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REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SULFITE WASTE LIQUOR[1]

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In a recent paper (1) a comprehensive study of the reduction of nitrobenzene with sulfite waste liquor was reported. The results obtained, and the possibility of using sulfite waste liquor as a substitute for metals in commercial organic reductions led to other studies of sulfite waste liquor as a reducing agent. This paper recites a number of experiments on the reduction of aromatic nitro compounds which, at the present time, are reduced commercially by other means to give valuable intermediates for use in the dyestuff, pharmaceutical, and organic chemical industries. The compounds selected were 2- and 4-nitrophenol, 2- and 4-nitrotoluene, 2-nitroanisole, 2-nitrocymene, 2-nitrobiphenyl, and 2-nitrochlorobenzene.

These compounds were treated with sulfite waste liquor and alkali at both atmospheric and superatmospheric pressures, employing reactant ratios and reaction conditions which were found to give total reduction of nitrobenzene (1). Table I[2] gives the data and results of those reductions using reaction mixtures of 0.6 mole of the nitro compound, 300 g. of sulfite waste liquor containing 50% solids, 90 g. of sodium hydroxide, and 100 g. of water. All experiments were performed in the same general manner as outlined in the experimental part.

Schulz (2) claimed that nitrophenols and alkali oxidized sulfite waste liquor to vanillin at elevated temperatures. From this, one would assume simultaneous reduction of the nitro compounds. Experiments at atmospheric pressure indicated that neither 2- nor 4-nitrophenol yielded increased quantities of vanillin with sulfite waste liquor. Furthermore neither compound was reduced by the alkaline liquor. Condensation with the lignin or some other component of the waste liquor must have taken place because only a fraction of the nitrophenol could be recovered. Raising the temperature of the reaction mixture resulted in reduction to aminophenols. No other reduction product was obtained.

The facts that *p*-cymene is formed, together with sulfite waste liquor, as a by-product of the sulfite pulp industry, and that reduction products of nitrocymene have recently attained commercial importance, led to the selection of 2-nitrocymene for reduction studies. The crude 2-nitrocymene used in the

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[2] Whereas this paper is concerned chiefly with the reduction products of the nitro compounds, the simultaneous vanillin yields from the oxidation of the lignin have been included in Table I. Under the conditions of these experiments, vanillin is the principal and substantially the total recovered oxidation product of the lignin, the remainder being mostly degraded lignin material (1).

atmospheric reductions contained 5% of 4-nitrotoluene. Only a small amount of 2-aminocymene was obtained from the nitrocymene in the reductions, but the 4-nitrotoluene was quantitatively reduced to *p*-toluidine. Reduction of pure nitrocymene at 130° resulted in the formation of 2-aminocymene and a new compound, 2,2′-azoxy-*p*-cymene (2,2′-dimethyl-5,5′-diisopropylazoxybenzene).

