rate of hydrolysis of ethyl acetate in solutions of barium hydroxide partially neutralized by the oxime. This agrees with our value at $\mu \sim 0.075$ but is based on $K_w = 1 \times 10^{-14}$ which is correct only at $\mu = 0$.

Summary

The rate of decomposition of nitrosotriacetonamine, catalyzed by hydroxyl ion, has been measured as a function of ionic strength at 24.9°, up to $C_{OH^-} = 0.05$ and $\mu = 0.22$ and may be expressed in the equation

$$k = (1.209 - 0.479\,\mu)\,C_{OH^-}$$

Using this catalytic reaction to measure hydroxyl ion concentration in solutions of sodium hydroxide partially neutralized by acetoxime, methyl ethyl and diethyl ketoximes, the acid dissociation constants of these oximes have been determined as a function of ionic strength.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System Silver Bromate–Sodium Bromate–Water

BY JOHN E. RICCI AND JACK J. ALESHNICK*

Introduction.—The formation of a compound or of a solid solution of silver bromate and sodium bromate from aqueous solutions of the salts came to be suspected from certain difficulties encountered in attempts to determine bromate ion in the presence of sodium ion, using silver nitrate as precipitant. Estimated gravimetrically the precipitate was always too light. Volumetric determination of the excess of silver ion in the filtrate by the Volhard method revealed the same error, in that too much silver ion was found unprecipitated. These analytical errors appeared regularly and despite care in the original precipitation of the bromate ion with silver nitrate.

The equilibrium relations at room temperature in the ternary system consisting of silver bromate, sodium bromate and water were therefore investigated. The isotherm at 25° shows the formation of a 1:1 double salt capable of forming continuous solid solutions with silver bromate. The salts actually form two solid solutions: sodium bromate containing up to about 3% of silver bromate, and silver bromate containing up to 39.0%, a limit corresponding to the compound $AgBrO_3 \cdot NaBrO_3$.

The consequent contamination (which is of an equilibrium nature and therefore unavoidable) of silver bromate with sodium bromate whenever the silver salt is precipitated from solution containing sodium ion, and especially in the presence also of excess of bromate ion, not only explains the abovementioned analytical difficulties in the attempted determination of bromate by precipitation as silver bromate, but also accounts, presumably, for the difficulty experienced in the preparation of pure silver bromate.[1-4] This difficulty is obvious from the great variation in the values of the aqueous solubility of the salt reported in the literature. In fact, even the C. P. grade of silver bromate used in the present experiments was found to contain about 1.8% of sodium bromate.

Such behavior on the part of silver bromate appears important not only in connection with possible applications of silver bromate in analytical procedures, but also because of its frequent use in experimental tests of theoretical principles involving solutions of electrolytes.[1-7]

Experimental Procedure

The solubility measurements were made by methods already described for similar determinations. The ternary complexes were made up by weight, using distilled water, C. P. sodium bromate and C. P. silver bromate. The sodium bromate was found to be of satisfactory purity (100.0 ± 0.1%) by iodometric titration using standard thiosulfate. The silver bromate was analyzed in several ways: (1) after reduction with sodium nitrite in the presence of nitric acid and of a small excess of sodium bromide, the precipitate of silver bromide was weighed and was found to correspond to 98.4% silver bromate. (2) After reduction with sulfur dioxide in the presence of nitric and hydrochloric acids, thus precipitating all the silver as silver bromide and chloride, the filtrate was evaporated, finally with sulfuric acid, and weighed, after recrystallization, as sodium sulfate; the sodium was evident in this residue, from ordinary flame tests. The result showed about 1.8% sodium bromate. (3) After reduction with sodium nitrite in the presence of nitric acid and of a small excess of silver nitrate, the precipitate of silver bromide was weighed, and, on the assumption that the original sample consisted of silver and sodium bromates, a purity of 98.0% silver bromate was calculated. These analyses were all done in duplicate and with blank corrections for reagents and apparatus. A value of 98.2% silver bromate and 1.8% sodium bromate was therefore assumed in calculating the compositions of ternary complexes prepared from the C. P. silver bromate.

