

THE DETERMINATION OF HYDRAZOBENZENE BY THE DIE METHOD WITH HYDROGEN PEROXIDE CATALYZED WITH VANADIUM

F. TRISCHLER

Phys. Chem. Dept., Gedeon Richter Chem. Works, Budapest, Hungary

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Hydrazobenzene cannot be oxidized to azobenzene with hydrogen peroxide in ethanol-containing medium. Vanadium(V) ions catalyze the oxidation; in their presence the reaction takes place rapidly. A thermometric (DIE) method was developed for the determination of hydrazobenzene, based on the oxidation reaction with hydrogen peroxide catalyzed by vanadium(V). The reaction is initiated by the addition of the solution of the catalyst, which is applied in small amount (100 μ l). Thus, the application of the immersion pipette is not necessary. The standard deviation of the determination is ± 0.42 mg hydrazobenzene in 50 ml ethanol.

The methods available in the literature for the quantitative determination of hydrazobenzene (HB), and mainly the early ones, are based on the photometric measurement of benzidine formed during re-arrangement of the molecule in acidic media [1–2, 6]. A common drawback of these methods is that during the re-arrangement not only benzidine but also 2,4'-diamino diphenyl is formed, the characteristics of which differ from those of benzidine. The iodometric method of Ries [3] after permanganate oxidation, and the direct iodometric method of Ashworth [4], are based on the oxidizibility of the molecule. Bottei [5] reduced the material with chromium(II) ions and back-titrated the excess reducing agent with iron(III) sulphate.

In order to develop a more reliable method than the above-mentioned ones, the reactivity of HB towards various oxidizing agents was investigated. It has been found that the reaction with iodine is quantitative only in neutral or well-buffered basic solutions, but the titration becomes extremely sluggish even in these instances. In acidic media no oxidation takes place. No well-defined reaction product could be obtained in a reaction with bromine, the reaction being mainly of a substitution character.

HB cannot be oxidized to azobenzene by hydrogen peroxide in neutral ethanol, but the reaction was found to be quantitative and rapid in the presence of a suitable catalyst.

According to Yatsimirskii [7], the oxidizing agent is not hydrogen peroxide itself but the ions and radicals (OH^+ , O^{\cdot} , OH^{\cdot} , $\text{O}_2\text{H}^{\cdot}$) produced from it, their formation being endothermic. The catalyst forms a complex with hydrogen peroxide and therefore, decreases the endothermicity of the formation of radicals. Of the potential catalysts, the best results were obtained with vanadium(V). As low

a concentration of ammonium metavanadate as $5 \cdot 10^{-4}$ mole \cdot l $^{-1}$ greatly accelerates the oxidation of HB. The oxidation was followed by thermometry, and an analytical procedure was developed for the quantitative determination of HB based on measurement of the heat of the reaction.

Experimental

Apparatus

The change of the temperature of the reaction mixture was followed with a thermistor (Siemens 4 Kohm, 25°) built into a Wheatstone bridge, and the change of the signal was scanned with a strip chart recorder (Radelkis OH-814/1) after being amplified by an IC amplifier.

The reaction vessel was a 100 ml plastic beaker insulated with polyurethane. The thermistor is fixed to the lid closing the cell in such a way that it is immersed in the solution when the cell is closed. The solution is stirred with a magnetic rod.

The solution containing the catalyst is added to the mixture with a 100 μ l Hamilton syringe. The volume of the solution of the catalyst is negligible compared to that of the reaction mixture, and thus thermostating is not necessary.

The measurements were carried out at 25° by means of a calibration graphs and a simultaneously run standard.

Reagents

Solvent: ethanol, 96 v/v%.

Hydrogen peroxide solution: 30 ml 30 v/v% hydrogen peroxide is diluted with 150 ml distilled water.

Catalyst solution: 1 g ammonium metavanadate is dissolved in 50 ml 2 N hydrochloric acid and diluted to 100 ml with distilled water.

All materials and solvents used in this study were of analytical reagent grade purity.

