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THE ACTION OF IODINE ON PINENE
AND THE RESINS FORMED BY THE
ACTION OF IODINE ON PINENE.

By

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The Action of Iodine on Pinene and the Resins
Formed by the Action of Iodine on Pinene.

It has been shown (This Journal, 28, p.1461) that when pinene is treated with nascent chlorine under proper conditions, common pinene hydrochloride is first formed: then there follows a series of reactions in which chlorine is substituted for hydrogen in the pinene molecule, resulting in the formation of mono, tetra and pentachlorohydrochlorides.

The complex reactions which take place when pinene is treated with bromine and iodine indicate that perhaps under similar conditions, analogous derivatives are formed. It required but a few experiments to show that bromine, while acting quite differently from chlorine readily formed a dibromide together with higher brom-compounds (Wagner and Brickner, Ber. 32, 2302). Unless ^{is} bromine added cautiously, however, it decomposes the pinene molecule. As iodine gave more satisfactory results than bromine, it was chosen instead of bromine

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in the experiments which follow.

Armstrong(Ber. 12, p. 1756), in studying the action of iodine on pinene or turpentine, found that by following out experiments similar to those which he and Gaskell(Ber. 11, p. 151) used in studying the action of iodine on camphor, obtained by distilling at 250° C an oil representing about one half the total weight of the turpentine used. The residue he recognized as colophene but containing a considerable free iodine. It began to decompose at the above temperature liberating a number of substances, among them ethyl iodide and cymene.

The same year Armstrong and Tilden(Jour. Chem. Soc. 35, p. 733) repeated the work of Rebau obtaining colophene. They were unable, however, to obtain it from either American or French turpentine.

Nothing is known of the structure of colophene molecule further than the fact that it has the formula, $C_{20}H_{32}$, and is, therefore, a polymer of pinene. From the above formula, colophene seems closely related to common resin, the principal constituent of which is sylvinic

acid with the probable formula, $C_{20}H_{32}O_2$.

That common resin should be formed from pinene seems in perfect accord with what takes place in nature. In fact, the relationship between pinene and resin has long since been recognized. As early as 1840, Deville, (Ann. Chim. Phys. 75, p.37) succeeded in converting pinene into terebene, an optically isomer of pinene and colophene the polymer of pinene. Rebau, (Compt. rend. 76, p.1547) in studying the action of concentrated sulphuric acid on turpentine, obtained an oily liquid boiling at 318-320°C. This oil he recognized as identical with that obtained by distilling colophony. It is perhaps identical with the colophene of Deville.

When iodine is brought in contact with pinene at the ordinary temperature, a violent reaction takes place with a rapid rise in temperature and the evolution of a large amount of hydriodic acid. When equal parts of iodine and pinene are brought together cautiously, the temperature rises to 166 to 180°C, a temperature above the boiling point of pinene. If the iodine is added all

at once, the reaction is extremely energetic, liberating both iodine and hydriodic acid with explosive violence. If the temperature is allowed to rise, a complex reaction takes place resulting in the actual decomposition of some of the pinene and the forming of a number of substances, including ethyl iodide and cymene. If the iodine is slowly added, a different reaction takes place, There is no indication of decomposition but the hydriodide and the diiodide are the chief substances formed.

In the first experiments iodine was used alone and the temperature kept below 10°C. The quantity of iodine which combined with pinene was small, being less than one third the weight of the pinene taken. Even when this quantity of iodine was used and the precautions concerning the temperature taken, a vigorous reaction, to be called an explosion, followed an attempt to distil the liquid at ordinary atmospheric pressure.

The first attempt to bring about a more complete reaction at the ordinary temperature was made by using aluminum chloride with the iodine. The results were unsatisfactory as pinene hydrochloride was formed and

constantly appeared in the distillates in fractioning off iodides. The above experiment was repeated, using AlI_3 .

