

CCCCVI.—*The Action of Bromine on Strontium Oxide and its Hydrates.*

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THE action of halogens on slaked lime was studied by Wilks (J., 1912, **101**, 366), and we now describe the action of bromine both as vapour and as a solution in carbon tetrachloride on strontium oxide and its hydrates.

*The Action of Bromine on Anhydrous Strontium Oxide.*—Merck's pure strontium oxide was used. Pure carbon tetrachloride (Kahlbaum) was distilled over calcium chloride; and bromine was purified by a modification of Brauner's method (*J. Amer. Chem. Soc.*, 1920, **42**, 921). After exposure to bromine vapour for some days, strontium oxide adsorbed about 1% of its weight of bromine, giving a pale dirty-brown product containing a few scarlet specks. The same proportion of bromine is adsorbed under identical conditions by dry, powdered silica. Strontium oxide shaken with a 2% solution of bromine in carbon tetrachloride for 48 hours took up 1.5% of its weight of bromine, as determined by loss of bromine from the solution. In both cases the solid lost the adsorbed bromine on exposure to the air, so chemical action had not taken place.

*The Action of Bromine on Strontium Hydroxide Monohydrate.*—Kahlbaum's strontium hydroxide octahydrate was recrystallised in a carbon dioxide-free atmosphere (Found: SrO, 39.15. Calc.: SrO, 39.06%). The powdered octahydrate was extracted with alcohol (b. p. 78.2°/742 mm.) in a Soxhlet apparatus under 150—170 mm. pressure for 10 hours: this is a new method for the preparation of strontium hydroxide monohydrate (Found: SrO, 73.87. Calc.: SrO, 74.21%). When the monohydrate is exposed to excess of bromine vapour, it yields a dark brown substance which resembles brom-bleaching powder (Wilks, *loc. cit.*), and from which carbon tetrachloride extracts some bromine. When this substance is kept

in a closed vessel, the brown colour gradually disappears, giving a pale yellow substance which yields no bromine to carbon tetrachloride. Quantitative action was not observed, but in a typical sample exposed for 12 days to the action of bromine vapour and then set aside in a large empty vessel until the colour was pale yellow 77% of the hydroxide had been attacked, giving, on solution in water, bromide (2.2 mols.) and hypobromite (1 mol.); bromate was absent. When exposed to moist air, the substance becomes pasty and finally contains bromide and bromate, but no hypobromite.

To investigate the nature of the reaction between carbon tetrachloride solutions of bromine and strontium hydroxide monohydrate, quantities of 1 g. of the hydroxide were shaken with bromine solutions in a thermostat at 20° for 24 hours. The liquid was then filtered from the solid, special precautions being taken to avoid loss of bromine, and the amount of bromine remaining in the solution was determined volumetrically. In Table I,  $c$  and  $(c-x)$  show respectively the initial and final concentrations of bromine (mg. per 100 c.c. of solution),  $x$  mg. therefore reacting with 1 g. of the hydroxide.

TABLE I.

*Action of Bromine in Carbon Tetrachloride Solution on Sr(OH)<sub>2</sub>.H<sub>2</sub>O.*

$c$ .	$(c-x)$ .	$x$ .	$\log(c-x)$ .	$\log x$ .	$\log(x-450)$ .	$\frac{(x-450)}{(c-x)^2}$ .
450	Traces	450	—	—	—	—
473	6	467	0.778	2.669	1.230	—
574	15	559	1.176	2.747	2.037	44
695	110	585	2.041	2.767	2.303	42
951	239	712	2.378	2.853	2.415	42
1219	427	792	2.630	2.891	2.534	45
1515	716	799	2.855	2.903	2.543	39
1838	1025	812	3.011	2.910	2.559	36
2949	2137	812	3.330	2.910	2.559	—

When  $(c-x)$  is plotted against  $x$ , a curve suggesting adsorption is obtained which cuts the axis at  $x=450$  mg., and if  $\log(c-x)$  is plotted against  $\log(x-450)$ , the points lie practically on a straight line. It therefore appears that a very rapid chemical action takes place in which 0.45 g. of bromine reacts with 1 g. of the hydrate in the molecular proportion  $\text{Br}_2 : \text{Sr(OH)}_2 \cdot \text{H}_2\text{O} = 1 : 2.5$ . After that, the resulting mixture adsorbs bromine until, at high concentrations, 1 mol. of the hydroxide has reacted with a maximum of 0.7 mol. of bromine: it is not possible to wash this product completely free from bromine. The substance obtained by desiccation to constant weight was analysed for bromine, bromide, hypobromite, and bromate by Dehn's method (*J. Amer. Chem.*

*Soc.*, 1909, **31**, 525), and strontium was determined as sulphate (Found : Sr, 32.36; Br, extracted by  $\text{CCl}_4$ , traces; Br, as bromide, 36.10; as hypobromite, 4.54; as bromate, nil). The bromide and hypobromite correspond to 61.3% of the strontium present. Thus, when treated either with bromine vapour or with bromine in carbon tetrachloride, strontium hydroxide monohydrate gives appreciable amounts of hypobromite. Reference to the action of bromine on the octahydrate (below) shows that, when greater quantities of water are present, the hypobromite is decomposed almost as quickly as it is formed.

