The concentration of free bromine can be shown to be equal to

$$y = 1/2\{\sqrt{[1/6(\zeta_0 - \zeta) + 5/6\,(T_0 - T) - T/2 + K + b]^2 + 2KT} - [1/6\,(\zeta_0 - \zeta) + 5/6\,(T_0 - T) - T/2 + K + b]\} \quad (2)$$

K being the dissociation constant of tribromide and b the initial normality of bromide. This value of y may be inserted into the rate equation (1), but it is impossible to carry out the integration without a knowledge of the functional relation between any two of the three variables $(T_0 - T)$, $(\zeta_0 - \zeta)$ and t.

If we combine the rate equation for the liberation of bromine from bromate and bromide[2] with equation (1), we obtain

$$d[H^+]/dt = -dT/dt = 2ky - 2k_4[Br^-][H^+]^2[BrO_3^-] \quad (3)$$

where k_4 is the rate constant of the forward reaction II in alcoholic solution.

Figures 1 and 2 show that T and $[H^+]$ behave in qualitative accordance with this equation, both changing rapidly in the beginning, when the concentration of hydrogen ion is very low, and tending to an almost constant value when the two terms on the right hand become commensurate.

The quantitative estimation of dT/dt, however, cannot be carried out since k_4 has not been determined, and in any case would be rather involved. Therefore, the rate constant was evaluated from the expression

$$-\frac{\Delta\zeta}{\Delta t} \times \frac{1}{2y} = k \quad (1a)$$

using the values of y calculated by equation (2).

Several experiments were carried out at a bromine titer ranging from 0.013 to 0.13 and a normality of total oxidizing agent of 0.3 to 0.4. Experiments with bromide added initially were also carried out. The results of two typical experiments are shown in Tables II, A and B.

The average value of k as defined by eqn. (1) between each two values of ζ has been estimated by the method indicated in our previous communication[1] and is shown as $k_{\text{theor.}}$ in the last column of Tables II, A and B, using $k_I = 0.094$. The deviations between k and $k_{\text{theor.}}$ are not larger than the experimental error and the inaccuracy introduced by using the interpolations of equation (1a).

It can be concluded that the oxidation of alcohol by a mixture of bromine and bromate proceeds according to the same rate equation as the oxidation with bromine alone.

Summary

The oxidation of alcohol by a mixture of bromine and bromate has been investigated.

The ratio of aldehyde to acetate in the reaction product is identical with the ratio found in the case of the oxidation by bromine alone.

The reaction in the presence of bromate proceeds according to the same rate equation as the reaction with bromine alone. The two reactions are fundamentally identical, the bromate merely supplying the free bromine necessary for the reaction to proceed.

The rate of formation of hydrobromic acid in the course of the oxidation of alcohol is faster than, but commensurate with, the rate of liberation of bromine from bromate and hydrobromic acid. Thus, the concentration of hydrobromic acid increases, and the bromine titer decreases during the reaction.

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[2] Sclar and Riesch, THIS JOURNAL, **57**, 667 (1936) (*cf.* also literature quoted in that paper.)

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

The High Field Conductance of Some Paraffin Chain Electrolytes[1]

BY WILLIS A. ADCOCK[2] AND ROBERT H. COLE

1. Introduction

To complement the researches which have been carried out in this Laboratory on colloidal electrolytes, an apparatus has been constructed to measure the high field conductance of these electrolytes. The apparatus is described below and preliminary data are given for the high field conductance of hexadecylpyridonium iodate and octadecylpyridonium iodate.

The high field conductance of hexadecylpyridonium chloride was first reported by Malsch and Hartley.[3] These investigators employed the barretter bridge method developed by Wien.[4]

In the barretter bridge method, a damped sine wave voltage pulse is applied to a bridge network and the currents which pass in each side of the bridge are averaged by means of the barretter elements. This method measures the average conductance during the duration of the pulse. Other investigators[5,6] have utilized oscilloscopic recorders to investigate the effect of

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[1] This paper is based on a portion of a thesis presented by Willis A. Adcock in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

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[3] J. Malsch and G. S. Hartley, *Z. physik. Chem.*, **A170**, 321 (1934).

[4] H. C. Eckstrom and C. Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

[5] W. Fuchs, *Ann. Physik*, **12**, 306 (1932).

