

The Texas Company

Circulation of this report outside the laboratory premises is authorized only upon express permission of the laboratory superintendent.

SECRET

TOM REEL 55, BAG 2523, DOCUMENT 88

Assignment: 820

Subject: The treatment of oxo- and synol alcohols.

In Charge: Berg, Gemassmer, Meusel.

Situation as of 1 February 1944

- 1.) The preparation of wetting-agents from brown coal low temp. carbonization fuel* (Berg, Gemassmer).

First, the model experiments with benzol and C₈-oxo alcohol from cracked olefin were continued and expanded to include toluol. The condensation of the C₈-oxo alcohol with toluol and simultaneous sulfonation to alkyl-aryl sulfonic acid is somewhat more difficult than with benzol. This is due to the presence of the methyl group. The corresponding experiment with naphthalene went smoothly.

The analytic examination of the wetting-agents of the nekal-type** which are present consists in boiling with hydrochloric acid and subsequent neutralization. This allows the separation of the sodium salt of the alkyl aryl sulfonic acid from the alcohol sulfate still present (when the condensation is incomplete). From the quantity of alcohol formed after the boiling with hydrochloric acid, the extent of the condensation between the alcohol and the aromatic compounds was deduced. With benzol, the alkylation with oxo-octyl alcohol was complete; the molar

*Schwelbenzin = fuel obtained by low temperature carbonization of German brown coal, \approx lignite. (Transl.)

**A naphthalene condensation product. (Transl.)

ratio of octyl alcohol : benzol was 1:2. With toluol, the alkylation was not complete when this ratio was used, whereas with naphthaline the condensation was almost total with a ratio of 1:1. After the conclusion of the model experiments, the benzol-, toluol- and xyolol fractions of Deuben brown coal low temp. carbonization gasoline were processed under the conditions which had been found to be most favorable in the model experiments (See report of 1 February 1943) and converted into wetting-agents. The alkyl aryl sulfonates thus obtained were of brownish color and brittle. Their examination shows that, especially with the benzol fraction, the aromatic content is insufficient to allow complete condensation of the alcohol formed in the fraction by the oxo reaction. About one half of the wetting-agent consisted of alcohol sulfate if the sodium sulfate was disregarded. Conditions were somewhat better in the xyolol and toluol fraction. Experiments were begun for the conversion of the corresponding fractions of gasoline obtained by low temp. coal carbonization (OHWI Blechhammer) into wetting-agents. After conclusion of the experiments, the products will be sent to Dr. Richter for examination.

2.) Sulfonation of oxo-alcohol/hydrocarbon mixtures with SO_3 dissolved in SO_2 .

As suggested by Dr. Reisinger, experiments for the sulfonation of fatty alcohols with SO_3 were started. For these experiments, a $\text{C}_{12}/\text{C}_{13}$ oxo alcohol from primary olefin of 50% alcohol content, was used. The sulfonation was carried out with freshly distilled SO_3 dissolved in liquid SO_2 ($\text{SO}_3:\text{SO}_2 = 1:3$). The mixture was added to the alcohol/hydrocarbon mixture at -20°

to -30° in a stirring vessel. A slight excess SO_2 (5-10% as calculated on the alcohol) was added. The components which crystallize at this low operating temperature from the alcohol/hydrocarbon mixture easily re-dissolve during the course of the sulfonation.

The sulfonation followed a course analogous to that of the chlorosulfonic acid; 95% sulfonation was achieved. The alcohol sulfates obtained were somewhat more yellowish than the products obtained with chlorosulfonic acid. The advantage expected from this procedure consisted in the easier separation of the non sulfonable components before neutralization. The experiments showed however that with 200% by vol. SO_2 (the oxo alcohol-hydrocarbon mixture being taken as 100), which corresponds to about 400% as calculated on the alcohol, a separation of layers occurs. The upper layer, however, consisted mainly of the ester acid, the neutral oil and some SO_2 ; the lower layer contained only SO_2 and very small amounts of ester acid and neutral oil. The separation of the layers occurred at -25°C . By addition of methanol (which furthers the solubility) the following result was achieved: the ester acid dissolved in the SO_2 and a large portion of the neutral oil (about 70%) separated in the upper layer. The amount of methanol necessary for this separation is about 20% (the oxo alcohol-hydrocarbon mixture being = 100). The residual neutral oil in the SO_2 solution could be removed by extracting three times with pentane at -25° (pentane : SO_2 = 1:2). Here again it was noticed that the hydrocarbons may be extracted much more easily than the small amounts of non-sulfonated alcohols which were present especially in the last pentane extract. Very small amounts of ester acid

also seem to be present in the pentane. After evaporation of the SO_2 and removal under vacuum of the last traces of SO_2 at temperatures not exceeding 20° , the alcohol sulfate was prepared by neutralization with aqueous alkali solution and subsequent desiccation. The necessary addition of methanol gives rise to the problem of the separation of SO_2 from methanol and furthermore to the problem of how to avoid the loss of methanol by recovering the methanol portion which remains in the ester acid after neutralization during the desiccation; and also, its subsequent separation from water. A complete removal of the methanol from the ester acid by distillation is probably not feasible due to the temperature-sensitivity of the ester acids.

