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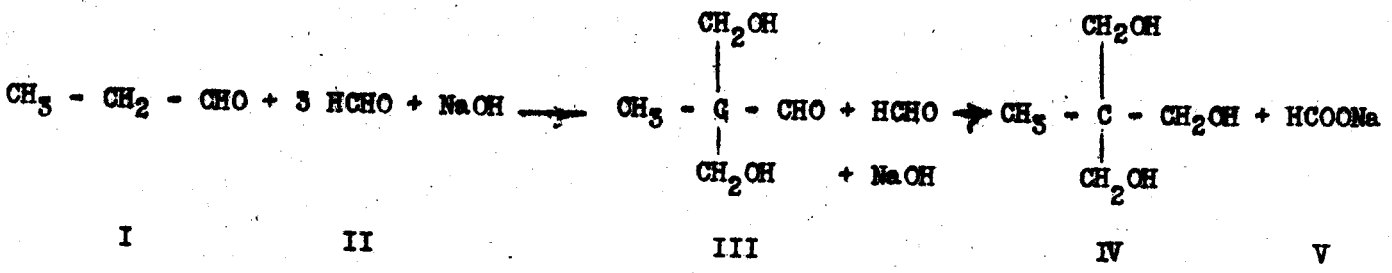
The reaction investigated is that whereby one mole propionic aldehyde (I) condenses by the addition of sodium hydroxide solution with 2 moles formaldehyde (II) to 2,2'-dimethylol-propanol, which, by the addition of a third molecule of formaldehyde is changed in accordance with the Cannizzaro rearrangement into tri-methylol-ethane (IV) and sodium formate (V).



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The heat evolved has been found to be 45,240 calories per mole propionic aldehyde. The apparatus used is described.

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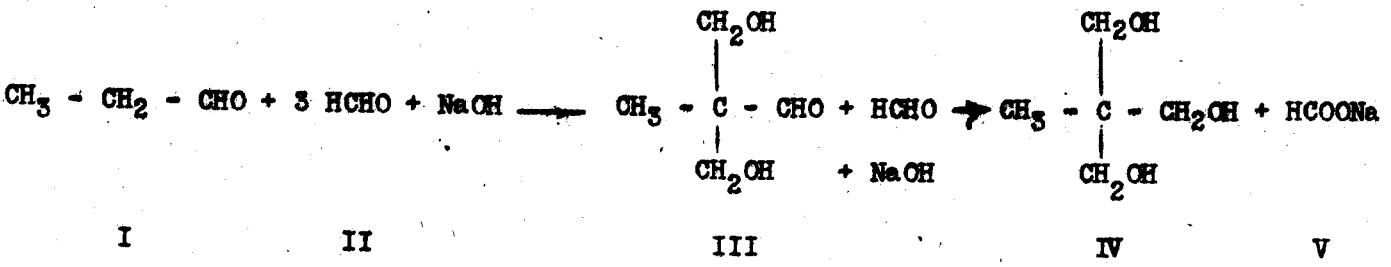

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25. Preparation, properties, and comparative capillary chemistry research on eight sulfonates and sulfates derived from hexadecane. Leuna, January, 1941.

Table of Contents:

Purpose of the research.

Choice of raw materials.

Raw material workup.

Survey of the products investigated.

(A) Sulfonated products from alcohols.

(B) Sulfonated products from olefins.

(C) Sulfonated products from saturated hydrocarbons.

Preparation of individual products.

Properties of individual products.

(A) Appearance.

(B) Solubility in water.

(C) Hygroscopicity.

(D) Resistance to hard water.

(E) Lime soap dispersive power.

(F) Wetting power.

(G) Foaming action.

(H) Detergency.

Summary.

The summary and conclusions follow:

(1) The wetting and foaming properties of the alcohol sulfates, olefin sulfonation products and cetane sulfonates prepared in this research differ very little. (The lime soap dispersive power of the alcohol sulfates in water could not be exactly determined due to their poor solubility). Cetane sulfonate was the worst of all products investigated.

(2) Wide difference in detergent properties were found, when the products were tested in white washing, using distilled water without addition of soda. The best products were the sulfates from n-cetyl alcohol also from the oxoalcohols from the cracked olefins from Ruhrchemie.

