Reduction of NITROBENZENE with SULFITE WASTE LIQUOR

Conditions necessary for the reduction of nitrobenzene by sulfite waste liquor and alkali have been studied. Variables considered were: time of reaction, temperature, concentration and order of introduction of reactants, and nature of sulfite waste liquor. The reaction mechanism has been investigated, and sodium p-azobenzenesulfonate was identified as an important product of the reaction when carried out at atmospheric pressure. Other reduction products obtained in high yield, depending upon conditions, were azoxybenzene, azobenzene, and aniline. Optimum conditions for maximum yield of each have been determined. Sulfite waste liquor is indicated as a good substitute for zinc dust in the preparation of a mixture of azoxybenzene and sodium p-azobenzenesulfonate for direct conversion to benzidine. Vanillin is a by-product of the simultaneous oxidation of the lignin in the sulfite waste liquor, and recoveries up to 25%, based on lignin, are obtained. Material balances were made on the nitrobenzene, lignin, and methoxyl entering into reaction. The re-use of desulfonated lignin resulting is considered.

R ECENTLY Schulz (4) and Freudenberg, Lautsch, and Engler (2) reported the preparation of vanillin in greatly increased yields when sulfite waste liquor or isolated calcium lignosulfonate was oxidized by nitrobenzene and alkali at high temperatures and pressures. Although Schulz's patent was directed toward the production of vanillin, an 80% yield of azobenzene was noted. Freudenberg *et al.*, being interested only in the oxidation of the lignin, noted the formation of aniline and azoxybenzene, but recorded no yields.

The present shortage of vital materials makes an investigation of the reducing action of sulfite waste liquor desirable. There is a shortage of the reducing agent, zinc, and a need for a cheap reducing agent. The possible use of sulfite waste liquor to replace zinc in certain organic reduction processes would be of value to the chemical industry in supplying immediately and without expensive modification of present processes an almost inexhaustible amount of organic reducing agent.

Because it was known that nitrobenzene could be reduced by sulfite waste liquor, nitrobenzene was used as the substrate in the first quantitative studies of sulfite waste liquor as a reducing agent. The purpose of this investigation was to study the reducing action of sulfite waste liquor upon nitrobenzene and to determine the conditions necessary for obtaining maximum reduction and maximum yields of the various reduction products, with special emphasis on the production of aniline and the reduction products which could be converted easily to benzidine.

The first experiments were arbitrarily patterned after Freudenberg *et al.* (2). The nature and yields of reduction products under varying conditions of time, temperature, concentration ratio, and type of liquor were studied at superatmospheric pressure. Azobenzene and aniline were the chief reduction products at 160° C. for reaction times of 1 hour and longer. For shorter reaction times at lower temperatures (130° C.) and in cases of excessive dilution, azoxybenzene and a new reduction product identified as sodium *p*-azobenzenesulfonate were obtained in amounts depending upon conditions. These observations and the fact that the reduction products were more easily isolated from the re-

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actions at 130° C. led to the investigation of the reduction of nitrobenzene with sulfite waste liquor at reflux temperatures and atmospheric pressure. Under these conditions azoxybenzene and sodium p-azobenzenesulfonate were obtained as the chief reduction products.

ATMOSPHERIC PRESSURE

A standard experiment for comparison was arbitrarily set as a mixture of 350 grams of sulfite waste liquor (containing 50% or 175 grams of sulfite waste liquor solids), 90 grams of sodium hydroxide dissolved in 90 grams of water, and 72 grams of nitrobenzene; this mixture was heated at the boiling temperature and atmospheric pressure with efficient stirring for 8 hours under a reflux condenser. The effect of different conditions was studied by changing one or more of the following: time of reaction, temperature, concentration of reactants, order of introduction of reactants, nature of sulfite waste liquor. Differences in the total solids content of the various liquors were adjusted by varying the amounts of liquor and water. In some cases the liquors had to be further concentrated.

PROCEDURE. The sulfite waste liquor was placed in a three neck flask of one-liter capacity fitted with a reflux condenser and a mechanical stirrer under a mercury seal. Stirring was started, and sodium hydroxide solution was added. The flask was then closed by a rubber stopper carrying a thermometer reaching below the surface of the reaction mixture. Nitrobenzene was added slowly through the top of the condenser, whereupon the temperature of the mixture rose. The flask was placed on a sand bath heated by an electric hot plate, and the mixture was brought to a gentle boil within approximately an hour. The temperature rose to 103-114° C., depending upon the concentration of reactants. Boiling and stirring were continued for the time of the experiment, and the reaction mixture was then allowed to cool with When cool, the mixture was steam-distilled until stirring. practically no oily material passed over with the steam. The steam distillate was acidified with dilute hydrochloric acid to dissolve the aniline, and was then extracted with ether to remove unreduced nitrobenzene and the azoxybenzene that was volatile with the steam. The ether solution was dried with anhydrous sodium sulfate and, after the ether was distilled on the steam bath, the oily residue was fractionated under reduced pressure to recover pure nitrobenzene and azoxybenzene.