Several experiments are being carried out with the purpose of sulfonating with SO_3/SO_2 mixtures at higher temperatures in pressure containers.

3.) Alkylating sulfonation.

It was attempted in several experiments to use short chain oxo-alcohols and to arrive at longer chain alcohol sulfates by alkylating sulfonation. The presence of considerable amounts of alcohols with tertiary C-atoms (branched oxo-alcohols) indicated that the sulfonation should be guided along somewhat different lines by changing the experimental conditions; the reaction should run so as to give ester acids whose molecular weight is twice as high. The experiments were carried out with $\text{H}_2\text{SO}_4/\text{ClSO}_3\text{H}$ mixtures and the alcohol was led into the excess sulfonation mixtures. The experiments were conducted at different temperatures and with different reaction times, but since they did not lead to any consider-

able dimerization, they were discontinued.

4.) Migration of the double bond in branched olefins under the influence of cobalt carbonyl (with Dr. Asinger).

In continuation of previous experiments (see report of 1 April 1942 and illegible (1 June ?) 1943), it was attempted to prepare a well defined branched olefin with terminal double bond, with the purpose of treating it at higher temperature with cobalt carbonyl and finding out whether the double bond shift is hindered by the presence of the branches. These experiments should also clarify the problem of the difficulty of the oxo reaction with branched olefins. The preparation of a 4-methyl tetra decene (1) has already begun. The preparation is to be achieved by treating dodecyl chloride with Grignard reagent and conversion with acet-aldehyde into dodecyl alcohol (2); then, by converting the latter into dodecyl bromide (2), preparation of the Grignard compound of this bromide and conversion with allyl bromide along the lines of the Wurtz reaction.

Extraction of synol alcohols (Meusel).

By extraction of the crude synol fraction 120-250° with 2-1/2 times the amount of 73% methanol in countercurrent, a considerable amount of synol alcohols was prepared in the technical plant. The alcohols were then fractionally distilled according to their chain length. ~~At the present time, 50 liters each of~~ the (straight chain) synol alcohols C₅ to C₉ (degree of purity = 94-97%) are available; they were handed over in part to the storage room.

During the extraction itself, experiments concerning the

capacity of the Raschig column were performed. The column, which had an inner diameter of 5.5 cm, operated satisfactorily with a charge rate of 15 liters synol product and 37 liters aqueous methanol per hour. This was the limit; however, the limiting factor is not so much the diameter of the column; but rather the difficulty of the feeding and removal of the products and the consequent difficulty in the maintenance of a constant separation level.

For one ton per day of crude synol product a column of about 10 cm diameter would therefore be necessary.

Further experiments were made in order to determine whether the separation level in the column would be more advantageous in the upper or in the lower part. It must be stated here that the neutral oil, when leaving the column, is absolutely clear. When the separation level is low, the neutral oil has an OH number of 1; when the level is kept high, the OH number is 2-3; from an absolute point of view, the purity of the neutral oil is exceptionally high in both cases.

The extract is turbid in both cases. For this reason, a large, wide settling vessel was attached to the lower part of the column, in which the emulsified small neutral amounts had the opportunity of returning to the column.

When the separation level was high, the alcohols obtained were about 96% pure; when it was low, they were only 95% pure.

When the level was kept low, rather large extract droplets took shape in the oil and then migrated downwards; by funnel-shaped installations, the extraction effect may thus be bettered. But since this effect differs very little whether the level is

kept high or low, I think it best to keep the separation level in the center because it is easiest to maintain it there.

Extraction of the alcohols from the oxated yellow oil from 458a.

By distillation, only an unsatisfactory separation is possible. Experiments were made to determine whether a more advantageous separation may be achieved by extraction with methanol. Since the neutral oils to be separated contain 1 C-atom less than the alcohols while, with the synol products, they are larger by 3 to 4 C-atoms, a lesser effect is to be expected for this reason alone. Furthermore, the yellow oil contains a number of other solubility-furthering substances such as esters, aldehydes and "heavy oil." An alcohol richer extract and an alcohol poorer "neutral oil" was obtained, but the effect was far below that of the distillative separation as long as the amounts of methanol used for the extraction were kept within the limits of technical possibility.

Rehydrogenation of high boiling synol residue.

After it had been recognized that the iron contained in the crude synol residue deposited on the catalyst and thus rendered it unserviceable, the problem of whether one can hydrogenate at all by means of an iron catalyst was studied. WK 17 gave approximately the same yields as catalyst No. 3076 during one week of operation. With this catalyst too, an almost white product was obtained. The iron which deposits from the product is less active. Since the reactor had to be given to somebody else, the experiments had to be discontinued.

Mesamoll residue oil extraction.

