solution patterns, the molecular weights, the density of the solid mercurous halides and the effective area of our indicator electrode, were calculated the thickness of the halide films expressed in Å. and also in molecular diameters. Diameters were evaluated from interatomic distances given by Wyckoff[9] for linear molecules of the type X–Hg–Hg–X of which the tetragonal crystals of the mercurous halides are built.[10] The data are presented in Table I.

TABLE I

THICKNESS OF MERCUROUS HALIDE FILMS ON THE MERCURY CONVECTION ELECTRODE

Halide	Concn. (moles/l.)	Approximate thickness of film	
		Å.	Mol. diameter
Chloride	1.00×10^{-4}	50	7
Bromide	1.00×10^{-4}	370	48
Iodide	1.00×10^{-4}	440	55
Iodide	2.32×10^{-4}	90	11
Iodide	1.77×10^{-3}	180	22

The most striking result in Table I is that the film obtained in 10^{-4} M iodide was about 5 times and 2.5 times as thick as those observed in 2.3×10^{-4} and 1.8×10^{-3} M solutions. In spite of this, in 10^{-4} M solution the true convection current was measured which remained constant with time, while the limiting currents in the more concentrated solutions were much smaller than the convection currents and decayed with time. In agreement with Majer[1]) and Müller, *et al.*,[11] it is concluded that the resistance exhibited by the film is not determined by its thickness but by its structure which in turn determines its permeability to the electroactive species. According to Müller, this permeability is determined by the structure of the first molecular layer which is formed. The convection electrode appears to be ideally suited for a systematic study of the permeability of films formed under various conditions. Our estimates of between 5 and 50 molecular diameters (Table I) are of the same order of magnitude as Majer's value[1] of 23 to 29 molecules for films of mercurous chloride and bromide at the dropping mercury electrode.

Acknowledgment.—This investigation was supported by research grants from the National Science Foundation and the Graduate School of the University of Minnesota.

[9] R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1951, Chapter III, table, page 43.

[10] R. J. Havighurst, THIS JOURNAL, **48**, 2113 (1926).

[11] W. J. Müller, *Z. Elektrochem.*, **38**, 854 (1932); **40**, 119 (1939); **41**, 83 (1935); W. J. Müller and K. Konopicky, *Monatsh.*, **48**, 711 (1927); W. J. Müller and L. Holleck, *ibid.*, **52**, 409, 425 (1929).

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Rates of Neutralization of C_1 to C_4 Nitroparaffins

BY PHILIP J. ELVING AND JULIAN LAKRITZ

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The kinetics of neutralization of the C_1 to C_3 nitroparaffins by hydroxide ion

$$R_1R_2CHNO_2 + OH^- = R_1R_2CNO_2^- + H_2O \quad (1)$$

have been studied by 1000-cycle conductivity[1a,b] at 0 and 5° and by polarography[1c] in buffered solution at 25°. The mechanism of the reaction has been thoroughly discussed.[1] The C_4 nitroparaffins have apparently not been investigated; neither have the compounds been studied at 25° in unbuffered medium.

The present investigation describes measurement of the neutralization rates of six lower C_1 to C_4 primary and secondary nitroparaffins by a megacycle frequency oscillator circuit, using an insulated cell. Such application is possible because of the large change in solution conductivity as the reaction of equation 1 occurs, and hydroxide ion is replaced by the anion. If equivalent conductances do not change over the range of ionic concentration encountered in an experiment (as was assumed by Pearson[1b] and others for higher concentrations than those used here), the changes in reaction (1) can be expressed in terms of measured items which are linear functions of conductance.[2]

Kinetic Data.—The data are summarized in Table I; standard deviations of the mean of the second-order rate constant range from 0.8 to 5.6% with only one exceeding 3.2%.

TABLE I

RATE DATA FOR CONVERSION OF NITROPARAFFINS TO THE ANION

Compound and concn. mM	NaOH concn., mM	No. of runs	Av. second-order rate constant, k, l. mole^{-1} min.$^{-1}$	Av. $t_{1/2}$, min.
Nitromethane, 2.42	0.514	2	1026 ± 8.5 (0.8%)	0.280
Nitroethane, 9.14	.919	3	236 ± 7.6 (3.2%)	0.321
1-Nitropropane, 9.20	.999	3	195 ± 2.1 (1.1%)	0.384
2-Nitropropane, 9.11	.999	5	16.4 ± 0.92 (5.6%)	4.44
1-Nitrobutane, 9.11	.999	4	192 ± 6.2 (3.2%)	0.397
2-Nitrobutane, 9.31	.999	5	8.78 ± 0.162 (1.8%)	8.49

Effect of Possible Reverse Reaction.—The present treatment, which does not make explicit allowance for the effect of opposing reactions, is strictly valid only when the equilibrium in equation 1 lies so far to the right that secondary effects become negligible; consequently, the slopes of the curves have been calculated from the initial values so as to minimize the influence of the reverse reaction. However, when the equilibrium concentration is explicitly introduced in the calculations, a first-order expression is observed for a reversible reaction with the effective rate constant being the sum of the constants for the forward and reverse directions.[3] It is possible to estimate, at least qualitatively, the effect of the reverse reaction for the specific compounds studied.

