recombination would be at least 10^5 times more rapid. In the light of these facts it seems extremely improbable that the wall as a whole adsorbs atomic hydrogen. There remains the possibility that isolated points on the wall are absorbent and hence catalytic. Such a possibility is unlikely since if this were the case duplicate results could not be obtained in different apparatus.

In conclusion the author wishes to express his indebtedness to Dr. H. C. Urey and to Professor K. F. Herzfeld for their advice during the course of this work.

Summary

1. A calorimetric method for the estimation of the amount of atomic hydrogen obtained from a Wood tube is described, together with the application of this method to the measurement of the rate of recombination of the hydrogen atoms.

2. This rate has been measured through the pressure range 0.5–0.9 mm. of mercury.

3. It was found that, under the conditions of the experiment, one-fifth to one-sixth of the atomic hydrogen present reacted with solid sulfur and that nitric oxide catalyzes the recombination of the atomic hydrogen.

4. The data obtained for the rate of recombination are discussed and it is concluded that they are in accordance with the predicted three-body mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE REACTIVITY OF IODINE CYANIDE IN DIFFERENT ORGANIC SOLVENTS

BY ERWIN CHARGAFF[1]

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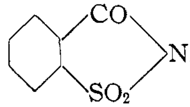
F. Feigl and the author have stated[2] that the reactivity of iodine toward the silver salt of saccharin depends upon the solvent used. In the so-called active solvents, which give brown solutions of iodine (*viz.*, ethyl ether, ethyl alcohol, etc.), almost only AgI is formed. In the inactive solvents (*viz.*, carbon disulfide, carbon tetrachloride, etc.), in which iodine dissolves with a violet color, there apparently is formed an addition compound



NAg...I_2, which, being unstable, easily decomposes into

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[1] Milton Campbell Research Fellow in Chemistry, 1928–1929.

[2] F. Feigl and E. Chargaff, *Monatsh.*, **49,** 417 (1928). (In *C. A.*, **22,** 3816 (1928), and **22,** 4083 (1928), both times the second author's name is incorrectly reported.)

silver saccharate and iodine. This remarkable difference in reactivity is attributed by the authors to the fact that in the brown solutions the iodine is present in a molecular compound with the solvent, whereas in the violet solutions we are dealing with uncombined molecules of iodine. The absorption spectra of these violet solutions are almost identical with that of iodine vapor. Therefore it was of some interest to compare the reactivity of an interhalogen compound with that of iodine in the same solvents. For this purpose the reaction of silver saccharate in solutions of iodine cyanide with different solvents has been investigated under identical conditions.

Experimental Part

The silver saccharate used was prepared by adding a boiling aqueous solution of 8 g. of silver nitrate to a boiling solution of 10 g. of sodium saccharate. The precipitate was washed with water, acetone and ether. By analysis it was shown to be pure silver saccharate. The best method for preparing iodine cyanide proved to be that recommended by V. Grignard and P. Crouzier,[3] which consists in passing a stream of chlorine through a solution of iodine in aqueous sodium cyanide, and subsequently removing the iodine cyanide by extraction with ether. In order to obtain a good yield of the cyanide it was found to be desirable to remove the ether by distillation in a vacuum at room temperature and not on a steam-bath, as iodine cyanide is very volatile even below 40°. Out of the highly concentrated ether solution the iodine cyanide is then precipitated by adding carbon tetrachloride. The product thus obtained is almost pure (m. p. 145.5° instead of 146.5°). For ordinary purposes the very unpleasant sublimation thus may be avoided. However, for the experiments given here the original product was slowly sublimed in small portions at 40°, whereupon the melting point rose to 146° in the closed capillary tube. From 31.5 g. of iodine 35.2 g. of iodine cyanide was obtained (92.6% of the iodine used). The solvents were all freshly distilled and dried. The carbon disulfide was shaken with mercury and calcium chloride and then distilled.[4]

In all cases the reactions were carried out by refluxing 0.6 g. of silver saccharate with solutions of 0.8 g. of iodine cyanide in 80 cc. of the respective solvents for two hours. Longer heating does not change the results. When still hot the solution then was decanted from the silver salt and the latter heated with fresh solvent several times until a sample of the solvent did not liberate iodine from a potassium iodide solution. To determine the silver in the reaction product the previous method of analysis could not be employed. A method was necessary which allowed the determination of silver iodide and at the same time of the amount of silver cyanide which may have been formed. Therefore, each time a weighed sample of the product was heated with dilute nitric acid and the liquid separated from the silver iodide and silver cyanide with a filter crucible. In the filtrate the amount of silver, which came from unchanged silver saccharate, was determined by titration with 0.1 *N* ammonium thiocyanate solution after the method of Volhard. The residue in the crucible was washed with warm aqueous ammonia after weighing and the loss of weight indicated the amount of silver cyanide dissolved by the ammonia. However, as the amounts of silver iodide and silver cyanide insoluble in nitric acid were very slight, great accuracy

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[3] Grignard and Crouzier, *Bull. soc. chim.*, [4] **29,** 214 (1921).

