The Exchange Reaction of 3-Bromo-2-iodonitrobenzene with Tetrabutylammonium Bromochlorocuprate(I) in Chlorobenzene

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Liedholm, B., 1988. The Exchange Reaction of 3-Bromo-2-iodonitrobenzene with Tetrabutylammonium Bromochlorocuprate(I) in Chlorobenzene. – Acta Chem. Scand., Ser. B 42: 237–241.

In the halogen exchange reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium bromochlorocuprate, Br as well as Cl of the bromochlorocuprate(I) ion are available for exchange with I of the aryl halide. Simulated values of the rate constants for the formation of the end product, 3-bromo-2-chloronitrobenzene, are given.

The copper(I) catalyzed halogen exchange reactions of 3-bromo-2-iodonitrobenzene with tetrabutylammonium dibromo- and dichlorocuprates (I) have previously been studied kinetically in chlorobenzene.[1] The reaction of the halogenoarene with the dibromocuprate anion was a reversible second-order reaction, first-order in both arene and anion, whereas no appreciable reversibility was noticed in the exchange with the dichlorocuprate anion, also of second order. The exchange reactions of 2,3-dibromonitrobenzene with tetrabutylammonium dichloro- and bromochlorocuprates(I) have also been investigated[1] (see Table 1).

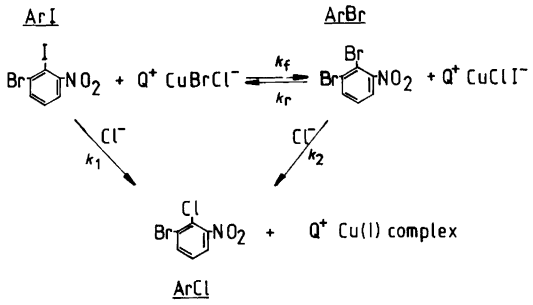
The crystal structures of the tetrabutylammonium salts have been determined from single-crystal X-ray diffraction data. The dibromo- as well as the dichlorocuprates(I) are linear monomers.[2] The most plausible description of the structure of bromochlorocuprate(I) entails one dichlorocuprate(I) ion, one dibromocuprate(I) ion and two bromochlorocuprate(I) ions per unit cell.[3] This was confirmed by an infrared spectrum.

This paper describes the completion of the previous studies with a kinetic study of the exchange reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium bromochlorocuprate(I) in

Table 1. Rate parameters for exchange reactions of 2-halogeno-3-bromonitrobenzenes and tetrabutylammonium dihalogenocuprates(I) ($Q^+CuX_2^-$) in chlorobenzene at 90 °C.[a]

Aromatic compound/M	$Q^+CuX_2^-$	X/M	K_{eq}	$k_f/10^{-4}M^{-1}s^{-1}$	$k_r/10^{-4}M^{-1}s^{-1}$
3-Bromo-2-iodonitrobenzene					
0.0546	$Q^+CuBr_2^-$	0.1638	1.819	18.49	10.16
0.0546	$Q^+CuCl_2^-$	0.1638	>50	3.20(3)	
2,3-Dibromonitrobenzene					
0.0551	$Q^+CuCl_2^-$	0.1102	>50	2.66(2)	
0.0541	$Q^+CuBrCl^-$	0.1082[b]		2.04(2)	

[a]From Ref. 1. [b]As Cl.



Scheme 1.

chlorobenzene. In this reaction, Br as well as Cl of the $CuBrCl^-$ anion are available for exchange with I of 3-bromo-2-iodonitrobenzene.

