The Rate of the Color Reaction of m-Dinitrobenzene with Sodium Hydroxide in Acetone

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Investigations of kinetics of the color reactions producing Meisenheimer's intermediates[1] have been studied by Caldin, Long and Ainscough[2,3] on the coloration reactions between trinitrobenzenes and ethoxide ion, and also by Nagakura, Oosawa and Tsubomura[4] on the decoloration reaction of the color product between 2, 4-dinitroanisole and hydroxyl.

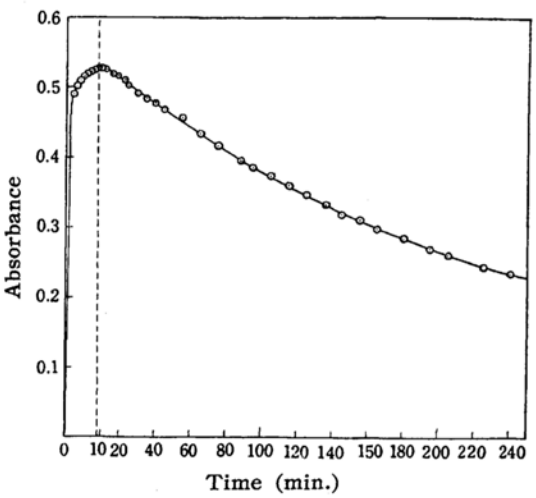
The author has succeeded in pursuing changes in absorbance of a visible absorption of a colored species through both coloration and decoloration reactions in a whole substitution reaction of *m*-dinitrobenzene with sodium hydroxide in acetone.

In the previous paper[5], the author has reported the visible absorption curve (530～600 mμ) of the colored solution produced by adding sodium hydroxide to *m*-dinitrobenzene in acetone. This color becomes more intense for several minutes and then fades slowly. The result in Fig. 1 was obtained by following the absorbance d of the 560 mμ absorption of the colored species at 25°C. The coloration and decoloration reactions are formulated provisionally as

$$m\text{-Dinitrobenzene} + \mathrm{NaOH} \xrightarrow{\text{Coloration}} [m\text{-Dinitrobenzene}\cdot\mathrm{OH}]^- \text{ Colored species (transition complex)} \xrightarrow{\text{Decoloration}} \text{A final product}$$

Although both the coloration and the decoloration are actually concurrent, we assume that only coloration reaction proceeds till nine minutes, at which time the maximum absorbance is obtained, and that only the decoloration occurs from that time,

1) J. Meisenheimer, *Ann.*, **323**, 214, 241 (1902).
2) E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).
3) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
4) S. Nagakura, S. Oosawa and H. Tsubomura, Presented at the Symposium on Electron States of Molecules at Kyoto in October, 1958.
5) T. Abe, This Bulletin, **32**, 775 (1959).
6) T. Abe, to be published in ibid., **32**, No. 9 (1959).



Flg. 1. Change in the absorbance of the 560 mμ absorption for the colored solution of *m*-dinitrobenzene (2.33×10^{-5} M) and sodium hydroxide (3.49×10^{-3} N) in acetone, at 25°C (path length of absorption cells, 1 cm.).

since the rate of the coloration reaction is much greater than that of the decoloration, as can be known from Fig. 1. Moreover, on an assumption that *m*-dinitrobenzene completely changes into the colored species just after nine minutes, a value of 2.27×10^{4} can be obtained as a molar extinction coefficient ε of the 560 mμ absorption of the colored species. This value is of the same order, as compared with the molar extinction coefficients of the red complexes of trinitrobenzene and its derivatives with ammonium hydroxide[6]. From this it is, therefore, known that the above assumptions are very good. Under a condition that the concentration of sodium hydroxide is sufficiently larger than that of the colored species produced, the rate constant k_C of the coloration reaction of the second can be derived as follows:

$$k_C=\frac{1}{0.4343(C_{DNB}-C_{OH})(t-t_{0C})}\log\frac{C_{DNB}-d/\varepsilon}{C_{DNB}-d_{0C}/\varepsilon} \quad (1)$$

where C_{DNB} is the initial concentration of *m*-dinitrobenzene, C_{OH}, the initial concentration of sodium hydroxide, d, the absorbance of the colored species after t minutes, and d_{0C}, the value of d after arbitrary t_{0C} minutes. On the other hand, the following empirical formula of the first order satisfactorily represents the observed rate constants, as in the case of the decoloration of 2, 4-dinitroanisole[4].

$$k_d=\frac{1}{0.4343(t-t_{0d})}\log\frac{d}{d_{0d}} \quad (2)$$

Here d_{0d} is the value of d after t_{0d}. By taking $t_{0C}=2$ and $t_{0d}=12$ in Eqs. 1 and 2, the values of k_C and k_d at 25°C are calculated respectively, as indicated in Table I.

TABLE I

t(min.)	k_C(mol^{-1}·sec^{-1})	t(min.)	k_d(sec^{-1})$\times10^3$
3	101	25	3.35
4	109	30	3.71
5	99.8	35	3.61
6	104	40	3.37
7	99.7	45	3.47
8	103	55	3.26
	mean 103	65	3.54
t	$k_d\times10^3$	t	$k_d\times10^3$
75	3.64	155	3.64
88	3.71	165	3.68
95	3.64	180	3.64
105	3.68	195	3.64
115	3.64	205	3.61
125	3.61	225	3.57
136	3.64	240	3.54
145	3.75		mean 3.57

The means of k_C and k_d are 103 mol^{-1}·sec^{-1} and 3.57×10^{-3} sec^{-1}, respectively. In the decoloration reaction sodium hydroxide may probably interact with the colored species, because the higher the concentration of alkalies contained, the faster disappear the colors of the complexes of polynitrobenzenes with alkalies[4,6].

It is in progress to investigate the effect of the concentration of sodium hydroxide of the rate of the decoloration reaction, and to obtain energies of activation for the coloration and docoloration.

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