[4] Th. Sidot, *Compt. rend.*, **69,** 1303 (1869); H. Arctowski, *Z. anorg. Chem.*, **6,** 255 (1894); M. v. Unruh, *ibid.*, **32,** 407 (1902).

could not be expected for the determination of the silver cyanide. Some of the results obtained are given in Table I.

Table I

Results of Experiments

Solvent	Digest., hours	Silver salt, g.	Insol. res., g.	Sol. in NH_4OH, g.	NH_4SCN $N/10$, cc.	Silver saccharate recovered, g.	%
Abs. ether	2	0.2046	0.0007	....	7.02	0.2035	99.47
Ether	2	.3757	.0015	0.0004	12.89	.3737	99.46
Ether	5	.3215	.0016	.0003	11.02	.3195	99.37
Abs. alc.	4	.2927	.0020	.0008	10.00	.2900	99.06
Abs. alc.	2	.3434	.0024	....	11.74	.3403	99.11
Benzene	4	.2772	.0009	....	9.52	.2760	99.56
Benzene	2	.3988	.0008	....	13.72	.3977	99.73
Carbon tet.	2	.2189	.0012	....	7.50	.2174	99.32
Chloroform	2	.3423	.0015	....	11.74	.3403	99.42
Carbon disulfide	4	.3158	.0022	.0009	10.81	.3134	99.24
Carbon disulfide	2	.3968	.0021	....	13.59	.3940	99.29

Discussion of the Results

The experiments described above gave the result that iodine cyanide does not act on silver saccharate at all, whereas iodine does, and there cannot be found any influence due to the nature of the solvent used. In Table II are recorded the respective amounts of silver iodide expressed as percentage of the reaction products in the cases of both iodine and iodine cyanide.

Table II

Silver Iodide Expressed as Percentages

	Abs. ether	Ether	Abs. alc.	Benzene	Chloroform	Carbon tetrachloride	Carbon disulfide	Pet. ether
Reaction with I_2	90.15	95.76	91.30	88.20	86.94	24.57	0	0
Reaction with ICN	0.53	0.59	0.92	0.36	0.58	0.68	0.74	..

In the reaction with iodine there appears to be a decisive difference according to the use of an active or inactive solvent (with the exception only of chloroform and benzene),[5] while with iodine cyanide no influence of the solvent can be stated at all, the amount of silver iodide formed being very small in all cases. The statement of F. Ephraim[6] that the reactions of the interhalogen compounds are merely weakened reactions of the free halogens does not prove to be correct at least in this case. In order to explain these facts two assumptions could be made. Either it could be assumed that, contrary to the case of iodine, iodine cyanide does not give addition compounds with the active solvents and that to these addition compounds is due the formation of silver iodide in brown solutions of iodine, or (and this may be the more plausible explanation) that iodine cyanide—and perhaps other interhalogen compounds, too—

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[5] F. Feigl and E. Chargaff, ref. 2, pp. 418 f.

[6] F. Ephraim, "Anorganische Chemie," 2d and 3d ed., p. 300.

does not function as a "mixed halogen," but as a salt of hydrocyanic acid with the weak base iodine hydroxide.[7] The salt-like behavior of the iodine-halogen compounds is emphasized by several investigators.[8] In conclusion it may be said that according to the results which have been obtained the hypothesis that the structure of the iodine cyanide molecule is different from that of the iodine molecule is confirmed, and that it is to the different chemical nature of iodine cyanide that we may attribute its divergent reactivity.

Summary

The reactivity of iodine cyanide toward silver saccharate in various solvents has been investigated. It is shown that contrary to the behavior of iodine the reactivity of iodine cyanide is independent of the nature of the solvent. From this fact the conclusion may be drawn that iodine cyanide represents a heteropolar compound and does not function as a "mixed halogen." The yield of iodine cyanide has been increased by modifying the purification methods.

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[Contribution from the Chemical Laboratory of the University of Utah]

THE DENSITIES OF COEXISTING LIQUID AND GASEOUS NITROUS OXIDE

By Elton L. Quinn and Grant Wernimont

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During an investigation of the internal pressure of liquid nitrous oxide by the measurement of its surface tension, the authors found that no data existed on the densities of the liquid and its saturated vapor at temperatures below zero. As these data were necessary for calculating the surface tension, it became necessary to interrupt the investigation and to attempt a set of measurements for supplying these values. This paper describes the method of making these determinations and the results obtained over a temperature range from 30 to $-50°$.

The densities of liquid nitrous oxide and its saturated vapor were determined between the temperatures of 30 and 0° by Villard[1] in the year 1894. While the reliability of these determinations has never been questioned, the temperature range covered is not great enough for the work at hand. The advisability of extrapolating these values to the lower temperatures was carefully considered but it seemed best under the circumstances to make direct measurements.

[7] *Cf.* Abegg, "Handbuch der anorganischen Chemie," **1913,** Vol. IV, 2, pp. 455 ff.

[8] P. Walden, *Z. physik. Chem.*, **43,** 385 (1903); R. Abegg, *Z. anorg. Chem.*, **39,** 330 (1904).

[1] Villard, *Compt. rend.*, **118,** 1096 (1894).