

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY.]

## UNSATURATION AND MOLECULAR COMPOUND FORMATION.

## II.

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In our first paper on the effect of unsaturation on molecular compound formation it was pointed out that in the cases studied this is influenced by the structure of the remaining parts of the molecule. Thus benzene did not show the same evidence of molecular compound formation that toluene, ethyl benzene and mesitylene showed, hydrobromic acid being the second component. On examining the system acetylene-hydrobromic acid it was shown that no molecular compound was formed, and from the analogy to benzene it was proposed to study the system of a substituted acetylene and hydrobromic acid with the expectation that allylene, for instance, might behave like a substituted benzene in its tendency to form a molecular compound. This investigation is described in the following paper and incidentally the preparation of allylene is described in detail.

Of the several methods which are available for the preparation of allylene the only one in which it was found possible to obtain a product in which the impurities could be easily removed was a method due to Lebeau and Picon<sup>1</sup>. These authors outline the method as follows. Acetylene is passed into a solution of metallic sodium in liquid ammonia until the disappearance of the blue color shows the formation of sodium acetylide; subsequent addition of methyl iodide brings about the formation of allylene. As a considerable time was spent in discovering the best experimental conditions for obtaining a large yield by the above method, it may be worth while to describe these here.

The large tube T (Fig. 1), about 25 cm. long and 7 cm. wide, is evacuated and then filled with dry hydrogen. 15 g. of freshly cut sodium is placed on a perforated plate at the bottom of side tube S, a stream of hydrogen being forced in at A. T is placed in an oil-bath heated to 110° and the direction of the stream of hydrogen is reversed so that on gently heating the stream of hydrogen the molten sodium is forced through the perforated plate on which the scum remains behind. S is then sealed off. Pure dry ammonia is then sent through A and condensed in T which is surrounded with solid carbon dioxide-ether mixture. The rate of condensation is conveniently followed by means of manometer M, Y serving as exit tube when necessary. Some 300 cc. of liquid ammonia is condensed, Tube A being gradually withdrawn so that it always remains above the surface of the solution. Otherwise the solution creeps up the tube and the warm stream of ammonia causes the deposi-

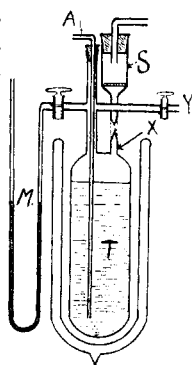


Fig. 1.

<sup>1</sup> Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913).

tion of metallic sodium on the walls of the tube. The stream of ammonia is then replaced by a current of pure dry acetylene, the end of tube A being now immersed well below the surface of the solution. The stream of acetylene must be maintained at a vigorous rate to prevent the clogging up of the inlet tube by precipitated sodium acetylide and also to help stir the liquid. The stirring of the liquid is essential, as otherwise the acetylene dissolves to excess in the lower layers. White crystals of acetylide separate out in the bottom of the vessel, the completion of the reaction is given fairly sharply by the disappearance of the blue color, provided the liquid is vigorously stirred. To eliminate any excess of acetylene which may be there, the vessel is allowed to warm up slowly and a portion of the ammonia distilled off; this is replaced by recondensation of an equal amount of fresh ammonia, and this process is repeated until a test of the gas coming off shows the complete absence of acetylene. Tube A is then replaced by a small dropping funnel and the calculated amount of methyl iodide added drop by drop, the whole apparatus being shaken from time to time. A white precipitate of NaI is deposited. As the temperature is maintained very low no gas is evolved. After standing for an hour at a temperature of about  $-50^{\circ}$  the vessel is allowed to warm up slowly, the gas evolved is passed through numerous wash-bottles filled with water to remove the ammonia, and collected in gasometers, the displaced liquid being a saturated sodium chloride solution in which allylene is less soluble than in water. Some 7 to 8 liters of allylene is obtained.

Tests showed the complete absence of iodide and of acetylene. The test for acetylene in the presence of allylene is one due to Berthelot.<sup>1</sup> The allylene is then further purified by passing slowly over phosphorus pentoxide at  $10^{\circ}$ , and condensing and distilling it a number of times. As the boiling point of allylene is fairly low special tubes were designed in which it could be kept at room temperature and from which it could be transferred to some other vessel when desired without the possibility of subsequent contamination. Fig. 2 illustrates such a tube. C is connected to a vacuum pump and a bulb containing the allylene immersed in liquid air. After evacuation the allylene is condensed in the tube and, after melting, it is again frozen, evacuated, and C is sealed off. The allylene is thus kept in an all-glass vessel which has been scrupulously cleaned and which can withstand the pressure at room temperatures. When the allylene is to be transferred to another vessel Tube B is glass-sealed to the latter, the space above evacuated, and after

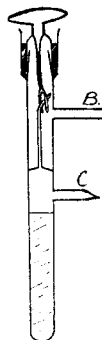


Fig. 2. cooling the liquid, connection is made by breaking the capillary in a manner made obvious by the diagram.

The freezing-point was found to be sharp at  $-105.0^{\circ}$  and the boiling-point  $-27.0^{\circ}$  as compared to  $-110^{\circ}$  and  $-23.5^{\circ}$  given in the literature for a product prepared by other methods. Subsequent molecular weight determination gave the value 40.0 under ideal conditions.

The allylene thus prepared was mixed with hydrobromic acid in various proportions and the freezing-points determined in the manner described for the system acetylene: hydrobromic acid in our previous paper.<sup>2</sup> The bulbs containing the mixtures were never allowed to warm up above  $-78^{\circ}$  and the freezing-point was taken immediately. Analysis of several of the bulbs afterwards showed that the atomic compound had not formed to an appreciable extent at that low temperature during the short time required

<sup>1</sup> *Ann. chim. phys.*, [4] 9, 423 (1866).