The acid aqueous solution was made alkaline with sodium hydroxide, saturated with sodium chloride, and extracted with ether. The ether extract was dried with anhydrous potassium carbonate, and the ether was removed by distilling on the steam bath. The light oil which remained was practically pure aniline and was weighed as such. If desired, the oil was distilled under reduced pressure to recover very pure aniline. The residuel alkaline solution from the steam distillation was

The residual alkaline solution from the steam distillation was centrifuged after cooling. The clear centrifugate was extracted with ether to recover a small amount of azoxybenzene which did not settle out on centrifuging. This recovered material was added to that collected from the steam distillate. The wet centrifuge residue (inorganic material, some lignin material, sodium *p*-azobenzenesulfonate, and azoxybenzene) was extracted with warm acetone. The azobenzenesulfonate and azoxybenzene dissolved in the acetone. The acetone was distilled almost to dryness, the residue was taken up in ether, and the mixture was filtered. Pure sodium *p*-azobenzenesulfonate, which is insoluble in ether, was obtained in this manner. The ether extract was dried with anhydrous sodium sulfate and distilled to remove ether. The azoxybenzene was added to the product obtained above.

The centrifugate, after ether extraction, was made up to a definite volume. An aliquot (usually 5%) taken for the vanillin determination was acidified and exhaustively extracted with ether. The ether solution was extracted with 5% sodium bisulfite solution to remove aldehydes. The bisulfite solution was acidified with sulfuric acid, and sulfur dioxide was removed by warming on the steam bath and aspirating with air under reduced pressure. The acid solution of vanillin was heated on the steam bath, filtered if necessary, and treated with a warm filtered solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid. Brickred vanillin 2,4-dinitrophenylhydrazone precipitated immediately. The precipitate was digested for half an hour on the steam bath, allowed to stand for several hours, filtered through a sintered crucible, dried at 105° C., and weighed. Vanillin was reported as the percentage of original lignin present in the sulfite waste liquor. The other ether-soluble substances originating from the lignin were not investigated.

SUPERATMOSPHERIC PRESSURE

The conditions of these experiments were also varied from an arbitrary standard. The standard reactant ratios were the same as those of the atmospheric pressure experiments, but the procedure was different:

Forty-five grams of sodium hydroxide were dissolved in 45 grams of water. This solution was mixed with 175 grams of sulfite waste liquor containing 87.5 grams of solids; the resulting mixture was introduced into a stainless-steel tube of approxi-mately 400-cc. capacity. Thirty-six grams of nitrobenzene were added, and the tube was sealed with a plug carrying a thermom-A lead gasket was used to effect a seal. The tube was eter. turned end over end several times to mix the contents and then placed in the electrically heated rocker. Rocking was com-menced, and the temperature was gradually raised to the desired temperature and kept at that point for the time of the exper-iment; the mixture was then allowed to cool in the rocker. When the temperature reached 50° C., the tube was removed from the rocker, cooled under tap water, and opened. The contents were transferred to a round-bottom flask and steam-distilled until no oily droplets passed over with the steam. The steam distillate was acidified with hydrochloric acid to dissolve the basic substances which were separated from the neutral sub-stances by extraction with ether. The aniline was recovered from the acid solution as described above. The neutral substances (azobenzene and, under some conditions, nitrobenzene and/or azoxybenzene) were obtained by drying the ether solution with sodium sulfate and removing the ether by distillation on the steam bath. On cooling, the azobenzene crystallized and was The vanillin was recovered by acidifying the weighed directly. The vanillin was recovered by acidifying the alkaline residue from the steam distillation and extracting with It was determined by the method outlined above. ether.

The data on a few of the experiments are listed in Table I. The following abbreviations are used:

| SPABS | Sodium p-azobenzenesulfonate |
|-------|---|
| SWL | Sulfite waste liquor |
| LCML | Laboratory-concentrated Mitscherlich liquor |
| CSWQC | Concentrated softwood quick-cook liquor |
| CNMS | Concentrated neutralized Mitscherlich spruce liquor |
| CNQCP | Concentrated neutralized quick-cook poplar liquor |

The more drastic reductions always gave reaction mixtures which could not be separated easily, and tars usually separated from the alkaline solutions. These facts lead to the inference that one or more of the nitrobenzene reduction products probably condense with lignin or one or more of its fission products; the result is lower recoveries of reduction products and lower yields of partially desulfonated lignin.

