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Kinetics of Chloride–Bromide Exchange at Tetrahedral Tetrahaloferrates(III) in Dichloromethane

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The kinetics of the reversible stepwise substitution of bromide by chloride on going from tetrahedral $FeBr_4^-$ to $FeCl_4^-$ was studied photometrically in dichloromethane. The dependence of the substitution rates on the nature of the counterion (tetraethylammonium, tetraphenylarsonium, and bis(triphenylphosphin)iminium) was interpreted with the aid of conductometrically determined ion-pair association constants. In this way evidence was found for an ion-pair, ion-pair mechanism. Activation parameters ($\Delta S^{\ddagger}$ between −150 and −110 J K^{-1} mol^{-1}; $\Delta H^{\ddagger}$ between 6 and 25 kJ mol^{-1}) indicate an associative mode of activation and an exceptional stability of the symmetrical five-coordinated intermediate or transition state with formula $FeBr_3Cl_2^{2-}$.

Introduction

In the past decade the increased interest in solvent effects on the kinetics of reactions of coordination compounds has brought a deeper insight into the mechanisms of complex formation.[1] In this respect a study of tetrahedral complexes seems to be worthwhile. Tetrahedral complexes, like the much more extensively studied square-planar d^8 complexes, have not attained the highest stable coordination number and consequently may easily increase their coordination number on going to the transition state and therefore are likely to show an associative activation mode. Illustrative examples are chloride exchange in aqueous $FeCl_4^-$[2] and $GaCl_4^-$[3] and triphenylphosphine (TPP) exchange in $CoBr_2(TPP)_2$.[4] In contrast to the square-planar d^8 complexes the tetrahedral complexes are not prone to addition of solvent donor molecules in the ground state, complicating the understanding of solvent effects.[5]

This advantage may be lost for the less stable tetrahedral complexes like $CoCl_4^{2-}$, where solvent donor molecules may substitute chloride.[6,7] The strongly covalent[8,9] tetrahaloferrate(III) complexes seem to be more promising because of their relative stability to even moderately donating solvents;[10] also mixed bromochloroferrates(III) seem to be stable.[11]

As a preliminary to a kinetic study of solvent effects in bromide–chloride exchange in ferrates(III), we report here a characterization in terms of activation parameters and medium effects of this system in one solvent, dichloromethane, chosen because of its negligible donor properties and the high solubility of the electrolytes used therein.[10] Unfortunately the most obvious approach, a chlorine-35 NMR study of chloride exchange in $FeCl_4^-$, was ruled out by the absence of a signal in dichloromethane solutions due to combined quadrupolar and paramagnetic broadening.

As cations proved to have a large specific effect on the reaction rates, the halide exchange was studied in the presence of small (tetraethylammonium) and large (tetraphenylarsonium) symmetrical ions and a large asymmetrical ion, the bis(triphenylphosphin)iminium (PNP) ion. The influence of the added cations on the rate is interpreted along the lines of the Davies ion-pair formalism.[12]

Experimental Section

Chemicals. The preparation and recrystallization of tetraethylammonium chloride and tetraphenylarsonium chloride, bromide, and perchlorate, as well as the tetrahaloferrates(III) of these cations, have been described elsewhere.[10] The bis(triphenylphosphin)iminium (PNP) chloride and bromide were prepared as described by Martinsen and Songstad.[13] The tetrahaloferrates(III) of this cation were prepared by mixing equivalent amounts of the anhydrous iron(III) halide and the PNP halide in anhydrous ethanol. The precipitates formed were filtered off and recrystallized from anhydrous ethanol.[14] All compounds were dried and stored over phosphorus pentoxide under vacuum. The analysis results were better than 1% relative for iron and better than 2% relative for the halide.

Dichloromethane (Merck, pa) was purified immediately before use as described earlier.[10]

Kinetic Measurements. All kinetic measurements were performed in a full-glass stopped-flow apparatus (Nortech Ltd.), having a 2-mm quartz mixing-observation cell, contained in a thermostat giving a temperature constancy better than 0.1 K. Solutions were made by weighing and converted to molarities with the aid of solvent densities.[15]

The halide-exchange reactions were performed under pseudo-first-order conditions with respect to the halide; i.e., the mole ratio of the halide to the iron(III) complex ranged from 6 to 50. The iron(III) concentration was varied between 6×10^{-5} and 10^{-3} M (mol dm^{-3}). In a typical series a tetrahaloferrate(III) in a fixed initial concentration was reacted with excess halide ion in nine different concentrations.

