

A grant from *Knut och Alice Wallenbergs Stiftelse* made possible the purchase of the gas chromatographic apparatus used in this work.

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Nucleophilic Substitution of Aromatic Chlorine in Diazonium Ions by Bromide Ion

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It is known^{1,2} that aromatic bromine atoms in diazonium compounds may be replaced by chlorine atoms in reactions involving a nucleophilic attack by chloride ion. The opposite reaction, namely substitution of aromatic chlorine by bromide ion has not hitherto been reported to take place in diazonium compounds. However, the substitution of a nitro group by bromide ion in a diazonium compound has been reported by Sihlbom.³ For comparison it may be mentioned that among the 1-halo-2,4-dinitrobenzenes, substitution of chlorine by bromide ion as well as the opposite reaction take place⁴, the specific rates of the two reactions being of the same order of magnitude, so that all four molecular species in question may be present in

comparable amounts at equilibrium (measured at 175 and 195°C).

Bearing this evidence in mind, it seems rather difficult to understand why a chlorine atom in a suitably substituted diazonium ion should not be replaced by bromide ion. In actual fact, the present author has found that 2-chloro-5-nitrobenzenediazonium ion and 4-chloro-3-nitrobenzenediazonium ion in a hydrobromic acid-acetic acid-water medium at 25°C are converted to the corresponding bromine compounds through halogen exchange. The conversions are, however, not quantitative for reasons which will be presented below.

Experimental. About 1 g 2-chloro-5-nitroaniline or 4-chloro-3-nitroaniline, prepared by nitration in conc. sulphuric acid solution of *o*-chloroaniline and *p*-chloroaniline, respectively, was dissolved in 75 ml glacial acetic acid and the solution gradually added to a solution of the required amount of sodium nitrite, dissolved in 15 ml conc. sulphuric acid, while cooling in an ice-bath. 75 ml freshly redistilled constant-boiling-point hydrobromic acid was added, and the mixture was placed in a thermostatic bath at $25.0 \pm 0.1^\circ\text{C}$. After one week, no more diazonium compounds were present (negative reaction with 2-naphthol and sodium acetate), and the mixture was distilled with steam until no more organic material was carried over. The distillate was made alkaline and extracted with ether, the combined ether extracts were washed and dried with calcium chloride and finally, the ether was allowed to evaporate at room temperature. The solid remainder was dissolved in 2 ml toluene, and a few microlitres of this solution was analyzed on a Perkin-Elmer Model 116E Fractometer. Conditions: 2 m silicon grease-on-chromosorb column "O", i.d. 4 mm, temp. 185°C, flow

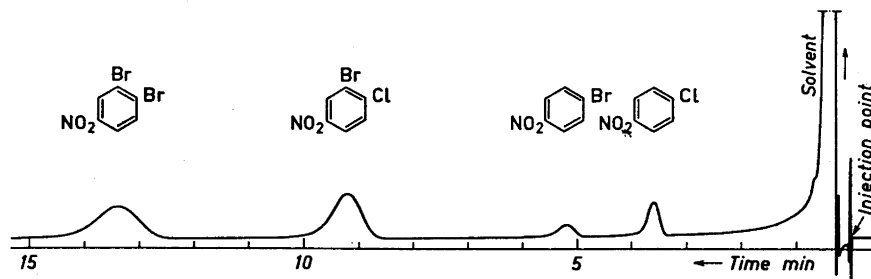


Fig. 1. Fractogram of substances formed in the reactions of 2-chloro-5-nitrobenzenediazonium ion in a hydrobromic acid-acetic acid-water medium.

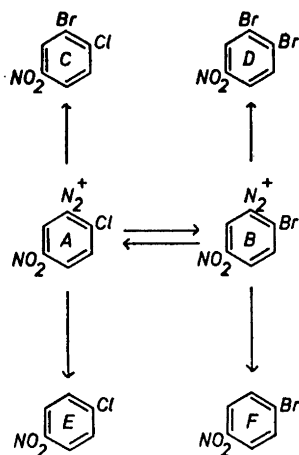


Fig. 2. Reactions of 2-chloro-5-nitrobenzenediazonium ion in a hydrobromic acid-acetic acid-water medium.

rate (He) 85 ml/min. The peaks obtained were easily identified by comparing the retention times with those of authentic samples of the compounds suspected to be present. The fractogram obtained in the experiment with 2-chloro-5-nitrobenzenediazonium ion as the starting material is shown in Fig. 1. The areas under the peaks give a semi-quantitative idea of the molar proportions of the compounds present. In quantitative work, calibrations with known mixtures should always be made.

The experiment with 4-chloro-3-nitrobenzenediazonium ion as the starting material gave a qualitatively analogous result, other isomers being formed.

Discussion. In Fig. 2, a reaction scheme is given for the case of 2-chloro-5-nitrobenzenediazonium ion. In the scheme, all the products observed in the fractogram are accounted for.

One possible explanation for the fact that the compounds are formed in comparable amounts is that the reactions $A \rightarrow C$, $A \rightarrow E$, $B \rightarrow D$ and $B \rightarrow F$ take place at rates comparable to that of $A \rightarrow B$ (the symbols are taken from Fig. 2). As a consequence, some of the aromatic chlorine will be "frozen in" and thus no quantitative conversion of aromatic chlorine into aromatic bromine can take place.

A further reaction which must be considered is the back-reaction $B \rightarrow A$. The

rate of this reaction has been studied in previous work², and it is considerably more rapid than $A \rightarrow B$. It can therefore be estimated, that under the conditions of this work, the small amount of chloride ion generated in the exchange reaction $A \rightarrow B$ was sufficient to produce a condition of equilibrium at a stage when A and B were present in comparable amounts, despite the large excess of hydrobromic acid. It is, however, impossible to conclude how close to equilibrium the reaction $A \rightleftharpoons B$ had approached before the diazonium compounds were consumed. A possible equilibrium is of course also continually being perturbed by the side-reactions.

The nature of the reactions $A \rightarrow C$ and $B \rightarrow D$ is known from the work by Lewis and Hinds⁵. These authors have shown that the rate expression for the reaction between a diazonium ion and bromide ion consists of a monomolecular term arising from the spontaneous decomposition of the diazonium ion, and a bimolecular term ascribed to a nucleophilic attack of bromide ion on the carbon atom carrying the diazonium group. It is thus impossible to suppress the reactions $A \rightarrow C$ and $B \rightarrow D$ compared to $A \rightarrow B$ by increasing the bromide ion concentration.

The reactions $A \rightarrow E$ and $B \rightarrow F$ are somewhat unexpected and cannot at present be explained in detail. A plausible mechanism involves the reduction of the diazonium ion by bromide ion as the initiating step. It would be an interesting task to trace the origin of the hydrogen atom which replaces the diazonium group.

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