Results and calculations

The reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium bromochlorocuprate (I) was studied by means of GLC and ^1H NMR at 90 °C. From the results of the preceding investigations of the kinetics of the reactions of 3-bromo-2-iodonitrobenzene and 2,3-dibromonitrobenzene with tetrabutylammonium bromo- and chlorocuprates(I),[1] it was possible to predict the course of the reaction (Scheme 1). The following rate expressions are applicable:

$$-\frac{d[ArI]}{dt} = k_f [ArI][Br^-] - k_r [ArBr][I^-] + k_1 [ArI][Cl^-] \quad (1)$$

$$-\frac{d[ArBr]}{dt} = k_2 [ArBr][Cl^-] + k_r [ArBr][I^-] - k_f[ArI][Br^-] \quad (2)$$

$$\frac{d[ArCl]}{dt} = k_1 [ArI][Cl^-] + k_2[ArBr][Cl^-] \quad (3)$$

The progress of the exchange reaction is illustrated in Fig. 1 with the formation and subsequent disappearance of 2,3-dibromonitrobenzene together with the growth of the end product, 3-bromo-2-chloronitrobenzene. The reaction is followed to 98 % consumption of the 3-bromo-2-iodonitrobenzene.

The rate expression (3) for the formation of

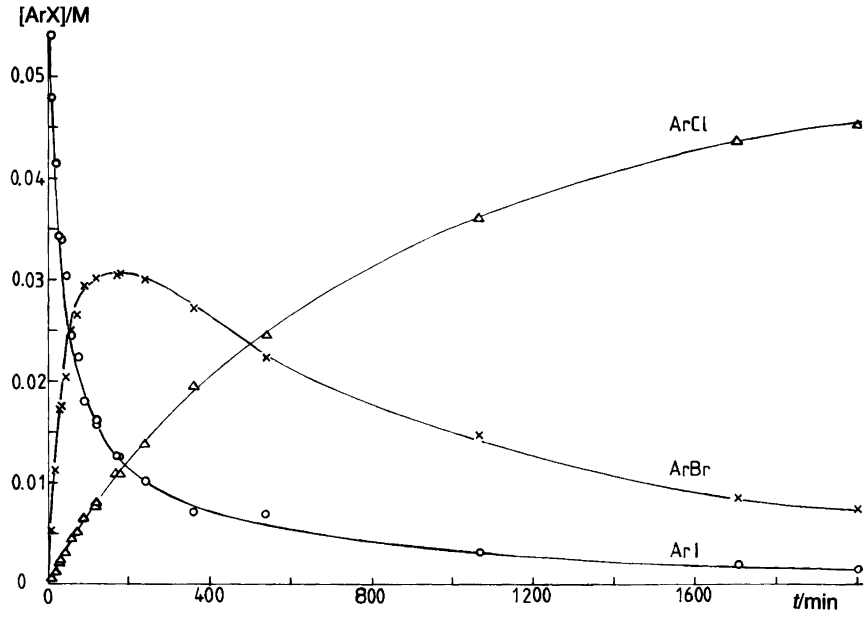


Fig. 1. The exchange reaction of 3-bromo-2-iodonitrobenzene (ArI = 0.0541 M) with tetrabutylammonium bromochlorocuprate(I) (0.1082 M) with the formation of 2,3-dibromonitrobenzene (ArBr) and 3-bromo-2-chloronitrobenzene (ArCl) at 90 °C.

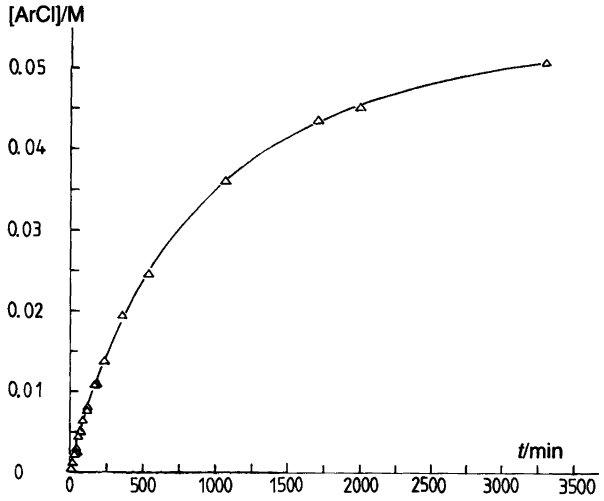


Fig. 2. The formation of 3-bromo-2-chloronitrobenzene. The triangles are the experimental results and the curve is calculated in the simulation procedure.