It must be pointed out that these quantitative analyses of the silver bromate, with consequent correction of the compositions of the synthetic ternary complexes, were performed after a preliminary study of the ternary isotherm had indicated first of all the extensive formation of solid solution between the two salts, and, second, from certain consistent deviations of the tie-lines from the stoichiometric composition of the 1:1 compound, the probability of the presence of a definite amount of sodium bromate in the supposedly C. P. silver bromate.

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* Present address: U. S. Army.

[1] Hill, THIS JOURNAL, **39**, 220 (1917).

[2] Reedy, *ibid.*, **43**, 1443 (1921).

[3] Dalton, Pomeroy and Weymouth, *ibid.*, **46**, 61 (1924).

[4] Vosburgh and McClure, *ibid.*, **65**, 1062 (1943).

[5] Noyes, *Z. physik. Chem.*, **6**, 246 (1890).

[6] Owen, THIS JOURNAL, **55**, 1922 (1933).

[7] Neuman, *ibid.*, **56**, 28 (1934).

TABLE I

SYSTEM $AgBrO_3$–$NaBrO_3$–H_2O

Temp., °C.	No.	Original complex		Liquid Solution		% $AgBrO_3$ in solid phase, by extrapolation	Solid phase
		Wt., % $NaBrO_3$	Wt., % $AgBrO_3$	Wt., % $NaBrO_3$	Density		
25	1	..	0.0	28.26 (±0.02)	1.264 (±0.002)		$NaBrO_3$
	2	30.0	.0027	28.26	1.264	0.11	S.S.I.[a]
	3	29.98	.0105	28.24	1.261	.43	S.S.I.
	4	30.0	.0244	28.21	1.262	.97	S.S.I.
	5	29.80	.0401	28.16	1.261	1.7	S.S.I.
	6	29.94	.0590	28.14	1.260	2.3	S.S.I.
	7	30.17	.0779	28.08	1.260	2.6	S.S.I.
	8	30.0	.0941	28.00	1.261	3.2	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	9	29.8	.490	27.96	1.259	15.3	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	10	29.7	.970	27.96	1.262	25.9	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	11–21						S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	22	31.18	14.71	27.94	1.258	59.1	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	23	30.99	14.71	28.00	1.260	59.8	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	24	30.76	14.71	27.99	1.261	60.8	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	Average (8–24)			27.97 (±0.02)	1.260 (±0.001)		S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	25	28.48	3.426	27.84	1.257	60.74	$AgBrO_3 \cdot NaBrO_3$
	26	28.27	2.747	27.78	1.257	61.23	$AgBrO_3 \cdot NaBrO_3$
	27	28.29	3.424	27.66	1.256	61.16	$AgBrO_3 \cdot NaBrO_3$
	28	27.99	3.00	27.41	1.252	60.83	$AgBrO_3 \cdot NaBrO_3$
	29	28.01	3.431	27.35	1.251	60.95	$AgBrO_3 \cdot NaBrO_3$
	30	27.72	3.430	27.05	1.248	61.03	$AgBrO_3 \cdot NaBrO_3$
	31	27.07	2.939	26.42	1.241	60.24	$AgBrO_3 \cdot NaBrO_3$
	32	26.02	2.98	25.36	1.232	61.11	$AgBrO_3 \cdot NaBrO_3$
	33	25.07	3.140	24.32	1.220	61.09	$AgBrO_3 \cdot NaBrO_3$
	34	23.62	3.45	22.71	1.203	61.16	$AgBrO_3 \cdot NaBrO_3$
		Average	(25–34)			60.95	(Theoretical: 60.98)
	35	22.20	3.441	21.28	1.185	62.13	S.S. II
	36	18.07	3.443	16.99	1.143	63.23	S.S. II
	37	14.09	3.439	13.04	1.108	66.60	S.S. II
	38	11.07	3.427	10.28	1.079	72.86	S.S. II
	39	9.14	4.41	8.39	1.062	78.3	S.S. II
	40	7.582	3.932	7.17 (0.01% $AgBrO_3$)	1.051	84.0	S.S. II
	41	3.968	3.854	3.92 (0.03% $AgBrO_3$)	1.025	94.8	S.S. II
	42	0.0	...	(0.204 ±0.004, % $AgBrO_3$)	0.9985 (±0.0003)		$AgBrO_3$
50	1	..	0.0	35.64	1.341		$NaBrO_3$
	2	36.60	14.71	35.25	1.333	59.3	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	3	36.36	14.71	35.21	1.335	60.1	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	4	36.18	14.71	35.25	1.335	60.9	S.S.I. + $AgBrO_3 \cdot NaBrO_3$
		Average (2–4)		35.24	1.334		S.S.I. + $AgBrO_3 \cdot NaBrO_3$
	5	35.98	14.71	35.05	1.334	61.09	$AgBrO_3 \cdot NaBrO_3$
	6	35.79	14.71	34.73	1.331	60.88	$AgBrO_3 \cdot NaBrO_3$
	7	35.59	14.71	34.57		61.19	$AgBrO_3 \cdot NaBrO_3$
	8	30.00	9.80	28.77	1.258	63.29	S.S. II
	9	25.18	10.81	23.32	1.196	65.42	S.S. II
	10	0.0	...	(0.430% $AgBrO_3$)	0.9934		$AgBrO_3$
5		..	0.0	21.41	1.192		$NaBrO_3$
		Average of 4 detns.		21.32	1.190	57–60.3	S.S.I + $AgBrO_3 \cdot NaBrO_3$
		0.0	...	(0.0905% $AgBrO_3$)	0.9998		$AgBrO_3$