Reactions obeying a first-order rate law were followed to at least 90% completion. More complicated rate patterns were analyzed by the initial-rate method. Molar absorbance coefficients for starting and end products were obtained from mole ratio plots. To this end UV–visible spectra of 40 mixed solutions (equally spaced on the mole ratio scale) of tetraethylammonium tetrachloroferrate(III) and tetrabromoferrate(III) in dichloromethane were recorded. The fixed total ferrate(III) concentrations were 5×10^{-4} and 4×10^{-5} M. For each wavelength a plot of absorbance vs. mole ratio showed three changes of slope, indicating the existence of all three discrete intermediate compounds possible. The usual extrapolation procedure gave the molar absorbance coefficients. Comparison with the measured values indicated <5% disproportionation for $FeBr_3Cl^-$ and $FeBrCl_3^-$, but ca. 20% disproportionation for $FeBr_2Cl_2^-$. At the wavelength (472 nm) used for the kinetics the molar absorbance coefficients are 6050 ($FeBr_4^-$), 3900 ($FeBr_3Cl^-$), and 2000 ($FeBr_2Cl_2^-$) cm^{-1} mol^{-1} dm^3. It was checked that the molar absorbance is cation independent.

The first-order character of the reactions was checked in two ways. First, the wavelength dependence was studied. Rate constant k_4 (see Results) was measured at 420 and 363 nm, with tetraphenylarsonium as the counterion. The observed rate constants were the same within 3.5%, which implies that no intermediate compounds of reasonable

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Table I. Ion-Pair Association Constants[a] (in mol^{-1} dm^3) from the Analysis of Conductivity Data Using the Fuoss-1978 Theory

compd	278.65 K	284.15 K	289.65 K	293.15 K	298.15 K	Λ^0 [b]
Et_4NCl	71700	82100	93900[c]	96100	99800	122.7
Et_4NFeCl_4	15600[c]	17500	20900	21700	24600	159.0
Et_4NFeBr_4	15200	16600	17900	18100	19400	139.7
$(C_6H_5)_4AsCl$	2760	2960	3300	3340	3630	111.3
$(C_6H_5)_4AsBr$	3170	3260	3490[c]	3650	3880	116.0
$(C_6H_5)_4AsClO_4$					4390	120.3
$(C_6H_5)_4AsFeCl_4$	3330	3520	3730	3850	4090	118.9
$(C_6H_5)_4AsFeBr_4$	3130	3450	3770	3930	4250	116.3
PNPCl	1790[c]	1830	1900	1960	2060	101.0
$PNPFeCl_4$	2260	2300	2370	2440	2590	109.7
$PNPFeBr_4$	2050	2130	2200	2370	2600	109.8
$(C_6H_5)_4AsB(C_6H_5)_4$					2590	84.9

[a] Standard deviation is better than 1%. [b] Equivalent conductance at zero concentration in units cm^2 Ω^{-1} M^{-1}. [c] Calculated from eq 1.

stability, other than described by Scheme I, exist. Consequently the rate data were obtained at one wavelength: 472 (for k_1 and k_2) and 420 nm (for k_4 and k_{-4}), chosen for the most favorable difference in absorbance. Second, the dependence of the rate constants on the iron(III) complex concentration was investigated. No influence was found, if experiments were carried out under pseudo-first-order conditions for the halide and the iron concentration was varied between 6×10^{-5} and 10^{-3} M. This is exemplified by $k_{2,1}$ and $k_{4,1}$ (see Results) in Table II, comprising the results of experiments with three different iron(III) concentrations. The temperature dependence of the reactions was studied between 298.1 and 278.6 K. UV–visible spectra were recorded on a Beckman Acta M IV spectrophotometer, using 2 - and 10-mm quartz cells.

Conductivity Measurements. The procedure for measuring the conductivity has been described earlier.[10] Some modifications, mainly aimed at increasing the accuracy, were introduced. A closed all-glass cell with a cell constant of 0.042 ± 0.001 cm^{-1} was used, and the conductivity was measured with a Wayne Kerr B 331 autobalance precision bridge. The temperature was measured with a platinum resistance thermometer by using a Leeds-Northrup 8078 precision temperature bridge and was kept constant within 0.005 K.

