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THE BENZIDINE REARRANGEMENT V
2-Chloro-2'-methylhydrazobenzene

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$$\left(\frac{\partial \ln k}{\partial S}\right)_{T,P,\dots} = 0. \quad (6)$$

The constant β is likely to be closely related to the acidity of alcohol as cosolvent, as described previously¹⁾.

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The effect of pressure on the rate of the acid-catalyzed rearrangement of 2-chloro-2'-methylhydrazobenzene in 85 vol% aqueous ethanolic solution was studied under the conditions of 15~30°C and 1~1,500 kg/cm². As a result, it was observed that two different reactions concurred; one was of first order with respect to [HCl] (one-proton mechanism) and the other was of second order (two-proton mechanism), and the former was fairly, while the latter was slightly accelerated by pressure.

Based on the activation parameters obtained, *i.e.* $E^\ddagger = 22.2$ kcal/mole, $\Delta S^\ddagger = -1.6$ e. u., $\Delta V^\ddagger = -6.8$ cm³/mole for one-proton mechanism and $E^\ddagger = 18.0$ kcal/mole, $\Delta S^\ddagger = -12.4$ e. u., $\Delta V^\ddagger = -3.2$ cm³/mole for two-proton mechanism, the reaction mechanisms and the transition states were discussed. The existence of a linear relationship between the logarithms of the rate constants of the rearrangement and pK_a values of ortho-substituted anilinium ions was suggested, by correcting pK_a for the steric effect of ortho-substituents.

Introduction

The so-called benzidine rearrangement is an acid-catalyzed rearrangement and the rate of the rearrangement of hydrazobenzene is of second order with respect to the acid concentration (two-proton mechanism). But in the cases of 2, 2'-dimethyl-^{1a)}, 2, 2'-dimethoxy-^{1b)} and 2, 2'-dibromohydrazobenzene^{1c)}, it was observed that the order of reaction in acid fell to one (one-proton mechanism) and that two reactions of first and of second order concurred, depending on the electrostatic character of the substituents. The reactions of one-proton mechanism was found to be always accelerated by pressure irrespective of the substituents.

Considering the negative values of the volume of activation for one-proton mechanism, it was presumed that the transition state of one-proton mechanism was polar, strongly solvated and compact. As the compounds treated previously were all symmetrical, in order to obtain further information about an unsymmetrical compound, the effect of pressure on the rate of the rearrangement of 2-chloro-2'-

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- b: J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **40**, 39 (1970)
- c: J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **39**, 57 (1969)

