37. On the nature of the aromatic hydrocarbons present in prehydrogenation products. Leuna, April, 1931.

Summary:

1. The nature of the aromatic hydrocarbons present in the Leuna product P 813 before hydrogenation has been investigated.

2. It has been concluded on the basis of their aniline points and hydrogenation characteristics that these hydrocarbons are most likely partially hydrogenated bicyclic hydrocarbons of the tetraline type.

38. Quantitative determination of ethylene oxide. Oppau, January 31, 1938.

Summary:

A gas containing 1% ethylene oxide was passed, in the order mentioned below, through sulfuric acid solutions of various concentrations, calcium chloride solutions acidified with hydrochloric acid and aqueous urotropine solutions. It was found that:

1. Sulfuric acid, diluted with 15 parts of water, will absorb the ethylene oxide quantitatively, even when a volume of 100 ml. of the acid solution and a gas velocity of 100 litres per hour are used. The dissolved ethylene oxide can then be determined by oxidation with bichromate. The excess bichromate can then be titrated back with iron sulfate and diphenylamine used as a Redox indicator.

2. Calcium chloride in concentrated HCl is not satisfactory.

3. A warmed (75°C.) and dilute (0.1 N) urotropine solution (100 ml. solution and 20 litres per hour gas velocity) absorbs the ethylene oxide quantitatively, but the determination of the dissolved gas gives uncertain results.

Static methods in which a given volume of the gas containing 1% ethylene oxide were left in contact with measured volumes of the above reagents. Calcium chloride solutions prepared according to Kerchow reacted very rapidly.

(1) Sulfuric acid requires 15 minutes for quantitative decomposition.

(2) Calcium chloride solutions prepared according to Kerchow required 1/2 hour for complete transformation of the ethylene oxide to ethylene chlorhydrin.

(3) Urotropine showed the peculiarity that it does not form

ethanolamine quantitatively as expected, but through some obscure reaction, forms more alkalinity than would be present by the formation of ethanolamine.

It is therefore recommended to use:

Sulfuric acid for absorption in either a stream or static gas. Accuracy on a 1% ethylene oxide content:

± 0.03% on the total sample.

Calcium chloride as a convenient reagent, to be used only statically. It gives the same accuracy as sulfuric acid.

Urotropine with both streaming and static gases, provided care be taken of using reproducible absorption conditions.

39. The vacuum rectification of the mixture phenetol-benzylamine in empty glass tubes. (Investigation to determine the efficiency of rectification columns with perpendicular contact surfaces). Leuna, October 23, 1944.

Table of contents:

I. Introduction.

II. Products

III. Theoretical.

(a) Vapor pressure curves and heats of vaporization.

(b) Equilibrium diagram.

IV. Determination of plate efficiency.

(a) Apparatus used.

(b) Method.

V. Results.

As a result of this work, the following equation has been devised:

$$h = 0.17 \frac{Wr^2M}{\gamma}$$

where W = vapor velocity in Mol. cm^{-2}

M = molecular weight

r = radius of the tube in cm.

7 = viscosity of the vapor in poises

The columnar height can be calculated by this equation also for other mixtures with good approximation.

40. Volumetric analyses with iron salts. (Ferrometry). Leuna, December, 1941.

Summary:

The system Fe "/Fe"' can be used as basis for gas analytical-oxydimetric purposes; the remaining divalent iron can be measured by a final permanganate titration. The determination with either iodine or cadmium is cited as an example and has been investigated.

The addition of barium (fresh precipitation of $BaSO_4$ in the titrating solution) in the permanganate titration was found to be helpful in the H_2S determination and will be brought into general use.

Oxidation agents can also be determined ferrometrically. The simple and sure bichromate determination can be generally used and a new method for the determination of SO_2 is described.

Comments: The addition of barium acetate in the permanganate titration serves to correct for 3 possible sources of error in the determination of H_2S by the addition of excess ferric salt according to the reaction:

$$S'' + 2\ Fe^{\cdot\cdot\cdot} = S + 2\ Fe^{\cdot\cdot}$$

and the ferrous salt produced is titrated with permanganate.

The errors are:

1. Effect of the oxygen from the air on the ferrous salt during the titration.

2. Action of the permanganate on the liberated free sulfur.

3. Recognizing the permanganate end point, which is not always easy due to the brown coloration of the solution.

It is not clear how freshly precipitated barium sulfate prevents oxidation of the ferrous salt. A statement is made, however, that the finely divided sulfur is occluded with the barium sulfate and thereby protected from oxidation by the permanganate. A white precipitate in the solution will also be of help in detecting the pink end point.