NATURE OF SULFITE WASTE LIQUOR

The preliminary experiments were made with both Mitscherlich and quick-cook spruce sulfite waste liquors and their concentrates obtained by evaporation under reduced pressure. Little difference was found between the liquors under identical reduction conditions. For a large-scale investigation it seemed desirable to determine whether significant differences existed in the reducing action on nitrobenzene of the several sulfite waste liquor products available commercially. Accordingly the following products were obtained for experiment: Mitscherlich spruce liquor concentrated by evaporation at atmospheric pressure; Mitscherlich spruce liquor neutralized to pH 8 with sodium hydroxide and evaporated at atmospheric pressure, maintaining the pH with sodium hydroxide; quick-cook spruce liquor evaporated under the same conditions; quick-cook softwood (90% white spruce and 10% balsam fir) liquor neutralized with magnesium oxide to pH 5.8 and evaporated in a double-vat evaporator; and quick-cook softwood liquor solids obtained by vacuum drum drying of the last mentioned concentrated liquor.

Experimental data indicated that the various liquors reacted in substantially the same manner in the nitrobenzene reduction reaction when compared on the solids basis. The hardwood poplar liquor was slightly more reactive as a reducing agent and at the same time gave higher aldehyde yields. In the case of the hardwood waste liquor studies, the aldehyde fraction was a mixture of vanillin and syringaldehyde. From the methoxyl contents of the various 2,4-dinitrophenylhydrazone precipitates, aldehydes were found present in the ratio of approximately 1 part syringaldehyde to 2.5 parts vanillin. This value varies markedly from the ratio of syringaldehyde to vanillin of 3 to 1 found by Creighton, McCarthy, and Hibbert (1) in the oxidations of hardwoods by nitrobenzene and alkali. The fact that these authors obtained 40 to 45% aldehydes from drastic oxidations of hardwoods and only 25% aldehydes from oxidation of spruce wood concurs with our findings.

ORDER OF ADDITION OF REACTANTS

During the investigation an attempt was made to obtain a single reduction product from the reaction mixture by changing the order and manner of introduction of the various reactants. A series of experiments proved that nothing could be gained by attempting to increase the yield of one reduction product at the expense of the others in this manner. The addition of nitrobenzene over a period of 3 or 6 hours or the gradual addition of the sulfite waste liquors with or without sodium hydroxide had little influence on the course of the reaction. The addition of sulfite waste liquor over a period of time resulted in a lower vanillin yield. This lower yield was due to the fact that a large part of the lignin was subjected to oxidizing conditions for too short a time. In general, the decreased reaction time of one of the reactants resulted in an actual decrease in the amount of total reduction products.

CONCENTRATIONS OF REACTANTS

' It soon became evident that the conditions selected for the standard experiment were far from ideal. The pattern for successive experiments was formulated from day to day. Promising experiments were studied in detail, and those which appeared to offer little success were dropped without further investigation. A decrease in the sodium hydroxide ratio resulted in a higher aniline yield but a large drop in the azoxybenzene and vanillin recoveries. Under these conditions sodium p-azobenzenesulfonate was formed only in minute quantities.

A decrease in the sulfite waste liquor ratio or, in other words, an increase in both the nitrobenzene and sodium hydroxide ratios, had an opposite effect (Figure 1). Under these conditions, the aniline yield was lowered, and azoxybenzene and vanillin yields were increased considerably; the azoxybenzene yield of 67.5% was the highest recorded. Because both azoxybenzene and sodium *p*-azobenzenesulfonate are intermediates in the manufacture of benzidine, these conditions can be used advantageously for preparing a mixture of the two compounds for direct conversion to benzidine.



A series of experiments indicated that dilution without changing the ratio of the other reactants resulted in greatly increased yields of sodium p-azobenzenesulfonate. At the same time, dilution decreased the total reduction of nitrobenzene, probably because of the lower reaction temperature.

Under standard conditions at 160° C., dilution caused little change. However, at the higher temperature using half quantities of waste liquor and alkali, dilution produced an increase in the yield of azobenzene at the expense of aniline. These results paralleled the atmospheric pressure reductions which yielded increased azoxybenzene recoveries at the expense of the aniline.

Schulz (4) noted an 80% recovery of azobenzene as a byproduct of his process for making vanillin by the oxidation of sulfite waste liquor by nitrobenzene and alkali. Inasmuch as this yield is much higher than any obtained in the present work, the reduction of nitrobenzene by sulfite waste liquor and alkali, using Schulz's proportions at atmospheric and higher pressures, was investigated. The results indicated that little reduction took place at atmospheric pressure, even for long reaction times (Figure 2). Since these reaction mixtures were very dilute, yields of sodium *p*-azobenzenesulfonate were increased. The vanillin yields were not affected. Schulz's proportions at 160° C. for 1 hour gave 15.6% pure sodium p-azobenzenesulfonate. This was an unusual result for pressure experiments but is related to the fact that great dilution favors azobenzenesulfonate formation. The 80% yield of azobenzene reported by Schulz (4) could not be realized; in fact, the conditions which he reported for this yield actually give a much lower yield than other temperatures and reaction times. These proportions at the higher temperatures caused increased vanillin yields (Figure 4).

