TABLE IV.—$K_1/K_2 \doteq 1/3$. Temperature = 25°.

Time in minutes.	Conc. of acids by titration.	Conc. of $CH_2=N.CH_2.CH_2.CH_2.NH_2$.	$K_2 \times 10^3$.
Experiment 11.	$C_2H_5.OH$ = 6.81 M.		
0	0.2215	0.0223	..
17.6	0.2113	0.0121	15.8
39.9	0.2065	0.0073	13.2
∞	0.1992	0.0	..
			Mean, 14.5
Experiment 12.	NaCl = 0.0573 M.		
0	0.2206	0.0279	..
10.9	0.2164	0.0237	6.17
32.4	0.2106	0.0179	5.87
71.8	0.2043	0.0116	5.50
	0.1927	0.0	..
			Mean, 5.85
Experiment 13.	NaCl = 0.1039 M.		
0	0.2222	0.0276	..
24.25	0.2145	0.0199	5.78
46.7	0.2100	0.0154	5.53
∞	0.1946	0.0	..
			Mean, 5.66
Experiment 14.	NaCl = 0.173 M.		
0	0.2223	0.0278	..
22.9	0.2153	0.0208	5.39
45.75	0.2119	0.0174	4.49
∞	0.1945	0.0	..
			Mean, 4.94
Experiment 15.	NaCl = 1.614 M.		
0	0.2185	0.0322	..
27.3	0.2136	0.0273	2.29
53.6	0.2107	0.0244	1.99
∞	0.1863	0.0	..
			Mean, 2.14

Summary.

The effect of hydrogen ion on addition reactions of any allelotropic mixture, involving a tautomeric shift about a nitrogen atom, is discussed. It is pointed out that in such cases hydrogen ion may be expected to act as a negative catalyst.

The rate of hydrolysis of hexahydropyrimidine was measured under varying concentrations of hydrogen ion, and at two temperatures. Both the effect of hydrogen ion and of temperature on the rate of this reaction were found to be in agreement with this theory.

Alcohol was found to increase the rate of hydrolysis of hexahydropyrimidine.

Sodium chloride in low concentrations was found to increase the rate of this reaction, while in higher concentrations it acts as a negative catalyst.

BERKELEY, CAL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE SILVER SALT OF TRIIODOPHENOL AND ITS CATALYTIC DECOMPOSITIONS.

BY G. H. WOOLLETT.

Received August 21, 1916.

In the course of further study of the catalytic decomposition of silver salts described by Hunter,[1] *et al.*, it became necessary to investigate the

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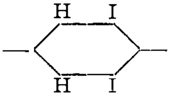
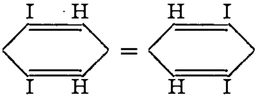
[1] THIS JOURNAL, 38, 1761 (1916).

behavior of the silver salt of triiodophenol. On account of its symmetrical nature, it was expected that this salt would give a smooth catalytic decomposition, comparable to that of the salt of tribromophenol, giving silver iodide, and a residue —O— which should then polymerize as did those already studied. Further, the result of this polymerization could not fail to be of interest, in comparison with the colored compound, of like empirical composition, already studied by several chemists, and now known as tetraiododiphenylenequinone.

This had been originally obtained by the action of iodine and sodium carbonate on phenol, by Lautemann[1] who believed it to be an aromatic oxide and called it diiodophenylene oxide. Kammerer and Benzinger[2] ascribed it to the formula of a tetraiododiphenoquinone, O =  = O and this formula has since been retained. It is proposed to show in a later communication that this formula also is erroneous.

On making very pure samples of the silver salt, it was discovered that it was possible to obtain from it at will either a white amorphous product exactly like those described in the paper already cited, or a red substance, which was easily shown to be identical with Lautemann's red substance.

The present preliminary paper will contain a description of the properties of the silver salt, and of the conditions under which each of the above transformations occurs.

