NOTES

The Effect of Aluminum Chloride and Antimony Trichloride on the Solubility of Cesium Antimony Chloride in Hydrochloric Acid Solutions

By Paul Bender and Robert E. Bunde

The precipitation of cesium antimony chloride is often carried out in the presence of aluminum chloride, and an excess of antimony trichloride is employed in any case. The effects of these reagents on the solubility of the double salt in hydrochloric acid solutions are reported in Tables I and II. The accuracy of the data of Table I is estimated as 0.3%, for that of Table II, 1%. For pure hydrochloric acid solutions the solubilities here given are in good agreement with those previously published.[1]

Table I

Effect of Aluminum Chloride on the Solubility of Cesium Antimony Chloride in Hydrochloric Acid Solutions at 25°

m HCl	m $AlCl_3$	G. salt/100 g. solution	G. salt/100 cc. solution
2.988	0.000	1.381	1.457
	0.48	1.143	1.263
	0.89	1.036	1.189
	1.33	0.960	1.144
	1.77	0.901	1.110
3.529	0.000	1.275	1.354
	0.48	1.099	1.224
	0.96	0.992	1.152
	1.43	0.918	1.110
	1.91	0.860	1.077
4.446	0.000	1.194	1.280
	0.47	1.088	1.223
	0.96	0.998	1.171
	1.39	0.947	1.155
	1.43		1.142
6.268	0.000	1.120	1.228
	0.50	1.054	1.212
	0.73	1.015	1.192
	1.02	0.982	1.184
10.75	0.000	1.072	1.225
	0.17	1.083	1.261
	0.26	1.089	1.278
	0.29	1.094	1.286

Table II

Effect of Antimony Trichloride on the Solubility of Cesium Antimony Chloride in Hydrochloric Acid Solutions at 25°

m HCl	m $SbCl_3$	G. salt/100 g. solution	G. salt/100 cc. solution
6.718	0.000	1.104	1.218
	.00863	0.985	1.085
	.01250	.925	1.020
	.01707	.890	0.980
	.02205	.840	.925
	.03168	.760	.840
	.04487	.680	.750
	.06594	.580	.645
	.09830	.485	.540
	.1966	.365	.410
12.11	.000	1.075	1.245
	.01550	0.940	1.090
	.02760	.835	0.965
	.05545	.675	.785
	.1108	.495	.575

Experimental

Preparation of Materials.—Cesium antimony chloride free from thallium[1] was synthesized from reagent grade antimony trichloride and cesium chloride prepared by the method of Wells.[2] Other reagents employed were of analytical grade.

Solubility Measurements.—Standard procedures were followed in the solubility determinations. The thermostat temperature was maintained at 25.00 ± 0.02°; the thermometer was calibrated before use. Weld specific gravity bottles were used in the density determinations required for conversion of the results to the volume concentration basis. Calibrated weights and glassware were used throughout the work.

Analytical Methods.—Samples of the saturated solutions were transferred to weighing flasks by air pressure; glass wool plugs were used as filters in the delivery tubes. The solutions were analyzed by volumetric determination of the antimony present by iodometric titration; when an excess of antimony trichloride was present this procedure was checked by removal of antimony as the sulfide and weighing the residual cesium chloride. The hydrochloric acid solutions were standardized gravimetrically by means of silver chloride. Aluminum chloride solutions were made up by weight from the anhydrous salt. Solvent solutions containing an excess of antimony trichloride were prepared by weight from hydrochloric acid and either antimony trioxide or freshly distilled antimony trichloride.

Madison, Wisconsin Received November 11, 1949

---

[1] P. Bender, This Journal, **67**, 1771 (1945).

[2] H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

The Absorption Spectrum of Iodine in Acetone

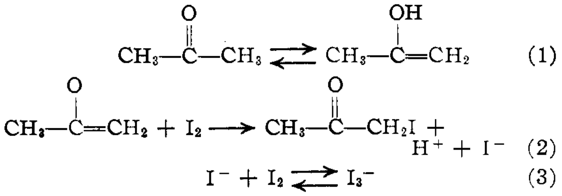
By H. A. Benesi and J. H. Hildebrand

In an earlier publication[1] we briefly reported that the absorption spectrum of iodine in pure acetone was characterized by a single, intense absorption peak, $\epsilon_{\text{max.}} = 6100$ at 363 mμ. The absorption was reproducible, and remained unchanged for several hours, but noticeably decreased during a two- or three-day period. In view of this evidence we had tacitly assumed that the normal absorption peak of iodine ($\epsilon_{\text{max.}} = 1000$ at 520 mμ) had been shifted into the ultraviolet region in its acetone solutions because of some form of solvent interaction, like that between

---

[1] H. A. Benesi and J. H. Hildebrand, This Journal, **71**, 2703 (1949).