The solutions were made by adding aliquots of a concentrated electrolyte solution, contained in a Hamilton syringe, to the solvent (ca. 90 mL) in the conductivity cell. The amount of stock solution transferred was determined by weighing. In this way for a complete series (one compound at one temperature) a concentration range from 6.6×10^{-6} to 2.2×10^{-4} M (14 measuring points) was realized, which is in accord with the limiting concentration set by Fuoss[16] at $3.2 \times 10^{-7}D^3$ M, which in the present case is 2.3×10^{-4} M.

Literature values for the dielectric constant[17,18] and the viscosity of the solvent[10,19,20] were used for the evaluation of the association constants. Because of the small influence (<0.5%) of the measuring frequency (varied between 5000 and 10 000 Hz) on the measured conductance and the uncertainty in the extrapolation procedure,[21] all conductances were taken at a fixed frequency of 10 000 Hz.

The conductance data were analyzed in terms of the equations of Pitts,[22,23] Fuoss,[24,25] and Lee and Wheaton,[26-28] using the computer program HUNTER written by Dr. A. D. Pethybridge.

Results

Ion-Pair Association Constants from Conductivity Measurements. The conductance data were analyzed by means of three different equations, the Lee–Wheaton equation, the Fuoss-1978 equation, and the Pitts equation. As expected[18,29] two least-squares minima were found on fitting the data to the Fuoss-1978 and the Pitts equations; these minima generally were found for values of the distance parameter R around 500 and 3500 pm. However, the Lee–Wheaton equation only yielded one minimum. Because of the small variation of the resulting association constants K_{ip} as a function of the distance parameter the usual practice[30] of giving K_{ip} at the Bjerrum critical distance (3150 pm for the present case) will be adhered to in the following.

The variation of K_{ip} obtained from different equations is smaller than 8%; this result agrees with the conclusion of Beronius[31] that for larger association constants the choice between rival conductivity equations becomes less important. For the calculations in the following sections the Fuoss-1978 values of Table I were used, as this theory gave the best fit for the experimental conductivities: 0.10% compared to 0.16% for the other theories. The standard deviation of the constants in Table I is better than 1%. Due to a more sophisticated procedure of the present study this means a considerable increase of accuracy compared to a more limited set of older results from this laboratory with an average error in K_{ip} of 5%.[10]

The temperature dependence of the association constants of Table I does not follow the van't Hoff equation, although a reasonable fit (better than 1%) was obtained with the empirical equation[32]

$$\ln K_{ip} = AT^{-2} + BT^{-1} + C \qquad (1)$$

Kinetics of Halide Exchange. Addition of chloride to $FeBr_4^-$ in dichloromethane in only a small excess over the molecular ratio (4:1) produces $FeCl_4^-$ to completion, proving the greater stability of the chloro complex. Since all intermediate compounds can be prepared, both in the solid state[11] and in solution,[10] the complete reaction appears in Scheme I. The mixed complexes can be prepared in solution by adding $FeBr_4^-$ and $FeCl_4^-$ in the calculated ratio. As the constants k_1, k_2, k_3, and k_4 are of comparable magnitude, a straightforward first-order treatment could only be attempted for the last step (k_4) of the tetrachloroferrate(III) formation. The other constants were obtained by the initial-rate method, starting from the complexes prepared in solution and using the molar absorbance coefficients from the mole ratio plots. Due to the relative instability of the bromo complexes only the fastest

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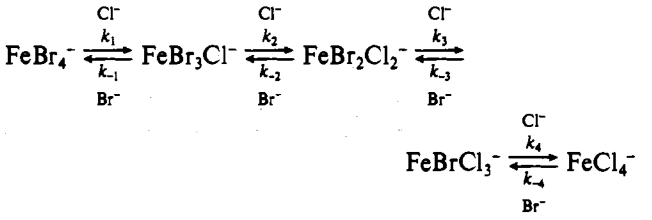
reverse reaction (k_{-4}) could be studied. The fact that $k_1 \simeq k_2 \simeq k_3 \simeq k_4$ and the negligible disproportionation means that $k_{-1} < k_{-2} < k_{-3} < k_{-4}$. Consequently the remaining reverse constants need a higher bromide concentration, which could not be realized. No attempt to measure k_3 was made because of the disproportionation of the starting product, $FeBr_2Cl_2^-$.