[6] W. Hüter, *ibid.*, **24**, 253 (1935).

high potentials on the conductance of electrolytes. In the present investigation the transient unbalance of a bridge circuit fed by a square pulse was recorded, to obtain the advantages of a difference method and a simple observed pulse form.

II. Apparatus

The essential part of the apparatus is shown in Fig. 1. When the thyratron, type 4C35, is triggered by an applied pulse; the charged cable discharges into the conductance bridge, the impedance of which is matched to the surge impedance of the coaxial cable. A negative high voltage pulse with a duration of 2.15 microseconds is thus applied to the conductance bridge. The voltage of the pulse is approximately equal to one-half of the initial potential to which the cable is charged. This method for the production of high voltage square pulses has proved convenient and reliable. The shape of the pulse produced by this circuit is shown in Fig. 2A.

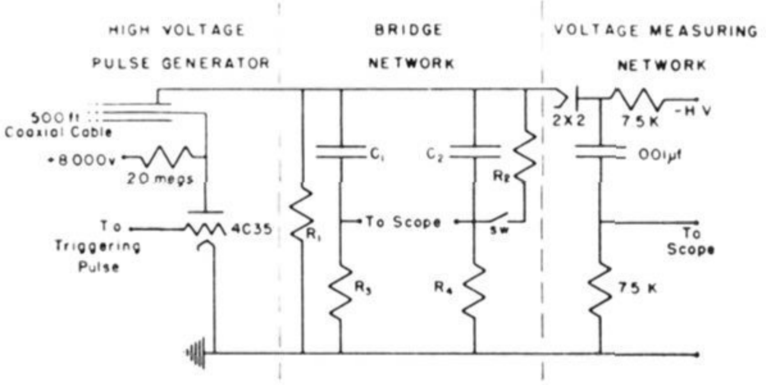


Fig. 1.—High field conductance apparatus.

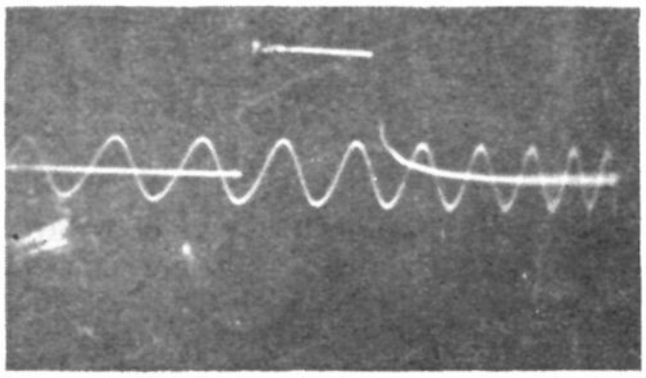
Two of the arms of the bridge network are formed by high field conductance cells, C1 and C2, with an electrolytic resistor R2 in parallel with C1. General Radio Type 510 Decade Resistance Units with ten-ohm steps are used to form the other two arms of the bridge, R3 and R4. An electrolytic resistor R1 is used to adjust the resistance of the bridge to the 70 ohms surge impedance of the cable, type RG-41-U.

The high field conductance cells utilize 0.5-inch diameter platinized platinum iridium (10%) electrodes. The electrode separation is made variable by a screw mechanism. The platinum leads to the electrodes and the backs of the electrodes are coated with lead glass to confine the lines of electrical flux. The high field cells and the electrolytic resistors are immersed in an oil-bath thermostat maintained at 25 ± 0.01° by means of a thyratron controlled heater actuated by a mercury thermoregulator.

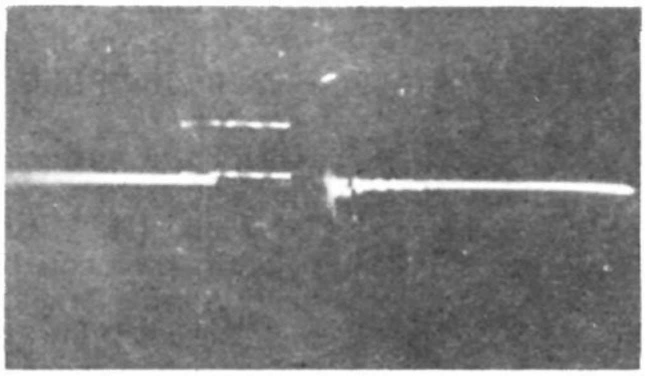
To measure the voltage of the square pulse a biased 2X2 diode is used as shown in Fig. 1.