iodine and aromatic hydrocarbons,[1] and that the subsequent drop in absorption had been due to the slow reaction of iodine to form iodoacetone. We now wish to report that a more detailed investigation indicates that iodine, in the concentrations used in our absorption measurements, reacts with acetone almost instantaneously to form iodide ion and, supposedly, iodoacetone. The iodide ion evidently establishes equilibrium with the remaining iodine very quickly to form triiodide ion, which gives the strong ultraviolet band reported above. The equations are given



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \qquad (1)$$

$$CH_3-\overset{\overset{O}{|}}{C}=CH_2 + I_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2I + H^+ + I^- \qquad (2)$$

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (3)$$

The experimental evidence for our conclusions can be summed up as follows: (1) Successive additions of acetone to a solution of iodine in carbon tetrachloride caused small, progressive shifts of the normal iodine peak toward shorter wave lengths, but no absorption in the ultraviolet region. Upon standing, however, these solutions underwent a remarkable change. The absorption peak in the visible region began to drop and an absorption peak appeared in the ultraviolet having the same form and $\lambda_{max.}$ as had been earlier observed in solutions of iodine in pure acetone. In the light of the evidence which follows we designate this as the triiodide peak. The simultaneous disappearance of free iodine and the appearance of triiodide ion is good evidence for reactions (2) and (3).

(2) When acetone containing a small amount of dissolved potassium iodide was added to a solution of iodine in carbon tetrachloride, the characteristic peak in the ultraviolet region instantly appeared and the free iodine peak was not obtained at any time. This evidence, together with the fact that triiodide ion in its aqueous solutions has an intense absorption peak[2] ($\lambda_{max.} = 353$ mμ) almost identical in position with the peak observed above, seems to show unmistakably that triiodide ion is being formed when iodine reacts with acetone.

(3) The purified acetone used to make up our solutions was neutral toward litmus, but its iodine solutions gave a distinct acid reaction furnishing more evidence for the occurrence of reaction (2).

(4) Conductivity measurements of a 0.008 molar solution of iodine in acetone at room temperature gave a value of 90 for the molar conductivity of iodine. This value can be compared to the molar conductivity of potassium iodide, which is 100 at the same concentration and temperature.[3] The high molar conductivity of iodine in acetone furnishes definite proof that the reaction of iodine with acetone produces ionic species.

Reactions (1) and (2) are well known, from the work of Lapworth,[4] Bartlett,[5] and Ingold, *et al.*,[6] on the kinetics of the halogen–acetone reaction. These investigators have shown that reaction (1) is the rate controlling step and that the over-all reaction rate is therefore independent of the halogen concentration. We did not observe a reaction rate of this kind in our original absorption measurements because of the low concentration of iodine used (5×10^{-5} molar). It now seems evident that the minute amount of iodine reacted to completion within the time required to make up the solution.[7,8]

---

[2] W. R. Brode, This Journal, **48**, 1877 (1926).

[3] P. Walden, H. Ulrich and G. Busch, *Z. physik. Chem.*, **123**, 459 (1926).

[4] A. Lapworth, *J. Chem. Soc.*, **85**, 30 (1904).

[5] P. D. Bartlett, This Journal, **56**, 967 (1934).

[6] S. K. Hsu, C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 78 (1938).

[7] For experimental details see reference 1.

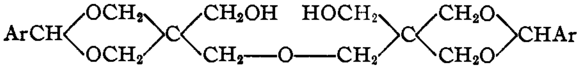
[8] We gratefully acknowledge the support of this research by the Atomic Energy Commission.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.
RECEIVED JANUARY 23, 1950

Acetals of Dipentaerythritol

BY ELIAHU BOGRACHOV[1]

In connection with an investigation in the pentaerythritol series,[2] it became desirable to study the hitherto unknown acetals of dipentaerythritol. When the latter is treated with aromatic aldehydes in presence of an acidic catalyst and under conditions under which the water formed is continually (azeotropically) removed, diacetals



are formed. The two remaining hydroxyl groups are incapable—at least under these conditions—of reacting with a third molecule of the aldehyde, forming an eight-membered ring; they can be acylated in the normal manner.

The diacetals decompose even in contact with humid air. This is the reason why the acetalisation of pentaerythritol according to Kraft[3] can be used for the quantitative determination of the tetrahydric alcohol in presence of dipentaerythritol.

Experimental

Preparation of Dipentaerythritol.—Friedrich and Bruen's[4] method for preparing dipentaerythritol is not satisfactory on any larger scale, and the following procedure is preferred: starting from the double compound of 4 moles of pentaerythritol and 1 mole of dipentaerythritol,[5] the former was separated as dibenzal derivative and the mother liquor evaporated to dryness. Acetylation of the residue

---

[1] Present address: Division of Plant Protection, Ministry of Agriculture, Tel-Aviv, Israel.

[2] Bograchov, This Journal, **72**, 2268 (1950).

[3] Kraft, *C. A.*, **25**, 5114 (1931).

[4] Friedrich and Bruen, *Ber.*, **63**, 2681 (1930).

[5] Wyler, U. S. Patents 2,270,839 (1942); 2,288,929 (1942); Wyler and Wernett. U. S. Patents 2,251,236 (1941), 2,299,048 (1942).