Scheme I



$$FeBr_4^- \underset{\underset{Br^-}{k_{-1}}}{\overset{\overset{Cl^-}{k_1}}{\rightleftharpoons}} FeBr_3Cl^- \underset{\underset{Br^-}{k_{-2}}}{\overset{\overset{Cl^-}{k_2}}{\rightleftharpoons}} FeBr_2Cl_2^- \underset{\underset{Br^-}{k_{-3}}}{\overset{\overset{Cl^-}{k_3}}{\rightleftharpoons}}$$

$$FeBrCl_3^- \underset{\underset{Br^-}{k_{-4}}}{\overset{\overset{Cl^-}{k_4}}{\rightleftharpoons}} FeCl_4^-$$

The measured rates are markedly dependent on the nature of the counterion present: under similar conditions tetraethylammonium salts react 20–50 times faster than the tetraphenylarsonium salts. This so-called[33,34] Olson–Simonson effect is diagnostic of specific effects, commonly interpreted in the line of Davies[12] as the appearance of ion pairs in the reaction route. In the present case three ion-pair routes (eq A–C) are possible, of which two—(B) and (C)—are mathematically equivalent in which X, Y = Br and Cl and Cat^+ symbolizes the organic cation; i-p = ion pair.

(A) (i-p, i-p) $Cat^+{\cdot}FeX_mY_{4-m}^- + Cat^+{\cdot}Y^- \rightarrow$

$$k_{obsd} = k_{n,0} + k_{n,1}(1 - \alpha)(1 - \beta)[Y^-]_{tot} \tag{2}$$

(B) (i-p, i) $Cat^+{\cdot}FeX_mY_{4-m}^- + Y^- \rightarrow$

$$k_{obsd} = k_{n,0} + k_{n,1}(1 - \alpha)\beta[Y^-]_{tot} \tag{3a}$$

(C) (i, i-p) $FeX_mY_{4-m}^- + Cat^+{\cdot}Y^- \rightarrow$

$$k_{obsd} = k_{n,0} + k_{n,1}\alpha(1 - \beta)[Y^-]_{tot} \tag{3b}$$

Because in reactions A, B, and C the ionic charge does not change on going to the transition state, no primary kinetic salt effect[34] is expected and concentration units must be used in the rate equations. k_{obsd} is the observed photometric pseudo-first-order rate constant obtained at excess halide; $k_{n,0}$ takes the possibility of a solvent path into account, analogous to the two-term rate law for square-planar systems;[35,36] α and β denote the degree of dissociation of the iron(III) complex ion pair and the halide pair, respectively.

For a decision between the different reaction routes, the measured reaction rates as a function of the total halide concentration were fitted to eq 2 and 3 with use of least-squares linear regression. Values of α and β were calculated from the thermodynamic ion-pair association constants obtained from the conductivity measurements. As shown by Balt et al.[10] the ion-pair association constants for the mixed complexes can be obtained by linear interpolation between the values of the tetrabromoferrate(III) and tetrachloroferrate(III) complexes. Reaction patterns were established by using two criteria: the *F* test[37] and the intercept $k_{n,0}$. The *F* values were obtained from a regression analysis of the data for every possible reaction route. The total sum of squares of deviations of the rate constants about their mean can be divided into two components: one component is given by the variance of the regression line about the mean of the observed *k* values (reduction due to regression) and the other component represents the variance of the observed *k* values about the regression line (residual). The quotient of these two components is called the *F* value. Then, a null hypothesis was carried out to test the significance of the differences in the *F* values. A comparison of the quotient of the *F* values for route A and route B and the values of the *F* distribution showed the preference of route A over route B to be scattered around the 95% probability limit. In the second place the value of the intercept $k_{n,0}$ was used as a criterium, because for the present series of simple substitution reactions negative intercepts do not seem probable. Representative results for 298.1 K are given in Table II. In a more graphic way Figure 1 illustrates eq 2 (route A) to give a better linear relation for k_{obsd} than eq 3a (route B).