3-bromo-2-chloronitrobenzene can be transformed into eqn. (4), where $X_{ArI} + X_{ArBr} = 1$.

$$\frac{d[ArCl]}{dt} = [(k_1 - k_2)X_{ArI} + k_2]([ArI] + [ArBr])[Cl^-] \quad (4)$$

The rate constants, k_1 and k_2, were determined using a simulation procedure for the solution of the differential eqn. (4).[1]

The triangles in Fig. 2 are the experimental results obtained by GLC. The curve has been calculated by the simulation procedure for the formation of 3-bromo-2-chloronitrobenzene. The simulated rate constants k_1 and k_2 were 2.17(5) $\times 10^{-4}$ and 1.92(5)$\times 10^{-4}$ $M^{-1}s^{-1}$, respectively.

Conductance measurements on the tetrabutylammonium dihalogenocuprates(I) in chlorobenzene in the concentration range 0.0015–0.05 M at 21.5 °C were performed to elucidate the "state" of the salts in this solvent. The low solubility of the salts in chlorobenzene at this temperature prevented the use of higher concentrations. In solvents of low polarity, like chlorobenzene, ions, contact ion-pairs, loose ion-pairs, triple ions or higher aggregates are possibly involved. The concentration range of interest was 0.025–0.10 M, within which the kinetic investigations were carried out. A weak minimum in the $\Lambda - c^{1/2}$ plot is observed at a concentration of 0.015 M for the dichloro- and bromochlorocuprates(I), and at 0.02 M for the dibromocuprate(I) salt. However, the molar conductivities, Λ, are seen to be almost constant in the 0.005–0.05 M range of concentrations of the salts (see Fig. 3).

Discussion

The rate constants k_1 and k_2, 2.17×10^{-4} and 1.92×10^{-4} $M^{-1}s^{-1}$, respectively, for the exchange reaction of 3-bromo-2-iodonitrobenzene with tetrabutylammonium bromochlorocuprate(I) are of the same magnitude as the rate constants for exchange reactions obtained in the preceding investigations in chlorobenzene.[1] k_2 in this work (1.92×10^{-4} $M^{-1}s^{-1}$) should be compared with k_f for the exchange reaction of 2,3-dibromonitrobenzene with bromochlorocuprate(I) anion found in the preceding paper (2.04×10^{-4} $M^{-1}s^{-1}$).[1] The rate constant k_1, 2.17×10^{-4} $M^{-1}s^{-1}$, can be compared approximately with the rate constant k_f, 3.20×10^{-4} $M^{-1}s^{-1}$ for the exchange reaction of 3-bromo-2-iodonitrobenzene with the dichlorocuprate(I) anion[1] (see Table 1). However, two Cl of the dichlorocuprate(I) anion may be in position for a possible reaction following a molecular collision with the halogenoarene, and a higher value of the rate constant k_f should therefore be expected. This was also found. In addition, we must take into consideration the fact that the rate constants k_1 and k_2 determined in this work are dependent on the preceding reversible step [eqn. (5)]. The ^1H NMR investigations