TABLE I

REDUCTIONS OF AROMATIC NITRO COMPOUNDS WITH SULFITE WASTE LIQUOR

EXPT.	NITRO COMPOUND	TEMP., °C.	TIME, HOURS	RECOVERED NITRO COMPOUND, %	AMINO COMPOUND, %	AZOXY COMPOUND %	AZO COMPOUND, %	TOTAL REDUCTION OBSERVED, %	TOTAL NITRO COMPOUND ACCOUNTED FOR, %	VANILLIN,[a] %
1	4-Nitrophenol[b]	108	8	49.6	0	0	0	0	49.6	1.2
2	4-Nitrophenol	120	4	38.1	22.0	0	0	22.0	60.1	Not det'd.
3	2-Nitrophenol	140	4	2.5	56.0	0	0	56.0	58.5	2.2
4	2-Nitrocymene (crude)	108	8	88	10.2	0	0	10.2	98.2[c]	8.8
5	2-Nitrocymene (pure)	130	6	39.5	32.9	22.6	0	55.5	95.0	17.5
6	4-Nitrotoluene	108	8	34.7	13.0	32.1	4.2	64.9[d]	99.6	12.7
7	4-Nitrotoluene	130	5	0	26.3	0	73.1	99.4	99.4	19.8
8	2-Nitrotoluene	108	8	53.4	13.0	22.7	0	41.0[e]	95.4	11.5
9	2-Nitrotoluene	130	5	0	50.3	0	52.4	102.7	102.7	18.7
10	2-Nitrotoluene	130	2	37.5	20.0	0	40.0	61.1[f]	98.6	14.0
11	2-Nitrobiphenyl	108	8	80.8	6.7	3.9	0	10.6	91.4	10.9
12	2-Nitrobiphenyl	130	6	0	40.9	52.2	0	93.1	93.1	22.3
13	2-Nitroanisole	108	8	53.2	12.9	26.4	0	38.3	91.5	Not det'd.
14	2-Nitroanisole	140	2	0	91.5	0	0	91.5	91.5	Not det'd.
15	2-Nitrochlorobenzene	108	7	24.7	12.2	21.0	0	33.2	99.0[g]	10.2

[a] Vanillin is reported as percentage of initial lignin present in the sulfite waste liquor.

[b] In Experiments 1, 2, and 3 an additional amount of sodium hydroxide was added equivalent to the phenolic hydroxyl of the nitrophenol.

[c] In addition to the products listed, *p*-toluidine was recovered in an amount corresponding to 5% of the 4-nitrotoluene in the original crude 2-nitrocymene. Therefore, the yields of recovered 2-nitrocymene and 2-aminocymene are based on 95% of the crude nitrocymene used.

[d] This value includes 15.7% of sodium 4,4′-dimethylazobenzene-3-sulfonate obtained in this experiment.

[e] Includes 6.3% of sodium 2,2′-dimethylazobenzene-4-sulfonate.

[f] Includes 1.1% of sodium 2,2′-dimethylazobenzene-4-sulfonate.

[g] Includes 41.1% of 2-nitrophenol which was formed by hydrolysis of the nitrochlorobenzene.

Because all the 4-nitrotoluene present as an impurity in the crude 2-nitrocymene was reduced to *p*-toluidine in the atmospheric reduction of 2-nitrocymene, it was assumed that sulfite waste liquor would quantitatively reduce 4-nitrotoluene to *p*-toluidine at atmospheric pressure. The data of Experiment 6 indicate that this assumption was far from correct. In the nitrocymene experiment the large excess of reducing agent must have caused the quantitative reduction of the small amount of 4-nitrotoluene, the 2-nitrocymene being inert. The chief reduction product of this experiment was 4,4′-azoxytoluene. In addition to the known products obtained in this experiment a yellow, crystalline, sodium-containing compound was obtained. Reduction of this compound with tin and hydrochloric acid yielded *p*-toluidine and 4-amino-2-toluenesulfonic acid, indicating that the unknown compound was sodium 4,4′-dimethylazobenzene-3-sulfonate, which was also prepared according to Janovsky (3). The formation of this compound is analogous to the formation of sodium *p*-azobenzenesulfonate in nitrobenzene-sulfite waste liquor reaction mixtures (4).

Sulfite waste liquor reductions of 2-nitrotoluene at atmospheric pressure gave 2,2′-azoxytoluene as the chief reduction product, together with a smaller amount of *o*-toluidine. Reduction for 5 hours at 130° resulted in approximately equal amounts of *o*-toluidine and 2,2′-azotoluene and lower ratios of toluidine for shorter reaction times. Complete reduction took place in 5 hours. The presence of sodium 2,2′-dimethylazobenzene-4-sulfonate was definitely established in reaction mixtures of 2-nitrotoluene and alkaline sulfite waste liquor. The golden crystals obtained were dissolved in boiling dilute alkali and treated with sodium hydrosulfite. The colorless solution, upon acidification and re-alkalization yielded *o*-tolidine (3,3′-dimethylbenzidine). The formation of *o*-tolidine indicates that 2,2′-dimethylhydrazobenzene or 2,2′-dimethylhydrazobenzene-4-sulfonic acid must have been formed during the reaction. Since these compounds could be formed only by reduction of the corresponding azo or azoxy compounds and since analytical data agreed with the azo structure, the unknown golden crystals must have been sodium 2,2′-dimethylazobenzene-4-sulfonate. The method of proof of structure is analogous to that used for sodium *p*-azobenzenesulfonate (4).