Table II. Statistical Regression Analysis on the Rate Constants for Halide–Halide Exchange at Tetrahaloferrates(III) as a Function of the Halide Concentration at 298.1 K

rate const	cation	$k_{n,0}$, s^{-1}	$k_{n,1}$,[a] s^{-1} mol^{-1} dm^3	reaction route[b]	*F* value
k_1	$(C_6H_5)_4As^+$	−0.2	7.60×10^3	A	1040
k_1	$(C_6H_5)_4As^+$	−6.9	2.18×10^4	B	350
k_2	$(C_6H_5)_4As^+$	1.6	6.57×10^3	A	5110
k_2	$(C_6H_5)_4As^+$	−0.9	1.59×10^4	B	1570
k_4	$(C_6H_5)_4As^+$	1.6	6.88×10^3	A	6500
k_4	$(C_6H_5)_4As^+$	−3.0	2.16×10^4	B	340
k_4	PNP^+	0.2	1.96×10^3	A	8930
k_4	PNP^+	−1.7	4.25×10^3	B	1740
k_4	Et_4N^+	15.9	1.55×10^5	A	15140
k_4	Et_4N^+	−0.5	1.28×10^6	B	600
k_{-4}	$(C_6H_5)_4As^+$	0.1	2.05×10^2	A	770
k_{-4}	$(C_6H_5)_4As^+$	−0.2	7.19×10^2	B	450

[a] Standard deviation is better than 2%. [b] A = ion pair, ion pair; B = ion pair, ion.

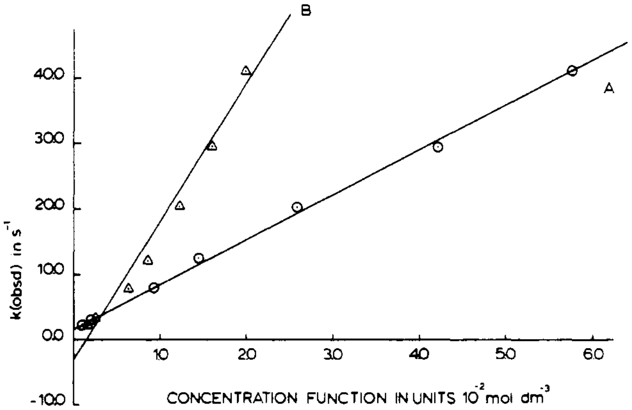


Figure 1. Plot of *k*(obsd) vs. concentration function for comparison of the ion-pair, ion-pair route A and the ion-pair, ion route B. Results are for rate constant k_4 at 298.1 K with tetraphenylarsonium as the counterion. For route A the concentration function is $(1 - \alpha)(1 - \beta)[Cl^-]$ and for route B $(1 - \alpha)\beta[Cl^-]$. (For clarity two points at the low end of the *x* axis have been omitted.)

The results thus obtained made a choice between reaction patterns in favor of A (ion pair, ion pair) straightforward in all cases except one. For rate constant k_4 and the Et_4N^+ ion as cation, it is difficult to make a distinction between the two routes. Comparison of the results obtained for other temperatures shows the *F* values to be of the same order of magnitude, ranging from 600 to 2500 and from 15 100 to 750 for routes B and A, respectively. On the other hand the values for $k_{4,0}$, the intercept, are zero within experimental error for case B and large and positive for case A (ranging from 10–16 s^{-1}). A comparison with the other systems makes it improbable that only in this particular case a solvent path is operative.

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Table III. Temperature Dependence of the Exchange Rates with Different Counterions[a]

rate const	cation	278.6 K		284.1 K		289.6 K		293.1 K	
		$k_{n,0}$[c]	$k_{n,1}$[c,d]	$k_{n,0}$[c]	$k_{n,1}$[c,d]	$k_{n,0}$[c]	$k_{n,1}$[c,d]	$k_{n,0}$[c]	$k_{n,1}$[c,d]
k_1	$(C_6H_5)_4As^+$	0.4	4.06×10^3	−0.6	5.31×10^3	−0.5	6.06×10^3	−0.2	6.89×10^3
k_2	$(C_6H_5)_4As^+$	−0.9	5.28×10^3	0.4	5.54×10^3	0.2	5.91×10^3	1.2	6.47×10^3
k_4	$(C_6H_5)_4As^+$	−0.4	3.95×10^3	0.9	4.13×10^3	−0.1	5.63×10^3	−0.1	6.17×10^3
k_4	PNP^+	0.2	1.06×10^3	0.1	1.31×10^3	0.1	1.65×10^3	0.2	1.69×10^3
k_4	Et_4N^+	2.8	7.39×10^5	1.6	8.37×10^5	−0.9	1.14×10^6	1.3	1.14×10^6
k_4	Et_4N^+[b]	10.9	1.12×10^6	9.9	1.23×10^6	11.4	1.54×10^6	13.4	1.50×10^6
k_{-4}	$(C_6H_5)_4As^+$	0.0	9.20×10^2	0.0	1.21×10^2	0.1	1.54×10^2	0.2	1.31×10^2

