

changes from hexahydrate to mixed hexasolvate to dihydrate with the preponderance of the blue<sup>7</sup> 4-coördinated [CoCl<sub>2</sub>·2(H<sub>2</sub>O, alcohol)] in the solution. The maximum solubility of 15.35% for the salt is found at the liquid composition at which the equilibrium solid is changing from the monohydrate to the anhydrous form, and may perhaps be a basis for considering the solute form achieving maximum concentration to be (CoCl<sub>2</sub>·H<sub>2</sub>O·(CH<sub>3</sub>)<sub>3</sub>OH). The decrease in solubility as the system becomes anhydrous is found also in the CoCl<sub>2</sub>-water-acetone system, and the cobaltous nitrate-water-solvent systems.

The equilibration data alone give no clear answer to the question of whether the anhydrous solid is alcoholated. The physical nature of the solid makes it difficult mechanically to separate the liquid phase sufficiently to be sure whether or not the solid might contain solvation alcohol. Two samples of anhydrous CoCl<sub>2</sub> were therefore refluxed with *t*-butyl alcohol for periods of several hours, and allowed to cool. In one sample the supernatant was poured off, the residual solid press-dried between sheets of filter paper, and analyzed. In the second sample, the light-blue solid formed a recrystallization ring above the top of the liquid, which could be cleanly separated to leave a fairly dry brittle solid which was allowed to drain further. The analysis of the first solid was 13.26% cobalt, 0.65% water; of the second solid, 14.06%

(7) L. I. Katzin and E. Gebert, *THIS JOURNAL*, **72**, 5464 (1950).

cobalt, 1.93% water. For CoCl<sub>2</sub>, Co = 45.4%. The alcohol is equivalent to about 4 molecules per cobalt, which for the second sample is certainly beyond the amount for which mere physical wetting might readily account. Alcoholation of the anhydrous solid therefore seems probable. Stable alcoholates of CoCl<sub>2</sub> are known for other alcohols.<sup>8-12</sup>

The pair of equilibrium liquids obtained closest to the plait point (Table I) analyzed 41.25% water-4.30% CoCl<sub>2</sub> and 64.53% water-8.82% CoCl<sub>2</sub>, respectively. Points in between these compositions were covered with particular care by the method of phase separation described above. At a composition 51.74% water-5.93% CoCl<sub>2</sub>-42.33% alcohol the separation of phases could be distinguished only with difficulty on approaching from the high-water side. The next point, at 49.34% water-5.50% CoCl<sub>2</sub>-45.16% alcohol, showed a reversal in relative densities of the more abundant and less abundant phases. The plait point is therefore near the composition 51.74% water-5.93% cobaltous chloride-42.33% *t*-butyl alcohol, which is reasonable from the symmetry of the solubility curve and the tie-lines.

(8) F. Bourion, *Compt. rend.*, **134**, 556 (1902).

(9) A. Benrath, *Z. anorg. Chem.*, **54**, 328 (1907).

(10) A. Hantzsch and F. Schlegel, *ibid.*, **159**, 273 (1927).

(11) E. Lloyd, C. B. Brown, D. G. R. Bonnell and W. J. Jones, *J. Chem. Soc.*, 658 (1928).

(12) O. E. Zvyagintsev and S. N. Matatshvili, *Bull. Acad. Sci. Georgian S.S.S.R.*, **3**, 1035 (1942); cited in *C. A.*, **41**, 2956 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY UNIVERSITY OF CALIFORNIA, BERKELEY]