TIME OF REACTION

At atmospheric pressure the yields of aniline generally increase with time. The yields of azoxybenzene increase up to approximately 10 hours and then drop off in favor of aniline. The sodium p-azobenzenesulfonate yields increase somewhat with time but are primarily a function of concentration ratios. Vanillin recoveries increase slightly with time.

Using half quantities of poplar liquor at atmospheric pressure, the azoxybenzene and sodium *p*-azobenzenesulfonate yields increase slightly with time. The aniline recovery appears to pass through a maximum between 6 and 14 hours, and the nitrobenzene recovered approaches zero at about 14 hours.

The solid curves in Figure 3 give the results of experiments on the effect of time on the reduction of nitrobenzene under standard conditions at 160° C. These results imply that a heating time of approximately 30 minutes between 100° and 160° C., with 2 hours at the latter temperature, gives the optimum yield (67.5%) of aniline with this reaction mixture. This was the highest aniline yield in any of the experiments.

A fairly sharp drop in the azobenzene yield during the first 2 hours—corresponding to the sharp increase in aniline yield during the same time—indicates that the azobenzene is further reduced to aniline by this reaction mixture at 160° C. The fact that the yield of aniline drops off after 2 hours and also that the total nitrobenzene accounted for drops off during the same time interval suggests that the aniline condenses with some other substance in the reaction mixture. The pressure reductions differ from the experiments performed at atmospheric pressure in that conditions are employed under which neither nitrobenzene nor its reduction products can escape except in the form of nonidentifiable products.

The effect of time on the reduction at 160° C. was also studied, using half quantities of sulfite waste liquor (Figure 3). Total recoveries were much better. Both aniline and azobenzene yields increased and finally totaled 100% after 3 hours. Azobenzene was the chief product of this reaction, obtained in 65% yield after 2 hours. In this series the aniline did not increase at the expense of the azobenzene. However, the series was not studied for more than 3 hours, after which time it is possible that the yields would have followed the pattern of the last series. The vanillin recovery was highest at 1/6 hour and decreased slightly with time. This suggests that the vanillin may condense

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TABLE I. REPRESENTATIVE REDUCTIONS OF NITROBENZENE BY SULFITE WASTE LIQUOR