[a] Reaction route A (ion pair, ion pair), unless indicated otherwise. [b] Reaction route B (ion pair, ion). [c] $k_{n,0}$ in s^{-1}; $k_{n,1}$ in s^{-1} mol^{-1} dm^3. [d] Standard deviation is better than 2%.

Table IV. Comparison between Observed Rate Constants as a Function of the Concentration of Added Tetraphenylarsonium Perchlorate and the Values Calculated from the Parameters of the Reaction without Addition of This Salt[a]

$10^3[ClO_4^-]_t$, M	k_4(obsd)[b]	k_4(calcd), model A[b]	k_4(calcd), model B[b]
1.22	7.87	7.60	8.57
2.81	8.24	8.37	7.93
3.61	8.61	8.66	7.65
4.64	8.72	8.98	7.35
6.93	9.30	9.56	6.74

[a] Temperature = 298.1 K; cation $(C_6H_5)_4As^+$; [Fe(III)] = 1.95×10^{-4} M; $[Cl^-]_t = 2.15 \times 10^{-3}$ M. [b] In units s^{-1} mol^{-1} dm^3.

Table V. Activation Parameters for the Halide–Halide Exchange Reactions at Tetrahedral Tetrahaloferrates(III)

rate const	cation	reaction route[a]	$\Delta H^‡$, kJ mol^{-1}	$\Delta S^‡$, J K^{-1} mol^{-1}
k_1	$(C_6H_5)_4As^+$	A	16.5 ± 1.6	−115 ± 6
k_2	$(C_6H_5)_4As^+$	A	6.0 ± 1.7	−152 ± 6
k_4	$(C_6H_5)_4As^+$	A	17.5 ± 1.1	−113 ± 4
k_4	PNP^+	A	19.2 ± 0.9	−118 ± 3
k_4	Et_4N^+	B	18.4 ± 1.7	−66 ± 6
k_4	Et_4N^+	A	9.3 ± 1.4	−114 ± 5
k_{-4}	$(C_6H_5)_4As^+$	A	25.4 ± 1.4	−115 ± 5

[a] A = ion pair, ion pair; B = ion pair, ion.

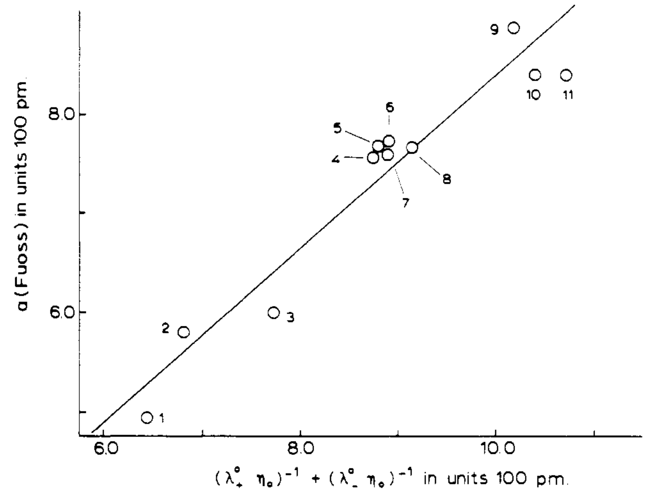

Figure 2. Plot of the *a* (Fuoss) values vs. the sum of the reverse individual Walden products for cations and anions, obtained by using the $(C_6H_5)_4As^+ \equiv B(C_6H_5)_4^-$ assumption: 1, Et_4NCl; 2, Et_4NFeCl_4; 3, Et_4NFeBr_4; 4, $(C_6H_5)_4AsClO_4$; 5, $(C_6H_5)_4AsFeCl_4$; 6, $(C_6H_5)_4AsBr$; 7, $(C_6H_5)_4AsFeBr_4$; 8, $(C_6H_5)_4AsCl$; 9, PNPCl; 10, $PNPFeCl_4$; 11, $PNPFeBr_4$. The line drawn was obtained from a linear regression analysis. Results are at 298.1 K.

