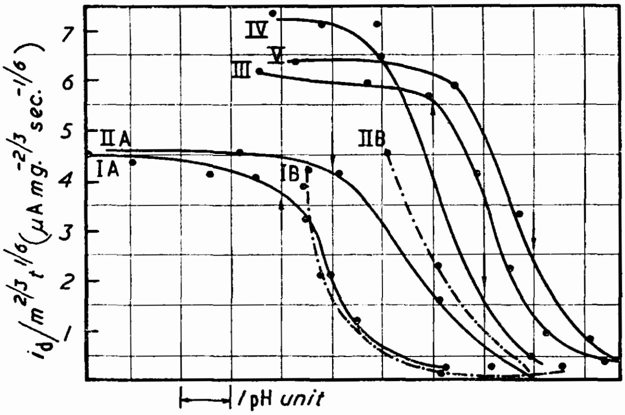

FIG. 2. *Limiting currents of the first wave at various* pH *for* 1·0mM-*solutions of the oximes. The curves are labelled for the particular compound and the buffered solution as described in the text. An arrow shows the position of* pH 7 *for each curve.*

The minimum currents for the first wave were expressed as a percentage of the maximum currents and some examples are given in Table 1, columns 4 and 9. Also recorded in Table 1 are the potentials ($E_{min.}$) at which the minima occur.

TABLE 1.

Compound	Buffer	pH	$i_{min.}/i_{max.}$ (%)	$-E_{min.}$ (v *v.* SCE)	Compound	Buffer	pH	$i_{min.}/i_{max.}$ (%)	$-E_{min.}$ (v *v.* SCE)
$COPh_2$ (I)	A	5·6	92	1·6	β-$C_{10}H_7$·COMe (III)	A	5·8	83	1·6$_5$
		6·5	75	1·6			6·8	55	1·6
		7·5	55	1·6			8·5	54	1·5
		9·0	25	1·4$_5$	Ph·COMe (IV)	A	3·3	97	1·4
,, ...	B	7·5	48	1·4$_5$			6·4	58	1·6$_5$
		8·5	60	1·3$_5$			7·1	43	1·5$_5$
p-C_6H_4Me·COPh (II)	A	9·1	60	1·4$_5$	*p*-C_6H_4Me·COMe (V)	A	5·6	51	1·6$_7$
,,	B	8·1	54	1·4$_5$			6·8	23	1·6$_3$
		9·1	78	1·3$_5$	$(COPh)_2$ (VI) *	A	6·23	72	1·6$_5$

* See also Langer.[1]

Benzophenone oxime and methyl *p*-tolyl ketoxime were also studied in sulphuric acid–water mixtures. With benzophenone oxime there was a single wave obtained at −0·60 v in 5—20% (w/w) sulphuric acid. The wave height in 5% sulphuric acid was nearly equal to the maximum wave height found in the pH range 2—*ca.* 10. When the solution was kept for 4

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[4] Brdička, *Coll. Czech. Chem. Comm.*, 1947, **12**, 212.

days the wave decreased in height by about 50% and moved to more negative potentials. At 50% sulphuric acid two waves of nearly equal height were found at −0·5 and −0·6 v respectively. The total wave height corresponded to that of the single wave above. At higher concentrations of acid the waves were obscured by the solution decomposition current. Methyl *p*-tolyl ketoxime gave two waves of equal height in 10—50% sulphuric acid. The half-wave potentials were −0·7 and −0·8 v respectively. The total wave height in 10% sulphuric acid was equal to that of the single wave obtained in the pH range 2—*ca.* 10.

In neutral to alkaline solutions the second wave of benzophenone oxime was sufficiently differentiated from the buffer decomposition current to permit measurement of the wave height except at pH 11·3. The results are plotted in Fig. 3. The second waves of the other oximes were not usually well-defined, being superimposed upon the buffer decomposition current which increases rapidly with applied potential. Some estimates of $i_d/m^{2/3}t^{1/6}$ are 5·4 and 7·7 μA mg.$^{-2/3}$ sec.$^{-1/6}$ per millimole, respectively, for methyl β-naphthyl ketoxime in the pH range 8—11, and acetophenone oxime at pH 8.

