the catalysts tend to associate the chlorine molecules into bi-molecules. Hence chlorination in the presence of catalysts may be called a bi-molecular reaction, while it is a mono-molecular reaction in the presence of actinic light. Thus it might be expected that methane, after chlorination, would give  $CH_2Cl_2$  and  $CCl_4$ , though Phillips claims to have obtained  $CH_3Cl$  and  $CCl_4$ .

This is an inviting field and more definite work must be done before any hypothesis is proposed.

NIAGARA FALLS, N. Y.

## THE ACTION OF CHLORINE UPON HYDRAZINE, HYDROXYL-AMINE AND UREA.

BY C. T. DOWELL.

Received November 2, 1918.

In the course of an investigation of the action of chlorine upon urea, a study was also made of the action of chlorine upon hydrazine and hydroxylamine. Evidence was obtained showing that in the reaction of chlorine, with hydroxylamine and with hydrazine, nitrogen trichloride was formed. This evidence was based upon the action of a solution of nitrogen trichloride in carbon tetrachloride with potassium iodide, in which nitrogen is always liberated. When hydroxylamine and hydrazine were allowed to react with chlorine in contact with carbon tetrachloride it was found by shaking the reaction mixture and later separating the carbon tetrachloride and treating it with a solution of potassium iodide that nitrogen was given off. Precaution was taken to have a large amount of chlorine present with a small amount of the hydrazine or hydroxylamine. It was not expected that very much nitrogen trichloride would be obtained on account of the fact that this substance reacts quite rapidly with hydrazine and hydroxylamine.

After completing the work on the reactions between chlorine and urea an article<sup>1</sup> was found in which Chattaway had made a study of the same reactions and had isolated dichlorourea and determined its properties. My work was in the main a confirmation of Chattaway's work as far as the properties of the dichlorourea were concerned. It was found that no nitrogen is oxidized to the nitrous or nitric form. Chattaway and the writer both found that when a solution of dichlorourea was allowed to stand, it decomposed, giving as one of the products nitrogen trichloride. Chattaway supposed that the reaction took place between dichlorourea and water in which carbonic acid and monochloroamine were formed and that monochloroamine decomposed giving ammonia and nitrogen trichloride. In the early part of my work I suspected that the oxidizing properties of the solution were due to monochloroamine and made several tests

<sup>1</sup> Chem. News, 98, 285 (1902).

to determine whether or not it was present. This test is made as directed by Raschig<sup>1</sup> by treating the solution with ammonia and then adding a small amount of benzaldehyde. The reaction between monochloroamine and ammonia is one of the methods for preparing hydrazine, and in this case if hydrazine were present it would react with benzaldehyde to form the very insoluble benzalazine. No evidence of the presence of monochloroamine could be obtained. It was found that when the solution was treated with an excess of chlorine the only oxidizing compound obtained was nitrogen trichloride. This would lead one to think that nitrogen trichloride was formed by the action of chlorine, which in turn was possibly a decomposition product of dichlorourea.

STILLWATER, OKLAHOMA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & CO.]

## DIGITALIS LEAVES: EFFECT ON ACTIVITY OF TEMPERATURE IN DRYING.

By HERBERT C. HAMILTON.

Received November 7, 1918.

Since the first attempt to standardize digitalis leaves and the extracts, it has been observed that they vary greatly in activity.

Bennefield,<sup>2</sup> in 1881, using a method almost identical with that suggested in the 9th Rev. U. S. P. for standardizing the digitalis series of heart tonics found a variation of about 500% in the activity of tinctures from digitalis leaves from various parts of Germany.

Bührer,<sup>8</sup> in 1900, found a difference of 400% in the activity of some fluidextracts. Fränkel<sup>4</sup> found variations of 300 to 400% in tincture and infusions. Edmunds,<sup>5</sup> in 1907, tested 17 commercial tinctures and found a variation of 400%.

Many other similar results have been recorded, in some cases the reason being assigned to climate, soil, variety, or the locality from which the leaves were obtained.

Focke<sup>6</sup> observed that wild digitalis is more toxic than the cultivated and the second year's growth than the first. He also observed that the leaves gathered at seeding time are less active than when collected earlier. He was the first to record his observations as to the causes of deterioration and the effect of light and heat in drying the leaves. The former is negligible but he considered that when dried in the air in the ordinary way without special care in preserving the activity is soon largely lost.

<sup>1</sup> Ber., 40, 4586 (1907).

<sup>6</sup> Focke, Arch. Pharm., 245, 646 (1907).

<sup>&</sup>lt;sup>2</sup> Bennefield, "Ueber Digitalis Tincturen," Inaug. Diss., Göttingen, 1881.

<sup>&</sup>lt;sup>3</sup> Bührer, Inaug. Diss., Basel, 1900.

<sup>&</sup>lt;sup>4</sup> Fränkel, Therap. Gegenw., 43, 106 (1902).

<sup>&</sup>lt;sup>5</sup> Edmunds, J. Am. Med. Assoc., 48, 1744 (1907).