41. Investigation of ketone oils. Leuna, February 23, 1943.

Table of contents:

VI. Residual oil from hydrogenation, Leuna.

(1) Composition.

(2) Separation of the C_5 ketones.

VII. Summary.

The following analytical methods were used and improved for use in this investigation:

Ketone number: The sample is treated with a 7% solution of hydroxylamine hydrochloride in dilute methanol and the separated HCl is titrated with a $\frac{N}{2}$ NaOH solution in comparison with a similar solution of pH 4.0, using bromphenol blue as indicator. The reaction is finished after 1 hour and gives 98% of the theoretical value.

Water: The sample is titrated with iodine-pyridine-SO_2 reagent (Karl Fischer's reagent). Since the CO group reacts with pyridine-SO_2 (see Centralblatt 1941 II 783), the carbonyl group is first converted to cyanhydrin. This conversion is carried out by treating a methanol solution of the sample for 1/2 hour (to saturation) with HCN gas before the titration.

Nitrogen: The semi-micro Dumas procedure was used.

Sulfur: The sample was burned in a stream of air according to the procedure of Grote-Krekeler and the H_2SO_4 formed determined gravimetrically.

Alcohols: Determined by acetylization with glacial acetic acid-pyridine solution. Reproducible and accurate results were obtained. Small amounts of H_2O, nitriles and ketones do not affect the results, but large amounts interfere.

Methanol: The determination by acetylization depends on the accuracy of the weighing and is consequently uncertain. The same objection applies to the oxidation procedure to formaldehyde and colorimetric determination with Schiff's reagent. The latter is, however, specific for methanol.

Hydrogenation for analytical purposes: Attention is called to the fact that the hydrogenation of fractions, if carried out quantitatively, yields useful information on the composition of the products under examination.

Comments: Except for the analytical procedures outlined therein, this report should not be included among analytical documents. The material investigated was a ketone oil from the Deuben carbonization plant. This report which describes a long and painstaking research should be of interest to coking and carbonization industries.

42. Investigation on the nature of the higher boiling half of the xylenol fraction of the M-phenolic oil, Leuna, October 12, 1942.

Summary:

The higher phenols from A-middle oil can be obtained, by step wise treatment, with excess caustic soda solution, in separate extracts possessing various physical properties and elementary compositions. It has been found that:

(1) The higher phenols possess various strong acid properties.

(2) The properties and elementary compositions of the acid extracts approach these of dioxy benzenes such as oxycoumarone derivatives.

(3) The weakly acidic extracts resemble, with regard to their physical properties also in their carbon and oxygen content, alkyl phenols with open side chains. However, the hydrogen contents of the higher boiling portions are remarkably lower. It can, therefore, be assumed that alkyl phenols with unsaturated or ring forming side chains are present.

(4) Conclusions 2 and 3 should only be considered as initial assumptions, since the higher boiling fractions contain considerable amounts of nitrogen and sulfur, the effects of which had not as yet been been studied and which influence the physical properties of the fractions.

Comments: This report cannot be strictly classified as an analytical document. Since the material investigated has been obtained from the hydrogenation of the middle oil obtained from the sump-phase hydrogenation of coal, this report should be of interest to hydrogenation specialists.

43. Investigation of the K-fraction. Leuna, February 23, 1943.

Summary:

A fraction boiling between 110°-130°C. from crude isobutyl oil was investigated.

The procedure for ketones determination according to the hydroxylamine method, has been modified for the determination of isobutyrone, in that a known excess of NaOH was added and the unreacted NaOH back titrated after standing 8 hours.

A number of fractionations were carried out on a K-fraction after converting the aldehyde present into acetal with methanol. The main fractions boiled at 106-107°C., 112-114°C., 121°C., and the isobutyrone fraction at 124-124.5°C. Pure ketones were obtained by converting these fractions to semicarbazides according to a new procedure, separating the semicarbazides and treatment of the latter with HCl.

A C_6 ketone boiling at 114.2-114.4°C., a C_7 ketone boiling at 132-133°C. were separated besides isobutyrone, the main constituent. The first ketone forms azeotropic mixtures boiling at 106-107°C. with isobutanol and at 112-114°C. with hydrocarbons or ether.