The dependence of the wave heights upon the mercury pressure, *H*, was tested for the first waves of oximes (I), (II), (III), and (V) and the second wave of oxime (I). The wave heights were found to be linear with $H^{\frac{1}{2}}$ at those pH where the wave height was at its maximum. When the height of the first wave fell owing to increasing pH the wave height was observed to be independent of *H*. Independence of *H* was also observed with the current minima of oximes (I) and (II).

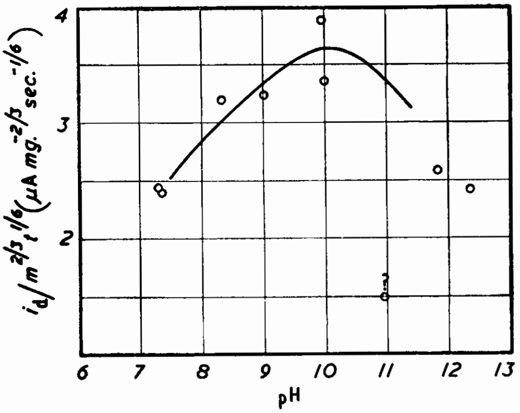

FIG. 3. *Limiting currents of the second wave at various* pH > 7 *for* 1·0mM-*benzophenone oxime and buffer mixture B.*

The half-wave potentials of the first waves were determined by using the current maxima as the limiting currents. As the pH was increased in the pH range 2—*ca.* 10 the half-wave potentials became more negative. The $E_{\frac{1}{2}}$–pH relations were linear with average deviations from linearity as shown in Table 2. The $E_{\frac{1}{2}}$–pH coefficients are also given in Table 2, together with the half-wave potential extrapolated to zero pH. For the second wave the $E_{\frac{1}{2}}$–pH coefficients are about zero (see Table 2).

TABLE 2.

Compound	(I)			(II)		(III)		(IV)		(V)	(VI)
Buffer solution	A	B	B	A	B	A	B	A	B	A	A
Wave (first or second)...	1st	1st	2nd	1st	1st	1st	2nd	1st	2nd	1st	1st
$E_{\frac{1}{2}}$–pH coefficient (mv per pH unit)	−78	−10	5	−63	0	−71	−10	−71	(0)	−71	−77
pH range	2—8	7—11	9—11	2—10	8—12	2—5	10—11	2—7	11	2—8	4—6
No. of points plotted ...	6	4	4	5	5	3	2	6	1	4	2
Average deviation (mv) from linear $E_{\frac{1}{2}}$–pH relation	2	10	1	13	40	2	—	4	—	5	—
$-E_{\frac{1}{2}}$ at pH 0	0·522	1·07	—	0·525	1·11	0·676	—	0·710	—	0·742	0·68
$-E_{\frac{1}{2}}$ at pH 10	—	—	1·635	—	—	—	1·75	—	1·78	—	—

Linear relations between wave height and concentration were obeyed to within 2% at 0·3, 0·6, 1·0, and 1·3mM-concentration by benzophenone oxime, methyl β-naphthyl ketoxime, and methyl *p*-tolyl ketoxime and the straight lines when extrapolated passed through the origin.

The half-wave potentials for both benzophenone oxime and methyl β-naphthyl ketoxime became more negative by 27 mv per 10-fold increase of concentration, and by 13 mv for methyl *p*-tolyl ketoxime. The relation was nearly linear for methyl β-naphthyl ketoxime.

A 20 ml. polarographic solution of benzophenone oxime at pH 5 was reduced *in situ* with 1 mg. of palladium–carbon catalyst and hydrogen. The limiting current decreased to zero but no anodic wave appeared before +0·1 v, even when the solution was made alkaline to pH 13.

Dimethylamine was prepared and tested for possible anodic waves at both pH 4·25 and pH 10·25. No anodic wave was observed before the decomposition potential of the solution. Air was then bubbled through in an attempt to form oxidation products of the amine but, if formed, they yielded no cathodic wave. Potassium permanganate was also added, hydrogen being then passed in until the solution was colourless, but again there was no cathodic wave.

DISCUSSION

Oximes are converted into amines by the action of a variety of reducing agents.[5, 6] The results in the present paper will now be discussed, it being assumed that with polarographic reduction also an oxime is converted into the corresponding amine.

The reduction of benzophenone oxime is irreversible since methyldiphenylamine gives no anodic polarographic wave. Also there is no anodic wave produced when benzophenone oxime is hydrogenated *in situ* with palladium–carbon as catalyst.

