

## THE CHEMISTRY OF HEPTANE AND ITS SOLUTION.\*

BY EDWARD KREMERS.

## 5. SOME THREE-PHASE OBSERVATIONS.

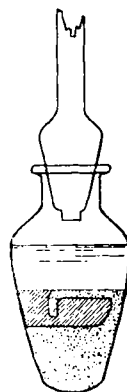
The first of these observations was made because of certain phenomena noticed in connection with an experiment made in the spring of 1919; the second in connection with certain lactone experiments that were started in the fall of 1921. Inasmuch as they have already led to similar observations with other materials and may lead to many more, it seemed worth while to record them.

I. Under date of October 14, 1919, the following observations were recorded: To 10 Gm. of molten phenol, 20 cc of heptane dried over sodium and 20 Gm. of arsenic trichloride were added. The mixture was shaken but separated into three layers. It was again shaken, this time more violently, but again separated into three layers and was allowed to stand for several days.

In earlier experiments it had been observed that arsenic trichloride is miscible with heptane in all proportions. In order to determine the solubility of crystalline phenol in heptane, the crystals had been liquefied by heat before the solvent was added. After shaking solute and solvent and allowing the mixture to cool, the excess of phenol separated in beautiful needle-shaped crystals. Upon melting these crystals and resolution of the molten phenol in heptane, several interesting observations were made which, however, have nothing to do with the triphase observations here recorded. With these observations having been made previously, the separation of the mixture of phenol, heptane and arsenic trichloride seemed rather peculiar.

When the phenomenon was brought to the attention of those colleagues of the writer who have specialized in physical chemistry, he was informed that they did not know of a similar case. One of them informed the writer that for the purpose of lecture demonstrations he had been in the habit of camouflaging, as it were, a triphase by carefully forming layers of carbon disulphide, water and petroleum. In a sense this is not a true triphase, certainly not a permanent one, for, upon shaking, the carbon disulphide and petroleum will mix, resulting in a two-phase affair.

After standing for several days, the triphase liquids were heated in an acetylation flask with glass-ground air condenser tube. At 60° no appreciable change in the depths of the layers was noticeable. Above 70° small bubbles (probably hydrogen chloride) rose, but not very many. At about 80° the two lower layers became active. The lowest layer rose at the side of the flask to the lower surface of the uppermost layer, spread out below the surface of contact and then dropped back like a water spout as indicated in the accompanying figure. A little later two such spouts formed, then three and finally they became too numerous to be differentiated. This stage was superseded by what might be called a homogeneous emulsion and, as the lower mixture began to boil smoothly, the liquid became clear. There were now two distinct layers, the two lower ones of the triphase having blended into one. The uppermost layer of the triphase seemingly had held its own for it did not appear to have diminished



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in depth. Assuming that the uppermost layer consisted principally of heptane, which boils at  $98^{\circ}$  to  $99^{\circ}$ , it is noteworthy that the lower mixture, consisting principally of phenol and arsenic trichloride, not to mention their reaction products at present, boiled actively before the upper hydrocarbon layer was in ebullition.

After about an hour's heating, the heat was withdrawn. The lower layer soon became turbid, separating into two layers so that the original triphase was reestablished. Since then the change from the triphase to diphasic by the aid of heat has been repeated again and again. At the time of writing, almost three years after the experiment was started, the change was once more effected only to return to the triphase as usual.

It would be of no little interest to determine, as accurately as possible, the composition of each of the three phases at temperatures varying from  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$  up to  $70^{\circ}$  and then to ascertain the composition of each of the two phases at  $80^{\circ}+$ . Under pressure, it may be assumed that a monophase would ultimately result with the further rise in temperature. In this connection it should be pointed out that the analyses may not prove quite as simple as would seem at first sight. Experiments as well as observations have revealed, as might be expected, that arsenic chloride is not without chemical reaction on both phenol and heptane. For a first series of determinations, however, these reaction products might be ignored for the time being and the three phases regarded as merely physical solutions.

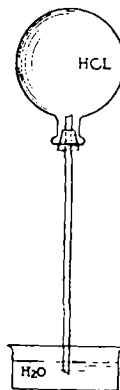
II. The second observation to be recorded in a preliminary manner was first made last fall when the writer had occasion to include the lactone, supposed by Professor E. R. Miller to be contained in catnep oil, in a series of experiments with these "inner anhydrides" of hydroxy acids. The lactone had been removed from the oil by shaking the latter repeatedly with a 10 percent potassium hydroxide solution until the volume of the oil was no longer reduced. From the aqueous alkaline solution the lactone was precipitated in the form of an oil by means of hydrochloric acid. The appearance of the non-acid aqueous layer indicated that appreciable lactone (or corresponding hydroxy acid) was held in solution or rather suspension or probably both. Hence this aqueous portion was shaken with heptane to recover lactone or acid or a mixture of both. While standing in a large separating funnel from which most of the aqueous layer had been withdrawn it was observed that three layers had formed: 1, an aqueous layer (containing potassium chloride from the reaction indicated above); 2, a yellowish oily layer, corresponding to the lactone the bulk of which had previously been separated mechanically; and 3, the heptane solution, presumably saturated with lactone, as the lactone is, no doubt, saturated with heptane or water or both (provided the one does not well nigh exclude the other).