The above experiment was repeated using 500 grams of pure pinene with 50 grams of sublimed aluminum iodide. The aluminum iodide had to be cautiously added on account of the violence of the reaction. After the iodide had been added and the pinene cooled down to about $10^{\circ}C$, one half its weight of iodine was added a little at a time until the whole amount had been added. After standing for a day in warm room, the temperature was gradually raised to $100^{\circ}C$ and kept at that temperature for several hours. The whole was then transferred to a distilling flask and distilled at a pressure of 5 to 15 millimeters. An examination of the heavy oily liquid before the distillation began, showed that at least three substances were present. On agitating this oil with water a part was lighter than water. This proved to be a hydrocarbon though not common pinene with traces of pinene hydroiodide.

The greater part sunk to the bottom having a specific gravity much greater than water. The heavy liquid contained the hydroiodide together with the higher iodides. On distilling the liquid in vacuo a small amount of liquid passed over at 50°C. This appeared to be largely pinene. The temperature then rapidly rose to 120°C at which point about one third passed over. The first of the distillate came over colored from the presence of free iodine. The latter part, however, passed perfectly clear. An examination of the clear liquid showed it to be an iodide of pinene. It had a specific gravity of 1.447 and an index of refraction of 1.6245. It decomposed rapidly on standing, liberating iodine. Analyses gave numbers for the hydroiodide notwithstanding the fact that the properties were somewhat different from those given for the simple iodide. (Wagner and Brickner, Ber. 32,2302). Two analyses gave an average of 48.02 per cent of iodine: theoretical amount is 48.13.

Pinenediodide, $C_{10}OH_{16}I_2$.— After the above iodide had been removed the distillation was continued, the

temperature rising rapidly to 180°C. About one fifth of the total distilled over between 150 and 180°C most of the distillate coming over about 160°C. Distillation at from 5 to 10 mm. failed to yield a colorless oil. At the time of distillation it had an amber color but rapidly turned dark brown due to liberation of iodine. It has a specific gravity of 1.69. Analysis gave the following:

Found: I, 64.65 and 64.85, Calculated for $C_{10}H_{16}I_2$, I, 64.12. Since the diiodide was prepared and analyzed, Casanova, (Boll. Chim.Farm. 48,684) obtained by treating pinene with iodine in the presence of almond oil a diiodide with a yellowish color and a boiling point of 170°C.

Pinene tetraiodide, $C_{10}H_{16}I_4$:- By continuing the distillation after the diiodide had passed over, the temperature again rapidly rose 250°C. A thick heavy amber colored liquid passed over between 240 and 250°C. The liquid was redistilled at 10 mm. pressure when most of the oil passed over at near 250°C. It proved to be a semi-solid at the ordinary temperature. It was very

unstable, turning brown in a short time from liberation of iodine. Minimum decomposition occurred when the oil was thoroughly cooled in vacuo before exposing to the air. Analysis of the slightly colored oil gave the following:

Found I, 77.66 and 77.15, Calculated for $C_{10}H_{16}I_4$:
I, 78.88. The low results here are doubtless due to decomposition. It was found that the substance could not be kept even in a vacuum desiccator without rapid decomposition.

Aluminum iodide was then tried. It was found that when one part weight of aluminum iodide was added to two of pinene an energetic reaction took place. The liquid turned brown and boiled vigorously, the temperature rising to $183^{\circ}C$. The hydroiodide and the diiodide are formed.

The Resins. - The temperature was now raised to 260 to $270^{\circ}C$. At the latter point the distillation had practically stopped except a small amount of dark colored semi-solid. The whole mass in the flask began to fluoresce. After half an hour at a temperature of $270^{\circ}C$

the fluorescence was brilliant. At this point the distillation was stopped and the mass cooled down to the ordinary temperature. The substance was solid with a melting point of about 100°C . It has a light resin color, was brittle and broke with the conchoidal fracture of ordinary resin. In general properties it resembled resin with the exception of its solubility. It is only moderately soluble in absolute alcohol and slightly in 95 per cent alcohol. By this means the substance was obtained as a light yellow crystalline powder which after recrystallization had a melting point of 102°C .

In order to obtain a sufficient quantity of these polymerized forms of pinene for experimental purposes, the above experiment was repeated, using a larger quantity of pinene.

A liter of pinene, excess of iodine, and anhydrous aluminium iodide was allowed to stand for over a year in order to secure complete reaction. At the end of this time, the mixture had separated into two distinct substances, a light liquid, deeply colored red and a

heavy, black, gummy substance.

