

On the Spontaneous Decomposition of 2,4,6-Tribromobenzenediazonium Ion in Aqueous Hydrobromic Acid

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The spontaneous decomposition of 2,4,6-tribromobenzenediazonium ion in aqueous hydrobromic acid has been studied. No 2,4,6-tribromophenol is formed. Instead, the reaction yields a mixture of 1,3,5-tribromobenzene and 1,2,3,5-tetrabromobenzene. Deuterium labelling has further shown that the hydrogen atom replacing the diazonium group in the formation of 1,3,5-tribromobenzene originates from the solvent and not from another aromatic molecule. A free-radical mechanism that explains the features of the reaction is suggested.

In connection with a kinetic study of the exchange reactions between chloride ion and bromine or chlorine in a number of 2,4,6-trihalobenzenediazonium ions,¹ a side reaction was observed in which 2,4,6-trichlorobenzenediazonium ion was slowly converted to 1,3,5-trichlorobenzene in aqueous hydrochloric acid medium.

The reductive replacement of the diazonium group by hydrogen is a well-known preparative method.^{2,3} It usually requires a reducing agent like ethanol or hypophosphorous acid. In the present case, it is difficult to envisage a "reducing agent" other than some aromatic compound present in the system, *i.e.*, either the diazonium ion or the corresponding phenol.

A scrutiny of the literature revealed that the same reaction had been observed in aqueous sulphuric acid by Hodgson and Mahadevan.⁴ In one of their experiments, a catalytic amount of divalent copper was present, and the medium also contained some acetic acid. Under these conditions the reductive displacement of the diazonium group by hydrogen was found to take place both in 2,4,6-tribromo- and 2,4,6-trichlorobenzenediazonium ion. In the discussion presented in the paper,⁴ copper is referred to as the reducing agent. It is hard to understand how divalent copper can perform this function. It is not wholly inconceivable that acetic acid could act as a reducing agent in a free-radical process, but the authors do not discuss this possibility. They do comment on the remarkable fact that no 2,4,6-trihalophenol is observed among the products, which they ascribe to steric factors.

To obtain an insight into the mechanism of this reductive replacement of the diazonium group by hydrogen, we decided to trace the origin of the entering hydrogen atom with the aid of deuterium labelling. We were unable to duplicate the original side reaction in the system 2,4,6-trichlorobenzene-diazonium ion in hydrochloric acid and obtained in later runs 1,2,3,5-tetrachlorobenzene. We therefore turned to the system 2,4,6-tribromobenzene-diazonium ion in hydrobromic acid. It may be noted that in the solvent system water-hydrobromic acid-acetic acid, replacement of the diazonium group by hydrogen has previously been observed.⁵

In actual fact, 2,4,6-tribromobenzene-diazonium ion in aqueous hydrobromic acid was found to yield 1,3,5-tribromobenzene, among other products. No copper compounds were added, and the diazonium compound was added to the solvent as its tetrafluoroborate salt, which could be prepared in a pure state. Together with 1,3,5-tribromobenzene, a comparable amount of 1,2,3,5-tetrabromobenzene was formed.

A priori, the replacement of the diazonium group by hydrogen can take place *via* a proton transfer step, a free radical process, or a hydride transfer step. The first possibility appears very unlikely, since it would involve an electrophilic attack at a positive site in the diazonium ion. To distinguish between the other two possibilities, an experiment was devised involving the decomposition of fully deuterated 2,4,6-tribromobenzene-diazonium ion in light aqueous hydrobromic acid. If, on one hand, the 1,3,5-tribromobenzene formed were to contain *two* deuterium atoms and *one* protium atom per molecule, the hydrogen would originate from the solvent. If, on the other hand, the 1,3,5-tribromobenzene were to contain *three* deuterium atoms per molecule, the new hydrogen atom must originate from a different aromatic molecule. The latter alternative would nearly prove a free-radical process, since hydride transfer from an aromatic position appears very unlikely in the present case.

