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# Reversible Substitution Reactions of Tetrahedral Tetrahaloferrates(III) with Thiocyanate

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*The kinetics of the reversible substitution reactions of $SCN^-$, $Cl^-$ and $Br^-$ ligands at tetrahedral tetrahaloferrates(III) were studied photometrically in dichloromethane. Infrared spectra show thiocyanate to be N-bonded in these complexes. With the aid of conductometrically-determined ion-pair association constants, evidence was found for an ion-pair, ion-pair mechanism. The activation parameters ($\Delta H^{\ddagger}$ between 3 and 30 kJ $mol^{-1}$, $\Delta S^{\ddagger}$ between $-77$ and $-155$ J $K^{-1}$ $mol^{-1}$) indicate an associative mode of activation. A linear enthalpy relationship was found (slope 0.57), implying substantial bond-breaking and bond-making in the transition state ($I_a$ mechanism). The relative bond strengths of the $(FeX_3)Y^-$ combinations, with $X^- = Cl^-$ or $Br^-$ and $Y^- = Br^-$, $Cl^-$ or $NCS^-$, vary in the order $Br^- < Cl^- \ll NCS^-$.*

## Introduction

It is well established that substitution reactions of four-coordinate transition metal complexes in general proceed via a limiting associative or an associative interchange mechanism [1, 2]. However, in depth mechanistic information is available mainly for reactions at square-planar complexes, notably of platinum(II), palladium(II) and nickel(II) [3–5].

To fill this gap, we recently reported on substitution reactions at tetrahedral tetrahaloferrates(III) in dichloromethane [6]. The importance of ion-pairing and the associative character of the reaction mechanism were inferred from this study. It seemed worthwhile to extend the study in dichloromethane to thiocyanate as the incoming and leaving ligand, involving the possibility of linkage isomerism as found for substitution reactions in square-planar palladium(II) complexes [7, 8].

We report here a study of reversible substitution reactions at tetrahedral iron(III) complexes with the (pseudo)halide ligands $SCN^-$, $Cl^-$ and $Br^-$ in dichloromethane. The reactions studied can be represented by the general reaction scheme:

$$(FeX_3)Y^- + Z^- \rightleftarrows (FeX_3)Z^- + Y^- \qquad (1)$$

in which the $(FeX_3)$-moiety of the complex can be regarded as the inert 'skeleton'. The results will be interpreted in terms of entering group and substrate dependence.

Although cations have substantial effects on the reaction rates [6], only one counterion, bis(triphenylphosphine)iminium (PNP), was used throughout in this study. The reason is that most thiocyanate salts of organic cations are very hygroscopic and therefore difficult to handle, with the exception of the PNP salt. Furthermore, the choice of cation is restricted by the overall limited solubility of the salts in dichloromethane.

## Experimental

### *Chemicals*

Bis(triphenylphosphine)iminium chloride, bromide and thiocyanate were prepared as described by Martinsen and Songstad [9]. The tetrachloroferrate(III) and tetrabromoferrate(III) compounds of the PNP ion were prepared as described [6]. The results of the analyses agreed within 1% for the (pseudo)halide and within 2% for iron. The tetrakis(isothiocyanato)ferrate(III) complex was prepared in solution. Commercial iron(III) thiocyanate (K and K Fine Chemicals) was purified by dissolving the salt in dichloromethane and filtering off the insoluble part. The filtrate was then partly evaporated. After analysis one equivalent of PNP(SCN) was added to the $Fe(NCS)_3$ solution.

Dichloromethane (Merck, *p.a.*) was purified immediately before use, as described in [10].

### *Kinetic Measurements*

To verify the existence of mixed halo–thiocyanatoferrate(III) complexes the UV–visible spectra of 20 solutions of different molar ratios (equally spaced on the molar ratio scale) of the tetrakis(isothiocyanato)ferrate(III) and the tetrahaloferrate(III) complexes were recorded. The total iron(III) concentration was fixed at $1.19 \times 10^{-4}$ *M*. For all wavelengths plots of

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absorbance *vs.* molar ratio showed three changes of slope. This indicates the existence of all three intermediate complexes. Comparison of the extrapolated *vs.* measured absorbances showed less than 5% disproportionation for all compounds with formulae $Fe(NCS)_3X^-$, $Fe(NCS)_2X_2^-$ and $Fe(NCS)X_3^-$, with $X = Cl^-$, $Br^-$. The $Fe(NCS)_4^-$ complex dissociates between 5 and 10%. The molar ratio curves yielded the molar absorbance coefficients needed for the evaluation of the rate constants: 8330 ($FeCl_3NCS^-$; 470 nm), 750 ($FeCl_3Br^-$; 470 nm; ref. [6]), 7170 ($FeCl_3NCS^-$; 480 nm), 8130 ($FeBr_3NCS^-$; 520 nm) and 1530 ($FeBr_4^-$; 520 nm) $M^{-1}$ $cm^{-1}$.