The cathodic wave found in the pH range 2—6 is probably due to the uptake of four electrons per molecule since the wave height is nearly four times that of the first one-electron wave of the parent ketone in a similar solution; twice that of the two-electron wave in the case of benzoin.[7] The individual factors are: (I), 3·7; (II), 3·5; (III) 4·6; (IV), 3·9; (V), 4·6; (VI), 4·3. In the pH range 2—6 the limiting current is diffusion controlled as shown by its linearity with $H^{1/2}$. In the pH range 6—*ca.* 10 the limiting current becomes independent of H and indicates that the electron transfer is preceded by a reaction the rate of which controls the current.[4]

In equation (1) the oxime is shown in equilibrium with its conjugate acid; HB represents proton donors in the solution, *i.e.*, either buffer weak acid or hydrogen ion and hence its electric charge is not specified.

$$R_2C{:}N{\cdot}OH + HB \rightleftharpoons (R_2C{:}N{\cdot}OH)H^+ + B \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When $(R_2C{:}N{\cdot}OH)H^+$ is removed at the electrode surface by reduction the equilibrium is displaced to the right and continuous protonation of the oxime occurs. With increasing pH the donor HB may be unable to maintain protonation and the reaction becomes slower than the diffusion of oxime to the electrode surface. The decrease in wave height at pH *ca.* 6 is thus explained.

The addition of the four electrons to $(R_2C{:}N{\cdot}OH)H^+$ follows protonation and is probably irreversible since the α values are less than unity.[8, 9] To a first approximation the waves are symmetrical. The methods of either Saito [10] or Tanaka and Tamamushi [11] are therefore applied and equation (2) is derived:

$$-E = \text{constant} + (0{\cdot}015/\alpha)\log[i/(i_d - i)] + (0{\cdot}015/\alpha)\log[(h + K_a)/h] \quad . \quad (2)$$

E is the electrode potential, i the current, i_d the limiting current of the wave, h the hydrogen-ion concentration, K_a the dissociation constant of the protonated oxidant, and the coefficient 0·015 is equal to $2{\cdot}303\boldsymbol{R}T/4\boldsymbol{F}$, where $\boldsymbol{R}$, T, and $\boldsymbol{F}$ are the gas constant, absolute temperature, and faraday, respectively; the coefficient α is regarded by Butler [12] and by

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[5] Schöll, *Ber.*, 1927, **60**, 1247.

[6] Kaplansky, *Ber.*, 1927, **60**, 1842.

[7] Gardner, Ph.D. Thesis, Univ. W. Australia, 1954.

[8] Goto and Tachi, *Proc. Intern. Pol. Congr.*, 1951, **1**, 69.

[9] Gardner and Lyons, *Rev. Pure Appl. Chem.*, 1953, **3**, 134.

[10] Saito, *Bull. Soc. chim. France*, 1948, 404.

[11] Tanaka and Tamamushi, *Proc. Intern. Pol. Congr.*, 1951, **1**, 486.

[12] Butler, " Chemical Thermodynamics," Macmillan, London, 1946.

Eyring, Marker, and Kwoh[13] as the fraction of potential assisting the forward reaction (but see also Evans and Hush[14] for an alternative explanation).

Equation (2) gives rise to two predictions by which it may be tested. First, the term $(0{\cdot}015/\alpha)\log[i/(i_d - i)]$ becomes equal to zero at $E = E_{\frac{1}{2}}$ ($E_{\frac{1}{2}}$ is the half-wave potential) and hence $E_{\frac{1}{2}}$ should vary with the hydrogen-ion activity as described by the last term of (2). At pH $<$ pK_a, $E_{\frac{1}{2}}$ should be pH-independent; at pH $>$ pK_a, $E_{\frac{1}{2}}$ should become more negative by $0{\cdot}015/\alpha$ v per pH unit. In the second place α may be calculated from the variation of $E_{\frac{1}{2}}$ with pH and also from the variation of E with $\log[i/(i_d - i)]$. The results for α should agree.