Isobutyrone boils at 124-124.5°C. when 92% pure (22% in K-fraction) and constituted 46% of the fraction boiling between 120-125°C. In the fraction boiling about 125°C., besides isobutyrone, were increasing amounts (with increasing temperature) of another C_7 ketone which could not be entirely separated despite several fractionations.

The use of a higher boiling alcohol, such as isobutanol is necessary for the transformation of aldehydes into higher boiling acetals.

Analytical determinations:

It was found that the customary procedure with hydroxylamine hydrochloride for determination of ketones gave much too low results with isobutyrone, the principal product. This is due to the fact that the reaction with hydroxylamine is much slower and takes several hours to complete. A modification of the procedure in which a known excess of NaOH solution was added to the reaction mixture and the unconsumed NaOH titrated after standing 8 hours, was found to be satisfactory.

44. Determination of benzoyl peroxide. Leuna, April 29, 1942.

A number of procedures for the determination of peroxides were tested on benzoyl peroxide solutions of known concentration. These procedures were classified as follows:

1. Methods based on oxidation of $SnCl_2$.

2. Methods based on oxidation of Na_2SO_3.

3. Methods based on separation and determination of iodine.

The Vanino and Henzer method (Arch. f. Chem. u. Pharm. 253 (1915); 426) gave generally high results. The Hock and Schrader method (2. analyt. Chem. 70 (1927), 57) was also unsatisfactory.

The I.G. Hoechst method based on Na_2SO_3 oxidation gave low results with benzoyl peroxide.

The procedure of Gelisse and Herman (Ber. 58 (1926), 63) was unsatisfactory due to the fact that only the peroxide which was hydrolyzed released iodine. A later modification by these investigators gave high results.

The procedure of Kokatnur and Jelling (J. Am. Chem. Soc. 63 (1941), 1432) gave low results, particularly with larger amounts of benzoyl peroxide.

Finally, the procedure of Liebhafsky and Sharkey (J. Am. Chem. Soc. 62 (1940), 190), was modified in that the addition of sodium bicarbonate was replaced by a stream of CO_2, thus avoiding the use of water and found to be satisfactory. This method is as follows:

A 10 gram sample is dissolved in purest water-free glacial acetic acid obtainable and a 50 ml. aliquot pipetted into a 50 ml. flask. A stream of CO_2 is passed through the solution for 5 minutes, 1 g. solid KI added and allowed to stand 15 minutes. Fifty ml. water are then added and the liberated iodine titrated with thiosulfate, using starch as an indicator.

45. Patent Application. Frankfurt am Main, March 18, 1940. Procedure for the separation of aliphatic oxygenated compounds, as well as straight chain hydrocarbons containing at least 6 carbon atoms, from mixtures containing these compounds.

The procedure is based upon the fact that aliphatic oxygenated compounds as well as straight chain hydrocarbons containing at least 6 carbon atoms form well crystallizable addition products with urea, whereas branched hydrocarbons are left untouched. The reaction is carried out simply by shaking the product with a methanol solution of urea. In the case of petroleum products such as gasolines, gas oils, or lubricating oils, a methanol solution of urea is shaken with the product and the urea-saturated hydrocarbon addition product separates after a short time.

Comments: No examples on synthetic mixtures are given. Aside from the commercial possibilities, the procedure would be extremely interesting from an analytical viewpoint if it is quantitative.

46. Analytical and preparative accurate separation of hydrocarbon mixtures. Oppau, March 14, 1930.

New methods for the separation and determination of hydrocarbons in mixtures are presented. These methods were developed in the last decade in the Oppau plant in order to obtain an idea of the composition of the pressure oil which is produced under various conditions in the methanol synthesis, also the products obtained from thermal cracking.

Compounds present in the latter occur also in products from coal liquefaction. Since cracked oils are produced in large quantities in foreign countries, it was very important to establish which individual compounds were present, how these individual compounds could be exploited and what effect (from the foreign side) this will have on German economy.

The analytical procedures, also examples, are given in the appendices.

These methods are presented in the order in which they originated: the accurate separation by distillation by the Oppau apparatus, the olefins determination, the dienes, which came last, except for butadiene, the principal product of thermal cracking. Finally, an example is shown of an investigation of a complex $CO-H_2$ pressure oil.