Substantial reduction of 2-nitrobiphenyl took place only at elevated pressures. Under those conditions 2,2′-azoxybiphenyl and 2-aminobiphenyl were the reduction products. In addition to the known 2,2′-azoxybiphenyl melting at 157–158° (5), a product melting sharply at 149–150° was obtained in substantial yield. This compound gave analysis for azoxybiphenyl and upon reduction with tin and hydrochloric acid, it yielded only 2-aminobiphenyl. Therefore, this compound must be a geometric isomer of Friebel and Rassow's (5) compound and, for convenience, has been called iso-2,2′-azoxybiphenyl.

Of all the nitro compounds studied, 2-nitroanisole was the only one that yielded the amino compound as the sole reduction product in practically quantitative yield. The facts that a fair yield of 2,2′-azoxyanisole was obtained at atmospheric pressure and that at 140° the yield of 2-anisidine was practically quantitative indicate that at some temperature between 108° and 140°, all of the intermediate reduction products of 2-nitroanisole are further reduced to the ultimate reduction product, 2-anisidine.

Reduction studies on a halogen-substituted nitro compound (2-nitrochlorobenzene) indicated that the halogen was more susceptible to hydrolysis by the alkaline solution than the nitro group was to reduction by the sulfite waste liquor. It is interesting to note that the 4-nitrophenol obtained in Experiment 15 was recovered quantitatively, whereas only 50% was recovered in the atmospheric reduction of 4-nitrophenol (Experiment 1). Because of the large degree of hydrolysis taking place at atmospheric pressure, no high-temperature experiments were made on 2-nitrochlorobenzene. The reduced chlorobenzenes were stable toward hydrolysis—no amino or azoxy-phenol was found.

The experiments in this study demonstrate that these high-boiling nitro compounds, which contain no strongly active group, can be totally reduced by sulfite waste liquor and alkali at temperatures higher than reflux temperatures. Except in the reduction of 2-nitroanisole under pressure, the largest part of these compounds is reduced to bimolecular products instead of to monomolecular compounds. Lower temperatures favor azoxy compound formation and higher temperatures favor the production of azo and amino compounds. The yields of vanillin obtained in these experiments from the simultaneous oxidation of the sulfite waste liquor were a function of the total reduction observed. The vanillin yields agreed remarkably with those obtained in the nitrobenzene study (1).

EXPERIMENTAL

All melting points given are uncorrected.

Starting materials. The sulfite waste liquor used was a concentrate prepared from a spruce Mitscherlich liquor. The digester-strength liquor was concentrated at atmospheric pressure to 50% solids (7.16% methoxyl). Assuming that 90% of the methoxyl belonged to lignin and that lignin has a methoxyl content of 14.5%, the lignin content of the sulfite waste liquor was 22.2%.

2-Nitrocymene was prepared from *p*-cymene by the method of Doumani and Kobe (6). The product obtained boiled at 128–132° at 13 mm.; n_D^{20} 1.5299. Under the conditions of nitration some 4-nitrotoluene was formed and, because it could not be separated by distillation, the resulting 2-nitrocymene contained 4-nitrotoluene. From the refractive index-composition diagram of Doumani and Kobe (6) the amount of 4-nitrotoluene was found to be approximately 5%. The pure 2-nitrocymene used in several experiments was that recovered from atmospheric sulfite waste liquor reductions in which all the 4-nitrotoluene was reduced. Upon distillation pure 2-nitrocymene was obtained, n_D^{20} 1.5287.