## The Heat and Free Energy of Formation of Bromate Ion

BY HOWARD C. MEL, WILLIAM L. JOLLY AND WENDELL M. LATIMER

RECEIVED APRIL 30, 1953

In an effort to clear up an inconsistency in the thermodynamic data for BrO<sub>3</sub><sup>-</sup> ion, the heat of solution of KBrO<sub>3</sub> and the heats of reduction of KBrO<sub>3</sub> with I<sup>-</sup> and Br<sup>-</sup> have been measured calorimetrically at 25°. For KBrO<sub>3</sub>(c) = K<sup>+</sup> + BrO<sub>3</sub><sup>-</sup>, ΔH<sup>0</sup> = 9.76 ± 0.05 kcal./mole; for KBrO<sub>3</sub>(c) + 9I<sup>-</sup> + 6H<sup>+</sup> = 3I<sub>2</sub> + K<sup>+</sup> + Br<sup>-</sup> + 3H<sub>2</sub>O, ΔH<sup>0</sup> = -122.26 ± 0.8 kcal./mole; and for KBrO<sub>3</sub>(c) + 8Br<sup>-</sup> + 6H<sup>+</sup> = 3Br<sub>2</sub> + K<sup>+</sup> + 3H<sub>2</sub>O, ΔH<sup>0</sup> = -42.17 ± 0.3 kcal./mole. Combining these heats with other heat and entropy data, we have calculated for BrO<sub>3</sub><sup>-</sup> ion: ΔH<sub>f</sub><sup>0</sup> = -18.3 kcal./mole and ΔF<sub>f</sub><sup>0</sup> = 2.1 kcal./mole. These values have been discussed with respect to other experimental data.

### I. Introduction

Lewis and Randall<sup>1</sup> calculate from the measurements of Sammet<sup>2</sup> on the bromine-bromate electrode that the free energy of formation of BrO<sub>3</sub><sup>-</sup> is 2.3 kcal./mole. The National Bureau of Standards<sup>3</sup> gives 10.9 kcal./mole for the free energy of formation. This latter quantity was calculated from Thomsen's<sup>4</sup> heat for the reduction of BrO<sub>3</sub><sup>-</sup> by Sn<sup>++</sup> and Ahlberg and Latimer's<sup>5</sup> entropy data for BrO<sub>3</sub><sup>-</sup>. The large discrepancy was thought to be primarily

(1) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 521.

(2) V. Sammet, *Z. physik. Chem.*, **58**, 678 (1905).

(3) National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952.

(4) J. Thomsen, "Thermochemische Untersuchungen," Leipzig, J. A. Barth, 1882.

(5) J. E. Ahlberg and W. M. Latimer, *THIS JOURNAL*, **56**, 856 (1934).

due to an inaccurate value for the heat of formation of BrO<sub>3</sub><sup>-</sup>. Hence, the present investigation was undertaken to establish a more accurate value for this quantity. Two main reactions were studied, (1) the heat of reduction of KBrO<sub>3</sub> by iodide, and (2) the heat of reduction by bromide. The heat of solution of KBrO<sub>3</sub> in water was also measured.

Unless specifically stated, all heat calculations were made using heats of formation tabulated by the Bureau of Standards.<sup>3</sup>

### II. Experimental

**Calorimeter.**—The calorimeter has been described previously.<sup>6,7</sup> The possibility of variation in the calorimeter stirring rate has been reduced by the use of a synchronous motor with chain and sprocket drive. The standard re-

(6) B. J. Fontana, "National Nuclear Energy Series IV-19B," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

(7) H. W. Zimmerman and W. M. Latimer, *THIS JOURNAL*, **61**, 1680 (1939).

sistances in the calorimeter circuit were calibrated against resistances recently certified at the Bureau of Standards.

The samples of  $\text{KBrO}_3$  (weighed in thin-walled glass bulbs) were either fastened to a glass rod running through the calorimeter stirring shaft and broken on the bottom of the calorimeter, or were fastened directly to the stirring shaft itself and broken by thrusting a rod through them. The reactions were calorimetrically complete in 5 to 25 minutes. The heats were measured at  $25.0 \pm 0.5^\circ$  and are reported in terms of the defined calorie.

**Reagents.**—All weighings were corrected to weight *in vacuo* when necessary. Two separate lots of reagent grade  $\text{KBrO}_3$  were recrystallized and dried for several hours at  $160^\circ$ . One lot was analyzed by gravimetric titration with thiosulfate and was found to be 100.17% pure. The other lot was not analyzed, but samples from it were used at random, with no systematic differences in the calorimetric results. The thiosulfate solution was standardized with recrystallized  $\text{KIO}_3$ . The  $\text{KI}$ ,  $\text{NaI}$ ,  $\text{KBr}$  and  $\text{NaBr}$  used in the reduction runs were reagent chemicals dried for several hours at  $110^\circ$ . The perchloric acid was a double vacuum distilled reagent and was standardized before use.

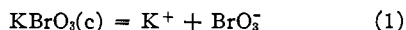
### III. The Heat of Solution of $\text{KBrO}_3$

Three determinations were made of the heat of solution of  $\text{KBrO}_3$  in water. The details are given in Table I.

