

The compound formed with cinnamic aldehyde is a brick-red pasty mass. It also is soluble in ether, and from this solution hydrochloric acid precipitates a flocky red salt.

The condensation product with piperonal is a greenish yellow slime. When hydrochloric acid is added to its solution in dry ether, the precipitate first formed is pale yellow. A little more acid changes this color to a light red, and an excess to a bright lemon-yellow.

The compound formed with vanillin is a dark, blood-red, transparent jelly. Hydrochloric acid precipitates yellow salts.

#### Summary.

The salts of bases formed by condensing *m*-aminodimethylaniline and *m*-aminodiethylaniline with aldehydes do not show the same peculiarities of color as the corresponding salts of the *p*-compounds.

From this the conclusion might be drawn that the dark-colored salts of the latter were quinoid, but the force of this argument is a good deal weakened by the probability that these *m*-bases are polymers.

The amorphous character of these compounds (perhaps due to polymerization) in contrast to the crystalline nature of the *p*-compounds suggests applications to the benzene problem which are worthy of future study.

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## THE ACTION OF MAGNESIUM UPON THE VAPORS OF ORGANIC COMPOUNDS.

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In 1894 Edward H. Keiser and M. B. Breed<sup>1</sup> studied the action of metallic magnesium upon the vapors of some of the aliphatic alcohols and found that when the metal is heated in a tube through which the vapor of the alcohol is passing it soon begins to glow and after the action has ceased and the tube allowed to cool, a black residue is left. This residue when put into water evolves a gas slowly and on the addition of a few drops of ammonium chloride a more rapid evolution of gas is obtained. It was shown that the gas thus given off consisted of hydrogen mixed with small quantities of allylene.

In a subsequent paper by Edward H. Keiser<sup>2</sup> the work was continued, other alcohols and acetone were subjected to the action of magnesium, and it was shown that in every case the black residue gave off allylene when treated with water. The best yield of allylene was obtained from

<sup>1</sup> *J. Franklin Inst.*, Dec., 1894.

<sup>2</sup> *Am. Chem. J.*, 18, 328.

the black mass formed by the action of magnesium upon acetone. It was also shown that when magnesium is heated in an atmosphere free from hydrogen, as for instance, in carbon monoxide and carbon dioxide, a very hard compact black mass is obtained which gives only small quantities of allylene on treatment with water. The conclusion was, therefore, drawn that a magnesium compound of allylene was probably present in the black residue.

We have now endeavored to determine whether a magnesium compound of allylene or simply a carbide of magnesium is present in the black residue. In the earlier experiments several of the aliphatic alcohols, allyl alcohol and acetone had been acted upon by the magnesium; we now extended the work so as to include other classes of compounds such as paraffin and aromatic hydrocarbons, aliphatic acids and esters, aromatic alcohols, halogen derivatives, acetylene, cyanogen, etc.

The method of operating was the same as before, the metal in an iron boat was placed in a combustion tube of glass, the tube was heated in a small furnace and the organic compound was passed through the tube in the form of vapor. After the action was over the black magnesium residue was allowed to cool off in the vapor. The black residue was then put into a dry evolution flask provided with a separatory funnel and water containing a few drops of ammonium chloride was allowed to drop upon it. The gases evolved were passed into an ammoniacal solution of silver nitrate. The silver precipitates thus obtained were analyzed. The following table (see p. 390) contains the results of these analyses.

These results show that in every case when magnesium is heated in the vapor of a compound containing hydrogen the unsaturated hydrocarbon evolved from the black residue is chiefly allylene. When hydrogen is absent, as in the cases of cyanogen and carbon monoxide a very poor yield of unsaturated hydrocarbon is obtained; four to five times as much of the black magnesium residue must be used in order to obtain sufficient of the silver precipitate for analysis. The analytical results show that even in these cases the gas evolved is not pure acetylene but contains some allylene. Thus from cyanogen the silver precipitate was found to contain but 82.95 and 82.72 per cent. of metal whereas pure silver acetylide contains 89.9 per cent.; and in the case of carbon monoxide the silver precipitate gave 78 per cent. of silver. These low results indicate a mixture of allylene and acetylene and at first thought it would appear that a carbide of magnesium is formed in all these experiments and that the allylene is formed by the action of water upon this carbide. This conclusion would be justified were it not for the fact, noted in the earlier paper, that magnesium powder contains hydrogen, either as occluded hydrogen, or hydroxide or both. This has been proved by burning weighed amounts of magnesium powder and weighing the water formed.

The average result of two combustions of magnesium powder, previously dried for several hours at  $120^{\circ}$  in an air bath, gave 0.065 per cent. of hydrogen.