[a] S.S.I.: $NaBrO_3$ containing up to 2.5–3.0% $AgBrO_3$.

The solubilities of "pure" silver bromate reported below were determined on samples of this C. P. salt which were repeatedly washed with considerable quantities of water. As may be seen from the ternary diagram, however, such a process of purification would be slow and incomplete. A purity of about 99.7% was finally thus attained, but it is evident that great accuracy cannot be claimed for these solubilities. The ternary diagram, however, and the reported relations of the two salts involved, are independent of the exact solubility of pure silver bromate, the ternary measurements possessing actually a very high degree of accuracy. They involve simply the weighing operations of preparing the original complexes, and the sampling and analysis of the filtered liquid solutions at equilibrium. Because of the high concentration of bromate ion in these solutions, the silver ion concentration was so small as to be not even detectable in all but the last one or two complexes in Table I (at 25°). In these the silver bromate content was determined gravimetrically as silver bromide after reduction with sodium nitrite. In all other cases, it was sufficient simply to evaporate the solution to dryness and to assume the residue to be sodium bromate.

The composition of the solid phase was calculated by algebraic extrapolation of the tie-lines joining the composition of the saturated liquid solution with that of the total original complex.[8] Attainment of equilibrium was proved in almost all cases by repeated analysis of the solution after further stirring. The complexes were stirred for periods of two to eight weeks. The densities were determined by using calibrated pipets for the withdrawal of samples to be weighed for analysis.

Results

The results are presented in Table I, which includes the complete 25° isotherm and some data at 50 and 5°, and in Fig. 1, the usual graphical representation of the 25° isotherm. The compositions in Table I are given in terms of weight per cent.

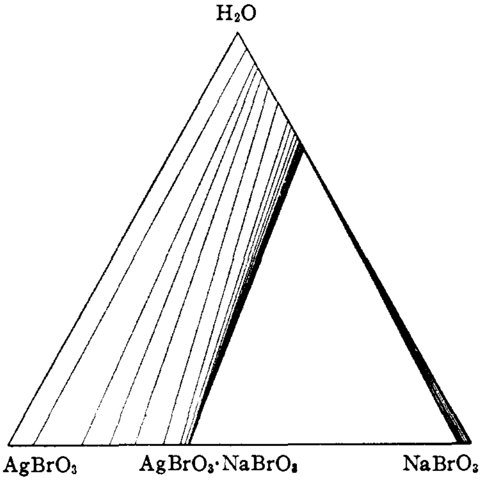

Fig. 1.—System $AgBrO_3$–$NaBrO_3$–H_2O at 25°.

