

MISCELLANEOUS CHEMICAL PAPERS.*

ABSORPTION OF GASES BY PINENE.

BY W. F. SUDRO.

Kindt,¹ in 1802, obtained pinene hydrochloride by saturating well-cooled, dry pinene with dry hydrochloric acid gas. Subsequently, somewhat similar compounds were formed by the action of hydrobromic and hydriodic acids. By heating pinene with paraformaldehyde, resulting most likely in the dissociation to formaldehyde, Kriewitz² obtained an alcohol corresponding to the formula $C_{11}H_{18}O$. Various attempts have been made to combine hydrogen with pinene in order to study the reduction compounds. Pinene is reported³ as forming no characteristic derivatives when treated with CO and CO₂. The absorption of oxygen by pinene, reported first by Kingzett,⁴ has been well established as have also the resulting products formed therefrom. Papasogli,⁵ in 1876, asserted that the oils (such as turpentine oil) absorb nitrogen as well as oxygen from the air, as did also Bardsky⁶ in 1882. With the exception of the above the literature on pinene is practically devoid of any reference to the absorption of gases by that substance. Whereas the absorption of HCl, etc., has led to the formation of distinct chemical compounds, the absorption of so-called indifferent gases has thus far received little or no attention.

CARBON DIOXIDE.

In connection with the purification of pinene and the well-known oxygen absorption by this hydrocarbon with the changes subsequent thereto, the possibility that it might also absorb carbon dioxide suggested itself. Although *a priori* it did not seem probable that such absorption would take place to any appreciable extent or have any marked influence on the pinene, at all comparable to that produced by the absorbed oxygen, it seemed desirable to ascertain the facts whatever they might prove to be. Hence, a few experiments in this direction were made, more with the desire to satisfy the curiosity roused by the suggestion than with the expectation of the results which were obtained.

Thirty ccm. of pinene were transferred to the graduated tube of a Lunge nitrometer and supported by water. Carbon dioxide was then passed into the apparatus so that it came in contact only with the pinene. Whether the carbon dioxide was under slight pressure or not, its absorption was very noticeable. In 24 hours, all but 1.4 cc of 37.8 cc of gas, *viz.*, 36.4 cc CO₂, had been absorbed. The remaining gas was discharged and the apparatus recharged with an additional 30 cc of gas. After 24 hours all but 2.6 cc had been absorbed, *viz.*, 27.4 cc. The operation was repeated and after a third 24 hours all but 10 cc of 30 cc gas, *viz.*, 20 cc of CO₂, had been absorbed. In all 30 cc of pinene had absorbed 73.8 cc of CO₂ in three times 24 hours.

In the course of time the water column underlying the pinene became turbid as though the modified pinene had gone into partial solution. Tested with lime water, the aqueous layer gave a heavy precipitate. When previously boiled, no such precipitation occurred. This would seem to indicate that some of the carbon dioxide, first absorbed by the pinene, passed through the column of 30 ccm. of hydrocarbon and by it was given off to the water and that some of the modified pinene had gone with it.

* From the laboratory of Edward Kremers.

A portion of the pinene was then shaken with lime water resulting in a copious precipitate. Another portion was boiled before being shaken with lime water, but this also gave a precipitate with the reagent. This would indicate that whatever the physical or chemical union between pinene and carbon dioxide, enough of the latter remains with the pinene after heating to 155°, the boiling point of pinene, to give the characteristic reaction with lime water reagent. Fresh pinene shaken with lime water gave not even a turbidity.

In order to ascertain something more about the nature of the carbon dioxide solution in pinene, 100 Gm. of freshly distilled hydrocarbon (b. p. 155–156°) were transferred to a shaking tube and CO₂ slowly forced into the tube for 48 hours. No increase in weight could be detected. However, the liquid had acquired a faint yellowish color, also a number of small, colorless granules had been formed. The following constants were ascertained: (1) for the rectified pinene; (2) for the hydrocarbon after it had been charged with CO₂; and (3) for the charged hydrocarbon after direct distillation. Fifty-five Gm. of charged hydrocarbon upon distillation yielded 0.1724 Gm. of gas, collected by passing it through potash bulbs, corresponding to 0.31 percent of the carbonated product.