(3) The white wash detergency of individual products cannot be well differentiated in distilled water in the presence of soda. The influence of addition products such as pyrophosphates, silicates, Trillon, Tylox, etc., were not investigated.

(4) Great differences can be observed in the defattening properties of the products when used for wool washing in the presence of soda. Here again the best products are the sulfates from n-cetyl alcohol and from the oxoalcohol obtained from cracked olefins from Ruhrchemie.

(5) A remarkable fact is that the sulfided product from KW Sy(1)

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(1) Catalytic reduction of carbon monoxide at 20 atmospheres pressure and a temperature of 230-250°C. (K.W. Sy-Research, Leuna).

olefins, in the white as well as in the wool wash behave as well as the sulfate from oxoalcohol and the pentadecene fraction from the KW Sy product.

(6) The influence of salts, such as Glauber salt, on individual products was not tested in wool washing.

(7) The fact that the poor capillary chemical behavior of the sulfonates containing lyophil groups at the end of the chain as compared with the excellent properties of the products prepared by sulfochlorination (possibly due to a preponderance of inner sulfo-groups) explains the good properties of the Mepasin sulfonate.

Comments: This appears to be an outstanding research which should be called to the attention of those interested in the Oxo-process also on general detergency tests.

26. Volumetry of non-ideal gases. Mole volume of butadiene. Leuna, March, 1939.

The determination of the behavior of gases toward compression is necessary for correct calculations in gas analysis. If the properties of the gas do not follow those of an ideal gas, the deviations from the ideal gas laws must be determined and suitable corrections calculated and applied if more exact analytical results are desired.

Such work was carried out on butadiene. It was found that by subjecting known volumes of the gas (of known butadiene concentration) to pressures varying between 0 and 760 mm. a curve could be constructed showing the relation of the mole volume as function of the pressure and composition, or butadiene content.

The deviations can be neglected under 30% butadiene by volume. With the pure gas, this deviation amounts to -2.7% at 760 mm. pressure.

27. Comparison of various procedures for the determination of olefins. Leuna, February 15, 1943.

Summary:

Further tests of the methods of Kaufmann, Winkler, Hanus, and McIlhiney for olefin determinations were carried out on a large number of olefins which were of interest to Leuna, including various dienes. The Kaufmann method requires mild reaction conditions (short bromination times, small excess of bromine) to avoid substitution. Reaction times of 1 to 2 hours are necessary to completely saturate the double bonds of conjugated diolefins and other olefins showing steric hindrance. Potentiometric methods were used to determine the endpoint in the titration of dark-colored olefins.

The method of Winkler (bromide-bromate) gives high results when 2-hour reaction times are used with compounds where substitution easily occurs, but gives correct results for dienes. A bromination time of 15 to 20 minutes is sufficient for normal compounds and when substitution can easily occur. Hanus' method fails with most olefins.

The determination of iodine number according to McIlhiney does not give good results. It appears that with a number of compounds longer bromination times produce addition, but that the added bromine later splits off as HBr; thus giving too high substituted values.

With olefins of unknown characteristics, it is necessary to try various methods and the reaction conditions should be determined and varied to suit the case. The methods of Kaufmann and Winkler are the safest to use.

Comments: This report represents a large amount of work. It adds greatly to the large amount of information already available on the subject and is of interest mainly from this viewpoint. From the literature reference it appears that the Germans were unaware of the work carried out in the United States.

28. The ultraviolet colorimeter, a control apparatus for the determination of phenol and other substances. Leuna, October 2, 1941.

A control apparatus is described which operated as a photoelectric colorimeter based on short ultraviolet waves. A new filter combination, as well as a special mercury lamp was developed which gives such a strong light that the current from the photoelement can be registered and the analytical values written with a bicolored pen (50 mV.). The apparatus has been especially set up for the determination of phenol (0 to 0.1%) in cyclohexanol, but was also useful for the determination of many organic compounds (all aromatics) and inorganic compounds in non-absorbing solvents. The determination of chlorine gas when present in other gases can also be carried out by ultraviolet absorption.

Comments: Methods and apparatus are fully described including absorption curves and diagrams. The procedure is of definite interest.

29. Analytical methods for Mersol, Mersolate, and wetting agents containing Mersolates. Further developments in 1942. Leuna, January 27, 1943.