The exclusive introduction of light hydrogen was found to occur. The implications of this result will be discussed at the end of this paper.

EXPERIMENTAL

I. Preparation of compounds

Aniline-d₅. Benzene-*d₆* (Ciba, Basel, 99 % D) was nitrated,⁶ and the nitrobenzene-*d₅* was reduced with tin and hydrochloric acid.⁶ The over-all yield was 65 %.

2,4,6-Tribromoaniline-d₂ was obtained from aniline-*d₅* by bromination in glacial acetic acid.⁷ M.p. 121°C, lit.⁷ 120°C (for the light compound).

2,4,6-Tribromobenzene-diazonium-d₂ fluoborate. Of the preceding compound, 8.25 g (0.025 mole) was dissolved in 50 ml of hot 70 % sulphuric acid. The solution was stirred and rapidly cooled to 10°. A solution of 1.75 g (0.025 mole) of sodium nitrite in 10 ml of water was carefully added. A clear, pale green solution was obtained, which was allowed to stand at room temperature for 30 min. Ice (75 g) was added, followed by a cold, concentrated solution of 33 g (0.3 mole) sodium tetrafluoroborate in water. After 30 min the white precipitate formed was filtered off, washed with aqueous sodium tetrafluoroborate solution, cold methanol and ether, and dried *in vacuo*. Yield 8.5 g (79 %), decomposition temp. 243°C, lit.⁸ 243°C. The unlabelled compound was prepared in the same way, starting from aniline.

1,2,3,5-Tetrabromobenzene was prepared by diazotization of 2,4,6-tribromoaniline, followed by a Sandmeyer reaction with cuprous bromide in hydrobromic acid according to Hodgson and Mahadevan.⁴ M.p. 98°C, lit.⁴ 98°C.

All melting points were determined on a Kofler "Heizbank". The purity of the compounds was checked with NMR and (in applicable cases) GLC.

II. Decomposition experiments

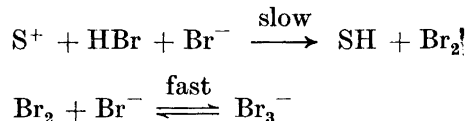
2,4,6-Tribromobenzenediazonium-*d*₂ fluoborate (2.0 g, 0.0047 mole) was dissolved in 50 ml of 5 M hydrobromic acid. This solution was placed in a thermostatic bath at 30.0 ± 0.1°C. After 15 days all of the diazonium ion was consumed as indicated by a negative colour reaction with acetate-buffered 2-naphthol solution. The solution was brought to pH 8 with sodium carbonate solution and extracted with ether. After having been dried over calcium chloride and filtered the ether was allowed to evaporate at room temperature. Without undue delay the remainder, weighing about 1.4 g, was dissolved in carbon tetrachloride and analyzed on a Perkin-Elmer Model 116 gas chromatograph equipped with a Model D 2 digital integrator. A 4 mm i.d., 2 m Perkin-Elmer "O"-column was used (silicon grease on Chromosorb), temp. 195°C, flow rate 80 ml/min, carrier gas helium. Three separate runs were made. The reaction product was found to contain 5 ± 1 mole % 1,3,5-tribromobenzene and 95 ± 1 mole % 1,2,3,5-tetrabromobenzene, based on a calibration with known mixtures of the pure compounds.

A preparative GLC separation of the solution was then carried out on an Aerograph, Autoprep Model A-700. A 3/8" i.d., 2 m column with 20 % SE-30 on Chromosorb W was used, temp. 180°, flow rate 200 ml/min, carrier gas nitrogen. The isotopic composition of the tribromobenzene contained in the mixture was then determined by mass spectrometry at the Department of Chemistry, University of Lund. The characteristic four-peak pattern of a tribromo compound was obtained at *m/e* 314, 316, 318, and 320, which is in agreement with C₆HD₂Br₃ or 1,3,5-tribromobenzene-*d*₂. Similarly, a mass spectrum of the tetrabromo compound proved the presence of two deuterium atoms per molecule, as expected.