In all cases a combination of both pathways did not improve the fit. In Table III the kinetic results for four other temperatures and different counterions are given.

The reaction path i-p, i-p established so far was checked by studying reaction k_4 for the tetraphenylarsonium counterion under conditions of a fixed chloride concentration (2.15×10^{-3} M) and varying concentrations of added tetraphenylarsonium as the supposedly innocent perchlorate.

From Table IV it is seen that the observed rate constants follow the ones predicted from eq 2 and the parameter values in Table II, whereas eq 3a gives calculated values that follow the reverse order and therefore never can match the observed rate constants. This strongly confirms the description of the reaction in terms of two ion pairs.

Finally, so that information about the accuracy of the analysis could be obtained, the association constants used in the calculations were changed by ±20%. The regression analysis was then repeated, which resulted in a pattern similar to the one represented by Table II, with resulting values of rate constants changed by less than 10%. The activation parameters, obtained from a weighted least-squares Eyring analysis, are given in Table V.

Discussion

Although the main object of the conductometric study is the availability of the ion-pair association constants, a few additional conclusions may be drawn from the results obtained, which can be used in discussing the kinetic results. An earlier conclusion[10] that no extensive solvation occurs for the salts studied in dichloromethane is reinforced by using the reliable Λ^0 (equivalent conductance at zero concentration) values that result from this study. From these Walden products[38] were calculated, which were constant (within an average of 3%) in the temperature range employed, indicating a small extent of solvation.[39] Moreover, with the $(C_6H_5)_4As^+ \equiv B(C_6H_5)_4^-$ assumption,[40] individual ionic Walden products $\lambda_\pm^0\eta_0$ could be calculated; on the basis of Stokes' Law[41] these should be inversely proportional to the radii of the solvated ions. We have compared these with the *a* values of the Fuoss equation[42]

$$K_{ip} = (4\pi N a^3/3000) \exp(e^2/aDkT) \qquad (4)$$

using the conductometrically determined K_{ip} values. Figure 2 displays the relation between *a* (Fuoss) and $(\lambda_+^0\eta_0)^{-1} + (\lambda_-^0\eta_0)^{-1}$. Both functions should be proportional to the sum of cation and anion radius of the salt. The proportionality of the two sets for different cations can only mean that none of the ions studied is exceptional in the extent of desolvation on going from the free to the ion-paired state. A similar conclusion may then be drawn for the association on activation. This conclusion does not answer the question[25] whether sol-

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(38) Monk, C. B. "Electrolytic Dissociation"; Academic Press: London, 1961; p 45.

(39) Stern, K. H.; Amis, E. S. *Chem. Rev.* **1959**, *59*, 1.

(40) Cox, B. G.; Parker, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 402.

(41) Reference 38; p 267.

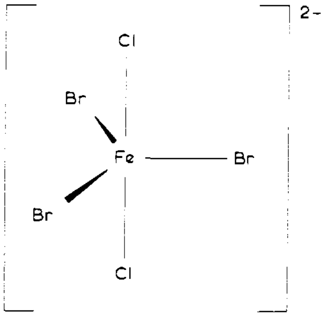
(42) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

vent-separated or contact ion pairs are present. Because of the difficulties involved in correcting Stokes' radii, no attempt for a complete analysis of our limited number of data in dichloromethane to yield absolute radii of the solvated ions was undertaken.

The form of the rate equation and the order of magnitude of the activation parameters—the small value of the enthalpy and the markedly negative value of the entropy of activation—are reminiscent of the substitution reactions of square-planar d^8 complexes, for which an associative mode of activation is well established.[35] This is in agreement with the associative activation postulated for the tetrahedral complexes mentioned in the Introduction.