The kinetic measurements were performed with stopped-flow equipment [6]. Solutions of the mixed iron(III) complexes were prepared by mixing the (pseudo)haloferrate(III) complexes in the appropriate molar ratio. The reactions were carried out under pseudo first-order conditions using excess (pseudo)-halide. The mole ratio of the (pseudo)halide to the ferrate(III) complex was varied (taking at least 6 different concentrations), from at least 7 to 40 (for the fastest reactions) or from 7 to 200 (for the slowest reactions). The reactions (forward and reverse reactions) were followed at 420 nm ($FeCl_4^- + Br^-$), 470 nm ($FeCl_3Br^- + NCS^-$), 480 nm ($FeCl_4^- + NCS^-$) and at 520 nm ($FeBr_4^- + NCS^-$). The changes in absorbance resulting from the reactions are most favourable at these wavelengths.

The first-order character of the reactions was checked by variation of the iron(III) complex concentration. No influence was found if the experiments were carried out under excess of the (pseudo)halide. This is exemplified by the rate constants $k_1$ in Table II in case of the reactions of $FeCl_3NCS^- + Cl^-$ and $FeBr_3NCS^- + Br^-$, which originate from experiments with iron(III) concentrations varying between $7 \times 10^{-5}$ and $2 \times 10^{-4}$ *M*.

The observed rate constants were evaluated in several ways. The initial rate method was used for the reactions of $FeBr_4^- + NCS^-$ to eliminate contributions of subsequent bromide–isothiocyanate substitutions, and for the reactions of $FeCl_4^- + NCS^-$, $FeCl_3Br^- + NCS^-$, $FeBr_3NCS^- + Br^-$ and $FeCl_4^- + Br^-$ to eliminate contributions of the reverse reactions. All other reactions were followed to at least 85% completion and rate constants were calculated by a least-squares analysis. The temperature dependence of the reactions was studied between 298.1 K and 278.6 K. The temperature was kept constant within 0.1 K.

### *Apparatus*

Kinetic experiments were performed on a Nortech Ltd. stopped-flow apparatus and on a home-made stopped-flow apparatus made of stainless steel and equipped with quartz windows. The apparatus has a pneumatic drive and UV–visible light is transmitted via quartz fibre optics. The dead time is about 3 ms.

TABLE I. Ion-Pair Association Constants[a] (in $M^{-1}$) from the Analysis of Conductivity Data Using the Fuoss-1978 Equation.

| Temperature (K) | Compound | |
|---|---|---|
| | PNP Br | PNP (SCN) |
| 298.15 | 1750 | 1860 |
| 293.15 | 1690 | 1770 |
| 289.65 | 1620 | 1700 |
| 284.15 | 1550 | 1610 |
| 278.65 | 1440 | 1450 |

[a] Equivalent conductance at zero concentration at 298.15 K is 81 (PNP Br) and 86 (PNPSCN) $cm^2$ $\Omega^{-1}$ $M^{-1}$.

TABLE II. Regression Analysis on the Rate Constants for the Reaction[a] $(FeX_3)Y^- + Z^-$ as a Function of the (Pseudo)-Halide Concentration at 298.1 K.