The bulk of the lactone which had been separated from the catnep oil soon crystallized. One lot crystallized after standing a few days, a second lot after standing from eight to ten days. The oily layer referred to above as "lactone," however, has neither crystallized nor shown the signs of a crystal thus far after several months' standing. If it were removed from the water below and the heptane above it might be expected to crystallize as have other samples. Whether this experiment can be repeated with pure lactone which has since been obtained in quantity, remains to be seen.

## 6. ON THE SOLUBILITY OF SEVERAL GASES.

The solubility of the hydrohalogens in heptane has been reported on, not only in a general way (No. 1), but the strength of the respective solutions at different temperatures has been studied and reported by Sherk (Nos. 3 & 4). Among the earliest experiments recorded (No. 1) the solubility of ammonia is indicated in connection with the observation that when a heptane solution of hydrogen chloride is added to a heptane solution of ammonia, insoluble ammonium chloride is formed by addition. Since then the solubility of other gases has been studied more or less, *e. g.*, that of hydrogen sulphide as reagent for some of the heavy metals in heptane solution as oleates, etc. The object of this report is not to render a complete account of numerous experiments and observations, but to pick out a few instances that are rather striking for reasons to be pointed out.

I. Previous reports on the solubility of hydrogen chloride in heptane, qualitative and quantitative, have been referred to above. In this brief report the writer desires to supplement the earlier reports by recording an observation not without a lesson. Every beginner in chemistry is acquainted with the lecture experiment that is made in general chemistry to demonstrate the affinity of hydrogen chloride for water. A large glass flask is filled with hydrogen chloride (gas), and the inverted flask connected by means of a long tube with a reservoir of water. In order to be able to make the demonstration at a given moment, the tube is provided with a stopcock not shown in the accompanying figure. As soon as the stopcock is opened, the affinity of the water for the hydrogen chloride, or *vice versa*, becomes apparent by the rising of the water in the tube. As the water overflows, the absorption becomes more rapid due to the increased surface of the solvent. The water may even spout into the large flask until it has risen to the level of the tube. In case all of the air in the flask has been replaced by hydrogen chloride, the flask will ultimately be filled with water.



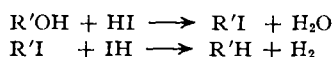
This experiment was repeated, not only with water, but with pinene and heptane. The former was chosen as an unsaturated hydrocarbon known to combine chemically with hydrogen chloride to form the so-called artificial camphor of Kindt. The latter was selected because it is saturated, hence did not admit of the ready chemical explanation applicable in the case of water ( $\text{HCl} \cdot 5\text{H}_2\text{O}$ ) and of pinene ( $\text{C}_{10}\text{H}_{16} \cdot \text{HCl}$ ). The striking fact was that the heptane rose in the tube almost as rapidly as the pinene and did not rise very much slower than did the water.

The offhand explanation is that we have here a case of physical solution. However, before making such a dogmatic assertion, it may be well to consider other possible explanations, though they may not have much probability in their favor.

Every organic chemist at all familiar with the evolution of his science knows that the point of view of organic chemistry as the chemistry of the hydrocarbons and their substitution products did not always obtain. Liebig's definition of organic chemistry as the chemistry of the compound radicles was based upon the parallel with the inorganic chemistry of acids, bases and salts, which, in turn, was nothing more than an imperfect systematization of Lavoisier's chemistry of

oxygen. Liebig's scheme had to be abandoned long before the inorganic parallel, upon which it was based, was given up. Kekulé's definition of organic chemistry as the chemistry of carbon compounds has led nowhere as a principle of systematization though it served the extremely useful purpose of drawing a hard and fast line—such as does not exist in nature—between organic and inorganic.

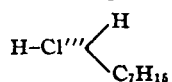
During the early days of Kekulé's definition the hydrocarbons were, in part at least, regarded as the hydrides of the alkyl radicles, thus reflecting their method of preparation symbolized by the following formulas:



In accordance with this viewpoint they were regarded as, *e. g.*, ethyl hydride, butyl hydride, pentyl hydride, etc., before their respective names became ethane, butane, pentane, etc. This viewpoint has largely been lost to the modern student of organic chemistry. True, it is a one-sided viewpoint. The reduction, by means of hydrogen iodide, of diiodides such as  $CH_3CHI_2$  (from acetaldehyde) or of  $CH_3CI_2CH_3$  from acetone might as well suggest such names as ethylenedene dihydride, aceto dihydride (in other words, alkyledene dihydrides). Theoretically, we might carry this point of view *ad absurdum*. However, it is not from the point of view of nomenclature that we wish to consider this problem.