	Before charging.	After charging.	After distillation.
Sp. gr. at 20°.....	0.860	0.862	0.861
α_D^{20} for 100-mm. tube.....	24.1°	24.1°	24.1°
n_D^{20}	1.4678	1.4681	1.4680
A. V.....	0.56	0.54	0.54
S. V.....	0.0	2.2	2.1
S. V. after acetylation.....	12.0	10.8	19.0

The changes in density and refractive index are just what one might expect. However, the differences are so small that it might not be an easy matter to duplicate the exact results. The angle of rotation apparently is not affected at all.

The acid values would seem to indicate that the presence of CO₂ had a negative effect, which does not seem correct. However, the differences are so small that they may be within experimental error. Of the chemical constants the saponification values are the most striking. Moreover, they seem to indicate that it is chemically combined and not merely physically dissolved carbon dioxide which affects this constant. The saponification values after acetylation reveal the greatest differences, but these differences are of such a nature as not to admit of rational interpretation, at least at present.

In order to secure data on the relative length of time for the CO₂ to penetrate the layer of pinene the following experiments were performed.

A Lunge nitrometer was filled with lime water, 30 ccm. of pinene were allowed to flow in from the top of the tube, and 30 ccm. of CO₂ forced in, atmospheric pressure being maintained in the nitrometer. The following results were recorded:

	I.	II.
First appearance of cloudiness in the lime water.....	10 minutes	9 minutes
CO ₂ absorbed in that time.....	6 ccm.	5.2 ccm.
15 ccm. of CO ₂ absorbed in.....	50 minutes	40 minutes

A third experiment was performed in like manner to the above, the results of which are as follows:

1 ccm. of CO ₂ absorbed in	3 minutes	6 ccm. of CO ₂ absorbed in	12½ minutes
2 " " " " "	5 "	7 " " " " "	14½ "
3 " " " " "	7 "	8 " " " " "	17 "
4 " " " " "	8¾ "	9 " " " " "	19½ "
5 " " " " "	11½ "	10 " " " " "	22 "

The results are somewhat variable, being due, no doubt, to the presence of moisture in the upper portion of the tube.

For that reason a second series of experiments was run as follows: the nitrometer was thoroughly dried, 35 ccm. of pinene were placed in the bottom of nitrometer and forced up the tube by the lime water, thus preventing the upper portion of tube from becoming moistened by the lime water. The results obtained are as follows:

1 ccm. CO ₂ absorbed in	2 minutes	0.3 ccm. CO ₂ absorbed in	1 minute
2 " " " " "	3½ "	0.9 " " " " "	2 "
3 " " " " "	5½ "	1.6 " " " " "	3 "
4 " " " " "	7 "	2.1 " " " " "	4 "
5 " " " " "	9 "	2.7 " " " " "	5 "
6 " " " " "	11 "	3.4 " " " " "	6 "
7 " " " " "	13 "	4.0 " " " " "	7 "
8 " " " " "	15 "	4.6 " " " " "	8 "
9 " " " " "	17 "	5.1 " " " " "	9 "
10 " " " " "	19 "	5.6 " " " " "	10 "
11 " " " " "	22 "	7.0 " " " " "	13 "
12 " " " " "	24½ "	8.0 " " " " "	15 "
13 " " " " "	27½ "	10.0 " " " " "	20 "
14 " " " " "	30½ "	11 " " " " "	22½ "
15 " " " " "	34½ "	12 " " " " "	26 "
29.8 " " " " "	5 hours	13 " " " " "	29 "
Cloudiness noted in lime water in		14 " " " " "	32 "
24½ minutes		15 " " " " "	35½ "
		Cloudiness noted in lime water in	23 minutes

As was indicated in a previous experiment, the CO₂ evidently passes through the pinene layer into the underlying medium. Therefore, in order to ascertain the absorption power of pinene itself the following experiment was performed:

Five ccm. of pinene were placed in a dry tube and forced up by means of mercury. Fifty ccm. of CO₂ were then forced in with the following results.

1.4 ccm. CO ₂ absorbed in	5 minutes
3.7 " " " " "	20 "
4.5 " " " " "	30 "

The absorption is very slow and small in amount indicating that the pinene itself possesses but little absorptive power in reference to CO₂.

SULPHUR DIOXIDE.

