of the University of Wisconsin. The frequency of the tuning-fork controlled power supply used to operate the timing clock was determined by use of the time signals from station WWV.

Temperature measurements were made by use of a Leeds and Northrup Co. calorimetric type platinum resistance thermometer, calibrated by the National Bureau of Standards. The Rubicon Company Mueller bridge employed was also calibrated. The corrected temperature rise was calculated on the standard assumptions of Newton's law and a constant heat of stirring. The required time–temperature readings were recorded photographically.[2] A temperature rise of about three degrees was regularly used; the initial conditions were adjusted so that the mean temperature of the interval was very close to 25 or 30°. The heat capacity of the calorimeter was determined with a precision of ±0.03%, by use of water as a standard; the reference data were those of Osborne, *et al.*[3]

Solutions.—Concentrated stock solutions of reagent grade sodium and potassium bromide were diluted quantitatively to lower concentrations as required. All solutions used were analyzed gravimetrically by the silver bromide method, to avoid the uncertainty otherwise present due to the water retained by the salts even after prolonged drying. The molalities specified are considered accurate to ±0.03% or better; calibrated weights were employed, and all results correspond to weights *in vacuo.*

Experimental Results

The results obtained are presented in Table I. Except where noted the values given represent the average of duplicate or (usually) triplicate determinations in which the deviation from the mean averaged ±0.05%. The apparent molal heat capacity of the solute, in defined calories deg.$^{-1}$ mole^{-1}, was calculated for each solution (for the solvent the specific heat data of Osborne, *et al.*,[3] were used) and by the method of least squares there were obtained the following equations, which are presented for interpolation purposes only:

TABLE I

SPECIFIC HEATS OF SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS

m = molality solute, C_p = specific heat, defined calories deg.$^{-1}$ g.$^{-1}$.

m	C_p, 25°	C_p, 30°
A. Sodium Bromide Solutions		
0.9675[a]	0.8983	....
0.9990	.8955	0.8973
2.2050	.8078	.8102
2.2165[a]	.8076	....
3.8495	.7247	.7256
5.9985	.6534	.6528
8.3735	.6028	.6020
B. Potassium Bromide Solutions		
0.9985	0.8746	0.8764
1.9960	.7838	.7850
2.9945	.7133	.7142
3.9795	.6561	.6576
4.9985	.6082	.6095
5.5245	.5875	.5885

[a] One run only.

$$\text{KBr:}\ \begin{cases} 25^\circ,\ \phi_{c_p} = -38.167 + 20.460m^{1/2} - 2.645m \\ 30^\circ,\ \phi_{c_p} = -31.135 + 14.111m^{1/2} - 1.133m \end{cases}$$

$$\text{NaBr:}\ \begin{cases} 25^\circ,\ \phi_{c_p} = -29.715 + 20.049m^{1/2} - 1.625m \\ 30^\circ,\ \phi_{c_p} = -24.467 + 16.453m^{1/2} - 1.034m \end{cases}$$

The deviations of the experimental values for the specific heats from the comparison values given by the preceding equations average ±0.04%, in confirmation of the internal consistency of the results at the different concentrations involved. It is considered that an accuracy of the order of ±0.15% can be assigned to the specific heat data reported. This claim is supported by a comparison of the present results with those derived from the work of Randall and Rossini[1]; for one molal solutions at 25°, the deviation between the two sets of results amounts to 0.16% for the potassium bromide solution, and 0.08% for the sodium bromide solution, the present results being the lower in each case. For proper comparison, the apparent molal heat capacities given by Randall and Rossini were converted to defined calories, and the specific heats calculated by use of the data of Osborne, *et al.*,[3] for the solvent.

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[2] P. Bender and W. J. Biermann, THIS JOURNAL, **74**, 322 (1952).

[3] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bureau Standards*, **23**, 197 (1939).

Polarographic Reduction of the Nitrobenzaldehydes

BY R. A. DAY, JR., AND R. M. POWERS

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Korshunov and Sazanova recently[1] reported a study of the polarography of *o*-, *m*- and *p*-nitrobenzaldehydes in buffered ethanol–water media. They found abnormally high diffusion currents for the *ortho* isomer and three waves for the *para* isomer in basic solution, suggesting secondary reactions between the groups in the molecule and reduction of the resulting products.[2] Since these results do not appear consistent with usual carbonyl behavior we decided to repeat these experiments. We found that the behavior of these compounds upon polarographic reduction is consistent with the known behavior of both the nitro and carbonyl groups.

