SOME HYDROCHLORATED SULPHATES.

BY CHARLES BASKERVILLE.

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SMITH and Tunnell[1] have published experiments on the removal of the acid radical in sodium and potassium sulphates by gaseous hydrochloric acid under the influence of heat. The volatilization, rather substitution, of sulphuric acid by hydrochloric acid has been pointed out in papers presented before the North Carolina Section by the writer. Heusgen[2] had previously noted that gaseous hydrochloric acid acted upon potassium sulphate cold. Prescott[3] observed substitution when the same salt and concentrated hydrochloric acid were evaporated together. Smith obtained addition products, *i. e.*, $K_2SO_4.xHCl$ (x not stated), in the course of the reaction, but a complete elimination of the sulphuric acid was not observed. The reaction is attributed to mass action.

Our observations on somewhat similar reactions were made with salts of zinc, cadmium, and mercury. The experiments demonstrate without doubt the effect of mass action, but time, temperature, and the removal from the sphere of action of certain agents involved have a decided influence on the observed changes.

The degree of substitution depends entirely upon the temperature and time of the action as well as mass. The preparation of new bodies like these is of no great importance. The point of interest rests in the graduated substitution of water by hydrochloric acid, molecule for molecule, in crystalline bodies. This substitution may throw some light upon the discussed "molecular compounds."

MERCURIC COMPOUNDS.

(WITH LIONEL WEIL.)

According to Berzelius, if a stream of hydrochloric acid gas be passed over mercuric sulphate, mercuric chloride and sulphuric acid will result. Ditte[4] states that if gentle heat be applied, the mercuric sulphate combines with hydrochloric acid, melts and snow-white crystals of $HgSO_4.HCl$ are sublimed. Further the same compound may be obtained by evaporating mercuric sulphate and concentrated hydrochloric acid, or mercuric chloride and

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[1] This Journal, **21**, 930 (1899).

[2] *Ber. d. chem. Ges.*, p. 1671 (1876).

[3] *Chem. News*, **36**, 178.

[4] *Ber. d. chem. Ges.*, **12**, 361 (1879).

sulphuric acid with 1 molecule of water. By gentle heat, white needle crystals are obtained.

The experiments were repeated successfully in the following way: Twenty grams mercuric sulphate were treated with 20 cc. concentrated hydrochloric acid in a porcelain dish, the excess of acid being first driven off by a free flame; the substance was dried on a sand-bath and sublimed at 240° C. into a funnel, through which a rapid stream of air was drawn. The crystalline sublimate was treated in turn with alcohol and a mixture of alcohol and ether to remove the free acid and mercuric chloride and sulphate. The insoluble portion was not affected by hydrochloric acid and was only slightly soluble in nitric acid. It was fused with sodium carbonate, leached, and the chlorine determined.

	Calculated for $HgSO_4.HCl$.	Found.
Chlorine	10.67	10.81

The yield was small and not improved by varying the amounts of the substances used.

In following out another method for preparing hydrochlorated mercuric sulphate, namely, by gently heating the mercuric sulphate in a stream of dry hydrochloric acid, only a small amount of the substance was obtained. A new white, crystalline, very deliquescent body was obtained however which proved on analysis to be the dihydrochlorated body, which is very soluble in water.

	Calculated for $HgSO_4.2HCl$.	Found.
Sulphur trioxide	18.65	18.18

Roscoe and Schlorlemmer state that mercuric chloride dissolves without decomposition in concentrated sulphuric acid. This seems to be true, but, on heating, a crystalline sublimate was obtained in the funnel suspended above the dish in which the reaction occurred. If the heating be too prolonged some free sulphuric acid will volatilize and condense on the crystals. Molecular amounts of mercuric chloride and $H_2SO_4.H_2O$ were carefully heated in a porcelain dish. Clean, dry, well-formed monoclinic crystals were selected from the sublimate in the neck of the funnel suspended above. On analysis these crystals gave the following results:

	Calculated for $HgSO_4.2HCl.H_2O$.	Found.
Chlorine	18.34	19.89

The substance was not further worked with.

CADMIUM COMPOUNDS.

(WITH ISAAC F. HARRIS.)

