

치환 벤젠디아조늄 이온의 수용액내에서의 분해반응에 관한 연구

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(1975. 9. 4 접수)

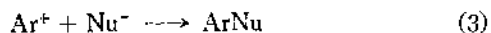
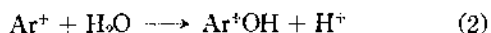
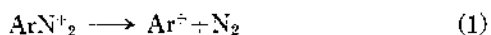
A Study on the Decomposition of Substituted
Benzenediazonium Ion in Aqueous Solution

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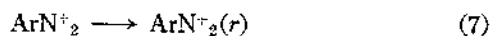
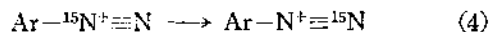
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(Received Sept. 4, 1975)

The decomposition of aryldiazonium salts in aqueous solution has been investigated extensively.¹ This reaction has long been thought to pass through an intermediate aryl cation, which then reacts very rapidly with solvent or other nucleophiles (Eq. (1)~(3)). An effect of substituent on the decomposition rate² would



support the above S_N1 mechanism. However, a small increase in rate under the presence of a high concentration of a nucleophilic anion³ has made the above simple S_N1 interpretation doubtful. Through the observation of an isotopic rearrangement (Eq. (4)),⁴ Lewis *et al.* have modified the mechanism as in equations (5)~(7).⁵ In equations (7), $\text{ArN}_2^+(r)$ refers to the diazonium ion in which the two nitrogens



rearranged each other. This alternative mechanism, however, does not seem feasible considering substituent effects which are consistent with a transition state resembling the aryl cation.

In this work, we have done further detailed studies on the effect of substituent in order to pursue a more pertinent mechanism for the decomposition of benzenediazonium ion, and presented a part of its results.

EXPERIMENTAL

Materials. Substituted benzenediazonium fluoroborate was prepared by the addition of excess cold 42 % aqueous fluoroboric acid to a solution of diazotized corresponding ring-substituted aniline in hydrochloric acid. The resulting yellow crystalline material was washed with cold ethanol and cold ether. Recrystallized the crude product from acetone and then from chloroform. The synthetic procedure was mainly based on the method described by Sheats and Harbison.⁶

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Kinetic Measurement. In a 100 ml volumetric flask containing 50 ml of 0.05 M aqueous hydrochloric acid, added about 20 mg of corresponding diazonium fluoborate. At appropriate intervals, 1 ml of reaction mixture was removed and in which 5 ml of aqueous 0.01 M R salt (2-naphthol-3,6-disulfonic acid disodium salt) (Tokyo Kasei, Japan) in 0.2 M sodium bicarbonate was added. A pink color appeared immediately. This color is resulted from the coupled compound derived from R salt and the undecomposed diazonium ion. Measured the absorbance of the colored solution at an appropriate wave length. Maximum absorbances of these coupled compounds were found in the range of 490~505 nm. First-order rate constants were obtained from

equation (8). In this equation, ϵ_0 and ϵ denote

$$k = \frac{2.303}{t} \log \frac{\epsilon_0}{\epsilon_t} \quad (8)$$

absorbances measured at time zero and time t respectively. An example of measurements is shown in Table 1 and Fig. 1.

RESULTS and DISCUSSION

In aqueous hydrochloric acid, monosubstituted benzenediazonium fluoborate is decomposed according to strictly first-order kinetics since the time-dependent rate constant derived from equation (8) which is based on the first-order kinetics, showed an excellent linearity (Fig. 1). Activation energy (E_a) of this reaction derived from Arrhenius equation is 28.168 kcal/mole, and enthalpy of activation (ΔH_{25°) and entropy of activation ($S^*_{25^\circ}$) are 27.556 kcal/mole and 3.028 e. u. respectively. Rate constants of several monosubstituted benzenediazonium fluoborates are given in Table 2.

In contrast to Lewis and Holliday's result,²

Table 2. First-order rate constants (k 's) for the decomposition of substituted benzenediazonium fluoborates at $50 \pm 0.05^\circ\text{C}$.

Substituents	$k \times 10^4, \text{sec}^{-1}$
<i>p</i> -CH ₃	1.645
<i>m</i> -CH ₃	52.340
H	14.394
<i>m</i> -C ₆ H ₅	20.319*
<i>m</i> -CH ₃ O	53.736
<i>p</i> -Cl	0.041
<i>o</i> -Br	0.0198
<i>m</i> -Cl	0.670
<i>m</i> -Br	1.267
<i>p</i> -CO ₂ H	1.844*
<i>p</i> -NO ₂	0.080
<i>m</i> -NO ₂	0.028

*Calculated from the values which appeared in Ref. (2) using activation energy and frequency factor.