The determinations at 25° show first of all a variable solid phase based on sodium bromate and containing up to 2.5–3.0% of silver bromate. This is seen in the first seven points, in which the liquid and solid compositions (the latter as determined by algebraic extrapolation) vary simultaneously and concomitantly. When this first solid solution (S.S.I.) reaches its limiting composition, a second solid phase evidently appears, and the liquid solution becomes isothermally invariant; the composition of this liquid solution, averaged from a great number of determinations, is 27.97 (±0.02) % sodium bromate, the percentage of silver bromate being analytically zero; its density is 1.260 (±0.001). The second solid is a saturated solid solution of the two salts containing, by extrapolation, 60.95 (±0.17) % silver bromate. This at any rate is the evidently constant composition of the solid in equilibrium with liquids ranging from 27.97 to about 22% sodium bromate, where, without the appearance of any break in the solubility curve, the solid composition begins to vary, gradually and continuously, increasing in silver bromate content until the composition of the pure salt is reached.

The second branch of the solubility curve therefore represents liquid solutions saturated with a second solid solution (S.S. II) starting at pure silver bromate, and whose limiting binary composition can be fixed very precisely because of the sharp convergence of the tie-lines at the binary limit. This sharp convergence indicates the existence of a definite compound, and the observed composition (by extrapolation of tie-lines) agrees very well with that theoretically required for the 1:1 compound, $AgBrO_3 \cdot NaBrO_3$, namely, 60.98% silver bromate.

Only a few determinations were made at 50°, so chosen as to verify the same general behavior. The isothermally invariant solution contains 35.24% sodium bromate as compared with 35.64%, the solubility of pure sodium bromate at this temperature. Since the relationship of these two points is the same as that of the corresponding points at 25°, it may be inferred that here too one of the solid phases is a solid solution of some small amount of silver bromate in sodium bromate. The second solid phase, as shown by the extrapolations, is again the compound, $AgBrO_3 \cdot NaBrO_3$, representing the limit of a solid solution presumably extending to pure silver bromate.

The nature of the limit of this second solid solution as a definite chemical compound, $AgBrO_3 \cdot NaBrO_3$, is of course corroborated by the constancy of the limiting composition at the two temperatures, 25 and 50°.

At 5° only the points of the isotherm have been determined; but the relation of the invariant point to the solubility of sodium bromate is still the same, indicating the probability of the same reaction and relationship between the salts at this as at the higher temperatures studied.

Discussion

The conclusion from this equilibrium study is that silver bromate precipitated in the presence of sodium ion and particularly in the presence also of excess of bromate ion, must be contaminated with sodium bromate. Mere recrystallization or digestion in water cannot be expected to purify it "completely" or analytically except through repeated and prolonged treatments. It may be suggested that this effect of sodium bromate is probably the reason for the disagreement in the published values for the solubility of this salt, and for the difficulties experienced by careful workers in attempting to obtain samples of constant and reproducible solubility. Thus, in a recent article on the silver–ammine ions, Vosburgh and McClure[4] state that their two different samples of the salt "gave appreciably different solubilities

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[8] Hill and Ricci, This Journal, 53, 4305 (1931).

in water," and they do not consider these solubilities worth reporting.

The solubility here reported, of 0.204% at 25°, is not claimed to be final and accurate, and is to be compared with the following literature values (recalculated into units of weight per cent.)

Longi (1883)[9]	0.166 at 25°
Noyes (1890)[5]	.192 at 24.5°
Böttger (1903)[10]	.159 at 25°
Whitby (1910)[11]	.171 at 27°
Hill (1917)[1]	.195 at 25°
Reedy (1921)[2]	.196 at 25°
Dalton, Pomeroy and Weymouth (1924)[3]	.189–0.191 at 25°
Owen (1933)[6]	.192 at 25°
Neuman (1934)[7]	.192 at 25°

The highest values reported are those of Hill and of Reedy. The latter apparently took the greatest pains in purifying the salt by recrystallization. The present investigation shows that the presence of even small amounts of sodium bromate reduces considerably the solubility of silver bromate.