III. Method

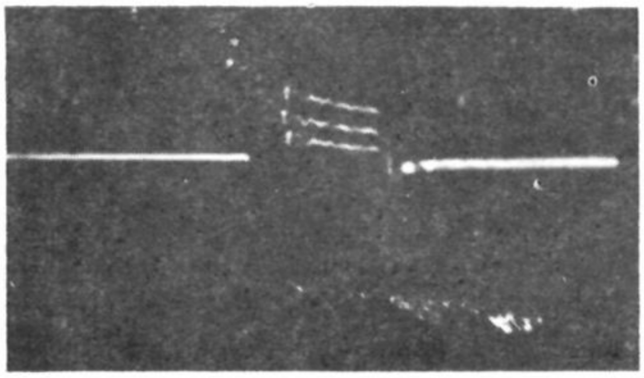
The solution whose high field conductance is to be measured is placed in the high field cell Cl and a potassium chloride solution of approximately the same specific conductance is placed in C2. R3 is made equal to R4, R2 is connected and R1 is adjusted so that the impedance of the bridge network is 70 ohms which matches the surge impedance of the cable used. A high voltage pulse, approximately 3500 volts, is applied to the bridge network from the high voltage pulse generator.



A—Output pulse from H. V. pulse generator, 866 kc. sine wave.



B—Unbalance signals from conductance bridge.



C—Signals from pulse voltage measuring circuit.

Fig. 2.

The first pulse is applied to the bridge with R2 disconnected and then another pulse is applied with R2 connected, R2 having been adjusted to such a value that the parallel combination of C2 and R2 will have the resistance which C1 is estimated to have under the high field conditions. These two pulses are photographed on the same frame and a typical pair is shown in Fig. 2-B. The higher pulse in Fig. 2B is produced with R2 disconnected.

To determine the voltage of the pulse, the scope is connected into the voltage measuring circuit and the variable negative high voltage supply supplying the biasing voltage to the 2X2 diode is adjusted to about one hundred volts less than the expected voltage of the pulse. The voltage of this voltage supply is determined by means of a Type K potentiometer using a bleeder circuit. A pulse is then applied to the bridge network with R2 disconnected (Fig. 1) and the scope records the difference between the pulse voltage and the high voltage supply. Two other pulses are applied when the biasing voltage is changed by plus and minus 45 volts in order to calibrate the sensitivity of the scope. A typical set of three such pulses is shown in Fig. 2-C.

The method of calculating the data and a sample calculation are given in the following paragraphs.

Let E represent the voltage of the pulse applied to the bridge network and E_1 and E_2 represent the voltages developed across C1 and C2, respectively. Then $E_1 = (R_{C1}/R_{C1} + R_3)\,E$, where R_{C1} is the high field resistance of C1 and similarly $E_2 = (R_{C2}/R_{C2} + R4)E$ with R2 disconnected. R_{C2} is the high field resistance of C2 and this is assumed to be equal to that determined by conventional audio frequency bridge measurements. $E_2' = (R_{C2}'/R_{C2}' + R4)E$ where R_{C2}' is the resistance of C2 and R2 in parallel combination.

The larger deflection shown in Fig. 2-B is proportional to $E_2 - E_1$ and the smaller deflection is proportional to $E_2' - E_1$. Let d_1 and d_2 represent the magnitudes of these deflections, respectively, as measured on the photographic record. Thus with the proportional factor k, relating the magnitude of these deflections to the magnitude of the voltages producing them, one has $E_2 - E_1 = kd_1$ and $E_2' - E_1 = kd_2$. These above expressions can be combined as

Equation 1. $E_2 - E_1 = kd_1 =$

$$\frac{R_{C2}}{R_{C2} + R4}\,E - \frac{R_{C1}}{R_{C1} + R3}\,E$$

Equation 2. $E_2' - E_1 = kd_2 =$

$$\frac{R_{C2}'}{R_{C}' + R4}\,E - \frac{R_{C1}}{R_{C1} + R3}\,E$$

In order to be able to calculate R_{C1} from the measured values of d_1, d_2, R_{C2}, R_{C2}', $R3$ and $R4$, equations 1 and 2 can be combined to eliminate k/E as is shown in Equation 3.