| $X^-$ | $Y^-$ | $Z^-$ | $k_0$ ($s^{-1}$) | $k_1$ ($s^{-1}$ $M^{-1}$) | Reaction Route[b] | F-value |
|---|---|---|---|---|---|---|
| $Cl^-$ | $NCS^-$ | $Cl^-$ | 7.8 | $5.8 \times 10^4$ | A | 3710 |
| | | | −5.6 | $7.9 \times 10^4$ | B | 190 |
| $Cl^-$ | $NCS^-$ | $Br^-$ | 6.1 | $1.3 \times 10^4$ | A | 4190 |
| | | | −1.8 | $2.2 \times 10^4$ | B | 230 |
| $Br^-$ | $NCS^-$ | $Br^-$ | 1.1 | $2.8 \times 10^3$ | A | 3350 |
| | | | −0.9 | $5.4 \times 10^3$ | B | 170 |
| $Cl^-$ | $Cl^-$ | $NCS^-$ | 1.6 | $1.2 \times 10^3$ | A | 6220 |
| | | | −8.4 | $6.0 \times 10^3$ | B | 250 |
| $Cl^-$ | $Cl^-$ | $Br^-$ | 0.0 | $6.3 \times 10^1$ | A | 2260 |
| | | | −0.4 | $2.7 \times 10^2$ | B | 280 |
| $Br^-$ | $Br^-$ | $NCS^-$ | 1.6 | $2.9 \times 10^4$ | A | 1430 |
| | | | −20.8 | $5.6 \times 10^4$ | B | 790 |
| $Cl^-$ | $Br^-$ | $NCS^-$ | 1.5 | $1.5 \times 10^4$ | A | 1430 |
| | | | −3.9 | $2.2 \times 10^4$ | B | 430 |

[a] In all cases PNP is the counterion. [b] A = ion-pair, ion-pair; B = ion-pair, ion.

Transient UV–visible spectra were recorded on a rapid-scanning spectrophotometer. To this end the Nortech Ltd. stopped-flow apparatus was coupled to an EG and G OMA2 system, consisting of a 1420 S solid-state detector, a model 1218 detector controller and a model 1215 processor.

UV–visible spectra were recorded on a Beckman M IV spectrophotometer using 10 mm quartz cells. Infrared spectra were recorded on a Perkin Elmer 580 B spectrophotometer using KBr pellets.

### *Conductivity Measurements*

The apparatus and procedure used for the conductivity measurements have been described before [6]. A 250 ml Kraus-Erlenmeyer type cell with a cell constant of 0.041 ± 0.001 $cm^{-1}$ was used.

Literature values of the dielectric constant [11, 12] and the viscosity of the solvent [10, 13, 14] were used for the evaluation of the ion-pair association constants. The conductance data were analyzed in terms of the Fuoss-1978 equation [15, 16].

## Results

### Ion-Pair Association Constants from Conductivity Measurements

The conductance data were analyzed by means of the Fuoss-1978 equation. Two least-squares minima were found for the distance parameter, at 500 pm and at 3500 pm. Because of the small variation of the ion-pair association constants with the distance parameter, the ion-pair association constants were evaluated at the Bjerrum distance. This is the usual procedure for solvents with low dielectric constants [17]. In addition, the obtained ion-pair association constants can now be compared with previously reported constants [6]. Results are given in Table I.

### Kinetics of (Pseudo)Halide Exchange

The reactions studied can be represented by eqn. 1, with $X^- = Cl^-$ or $Br^-$ and $Y^-, Z^- = Br^-, NCS^-$ or $Cl^-$. The observed rate constants were interpreted according to the model outlined before [6]. In this way a distinction can be made between the following reaction routes:

(A) an ion-pair, ion-pair mechanism, with

$$k(\mathrm{obsd}) = k_0 + k_1(1-\alpha)(1-\beta)[\mathrm{Hal}]_{\mathrm{tot}} \qquad (2)$$

(B) an ion-pair, ion mechanism, with

$$k(\mathrm{obsd}) = k_0 + k_1(1-\alpha)\beta[\mathrm{Hal}]_{\mathrm{tot}} \qquad (3)$$

and

(C) an ion, ion mechanism, with

$$k(\mathrm{obsd}) = k_0 + k_1\alpha\beta[\mathrm{Hal}]_{\mathrm{tot}} \qquad (4)$$

In these expressions k(obsd) is the observed pseudo first-order rate constant, and $\alpha$ and $\beta$ represent the degree of dissociation of the iron(III) complex ion-pair and the (pseudo)halide ion-pair respectively. The total (pseudo)halide concentration is represented by $[\mathrm{Hal}]_{\mathrm{tot}}$; $k_0$ reflects a solvent route in the mechanism. The criterion used to distinguish between the routes is the F-value, calculated from the regression analysis carried out for all possible routes.

Values of $\alpha$ and $\beta$ were calculated from the thermodynamic ion-pair association constants. The ion-pair association constant of the tetrakis(isothiocyanato)ferrate(III) complex could not be determined, due to the dissociation of this complex [18, 19] into $Fe(NCS)_3$ and $NCS^-$. This value was therefore assumed to be equal to that of the tetrabromoferrate(III) complex. In view of the similarity between the ion-pair association constants of PNPBr and PNP (SCN) this is a reasonable assumption. As shown by Balt *et al.* [10] values of the ion-pair association constants of the mixed (pseudo)halide ferrate(III) complexes can be obtained by linear interpolation between the values of the parent complexes.