| | Reactants, Grams | | | | | | Azoxy- ben- | | Nitrobenzene, % | | Total Re- duction | | · · · · | |
|---|--|--|--|---|--|---|--|---|---|--|---|---|---|--|
| Expt. No. | SWL | Nitro- benzene | NaOH | Water | Temp., °C. | Time, Hr. | Aniline, | zene, % | SPABS | Re- A | for | Obsvd., | Vanillin, | Remarks |
| 13 15 17 18 19 20 23 33 | 175 350 175 350 350 350 350 350 350 | 72 72 72 72 72 72 72 72 72 72 | 45 90 45 90 90 90 45 90 | 90 90 90 90 90 90 90 90 | 104 105 104 105 105 105 104 105 | 19 14 10 23 5 8 5 8 8 | 11.024.112.518.023.925.416.720.0 | $\begin{array}{c} 30.5\\ 38.9\\ 34.0\\ 34.6\\ 46.0\\ 52.7\\ 27.1\\ 44.0\end{array}$ | 22.9 28.0 3.1 25.2 29.9 23.9 28.2 4.4 | $\begin{array}{c} 30.5 \\ 8.2 \\ 49.3 \\ 0 \\ 0 \\ 28.4 \\ 29.3 \end{array}$ | 94.9 99.2 98.6 97.8 99.8 101.0 100.0 97.7 | $\begin{array}{c} 64.4\\ 91.0\\ 49.6\\ 97.8\\ 99.8\\ 101.0\\ 71.6\\ 68.4 \end{array}$ | $12.6 \\ 14.3 \\ 11.6 \\ 10.1 \\ 16.3 \\ 10.5 \\ 4.7 \\ 9.0$ | ^{1/2} NaOH and ^{1/2} SWL, LCML Standard expt., LCML ^{1/2} NaOH and ^{1/2} SWL, LCML Standard expt., LCML Standard expt., LCML Standard expt., LCML ^{1/2} NaOH, LCML SWL added gradually over 4 hr., |
| 34 | 350 | 72 | 90 | 90 | 100~5 | 8 | 10.8 | 21.6 | 3.6 | 53.6 | 89.6 | 36.0 | 8.6 | SWL + NaOH + H ₂ O added |
| . 37 | 350 | 72 | 90 | 90 | 105 | 8 | 14.9 | 43.1 | 9.2 | 24.9 | 92.1 | 67.2 | 9.9 | Nitrobenzene added over 3 hr., |
| 43 | 350 | 72 | 45 | 90 | 104 | 8 | 13.7 | 8,3 | 1.0 | 69.6 | 92.6 | 23.0 | 1.5 | ¹ / ₂ NaOH; nitrobenzene added |
| $\begin{array}{c} 44 \\ 45 \end{array}$ | 350 350 | 72 72 | 45 45 | 90 180 | 104 10 3 | 8 8 | $\substack{18.4\\20.2}$ | $\begin{array}{c} 28.4 \\ 28.7 \end{array}$ | $1.5 \\ 1.4$ | $34.8 \\ 38.8$ | $\begin{array}{c} 83.1 \\ 89.1 \end{array}$ | $\begin{array}{c} 47.3 \\ 50.3 \end{array}$ | 3.1 1.1 | ^{1/2} NaOH, CSWQC ^{1/2} NaOH, twice amount of added H-O. CSWQC |
| 46 47 | 175 175 | 72 72 | 90 90 | 90 180 | $\begin{array}{c} 105 \\ 104 \end{array}$ | 8 8 | $\substack{12.1\\10.1}$ | $\begin{array}{c} 65.0\\ 55.2 \end{array}$ | $\frac{4.2}{8.6}$ | $\begin{array}{c} 9.1 \\ 19.1 \end{array}$ | $\begin{array}{c} 90.4\\ 93.0 \end{array}$ | $\begin{array}{c} 81.3 \\ 73.9 \end{array}$ | $\begin{array}{c} 9.0\\ 11.4 \end{array}$ | 1/2 SWL, CSWQC 1/2 SWL, twice amount of added H ₂ O, CSWQC |
| 51 | 350 | 72 | 90 | 90 | 105 | 8 | 18.2 | 40.5 | 9.3 | 26.0 | 94.0 | 68.0 | 10.5 | Nitrobenzene added over 3 hr., |
| 52 | 350 | 72 | 90 | 90 | 105 | 8 | 20.4 | 47.6 | 4.9 | 24.2 | 97.1 | 72.9 | 8.2 | SWL added gradually over 4 hr., |
| 53 | 350 | 72 | 90 | 355 | 103 | 8 | 13.6 | 31.8 | 14.6 | 31.7 | 91.7 | 60.0 | 9.2 | Twice amount of total H ₂ O, CNMS |
| 54 | 350 | 72 | 90 | 355 | 103 | 8 | 13.2 | 20.0 | 18.4 | 29.6 | 81.2 | 51.6 | 11.7 | Twice amount of total H ₂ O; nitro- benzene added over 3 hr., CNMS |
| 55 | 350 | 72 | 90 | 355 | 103 | 8 | 13.1 | 27.6 | 7.1 | 41.4 | 89.2 | 47.8 | . 7.9 | Twice amount of total H ₂ O; SWL added gradually over 4 hr., CNMS |