The Hahn apparatus (Appendix 2) is used for accurate fractionation. The walls which are in contact with the vapors are surrounded by a boiling bath. The heat of the jacketed bath is not provided by the circulating vapors, but by an auxiliary electric heater. The apparatus will show the same efficiency even for small samples. Only a narrow ring space was used at first, without attached spiral, then by the provision of a two-way platinum wire spiral the path of the vapors was lengthened and the vapors forced through even at low velocities. The best solution was to use the Widmer sliding glass spiral which has been fused to the inner tube. It fits tighter but requires excellent glass blowing technique for its manufacture particularly for the larger sizes. Metal wires, such as silver, can also be used, according to the composition of the distillate. The sharpness of the separation suffers little, but these distillates are not suitable for spectroscopic investigations. Dimpled glass columns are unsuitable.

Accurate separation requires constant pressure, so that each apparatus should be provided with individual pumps. Drawings of the appparatus, pressure regulator, etc., are given in Appendix 7. The temperature is best regulated by regulating the pressure of the constant boiling point bath.

As an example of accurate fractionation the separation of equal parts of o-, m-, and p-xylene may be cited. After two fractionations about half of the o-xylene was obtained as a 95% pure product in the last fraction, the first fraction being an o-free mixture of m- and p-xylol. The ternary mixture composing the main fraction can no longer be separated. The determination of the xylene content is carried out by Raman spectrography.

These columns are more efficient than even our large plant columns. They were tested in the plant and gave at least the same order of separation.

The determination of olefins in hydrocarbon mixtures will now be discussed. Our so-called chemistry of hydrocarbons in dye and pharmaceutical chemistry is in reality a chemistry of aromatic compounds. Cracking of petroleum oils and tars, the synthesis of hydrocarbons from CO and H_2 and the products from further processes give crude materials consisting mostly of olefins. It is possible to separate individual isomers from mixtures, such as represented by a cracked oil, by accurate fractionation. The separation of the individual pentene isomers in a mixture is given as an example, and it is hoped that similar methods may be applied for the separation of thehexenes and heptenes. The problem cannot completely be solved since both pentenes and hexenes may be present in the same group and determined together. This problem has been studied for the last decade and Professor Mohr of the Ludwigshafen Research Laboratory has tried to solve it by bromination and fractionation of the bromides. This procedure was unsuccessful since bromine forms substitution as well as addition products and, moreover, many of the substitution products are unstable. The addition of HBr was then used and it was possible by means of this reaction to separate the pentenes and the paraffins into four groups. The reactions of pentenes with HBr were studied by Michael and Zeidler for the last decade.

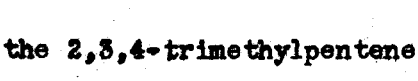
The olefins-paraffins mixtures are shaken with 4.5 N.HBr in a suitable reaction vessel consisting of a V shaped tube with two arms (Appendix 11), the bromine addition determined (description of procedure, Appendix 9), and the tertiary bromides formed by the trimethylethylene and assymetric methylethyl-ethylene decomposed with water and determined by titration of the liberated HBr. All the olefins are then brominated at 0°C. with HBr and the paraffins separated in the other arm of the apparatus and determined. Any isopropylethylene which may have been originally present can be calculated from the determination carried out after the decomposition of the tertiary bromides by taking into consideration the transposition factor 2. The excess bromine then corresponds to that taken up by the straight chain pentenes. Consequently, three pentene groups are thus separated from the paraffins, namely (1) tertiary olefins, i.e., trimethylethylene, assymetric methylethylethylene, (2) isopropyl ethylene, and (3) straight chain pentenes. (see scheme, Appendix 12).

With hexenes, a fourth group is added (IIIa) between the isopropylethylene group and the straight chains, i.e., the tertiary butylethylene. Its bromide can be saponified according to the Retrov pinacoline rearrangement into 2, 3-dimethyl-2-butanol and this alcohol changes almost completely under the conditions into tetramethylethylene. Further details are given in the analytical scheme. This method was not used for the hexenes, the separation in the V tube being incomplete.