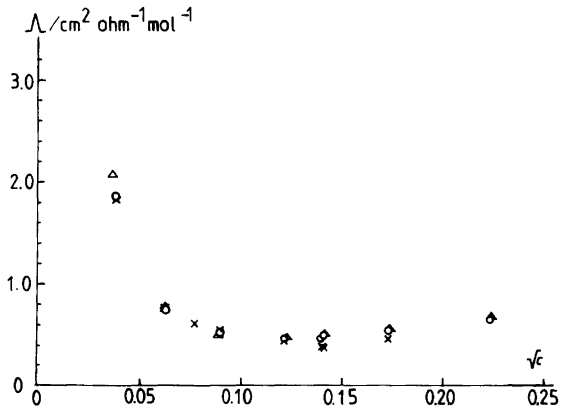


Fig. 3. Plots of the molar conductivities, Λ, against $c^{1/2}$ for the tetrabutylammonium dihalogenocuprates(I) in chlorobenzene at 21.5 °C (○ $Q^+CuCl_2^-$, △ $Q^+CuBrCl^-$ and × $Q^+CuBr_2^-$). The Λ values are relative values.

of the tetrabutylammonium dihalogenocuprates (I) in chlorobenzene[1] revealed that all the salts, irrespective of the nature of the anion species (CuI_2^-, $CuBr_2^-$, $CuCl_2^-$ or $CuBrCl^-$), had identical chemical shifts. This result suggested that ion pairing must be relatively unimportant for the tetrabutylammonium dihalogenocuprates(I) in chlorobenzene.

$$ArI + Q^+CuBrCl^- \rightleftarrows ArBr + Q^+CuClI^- \quad (5)$$

Fuoss and Kraus[4] have proposed that the presence of triple ions accounts, to a large measure, for the appearance of minima in the $\Lambda - c^{1/2}$ curves of salts in solvents of low dielectric constants (see Fig. 3). The original treatment by Fuoss and Kraus assumed that the triple ion formation constants K_{+-+} and K_{-+-} were equal. In most cases this assumption is not correct.[5] Grigo[6] has shown that it is possible to fit conductance data in solvents of low dielectric constant without assuming triple ion formation. Association constants are derived from conductivity data in the 10^{-6}–10^{-5} M concentration range. For higher salt concentrations, viz. 10^{-3}–10^{-1} M, no mathematical equations of any reliability are available. Svorstøl and Songstad[7] have studied the variation of conductivity with concentration for some tetraalkylammonium halides in dichloromethane at 25 °C. They found a minimum in their $\Lambda - \log c$ curves at a concentration of the salts of ~0.029 M but, in addition, a maximum at higher concentrations, viz. ~0.2 M. Such high concentrations are impossible for us to obtain because of the low solubility of the tetrabutylammonium dihalogenocuprates(I) in chlorobenzene. We find minima in our $\Lambda - c^{1/2}$ curves in the concentration range 0.015–0.020 M. The concentration at which these minima are observed is known to depend on the dielectric constant (ε) of the solvent. The conclusion of Svorstøl and Songstad is that an increase in ε at higher salt concentrations causes a decrease of the association constant and hence higher molar conductivity.

The concentrations of the various species, free ions, ion-pairs or triple ions are unknown due to the present lack of information on concentrated salt solutions in solvents of low ε.

Experimental

The reaction between 3-bromo-2-iodonitrobenzene and the tetrabutylammonium bromochlorocuprates(I) in chlorobenzene was performed in an argon atmosphere and was followed by means of GLC. Aliquots taken from the reaction mixture were quenched in ice-water, made alkaline and extracted with ether. The ether solutions, containing the aryl halides, were analyzed on a Perkin Elmer 3920-B gas chromatograph with a hot wire detector. Other conditions are described in Ref. 1. The aryl halides were also identified by ^1H NMR spectra and mass spectra (see Ref. 1). The conductivity measurements were performed with a Tetramatic 4-electrode MHO-Meter.

All calculations were made on a Compucorp 625 Mark II computer.

Chlorobenzene was distilled before use. 3-Bromo-2-iodonitrobenzene and tetrabutylammonium bromochlorocuprate(I) have been described in a previous paper.[1]

Acknowledgements. I am very grateful to Dr. Stig Fredriksson and Dr. Mats Jonsson, Department of Physical Chemistry, Chalmers University of Technology, for valuable help and discussions. A grant from the Gothenburg Board of Education is highly appreciated.

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Received November 17, 1987.