TABLE I  
THE HEAT OF SOLUTION OF  $\text{KBrO}_3$

Run	$\text{KBrO}_3$ , g.	$\text{H}_2\text{O}$ , g.	$\Delta H_1$ , kcal./mole
1	2.4074	1053	9.74
2	1.5186	1053	9.79
3	2.8477	1043	9.80
			Av. 9.78

Using the heat of dilution calculated from the Bureau of Standards data,<sup>3</sup> we correct the average value to  $\Delta H^0 = 9.76 \pm 0.05$  kcal./mole for



This compares with the value 9.8 kcal./mole calculated from the Bureau of Standards data.<sup>3</sup>

### IV. The Heat of Reduction of $\text{KBrO}_3$ with $\text{I}^-$

In this series of measurements, solid  $\text{KBrO}_3$  was dissolved in an aqueous solution of  $\text{HClO}_4$  and either  $\text{NaI}$  or  $\text{KI}$ . The details are given in Table II.<sup>8</sup>

TABLE II  
THE HEAT OF REDUCTION OF  $\text{KBrO}_3$  WITH  $\text{I}^-$

Run	$\text{KBrO}_3$ , g.	$\text{H}_2\text{O}$ , total g.	$\text{KI}$ , g.	$\text{HClO}_4$ , moles	$Q_5$ , cal.	$Q_2$ , cal.	$-\Delta H_1$ , kcal./mole
1	0.3787	1060	10.07	0.139	273.48	0.90	121.01
2	.5460	1057	17.74	.093	410.6	.69	125.8
3	.4996	1066	16.96	.093	367.40	.65	123.04
4	.4162	1060	11.39 <sup>a</sup>	.116	304.94	.75	122.67
5	.3070	1057	17.00	.093	225.82	.35	123.04
6	.5299	1070	17.74	.093	388.27	.67	122.59
7	.3872	1060	7.92 <sup>a</sup>	.116	285.11	1.15	123.47
							Av. 123.09

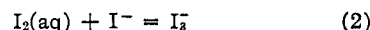
<sup>a</sup>  $\text{NaI}$  used.

$Q_5$  refers to the heat evolved in the calorimeter.  $Q_2$  refers to the calculated heat for the conversion of the aqueous iodine (formed in the calorimetric reaction) to triiodide<sup>9</sup>

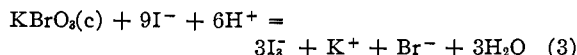
(8) One run, not described because of the possibility of the precipitation of  $\text{KClO}_4$ , gave a value of  $\Delta H_1 = -123.0$  kcal./mole.

(9) In calculating  $Q_2$ , we have used the iodine-triiodide constant of Davies and Gwynne.<sup>10</sup> It can be seen that  $Q_2$  is of the order of 0.2% of  $Q_5$ , and errors due to neglect of activity coefficients and heats of dilution in the calculation of  $Q_2$  are negligible.

(10) M. Davies and E. Gwynne, *This Journal*, **74**, 2748 (1952).



The sum of  $Q_5$  and  $Q_2$  is then the heat of the hypothetical calorimetric reaction where all the oxidized iodide has formed triiodide



The quantity  $\Delta H_3$  refers to the heat (in kcal./mole) for reaction (3), uncorrected to infinite dilution. We shall use our weighted average,  $\Delta H_3 = -122.98$  kcal./mole. By assuming that the heats of dilution of  $\text{HI}$  and  $\text{KBr}$  (in our calorimetric solutions<sup>11</sup>) are the same as those for 0.18 *M*  $\text{HI}$  and 0.18 *M*  $\text{KBr}$ , we calculated  $\Delta H_3^0 = -122.26 \pm 0.8$  kcal./mole for the infinitely dilute ions.

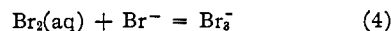
### V. The Heat of Reduction of $\text{KBrO}_3$ with $\text{Br}^-$

Solid  $\text{KBrO}_3$  was dissolved in an aqueous solution of  $\text{HClO}_4$  and  $\text{NaBr}$ . The details are given in Table III.<sup>12</sup>

TABLE III  
THE HEAT OF REDUCTION OF  $\text{KBrO}_3$  WITH  $\text{Br}^-$

Run	$\text{KBrO}_3$ , g.	$\text{H}_2\text{O}$ , total g.	$\text{NaBr}$ , g.	$\text{HClO}_4$ , moles	$Q'_c$ , cal.	$Q_4$ , cal.	$Q_5$ , cal.	$-\Delta H_3$ , kcal./mole
1	1.1417	1061	15.32	0.174	280.38	15.59	0.16	43.32
2	0.6897	1058	14.89	.174	170.64	8.65	.09	43.44
								Av. 43.38