| 56 57 58 60 62 63 64 69 | 175 175 175 122 122 122 122 350 | 72 72 72 72 72 72 72 72 72 | 90 90 90 72 72 72 90 | 90 90 90 299 299 299 355 | 105 105 105 105 103 103 103 103 | 6 8 10 14 6 8 16 8 | 2.412.114.020.96.47.78.126.1 | $\begin{array}{r} 42.8\\ 56.7\\ 67.5\\ 62.5\\ 13.3\\ 19.5\\ 24.8\\ 22.1 \end{array}$ | 3.9 7.0 5.9 8.6 7.3 7.8 9.3 22.7 | $17.8 \\ 2.5 \\ 2.2 \\ 0 \\ 67.8 \\ 64.7 \\ 54.9 \\ 24.9 \\ 24.9 \\$ | 66.9 78.3 89.6 92.0 94.8 99.7 97.1 95.8 | $\begin{array}{r} 49.1 \\ 75.8 \\ 87.4 \\ 92.0 \\ 27.0 \\ 35.0 \\ 42.2 \\ 70.9 \end{array}$ | $\begin{array}{c} 9.3 \\ 15.4 \\ 8.7 \\ 12.8 \\ 12.1 \\ 15.7 \\ 15.7 \\ 12.7^{a} \end{array}$ | 1/2 SWL CNMS 1/2 SWL, CNMS 1/2 SWL, CNMS 1/2 SWL, CNMS 1/2 SWL, CNMS Schulz's proportions, (4), CNMS Schulz's proportions, CNMS Twice amount of total H20 Twice amount of total H20 CMCC2 |
| $\frac{74}{76}$ | $\begin{array}{c} 175\\175\end{array}$ | 72 72 | 90 90 | 90 278 | $\begin{array}{c} 105 \\ 103 \end{array}$ | $\begin{array}{c} 10 \\ 14 \end{array}$ | $\begin{array}{c} 19.9 \\ 12.7 \end{array}$ | $\begin{array}{c} 60.0 \\ 27.3 \end{array}$ | $\begin{smallmatrix}&6.2\\12.1\end{smallmatrix}$ | $\begin{smallmatrix}&2.6\\&39.3\end{smallmatrix}$ | $\frac{88.7}{91.4}$ | $\substack{ 86.1 \\ 52.1 }$ | $^{17.3^a}_{28.2^a}$ | ^{1/2} SWL, CNQCP ^{1/2} SWL, twice amount of total H ₂ O, CNOCP |
| $ \begin{array}{r} 111 \\ 112 \\ 113 \\ \end{array} $ | 11,550 5,660 5,660 | 2040 2040 2040 | 2490 2490 2490 | 0 3,395 13,250 | 106 105 103 | $11 \\ 7.5 \\ 10$ | $12.8 \\ 12.7 \\ 7.5$ | 60:0 27.5 9.1 Azo- benzen | 15.3 24.1 20.1 | $0.5 \\ 30.3 \\ 53.8 \\$ | $ 88.6 \\ 94.6 \\ 90.5 $ | $88.1 \\ 64.3 \\ 36.7$ | 26.7ª 29.8ª 29.2ª | Small pilot-plant expt. Small pilot-plant expt. Small pilot-plant expt. |
| 79 | 175 | 36 | 45 | 45 | 160 | 1/6 | 30.9 | 51.4 | 0 | 0 | 82.3 | 82.3 | 13,8 | Standard expt., CNMS |
| 81 82 83 85 | $175 \\ 175 $ | 36 36 36 36 | 45 45 45 45 | 45 45 45 45 | 160 160 160 170 | 2 3 4 1 | $67.5 \\ 59.2 \\ 54.7 \\ 53.2 \\ $ | $ \begin{array}{r} 6.4 \\ 14.2 \\ 1.8 \\ 4.5 \\ \end{array} $ | 0 0 0 | 0 0 0 0 | 73.9 73.4 56.5 57.7 | 73.9 73.4 56.5 57.7 | ь ь ь | Standard expt., CNMS Standard expt., CNMS Standard expt., CNMS Standardproportions, higher |
| 87 | 87.5 | , 36 | 22,5 | 90 | 160 | 8 | 18.0 | 49.5 | 0 | 0 | 67.5 | 67.5 | 11.9 | ¹ / ₂ SWL and NaOH; twice |
| 88 89 91 92 93 94 95 97 99 | $175 \\ 87.5 \\ 87.5 \\ 61.2 \\ 61.2 \\ 61.2 \\ 175 \\$ | 36 36 36 36 36 36 36 36 36 | 45 45 45 36 36 36 45 45 | $\begin{array}{r} 0 \\ 45 \\ 45 \\ 149.5 \\ 149.5 \\ 149.5 \\ 45 \\ 45 \\ 45 \end{array}$ | 160 160 160 160 180 200 160 160 | 3 2 3 1 1 1 3 | $50.3 \\ 18.0 \\ 21.3 \\ 37.1 \\ 9.5 \\ 24.2 \\ 27.9 \\ 41.9 \\ 60.0 $ | $\begin{array}{c} 12.4\\ 56.4\\ 65.0\\ 63.3\\ 56.0\\ 61.5\\ 39.8\\ 36.8\\ 10.7 \end{array}$ | $ \begin{array}{c} 0 \\ 3.0 \\ 0 \\ 0 \\ 15.6 \\ 0 \\$ | | $\begin{array}{c} 62.7\\ 77.4\\ 86.3\\ 100.4\\ 81.1\\ 85.7\\ 67.7\\ 78.7\\ 70.7\end{array}$ | $\begin{array}{c} 62.7\\77.4\\86.3\\100.4\\81.1\\85.7\\67.7\\78.7\\70.7\end{array}$ | b 22.3 19.0 17.9 24.7 29.2° 18.7 23.2° 23.3° | amount of added h ₂ O, CNMS No added H ₂ O, CNMS 1/2 SWL, CNMS 1/2 SWL, CNMS 1/2 SWL, CNMS Schulz's proportions, CNMS Schulz's proportions, CNMS Schulz's proportions, CNMS Standard expt., CNQCP |