The associative character of the reactions is further established from the entering-group dependence (Cl^- or Br^-) of the rate for each ferrate(III), as can be inferred from the qualitative picture of the pattern of the rate constants of reaction scheme I, worked out in the preceding section. It is interesting to note that this discriminating factor diminishes on going from $FeBr_3Cl^-$ to $FeBrCl_3^-$, although far-infrared spectra seem to indicate that there is no significant change in Fe–Cl and Fe–Br bond strengths within the series of mixed ferrates(III).[11]

The picture of reactivity relations becomes less simple when, besides the free-energy changes, activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are also considered, as can be done for the tetraphenylarsonium series of reactions. Although an isokinetic relationship is strictly adhered to for all measured stepwise reactions, the differences in the absolute values are pronounced. Especially the comparatively small value of $\Delta H^{\ddagger}$ for the reaction $FeBr_3Cl^- + Cl^- \rightarrow$ is noteworthy. This value could reflect an extraordinary stability of the highly symmetrical five-coordinated transition state or intermediate



This behavior is not limited to the tetraphenylarsonium salts. A preliminary crude survey of the temperature dependence of the complete tetraethylammonium series of reactions yielded the same pattern of activation parameters. The higher $\Delta H^{\ddagger}$ value for the one measured reverse reaction (k_{-4}), compared to the values obtained for the forward reactions, will be due to the fact that on going to the transition state partial bond-breaking of the stronger Fe–Cl bond and bond-making of the weaker Fe–Br bond occur.

The mechanism of the halide-exchange reactions is not a direct attack of the halide ion on the ferrate(III) ion, as this reaction is preceded by a supposedly rapid formation of a quadruple ion, consisting of the two ion pairs of route A (eq 2).

Apparently the cations are needed to bring together the two negative ions before the bond to the incoming ligand can be formed. It is then obvious that the more bulky tetraphenylarsonium and PNP ions are less effective in this respect than the tetraethylammonium ion, as Table III clearly shows. This mechanism resembles the familiar Eigen–Wilkins mechanism for octahedral complexes.[43] In combination with the indications for an associative mode of activation set out above, we may then class the reaction as I_a, associative interchange.[44]

This makes it interesting to compare the overall rate constants with equilibrium parameters for the ion-pair, ion-pair preequilibrium in an electrostatic model. For this we used the ion-pair, ion-pair model of Paligorič and Gal.[45] On the basis of this purely electrostatic model ΔH° for $PNPFeBrCl_3$ + PNPCl, $(C_6H_5)_4AsFeBrCl_3 + (C_6H_5)_4AsCl$, and $Et_4NFeBrCl_3 + Et_4NCl$ is −11.9, −10.6, and −17.2 kJ mol^{-1}, respectively (with use of the Fuoss *a* values as discussed above). The difference in $\Delta H^{\ddagger}$ (k_4) for the PNP and $(C_6H_5)_4As$ (1.7 kJ mol^{-1}) and the $(C_6H_5)_4As$ and Et_4N systems (8.2 kJ mol^{-1}) is then nearly completely explained from this model. Acceptance of this simple electrostatic picture means that no extra steric factor due to the bulkiness of the $(C_6H_5)_4As^+$ ion comes in.

Finally the reaction route for the k_4 reaction in the presence of tetraethylammonium ions merits some comment. In the Results a statistical analysis proved to be unsuccessful in deciding between the ion-pair, ion-pair and the ion-pair, ion route.

From the preceding discussion it is clear that the enthalpy of activation of the ion-pair, ion-pair route will fit in smoothly with the values of other systems, within the framework of an electrostatic model. Also $\Delta S^{\ddagger}$ for route A agrees in magnitude with the two other cation systems. On the other hand deciding on the ion-pair, ion-pair mechanism for the tetraethylammonium system leaves us with the necessity to give an explanation for the fact that only in this case the reaction $FeBrCl_3^- + Cl^-$ gives a solvolysis path. The conclusion must be that, on the basis of the available evidence, no definite choice can be made. We intend to continue our study of the ferrate(III) system with an investigation of solvent effects.

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Registry No. Et_4NCl, 56-34-8; Et_4NFeCl_4, 14240-75-6; Et_4NFeBr_4, 21279-19-6; $(C_6H_5)_4AsCl$, 507-28-8; $(C_6H_5)_4AsBr$, 507-27-7; $(C_6H_5)_4As(ClO_4)$, 3084-10-4; $(C_6H_5)_4AsFeCl_4$, 21279-18-5; $(C_6H_5)_4AsFeBr_4$, 67709-35-7; PNPCl, 21050-13-5; $PNPFeCl_4$, 76137-12-7; $PNPFeBr_4$, 76137-13-8; $(C_6H_5)_4AsB(C_6H_5)_4$, 15627-12-0.

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(43) Reference 36; Section 4.2.
(44) Reference 35; Chapter 1.
(45) Paligorič, I.; Gal, I. J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 285.