Summary:

I.G. methods Nos. 625 and 626 developed in 1941 for the determination of impurities in Mersol and Mersolate have worked very satisfactorily in practice and have made possible a determination of the Mersolate content by difference when no other foreign substance is present.

The method for the direct determination of Mersolic acid by means of isobutanol and isoamyl alcohol developed in 1942 has been of considerable interest. The various sources of errors were investigated. It has been shown that all the tested methods did not give the free Mersolic acid, but rather its sodium salt. A large number of solvents were tested for the isolation of Mersolic acid. The best solvents were found to be alcohols containing 5-6 carbon atoms; this was also the case for Mersolate D which contains disulfonates and for almost pure disulfonates.

The I.G. and the Schicht methods for wetting agents containing Mersolate were critically investigated. As a result, of this work, a conference was held with Henkel and Schicht and it was decided to investigate cooperatively the individual procedures for Mersol, Mersolate, and washing products containing Mersolate.

Comments: The analysis of similar sulfonated products has been of interest in U.S. during the war, due to the many uses found for such products. The ASTM has recently worked out procedures similar to those mentioned in this long report. While the procedures probably apply only to the I.G. specialized products, the report should nevertheless be of interest to oil chemists.

30. Determination of minute amounts of carbon disulfide. Leuna, February 1, 1943.

The determination of small amounts of CS_2 in gases with the piperdine procedure (Brennstoff Chemie, 18, 465, 1937) gives good results. The solvent used, however, is critical. Alcohol, cyclohexane, acetone, and isobutyl alcohol gave poor results. Chloroform, carbon tetrachloride, and trichlorethylene gave occasionally good, but mostly low results. Benzene and monochlorbenzene were satisfactory, and should be used for scrubbing the gas. The velocity of the gas must not exceed 15 litres per hour. After absorption is completed, the solution is washed with the chosen solvent into a 50 ml. flask, decomposed with 5 ml. of a 0.25% copper oleate solution (in benzene or monochlorbenzene) and the flask filled to the mark. The colorimetric determination by comparison with a standard solution of known CS_2 content follows immediately. The procedure can also be used for determining CS_2 in solutions.

In view of the fact that the color of the standard solution of CS_2, piperdine and monochlorbenzene is not stable (it loses 14% of its color and 29% in 15 and 29 days, respectively, in brown bottles, and 73% in 30 days in clear containers), the color standard has been matched by inorganic solutions which have been found quite satisfactory. These solutions are:

Solution I, 23.26 g. $FeCl_3$ per litre and 42.06 g. $CuCl_2$ per litre.

Solution II, 0.2472 g. KCNS per litre.

Each ml. of the KCNS solution is equivalent to 0.20 mg. CS_2.

Comments: While the procedure is not novel, the details and precautions should be of interest.

31. Separation of the di- and polysulfochlorides in Mersol by precipitation with hydrocarbons. Leuna, February 1, 1943.

The method of Asinger and Naggatz for the separation of disulfochloride from sulfochloride mixtures by cooling a pentane solution to -35°C., has been tested with regard to its use in Mersol analysis. Using a 20 g. sample and 10 times the volume of pentane, by cooling at-35°C., too large a precipitate was obtained. Examination of this precipitate by determining the hydrolyzable chlorine showed the presence of sulfur monochloride. The optimum conditions for the separation of the dichloride was found to be from 12° to 15°C.

32. Volatility of H_2S in solution of various hydrogen ion concentrations. Leuna, November 18, 1929.

Summary:

The following conclusions were made (based on the law of mass action and the corresponding equilibrium constants) regarding the properties of aqueous sulfide solutions:

(1) Alkali- and alkali-earth metals sulfide solutions are strongly hydrolyzed; a one molar Na_2S solution, for example is 90% NaHS.

(2) Alkali-earth metals sulfides are practically soluble only as hydrosulfides.

(3) All aqueous sulfide solutions, due to the hydrolysis, possess a definite H_2S concentration, the amount of which depends on the hydrogen ion concentration. A lower H_2S concentration corresponds with lower hydrogen ion concentration.

(4) All of the sulfide sulfur can be volatilized from a sulfide solution.

(5) It is not possible to separate the so-called volatile (undissociated) and non-volatile (dissociated) sulfurs. Neither can be determined separately by analytical methods.

It was shown, in the second part of this work, that the so-called

H_2S curve can be used to characterize a sulfide solution. The data for these curves are obtained by passing a stream of inert gas through the solution and plotting the amount of volatile H_2S versus the amount of inert gas used.