The Silver Salt of Triiodophenol.—The phenol was made by the following method, which is based on that of Körner:[3] One-fifth gram molecule of phenol and the amounts of iodine and iodic acid required by the equation

$$5C_6H_5OH + 6I_2 + 3HIO_3 = 5C_6H_2I_3OH + 3H_2O$$

were each dissolved separately in a slight excess of 2 *N* potassium hydroxide solution. The three solutions were then mixed in a three-liter bottle with glass stopper, and diluted to two liters. To the solution dilute hydrochloric acid was slowly added, with good stirring. Iodine was liberated and at first very rapidly taken up, with formation of a white precipitate. After a while the color of free iodine remained for several minutes at a time. When this point was reached, the reaction mixture was rapidly made distinctly acid and placed on the shaking machine for two hours. The precipitate was then chiefly triiodophenol, colored with iodine, giv-

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[1] *Ann.*, 120, 309 (1861).

[2] *Ber.*, 11, 557 (1878).

[3] *Ann.*, 137, 214 (1878).

ing it a brown color. Dilute bisulfite solution was now added till the iodine color disappeared, and the precipitate was filtered off. It was a light pink, owing to the presence of a little of "Lautemann's red." This is formed by the action of free iodine on the alkaline solution.

The precipitate was dissolved in dilute alkali and filtered from the insoluble red substance. The mixture of triiodophenol with diiodophenol was reprecipitated from the filtrate by acetic acid, filtered, and washed. It was again dissolved in dilute alkali, treated with bone black without heating, and reprecipitated. It weighed about 80 g. It was purified by repeated solution in about 1500 cc. of alcohol and addition of an equal amount of water, until it gave the proper melting point, 156°. Less careful treatment yielded only products of much lower melting points. Our phenol agreed in every respect with the description of Körner.

From this very pure phenol a sample of silver salt was prepared in the usual way by precipitation from a solution of the potassium salt.

It was washed very carefully, dried on a porous plate, in the dark, then at 70° in a drying oven for nearly an hour, and finally over $CaCl_2$ *in vacuo*. The sample was a full lemon yellow, with no appearance of change at any time during the procedure. It was analyzed for both silver and iodine by the method of Carius.

For Ag, subst., 0.1831 g., AgI 0.0737 g.; for I, subst., 0.1114 g.; AgI, 0.1355 g.
Calc. for $C_6H_2I_3OAg$: Ag, 18.65%; I, 65.82%. Found: Ag, 18.55; I, 65.72.

Since this salt is described by Hantzsch[1] as white in color, several attempts were made to obtain a colorless variety, without success. To see if the color might be due to an impurity, a sample of yellow salt was reduced by zinc and sulfuric acid, and the phenol so obtained was used to make another sample of silver salt, which was again yellow. On acidification of an ammoniacal solution, the yellow salt reappeared. Finally, silver nitrate was added to a glacial acetic acid solution of triodophenol, when a yellow precipitate fell, which was collected, washed, and analyzed. It was low in silver, as was to be expected from its method of manufacture.

Subst., 0.1580 g., AgI, 0.0587 g. Calc.: Ag, 18.65. Found: Ag, 17.08.

Formation of the White Oxide from the Silver Salt.—On treating the silver salt with cold ethyl iodide, most of it was converted into the normal ether triiodophenetole. However, the formation of a small amount of amorphous substance could be demonstrated. If the tendency of the silver salt to decompose was increased by heating, the desired catalytic decomposition occurred, as in the following experiment:

Three grams of good silver salt, in small lumps and powder, were heated about five minutes on the water bath, in an Erlenmeyer flask. Ten cc. of cold ethyl iodide were then poured on the salt. A vigorous reaction at

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[1] *Ber.*, **40**, 4875 (1905).

once resulted, in every respect analogous to those observed with the salt of tribromophenol and other phenols, except that the color was grass green instead of blue. The color lasted for about fifteen minutes. The silver iodide was filtered off, and on addition of ethyl alcohol to the filtrate, there resulted a slightly pink precipitate. A single solution in bromoform and reprecipitation removed the color, giving a white, amorphous powder, of properties similar to those of the polydibromophenylene oxide of Hunter, except for a less degree of solubility—for instance, it is almost insoluble in chloroform. It was carefully dried and analyzed.

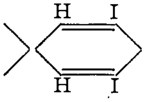
Calc. for $(C_6H_2I_2O)_n$: I, 73.82%. Found: I, 73.60, 73.80. Carius subst., 0.1394, 0.1063; AgI, 0.1902, 0.1452.