Preparation and purity control of standard HB

100 ml methanol is saturated at the boiling point with HB. The hot solution is filtered on a filter paper and cooled to room temperature. The large, white crystals obtained are filtered off, washed with two 10–15 ml portions of light petroleum and dried in an air stream at room temperature. The white crystalline HB becomes yellow rapidly when exposed to air, and therefore, it is advisable to prepare the calibration graph using freshly-crystallized HB. Yellow HB can also be used for the above purpose when its azobenzene content is corrected for. This can be done as follows: 0.25 g HB is dissolved in 20 ml chloroform in a 25 ml calibrated flask, and the solution is made up to the mark with chloroform. The absorbance of the resulting solution is measured immediately in a 1 cm cell at 445 nm, using chloroform as the blank. The azobenzene content of the HB is calculated as $A_{1\text{cm}}^{1\%} / 306$ of azobenzene.

Procedure

About 0.04–0.08 g HB is weighed into a 50 ml calibrated flask and dissolved in 40 ml 96 v/v% ethanol. 1 ml hydrogen peroxide solution is added by pipette, the temperature of the solution is set to 25° and the flask is filled to the mark with ethanol. The solution is transferred to a plastic beaker and placed into the isolated cell. After thermal equilibrium is reached (about 2–3 min), the Wheatstone bridge is set to zero. Then 100 μ l catalyst solution is added by means of a Hamilton syringe. The reaction starts immediately and is completed within 1–1.5 min. The HB content is calculated from the enthalpogram drawn by the recorder according to the known DIE principles.

Results

The results of measurements are given in Table 1.

Table 1

Hydrazobenzene, mg		Deviation, mg
taken	found	
31.17	30.78	–0.39
41.97	41.98	+0.01
51.28	51.62	+0.34
60.23	60.73	+0.50
71.89	71.35	–0.50

The standard deviation of the determination is ± 0.42 mg in the case of 40–80 mg HB (15 parallel runs).

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RÉSUMÉ — L'hydrazobenzène ne peut pas être oxydé par l'eau oxygénée dans un milieu contenant de l'éthanol. Les ions vanadium(V) catalysent l'oxydation et la réaction a lieu à grande vitesse en leur présence. Les auteurs ont développé une méthode thermométrique (DIE) afin d'effectuer le dosage de l'hydrazobenzène. Cette méthode repose sur la réaction d'oxydation

par l'eau oxygénée en présence de vanadium(V) comme catalyseur. La réaction est initiée par addition de la solution du catalyseur utilisée en faible quantité (100 μ l). Ainsi, l'emploi d'une pipette d'immersion n'est pas nécessaire. L'écart-type du dosage est ± 0.42 mg d'hydrazobenzène dans 50 ml d'éthanol.

ZUSAMMENFASSUNG — Hydrazobenzol kann in äthanolhaltigem Medium mit Wasserstoffperoxid nicht zu Azobenzol oxidiert werden. Vanadium(V)-ionen katalysierten die Oxidation, in ihrer Gegenwart vollzieht sich die Reaktion rasch. Der Autor entwickelt eine thermometrische (DIE) Methode zur Bestimmung von Hydrazobenzol, die auf der durch Vanadium(V)-katalysierten Oxidationsreaktion mit Wasserstoffperoxid beruht. Die Reaktion wird durch Zugabe der in kleinen Mengen (100 μ l) angewandten Katalysatorlösung ausgelöst. Dadurch erübrigt sich der Einsatz von Immersionspipetten. Die Standardabweichung beträgt ± 0.42 mg Hydrazobenzol in 50 ml Äthanol.

Резюме — Гидразобензол не может быть окислен до азобензола перекисью водорода в среде этанола. Ионы ванадия(V) катализируют это окисление и в их присутствии реакция протекает быстро. Автор разработал термометрический (ДИЕ) метод определения гидразобензола, который основан на реакции окисления перекисью водорода, катализируемой ванадием (V). Реакция начинается сразу же после прибавления малого количества (100 μ l) раствора катализатора. Применение погружающей пипетки не является необходимым. Стандартное отклонение определения гидразобензола составляет ± 0.42 мг в 50 мл этанола.