The definition of organic chemistry that it is the chemistry of the hydrocarbons and their substitution products, a definition not at all out of harmony with facts, implies that one hydrogen after another in the hydrocarbon may be replaced step by step by an equivalent element or radicle or both. That there is a decided difference in replaceability is clearly understood, though it has been difficult to formulate general rules. Thus, *e. g.*, it was formerly supposed that in a methane hydrocarbon all hydrogen atoms connected with one carbon atom were replaced by halogen before this substituting agent attacked the hydrogen of another carbon atom. This rule was brushed aside by Victor Meyer a generation ago when he showed that, *e. g.*, in hexane he could induce the halogen to substitute one hydrogen atom in connection with each carbon atom before a second halogen combined with any of the carbon atoms in connection with which monosubstitution had taken place, provided the substitution took place in the presence of certain chemicals employed by him. No doubt these agents are to be regarded as catalyzers so long as we do not understand how they act.

All of this is reviewed for the purpose of pointing out that the hydrogen atoms of a given hydrocarbon are not necessarily alike when it comes to substitution. Hand in hand with our concepts of substitution go our concepts of radicles. Varying with the point of view, we conceive of different radicles, *e. g.*, in connection with acetic acid:  $CH_3CO.O$ —(the ionists point of view);  $CH_3CO$ —(the acyl viewpoint); etc. So in connection with the hydrocarbons it may not be amiss to revive the alkyl hydride viewpoint of the older organic chemist of the middle of the last century. If we do, it is possible to conceive of heptane forming an addition product with hydrogen chloride, though this hydrocarbon is regarded as structurally saturated. The following formula will give better expression to this idea, *viz.*,



where heptyl hydride is supposed to have been added to halogen which has assumed trivalence to make possible this addition. Naturally, all we know about the valence of the halogens causes us to believe that such a compound, if formed, will be very unstable indeed. As, *e. g.*, the HCl addition product of cineol, a completely saturated compound itself, is broken up into its components by water, so the heptyl hydride "compound" of HCl may be even less stable. This explanation is given here for what it is worth merely to guard against any dogmatic statements about purely physical solution as the only way to account for the phenomena here recorded.

II. A year or two ago, an associate in plant physiology called me up over the 'phone wanting to know whether carbon dioxide is soluble in petroleum. It was one of those questions that will cause persons with some sense of humor left to smile rather audibly. No doubt, many if not most of our examiners of candidates for the doctor's degree find questions of this sort perfectly proper, but these seldom have the saving grace of the class referred to above. The sense of humor was doubly keen in this case because the writer was in a position to give an answer to the question. This possibility demands an explanation.

In connection with work being done on pinene, the question of the solubility of carbon dioxide in this hydrocarbon came up and the only answer the writer could give was: "Try it out." The results of the experimental "try out" are recorded in a separate report.<sup>1</sup> Inasmuch as pinene is an unsaturated hydrocarbon, the possibility of chemical addition was not excluded from a purely theoretical point of view, though the results showed that any chemical compound, if formed at all, was, for the most part, exceedingly labile. It was of some interest, therefore, to ascertain something about the solubility of carbon dioxide in heptane. Benefiting by the previous experience with pinene, the heptane was directly supported in the graduated tube of a Lunge nitrometer by lime water instead of water. In a comparatively short time the CO<sub>2</sub> had passed through the heptane as was indicated by the formation of calcium carbonate in the lime water. Unfortunately the notebook in which these experiments have been recorded is lost, hence no exact data as to time can be given at present.

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#### PHYTOCHEMICAL NOTES.\*

##### 90. The Seeds of *Bixa Orellana*.

BY S. S. AIYAR.

The seeds of *Bixa orellana* L., which yield the Annatto, have been investigated repeatedly because of their pigment which is used extensively in the dairying industries. Other constituents of the seed have received little or no attention.

The immediate impulse for this preliminary investigation along more general lines was twofold: First, the close relation between this species and that yielding chaulmoogra oil<sup>†</sup> and the medical importance which the latter has acquired recently, suggested an examination of the fatty oil for chaulmoogric acid; second, a visit to Mr. Marshall's factory in this city and the sight of a large quantity of

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<sup>1</sup> W. F. Sudro, "Absorption of Gases by Pinene."

• From the laboratory of Edward Kremers.

<sup>†</sup> † For references see Bibliography at end of article.