The results of the statistical analyses of the data at 298.1 K are given in Table II for the ion-pair, ion-pair route and the ion-pair, ion route. The ion, ion route could not accomodate the data and combinations of two or more routes did not improve the fit. As can be seen from the Table the choice in favour of the ion-pair, ion-pair mechanism is straightforward. The activation parameters obtained from a weighted least-squares Eyring analysis* are given in Table III.

To establish the bonding mode of the thiocyanate ligand infrared spectra were recorded of the compounds after evaporation of the solvent. The CN stretching vibration of these complexes is broadened and shifted to lower wavenumbers with respect to free thiocyanate. This is known [20] to indicate N-bonded thiocyanate. The conclusion agrees with the fact that iron–thiocyanate complexes are generally N-bonded [20–22].

TABLE III. Activation Parameters for the Reaction[a] $(FeX_3)Y^- + Z^-$.

| $X^-$ | $Y^-$ | $Z^-$ | $\Delta H^\ddagger$ (kJ $mol^{-1}$) | $\Delta S^\ddagger$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| $Cl^-$ | $NCS^-$ | $Cl^-$ | 23.0 ± 1.0 | −77 ± 3 |
| $Cl^-$ | $NCS^-$ | $Br^-$ | 23.6 ± 1.3 | −87 ± 5 |
| $Br^-$ | $NCS^-$ | $Br^-$ | 30.1 ± 1.5 | −78 ± 5 |
| $Cl^-$ | $Cl^-$ | $NCS^-$ | 9.1 ± 0.8 | −155 ± 3 |
| $Cl^-$ | $Cl^-$ | $Br^-$ | 18.8 ± 1.4 | −147 ± 5 |
| $Br^-$ | $Br^-$ | $NCS^-$ | 3.4 ± 1.3 | −148 ± 4 |
| $Cl^-$ | $Br^-$ | $Cl^-$[b] | 19.2 ± 0.9 | −117 ± 3 |
| $Cl^-$ | $Br^-$ | $NCS^-$ | 11.1 ± 1.1 | −124 ± 4 |

[a] With PNP as the counterion; all reactions follow the ion-pair, ion-pair route. [b] From our previous work [6].

## Discussion

The reactions studied proceed via an ion-pair, ion-pair mechanism, which is in agreement with our earlier findings on the chloride–bromide exchange [6]. The associative mode of activation of the reactions is inferred from the form of the rate law, the small values of the enthalpy of activation, and the large negative values of the entropy of activation. From Table III it is clear that the entropy of activation, unlike the enthalpy of activation, classifies the reactions. These classes may indicate differences in the change of solvation on going to the transition state.

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*Results obtained at four other temperatures are available on request.

The very small values of the enthalpy of activation for the reactions with thiocyanate could indicate a mechanism in which thiocyanate initially becomes S-bonded in an intermediate complex, which then rearranges to N-bonded thiocyanate in the final complex. However, experiments with a rapid-scanning spectrophotometer (low time limit, equal to the dead-time of the stopped-flow apparatus) could not substantiate this proposition.

The significantly large positive intercepts ($k_0$ of eqn. 2) of the reactions of $FeCl_3)NCS^-$ with halide merit some comment. A possible solvolysis pathway seems very unlikely, in view of the fact that all other reactions, including nearly all reactions reported previously [6], have zero intercepts within experimental error. In our opinion these intercepts originate from the small concentration range employed for these reactions, neccessitated by the large reaction rates relative to the dead–time of the apparatus.

The accuracy of the data can be checked by constructing a cyclic reaction scheme from the reversible substitution reactions between $(FeCl_3)Br^-$, $(FeCl_3)Cl^-$ and $(FeCl_3)NCS^-$. The thermodynamic parameters for each reaction can be calculated from the activation parameters for the forward and reverse reactions given in Table III. The changes in $\Delta H^0$ and $\Delta S^0$ calculated for the cyclic process, which theoretically should be zero, amount to $-1.0$ kJ $mol^{-1}$ and $-7$ J $K^{-1}$ $mol^{-1}$ respectively. These deviations are well within the confidence limits of the activation parameters of the six separate reactions. The thermodynamic parameters of the individual reactions cannot easily be obtained from an equilibrium study, as the equilibrium invariably contains many of the possible mixed complexes.