The testing of the first prediction of equation (2) requires a knowledge of pK_a for the conjugate acids of the oximes. The pK_a values are probably about zero since the solubility of the oximes is greatly increased in acid solutions stronger than normal. Therefore in the pH range 2—*ca.* 10, pH $>$ pK_a and in agreement with (2) the measured half-wave potentials are pH-dependent. The condition pH $<$ pK_a for the oximes is not possible in dilute aqueous solutions. However, if the Hammett acidity scale[15] be accepted for reference, then the solvent system sulphuric acid–water provides the condition $H_0 <$ pK_a where H_0 is the Hammett acidity function. It is found that in fresh solutions of benzophenone oxime in 5—20% sulphuric acid the half-wave potential is nearly constant, in agreement with (2). At higher concentrations of acid the division of the four-electron wave into two waves prevents further test of equation (2).

With methyl *p*-tolyl ketoxime two waves occur at all acid concentrations, each wave being due probably to the uptake of two electrons per molecule. An equation can be derived for two-electron uptake[10] which predicts constancy of $E_{\frac{1}{2}}$ for pH $<$ pK_a. In agreement, the half-wave potentials of both waves of methyl *p*-tolyl ketoxime are nearly constant for $H_0 <$ pK_a.

The second prediction of equation (2) is also largely fulfilled. In Table 3, α is shown at various pH for the lower and upper portions of the wave as α_1 and α_2, respectively. The methods of calculation of α_1, α_2, are from $\alpha_1 = 0{\cdot}0283/n(E_{\frac{1}{4}} - E_{\frac{1}{2}})$ and $\alpha_2 = 0{\cdot}0283/n(E_{\frac{1}{2}} - E_{\frac{3}{4}})$, which quantities are readily derived from equation (2). $E_{\frac{1}{4}}$, $E_{\frac{1}{2}}$, and $E_{\frac{3}{4}}$ represent the potentials at the quarter, half, and three-quarter wave heights, respectively. Also shown are values of α calculated from the pH dependence of the half-wave potential. The agreement between the α values from the above two methods of calculation is moderate with oximes (I), (II), (III), and (VI), and good with (IV) and (V).

The irreversibility of the electron uptake prevents polarographic examination of the subsequent electrode processes. The nature of the protonation which gives the amine must therefore be inferred by analogy with the reduction of carbon–carbon double bonds.[16] Sodium reduction of 1 : 1-diphenylethylene in liquid ammonia gives negative carbon centres which are highly reactive towards any proton donors present. Hence for the oximes it is suggested that the solvent water is the proton donor and that its reaction with negative nitrogen and oxygen centres is irreversible.

TABLE 3.

Compound	(I)		(II)		(III)		(IV)		(V)		(VI)	
	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
First wave (pH 2—*ca.* 8) :												
average values of α	0·21	0·30	0·14	0·20	0·23	0·27	0·18	0·21	0·21	0·21	0·14	0·16
α from $E_{\frac{1}{2}}$–pH coefficient	0·19		0·24		0·21		0·21		0·21		0·19	
Second wave (pH $>$8) :												
average values of α	0·13	0·13	—	—	0·16	0·16	0·13	—	—	—	—	—

The second wave of benzophenone oxime shows dependence of the wave height upon the pH. The maximum height is nearly equal to that of the first wave, and hence four

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[13] Eyring, Marker, and Kwoh, *J. Phys. Colloid Chem.*, 1949, **53**, 1453.

[14] Evans and Hush, *J. Chim. phys.*, 1952, **49**, C159.

[15] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940.

[16] Birch, *Quart. Rev.*, 1950, **4**, 69.

electrons are probably added to each molecule of oxime. The heights of the second waves of methyl β-naphthyl ketoxime and acetophenone oxime are also similar to those of the corresponding first waves. The half-wave potentials are measured with less precision than for the first wave because of the adjacent buffer decomposition current, but within the experimental error they are to be regarded as constant for change in pH.

The electrode processes which give rise to the second wave are probably similar to those for the first wave if the preprotonation is not considered. There would be, first, the irreversible uptake of four electrons by the neutral oxime, followed by irreversible reaction of negative nitrogen and oxygen centres with the aqueous solvent. The half-wave potential is independent of pH since the speed of the protonation reaction depends on the activity of the water, which is present in constant excess, rather than on the hydrogen-ion concentration.