By varying the temperatures we have succeeded in replacing variable amounts of water of crystallization in $3CdSO_4.8H_2O$. At 150° C. the sulphate loses 4 molecules of water; if subjected to the action of dry hydrochloric acid at that temperature 4 molecules of hydrochloric acid combine with the partially dehydrated body, giving $3CdSO_4.4H_2O.4HCl$.

At 200° C. the hydrated sulphate permits all its water to be expelled, giving $3CdSO_4.8HCl$. At that temperature under the prolonged influence of the hydrochloric acid, or at dull red heat for a shorter period, the sulphuric acid radical is displaced and finally $CdCl_2$ results. The observations noted took place with the hydrated sulphate, or material dried at 150° C. or completely dehydrated.

The bodies obtained are very deliquescent and present difficulties in obtaining them pure for analysis. Hydrochloric acid is held mechanically by the compounds and is difficult to remove. The method of procedure was to place the sulphates, hydrated and anhydrous, in a porcelain boat in combustion tubing fixed in an air-bath punctured to admit the tube. Dry hydrochloric acid was passed through the tube whose temperature was closely guarded. The material melted and crystallized out on cooling. If the temperature reached dull redness (with experiments over direct flame) the body was sublimed to the cooler portions of the tube. In order to remove the mechanically bound hydrochloric acid, the tube was allowed to cool for twelve hours, a steady stream of gas passing through all the while; afterwards dry air, free from carbon dioxide, was passed through for two or more hours. Some analyses are appended.

		Calculated.	Found.	
			I.	II.
Original sulphate $3CdSO_4.8.H_2O$	SO_3	31.2	31.4	
	H_2O	18.7	18.1	
$3CdSO_4.4H_2O.4HCl$. (at 150° C) ..	HCl	17.00	16.00 16.00	18.7
	SO_3	28.00	28.00	27.5
With prolonged heating	HCl		22.5	
	SO_3		23.5	
Fused and partially volatilized $3CdSO_4.8HCl$	HCl	31.00	30.1	30.2
Continued heat and sublimation $CdCl_2$	Cl	38.6	38.00	

A few experiments were made with zinc sulphate and the above observations extended, but not completed.

UNIVERSITY OF NORTH CAROLINA,
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THE ACTION OF ZINC ETHYL UPON NITRO AND NITROSO COMPOUNDS.

(A REPLY TO I. BEWAD.)

BY ARTHUR LACHMAN.

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IN a recent paper containing a wealth of experimental material, I. Bewad undertakes to prove the complete analogy of the action of zinc ethyl on carbonyl compounds on the one hand, and upon nitrogen-oxygen compounds on the other. This work was begun about fourteen years ago,[1] but its most important results were not manifest, or at any rate were not published in accessible journals, until last year.[2] In his last paper Bewad is anxious to claim priority for these results, evidently with reference to my own publications,[3] since the general subject has not been investigated by any third party.

Bewad's priority in this work is unquestioned. In fact, it was through a study of Bewad's own publications that I was led to attempt the main problem I have undertaken; *viz.*, the intimate structure of the nitro group. Priority, however, is no guarantee of accuracy; and since Beward has been, and is still, in error as to some matters of fact, and is entirely at sea with his explanations of other facts, I have thought it desirable to clear up several points that would seem reasonably certain, before proceeding with new experimental work.

In order to indicate that Bewad's results in the past have needed revision, let me briefly append a history of events. In his first papers (*cf.* above), Bewad asserted the following: That the action of zinc ethyl on nitroethane gave triethylamine oxide, $(C_2H_5)_3N=O$; that the reaction succeeds with only one molecule of zinc ethyl; that if two are taken, no amine oxide at all is obtained; that upon reduction the amine oxide forms triethylamine. On the other hand, I showed in my first paper that if two molecules of zinc ethyl are taken the yield of "amine oxide,"

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[1] *Cf. Ber. d. chem. Ges.*, **21**, ref. 479 (1887); **22**, ref. 250 (1888).

[2] *J. prakt. Chem.*, **63**, 94 (1901).

[3] *Am. Chem. J.*, **21**, 433 (1899); *Ber. d. chem. Ges.*, **33**, 1022 (1900).