$Q'_c$  refers to the heat evolved in the calorimeter.  $Q_4$  refers to the calculated heat for the conversion of the aqueous bromine (formed in the calorimeter) to tribromide<sup>13</sup>

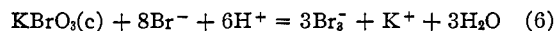


$Q_5$  refers to the calculated heat correction for the slight vaporization of bromine from the solution into the dead air space in the calorimeter



The partial pressure of  $\text{Br}_2(\text{g})$  was calculated assuming complete equilibrium. A calculation showed that the hydrolysis of bromine in our solutions was entirely negligible—as was also the case for our iodine solutions.

The sum of  $Q'_c$ ,  $Q_4$  and  $Q_5$  is then the heat of the hypothetical calorimetric reaction where all the oxidized bromide has formed tribromide



The quantity  $\Delta H_6$  refers to the heat (in kcal./mole) for reaction (6), uncorrected to infinite dilution. We shall use the average  $\Delta H_6 = -43.38$  kcal./mole. For these runs, the average ionic strength was about  $\mu = 0.29$ . Using methods similar to those described in Section IV, we correct this for dilution effects to  $\Delta H_6^0 = -42.17 \pm 0.3$  kcal./mole.

### VI. Interpretation of Data

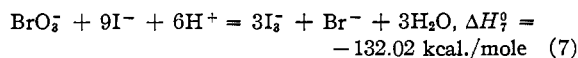
Subtracting reaction (1) from reaction (3) we obtain

(11) In all runs, the ionic strength was approximately the same and, since it changed little during the course of the reaction, we adopt the average  $\mu = 0.18$ .

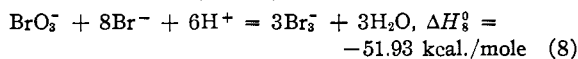
(12) One run, not described because of the use of  $\text{KBr}$  and the possible precipitation of  $\text{KClO}_4$ , gave a value of  $\Delta H_7 = -43.4$  kcal./mole.

(13) In calculating  $Q_4$ , we have used the bromine-tribromide constant Griffith, McKeown and Winn<sup>14</sup> corrected to  $25^\circ$ ,  $K_4 = 17 = (\text{Br}_3^-)/(\text{Br}_2)(\text{Br}^-)$ . Activity coefficient and heat of dilution corrections have been neglected.

(14) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).



Using Bureau of Standards heat data<sup>3</sup> we calculated  $\Delta H_f^\circ = -18.70$  kcal./mole for  $\text{BrO}_3^-$ . Similarly from reactions (1) and (6) we obtain



from which we calculate  $\Delta H_f^\circ = -17.82$  kcal./mole. Combining the average value of  $\Delta H_f^\circ$  ( $-18.3$  kcal./mole) with the entropy of formation,<sup>3</sup> we calculate  $\Delta F_f^\circ = 2.1$  kcal./mole. The close agreement with Sammet's<sup>2</sup> value may be fortuitous, as may be seen from a careful examination of the iodine and bromine heat data.

The Bureau of Standards value for  $\Delta H_f^\circ$  of  $\text{I}_2(\text{aq})$  (5.0 kcal./mole) is based on the temperature coefficient of fifty-year old solubility data. We calculate from more extensive and more recent data<sup>15</sup> the value 5.6 kcal./mole (corrected for hydrolysis). For the heat of iodide complexing of iodine (reaction (2)), the following values have been reported in the literature:  $\Delta H_f^\circ = -4.30$ ,<sup>16</sup>  $-3.87$ ,<sup>10</sup>  $-5.10$ <sup>17</sup> kcal./mole. All of these are based on the temperature coefficients of the equilibrium constant measured in different ways. From the Bureau of Standards heat data<sup>3</sup> one calculates the value  $-4.03$  kcal./mole. It is apparent that the consid-

(15) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940.

(16) Calculated by Davies and Gwynne<sup>10</sup> from the data of G. Jones and B. B. Kaplan, *THIS JOURNAL*, **50**, 1845 (1928).