*The Action of Bromine on Strontium Hydroxide Octahydrate.*—When strontium hydroxide octahydrate was exposed to bromine vapour, a yellow, gelatinous mass containing droplets of water was formed. After standing in a vacuum desiccator for 48 hours, it contained 37.51% of bromine as strontium bromide and 8.89% as bromate; hypobromite was absent. These results give a calculated value for strontium as bromide and bromate of 25.40%, whereas the proportion of strontium actually found was 25.16%. Hence the reaction is quantitative.

When first exposed to a solution of bromine in carbon tetrachloride, strontium hydroxide octahydrate turns brown. In the dark or in daylight the colour gradually fades, and a flocculent mass containing droplets of water is formed. After several weeks, colourless, needle-shaped crystals are found on the sides of the vessel and extend far above the level of the solid phase. These crystals (roughly dried, m. p.  $92^\circ$ ) are strontium bromide contaminated with a little bromate and water; their formation is accelerated by insolation.

In order to determine the time taken for the completion of the reaction, powdered strontium hydroxide octahydrate (1 g.) was shaken in a number of bottles at  $20^\circ$  with 100 c.c. of a solution of 1.594 g. (19.93 mg.-equivs.) of bromine in carbon tetrachloride for various intervals of time, and the loss of bromine from the liquid phase determined volumetrically. The results (Table II) show that, at first, a rapid chemical reaction with 200 mg. (2.50 mg.-equivs.) of bromine takes place. This is followed by a slower reaction, as shown by the increase in the value of  $x$  (mg.-equivs. of bromine consumed) with time ( $t$ , in hours), and if allowance be made for the 2.50 mg.-equivs. of bromine used in the primary reaction, a unimolecular velocity coefficient ( $k$ ) is obtained for the first hour of the second reaction; thus,  $a$  being the original concentration of bromine (19.93 mg.-equivs. per 100 c.c.),  $a_1 = a - 2.50 = 17.43$ , and putting  $x_1 = x - 2.50$ , we have  $k = 1/t \cdot \log a_1/(a_1 - x_1)$ . By application of the method of calculation given by Dunningcliff and

Butler (J., 1921, **119**, 1384), the preliminary reaction is found to be equivalent to the change which would have taken place in 1 hour if the unimolecular reaction had proceeded smoothly from the start, for, by adding 1 hour to the observed time and using the actual values for bromine concentration and amount of bromine taken up, we obtain  $k_1 = 1/(t + 1) \cdot \log a/(a - x)$ , the values of which are also shown in Table II. (This time-correction varies with the temperature of reaction and the concentration of the solution.) The final result of the reaction is a quantitative yield of strontium bromide and bromate (*vide infra*).

TABLE II.

*The Action of Bromine in Carbon Tetrachloride on Sr(OH)<sub>2</sub>.8H<sub>2</sub>O.*

<i>t</i> .....	0.000	0.083	0.25	0.50	0.75	1.00	2.00	5.00	24.00
<i>x</i> .....	2.50	2.71	3.16	3.73	4.29	4.75	6.00	7.20	7.48
<i>x</i> <sub>1</sub> .....	0.00	0.21	0.66	1.23	1.79	2.25	3.50	4.70	4.98
<i>k</i> × 10 <sup>4</sup> .....	—	636	632	636	628	600	487	273	—
<i>k</i> <sub>1</sub> × 10 <sup>4</sup> .....	582	578	600	600	602	591	518	325	—

*Effect of the Concentration of the Bromine Solution.*—Strontium hydroxide octahydrate (1 g.) was placed in 100 c.c. of solutions of bromine in carbon tetrachloride of various strengths for 24 hours at 20°. In dilute solutions the whole of the bromine was taken up, but in concentrated solutions the solid gelatinised and droplets of water were observed on the surface of the liquid. The original and final (equilibrium) concentrations of bromine and the differences were :

Conc. of bromine, g. per 100 c.c.			Conc. of bromine, g. per 100 c.c.		
Original.	Final.	Diff.	Original.	Final.	Diff.
0.391	0.000	0.391	0.895	0.313	0.582
0.488	0.013	0.475	1.567	0.959	0.608
0.527	0.020	0.507	1.771	1.199	0.572
0.623	0.085	0.538	2.550	1.946	0.604
0.786	0.224	0.562	2.925	2.302	0.623

} Mean = 0.598

Thus, 1 g. of Sr(OH)<sub>2</sub>.8H<sub>2</sub>O (0.390 g. of SrO) reacts with 0.598 g. of bromine, or SrO : Br<sub>2</sub> = 1 : 1.007, the proportion required for equimolecular quantities of strontium bromide and hypobromite.

The hypobromite formed in the earlier stages of the reaction was estimated by treating the solid phase (washed free from bromine by carbon tetrachloride) with ammonia in a Lunge nitrometer, and measuring the nitrogen evolved. The relationship between the hypobromite content (in terms of nitrogen) and the time of exposure of 1 g. of the octahydrate to a 1% solution of bromine in carbon tetrachloride at 20° was :

Time, hours .....	0.25	0.50	1.00	2.00	4.00	6.00	24.0
Nitrogen (c.c. at N.T.P.) ...	7.75	8.6	9.35	12.1	8.25	3.75	2.4

From this it is concluded that the hypobromite is formed and decomposed almost immediately, but that, up to 2 hours, the rate of formation exceeds the rate of decomposition. At the end of the reaction, hypobromite is negligible or absent.

TABLE III.

Conc. of Br <sub>2</sub> (g. per 100 c.c.).	SrBr <sub>2</sub> ·6H <sub>2</sub> O, %	Sr(BrO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O, %	Temperature, 15—17°.		Strontium, %.		Mol. ratio, brom- ide: bromate.
			Water, %.		Found.	° Calc.	
			Found.	° Calc.			
1.5	76.68	20.14	22.92	24.29	24.43	23.73	3.86
2.0	77.56	21.01	24.30	24.60	24.29	24.20	3.76
2.0	80.72	20.03	23.44	25.51	24.49	24.74	4.10
Temperature, 32—33°.							
1.5	76.79	20.74	—	24.35	24.92	23.94	3.76
3.0	79.54	20.48	—	25.18	24.80	24.56	3.95
3.5	80.56	19.42	—	25.43	—	24.55	4.21

\* From columns 2 and 3.

The gelatinous residue from each of several experiments was left in a desiccator until its weight was constant and then analysed. The vapour pressures of the crystalline bromide and bromate are low, and the water content of the final product, as found by heating with lead chromate in a current of dry air, is within reasonable agreement with the value (Table III, col. 5) found by calculation from the water of crystallisation of the salts (Table III, cols. 2 and 3). If, as these results indicate, the preliminary formation of equimolecular quantities of hypobromite and bromide is followed by the rapid decomposition of the hypobromite into bromide and bromate, one would expect the final proportion of bromide to bromate to be 5 : 1. Our ratio is uniformly lower and suggests that, in the presence of sufficient water, the excess of bromine oxidises some of the hypobromite to bromate direct (compare Dietzel and Schlemmer, *Z. anorg. Chem.*, 1925, **145**, 381). The following results, obtained by treating equal quantities of strontium hydroxide octahydrate with a 3% solution of bromine in the dark and in sunlight for 8 hours, show that the formation of bromate is favoured by insolation, and the values in the last two columns show that the reaction is quantitative :

	Br as bromide, %	Br as bromate, %	Strontium, %.	
			Found.	Calc.
In sunlight .....	34.88	9.66	24.69	24.39
In the dark .....	37.78	7.04	24.82	24.54

*The Action of Iodine on Strontium Oxide and its Hydrates.*—Rama Krishna Bahl has carried out a similar series of experiments with iodine. There was no action with strontium oxide. With the monohydrated hydroxide, the interaction was small and the

results were inconclusive. The analyses by Schulek's method (*Z. anal. Chem.*, 1925, **67**, 142) of the samples obtained by exposing the octahydrate to the action of 5% iodine in carbon tetrachloride for 5 days at 20° are given in Table IV. The reaction proceeds slowly and is not quantitative. The samples marked *a* were

TABLE IV.

*The Action of Iodine in Carbon Tetrachloride Solution on Sr(OH)<sub>2</sub>·8H<sub>2</sub>O.*

SrI <sub>2</sub> , %.	Sr(IO) <sub>2</sub> , %.	Sr(IO <sub>3</sub> ) <sub>2</sub> , %.	SrO, %.	Mol. ratio, iodide : iodate.
<i>a</i> 54·41	3·12	14·23	6·48	5·0
<i>a</i> 55·56	2·58	10·45	6·09	6·9
48·14	—	13·21	18·11	4·77
54·96	0·41	15·56	6·87	4·63
51·06	—	12·71	17·32	5·26
52·27	—	16·15	9·98	4·23

analysed immediately on dissolving in water, and the hypoiodite is probably due to the action of adsorbed iodine on free strontium hydroxide in solution. The other samples were analysed after being left in a desiccator until friable. The product was very hygroscopic.

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