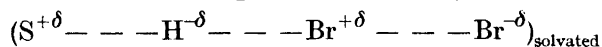
In a similar experiment, 2.0 g (0.0047 mole) of 2,4,6-tribromobenzenediazonium-*d*₂ fluoborate was dissolved in 75 ml of 1 M hydrobromic acid. After 5 days at 30°C the reaction was complete. The yield after ether extraction was about 1.5 g. Three separate experiments gave 53 ± 1 mole % 1,3,5-tribromobenzene-*d*₂ and 47 ± 1 mole % 1,2,3,5-tetrabromobenzene-*d*₂.

DISCUSSION

It was suggested above that the introduction of light hydrogen would speak in favour of a hydride transfer or radical mechanism. The only species present that might reasonably act as a source of hydride ions is undissociated hydrogen bromide, and we can hypothetically write



The transition state for the slow process can be represented by



S⁺ could be a diazonium ion or a species derived from it through loss of nitrogen. The concentration of undissociated hydrogen bromide is negligibly small, however, both in 1 M and 5 M aqueous solution. If anything, it should

be higher in 5 M acid where the over-all rate was found to be lower and where the yield of 1,3,5-tribromobenzene was only 5 mole %. We feel forced, therefore, to rule out this mechanism.

It is, however, possible to reconcile a free-radical process with the experimental results in the following way, and at the same time explain an apparent anomaly in the reaction, namely that no 2,4,6-tribromophenol is formed.⁴ Let us suppose that some of the diazonium ions initially present are nucleophilically attacked by water. This produces phenol, but it is rapidly consumed in a reaction with another aromatic species, in which the phenolic (light) hydrogen is transferred. The phenoxy radical left behind is subsequently lost, possibly giving rise to polymeric by-products. The 1,2,3,5-tetrabromobenzene is formed by a nucleophilic attack on the diazonium ion by a bromide ion, in a combined mono- and bimolecular process⁹ (a more recent interpretation is an exclusively bimolecular process with low specificity¹⁰), and it is then natural that this becomes the most important product in 5 M acid. Yet, the over-all rate is lower in the stronger acid, but this may well be due to a salt-effect. A reaction which proceeds *via* a transition state with less charge separation than that of the initial state becomes slower when the ionic strength of the medium increases.

For completeness, one final point requires comment. If the 2,4,6-tribromobenzenediazonium- d_2 ion had been contaminated with monodeuterated material the formation of 1,3,5-tribromobenzene- d_2 could have been explained as the result of a kinetic isotope effect on a reaction in which an aromatic hydrogen atom replaces the diazonium group. This possibility requires careful consideration particularly since such a hydrogen transfer step is expected to display a strong kinetic isotope effect. It can, however, be easily ruled out in the following way.

A careful examination of the mass spectrum of the 1,2,3,5-tetrabromobenzene- d_2 (another product formed from the diazonium ion), reveals a quintet at m/e 392, 394, 396, 398, and 400. The first peak of the corresponding monodeuterated compound should have appeared at m/e 391, but nothing was observed in the mass spectrum at this number. This proves that less than 2 % and probably less than 1 % of the monodeuterated species is present. (Note that the peaks m/e 393, 395, 397, and 399 are less useful in this connection, because of the ¹³C satellite peaks of the d_2 compound.) In fact, the specifications of the benzene- d_6 obtained from Ciba indicated an isotopic purity of at least 99 %. In the decomposition of 2,4,6-tribromobenzenediazonium- d_2 ion in 1 M hydrobromic acid, the yield of 1,3,5-tribromobenzene was never quantitatively determined, but a safe lower limit would be 20 %. It follows that the total amount of light aromatic hydrogen is insufficient to explain the isotopic composition of the tribromobenzene on the assumption that a kinetic isotope effect exists, and this possibility can thus be ruled out.

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