If both the salt and the ethyl iodide were heated before mixing, the action was very vigorous indeed, but gave the same white oxide. The pink color in the crude oxide was apparently due to the formation of a small amount of "Lautemann's red."

"Lautemann's Red" from the Silver Salt.—It was noticed that on long exposure to sunlight, the silver salt became red, suggesting the possibility of a second type of decomposition. Comparison with Lautemann's[1] method of making the red substance led to its preparation in the following manner:

A sample of the silver salt was ground up and suspended in water, and then treated with a single drop of a solution of iodine in potassium iodide. As the mixture was shaken, the silver salt became a dark purple in color, the solution still seeming to contain iodine. The colored solid residue was filtered off, dried, and extracted with carbon bisulfide. From this ligroin precipitated a dark red substance, entirely amorphous, and agreeing in every respect with samples made by the method of Lautemann. It was washed with alcohol, dried, and analyzed.

Subst., 0.1078; AgI, 0.1462. Calc. for $(C_6H_2I_2O)_n$: I, 73.82%. Found: 73.28.

That this formation of Lautemann's red instead of white amorphous substance is not due simply to the presence of iodine was easily shown by suspending dry salt in benzene, and adding a slight amount of iodine. This led to a formation of a white amorphous solid, only faintly tinged with pink, showing that iodine can also cause the formation of the white oxide. The question of the relation between the white and the red polymers of the unsaturated residues is being studied in this laboratory. It is perhaps worth pointing out, at this time, the possibility of a quinoid form of the unsaturated residue,  = O although any effect that could be due to such a form, could also result by a simple shifting of val-

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[1] *Loc. cit.*

ences without atomic rearrangement, after polymerization of the benzenoid form.

Summary.

The silver salt of triiodophenol has been prepared in a very pure state, but the colorless form described by Hantzsch has not been obtained, all the samples found being yellow.

This salt, when warmed, gives with ethyl iodide a reaction exactly like that shown by the silver salt of tribromophenol, yielding silver iodide and an unsaturated residue which polymerizes to a white oxide.

$$C_6H_2I_3OAg = AgI + (—C_6H_2I_2O—)$$

$$n(—C_6H_2I_2O—) = (C_6H_2I_2O)_n, \text{ white amorphous.}$$

The salt, when treated with a very little iodine in water, gives instead of the white oxide, the red substance first described by Lautemann.

$$C_6H_2I_3OAg = AgI + (—C_6H_2I_2O—)_n(—C_6H_2I_2O—) =$$

$$(C_6H_2I_2O)_n, \text{ red amorphous.}$$

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

STUDIES OF TRIMETHYLENE OXIDE.

I. PREPARATION AND CHARACTERIZATION.

BY C. G. DERICK AND D. W. BISSELL.[1]

Received September 9, 1916.

I. Introduction. II. Preparation and Purification of Trimethylene Oxide. III. Properties of Trimethylene Oxide. IV. Proof of the Atomic Linking Structure. V. Experimental Part.

I. Introduction.

The use of ethylene oxide and its homologs in organic synthesis has been well established in the field of amino alcohols, and more recently their value in the Grignard reaction has been demonstrated by the work of Grignard,[2] Blaise,[3] and Henry.[4] In the study of the scale of influence of substitution, by the senior author and his students,[5] it is necessary to synthesize substituted monobasic paraffin acids, in which the substituents are further removed from the carboxyl group than the delta position. It seemed probable that trimethylene oxide would be of great value in effecting these syntheses. With this in mind the only reported synthesis of this substance was studied.

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[1] Presented at the Urbana meeting of the American Chemical Society, 1916. From a thesis, submitted in partial fulfilment of the requirements for the degree of Master of Science at the University of Illinois.

[2] *Compt. rend.*, **136**, 1260 (1903); **141**, 44 (1905); *Ann. chim.*, [8] **10**, 23 (1907).

[3] *Compt. rend.*, **134**, 552 (1902).

[4] *Chem. Zentr.*, II, 445 (1907).

[5] THIS JOURNAL, **33**, 1167 (1911); **38**, 400 (1916).