[CONTRIBUTION FROM THE CHEMICAL LABORATORY, INDIANA UNIVERSITY]

Electrical Conductance of Aqueous Solutions. I. Sodium and Potassium Bromates at 25°, and the Conductance of the Bromate Ion

BY JAMES HOMER JONES

The electrical conductance of aqueous solutions of potassium bromate has been measured by Hunt[1] and by Walden,[2] and that of sodium bromate by Watkins and Jones.[3] The equipment and standards used by these investigators are outmoded. The conductance of the bromate ion calculated from work of Hunt on potassium bromate and Jones on sodium bromate differs by approximately 4.3%.

Shedlovsky[4] mentions that potassium nitrate and silver nitrate do not follow his linear relationship, and that chlorates and iodates behave similarly. No mention is made of bromates although they ought to be intermediate in behavior between chlorates and iodates.

The redetermination of the conductance of aqueous solutions of sodium bromate and potassium bromate was undertaken to clear up these discrepancies. Since the mobilities of the potassium ion and sodium ion are well known, the mobility of the bromate ion can be found.

Experimental

Purification of Material.—J. T. Baker reagent grade sodium bromate and potassium bromate were recrystallized three times from conductivity water. The hot solutions were allowed to stand until crystals began to appear, then they were filtered rapidly through glass filters into Pyrex filter flasks which served as crystallizing dishes. Only two crops of crystals were collected from any one solution. The purified salts were partially dried in an oven at 110°, the lumps broken up in a "mullite" crucible, and the drying completed in a vacuum desiccator over solid potassium hydroxide. The salts showed no evidence of bromides when tested with silver nitrate. A portion of the potassium bromate was dried in an oven at 180° for twenty-four hours before use. No difference in conductance between this part and the original sample was noted.

Apparatus.—The bridge, oscillator and amplifier used for the conductance measurements were those recommended for research by Leeds and Northrup.[5] The thermostat consisted of a double bath: the inner one filled with oil and the outer with water. The oil-bath was insulated with masonite to slow down the rate of cooling. With the outer water bath at a temperature of from 0.2 to 0.5 of a degree lower than that of the inner bath, the heating and cooling rates were about equal. The oil-bath has a capacity of about twenty gallons. It was heated by means of a 50-watt heater.

The temperature was measured by means of a Mueller Bridge and platinum resistance thermometer (NBS 642). A Leeds and Northrup HS galvanometer (0.08 μv./mm.) was used in conjunction with the Mueller bridge. The temperature was regulated by an electronic relay and photoelectric cell. A second light source with adjustable slit focused on the galvanometer mirror, reflected the light needed to activate the photoelectric cell. A change in temperature of less than 0.001° was sufficient to throw the image of the slit in or out of the photoelectric cell. Considering the lag always present in such relays, the temperature control should approximate $\pm$ 0.001°.

The temperature was set as close to 25° as possible by measuring the ice point of the platinum resistance thermometer, and calculating the resistance at 25° by means of the Callander formula.

The solutions were made up either by weight from the dry salt and water, or by weight dilution. When weight dilutions were made, no more than two solutions were made from any one of the original solutions.

The conductance cells were made entirely of "Pyrex" glass. The electrodes were platinized according to the directions of Jones and Bollinger.[6] Each cell was checked for polarization effects by determining the resistance of the cell at frequencies of 500, 1000 and 2000 cycles per second. Since no appreciable change in resistance was noted, it was assumed that the platinization was adequate.

Density of Potassium Bromate and Sodium Bromate Solutions.—The densities of several solutions of potassium bromate were determined. They agree with the values recorded in the literature[7] to within 0.01%. The densities at 25° may be represented by the equation $d_{KBrO_3} = 0.99707 + 0.12304c$, where c is the molar concentration. No data on the density of sodium bromate solutions at 25° were found. The densities of the solutions used in the conductance measurements were determined. The densities from 0–0.3 molar may be represented by the equation $d_{NaBrO_3} = 0.99707 = 0.11606\ c$, where c is the molar concentration.

The Conductance of Sodium and Potassium Bromate Solution.—The data obtained on the conductance of aqueous solution of potassium bromate and sodium bromate at 25° are recorded in Table I. In this table, C is the molar concentration, Λ is the observed equivalent conductance and Λ_0' is the computed value of the limiting conductance from the Onsager equation.

The cell constants were determined using the Jones and Prendergast[8] standards. The water used had a specific conductance of from 0.8–1.3 $\times$ 10^{-6} reciprocal ohm.

TABLE I

C_{KBrO_3}	Λ_{KBrO_3}	Λ_0'	C_{NaBrO_3}	Λ_{NaBrO_3}	Λ
0.14774	103.62		0.48193	75.07	
.13081	104.76		.28598	77.75	
.093616	107.53	135.48	.10579	85.93	114.04
.062524	110.49	133.20	.064229	89.27	110.49
.061555	110.68	133.21	.057283	89.97	110.45
.049083	112.26	132.33	.028252	93.85	108.15
.048959	112.26	132.31	.021905	95.09	107.67
.031380	115.19	131.20	.014252	96.98	107.11
.011069	120.37	129.83	.010836	97.97	106.79
.0043415	123.46	129.38	.0053638	100.12	106.32
.0037242	123.90	129.37	.0042144	100.77	106.26
.0032819	124.18	129.32	.0029153	101.58	106.10
.0024280	124.88	129.31	.0010531	103.28	106.03
.0019640	125.33	129.32	.0007800	103.61	105.97
.0010513	126.43	129.35	.0005078	104.12	106.00
.0008370	126.72	129.31			
.0005443	127.27	129.38			
0	129.31[a]		0	105.86[a]	

[a] By method of least squares applied to Onsager function.

