

anticipated that the characteristics of the hindered aromatic nitro compounds would show certain similarities to those of the aliphatic nitro derivatives. Unfortunately, however, the only data reported for the aliphatic compounds were determined in solutions in which nitromesitylene and nitrodurene are not sufficiently soluble to permit measurements to be made. The straight-chain primary and secondary aliphatic nitro compounds, with one to four carbon atoms resemble the hindered aromatic compounds in that they have been reported to yield only a single polarographic wave in acid solution; on the other hand, the aliphatic compounds are apparently non-reducible in 0.1 *M* aqueous sodium hydroxide or tetramethylammonium hydroxide solution.¹⁷ In 0.05 *M* aqueous sulfuric acid solutions the aliphatic compounds have half-wave potentials in the range -0.57 to -0.69 v. vs. S.C.E. and would appear to be somewhat more difficultly reducible in acid solution than any of the substances investigated in the present work. Although the shift in half-wave po-

tentials toward more negative values on going from the unhindered to the hindered aromatic derivatives is in the direction anticipated from the values reported for the aliphatic nitro compounds, closer comparison of the polarographic behavior of nitromesitylene and nitrodurene with that of aliphatic nitro derivatives must await re-examination of the characteristics of the latter and determination of the *n*-values of the polarographic waves for members of both series.

Summary

The polarographic characteristics of nitrobenzene, *o*-, *m*- and *p*-nitrotoluene, 2-nitro-1,4-dimethylbenzene, 3-nitro-1,2-dimethylbenzene, nitromesitylene and nitrodurene have been examined in buffered 80% aqueous dioxane solutions at pH 1.0, 7.2 and 12. The behavior of nitromesitylene and nitrodurene is distinctly different from that of the aromatic nitro compounds examined in which steric inhibition of resonance does not exist.

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RECEIVED¹⁸ OCTOBER 11, 1948

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(18) Original manuscript received June 2, 1948.

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Quantitative Interpretation of the Polarographic Hydrolysis Current of Chromic Ion

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Chromic ion undergoes stepwise reduction at the dropping electrode, the first wave corresponding to reduction to chromous ion and the second to complete reduction to the metal.^{2,3} Kolthoff and Lingane⁴ called attention to the fact that the height of the second wave is significantly larger than twice the height of the first when the supporting electrolyte is unbuffered, and they attributed the discrepancy to the simultaneous discharge of hydrogen ion from the hydrolysis of the chromic ion. This has also been noted by Willis.⁵

In the present study this phenomenon has been investigated systematically, and interpreted quantitatively on the basis of diffusion current theory. Relations have been derived which are of general applicability in polarographic studies of hydrolytic equilibria in metal salt solutions.

Experimental

Polarographic measurements were made in an H-type cell provided with a saturated calomel electrode as pre-

viously described.⁶ Atmospheric oxygen was removed by purified hydrogen or nitrogen. All measurements were made with the cell in a water thermostat at $25.0 \pm 0.1^\circ$. The drop time of the capillary varied from three seconds with an open circuit to about two seconds at an applied potential of two volts, and was timed as necessary at each potential. An automatic *m*-measuring device⁷ was employed.

Polarograms were either recorded with a Sargent Model XI Polarograph, or obtained with a manual apparatus based on a circuit previously described.⁸

Residual currents were obtained in all cases and the proper correction applied.

The pH of the solutions was measured with a glass electrode.

Chromic Solutions.—Stock solutions of 0.1000 *M* chromic chloride and chromic sulfate were prepared determinately by reduction of a known quantity of pure potassium dichromate with sulfur dioxide or hydrogen peroxide in the appropriate acid, and the excess reducing agent was removed by boiling. A neutral solution of chromic chloride was made up from the reagent grade hexahydrate and standardized by determination of the chromium content. The stock solutions were diluted to 0.01 *M* before use in order to increase the accuracy of measurement. The ionic state of the chromium in these solutions was believed to be an equilibrium mixture of the hexaquo- and the dichlorotetraquo-chromic ions.

A stock solution of 0.1 *M* chromic perchlorate was prepared by reduction of a known quantity of reagent grade sodium chromate with hydrogen peroxide in perchloric acid,

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(2) J. Prazler, *Collection Czechoslov. Chem. Commun.*, **3**, 406 (1931).