2-Nitrobiphenyl was a commercial product kindly furnished by Monsanto Chemical Company. All the other nitro compounds were Eastman Kodak Company products and were used without further purification.

The method for atmospheric pressure reductions may be illustrated by that used in reducing 4-nitrotoluene.

Reduction of 4-nitrotoluene with sulfite waste liquor at atmospheric pressure. Into a 1-liter, 3-neck flask fitted with a reflux condenser and a mercury-sealed stirrer were placed in order (with stirring) 300 g. of sulfite waste liquor, 90 g. of sodium hydroxide dissolved in 100 g. of water, and 82.5 g. of 4-nitrotoluene. The flask was closed with a rubber stopper carrying a thermometer reaching below the surface of the reaction mixture, and the mixture was heated to boiling. Refluxing and stirring were continued for 8 hours, after which the mixture was allowed to cool with stirring. After diluting with water the alkaline solution was distilled with steam. The steam distillate was acidified with hydrochloric acid to dissolve organic bases and extracted with ether. The ether solution, after drying, evaporating, and distilling the residue under reduced pressure, yielded 28.7 g. (34.7%) of 4-nitrotoluene as light yellow needles, m.p. 51–52°. The acid steam distillate was alkalized with sodium hydroxide, saturated with sodium chloride, and extracted with ether. The ether solution was dried, the solvent removed, and the residue distilled under reduced pressure. A yield of 8.4 g. (12.9%) of *p*-toluidine, m.p. 42–43°, was obtained. The alkaline residue from steam distillation was centrifuged, and the clear centrifugate reserved for vanillin determination. The residue from the centrifuging operation was extracted with wet acetone, and the acetone removed by distillation. The residual wet brown oil was extracted with ether. An aqueous layer formed and between the ether and aqueous layers a golden precipitate separated. The aqueous layer was drawn off, the precipitate was filtered, and the ether layer was distilled, leaving a residue which was separated by fractional distillation *in vacuo*. The residue consisted of 21.9 g. (32.1%) of 4,4′-azoxytoluene as microscopic yellow needles, m.p. 68–69° and 2.7 g. (4.2%) of 4,4′-azotoluene as microscopic orange crystals, m.p. 143–144°. Mixed melting points with authentic samples showed no depression. The golden precipitate (14.9 g.) was recrystallized from ethanol. Reduction with tin and hydrochloric acid yielded equivalent weights of *p*-toluidine and 4-amino-2-toluenesulfonic acid (identified as its amide, m.p. 164°), indicating it to be sodium 4,4′-dimethylazobenzene-3-sulfonate.

Anal. Calc'd for $C_{14}H_{13}N_2NaO_3S$: C, 53.8; H, 4.17; N, 8.97; S, 10.3; Na, 7.37.
Found: C, 53.7; H, 4.27; N, 9.06; S, 10.3; Na, 7.27.

An aliquot of the centrifugate was acidified with dilute sulfuric acid, and thoroughly extracted with ether. The ether solution was extracted with 21% sodium bisulfite solution. The bisulfite extract was acidified with dilute sulfuric acid, aspirated under reduced pressure to remove sulfur dioxide, and precipitated with 2,4-dinitrophenylhydrazine according to Pearl (7). The vanillin yield amounted to 8.45 g. or 12.7% on the basis of the lignin present in the sulfite waste liquor.

In experiments where steam distillation was not complete, an ether extraction of the alkaline solution was employed. Under these conditions all the basic and neutral substances were obtained in the ether extract.

Reductions at superatmospheric pressure. These experiments were made in a stainless steel autoclave which was shaken in a heated rocker at the desired temperature for the required length of time. Upon cooling, the tube was opened and the contents were transferred to a flask for steam distillation. After this, the mixture was worked up as described for the experiment at atmospheric pressure.

Variations in the physical and chemical properties of the different nitro compounds and their reduction products necessitated minor deviations from the standard procedure. However, these deviations were of little consequence.