Because forward and reverse reactions were studied the existence of a linear Gibbs energy relationship [23] was examined. There is a poor relation ($r = 0.54$) for $\Delta G^{\ddagger}$ and the calculated $\Delta G^0$. Remarkably, a much better relation exists between both $\Delta H^{\ddagger}$ and $\Delta H^0$, the reaction enthalpy, ($r = 0.95$) and $\Delta S^{\ddagger}$ and $\Delta S^0$, the reaction entropy, ($r = 0.90$). The correlations for the Gibbs energy and the entropy are not significantly improved by introducing correction factors for the entropies. Apparently $\Delta G$, as the difference between the generally much larger $\Delta H$ and $T\Delta S$ values, is much more sensitive to structural changes. The linear relationship between $\Delta H^{\ddagger}$ and $\Delta H^0$ has a slope of 0.57, implying the reactions to proceed via a common associative interchange ($I_a$) mechanism, with a substantial bond-breaking and bond-making in the transition state.

We found (Table IV) a difference between the equilibrium data of the chloride–bromide exchange with either the tetraphenylarsonium or the PNP counterion (both from ref. [6]). This difference can partly be accounted for by the difference in ion-pair association behaviour of initial and final states (*vide infra*). The remaining discrepancy is attributed to the fact that the ion-pair association constants as a function of temperature do not follow the van 't Hoff equation.

TABLE IV. Calculated and Corrected Thermodynamic Parameters for the Reaction[a] $(FeX_3)Y^- + Z^-$.

| $X^-$ | $Y^-$ | $Z^-$ | $\Delta H^0$ (kJ $mol^{-1}$) | $\Delta S^0$ (J $K^{-1}$ $mol^{-1}$) | $\Delta H^0$(corr.) (kJ $mol^{-1}$) | $\Delta S^0$(corr.) (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|---|
| $Cl^-$ | $Br^-$ | $Cl^-$ | 0.4 | 30 | −0.8 | 27 |
| $Cl^-$ | $Br^-$ | $Cl^-$ [b] | −7.9 | 2 | −4.7 | 12 |
| $Cl^-$ | $Br^-$ | $NCS^-$ | −12.5 | −37 | −10.8 | −31 |
| $Cl^-$ | $Cl^-$ | $NCS^-$ | −13.9 | −78 | −11.0 | −69 |
| $Br^-$ | $Br^-$ | $NCS^-$ | −26.7 | −70 | −25.0 | −64 |

[a] Unless stated otherwise, with the PNP counterion. [b] With tetraphenylarsonium as the counterion [6].

The values of $\Delta H^0$ and $\Delta S^0$ of the individual reactions can be used to calculate the relative bond strengths for the combinations $(FeX_3)Y^-$, with $X = Cl^-$ and $Br^-$ and $Y^- = Br^-, Cl^-$ and $NCS^-$. Before this comparison can be made the values of $\Delta H^0$ and $\Delta S^0$ should be corrected for differences in ion-pair association behaviour of the initial and the final states of the equilibria. To this end the correction factor C(T):

$$C(T) = \frac{K_{ip}((FeX_3)Z^-)K_{ip}(Y^-)}{K_{ip}((FeX_3)Y^-)K_{ip}(Z^-)} \tag{5}$$

was calculated for the reactions of eqn. 1 and fitted by the van 't Hoff equation. Reasonable fits (error 3%) were obtained, although the individual ion-pair association constants as a function of the temperature do not follow the van't Hoff equation. With the aid of the resulting enthalpy correction, $\Delta H^0_c$, and the entropy correction, $\Delta S^0_c$, the corrected values of $\Delta H^0$ [$\Delta H^0$(corr.)] and of $\Delta S^0$ [$\Delta S^0$(corr.)] were calculated. Results are given in Table IV. As can be seen from this Table the bond strengths in the $(FeCl_3)Y^-$ complex vary according to $Br^- < Cl^- \ll NCS^-$. It is remarkable that the difference in bond strength between $(FeX_3)$–$NCS^-$ and $(FeX_3)$–$Br^-$ is larger for $FeBr_3$ than for $FeCl_3$. The values of $\Delta S^0$(corr.) seem to follow the expected change in solvation of the (pseudo)halide anions.

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