(3) N. Demassieux and J. Heyrovsky, *J. chim. phys.*, **26**, 219 (1929).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 291.

(5) J. B. Willis, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 239 (1944).

(6) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(7) J. J. Lingane, *ibid.*, **16**, 329 (1944).

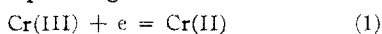
(8) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939).

thus eliminating the presence of chloride ion. Solutions of chromic perchlorate were polarographed in a cell with an internal mercury anode, in order to exclude chloride ion.

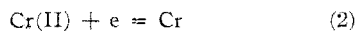
Supporting electrolytes were prepared from reagent grade chemicals. Commercial "Chemically pure" sodium perchlorate was found to contain a large amount (ca. 6%) of a basic impurity, which, from the shape of the titration curve with standard hydrochloric acid, appeared to be a mixture of sodium bicarbonate and sodium carbonate. Therefore, sodium perchlorate supporting electrolytes were prepared by careful neutralization of pure perchloric acid solutions with carbonate-free sodium hydroxide solutions to a pH of 6.5 to 7.0.

Results and Discussion

Figure 1 shows polarograms of various concentrations of chromic chloride in 0.1 M potassium chloride with 0.01% gelatin present as a maximum suppressor. The half-wave potential of the first wave, corresponding to



is -0.91 v. vs. S.C.E., and that of the second wave, corresponding to



is -1.47 v. vs. S.C.E. These values are in good agreement with previous determinations.⁴

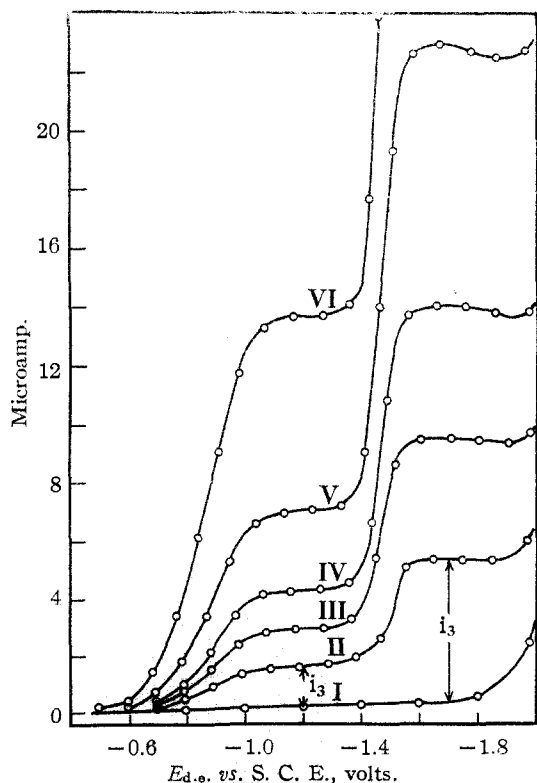


Fig. 1.—Polarograms of (I) 0, (II) 0.5, (III) 1.0, (IV) 1.5, (V) 2.5 and (VI) 5.0 millimolar chromic chloride in 0.1 M potassium chloride containing 0.01% gelatin.

Polarograms of chromous ion in 0.1 M potassium chloride, which will be described in a later paper, show a well-developed anodic wave. However, the half-wave potential of this wave is

several tenths of a volt more positive than the cathodic wave of chromic ion, showing that reaction 1 does not proceed reversibly at the dropping electrode.

The influence of pH on the polarograms of chromic ion in 0.1 M potassium chloride containing 0.01% gelatin is demonstrated in Fig. 2. The natural pH of 1 millimolar chromic chloride in 0.1 M potassium chloride resulting from hydrolysis is approximately 3.8. From Fig. 2 it is seen that when the pH is made smaller than this value the magnitude of the second wave increases greatly because of the simultaneous discharge of hydrogen ion with the chromous ion. When the pH is made larger than about 3.8 the first wave becomes poorly developed and a third wave appears at -1.7 v. This latter wave doubtless results from the reduction of a more highly hydrolyzed species in sluggish equilibrium with chromic ion.