Table 1. Decomposition of benzenediazonium fluoborate in aqueous hydrochloric Acid at $40 \pm 0.05^\circ\text{C}$

Time (sec)	Absorbance (ϵ_t)
0	0.448 (ϵ_0)
839	0.332
1234	0.287
1910	0.221
2416	0.180
3008	0.145
3462	0.113
∞ (47hrs)	0.000

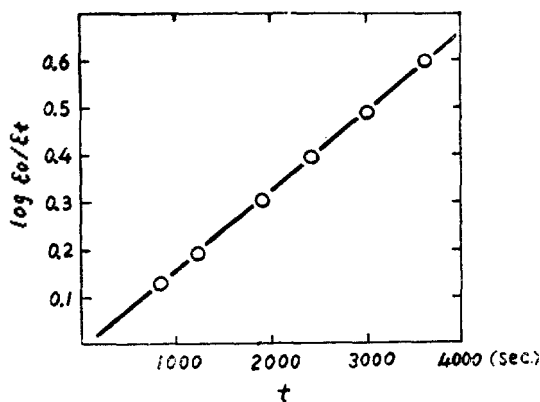


Fig. 1. A plot of $\log \epsilon_0/\epsilon_t$ against t (sec).

the Hammett equation⁷ was successfully applied to these reactions as shown in Fig. 2. Lewis and Holliday checked only three monosubstituted compounds and failed to find any applicability of the Hammett rule. The Hammett constant (σ) of ortho-substituent is taken from the value of para-substituent constant of the same substituent according to the results of evaluation reported by Solomon *et al.*⁸ In drawing the Hammett plot (Fig. 2), *p*-CH₃, *p*-Cl, and *o*-Br are excluded from the regression line, since these three substituents are supposed to retard the decomposition by direct resonance interaction with diazonium ion and strengthen the C—N bond as in I~III. Formerly Lewis *et al.* observed this phenomenon for *p*-CH₃O in a similar reaction.⁹

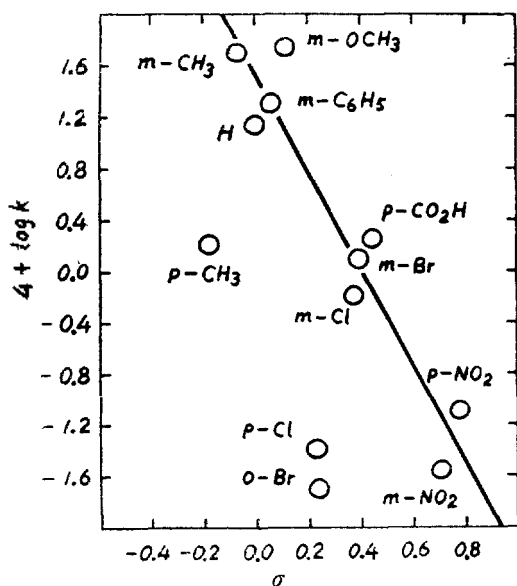
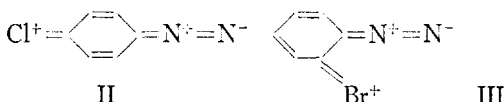
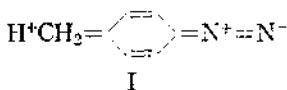
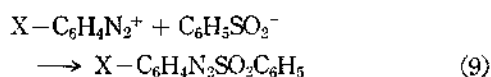


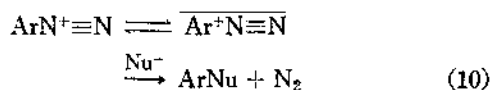
Fig. 2. Hammett plot for the decomposition of benzenediazonium fluoroborates.

This explanation seems reasonable when it is observed that *p*-CH₃, *p*-Cl, and *p*-CH₃O also obeyed the Hammett rule as other substituents in the reaction like equation (9)¹⁰ where the diazonium ion is included but the C—N bond breaking is not involved. Except the substituents capable of direct electron transfer by resonance,



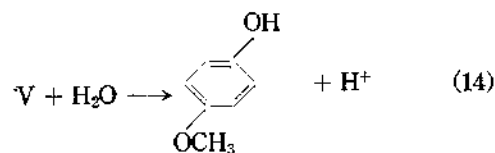
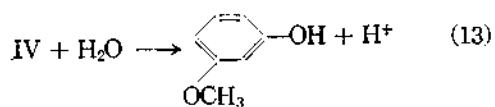
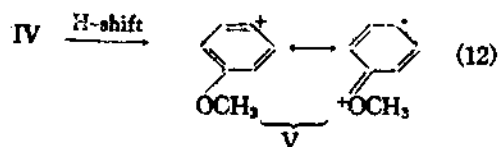
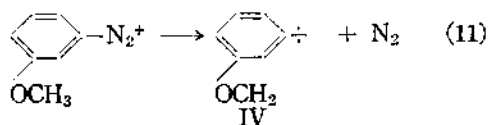
the Hammett rule was successfully applied in the relation between substituents and rate constants of decomposition of diazonium ions; the correlation coefficient was found to be 0.95 (Fig. 2). When σ^+ constant was employed instead of σ , the correlation coefficient was 0.80.

On the basis of present investigation together with the fact that two nitrogens in diazonium ion are indistinguishable from each other (Eq. (4)), we support the existence of "caged pair" intermediate, which was tentatively believed by Insole *et al.*³ Hence the decomposition of aryl-diazonium ion would be described as equation (10). In this equation, $\overline{\text{Ar}^+\text{N}\equiv\text{N}}$ denotes a caged pair intermediate where the two nitrogens are in equivalent position. This procedure is consistent with both nitrogen rearrangement and



observed kinetic substituent effect.

On the other hand, if the free aryl cation is produced during the decomposition process, *o*-methoxyphenyl cation will isomerize to energetically favored *p*-methoxyphenyl cation through hydrogen-shift during the hydrolysis of *o*-methoxybenzenediazonium ion, and thus *p*-methoxyphenol will accompany the main product *o*-methoxyphenol (Eq. (11)~(14)). A study on this possibility is in progress.



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