A series of experiments were also performed to determine the absorption of SO₂ in pinene.

Thirty-five ccm. of pinene were placed in the lower part of a Lunge nitrometer and forced up by means of water. Thirty-five ccm. of SO₂ were then forced in with results which show remarkable absorptive capacity on the part of pinene for SO₂. In 2½ minutes all but 0.6 ccm. of the gas had been absorbed. The reaction

proceeded at such a rapid rate that it was impossible to determine the absorption rate of any intermediate volumes. The absorption became fairly constant when a volume of approximately 0.5 ccm. of gas remained.

Thirty-five ccm. of SO_2 were forced in a second time with the result that in $2\frac{1}{2}$ minutes all the SO_2 but 2.6 ccm. had been absorbed, the volume of unabsorbed gas remaining fairly constant at 1.4 ccm.

Thirty-five ccm. of SO_2 were forced in a third time. In $2\frac{1}{2}$ minutes all but 7.4 ccm. of gas had been absorbed, the volume of unabsorbed gas remaining fairly constant at 2.6 ccm. in 4 minutes.

Thirty-five ccm. of SO_2 were forced in a fourth time. All the 12 ccm. of SO_2 was absorbed in $2\frac{1}{2}$ minutes, the volume of unabsorbed gas remaining fairly constant at 3.4 ccm. in $5\frac{1}{2}$ minutes.

For the fifth time 35 ccm. of SO_2 were forced in, leaving but 15.2 ccm. unabsorbed in $2\frac{1}{2}$ minutes. The volume of unabsorbed gas became fairly constant at 4.9 ccm. in $6\frac{1}{2}$ minutes.

In order to determine the solubility of the SO_2 in water under like conditions, 50 ccm. of SO_2 were forced into a Lunge nitrometer filled with water. In $2\frac{1}{2}$ minutes 14.5 ccm. of SO_2 were absorbed, in 5 minutes 26.8 ccm. and in 10 minutes all the gas was absorbed.

The same experiment was performed using 35 ccm. of SO_2 in place of 50 ccm. In $2\frac{1}{2}$ minutes 12.4 ccm. of SO_2 were absorbed and in 5 minutes 24.9 ccm. All the gas was absorbed in $7\frac{1}{2}$ minutes.

As the solubility of SO_2 in water is great, experiments were performed to demonstrate the solubility of SO_2 in pinene itself. In these experiments the pinene was placed in a dry, clean nitrometer and forced to the upper portion of tube by means of mercury. Five ccm. of pinene were used with 50 ccm. of SO_2 . Results are as follows:

Time in minutes.	Ccm. SO_2 absorbed.		
	I.	II.	IIA.
1	15.6	15.0	2.8
2	25.8	25.6	5.2
3	33.4	34.0	7.6
4	38.0	39.0	9.3
5	41.6	42.3	10.5
6	44.0	44.6	11.7
7	45.5	45.9	12.5
8	46.5	46.7	13.0
9	46.9	47.1	13.5
10	47.1	47.4	14.0
20	16.0
45	17.6
60	18.3

Column IIA records results attained by passing 50 ccm. of SO_2 a second time into II.

The mercury supporting the pinene showed no evidence of any action of SO_2 upon it.

The pinene layer of these experiments became cloudy at the beginning of the experiment and finally became clear with a yellow color.

Part of the pinene layer was shaken vigorously with an aqueous fuchsin solution with the result that a purple precipitate was formed.

Upon boiling the pinene before adding the fuchsin solution no change was noted.

In order to establish the true relationship between pinene and SO_2 further experimental evidence must be submitted.

AMMONIA.

A series of experiments were carried out using ammonia gas.

In the first experiment 30 ccm. of NH_3 and 30 ccm. of pinene supported by water were used. The absorption was very slow, 3 ccm. of the gas being absorbed in 1 hour. The pinene layer became very cloudy at the upper portion. The water layer did not react ammoniacal with cochineal solution as indicator.

The experiment was repeated using water colored with cochineal solution. No change was noticed until a drop of water, which had adhered to the side of the tube, fell down into the water layer. A purple color was at once imparted to the cochineal water solution.

A third experiment was performed using the same volumes of pinene and ammonia gas, the pinene being supported by water (neutral in reaction) colored with cochineal solution. Extreme care was observed in preventing the water layer from coming in contact with the upper portion of the tube.