Equation 3.

$$\frac{R_{C1}}{R_{c_1} + R3} = \left(\frac{d_1}{d_1 - d_2}\right)\left(\frac{R_{C2}'}{R_{C2}' + R4} - \frac{d_2}{d_1}\,\frac{R_{C2}}{R_{C2} + R4}\right)$$

The above equations are derived by assuming that the addition of $R2$ does not affect the voltage E of the pulse. Actually the addition of R2 lowers E by a calculable value and the value of R_{C1} obtained by the above calculation is approximately the actual value of R_{C1} for the lower value of E. A correction is therefore applied as shown in the following sample calculation.

The concentration of the solution in C1 is determined from previously established conductance–concentration curves.

Sample Calculation

Let R_{C1}' represent the low field resistance of C1. The following values are obtained by audio-frequency bridge measurements. The deflection

R_{C1}' 560.0 ohms, R_{C2} 561.0, $R2$ 1018.0, $R3$ 50.0, $R4$ 50.0

d_1 is 0.790 cm. and d_2 0.030 cm. The voltage E obtained with $R2$ disconnected is 3650 volts.

The resistance R_{C2}' is equal to $R2R_{C2}/R2 + R_{C2} = 361.7$ ohms. From equation 3, R_{C1} is calculated to be 356.5 ohms and the per cent. increase in conductance is equal to $100[(560 - 356.5)/356.5] = 57.1$.

The separation of the electrodes in C1 is 0.046 cm. and for E 3650 volts, the voltage across C1 equals $(356.5/(356.5 + 50))\,E = 3200$ volts and the field strength is therefore 69,570 volts/cm.

Initially the bridge network was adjusted to 70 ohms with $R2$ connected and this approximates the high field resistance with $R2$ disconnected as R_{C1} at high field strength is approximately equal to the parallel combination of R_{C2} and $R2$. The voltage E is obtained with R2 disconnected. The cable behaves as a voltage source of an internal impedance of 70 ohms and thus with $R2$ connected the voltage E is lowered, and in this example the voltage is lowered by 2.8%. The value of R_{C1} is obtained for this lower voltage and thus the corrected value for the increase in conductance at the field strength of 69,570 v./cm. is $(57.1 \times 1.028) = 58.7\%$.

Preliminary data for aqueous solutions of hexadecylpyridonium iodate taken at 25° are presented graphically in Figs. 3 and 4 and tabulated in Table I. In all cases the per cent. increase in conductance for 100 k.v./cm. is determined by extrapolating the data obtained for lower field strengths.

TABLE I

HEXADECYLPYRIDONIUM IODATE

Field strength volts/cm.	Per cent. increase in conductance	Field strength volts/cm.	Per cent. increase in conductance
$c = 5.88 \times 10^{-3}$ molar		$c = 2.01 \times 10^{-3}$	
20,600	5.5	41,910	11.7
35,000	11.0	69,650	23.5
51,860	20.3	89,600	32.1
52,420	19.5	100,000	36.6
100,000	45.0	$c = 1.43 \times 10^{-3}$	
$c = 2.39 \times 10^{-3}$		43,570	5.5
13,180	1.7	68,200	9.5
21,140	4.2	89,400	12.6
21,860	4.3	100,000	14.2
36,330	9.9	$c = 1.23 \times 10^{-3}$	
41,490	12.2	87,160	3.5
77,330	29.2	100,000	4.0
100,000	39.8	$c = 1.06 \times 10^{-3}$	
		90,410	1.7
		100,000	1.9

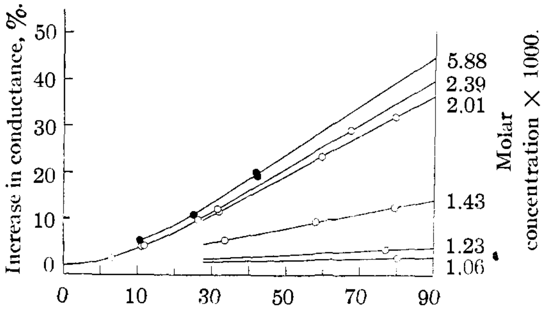


Fig. 3.—Hexadecylpyridonium iodate.