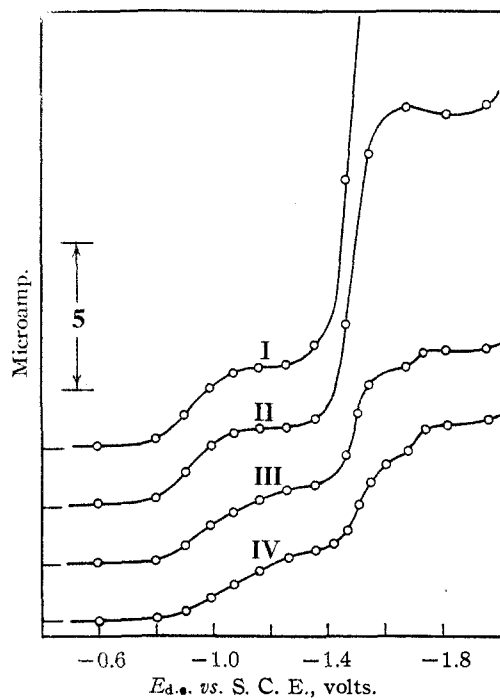


Fig. 2.—Effect of pH on the polarograms of 1 millimolar chromic chloride in unbuffered 0.1 M potassium chloride containing 0.01% gelatin. The pH values were (I) 2.80, (II) 3.38, (III) 4.63 and (IV) 5.00.

The effect of the concentration of potassium chloride in the supporting electrolyte was determined and a concentration of 0.1 M or less found to be optimum. With increasing chloride ion concentration, the magnitude of the diffusion current is decreased and the half-wave potentials shift to more negative values. This does not support the claim of Kalousek⁹ that the reduction proceeds reversibly in solutions containing a very large concentration of chloride ion.

(9) M. Kalousek, *Collection Czech. Chem. Commun.*, **11**, 592 (1939).

The polarographic characteristics of chromic chloride in ammonium, lithium, barium and calcium chloride solutions, and in sodium perchlorate solutions were found to be essentially the same as in a supporting electrolyte of potassium chloride.

Diffusion current data obtained with various concentrations of chromic chloride in 0.5 *M* sodium perchlorate and 0.25 *M* potassium chloride are given in Tables I and II. The solutions contained 0.005% gelatin. The chromic chloride stock solution used was prepared from pure chromic chloride hexahydrate without added acid, and it had aged for fifteen months prior to these experiments. The *pH* values listed are the "natural" values due to the hydrolysis of chromic ion, and they were measured for each solution with the glass electrode.

TABLE I

DIFFUSION CURRENTS IN 0.5 *M* SODIUM PERCHLORATE AT 25°

C_{Cr} milli- molar	<i>pH</i>	C_{H^+} milli- molar	i_1 , μa	i_3 , μa	I_3/I_1	i_H (obs.), μa	i_H (theor.), μa
0.495	3.84	0.193	1.24	4.82	4.12	1.31	1.35
0.980	3.60	.334	2.54	9.36	3.97	2.18	2.33
1.460	3.47	.452	3.76	13.82	3.91	3.29	3.16
1.925	3.37	.570	4.98	18.08	3.87	4.15	3.98
2.83	3.21	.823	7.36	26.22	3.82	5.67	5.73
3.70	3.12	1.010	9.58	34.04	3.79	7.24	7.05
4.54	3.03	1.245	11.78	41.94	3.76	8.94	8.69
6.52	2.89	1.720	16.76	59.84	3.76	12.74	12.00
8.33	2.77	2.27	21.44	77.28	3.76	16.18	15.85

TABLE II

DIFFUSION CURRENTS IN 0.25 *M* POTASSIUM CHLORIDE AT 25°

C_{Cr} milli- molar	<i>pH</i>	C_{H^+} milli- molar	i_1 , μa	i_3 , μa	I_3/I_1	i_H (obs.), μa	i_H (theor.), μa
0.465	4.05	0.114	1.28	4.78	3.97	1.15	0.78
0.922	3.80	.202	2.52	9.18	3.86	2.07	1.37
1.37	3.67	.274	3.75	13.28	3.76	2.68	1.88
1.81	3.58	.337	4.88	17.24	3.75	3.41	2.31
2.66	3.46	.445	7.18	24.70	3.64	4.35	3.05
3.49	3.39	.521	9.38	32.02	3.62	5.47	3.57
4.28	3.32	.614	11.40	38.48	3.57	6.23	4.20
6.14	3.20	.809	16.16	53.9	3.53	8.0	5.57
7.85	3.13	.905	21.26	71.3	3.54	10.7	6.50

In these tables i_1 is the diffusion current of the first wave, measured at -1.2 v., and i_3 is the total diffusion current of the doublet wave measured at -1.7 v.

