Spectrophotometric Determination of Cyclohexanone Oxime in a Sulfuric Acid Solution of ε-Caprolactam

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(Received October 4, 1966)

A previous work has shown that the trace amounts of cyclohexanone oxime in a Beckmann rearrangement solution can be spectrophotometrically determined by the analysis of the hydroxylamine derived from the hydrolysis of the oxime.[1] It has now been found that the same purpose can be achieved by the absorptiometry of cyclohexanone, which is another hydrolyzate of the oxime, with the aid of the diazonium salt of H-acid reported by Maslennikov.[2] Both methods are based on the analysis of diazo dyes derived from the oxime. The results obtained by the two methods proved to be in perfect accord.

Experimental

Procedure. Approximately 25 g of the reaction mixture from cyclohexanone oxime were weighed accurately and then diluted to 250 m*l* with distilled water. Out of the diluted sample, 10 m*l* was pipetted out into a 100 m*l* flask, which was then heated under reflux for 1 hr. After cooling, 2 m*l* of a 1% aqueous sodium nitrite solution was added and the mixture was left intact for 2 min. Then, 10 m*l* of 20% aqueous sodium hydroxide, 2.5 m*l* of a 5% aqueous sodium sulfite solution, and 10 m*l* of a 0.25% diazonium salt solution of H-acid (prepared by mixing 0.25% H-acid in 0.1 N sulfuric acid with 1% aqueous sodium nitrite 1 : 1)) were successively added. After 5 min, the whole solution was diluted accurately to 100 m*l* with distilled water, and the absorptivity was measured at 540 mμ. The reference material was prepared by the same procedure using a sulfuric acid solution of repeatedly-purified ε-caprolactam, the composition of which was in accord with that of the Beckmann rearrangement solution used.

Results and Discussion

Background. The diazotized H-acid solution is yellow or yellowish green and very unstable at room temperature. The apparent molar absorptivity, therefore, decreases gradually with the lapse of time when distilled water is used as a reference. However, when the reference is the diazonium salt solution, the absorptivity is not time-dependent.

The results obtained are shown in Fig. 1.

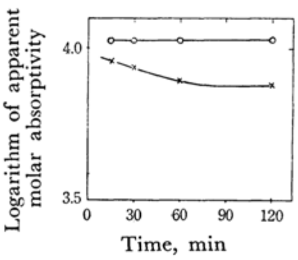

Fig. 1. The apparent molar absorptivities with elapse of time are compared between diazonium salt solution and distilled water as reference.

○ Diazonium salt solution

× Distilled water

Effect of Sodium Sulfate. For the coloration, the sample solution must be made basic to form a carbanion of cyclohexanone. The content of sodium sulfate, which is formed in neutralization with sodium hydroxide, proved to influence the

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[1] Y. Kobayashi, *Anal. Chem.*, **38**, 917 (1966).

[2] A. S. Maslennikov, *Zhur. Anal. Khim.*, **15**, 376 (1960).

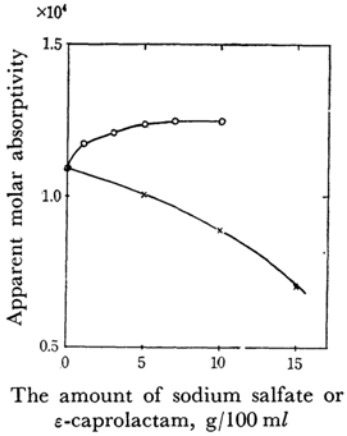

Fig. 2. The dependence of apparent molar absorptivity upon the amount of sodium sulfate or ε-caprolactam in the sample solution.

× Sodium sulfate
○ ε-Caprolactam

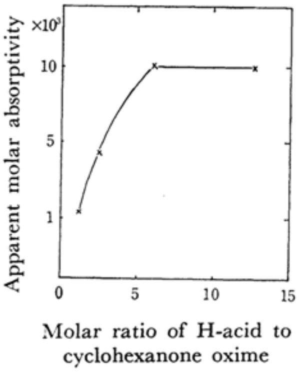

Fig. 3. The dependence of apparent molar absorption upon the molar ratio of H-acid to cyclohexanone oxime.

Table 1. The comparison of the contents of cyclohexanone oxime in the reaction mixture solution of Beckmann rearrangement between the present method and the method based on hydroxylamine analysis using Griess-Ilosvay reagent

Exp. No.	Griess-Ilosvay method, %	Present method, %	Difference %
1	0.019	0.019	0.000
2	0.020	0.014	0.006
3	0.021	0.018	0.003
4	0.020	0.016	0.004
5	0.021	0.015	0.006
6	0.019	0.015	0.004
7	0.017	0.022	−0.005
8	0.021	0.023	−0.002

absorptivity as Fig. 2 shows. Therefore, each solution must be made to contain a certain definite amount of sulfuric acid.

Effect of ε-Caprolactam. The content of ε-caprolactam also present proved to magnify the absorptivity. However, the increased sensitivity reached the saturation point at the concentration of 7 g per 100 m*l*. The behavior is shown in Fig. 2. To obtain stable conditions, it is recommended that the concentration of ε-caprolactam is kept at the saturation point of the sensitivity.

Amounts of Added H-Acid. To conclude the coupling reaction of cyclohexanone with diazonium salt of H-acid, it is necessary to add excessive amounts of the diazonium salt. From the viewpoint of obtaining stable measuring conditions, however, it is better to avoid the excessive addition of the diazonium salt because of its thermalunstability and the effect of the background. The investigation of the dependence of the apparent molar absorptivity upon the molar ratio of H-acid to cyclohexanone revealed that a molar ratio of more than seven to one is necessary for a complete coupling reaction. The results are given in Fig. 3.

Effects of Diverse Impurities. ε-Aminocaproic acid, which is formed by the hydrolysis of ε-caprolactam, proved to have no influence upon the absorptivity, even when all the lactam contained in the sample solution is transformed. Diverse metallic ions, such as ferric, ferrous, lead and zinc ions, were also confirmed not to interfere with the analysis if present in amounts less than 200 ppm.

Comparision of the Analytical Results of the Two Methods. From the continuous Beckmann rearrangement process of cyclohexanone oxime by sulfuric acid, sample solutions were taken out at constant intervals, the cyclohexanone oxime contents are simultaneously determined by both the method based on hydroxylamine using a Griess-Ilosvay reagent(1) and the present method. The results are shown in Table 1. The results are consistent within the range of experimental errors.