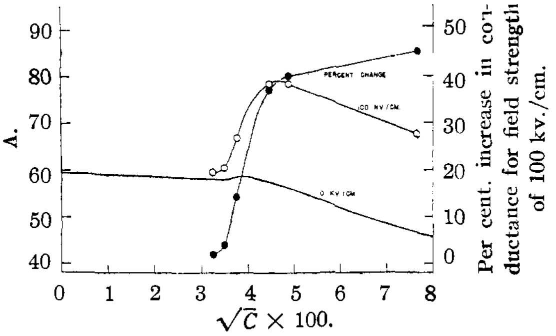


Fig. 4.—Conductance of hexadecylpyridonium iodate in water at zero and 100 kilovolts per centimeter field strengths.

Preliminary data for aqueous solutions of octadecylpyridonium iodate taken at 25° are presented graphically in Figs. 5 and 6 and tabulated in Table II.

TABLE II

OCTADECYLPYRIDONIUM IODATE

Field strength, volts/cm.	Per cent. increase in conductance	Field strength, volts/cm.	Per cent. increase in conductance
$c = 6.80 \times 10^{-3}$ molar		$c = 0.989 \times 10^{-3}$	
20,880	7.1	45,530	37.7
36,660	17.2	69,570	58.7
56,010	30.7	90,580	77.3
100,000	62.4	100,000	85.6
$c = 3.52 \times 10^{-3}$		$c = 0.622 \times 10^{-3}$	
21,520	9.3	38,280	25.3
45,070	29.9	67,680	46.8
72,320	55.0	87,280	60.8
100,000	80.0	100,000	69.8
$c = 1.71 \times 10^{-3}$		$c = 0.329 \times 10^{-3}$	
37,730	27.5	93,890	13.6
57,730	48.3	100,000	14.5
72,010	63.6	$c = 0.205 \times 10^{-3}$	
100,000	93.0	88,390	1.9
		100,000	2.2

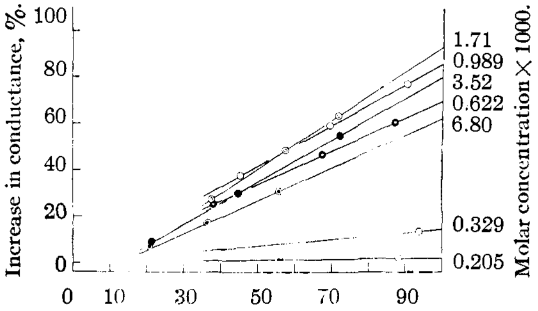


Fig. 5.—Octadecylpyridonium iodate.

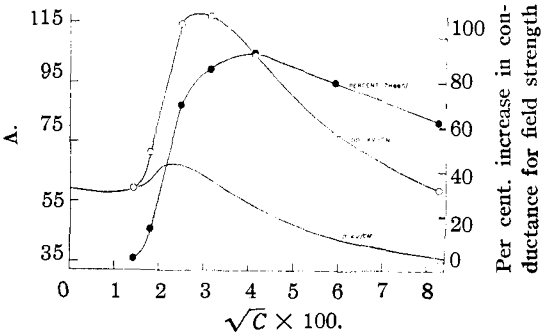


Fig. 6.—Conductance of octadecylpyridonium iodate in water at zero and 100 kilovolts per centimeter field strengths.

V. Summary

1. A bridge circuit method using a square voltage pulse has been described which is suitable for measuring the high field conductance of colloidal electrolytes.

2. The shape of the output pulse shows that there is no time delay greater than 0.1 microsecond in the establishment of the high field conductance upon the application of the square pulse. A greater time delay than this would cause a sloping of the front part of the output pulse.

3. Preliminary data for the high field conductance of aqueous solutions of hexadecylpyridonium iodate and octadecylpyridonium iodate are presented which confirm the earlier observations of Malsch and Hartley of the large effect produced by colloidal electrolytes at concentrations greater than the concentration of the break point.

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