The results are given in Table I for the *meta* and *para* isomers and in Table II for the *ortho* isomer. The *meta* compound reduces in two steps at low *p*H values. The first wave corresponds to the reduction of the nitro group to the hydroxylamine, four electrons being consumed. The second wave is a combination of the second nitro wave (reduction of the hydroxylamine to the amino group) and the first acid carbonyl wave. The second acid carbonyl wave is masked by liberation of hydrogen in these solutions. Since the hydroxylamine is stable toward further reduction at higher *p*H values, the second wave at *p*H 6.1 is evidently the first carbonyl wave alone. The current at this *p*H corresponds to this interpretation. At still higher *p*H values the second wave corresponds to the complete reduction of the carbonyl group to the carbinol. The current does not drop to half-value, as with the *ortho* and *para* isomers (below) and a wave at higher poten-

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[1] A. Korshunov and L. N. Sazanova, *Zhur. Fiz. Khim.*, **23**, 1299 (1949).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 755.

TABLE I

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE (ALL $E_{1/2}$ VALUES ARE NEGATIVE)

pH, aq.	First nitro wave $E_{1/2}$	Curr., μa.	Second nitro wave $E_{1/2}$	Curr., μa.	Carbonyl waves $E^1_{1/2}$	Curr., μa.	$E^{12}_{1/2}$[a]	Curr., μa.	$E^3_{1/2}$	Curr., μa.
					p-Nitrobenzaldehyde					
2.3	0.22	8.4	1.00	3.5	1.16	4.0	..	..	..	..
4.0	.31	9.0	1.11	3.3	1.23	3.2	..	..	..	..
6.1	.37	8.7	1.24	3.0	1.36	3.6	..	..	..	..
8.1	.50	8.4	1.36	3.9	..	..	1.61	4.0	..	..
10.1	.52	9.2	1.38	4.0	..	..	1.68	4.0	..	..
12.1	.56	8.0	1.48	3.1	..	..	1.72	3.0	..	..
12.0[b]	.51	8.0	1.32	1.7	..	..	1.64	2.8	1.93	2.4
					m-Nitrobenzaldehyde					
2.2	.28	8.6	1.08[c]	6.2			..	..	..	..
4.0	.35	8.8	1.24[c]	6.2			..	..	..	..
6.1	.49	9.8	..	..	1.30	2.5	..	..	..	..
8.0	.59	9.1	..	..	..	..	1.42	4.2	..	..
10.1	.73	9.0	..	..	..	..	1.46	4.8	..	..
12.1	.78	9.6	..	..	..	..	1.55	5.0	..	..
12.0[b]	.63	8.8	..	..	..	..	1.49	4.0	..	..

[a] $E_{1/2}$ of wave formed by merging two acid carbonyl waves; the second acid wave was masked by buffer decomposition in all solutions. [b] Calcium hydroxide–calcium chloride buffer. [c] Wave formed by merging second nitro and first carbonyl waves.

TABLE II

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE (ALL $E_{1/2}$ VALUES ARE NEGATIVE)

pH, aq.	First nitro wave $E^1_{1/2}$	Curr., μa.	$E^2_{1/2}$	Curr., μa.	Second nitro wave $E_{1/2}$	Curr., μa.	Carbonyl waves $E^1_{1/2}$	Curr., μa.	$E^{12}_{1/2}$[a]	Curr., μa.	$E^3_{1/2}$	Curr., μa.
					o-Nitrobenzaldehyde							
1.0	0.08	5.2	0.19	3.8	0.74	3.5	0.92	3.0	..	..	..	..
2.3	.18	5.8	.45	4.4	.97	2.2	1.12	3.1	..	..	..	..
3.3	.20	4.5	.39	3.5	1.00	2.4	1.20	2.8	..	..	..	..
4.2	.25	4.3	.62	3.5	1.16[b]	3.2			..	..	..	..
5.1	.32	4.5	.57	3.6	1.23[b]	4.0			..	..	..	..
5.8	.38	4.0	.66	3.8	1.27[b]	3.5			..	..	..	..
7.0	.42	4.4	.61	3.5	1.35[b]	3.9			..	..	..	..
8.0	.49	5.2	.69	2.6	1.45[b]	6.5			..	..	..	..
9.0	.53	8.2	..	..	1.39	3.9	..	..	1.58	3.3	..	..
10.1	.53	9.3	..	..	1.41	4.0	..	..	1.62	3.4	..	..
11.2	.55	8.3	..	..	1.41	3.9	..	..	1.60	3.0	..	..
12.0	.59	8.8	..	..	1.52	3.9	..	..	1.68	2.4	..	..
12.0[c]	.49	8.0	..	..	1.35	1.1	..	..	1.55	2.6	1.73	2.4