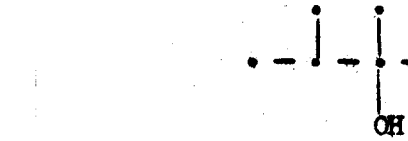
A second method (Appendix 15) for tertiary olefins is the selec- on catalytic transposition of HCl or HBr on a $BaCl_2$ or $BaBr_2$ catalyst ate tertiary olefins (Friedrichsen). It is possible, for instance to separate butenes, relatively small amounts of isobutylene as halogenide from other

A further procedure (Appendix 16) is the Tausch mercuric acetate method. This reagent reacts rapidly with primary, secondary, and tertiary olefins, but very slowly with ditertiary and tertiary olefins with adjacent quaternary groups. The reaction velocity can be measured by titration of the liberated acetic acid. (Table, Appendix 18). This procedure can be used to determine the amount of 2,4,4-trimethylpentene -1 in the presence of -2 in diisobutylene. Also, for example, it is possible to determine how much primary olefin, 1, 1-diisopropylethylene

, the 2,3,4-trimethylpentene -2



still contains by the water splitting of 1, 1-diisopropyl ethanol



Dienes interfere in the analysis of olefins, particularly in cracked products and must be determined and removed. Peroxides must also be removed before carrying out the distillation since they interfere with the tube analysis.

The dienes (Appendices 19-28) are removed by the stepwise addition of maleic anhydride and separation between each addition, identified by micro reactions or reacting with phthalic acid and determined.

As pointed out by Dr. Koch, the cyclic dienes can be determined by adding α-naphtho-quinone which reacts only slowly with straight chain dienes (Appendix 19). The acyclic dienes react with maleic acid, the branched dienes reacting first and the straight chains last (Appendix 28 and 29). These methods can be used for the separation and identification of small amounts of dienes in cracked products.

When the dienes are present in larger concentrations and the diene has been identified, it can be determined by the titration of the maleic acid produced by the water hydrolysis of the unreacted maleic anhydride (Appendix 30).

The determination of isomers of saturated paraffinic hydrocarbons is particularly difficult but in many cases very interesting as well as of great industrial importance. For instance, in the analysis of isooctane to be used for aviation gasolines, the determination of 2,4,4-trimethylpentane (which gives the product its high octane rating) is of great importance. Since the paraffins are not very reactive their molecular spectra has been used, particularly the Raman effect, for their determination. The Raman spectrum can be used for nonaromatics, when not more than 3 compounds are present in the mixture. A number of technical isooctanes were thus investigated in order to explain unexpected

differences in their octane number values. The 3 samples mentioned in Appendix 56 were fractionated in the Oppau apparatus and the fractions examined by the Raman technique. The data in the table showed that Sample II is composed mostly of a single component whereas I and III consist of 2 components in different amounts and appeared as important impurities in the first and last fractions. The main components were identified and determined by Dr. Timm as 2, 4, 4- and 2, 3, 4-trimethylpentane by Raman spectra and identified by their refractive indices. The first has an octane number of 100, the second was identified here for the first time, and after its synthetic preparation, was found to have an octane number of 95 (Appendix 35). The impurities which lowered the octane number of Sample III were found mostly in the last fraction which, however, contained also the largest amount of 2, 3, 4-trimethylpentane the octane number of which (95) does not produce any significant disturbance.

The next question was how to determine the composition of the pressure oil from the $CO-H_2$ synthesis. These products contain, besides hydrocarbons, also oxygenated compounds such as alcohols and acids among others (Appendix 41). Methods for the separation of alcohols and acids up to C_4 are known. The phthalic anhydride procedure (Appendix 42) for the determination of higher alcohols and, in general, the hydroxyl number, instead of acetic anhydride was used and found to be satisfactory. After separation of the esterified acids, the latter are transformed into methyl esters by the addition of diazomethane (since these esters hydrolyze less than the acetic esters) and the excess of unreacted phthalic anhydride can be easily determined. They are also less soluble and can be more easily separated from the hydrocarbons.

The composition of an oil is graphically shown in Appendix 50 and a comparison for several oils is given in Appendix 51.

It must be kept in mind, however, that general analytical procedures for such products cannot be given and that suitable procedures must often be worked out to suit individual cases.

Comments: This is a 60-page report including appendices found by the writer in Rector Muller-Cunradi's office at Oppau. The report itself is really a summary and has been completely translated above. It should be noted that many of the procedures are now and consequently should be of great interest to industry. Attention is particularly called to the scheme for separating some of the C_6 olefins, also the phthalic anhydride method for the determination of hydroxyl number. Procedures and apparatus are described in the appendices which should be fully translated.

References: Reports Nos. 1 to 45, inclusive, were abstracted from: Reel No. 15, Bag. No. 3043, Target 30/4.02 - Leuna; Report No. 46: Reel No. 34, Section 13, Items 11 and 12, Bag. No. 2168, Target 30/4.03 - Ludwigshafen.