The H_2S curves are given for series of synthetic sulfide solutions also crude waters containing sulfides.

These curves can be used as basis for calculating the amount of H_2S which can be separated under given conditions.

33. The preparation of methoxybutadiene from crotonaldehyde acetylization products. Leuna, May 14, 1942.

Note: This report has been found among analytical reports. Although it does not properly belong here, it is nevertheless summarized for the benefit of those who may be interested.

Summary:

The report covers:

(1) Research on the acetylization of crotonaldehyde with methanol. Here, not only was the aldehyde group acetylized but also a mole of methanol has been added to the double bond. A 1, 1, 3-trimethylmethoxybutane results therefrom.

(2) Research on the splitting of methanol from 1, 1, 3-trimethylmethoxybutane, which does not, as would be expected, give crotonaldehyde acetal but methoxybutadiene.

This procedure can be used for the preparation of methoxybutadiene.

34. Methods and apparatus for the determination of water vapor in gases by means of calcium nitride. (Water vapor register I) Ludwigshafen, February 7, 1942.

I. Summary.

An apparatus for registering the amount of water vapor in air and other gases is described. This apparatus is very versatile and was especially designed for the purpose. It is based on the decomposition of the water vapor with calcium nitride with formation of ammonia and determination of the latter by a special procedure. The ammonia is washed out by a boric acid solution and the change in conductivity of the boric acid solution is a measure of the ammonia absorbed, consequently a measure of the amount of water vapor originally present in the gas.

The described apparatus was installed as water vapor register I in the Oppau plant control.

II. General considerations on the procedure and apparatus.

(1) Introduction.

(2) Quantitative test of the decomposition of calcium nitride by water vapor.

(3) Measure of the ammonia produced by the reaction.

(4) Description of the apparatus for water vapor determination.

III. Description and operation of individual parts of the apparatus.

(1) The pressure regulator for holding a constant stream of gas.

(2) The calcium nitride reaction vessel.

(3) The ammonia scrubbing set up.

(4) The conductivity cell.

(5) The conductivity measuring apparatus

IV. Apparatus standardization.

V. Influence of gas velocity, chemical composition, temperature, etc.

(1) Passage of the gas and the lag of the indicator.

(2) Research on the decomposition of calcium nitride by water vapor, using the registering apparatus.

(a) Reaction time necessary.

(b) Indicator lag.

(c) Additional observations.

(3) Test of the decomposition of H_2O into NH_3 by titration of the ammonia.

(4) Control of the reaction mass by changing its temperature.

(5) Influence of the room temperature on the apparatus indications.

VI. Use of the apparatus.

Comments: The determination of traces of water in gases is of great importance and has been the subject of much work in the United States. Many reagents have been tried and, so far, the most satisfactory procedure is by the use of the infrared technique. This report is outstanding and if the claims are justified, the Germans have developed a most sensitive procedure for the determination. The instrument, which is capable of measuring quantitites of water vapor as low as 50 mg. H_2O per m^3 of air was used at Oppau for the determination of the water content of butadiene gas and found to be quite satisfactory. The apparatus cannot be used for acid gases which react with the nitride or which affect the conductivity of the boric acid solution. It is particularly useful for the determination of the moisture content of olefinic gases.

35. The physical-chemical principles of extinction spectrography and its uses in visible and long wave ultraviolet light. Leuna, October 3, 1942.

Summary:

The possibilities of extinction spectrography are discussed and the most important apparatus described. Applications of the methods to industrial laboratories are also discussed.

Comments: An excellent and very complete discussion.

36. Efficiency of laboratory columns. Leuna, December 5, 1940.

Summary:

The efficiences of three laboratory distillation columns were determined with ethanol-water mixtures. These Rashig ring columns were 1 m. high, 35 and 50 mm. cross-section and the rings of 5 and 10 mm. cross-section. It was found that a packing of 1 m. height gave only 9-10 theoretical plates and the efficiency of the column depends on the type of packing and not on the fortuitous arrangement of the packing.

A new bell type column made of Duran glass, 50 mm. in cross-section and of the same height as the Rashig type column, showed three times the efficiency of the latter. The advantages and disadvantages of the new column are discussed. Additional work on this subject will be carried out.