(17) A. D. Awtry and R. E. Connick, *ibid.*, **73**, 1842 (1952).

erable uncertainty in  $\Delta H_f^\circ$  of  $\text{I}_3^-$  causes three times this uncertainty in  $\Delta H_f^\circ$  for  $\text{BrO}_3^-$  (see reaction (7)).

In the case of bromine some calorimetric measurements have been made for the heat of solution of  $\text{Br}_2(\text{l})$  and for  $\Delta H_f^\circ$ . Again, however, the data are old, rather limited, and not obtained at 25°. Calculations from solubility data<sup>17</sup> lead to ambiguous results, so we must say that at least as much uncertainty exists in the Bureau of Standards value for  $\Delta H_f^\circ$  of  $\text{Br}_3^-$  as does in the  $\text{I}_3^-$  value, with the corresponding uncertainty existing in  $\Delta H_f^\circ$  for  $\text{BrO}_3^-$  calculated from equation (8). (Presumably,  $\text{I}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$  heats of formation are accurately enough known so that they will not introduce significant error.)

From this discussion it should therefore be evident that our final calculations of  $\Delta H_f^\circ$  for  $\text{BrO}_3^-$  from both types of reductions may be uncertain by as much as several kcal./mole. This uncertainty arises at least as much from the uncertainty in the heats of formation of triiodide and tribromide as from our own experimental uncertainties.

## VII. Conclusion

We will take as our final values for the heat and free energy of formation of  $\text{BrO}_3^-$  our calculated averages:  $\Delta H_f^\circ = -18.3 \pm 2$  kcal./mole and  $\Delta F_f^\circ = 2.1 \pm 2$  kcal./mole. Additional evidence for these values is provided by Myers<sup>18</sup> who has recently determined  $\Delta F_f^\circ$  to be  $2.5 \pm 0.3$  kcal./mole from kinetic measurements.

(18) O. Myers, private communication.

BERKELEY, CALIF.

## NOTES

### Isolation of Palmitic, Stearic and Linoleic Acids from Guayule Resin<sup>1</sup>

BY THOMAS F. BANIGAN, JR., AND JAMES W. MEEKS

RECEIVED APRIL 4, 1953

In processing guayule, *Parthenium argentatum* Gray, for the isolation of high-quality natural rubber<sup>2</sup> an acetone extract, termed guayule resin, is obtained as a principal by-product. Earlier investigations<sup>3,4</sup> on the composition of this material revealed the presence of parthenyl cinnamate, the ester of a sesqui-terpene tertiary alcohol whose structure was subsequently determined by Haagen-Smit and Fong.<sup>5</sup> A hard "wax-like" compound was also reported<sup>4</sup> and its distribution in the grow-

ing shrub determined.<sup>6</sup> The essential oil which constitutes about 3-5% of the resin was shown<sup>7</sup> to contain  $\alpha$ -pinene, 60%; dipentene, 9%; cadinene, 8%; and smaller percentages of sesqui-, di-, tri- and higher terpenaceous hydrocarbons and alcohols.

Studies conducted in this Laboratory have now revealed the presence of linoleic, stearic and palmitic acids, and confirmed the presence of cinnamic acid<sup>3,4</sup> in the resin saponifiables.  $\alpha$ -Linoleic acid, isolated and purified by solvent extractions and low-temperature crystallizations, has been found to be a major resin component (*ca.* 37%). Palmitic (4%) and stearic acids (1.6%) were isolated as the 72.5:27.5 mole per cent. eutectic, a mixture often encountered<sup>8</sup> when these two acids are obtained from natural sources. Linolenic acid (0.5%) was isolated only as a bromine addition product. Oleic

(1) From one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) F. E. Clark, T. F. Banigan, Jr., J. W. Meeks and I. C. Feustel, *Ind. Eng. Chem.*, **45**, 572 (1953).

(3) P. Alexander, *Ber.*, **44**, 2320 (1911).

(4) E. D. Walter, *THIS JOURNAL*, **66**, 419 (1944).

(5) A. J. Haagen-Smit and C. T. O. Fong, *ibid.*, **70**, 2075 (1948).

(6) T. F. Banigan, Jr., J. W. Meeks and R. W. Planck, *Botanical Gazette*, **113**, 231 (1951).

(7) A. J. Haagen-Smit and R. Siu, *THIS JOURNAL*, **66**, 2068 (1944).

(8) J. C. Smith, *J. Chem. Soc.*, 625 (1936).