The sixth column shows the corresponding ratio of the diffusion current constants, where $I = i_d/(Cm^{2/3}t^{1/6})$. The theoretical value of I_3/I_1 is 3, corresponding to the successive 1- and 3-electron reductions. The observed values of this ratio in Tables I and II are much larger than the theoretical value and the discrepancy increases with decreasing concentration of chromic ion. The abnormally large observed values of I_3/I_1

reflect the simultaneous reduction of the hydrogen ion formed by the hydrolysis of chromic ion



The relative concentration of hydrogen ion in this equilibrium increases with decreasing total concentration of the chromic salt.

The diffusion current of the first wave is directly proportional to the total chromic salt concentration. In 0.5 *M* sodium perchlorate at 25° the diffusion current constant $I_1 = i_1/(Cm^{2/3}t^{1/6})$ was found to be 1.46 ± 0.01 , and in 0.25 *M* potassium chloride it is 1.50 ± 0.015 , when 0.005% gelatin is present.

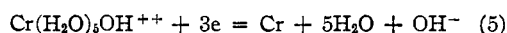
The *pH* values observed are consistent with the values for the hydrolysis constants of $Cr(H_2O)_6^{+++}$ (1.58×10^{-4}) and $CrCl_2(H_2O)_4^+$ (1.9×10^{-6}) reported by Bjerrum,¹⁰ Lamb and Fonda,¹¹ and Brönsted and King.¹² The predominant ion in perchlorate medium is $Cr(H_2O)_6^{+++}$, and in the chloride solutions the less-hydrolyzed $CrCl_2(H_2O)_4^+$ ion predominates.

The "hydrolysis current" resulting from the reduction of hydrogen ion is represented by i_H . The observed values of i_H listed in Tables I and II were computed from the relation

$$i_H = i_3 - 3i_1(t_2/t_1)^{1/6} \quad (4)$$

The values of t_2 and t_1 were measured with each concentration of chromic ion at the same time that the diffusion currents were measured.

At potentials corresponding to the second diffusion current plateau both unhydrolyzed and hydrolyzed chromic ions are reduced, and the reduction of the latter liberates hydroxyl ion at the electrode surface



The hydroxyl ions thus produced neutralize in the diffusion layer an equal number of the hydrogen ions that are diffusing up to the electrode surface. In the body of the solution the number of hydrogen ions is equal to the number of hydrolyzed chromic ions, and if the diffusion coefficients of the two were equal all of the hydrogen ions in the diffusion layer would be neutralized and there would be no contribution by hydrogen ion reduction to the second diffusion current. Actually, however, the diffusion coefficient of hydrogen ion is several times larger than that of the hydrolyzed chromic ion. Consequently the flux of hydrogen ion at the electrode surface is greater than that required to neutralize the hydroxyl ions produced by reaction 5, and it is the reduction of these additional hydrogen ions which produce the hydrolysis current i_H .

There is a larger proportion of hydrogen ion to chromic ion in the diffusion layer than in the body of the solution, and the proportion increases as the electrode surface is approached. As a con-

(10) H. Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907).(11) A. B. Lamb and G. R. Fonda, *THIS JOURNAL*, **43**, 1154 (1921).(12) J. N. Brönsted and C. V. King, *Z. physik. Chem.*, **130**, 699 (1927).

sequence, the hydrolytic equilibrium represented by eqn. 3 tends to shift to the left. Whether or not hydrolytic equilibrium is maintained in the diffusion layer during the life of each mercury drop obviously does not alter the net amount of hydrogen ion available for reduction, because it is immaterial whether hydrogen ion is neutralized by the hydrolyzed chromic ion (reversal of reaction 3) or by the liberated hydroxyl ion.