(1) Hunt, THIS JOURNAL, 33, 795 (1911).
(2) Walden, *Z. physik. Chem.*, 2, 48 (1888).
(3) Watkins and H. C. Jones, THIS JOURNAL, 37, 2626 (1915).
(4) Shedlovsky, *ibid.*, 54, 1409 (1932).
(5) Leeds and Northrup, Cat. EN-95.
(6) Grinnell Jones and Dorothy M. Bollinger, THIS JOURNAL, 57, 280 (1935).
(7) "International Critical Tables," Vol. III.
(8) Grinnell Jones and Maurice J. Prendergast, THIS JOURNAL, 59, 731 (1937).

Discussion

A plot of the Shedlovsky function was made

$$\Lambda_0' = \frac{\Lambda + 60.27\, c}{1 - 0.2294\, c}\ vs.\ c$$

for each salt. The lower end of these plots is shown in Fig. 1. As is seen, the data for potassium bromate deviate from the straight line at low concentrations in a manner analogous to those of potassium nitrate.[9] This behavior is typical of polyvalent salts but is usually absent from uni-univalent electrolytes. Since the Shedlovsky function did not yield a straight line, the Λ_0 value for potassium bromate was obtained from the Onsager limiting equation using the data on those solutions whose concentration was less than 0.005 molar. The method of least squares applied to these data yielded a straight line with an intercept of 129.31 and a slope of −89.10. The theoretical slope is −89.93. The estimated error is ±0.05 reciprocal ohms.

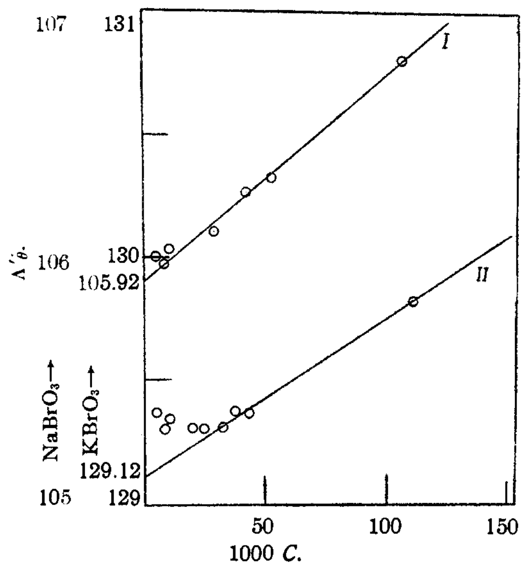

Fig. 1.—Plot of Shedlovsky function; Curve I, $NaBrO_3$; Curve II, $KBrO_3$.

(9) Shedlovsky, THIS JOURNAL, 54, 1409 (1932).

The Shedlovsky plot for sodium bromate was a straight line up to concentrations of about 0.06 molar. The intercept was 105.92. The Onsager limiting equation for solutions of concentration less than 0.006 molar yielded a straight line with an intercept of 105.86 and a slope of −79.22. The average of these figures, 105.89, is accepted as the Λ_0 value for sodium bromate. The estimated error is again ±0.05 reciprocal ohm.

The Conductance of the Bromate Ion.—The conductance of the potassium ion at infinite dilution and 25° is 73.52, and that of the sodium ion is 50.11 (on Jones and Bradshaw standard). If the value of Λ_0 for potassium bromate is taken as 129.31 ± 0.05, the conductance of the bromate ion would be 55.79 ± 0.05. The value for Λ_0 of sodium bromate yields a conductance value for the bromate ion of 55.78 ± 0.05. These values are in good agreement, and the average value of 55.78 ± 0.05 is assigned as the conductance of the bromate ion at 25° and infinite dilution.

Summary

1. The conductance of aqueous solutions of potassium bromate at 25° has been measured over the concentration range of 0.0005–0.15 molar, and that of sodium bromate from 0.0005–0.5 molar.

2. The densities of sodium bromate from 0.0005–0.3 molar have been determined at 25°.

3. The conductance of the bromate ion at 25° and infinite dilution has been calculated from the conductance of sodium and potassium bromates and the known conductances of the sodium and potassium ions.

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The Action of Chromia Catalyst on Aliphatic *Iso*-alcohols and *Iso*-aldehydes

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It was shown recently that primary straight chain aliphatic alcohols[1] when subjected to the action of chromia (Cr_2O_3) catalyst at atmospheric pressure and 400° underwent a combined *condensation–dehydrogenation* reaction resulting in the production of ketones with $2n - 1$ carbon atoms. The reaction was found to go through an aldehyde-aldol formation. This mechanism was supported by the fact that aldehydes and aldols gave the same reaction with higher yields in the above-mentioned order.

(1) Komarewsky and Coley, THIS JOURNAL, 63, 700 (1941). Komarewsky and Coley, *ibid.*, 63, 3269 (1941).

Straight chain aldehydes subjected to the action of the same catalyst but at super-atmospheric pressures underwent a combined *condensation–dehydration* reaction resulting in the formation of olefin hydrocarbons with $2n - 1$ carbon atoms.[2]

The present investigation extends the application of these reactions to isoalcohols and isoaldehydes. The following compounds were subjected to the action of chromia catalyst: isobutyl alcohol, 2-methylpentanol-1, isomyl alcohol, 2-ethylhexanol, isobutylaldehyde, isoamyl-

(2) Komarewsky and Kritchevsky, *ibid.*, 65, 547 (1943).