Reedy found that the purity of his silver bromate tended to be low, 99.6 to 99.8%, and he attributed this deviation from purity to the presence of air occluded in the crystals during precipitation. He even recommended the salt as a standard in iodimetry. But in view of the formation of a solid solution with sodium bromate, such use of silver bromate should obviously be undertaken only with serious precautions. The only other analysis of the silver bromate used for solubility work is given by Hill, who reported, without comment, that his salt gave 44.97 and 45.00% of silver (determined as silver chloride) as compared to the theoretical 45.75%. His sample was made by precipitation from potassium bromate and silver nitrate; the same reaction was used for the preparation of the material used in References 9, 10, 11, in which no analysis is given.

Summary

1. The system silver bromate–sodium bromate–water has been studied in detail at 25°, and, partially, at 50° and 5°.

2. The salts form a definite compound, $AgBrO_3{\cdot}NaBrO_3$, which forms a continuous solid solution with silver bromate. Sodium bromate also forms a solid solution containing up to 2.5–3.0% of silver bromate.

3. Some implications of these results on analytical procedures involving silver bromate are discussed. Precipitation of silver bromate from solutions containing sodium ion must result in an impure salt which can be purified by recrystallization only with difficulty.

4. The results may explain the great variation in the values of the solubility of silver bromate reported in the literature, and suggest that the samples of the salt used in various theoretical studies may have been contaminated with sodium bromate.

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[9] Longi, *Gazz. chim. ital.*, **13**, 87 (1883).

[10] Böttger, *ibid.*, **46**, 603 (1903).

[11] Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY AND POLYTECHNIC INSTITUTE OF BROOKLYN]

Mechanism of Peroxide Initiated Styrene Polymerization

BY HARRY F. PFANN[1] D. J. SALLEY[1a] AND H. MARK

Recent publications of Price and his co-workers[2] and of Kern and Kammerer[3] have succeeded in clarifying the mechanism of the peroxide initiated polymerization of styrene. Their results confirm and extend proposals advanced by Norrish,[4] Schulz[5] and others that the active centers for chain propagation are free radicals resulting from the decomposition of the peroxide as such or an addition compound between peroxide and styrene. As there appears to be continued interest[6,7,8] in this problem, the writers wish to present the following data obtained from experiments[9] in progress from 1940 to 1942, which were not published at that time due to the outbreak of the war.

In this work, halogen-containing polymer was prepared from styrene and *m*-bromobenzoyl peroxide. Non-combined initiator was removed by repeated extraction, and the presence of bromine in the polymer was demonstrated by combustion of the sample followed by determination of the halogen, as well as by measurement of the radioactivity of the polymer samples after neutron bombardment.

Experimental Procedure

Polymer samples were prepared by heating commercially pure styrene (Dow Chemical Company, 1941, n^{25}_{D} 1.5432, d^{24} 0.9025) with *m*-bromobenzoyl peroxide (m. p. 127–128°, 99% of theoretical active oxygen) in sealed glass tubes 38 mm. × 180 mm. immersed in an oil-bath at

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[1] (b) Present address: Koppers United Company, Butadiene Division, Kobuta (Monaca), Pennsylvania.

[2] Charles C. Price, *et al.*, THIS JOURNAL, **63**, 2798 (1941); **64**, 1103, 2508 (1942): **65**, 517 (1943).

[3] W. Kern and H. Kammerer, *J. prakt. Chem.*, **161**, 81–112 (1942); *C. A.*, **37**, 5381 (1943).

[4] Norrish and Brockman, *Proc. Roy. Soc.*, **A171**, 147–71 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1082 (1939).

[5] G. V. Schulz, *Naturwissenschaften*, **27**, 387, 456, 659 (1939).

[6] (a) Abere, Goldfinger, Mark and Naidus, *J. Chem. Phys.*, **11**, 379 (1943); (b) *Ann. N. Y. Acad. Sci.*, **44**, 267 (1943).

[7] Compare also Mayo, THIS JOURNAL, **65**, 2324 (1943).

[8] Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

[9] Taken in part from the Thesis for the Degree of Master of Science by Harry F. Pfann, Polytechnic Institute of Brooklyn, June, 1942.