XXXIX.—Action of Chloride of Iodine on Picric Acid.

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I HAVE already stated,* that when picric acid is digested with a strong aqueous solution of chloride of iodine, chloropicrin and chloranil are formed. From the manner, however, in which the experiment was then conducted, any other chlorinated products formed at the same time, could not be conveniently isolated. In the experiment just quoted, from the absence of any iodinecompound, it seemed that the chlorine was the active agent in the reaction between chloride of iodine and picric acid—the iodine merely serving as a sort of carrier for the chlorine.

Dinitrochlorophenic Acid.

From some experiments I have recently made, I found the following to be the most convenient method of treating picric acid with chloride of iodine :--- 3 parts of picric acid, 3 parts of water, and 1 part of iodine were introduced into a flask furnished with two tubes, one serving as a condensing-tube, and the other reaching nearly to the bottom of the vessel, through which a current of chlorine was passed. The contents of the flask were kept gently boiling, whilst chlorine was passed through it for some hours. In a short time, oily drops of chloropicrin condensed in the tube, but these gradually disappeared, and carbonic anhydride and nitric oxide were given off, together with a small quantity of nitrous fumes. The current of chlorine was then stopped, and the chloride of iodine distilled off as far as possible, in a paraffin-bath at about 120°-130° C. If. however, the reaction with chloride of iodine be continued sufficiently long, chloranil is the sole fixed product.

The crystalline residue, after being washed with a small quantity of cold water, is boiled with a considerable quantity of pure water, filtered, and allowed to crystallise. As the acid is but difficultly soluble, even in boiling water, the undissolved portion remaining on the filter should be extracted with the mother-liquors, from which the acid has separated by crystallisa-

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tion. The nearly pure crystals of the acid thus obtained, are readily purified by one or two recrystallisations from boiling water.

The acid melts at 103°, volatilises slightly at 100° C., and more readily in the vapours of boiling water. It separates almost entirely from its aqueous solutions when they are strongly acidulated with nitric or hydrochloric acids.

The acid, dried at 100° C., was subjected to analysis, with the following results :---

I. 468 grm. acid, gave 561 grm. carbonic acid, and 067 grm. water.

II. 185 grm. acid, gave 121 grm. chloride of silver.

			Theory.	I.	II.
C ₆	=	72	32.95	$32 \cdot 91$	
H ₃	=	3	1.37	1.59	
Cľ	=	35.5	16.25		16.18
N_2	=	28	12.81		
O_5	=	80	36.62		
		218.5	100.00		

This agrees with the formula $C_6H_2Cl(NO_2)_2$.H.O.

Dinitrochlorophenate of Silver.

This salt was prepared by neutralising a boiling solution of dinitrochlorophenic acid with argentic carbonate. The silversalt, after recrystallisation, was dried at 100° C, and analysed.

I. 260 grm. silver-salt, precipitated by hydrochloric acid, gave 114 grm. argentic chloride.

II. 494 grm. gave 216 grm. argentic chloride.

			Theory.	I.	II.
$C_6H_2Cl(NO_2)_2O$	-	217.5	66.83		
Âg	==	108.0	33.17	33.00	32.92
		325.5	100.00		

It will be seen, from these results, that the acid obtained by the above-described process is identical in composition with the dinitrochlorophenic acid of Griess*, with which it also agrees in all its properties.

* Ann. Chem. Phar., cix, 286.

Having submitted a specimen of the acid to Dr. Griess, he informed me that on comparing it with specimens of the dinitrochlorophenic acid, prepared by himself, "he found them the same in every respect." On treating the dinitrochlorophenic acid with sulphide of ammonium, it was converted into *amidonitrochlorophenic acid*, which is also identical with that obtained by Griess.

Dr. Griess's process for preparing dinitrochlorophenic acid consists, as is well known, in chlorinating phenol, and treating the resulting product with nitric acid. The red, oily mass thus obtained, is purified by converting it into the ammonium-salt. This method is tedious, and by no means productive, and, therefore, very interior to the process with picric acid, above described.

Action of Chloride of Iodine on Styphnic Acid.

When styphnic acid is treated with chloride of iodine in a similar manner to picric acid, it undergoes a very different kind of decomposition, being apparently resolved into chloropicrin and carbonic acid, no chlorinated acid or chloranil being produced. This result confirms the observation I have already made,* "that styphnic acid is not, as Erdmann erroneously supposed, merely oxidated picric acid, but must have a different nucleus, entirely unconnected with that of picric acid."