^a This was a poplar waste liquor; therefore, this value is actually a mixture of vanillin and syringaldehyde calculated as vanilin. ^b Not determined. ^c This vanillin value includes 6.1 per cent of a non-methoxyl containing aldehyde.

• Not determined. • This vanish value metades of per cent of a non-methody too saming accuration

with other material or it may be further oxidized under conditions existing in the reaction vessel.

TEMPERATURE

At atmospheric pressure total over-all reduction increased with increase in temperature. In this study increase in temperature was obtained only by concentration. Under pressure the temperature has a marked effect on the course of the reduction. Whereas at atmospheric pressure azoxybenzene is the chief reduction product and at 160° C. azobenzene is the chief product, at intermediate temperatures either or both may be obtained, depending upon the time and the concentrations. At 130° C. and for short reaction times azoxybenzene is formed in the greatest amount, but on continued reaction it is gradually changed to azobenzene. This transformation is increased by increased temperature and increased reaction time.

Under standard conditions, raising the temperature above 160° C. increased the formation of aniline at the expense of azobenzene. As in the 160° experiments, the total over-all recovery decreased with increased temperature for long reaction times.

A series of experiments was run on the effect of temperature on the pressure reduction of nitrobenzene using Schulz's proportions (Figure 4); data were obtained at 10° intervals from 160° to 200° C. The aniline yield increased with temperature and in that respect was similar to other series at superatmospheric pressure. The azobenzene increased somewhat at 180° C. but dropped off markedly at 200° C., an indication of further reduction or other reaction. The total reduction observed reached a maximum at 180° C., as did the yield of vanillin. The yield of 29.2% aldehydes at 180° C. (using Schulz's proportions) was the highest obtained in this type of experiment. A methoxyl analysis of the 2,4-dinitrophenylhydrazone precipitate indicated that some nonmethylated aldehyde was also formed during the reaction. Assuming that all the methoxyl of the precipitate originated in vanillin, the vanillin yield of this experiment was 23.1%.

SODIUM CARBONATE AS ALKALI

In studying the reduction of nitrobenzene by dextrose in alkaline solution, Opolonick (3) found that, if sodium carbonate was substituted for sodium hydroxide in the reaction mixture, nitrobenzene was reduced to aniline and no azoxybenzene or azobenzene was formed. Two identical experiments were run, substituting sodium carbonate for sodium hydroxide in the standard procedure at atmospheric pressure; the only reduction product isolated was aniline. However, the total reduction was so poor that no further work was done with this alkali. No vanillin was recovered from the reaction mixture, which indicates that strong alkali is necessary for the vanillin cleavage of lignin in sulfite waste liquor.

PILOT-PLANT REDUCTIONS AT ATMOSPHERIC PRESSURE

Small pilot-plant experiments were performed to obtain large quantities of the reduction products of nitrobenzene and the oxidation products of lignin, and to determine whether the laboratory results could be translated to pilot-plant operation. Large-scale reductions were made with softwood and hardwood liquors under varying conditions of time and concentration ratios, in essentially the same manner as the laboratory experiments. One series was run to determine the effect of concentration ratios on reduction with a concentrated neutralized quickcook poplar liquor containing 35.6% solids and having a calculated lignin content of 7.7%. The data are given in Table I as experiments 111-113.



Figure 4. Effect of Temperature on Pressure Reduction of Nitrobenzene with Concentrated Neutralized Mitscherlich Liquor (Schulz's Proportions for 1 Hour)

These experiments indicate the effect which changes in concentration ratios (especially dilution) have upon total reduction and nature of the reduction products. Although the over-all reduction is decreased by dilution, the SPABS-azoxybenzene ratio is increased to the point where SPABS is the chief reduction product. Inasmuch as nitrobenzene can be separated easily from the reaction mixture by steam distillation and then recycled in the process, the conditions of experiment 113 might prove interesting as a source of sodium p-azobenzenesulfonate. In Table II the data of experiments 111–113 are retabulated on the basis of nitrobenzene recovered instead of nitrobenzene used. These data would apply to continuous processes, using the conditions of the particular experiment and recycling the nitrobenzene.

