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Replacement of Bromine and Chlorine in 2-Halo-5-nitrobenzenediazonium Compounds by Chloride Ion

BO LAMM

Nobel Institute of Chemistry, Stockholm 50, Sweden

In a recently published paper¹, the present author reported that nucleophilic halogen exchange reactions take place at room temperature between bromine or chlorine in 4-halo-3-nitrobenzenediazonium ion and chloride ion. Analogous reactions have now been found to take place between bromine and chlorine in 2-halo-5-nitrobenzenediazonium ion and chloride ion.

A kinetic investigation of these reactions is in progress, and some preliminary results will be presented below.

As far as possible, the competitive technique is applied, which means that at least two reactions are studied in the same kinetic run. This makes a safer comparison between their specific reaction rates possible, since the medium effects cancel. For further information about the experimental conditions, reference should be made to previous work.¹ It should be remarked that instead of the infrared spectroscopic technique employed earlier, quantitative gas chromatography has been adopted as the method of assaying the mixtures of dihalo-nitrobenzenes resulting from the kinetic experiments, since the latter method is considerably faster and has also been found to make possible the quantitative assay of a four-component mixture consisting of two isomeric pairs. Thus, competitive runs with 4-bromo-3-nitrobenzenediazonium ion and 2-bromo-5-nitrobenzenediazonium ion

in a large excess of chloride ion have been made.

The competitive runs with the two isomeric bromonitrobenzenediazonium ions and chloride ion mentioned in the previous paragraph were carried out at two different temperatures. At 25°C, the ratio between the rate constants for the 4-bromo-3-nitro isomer and the 2-bromo-5-nitro isomer was found to be 1.32, and at 15°C, the same ratio was 1.61. (An extrapolation in an Arrhenius plot gives the ratio 1.00 at 40°C.)

Figures for the corresponding exchange reactions between ³⁶Cl-labelled chlorine compounds and non-radioactive chloride ion cannot easily be obtained from competitive runs for experimental reasons but may be calculated indirectly. At 25°C, the ratio for the corresponding chlorine compounds is 1.0. No value at 15°C has been obtained as yet.

Finally, the ratio between the specific reaction rates for 2-bromo-5-nitrobenzenediazonium ion and 2-chloro-5-nitrobenzenediazonium ion in the reactions with chloride ion at 25°C has been found to be 2.02. This further confirms the two-step mechanism postulated¹ for these reactions, with the absence of an "element effect". The very close agreement with the ideal value 2 is, however, fortuitous, because experiments which are in progress indicate that the reactions have different temperature coefficients.

One more conclusion may be drawn from the data presented above. Structurally, the 2-halo-5-nitrobenzenediazonium ions may be imagined to arise from the 4-halo-3-nitrobenzenediazonium ions by letting the diazonium group and the nitro group change places. It is interesting to note that this reversal does not have any substantial influence upon the halogen exchange reaction rate constants, since a diazonium group and a nitro group might be expected to interact to a different extent with a large halogen atom like bromine in an *ortho* position, in virtue of their different steric requirements. It is quite probable that solvation of the charged diazonium group makes it "larger" in the thermodynamic sense than would be apparent from the inspection of a molecular model.

Actually, the similarity of the specific reaction rates for the different isomers is nothing but a confirmation of an empirical multiple-substitution-additivity rule for the free-energy-of-activation changes due to substitution. Reference should be made to a review of this subject by Joffé.²

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Nucleophilic Substitution of Aromatic Chlorine in Diazonium Ions by Bromide Ion

BO LAMM

Nobel Institute of Chemistry, Stockholm 50, Sweden

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

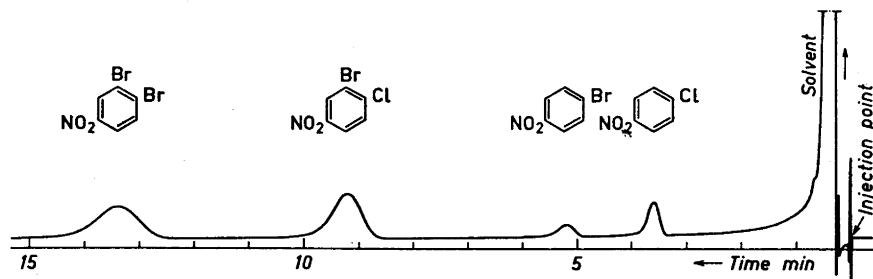


Fig. 1. Fractogram of substances formed in the reactions of 2-chloro-5-nitrobenzenediazonium ion in a hydrobromic acid-acetic acid-water medium.