$E_{1/2}$ of wave formed by merging two acid waves; the second acid wave was masked by buffer decomposition in all the solutions. [b] Wave formed by merging second nitro and first carbonyl waves. [c] Calcium hydroxide–calcium chloride buffer.

tials is not present in a calcium hydroxide buffer. Apparently the presence of the hydroxylamine group in the *meta* position decreases the tendency of the intermediate metal ketyl[3,4] to dimerize and the reduction occurs in a single step. We have observed this same effect in the reduction of *m*-nitroacetophenone.

The *para* isomer reduces in three steps in solutions of low *p*H. The first and second waves are those of the nitro group and the third is the first acid carbonyl wave. The current of the latter wave is somewhat higher than normal, but the value of the half-wave potential and the fact that it changes rapidly with *p*H are both characteristic of this wave. Other aldehydes containing an amino group in the *para* position, such as *p*-dimethylaminobenzaldehyde,[5] show similarly high currents. The second nitro wave is present in basic media also. It is known that phenylhydroxylamines which can be converted into quinoid forms are reducible in basic media.[6] The carbonyl wave at *p*H 8.1 is evidently the usual basic carbonyl wave formed by merging the two acid waves. The height of this wave drops to about half-value in 0.01 *M* sodium hydroxide, but the second wave can be observed in a calcium hydroxide buffer. This behavior is characteristic of aldehydes such as benzaldehyde and furfural.[3,7] In other words, in the calcium solution four waves are present, two nitro and two carbonyl waves. Calcium ions shift the half-wave potentials of both nitro waves as well as those of the carbonyl waves to more positive potentials.

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(3) M. Ashworth, *Collection Czechoslov. Chem. Communs.*, **13**, 229 (1948).

(4) R. A. Day, Jr., S. R. Milliken and W. D. Shults, THIS JOURNAL, **74**, 2741 (1952).

(5) J. W. Baker, W. C. Davies and M. L. Hemming, *J. Chem. Soc.*, 692 (1940).

(6) Reference 2, p. 748.

(7) R. A. Day, Jr., THIS JOURNAL, **76**, 280 (1954).

The wave height of the second nitro wave is appreciably reduced in the presence of calcium ions.

The behavior of the *ortho* isomer is somewhat more complex. In the first place the reduction of the nitro group to the hydroxylamine occurs in two steps below *p*H 9. The waves were very clearly separated in most cases. Although the first wave was normally higher than the second, the most apparent explanation for this separation is that the first step corresponds to reduction of nitro to nitroso, the second of nitroso to phenylhydroxylamine. Above *p*H 9 the two waves are merged into the usual single wave. The second nitro wave is present in solutions of low *p*H. Between *p*H 4.2 and 8.0 this wave is apparently merged with the first acid carbonyl wave. The height of this combined wave and of the nitro wave alone at lower *p*H is less than would be expected. This may result from the well-known rearrangement of the hydroxylamine to the *p*-aminophenol in acid solution. In basic solution this rearrangement would not take place and the height of the second nitro wave above *p*H 9.0 is about normal. The behavior of the carbonyl group at *p*H 9.0 is also normal, the single basic wave occurring at sufficiently more negative potentials to be separated from the second nitro wave. As the *p*H is further increased the height of the carbonyl wave falls to half-value and the second wave is observed in a calcium hydroxide buffer. The effect of calcium on the nitro waves is similar to that observed with the *para* isomer.