Dipinene($C_{10}H_{16}$)₂.

The liquid was subjected to fractional distillation under a reduced pressure of 8 mm. and at 172° a constant boiling point was obtained. The portion, which distilled over at this temperature, was redistilled several times, the final distillate being an almost colorless, oily, viscous liquid, with the following physical properties: readily soluble in ether or benzene, .947 sp.gr., viscosity 101 times greater than water at 25°C., optically inactive, and an index of refraction of 1.52517 at 23°.

Molecular weight determinations were made of this liquid, both by the freezing and boiling point methods, in the former benzene being used as a solvent while in the latter, ether. The results obtained were 290, 296, and 262, giving for an average, 282. If we consider the liquid as a polymerization product of pinene, theoretically, it would have a molecular weight of 272.

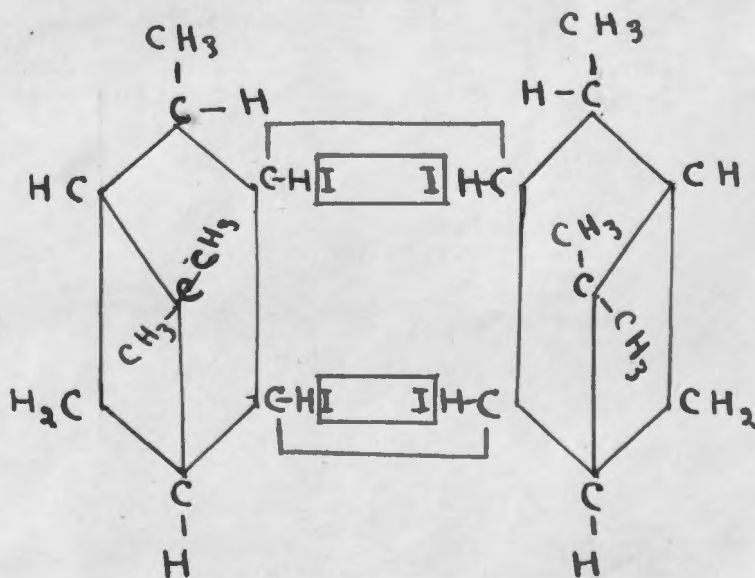
The question arises, if the liquid is a polymer of pinene, how does the polymerization take place, and the

following view is considered the most plausible:

Pinene is known to contain a double bond, and hence it has the power to take up 2 atoms of iodine. From observation it is known that these iodides break down, liberating iodine.

Now if two molecules of pinene lose their iodine, a combination may take place between the residues and the result would be a polymer of pinene.

The following graphical structure is given to show how this may take place:



Colophonene.- After the above liquid had distilled over, the distillation was carried on until a temperature of 240° was reached. On cooling, the contents of the flask solidified at once. The pure fluorescent resin has the following physical properties: melting point, 103°, easily soluble in chloroform, carbon-disulphide, benzene, slightly in alcohol, very stable; concentrated acids and alkalies do not attack it.

Molecular weight determinations were made of the colophonene by the freezing point method. Benzene was used as a solvent, which was agitated by means of an automatic stirrer. The results obtained were 533 and 546, calculated from the following formula:

$$\text{Mol. Wt.} = \frac{c \times x}{\Delta \times W}, \text{ where}$$

c = constant for solvent

w = weight of substance taken

W = weight of solvent taken

Δ = lowering of the freezing point

substituting values found in the above formula,

1st Determination

$$\text{Mol. Wt.} = \frac{500 \times .1148}{.039 \times 26.9074} = 546$$

2nd Determination

$$\text{Mol. Wt.} = \frac{5000 \times .1979}{.069 \times 26.9074} = 533.$$

Just as the liquid was considered as being built up by the union of two molecules after the iodine had been split off, so this resin is thought to have been built up by a combination of two molecules of the liquid polymer, hydriodic acid being eliminated very easily during the reaction. If this action does take place, then the formula for the resin should be $(C_{20}H_{30})_2$ and its molecular weight would be 540. From the above results, the molecular weight was found to be 539.5, thus agreeing with the theoretical value.

Graphically, the formation of the resin may be shown to take place as follows:

