of the pores from the experimental data given above is not regarded as justifiable, but does indicate that the internal surface of these oxides is very high. (2) The adsorption curve of the sample prepared in the presence of caustic soda does not differ materially from the other curves, and the effect of alkali in depressing the catalytic activity of these oxides cannot be due to a change in the physical structure of the oxide. Other work in this Laboratory[6] has shown that when finely divided manganese dioxide is prepared in the absence of alkali it is extremely active catalytically. The effect of the alkali adsorption must, therefore, be that of a so-called "catalytic poison." (3) There is no evidence from any of these curves for the existence of definite hydrates.

Summary

The author has investigated the adsorption of water vapor and carbon dioxide on samples of finely divided manganese dioxide and mixtures of this oxide with other metallic oxides. The results are given in the form of curves and the shape of these curves shows that in neither case is there evidence of the formation of definite chemical compounds, but brings out clearly the very fine porosity of these substances.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

CYANOGEN IODIDE AS AN IMPURITY IN IODINE. ITS DETECTION AND ELIMINATION

BY SAMUEL MORRIS, E. B. CALLAGHAN, AND LUCILE DUNLAP

RECEIVED APRIL 14, 1930 PUBLISHED JUNE 6, 1930

Cyanogen iodide is commonly considered one of the chief impurities in commercial iodine. According to Dammer[1] iodine has been known to contain as high as 28.75% of this impurity. Baxter,[2] in his work on the atomic weight of iodine, took great care to eliminate cyanogen iodide. In the method which he used, iodine was suspended in water and treated with hydrogen sulfide, which formed hydriodic acid and, in case cyanogen iodide was present, hydrocyanic acid also. The separation of these two acids, as employed by Baxter, involved long-continued boiling and was based upon the separation of hydrochloric and hydrocyanic acids by the method of Richards and Singer.[3]

In the present paper, study was made first of the separation of known mixtures of hydriodic and hydrocyanic acids. This suggested a procedure for the detection of small quantities of -CN in iodine, which was worked out

---

[6] Whitesell, THIS JOURNAL, **45**, 2841 (1923).

[1] Dammer, "Handbuch der Anorg. Chem.," Vol. I, p. 542.

[2] Baxter, THIS JOURNAL, **26**, 1579 (1904); **27**, 876 (1905).

[3] Singer, *Am. Chem. J.*, **27**, 205 (1902).

upon samples of iodine with a known content of –CN, and then used for the detection of this impurity in samples of iodine on the market.

Materials

Iodine 1.—Mallinckrodt's C. P. iodine.

Iodine 2.—C. P. iodine which was further purified by reduction to hydriodic acid and subjection to long-continued boiling to remove any possible hydrocyanic acid.

Iodine 3.—Crude Chilean iodine obtained from Mallinckrodt Chemical Works.

Iodine 4.—Seaweed iodine obtained in 1920 from the U. S. Kelp Products Company, Summerland, California.

Iodine 5.—Baker's C. P. iodine.

Cyanogen Iodide.—The general method of preparation by Linnemann[4] was followed and a very pure product was obtained.

Experimental

By reducing mixtures of known weights of iodine and cyanogen iodide with hydrogen sulfide, mixtures of hydriodic and hydrocyanic acids of known concentrations were obtained. These mixtures were boiled in a balloon flask connected with an ordinary water-cooled condenser. The volume of the undistilled mixture was kept practically constant by adding water from time to time. Successive portions (10 to 12 cc.) of the distillate were collected and these tested for –CN by the ordinary qualitative test involving the formation of Prussian blue.

Preliminary experiments, the results of which are not recorded in this paper, showed that upon distilling dilute mixtures of hydriodic and hydrocyanic acids, the hydrocyanic acid was concentrated in the first portions of the distillate. After about two hours of boiling, the concentration of the hydrocyanic acid in the distillate was so low that 10-cc. portions failed to show any test for the acid.

In all experiments in Table I the above procedure was carried out, except that in Expts. 6 to 9 no ICN was added. In Expts. 1 to 5, Table I, the percentage of ICN added in succeeding experiments was steadily decreased.

TABLE I

EXPERIMENTAL DATA

Expt.	HI and HCN soln., cc.	Iodine sample	Iodine, g.	ICN added, g.	ICN, %	–CN, %	12-cc. portions of distillate			
							Portion	–CN	Portion	–CN
1	500	1	8.994	0.029	0.323	0.055	1–4	Present	5–7	Absent
2	700	1	36.012	.031	.085	.014	1–5	Present	6–7	Absent
3	675	1	67.26	.0107	.015	.003	1–3	Present	4–7	Absent
4	700	1	133.93	.0109	.008	.0014	1–3	Present	4–7	Absent
5	1800	2	470.96	.0164	.00348	.0006	1–2	Present	3–7	Absent
6	700	1	57.31	...	....	..	1–6	Absent		
7	1700	1	455.0	...	....	..	1–7	Absent		
8	1700	3	412.0	...	....	..	1–23	Absent		
9	..	4	65.93	...	....	..	1–8	Absent		

---

[4] Linnemann. *Ann.*, **120**, 36 (1861).

The test for -CN in Expt. 5 was so slight, even in Portion I of the distillate, that the limit of detectability by this procedure, was considered substantially reached.

Since upon distilling mixtures of hydriodic and hydrocyanic acids the latter acid is concentrated in the first portion of the distillate, it seemed likely that by repeated redistillation the hydrocyanic acid could be concentrated in a small volume. To test this out, the first distillate was collected over a period of about nine hours and was large in volume. This in turn was distilled, but for a shorter time, resulting in a smaller distillate. After ten similar operations about 15 cc. remained, which was tested for -CN. This procedure was employed in all experiments in Table II, instead of the procedure involving a single distillation as used in Table I, and resulted in the detection of a considerably smaller percentage of -CN. The least amount detected by single distillation was 0.0006% in Expt. 5, while by repeated distillation, in Expt. 14, 0.00015% was detected.

Table II

Results of Experiments

Expt.	HI and HCN soln., cc.	Iodine, g.	Iodine sample	ICN added, g.	ICN, %	-CN, %	Times redistilled	-CN in final distillate
10	1500	226.0	5	None	....	....	10	None
11	1500	450.0	5	None	....	....	10	None
12	1500	450.0	2	0.0081	0.0018	0.000305	10	Present
13	1500	450.0	2	.0016	.00035	.00006	10	None
14	3000	902.0	2	.0081	.00089	.00015	10	Present

In Expts. 6 to 11 samples of iodine from various sources on the market today were examined for -CN, but none was found. A larger sample of iodine of seaweed origin was desired for Expt. 9 but could not be obtained.

Summary

1. Hydriodic and hydrocyanic acids, in dilute solution, can be separated by boiling.
2. A procedure is given by which a small percentage of -CN in iodine (approximately 0.00015%) may be detected by the Prussian blue test.
3. No cyanogen iodide could be detected in samples of iodine on the market today.

Morgantown, West Virginia