*2,2′-Azoxy-*p*-cymene.* The alkaline residue from steam distillation in Experiment 5 was extracted with ether. After removing basic substances with dilute hydrochloric acid, the ether was dried with calcium chloride, and distilled. The residue was fractionated under a high vacuum. A yellow crystalline product (10.7 g.), which boiled at 180–190°/1 mm. and which, when recrystallized from methanol, melted at 50–51°, was obtained. Reduction with tin and hydrochloric acid resulted in the recovery of only 2-aminocymene, b.p. 116–118°/12 mm., n_D^{20} 1.543.

Anal. Calc'd for $C_{20}H_{13}N_2O$: C, 77.5; H, 8.40; N, 9.04.
Found: C, 77.88; H, 8.55; N, 9.04.

Sodium 2,2′-dimethylazobenzene-4-sulfonate. This compound was isolated from 2-nitrotoluene and sulfite waste liquor reaction mixtures in a manner identical with that described for sodium 4,4′-dimethylazobenzene-3-sulfonate from 4-nitrotoluene reductions. The orange crystals were recrystallized from ethanol.

Anal. Calc'd for $C_{14}H_{13}N_2NaO_3S$: C, 53.8; H, 4.17; N, 8.97; Na, 7.37.
Found: C, 53.6; H, 4.52; N, 8.89; Na, 7.35.

One gram was dissolved in 100 g. of hot water, made alkaline with sodium hydroxide, and treated with sodium hydrosulfite. The colorless solution was acidified with hydrochloric acid, treated with decolorizing carbon, filtered, and the filtrate made alkaline with sodium hydroxide. Ether extraction, followed by drying and removal of the ether, yielded 0.5 g. of *o*-tolidine, m.p. 128–129° (ethanol-water); a mixed m.p. was not lowered. The yield of *o*-tolidine, recrystallized from dilute ethanol, was 74%.

Iso-2,2′-azoxybiphenyl. The neutral fraction of the ether extract of Experiment 12 yielded 17.4 g. (32.8%) of 2,2′-azoxybiphenyl, m.p. 157–158° (alcohol) [mixed m.p. with authentic 2,2′-azoxybiphenyl (5), 157–158°] and 10.3 g. (19.4%) of iso-2,2′-azoxybiphenyl, m.p. 149–150° (light tan crystals from methanol).

Anal. Calc'd for $C_{24}H_{18}N_2O$: C, 82.28; H, 5.14; N, 8.00.
Found: C, 82.28; H, 5.32; N, 7.98.

Reduction with tin and hydrochloric acid yielded only 2-aminobiphenyl, m.p. 44–45°. The m.p. of a mixture with authentic 2-aminobiphenyl was not depressed.

SUMMARY

A number of aromatic nitro compounds has been reduced with sulfite waste liquor and alkali at both atmospheric and superatmospheric pressures.

For total reduction of these high-boiling nitro compounds by sulfite waste liquor and alkali, temperatures higher than reflux temperatures are necessary.

Except in the reduction of 2-nitroanisole under pressure, the largest part of these compounds is reduced to bimolecular products instead of to monomolecular compounds.

The reaction between 2-nitrochlorobenzene and alkaline sulfite waste liquor results in the hydrolysis of a large part of the nitrochlorobenzene to 2-nitrophenol.

A number of new compounds has been isolated and identified.

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REFERENCES

(1) PEARL AND LEWIS, *Ind. Eng. Chem.*, **36**, 664 (1944).
(2) SCHULZ, U. S. Patent 2,187,366 (Jan. 16, 1940).
(3) JANOVSKY, *Ber.*, **21**, 119 (1888).
(4) PEARL, *J. Org. Chem.*, **9**, 424 (1944).
(5) FRIEBEL AND RASSOW, *J. prakt. Chem.*, **63**, 459 (1901).
(6) DOUMANI AND KOBE, *Ind. Eng. Chem.*, **31**, 257 (1939).
(7) PEARL, *J. Am. Chem. Soc.*, **64**, 1429 (1942).