At the beginning of the experiment a cloudiness appeared at the surface of the pinene. This cloud gradually became denser and slowly settled, reaching the bottom of the pinene layer in $6\frac{1}{2}$ minutes. No change of color was observed in the cochineal layer.

In 20 minutes approximately 1 ccm. of ammonia had been absorbed. At this time the meniscus between the pinene and aqueous layers was disturbed but no change in color took place. Observations made after 30 minutes showed an absorption of 2.2 ccm., after 1 hour 3.8 ccm., and after 24 hours 7 ccm. At the expiration of 24 hours no change of color was discernible in the cochineal solution.

A part of the pinene layer, when agitated with cochineal solution, gave a very slight change of color although another part, after first having been boiled, gave no change in color.

This evidence, then, together with the fact that in the experiment the ammonia had not penetrated into the aqueous cochineal layer, would appear to indicate that the pinene held gaseous ammonia in solution but only in very slight amounts, and that evidently the majority of the gas had entered into reaction with the pinene. However, this latter statement requires further experimental data for confirmation.

The absorption of ammonia by pinene over mercury was also demonstrated. Five ccm. of pinene and 50 ccm. of gas were used. The absorption was very slow, proceeding at the following rate:

0.4 ccm. NH_3 absorbed in	5 minutes
1.0 " " " "	10 "
1.2 " " " "	15 "
1.3 " " " "	20 "
1.4 " " " "	30 "

SUMMARY.

The results incorporated in this investigation warrant the statement that pinene possesses an absorptive capacity for certain gases, in some instances to a very high degree. Whatever fact of chemical significance may be attached to this phenomenon remains to be investigated.

This investigation is to be regarded as a preliminary one for it is the intention to pursue the investigation further, using such gases as HCN, H₂S, N₂, NH₂OH, C₂H₄, C₂H₂, CO, etc., in order to obtain true physical and chemical constants.

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DIETHYLPHTHALATE.*

BY J. A. HANDY AND L. F. HOYT.

I. SUMMARY OF AVAILABLE SCIENTIFIC DATA IN THE LITERATURE.

Of the three possible isomeric diethyl esters of phthalic acid, the one of the present commercial importance is the diethyl ester of ordinary or orthophthalic acid. This ester was first prepared by Laurent¹ in 1836, who was also the first chemist to prepare phthalic acid by the oxidation of naphthalene. Laurent states:

"When one boils a mixture of alcohol ('wine spirit'), hydrochloric acid and phthalic acid (called by him 'naphthalene acid') in a retort there is obtained at the end of the distillation an oily material which remains behind in the retort. This oily material is heavier than water and I believe it to be the ester of phthalic acid, without, however, having obtained a sufficient quantity to make further investigation of it."

There is no question that Laurent actually made the ester, as the procedure he used is a standard laboratory method for ester formation.

Von Graebe and Born² in 1867 state that the only existing data regarding this ester are those of Laurent. Von Graebe and Born prepared the ester by the same process as used by Laurent, and, after carefully purifying it, found it to be a colorless and odorless oil, boiling at 295° C. (cor.), and having the elementary composition of C₈H₈(CO₂C₂H₅)₂. It may be noted in passing that this b. p. of 295° C., as determined by these chemists over 50 years ago, checks exactly with that of the commercial product on the market to-day.

Michael³ in 1879 accidentally prepared diethylphthalate by the action of phosphorus trichloride on monoethylphthalate which he was studying at the time. (The monoethyl ester is described by Michael as an oil, moderately soluble in water and unstable towards heat, decomposing on distillation into ethyl alcohol and phthalic anhydride.) Michael gives no data on the constants of the diethyl ester.

Von Graebe and Born⁴ in 1883 studied further the ethyl and methyl esters of phthalic acid. They prepared the diethyl ester by three methods: (a) Ethyl iodide and silver phthalate, (b) sodium alcoholate and phthalyl chloride, and (c) phthalic anhydride and ethyl alcohol saturated with HCl gas. The esters obtained by these three methods showed the same b. p. of 294° C. at 734 mm., with the thermometer entirely in the vapor, and the sp. gr. (values not stated) differed only in the fourth decimal.

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