Miller, Arnold and Astle,[1c] using polarographic measurements, found the fraction of the nitroparaffin remaining in the nitro form in the equilibrium mixture at pH 8.9 to be 0.71, 0.20, 0.42 and 0.78 for nitromethane, nitroethane, 1-nitropropane

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[1] (a) S. H. Maron and V. K. La Mer, THIS JOURNAL, **60**, 2588 (1938); (b) R. G. Pearson, *ibid.*, **70**, 204 (1948); (c) E. W. Miller, P. A. Arnold and M. J. Astle, *ibid.*, **70**, 3971 (1948); (d) D. Turnbull and S. H. Maron, *ibid.*, **65**, 212 (1943); (e) C. M. Drew, J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 3098 (1954).

[2] Applicability of megacycle frequency oscillator circuits to reaction rate measurement with emphasis on moderately fast reactions is discussed in P. J. Elving, *Faraday Soc. Discs.*, **17**, 156 (1954). See also D. G. Flom and P. J. Elving, *Anal. Chem.*, **25**, 541, 544, 546 (1953).

[3] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173.

and 2-nitropropane, respectively. At this *p*H, our reactions should theoretically have gone 99% to completion. In the present calculations on nitromethane, where the half-life is of the order of 20 seconds and the equilibrium point is apparently unfavorable, the reverse reaction possibly played an important part. The unfavorable influence of reverse reactions on the rates of nitroethane and 1-nitropropane, which are almost as rapid, is offset, at least in part, by their more favorable equilibrium points; we can surmise that the same holds true for 1-nitrobutane. Consequences of the unfavorable equilibrium point of 2-nitropropane are considerably reduced by basing the calculations upon the first 2 to 3 minutes of the reaction; the half-life is about 4.5 minutes and, hence, secondary effects are probably small; the same argument probably holds for 2-nitrobutane (half-life of 8.5 minutes; calculations based on the first 2 to 3 minutes of reaction). Values for the equilibrium ratios of nitro to aci forms given by Miller, *et al.*, may be high[4]; if this were so, the effects of the reverse reactions would be even less than discussed in this paragraph.

Evaluation of the Results.—The present data agree qualitatively with those for the four compounds studied polarographically.[1c] The other two compounds fall into logical places; the rates decrease in the order: nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitropropane and 2-nitrobutane.

Duplication of the conditions used by Miller, *et al.*,[1c] was not feasible since the high ionic strength required for maintenance of a buffered solution would have made the measured conductance changes relatively small.[2]

A more pertinent comparison for the present results is with those of Maron and La Mer,[1a] who also worked in unbuffered solution. Their ratio of the second-order rate constants for 2-nitropropane, nitroethane and nitromethane at 0° is 1.0:18:114 as compared to 1.0:14:63 now found at 25°. Maron and La Mer give second-order rate constants at 0 and 5° for 2-nitropropane and nitroethane; values of 19.4 and 253 are calculated for 25° by the Arrhenius equation. In view of the uncertainty in the activation energy based on a 5° difference, these values are in good accord with those found in the present study, *i.e.*, 16.4 and 236.

The precision of the present results indicates that a megacycle frequency oscillator circuit can be used advantageously for studying the kinetics of certain types of ionic reactions whose half-lives are of the order of 20 seconds or longer in solutions of low ionic strength that are not hindered by unfavorable equilibria. By the addition of a recording potentiometer and suitable mixing arrangement, it would be possible to study much faster reactions.[2]

Experimental

Chemicals.—The nitro compounds had a molar purity of at least 99.9% as determined mass spectrometrically; 0.01 *M* stock solutions were prepared with carbon dioxide-free distilled water. The 0.01 *M* NaOH solution, prepared by diluting a saturated solution with carbon dioxide-free water, was standardized against reagent grade potassium hydrogen phthalate and was stored in a polyethylene bottle.

Apparatus.—The oscillator was the Sargent Model V Oscillometer which is of the capacitive retune type and operates at a frequency of about 5 megacycles.[5] The instrument response is primarily a measure of the change in capacitance of the sample cell, which is itself a function of the capacitance and conductance of the solution, the capacitance of the glass between solution and cell electrodes, and the cell geometry.[2,6] In the solutions studied, the principal effect is conductance change. The rates under the experimental conditions used were such that they could be followed by manual operation of the measuring apparatus. The capacitance cell, which was the 160-ml. size "titration" type furnished with the instrument, was maintained at a temperature of 25.0 ± 0.2° in an air-bath.

Procedure.—Dilution experiments indicated the instrument reading to be a linear function of NaOH concentration as long as the latter did not exceed 0.001 *M*.

In an actual experiment, 100 ml. of 0.01 *M* nitroparaffin solution was pipetted into a 125-ml. conical flask which was stoppered and suspended in a bath (25.0 ± 0.01°) to reach temperature equilibrium. This solution was then mixed with 10 ml. of 0.01 *M* base; a clock was started the instant nitro compound and base were mixed. To ensure adequate mixing, the resulting solution was poured twice between the vessels and was then transferred to the cell, which was stoppered with a cork covered with aluminum foil and placed in the cell-holder located in the air-bath. Readings were taken at 15-second intervals until the reaction was complete; the first reading was usually taken within 30 seconds of mixing the reactants. For reactions which reached equilibrium slowly, readings were taken for the first ten minutes; the solution was then returned to the constant temperature bath until equilibrium was reached. The equilibrium reading was then recorded.

Basis for Calculation.—If a large excess is taken of one reactant, *e.g.*, nitroparaffin, the reaction can be considered as *pseudo* first order, and

$$\ln (a - x) = k't + C \qquad (2)$$

where $(a - x)$ is the concentration of the reacting species present in smaller amount (original concentration $= a$) at time t, and k' is the *pseudo* first-order rate constant. Following the general equations for correlation of physical properties with concentration,[7] we can say for linear instrument response, that

$$(a - x) = K(C_t - C_\infty) \qquad (3)$$

and

$$C_t - C_\infty = (K' - K'')([OH^-]_t - [OH^-]_\infty) \qquad (4)$$

where K is a proportionality constant, C_t and C_∞ are the instrument responses to the conductances at time t and at infinite time, $[OH^-]_t$ and $[OH^-]_\infty$ are the concentrations of hydroxide ion at corresponding times, and K' and K'' are proportionality constants such that the instrument responses due to the hydroxide and nitroparaffin anion conductances are $K'[OH^-]$ and $K''[RNO_2^-]$. Consequently

$$\log (C_t - C_\infty) = -(k'/2.303)t + C' \qquad (5)$$

A plot of $\log (C_t - C_\infty)$ against t should give a straight line of slope equal to $-k'/2.303$. Dividing k' by the concentration of the reactant in excess gives the second-order rate constant.

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(4) There is a possible source of error in the polarographic measurements on the nitroparaffin–aci form equilibrium due to regeneration of the normal form from the aci form at the electrode–solution interface during the life-time of the mercury drop as the normal form is removed by reduction. This effect has been observed with other acid–anion systems, *e.g.*, Brdicka and Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947).

(5) A detailed mechanical and electrical description of the instrument and its cells is given in a publication of the Sargent Company: *Scientific Apparatus and Methods*, **5**, Winter Issue, 1 and 4, (1951–1952).

(6) C. N. Reilley in P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, Chap. 15.

(7) Ref. 3, pp. 28–29 and 35–37.

mercial Solvents Corporation for supplying the nitroparaffin samples.

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An Alternative Computation of the Transference Numbers in Zinc Sulfate Solutions

BY R. H. STOKES

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Lang and King[1] have recently published electromotive force measurements on the cell with transference

$$\underset{m_1}{\text{Pb–PbSO}_4 \mid \text{ZnSO}_4} \mid \underset{m_2}{\text{ZnSO}_4} \mid \text{PbSO}_4\text{–Pb (A, e.m.f. } E_t^A)$$

from which, in combination with activity coefficient data, they obtained by the method of Stokes and Levien[2] the transference numbers at 25° for the ions over the concentration range $m_2 = 0.005$ to 2 M. Their data are in satisfactory agreement with those obtained earlier by Purser and Stokes[3] using the cell

$$\text{Zn–Hg} \mid \underset{m_1}{\text{ZnSO}_4} \mid \underset{m_2}{\text{ZnSO}_4} \mid \text{Zn–Hg (B, e.m.f. } E_t^B)$$

The activity coefficient data used in both these researches were those of Bray[4] for solutions below 0.1 M in concentration, and of Stokes and Robinson[5]—above 0.1 M; the former were obtained from e.m.f. measurements on cells without transference, and the latter from isopiestic vapor pressure measurements. Now both sets of transference numbers exhibit rather sudden changes in the vicinity of 0.1 M, and there is clearly a possibility that this is a spurious effect arising from experimental errors in the activity data. Another possible source of spurious change lies in the fact that both transference number researches employed two separate equations to represent the relation between E_t and E (E = e.m.f. of cell without transference), *viz.*, a linear equation below 0.1 M and a quadratic above 0.1 M. The transference number is given by the differential relation $t = \mathrm{d}E_t/\mathrm{d}E$; differential coefficients are notoriously sensitive to experimental error near the ends of the range of the equations from which they are obtained, and the region of 0.1 M is subject to this objection. I have now made an alternative computation of the transport numbers, avoiding the use of the activity coefficient data altogether, and employing a single cubic equation to represent the relation between E_t and E over the entire range, as follows:

From cell A, we have $t_{Zn^{++}} = \mathrm{d}E_t^A/\mathrm{d}E$, and from cell B, $t_{SO_4^{--}} = 1 - t_{Zn^{++}} = \mathrm{d}E_t^B/\mathrm{d}E$. Hence $\mathrm{d}E = \mathrm{d}E_t^A + \mathrm{d}E_t^B$, and by integration between m_1 and m_2

$$E = E_t^A + E_t^B \qquad (1)$$

This of course assumes that m_1 and m_2 are the same in both cells. By graphical interpolation of suitable deviation functions, values of E_t^A were obtained corresponding to the e.m.f.'s of cell A for the molalities used in cell B by Purser and Stokes, and values of E were obtained from equation 1. The cubic equation 2 was then obtained by the method of least squares

$$E_t^B = 0.6281E + 1.257 \times 10^{-3}E^2 + 1.734 \times 10^{-5}E^3 \quad (2)$$

This reproduced the nine experimental E_t^B values with an average deviation of 0.08 mv. The transport numbers are therefore given by

$$t_{SO_4^{--}} = 1 - t_{Zn^{++}} = 0.6281 + 2.514 \times 10^{-3}E + 5.202 \times 10^{-5}E^2 \quad (3)$$

These values are shown in the figure along with those reported by Lang and King and by Purser and Stokes. The value obtained by equation 3 for the most dilute solution (0.373 at 0.0048 M) is omitted, as it is obtained from a differential coefficient at one extreme of the range of validity of equation 2; that for the most concentrated solution is also suspect, but is included since equation 2 fitted very accurately in this region, and also since the experimental e.m.f.'s in this region are more reliable.

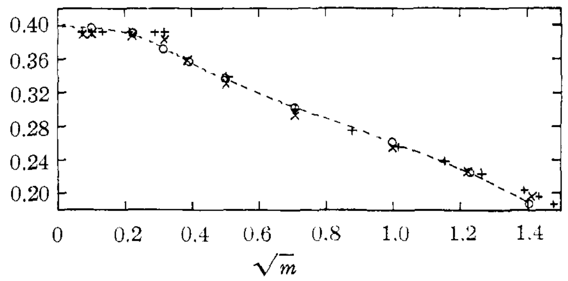

Fig. 1.—Zinc ion transference numbers *versus* square root of molality: ⊙, present method; X, data of Purser and Stokes (cell B); +, data of Lang and King (cell A).

Over most of the range, the transport numbers from all three methods differ only in the third place, which is as good as can be expected of the Helmholtz method. However, the new calculations reported here give a much smoother curve in the region of 0.1 M, suggesting that the abrupt change found by the earlier methods is in fact largely spurious.

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[1] R. E. Lang and C. V. King, THIS JOURNAL, **76**, 4716 (1954).

[2] R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333, 1852 (1946).

[3] E. P. Purser and R. H. Stokes, *ibid.*, **73**, 5650 (1951).

[4] U. B. Bray, *ibid.*, **49**, 2372 (1927).

[5] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

The Preparation of Iodopentamminecobalt(III) Salts from Cobalt(II)

BY RICHARD G. YALMAN

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Weak acid solutions of iodopentamminecobalt(III) ion react with iodide ion to form iodine and cobalt(II).[1] Because of this reaction iodopentamminecobalt(III) salts cannot be prepared in aqueous solution by the replacement of the water molecule in the aquopentamminecobalt(III) ion by iodide ion. Instead iodopentamminecobalt(III) iodide is prepared by heating aquopentammineco-

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[1] R. G. Yalman, THIS JOURNAL, **75**, 1842 (1953).