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Reduction of Organic Compounds by Ethanolamines

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During an investigation of the properties of triethanolamine the senior author noticed that the ethanolamines reduced aqueous solutions of silver, lead, mercury and other metallic salts. The literature records do not mention this reaction. The present paper reports the results of some experiments on the reduction of organic compounds of different types by the ethanolamines.

The reactions are very easily carried out, requiring the heating of the organic compound with one of the ethanolamines, preferably the diethanolamine. While all the end-products have not as yet been isolated, the reaction depends on the decomposition of the amino alcohol into ammonia and an aldehyde.

Table I records the compounds reduced and the reduction products isolated and identified.

TABLE I

Name of compound	Reduction products
Anthraquinone	Anthranol
Acetone	Isopropyl alcohol
Azobenzene	Aniline
Chrysoidine	1,2,4-Triaminobenzene
Nitrobenzene	Azobenzene, azoxybenzene, aniline
o-Nitrotoluene	*o*-Azotoluene, *o*-azoxytoluidine, *o*-toluidine

TABLE II

Nitro compound	Weight, g.	Amino alcohol	Weight, g.	NaOH	Time, hours		Yield, g.	
						Azo	Azoxy	Amino
Nitrobenzene	25	Monoethanolamine	48	None	4	1.9		2
Nitrobenzene	25	Diethanolamine	84	None	2	5.1		1.7
Nitrobenzene	25	Diethanolamine	64	None	2	3.5		1
Nitrobenzene	10	Diethanolamine	25	15 g.	2	6	1	Trace
Nitrobenzene	25	Diethanolamine	84	5 g.	2	9.3		0.7
Nitrobenzene	25	Triethanolamine	84	None	4	1.7		1
Nitrobenzene	10	Triethanolamine	25	20 g.	2	4	3	Trace
o-Nitrotoluene	27	Diethanolamine	84	None	2	1.9		2.6
o-Nitrotoluene	13	Diethanolamine	21	5 g.	2	0.2	6	0.3
o-Nitrotoluene	13	Diethanolamine	21	10 g.	2	.2	8.4	Trace
o-Nitrotoluene	13	Diethanolamine	21	15 g.	2	8.2		Trace

Table II shows the results of a more extended investigation of the reduction of the nitro group. It will be noticed that the nitro group on reduction yields azo, azoxy and amino compounds, the yields of each being dependent on the presence or absence of alkali, the amino alcohol and the time of reaction.

Experimental Part

Reduction of Anthraquinone.—Ten grams of anthraquinone and 32 g. of triethanolamine are heated in an oil-bath at 185° for six hours. The mixture is extracted with water and filtered. The insoluble portion is extracted with benzene and the benzene evaporated. The residue of anthranol is recrystallized and identified by its melting point and oxidation to anthraquinone.

Reduction of Azobenzene.—Thirty-two grams of triethanolamine and 10 g. of azobenzene are heated in an oil-bath at 185–190° for four hours. The resulting mixture was steam distilled. The excess azobenzene is filtered off from the distillate which after acidification with hydrochloric acid is evaporated to dryness. The residue was identified as aniline hydrochloride.

Reduction of Acetone.—Thirty-two grams of triethanolamine and 10 g. of acetone were refluxed for six hours. The solution was distilled and a fraction between 75–85° was collected. Isopropyl alcohol was identified by conversion into the 3,5-dinitrobenzoic ester.

Reduction of Nitrobenzene with Amino Alcohol and Alkali.—Ten grams of nitrobenzene and 25 g. of diethanolamine are mixed with a solution of 15 g. of sodium hydroxide in 10 cc. of water and heated with a small flame for two hours. After cooling, water is added and the mixture filtered. The solid residue is fractionally crystallized from alcohol and yields azobenzene (6 g.) and azoxybenzene (1 g.). The aqueous filtrate is steam distilled, the distillate acidified with hydrochloric acid and evaporated to dryness to yield aniline hydrochloride.

Conclusions

1. Ethanolamines have been found to act as reducing agents for inorganic salts and for some classes of organic compounds.
2. Nitro compounds when reduced with ethanolamines yield azo, azoxy and amino compounds.

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