The reaction mechanism of oximes is thus formulated :

(i) Acid pH at $\text{pH} > \text{p}K_a$:

$$\begin{aligned} R_2C{:}N{\cdot}OH &+ HB \rightleftharpoons (R_2C{:}N{\cdot}OH)H^+ + B^- \\ &+ 4e \longrightarrow (R_2C{:}N{\cdot}OH)H^{\ddagger} \\ &+ 3H_2O \longrightarrow R_2CH{\cdot}NH_3^+ + 4OH^- \end{aligned}$$

(ii) Alkaline pH :

$$\begin{aligned} R_2C{:}N{\cdot}OH &+ 4e \longrightarrow (R_2C{:}N{\cdot}OH)^{\ddagger} \\ &+ 3H_2O \longrightarrow R_2CH{\cdot}NH_2 + 4OH^- \end{aligned}$$

(The symbol ‡ represents an activation state or series of such states, the charge type being unspecified.)

The decrease in height of the second wave of benzophenone oxime in high pH is explicable by dissociation as in equation (3).

$$R_2C{:}N{\cdot}OH \rightleftharpoons R_2C{:}NO^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

If the rate of recombination is slow, then at $\text{pH} > \text{p}K$ there will be insufficient $R_2C{:}N{\cdot}OH$ formed at the electrode surface to maintain the maximum limiting current.

The rate of protonation in (i) above depends upon the source of protons HB. It might be expected that at $\text{pH} > 2$ the larger concentration of weak acid molecules than of hydrogen ions would make them the actual proton donors. The rate of protonation would then depend on the nature of HB. However, it is seen from Fig. 2 that when glycine buffers replace the acetic–phosphoric–boric acid mixture the pH of 50% wave height $(\text{pH})_{\frac{1}{2}}$ varies only to a small extent. It is possible therefore that hydrogen ions are the actual proton donors up to pH *ca.* 10. When the formula of Koutecký and Brdička [17] is used together with the estimated pK_a values of zero, and hydrogen ions are assumed to be the actual proton donors, the calculated protonation rate constants would be 10^{14} l. mole^{-1} sec.$^{-1}$.

EXPERIMENTAL

The current–voltage curves were obtained by using Lingane and Kolthoff's three-electrode circuit,[18] with a device for reproducible liquid junctions.[19] The average deviation of four half-wave potentials of benzophenone oxime corrected to pH 2·3 was 3 mv. The average deviation of the limiting currents of five waves at this pH was 1%. A series of saturated calomel electrodes was prepared with the precaution prescribed by Hills and Ives,[20] and their potentials were checked with hydrogen electrodes and with calomel electrodes containing 0·05M-potassium chloride. After they had been used for standards the reference calomel electrode of the polarograph was believed to be 0·242 v against the hydrogen electrode of unit activity at 25°. The polarograms were also taken at 25°, and the half-wave potentials are referred to the above calomel electrode.

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[17] Koutecký and Brdička, *Coll. Czech. Chem. Comm.*, 1947, **12**, 337.

[18] Lingane and Kolthoff, *J. Amer. Chem. Soc.*, 1939, **61**, 825.

[19] Gardner and Diamantis, *Austral. J. Sci.*, 1951, **14**, 23.

[20] Hills and Ives, *J.*, 1951, 301.

The ionic strengths in 25% (vol.) ethanol-in-water were calculated by using the apparent pK_a of the buffer acids. These pK_a were determined with a glass electrode and were in agreement with the apparent pK_a expected from the work of Grunwald and Berkowitz.[21]

The buffer solutions were: A, 0·1M each of acetic, phosphoric, and boric acid with sodium hydroxide to the required pH, and potassium chloride added to make $\mu = 0{\cdot}33$; B, Sörensen–Walbaum glycine buffers, with potassium chloride added to make $\mu = 0{\cdot}33$. Solutions contained 25% (vol.) of ethanol. The oximes were prepared by refluxing hydroxylamine with the parent ketone in alcoholic alkali, followed by precipitation with acid. They were identified by m. p. which were (recorded values in parentheses): (I), 143·5° (144°); (II), 153° (153°); (III), 145° (decomp.) (145°); (IV), 59° (59°); (V), 86·5—88° (88°); (VI), 163° (163—164°). On storage several of the oximes decomposed but the solutions in alcohol appeared to be stable. The methyldiphenylamine was prepared by Schöll's method [5] and melted at 186°.

A number of dropping-mercury capillaries were required for the work and hence the diffusion currents are divided by $m^{2/3}t^{1/6}$ where m is the rate of mercury flow (mg. per sec.) and t is the drop time (sec.).

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[21] Grunwald and Berkowitz, *J. Amer. Chem. Soc.*, 1951, **73**, 4939.