## ANALYSES OF SILVER PRECIPITATES.

Magnesium allylide from	Weight taken,	Wt. AgCl found.	Per cent. Ag.
<i>n</i> -butyl alcohol (a).....	0.1281	0.1262	74.16
(b).....	0.1422	0.1388	73.48
Benzyl alcohol.....	0.2715	0.2661	73.81
Ether.....	0.1271	0.1240	73.44
Ethyl bromide.....	0.0554	0.0543	73.78
Benzyl chloride.....	0.0898	0.0894	74.90
<i>n</i> -butyric acid.....	0.0336	0.0328	73.48
Isobutyric acid.....	0.1210	0.1190	74.30
Ethyl acetate (a).....	0.1042	0.1038	74.96
(b).....	0.0815	0.0812	74.98
Isobutyl acetate (a).....	0.1534	0.1496	73.42
(b).....	0.1447	0.1419	73.78
Amyl acetate (a).....	0.1423	0.1388	73.43
(b).....	0.1051	0.1027	73.53
Hexane.....	0.0400	0.0384	72.24
Benzene.....	0.1067	0.1062	74.81
Kerosene.....(a).....	0.0418	0.0417	75.11
(b).....	0.0599	0.0595	74.76
Illuminating gas (a).....	0.1370	0.1384	76.05
(b).....	0.1504	0.1522	76.17
(c).....	0.1290	0.1260	73.51
(d).....	0.1311	0.1280	73.50
(e).....	0.2340	0.2285	73.51
Cyanogen (a).....	0.1027	0.1132	82.95
(b).....	0.0637	0.0700	82.72
Acetylene (a).....	0.3213	0.3590	84.10
(b).....	0.1854	0.2063	83.80
Carbon monoxide.....	0.0818	0.0851	78.20
CO and nitrogen.....	0.0787	0.0814	77.83
CO + N <sub>2</sub> + HCl.....	0.0550	0.0547	74.80
Calculated for silver allylide, AgC <sub>3</sub> H <sub>3</sub> .....			73.45

This fact of the presence of hydrogen in the magnesium and the other fact that only a very small amount of the unsaturated hydrocarbons is obtained from carbon compounds containing no hydrogen led us to conclude that magnesium allylide is present in the black residue. There is undoubtedly a tendency on the part of magnesium, under the conditions of our experiments, to combine with carbon and hydrogen to form magnesium allylide and it is this compound which with water evolves allylene. This is shown clearly in the case of the experiments with acetylene. When magnesium powder is heated in this gas a black residue is obtained which with water gives off both allylene and acetylene. Here the conditions were favorable for the formation of only a carbide, as MgC<sub>2</sub>, yet the gas

given off consists of both hydrocarbons. Further, when carbon monoxide, diluted with nitrogen to make the action less violent, was acted upon by magnesium, the black residue gave very little silver precipitate, but when hydrochloric acid gas was added to the mixed gases then a good yield of unsaturated hydrocarbon was obtained and the analysis of the silver precipitate indicated nearly pure allylene. We conclude, therefore, that it is magnesium allylide that gives the allylene and not a carbide.

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## STUDIES IN THE ACTION OF HEAT ON MILK.<sup>1</sup>

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A number of experimenters<sup>2</sup> have noticed that when milk is heated, the lactose apparently diminishes in quantity. The subject, however, has not been systematically investigated.

Richmond<sup>3</sup> first called attention to the fact that the specific rotatory power of lactose in milk materially diminished on heating, but that the reducing power decreased only slightly. Later he and Boseley<sup>4</sup> determined lactose in samples heated for 1½ to 3 hours at 100° and found that there was a decrease of from 8.8 per cent. to 23 per cent. of the sugar as measured by the optical method. In another series where sugar was determined gravimetrically, no change was noticed. They offered the suggestion that this may be due to the formation of caramel, since the rotatory power decreased roughly in proportion to the increase of yellow color in the milk.

It did not seem to the present authors that caramelization could be the primary cause of the difference in the optical and gravimetric determinations, since the rotatory and reducing power should decrease nearly proportionally, due to the relatively large molecule of the caramel compared to that of lactose. It was for the purpose of investigating this that the following experiments were undertaken. We were particularly interested to find out the character and extent of the change taking place at the temperatures which might be used in pasteurization.

A number of possible causes for the change in rotatory power of the milk serum presented themselves among which may be mentioned changes

<sup>1</sup> Submitted by F. C. Ware, in partial fulfilment of the requirement for the degree of Master of Arts at Wesleyan University, June, 1908. The experimental work was carried on in the Chemical Laboratory, Stamford High School, Stamford, Conn.

<sup>2</sup> Wroblewski, *Oest. Chem. Ztg.*, **1**, 5 (1898); Leeds and Coon, *Pharm. J.*, **23**, 86; Cazeneuve and Haddon, *Compt. rend.*, **120**, 1272; and others.

<sup>3</sup> *Analyst*, **17**, 222.

<sup>4</sup> *Ibid.*, **18**, 141 (1893).