From well known diffusion relations at the dropping electrode,¹³ the flux of hydrogen ion at the electrode surface would be $(7/3\pi)^{1/2} (C_H D_H^{1/2}/t^{1/2})$ if there were no neutralization, where C_H and D_H are the concentration and diffusion coefficient of hydrogen ion in the body of the solution, and t is time during the life of each mercury drop. The flux of hydrolyzed chromic ion is expressible by an exactly similar relation, and, because of the neutralization, the net flux of hydrogen ion at any instant is the difference between the two, $(7/3\pi)^{1/2} (C_H D_H^{1/2} - C_{Cr} D_{Cr}^{1/2})/t^{1/2}$, where C_{Cr} and D_{Cr} refer to the hydrolyzed chromic ion in the body of the solution. Since $C_{Cr} = C_H$, and expressing the several quantities in the customary units¹³ and combining the numerical constants, the hydrolysis current at 25° should obey the equation

$$i_H = 605(D_H^{1/2} - D_{Cr}^{1/2})C_H m^2/t^{1/2} \quad (6)$$

It is more convenient to express i_H in terms of the diffusion current constants I , which for the 1-electron reductions involved are defined by $605 D^{1/2}$, and eqn. 6 then becomes

$$i_H = (I_H - I_{Cr})C_H m^2/t^{1/2} \quad (7)$$

This equation was used to compute the theoretical values of i_H in Tables I and II.

Since the diffusion coefficients of the hydrolyzed and unhydrolyzed chromic ions must be nearly identical, I_{Cr} was assumed equal to the measured diffusion current constant of the first wave (1.46 in 0.5 *M* sodium perchlorate and 1.50 in 0.25 *M* potassium chloride).

The diffusion current constant I_H of hydrogen ion was determined from measurements of the diffusion current of known concentrations (0.1 to 1 millimolar) of hydrogen ion in the same supporting electrolytes used to obtain the data in Tables I and II, and the same value, 5.64 ± 0.02 , was obtained in both cases. This value agrees well with the theoretical infinite dilution value 5.84 calculated from the equivalent conductance of hydrogen ion by means of the relation⁴ $D^0 = 2.67 \times 10^{-7}\lambda^0$. Special experiments showed that I_H was not altered by the simultaneous reduction of chromic ion.

Since *pH* numbers as ordinarily measured do not strictly correspond to either the concentration or activity of hydrogen ion, the glass electrode *pH*

meter was calibrated empirically in each of the supporting electrolytes with known small concentrations of hydrochloric acid. The data thus obtained were used to compute the concentrations of hydrogen ion in each solution of Tables I and II from the measured *pH* numbers, and these concentrations were then employed in eqn. 7 to compute i_H .

From Table I the agreement between the observed and theoretical values of i_H in 0.5 *M* sodium perchlorate is seen to be very good over the entire concentration range. The average difference between the two is only $\pm 3\%$, which is well within the limits of error of the measurements.

In 0.25 *M* potassium chloride the observed values of i_H average 45% larger than the theoretical values. This discrepancy can be accounted for by two factors which both operate to increase the observed value of i_H . First, the smaller ionic strength of the potassium chloride solutions leads to a greater possibility of some contribution by electrical migration⁴ to the total limiting current. Secondly, the predominant molecular state of the +3 chromium in 0.25 *M* potassium chloride is probably the $\text{CrCl}_2(\text{H}_2\text{O})_4^+$ ion, rather than the $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion which predominates in the perchlorate medium.^{10,11,12} The reduction of each chloro complex ion frees two chloride ions at the surface of the dropping electrode, which alters the potential gradient in the diffusion layer and produces a relatively larger negative charge at the electrode surface. This tends to accelerate the passage of hydrogen ion through the diffusion layer.

Summary

1. The polarographic behavior of chromic ion in potassium chloride and sodium perchlorate solutions has been investigated systematically. The optimum conditions for a well developed doublet wave are: (1) a concentration of supporting electrolyte of 0.1 *M* or less, (2) the natural *pH* (about 4) resulting from the hydrolysis of chromic ion, and (3) the presence of 0.005-0.01% gelatin as a maximum suppressor.

2. The first chromic wave is directly proportional to concentration. The second wave is relatively too large and becomes more so with decreasing concentration. The excess current results from the simultaneous reduction of hydrogen ion. The diffusion and reduction of the hydrolyzed chromic ion and hydrogen ion were analyzed with the aid of diffusion current theory, and equations were developed from which the magnitude of the "hydrolysis current" can be calculated. The latter was compared with the measured excess current, and the good agreement obtained verifies the interpretation.