

Correction to "The Stability of Metal Halide Complexes in Aqueous Solution III. The Chloride, Bromide and Iodide Complexes of Bismuth" *

STEN AHRLAND AND ING MARGREN THE

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

An error has crept into the calculations of the last column of Table 3B, where the head should read $X_5 \cdot 10^{-6} M^{-5}$ instead of $X_5 \cdot 10^{-7} M^{-5}$. As a consequence, the values of β_5 and β_6 for the chloride system have come out one power of ten too high. In Table 11, the correct values of $\log \beta_5$ and $\log \beta_6$ should therefore read 6.72 and 6.56 (instead of 7.72 and 7.56, respectively).

This correction means that the complex formation curve of the chloride system is much less steep in its upper part than was reported before. It is gratifying however that the new course, presented in the Fig. 1, fits much better

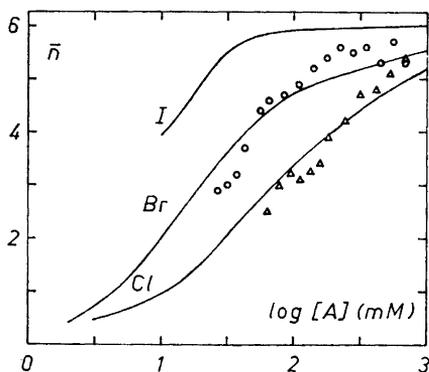


Fig. 1.

than the previous one to the experimental values of \bar{n} which are found from the slope of the C_M , C_A lines of constant E_M . In spite of their considerable random error, these values are therefore on the whole much more reliable than was once believed.

* *Acta Chem Scand.* **11** (1957) 1111.

The correction also implies that the range of existence of the third and, especially, the fourth complex is in reality wider and that of the fifth complex narrower than was reported in Fig. 3 of the original paper.

We are indebted to Dr G. A. Wright, University of Auckland, New Zealand, who kindly informed us of the error revealed by his careful reading.

Received May 12, 1961.

A Convenient Synthetic Route to ^{36}Cl -labelled Aromatic Compounds

B O L A M M

Nobel Institute of Chemistry, Stockholm 50, Sweden

The method generally applied¹ for introducing isotopically labelled chlorine into aromatic compounds is based on the well-known reaction

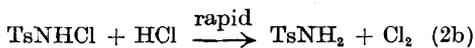
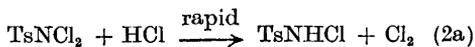


which has been carried out with chlorine gas containing the isotope in question, generally ^{36}Cl (ArH meaning, in general, any suitable aromatic compound). It is evident from formula (1) that half the amount of chlorine taking part in the reaction is lost as hydrochloric acid. For the sake of economy, it is generally necessary to recover the hydrochloric acid when working with ^{36}Cl in view of the high price² of this isotope, the recovered material being used in subsequent runs.

In the present communication, an alternative method of introducing ^{36}Cl into aromatic compounds will be described. This method has the advantage of utilizing in a single step almost all of the radioactive starting material (hydrochloric acid- ^{36}Cl) taking part in the reaction, albeit at the price of dilution with inactive chlorine. In the author's work, the latter circumstance does not cause any inconvenience, as the starting material obtained from The Radiochemical Centre, Amersham, England, has a sufficiently high specific activity to allow for about a tenfold dilution with inactive chlorine. Another advantage of the method suggested below is that the somewhat intricate preparation and handling of radioactive chlorine gas is completely circumvented, the aqueous solution of hydro-

chloric acid- ^{36}Cl obtained from the supplier being used as such.

The method of chlorination adopted was developed by Orton *et al.*^{3,4} An aromatic compound and a corresponding amount of dichloramine T (N,N-dichloro-*p*-toluenesulphonamide) are dissolved together in a suitable solvent. Upon addition of a catalytic amount of hydrochloric acid, a reaction sequence starts that may be formulated in the following way.



In the reaction scheme above, Ts denotes the *p*-toluenesulphonyl, "tosyl", group, and ArH means any aromatic compound. The relative significance of steps (2a) and (2b) is of no interest in the present case, since both reactions are rapid ones as compared to step (3). It simply bears a reference to the stoichiometrically stipulated fact that each mole of dichloramine T liberates two moles of chlorine and, in consequence, suffices for two moles of ArH, if monosubstitution is achieved.

The kinetic behaviour of the reaction sequence formulated above has been established from ^{36}Cl tracer experiments carried out by Olson *et al.*⁵ In fact, if labelled hydrochloric acid is added as the catalyst, there will be isotopic equilibrium between the hydrochloric acid and the molecular chlorine that is postulated as the chlorinating agent in step (3) above. Now, it was thought that this circumstance might serve as the theoretical foundation for a synthetic method in which the isotopic chlorine is introduced as hydrochloric acid- ^{36}Cl in the above-mentioned reaction sequence. If the molar amount of hydrochloric acid- ^{36}Cl is appreciably smaller than that of dichloramine T, a correspondingly high radiochemical yield of ^{36}Cl -labelled organic substance may be expected. In actual fact, this turned out to be true. The chlorination of acetanilide could be performed in 90 % radiochemical yield, the theoretically attainable value being 92 %. The chemical yield was 99 %. Indeed, practically quantitative chemical yields were also reported by Orton *et al.*⁴ The product resulting after hydrolysis of the chloroacetanilides ini-

ally formed, an isomeric mixture of chloroanilines, had the following composition (found by the isotope dilution technique): *o* 26 ± 2 %, *m* 2 ± 1 %, *p* 72 ± 2 %. These values are in fair agreement with those found by Orton *et al.*⁴, *o* 35 ± 5 %, *p* 65 ± 5 % (the *o/p*-ratio depending somewhat on the solvent employed).

Finally a few words might be said about the scope of the reaction. The "Orton" chlorination with dichloramine T and hydrochloric acid is generally applicable for compounds having a high reactivity, similar to that of acetanilide. Benzene itself failed to react in chloroform solution, and other solvents also gave negative results. On the other hand, the product of monochlorination of benzene, chlorobenzene- ^{36}Cl , may be prepared indirectly from an isomeric mixture of ^{36}Cl -labelled chloroanilines by diazotisation and reduction with hypophosphorous acid. The *ortho* and *para* isomers of chloroaniline- ^{36}Cl may each be isolated in the pure state from the isomeric mixture resulting from the synthesis in accordance with a procedure employed by Jones *et al.*⁶, which involves preferential steam-distillation of the *ortho* isomer from an acid solution of the amines. The *para* isomer is recovered from the nonvolatile part by acetylation, recrystallization of the anilide and hydrolysis.

A full experimental account will be published later.

Financial support from the *Swedish Natural Science Research Council* is gratefully acknowledged.

1. Murray, A. and Williams, D. L. *Organic Syntheses with Isotopes*, Interscience, New York and London 1958, Part II, pp. 1178—1194.
2. Sørensen, P. *Isotopfortyndingsanalyser* (Diss.) DTH, Copenhagen 1957, p. 34.
3. Orton, K. J. P. and King, H. *J. Chem. Soc.* **99** (1911) 1185.
4. Orton, K. J. P. and Bradfield, A. E. *J. Chem. Soc.* **1927** 986.
5. Olson, A. R., Porter, C. W., Long, F. A. and Halford, R. S. *J. Am. Chem. Soc.* **58** (1936) 2467.
6. Jones, W. J. and Orton, K. J. P. *J. Chem. Soc.* **95** (1909) 1056.

Received May 3, 1961.