The data of the small pilot-plant reductions indicate that slightly longer reaction times are necessary to obtain the same reduction results as those obtained from corresponding laboratory runs. Because the mechanical losses were smaller in the large experiments, over-all recoveries were much better. The vanillin was determined by weighing the isolated product. Agreement with the 2,4-dinitrophenylhydrazone precipitation method was close.

| TABLE II. | Results on Basis of Recovered Nitrobenzene | | | | | | | | | |
|-------------------|--|---|---|---------------------------------|------------------------|--|--|--|--|--|
| Expt. No. | Aniline, % | Azoxy- benzene, % | SPABS, % | Total Reduction Obsvd., % | Aldehydes, % | | | | | |
| 111 112 113 | $12.9 \\ 18.2 \\ 16.2$ | $ \begin{array}{r} 60.3 \\ 39.4 \\ 19.7 \end{array} $ | $\begin{array}{c}15.4\\34.6\\43.5\end{array}$ | 88.6 92.2 79.4 | $26.7 \\ 29.8 \\ 29.2$ | | | | | |

Material balances were made on the nitrobenzene, lignin, and methoxyl portions of the reaction mixtures. Nitrobenzene balances are apparent from the data of Table I. Lignin balances always indicated that a considerable portion of the material obtained as desulfonated lignin was actually nonlignin material. Methoxyl balances indicated close agreement between input and output in substantially all experiments.

RE-USE OF DESULFONATED LIGNIN AS REDUCING AGENT

Because of the large quantities of desulfonated lignin obtained as a by-product in the reduction of nitrobenzene with sulfite waste liquor and alkali, experiments were carried out to determine whether desulfonated lignin could be used for further reduction of nitrobenzene. Both desulfonated lignin prepared commercially by digesting calcium lignosulfonate with alkali under pressure and the desulfonated lignin prepared as a by-product in the nitrobenzene reductions were studied. The two products were compared as reducing agents at atmospheric and higher pressures.

Results indicated that desulfonated lignin is a poor agent for reducing nitrobenzene in the presence of alkali at atmospheric pressure. This is more true of the lignin desulfonated with nitrobenzene-alkali than of alkali-desulfonated lignin. On the other hand, at superatmospheric pressure the desulfonated products give almost the same reduction results as the original lignin material.

However, simultaneous vanillin yields resulting from the oxidation of the desulfonated lignin are substantially less. They confirmed the results of Freudenberg *et al.* (2), who found that a maximum of 25% total vanillin can be obtained from the lignin of sulfite waste liquor by repeated oxidation with nitrobenzene and alkali under pressure.

OPTIMUM REDUCING CONDITIONS

The optimum conditions for the preparation of aniline are those of experiment 81 which yielded 67.5% of the amine. The highest yield of azobenzene (65%) was obtained under the conditions of experiment 91. Azoxybenzene was found in a maximum yield of 67.5% in experiment 58. The highest actual yield of pure sodium *p*-azobenzenesulfonate (24.1%) was obtained in the small pilot-plant experiment 112. However, experiment 113 (Tables I and II) gave a much higher ratio of sodium *p*-azobenzenesulfonate to azoxybenzene and aniline and, in continuous process, would yield 43.5% sodium p-azobenzenesulfonate. The highest crude vanillin yield of 29.2% was obtained under the conditions of experiment 94. This crude vanillin consisted of over 80% of the pure compound.

ACKNOWLEDGMENT

This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Committee on Waste Disposal and conducted for the Committee by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the Committee to publish these results.

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PRESENTED before the Division of Cellulose Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa.

Correlating Vapor Pressure and Equilibrium Constant Data

Data for equilibrium constant K, used in distillation and gas absorption design calculations, are correlated by a logarithmic plot against vapor pressure of a reference substance at the same temperatures to give substantially straight lines. A nomogram has been prepared based on this correlation which gives K values for the hydrocarbons below nonane at different pressures and temperatures in a form which is useful when constant K values are to be compared. A second nomogram is also presented which is particularly useful for obtaining K values for hydrocarbons in this range at the same temperature and pressure as would be necessary, for example, in plate-to-plate calculations of a distilling column handling hydrocarbons.

N PREVIOUS articles (1, 2) a logarithm plot of vapor or related pressures of a compound against the pressures exerted by a reference substance at the same temperature was used

to correlate data of vapor pressures, latent heats, heats of chemical reaction, gas solubilities, heats of solution, adsorption equilibrium pressures, heats of adsorption, and other properties. It was also shown that the corresponding logarithmic plot of reduced pressures at the same reduced temperatures added somewhat to the precision of the plot and the accuracy of data obtained therefrom. It appeared that the same plot might be a useful tool for correlating values of the so-called equilibrium constant, K, used in the design of distillation, absorption, and related systems involving particularly hydrocarbons, such as petroleum fractions.

This equilibrium constant is usually derived, as by Sherwood (4), from Raoult's law

 $p = P_{-}x$ (1)

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and Dalton's law,

$$P = \Sigma p \qquad (2)$$

which, when combined with Avogadro's law, give the equilibrium relation:

$$p = P_v x = P y \tag{3}$$

where, at a given temperature, p is the partial pressure of the hydrocarbon under discussion in the gas phase; P_{v} is the vapor pressure of the pure component; P is the total pressure; x and y represent the mole fractions of the particular hydrocarbon in the liquid and the gas phase, respectively; and Σ_p repre-