<sup>2</sup> *THIS JOURNAL*, 40, 1561 (1918).

to determine the freezing-point. The values obtained for the freezing-points for various percentages by weight of hydrobromic acid are tabulated below.

FREEZING-POINTS OF THE ALLYLENE: HYDROBROMIC ACID SYSTEM.			
% acid by weight.	°C.	% acid by weight.	°C.
0.0	-105.0	68.0	-125.8
30.6	-112.3	70.5	-127.6
45.3	-121.5	73.9	-128.8
54.2	-129.6	81.5	-134.0
54.3	-129.5	85.0	-137.7
57.6	-129.1	90.3	-120.5
60.8	-127.2	95.4	-101.6
64.6	-126.1	100.0	- 86.0
66.3	-127.0	...	...

Fig. 3 shows the freezing-point curve of  $\text{CH}_3\text{—CH}\equiv\text{CH} + \text{HBr}$  and for purposes of comparison the dotted line representing the freezing-point curve of  $\text{CH}\equiv\text{CH} + \text{HBr}$ , previously determined, is inserted. It is evident that a molecular compound is formed between allylene and hydrobromic acid. There are two well-defined eutectics and the

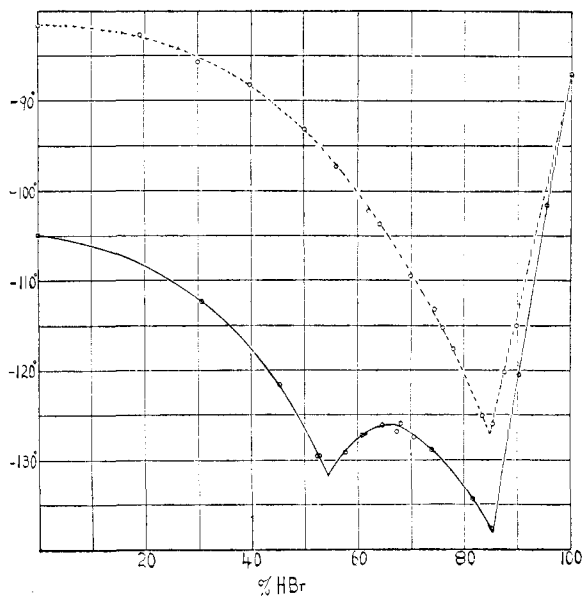


Fig. 3.

maximum corresponds to the compound  $\text{CH}_3\text{—CH}\equiv\text{CH.HBr}$  which has a theoretical composition of 67% by weight of acid. The corresponding compound in the case of acetylene would have a composition of 75.7% acid but the curve in this case gives no indication of the existence of such a compound.

On allowing the bulbs containing the allylene-hydrobromic-acid mixtures to warm up the atomic compound, the bromide was gradually formed. Acetylene-hydrobromic-acid mixtures, on the other hand, have been kept for a considerable time at room temperature without any reaction taking place.

As has been pointed out in our previous paper, the hydrocarbons, due to the well-defined valences of carbon and hydrogen, lend themselves admirably to an investigation of molecular compound formation, as it is possible to compare their relative tendency with one another. In benzene and acetylene the symmetry of the molecule leaves apparently no secondary valence due to unsaturation by means of which an attraction is exerted upon hydrobromic acid molecules, whereas in the case of alkyl substitutions such an attraction exists. This has an important bearing on the question of subsequent atomic compound formation, as is possible in the case of acetylene and allylene. It has been proposed that atomic compound formation is always preceded by molecular compound formation. The behavior of acetylene and allylene towards hydrogen bromide supports this idea to a modified extent inasmuch as acetylene which does not form a molecular compound does not combine readily (when pure and freed from the presence of catalysts) with hydrogen bromide to form the bromide, while allylene which forms a molecular compound will readily react with hydrogen bromide to form the atomic compound. That is, it is not unreasonable to suppose that the velocity of a chemical reaction is affected by the forces of attraction between the molecules as evidenced by molecular compound formation similar to the effect a catalyst would have on the velocity of a reaction.

An investigation of this is possible by quantitative measurements. Such an investigation, together with a study of systems of hydrobromic acid and chlorine with ethylene, propylene and other hydrocarbons, is now being carried out.

### Summary

The details of the preparation of pure allylene have been described. It was shown that, contrary to the behavior of acetylene, allylene forms a molecular compound with hydrogen bromide, and at higher temperatures combines with it to form an atomic compound.

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## A REVISION OF THE ATOMIC WEIGHT OF CADMIUM. V.

### The Electrolytic Determination of Cadmium in Cadmium Sulfate.

BY GREGORY PAUL BAXTER AND CARL HENRY WILSON.

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In confirmation of recent determinations of the atomic weight of cadmium completed in this laboratory,<sup>1</sup> the analysis of cadmium sulfate by the electrolytic precipitation of its metallic content has been carried out. Although cadmium sulfate is not particularly well suited for exact work,<sup>2</sup> owing to the danger of included mother liquor in the hydrated salt, and to the difficulty of freeing the anhydrous sulfate entirely from moisture owing to decomposition at high temperatures, yet this salt can at any rate be expected to give a minimum value for the constant in question. The

<sup>1</sup> Baxter and Hines, *THIS JOURNAL*, **27**, 222 (1905); Baxter, Hines and Frevert, *ibid.*, **28**, 770 (1906); Baxter and Hartmann, *ibid.*, **37**, 113 (1915); Baxter and Grose, *ibid.*, **28**, 857 (1916).

<sup>2</sup> Richards, *ibid.*, **33**, 890 (1911).