Experiments carried out together with Dr. Geiseler showed that residual oils extracted with methanol may be sulfochlorinated as easily as those extracted with NaOH. The methanol extraction has the further advantage that residual oils containing alcohols may also be extracted.

Specific sulfonation experiments (Reisinger).

It has been attempted to condense primary aliphatic alcohols with each other in acid medium, such as for instance under the influence of concentrated sulfuric acid or chloro-sulfonic acid, along the lines of the Guerbet reaction; this reaction consists in the alkylation of one alcohol by a second one. These attempts gave rise to a series of experiments for the direct sulfonation of the above mentioned alcohols by means of SO_3 . In our search for a satisfactory solvent for the SO_3 , carbon disulfide was found to be suitable initially. Several experiments with a solution of SO_3 in CS_2 for the sulfonation of alcohols gave surprisingly good results; on the basis of these results the following assumption was justified: that the extremely reactive SO_3 could be used for direct sulfonation only with diluting agents and then only in certain well defined doses.

Very soon, disadvantages of the CS_2 solution were discovered. Above all, the problem of the removal of the heat of sulfonation required immediate attention. This question may be considered as solved if, instead of the CS_2 , liquid SO_2 is used as solvent for the SO_3 , because then the heat of sulfonation can be used for the evaporation of a portion of the solvent. The

preliminary experiments were mainly concerned with solubility problems. Among other things it was determined that even the higher alcohols, such as those of the C₁₆ range, are sufficiently soluble in liquid SO₂, at least at room temperature, i.e. in the solvent contained in the pressure tube. Sulfonation experiments with such alcohols in liquid SO₃/SO₂ mixtures have so far been promising.

As far as the solubility of free alcohol sulfates or sulfonic acids of higher C-number ranges in liquid SO₂ is concerned, it was found that this solubility is not as high as expected. However, an appreciable solubility increase may be effected by addition of even small amounts of methanol to the liquid SO₂.

A conference held with the specialists in charge of the detergent research section was held. It was decided that these experiments point the way to a new direct sulfonation process which might be of importance to the Leuna Plant; and that the experiments should be carried further into several directions. The research should therefore be organized and distributed to various experts, each one of them being assigned a certain definite subject.

1.) Alcohol sulfonation.

In this field, Dr. Berg is to collaborate. The results of the experiments will be given in Dr. Berg's activity report.

2.) Olefin sulfonation.

This field was taken over by Dr. Reisinger at least as far as the basic research is concerned. So far, the experiments were limited to the study of the heptene sulfonation as a model reaction. The heptene was prepared from a highly refined C₇ synol

alcohol by dehydration; an extensive double bond shift to all possible positions is therefore to be anticipated. The following experiment will be chosen as illustrative example: 98 g of heptene (1 mol) were dissolved in 155 cc of liquid SO_2 in a three necked flask; the flask was immersed in a cooling solution kept at a temperature between -10 and -15°C . Under violent stirring, 150 cc of liquid SO_2 containing 80 g SO_3 (1 mol) were slowly and continuously added for a period of one hour. This SO_2/SO_3 mixture had been kept in a flask which had also been previously cooled to the same temperature. The reaction liquid assumed a red brown color. Subsequently, the SO_2 solvent was removed by evaporation and its last residues were removed by vacuum treatment of the residue left in the flask. The residue itself (173 grams) is then added, after determination of its acid number, to a corresponding amount of aqueous sodium carbonate solution; in this process, about 77 g of a non-soluble oil immediately settles to the bottom of the container; this oil is then separated by ether extraction of the sodium carbonate solution. It can then be saponified into the 96% alkali salt (by means of ethyl alcoholic alkali) of a sulfur containing acid, the aqueous solution of which possesses definite capillary-chemical properties. The chemical composition of this oil may so far only be guessed at.

That sulfonation component which immediately dissolved in the alkali solution does not differ from the saponification product of the heavy oil in aqueous solution, either in its appearance or in its capillary-chemical properties. It must therefore be observed that of 98 grams of initial heptene, at most 4.5 g,

i.e. 4.6% neutral oil appears after the sulfonation. 93.5 g, or 95.5% had thus been converted into water soluble, capillary-chemical substances. Their water solution is of yellow-brown color. The olefin sulfonation experiments are being continued.

3.) Direct sulfonation of paraffins.

Experiments for the direct sulfonation of dodecane have so far failed entirely. However, it could be shown that iso-paraffins such as isohexane, may be sulfonated directly. The corresponding model experiments were performed with molar quantities used in the heptene experiments. It was observed here that a homogeneous solution in SO_2 at -10° of the type obtained in the heptene experiments, could not be achieved. This factor must be considered in the critical study of the small sulfonation conversion: only 50% isohexane could be converted in the sulfonation experiments. Here too, water soluble and capillary-chemical substances are formed, which are identified as sulfonic acids. A formation of higher molecular secondary products (polymerization, alkylation) could so far not be observed. The experiments are being continued.

Signed

/GEMASSMER/ /BERG/ /MEUSEL/