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

BY RALPH G. PEARSON AND LAWRENCE H. PIETTE

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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

$$dA/dt = \pm u \mp kA \qquad (1)$$

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

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

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).

of perhaps 3×10^{-2} second can be studied. Another usually more important limitation is the minimum concentration of A which can be detected. Assuming this to be 10^{-6} *M*, reactions with half-lives of 7×10^{-2} second or more can be studied. We are using the method to study some rapid rates involving the reactions of complex ions.

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Dipole Moment Variations in the Hydrogen Halide Molecules[1]

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A two-electron approximation similar to Robinson's method[2] has been applied to the hydrogen halide molecules to determine the sign of $\partial\mu/\partial r$, whose magnitude can be obtained from infrared intensity or dispersion measurements. Using a linear combination of normalized covalent and ionic functions, respectively, of Heitler–London type and Weinbaum type, an equation for μ is obtained in terms of hydrogen-like atomic orbitals and an arbitrary coefficient of the ionic function, λ. 1s and pure p_z orbitals are used, respectively, for hydrogen and halide atoms. Differentiation of this equation with respect to internuclear distance, assuming λ to be a constant, allows one to calculate $\partial\mu/\partial r$. The values of the integrals involved and the parameters necessary are given in Table I. The origin of the coördinate system is chosen at the center of the internuclear distance with the positive *z*-axis going through the hydrogen atom. Effective nuclear charges of the halide atoms were taken from the work of Pauling and Sherman.[3]

TABLE I

VALUE OF INTEGRALS AND PARAMETERS

	r(Å.)	$\Delta = \int sp_z\,d\tau$	$\chi^a = \int sp_z\,z\,d\tau$	$\partial\Delta/\partial r^a$	$\partial\chi/\partial r$
HF	0.9171	0.3296	0.2667	−0.1167	−0.2514
HCl	1.275	.4852	.4939	− .1204	− .2874
HBr	1.414	.4922	.6988	− .0008040	− .1858
HI	1.604	.4294	.7728	+ .07104	− .04989

[a] In atomic units, $a_0 = 0.5282$ Å.

Results and Discussion.—In Fig. 1 μ and $(1/e)\ (\partial\mu/\partial r)$ are plotted as functions of λ for the compounds. The observed μ and $(1/e)\ (\partial\mu/\partial r)$ are indicated by the horizontal dashed lines. No reliable intensities are known for HF or HI. However, $|\partial\mu/\partial r|$ for HI is probably less than that for HBr.[4] Both positive and negative possibilities of the experimental values are shown.

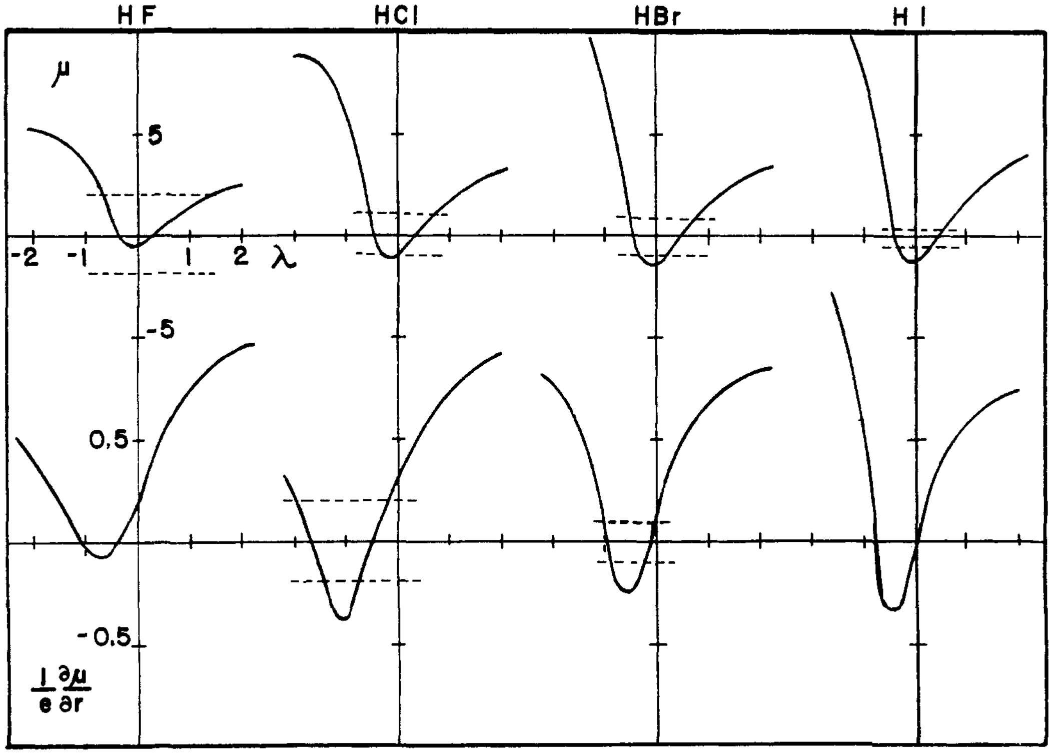

Fig. 1.—Variations of μ and $(1/e)(\partial\mu/\partial r)$ with respect to λ for the hydrogen halide molecules.

The λ values determined from the observed μ are used to establish the sign of $\partial\mu/\partial r$. The case of μ negative can be ruled out by Robinson's argument; namely, one obtains increasing λ for the sequence HCl and HI implying increasing ionicity in this direction. Furthermore, $|\partial\mu/\partial r|$ increases in the same direction contrary to the observed trend. For positive μ, if λ is negative $|\partial\mu/\partial r|$ again increases in the wrong direction. Moreover, the ionic characters one obtains from these λ values are too large. For positive λ one obtains $\partial\mu/\partial r$ and ionic character

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(1) Presented at the Northwest Regional A.C.S. Meeting, Washington State College, Pullman, Wash., June 12, 1953.

(2) D. Z. Robinson, *J. Chem. Phys.*, **17**, 1022 (1949).

(3) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(4) E. Bartholomé, *Z. physik. Chem.*, **B23**, 131 (1933).