Experimental

The current–voltage curves were determined with a Leeds and Northrup Electro-Chemograph Type E. The instrument was normally operated at a damping of 3. Half-wave potentials were corrected for lag at this damping and also for *IR* drop. The electrolysis cell, experimental procedure and buffer solutions were the same as previously described[4] except that buffers made from 0.1 *M* HCl and 0.1 *M* sodium diethylbarbiturate were used in place of borate buffers in the *p*H range 8–9.5.

All cell solutions were 25% by volume of 95% ethanol and the aldehyde concentration was 0.001 *M*. A single capillary of Corning Marine barometer tubing was used. Its characteristics were: droptime 6.0 sec., m = 1.291 mg./sec., determined in 25% ethanol, citrate–phosphate buffer of *p*H 5.5 with an open circuit. The aldehydes were Eastman Grade chemicals used without further purification. Measurements of *p*H were made with a glass electrode and a Beckman Model H-2 *p*H meter. All experiments were run at room temperature, which was normally between 21 and 25°.

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A Simple Steady State Method for Obtaining Rates of Rapid Reactions

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Suppose that in a first-order, or pseudo first-order reaction, the reagent is added to the system at constant rate u (or withdrawn at constant rate if the reaction produces the reagent). The rate equation becomes

$$\mathrm{d}A/\mathrm{d}t = \pm u \mp kA \qquad (1)$$

which can lead to a steady state[1] concentration of A given by

$$A_s = u/k \qquad (2)$$

A measurement of A_s and a knowledge of u enables the rate constant to be determined. The approach to the steady state is given by integrating 1.

$$t = (1/k) \ln (A_s - A_0)/(A_s - A) \qquad (3)$$

In many cases electrolytic methods can be used to directly or indirectly introduce or remove a reagent. In such cases u is easily determined and held constant. If A_s can be measured when very small, by e.m.f. for example, then it is clear that very rapid reactions can be studied using relation 2.

As an example we have studied the moderately rapid reaction whose rate constant is known to be

$$C_2H_5NO_2 + OH^- \xrightarrow{k} C_2H_4NO_2^- + H_2O \qquad (4)$$

350 l./mole min. at 25°.[2] A catholyte 0.10 *M* in nitroethane and in KCl was used as the reacting solution and hydroxide ion was generated electrolytically at a platinum gauze cathode. The extent of reaction was so small when steady states were reached (in less than one minute) that the reaction was pseudo first order. The steady state hydroxide ion concentration was measured with a *p*H meter. The catholyte was stirred at about 2000 r.p.m. Thermostatting was done manually.

The anode was a platinum foil immersed in a short bed of cation-exchange resin to pick up hydrogen ion produced by electrolysis. The anolyte was 1 *M* KCl and was contained in a glass tube separated from the catholyte by a cation-exchange membrane (Rohm and Haas Amberplex C-1). This combination formed an efficient salt bridge which would not leak hydrogen ion or hydroxyl ion and would pass very large currents.

For successful operation the anode tube was centered in the cylindrical cathode and the glass and calomel electrodes were as far as possible from the generating electrodes (a 400-ml. beaker contained the entire assembly). The indicating electrodes had to be well above or well below the plane of the membrane boundary between anolyte and catholyte.

Rate constants were calculated from the equation equivalent to 2

$$k = (It/FV)/(0.10)(\mathrm{OH}^-)_s \qquad (5)$$

where V is the volume of catholyte. For twelve runs on four separate solutions a mean rate constant of 355 l./mole min. with an average deviation of 33 was obtained. Currents ranged from 30 to 100 ma.

The slower reaction between ethyl acetate and hydroxide ion also was studied. Excellent agreement with literature values for the rate constant was obtained. Thus slow reactions can be studied by the steady state method, though the method is not convenient if the half life is greater than 20 minutes since the time required to establish the steady state is too long.

The big advantage lies in the study of rapid reactions. Here one limitation lies in the rate of mixing of the reagent which is introduced. It appears that the time of mixing can be reduced to about 10^{-2} second in which case reactions with half-lives

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[1] Steady states can be produced in general if the rate equation is of the form rate f(A).

[2] R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (*London*), **A212**, 16 (1952).