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Medium and Solvent Effects on the Kinetics of Chloride–Bromide Exchange at Tetrahedral Tetrahaloferrates(III)

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The kinetics of the final bromide–chloride substitution in the formation of $FeCl_4^-$ from $FeBr_4^-$ have been studied photometrically in six dipolar aprotic solvents. The role of the counterion could be evaluated with the aid of conductometrically-determined ion-pair association constants. Whether an ion-pair, ion-pair mechanism, an ion-pair, ion mechanism or an ion, ion mechanism is operative depends mainly on the dielectric constant of the solvent. The activation parameters ($\Delta H^{\ddagger}$ between 17 and 36 kJ mol^{-1}; $\Delta S^{\ddagger}$ between −83 and −27 J K^{-1} mol^{-1}) indicate an associative mode of activation. An initial-state transition-state dissection reveals the importance of donor and acceptor properties of the solvents for the ion-pair, ion-pair mechanism and the prime importance of the acceptor properties for the ion-pair, ion mechanism.

Introduction

Over the past two decades there has been much interest in the role of the solvent in reactions of coordination compounds. However, the interpretation of solvent effects in inorganic chemistry is in general less straightforward than in organic chemistry. It proved that these effects in the extensively-studied class of substitution reactions at square-planar transition metal complexes [1] are much more complicated than the seemingly similar ones at the saturated tetrahedral carbon [2]. Therefore it seemed worthwhile to study solvent effects on substitutions at tetrahedral transition metal complexes. Substitutions at tetrahedral tetrahaloferrate(III) complexes were chosen as the model system, because these iron(III) complexes are stable, even towards moderately donating solvents [3, 4]. This in contrast with the formerly-studied tetrahedral tetrachlorocobaltate(II), where solvent donor molecules may substitute chloride [5, 6], thus complicating the understanding of solvent effects.

As a preliminary to the kinetic study of solvent and medium effects on chloride–bromide exchange at tetrahedral tetrahaloferrates(III), the system has been characterized in dichloromethane [7, 8]. With the aid of conductometrically-determined ion-pair association constants, evidence was found for an ion-pair, ion-pair mechanism.

Because the approach seemed promising we extended the study of chloride–bromide exchange at tetrahedral tetrahaloferrates(III) to six dipolar aprotic solvents: acetone (Ac), acetonitrile (An), benzonitrile (BN), nitrobenzene (NB), nitromethane (NM) and propylene carbonate (PC). The solvents were chosen for their varying acceptor properties and for solubility reasons. In order to reveal the role of the cation in the mechanism, both tetraethylammonium and tetraphenylarsonium were used as counterions. Ion-pair association constants were determined conductometrically.

Experimental

Chemicals

Literature procedures were used for the purification of acetone (*p.a.*) [9], acetonitrile (*p.a.*) [10], nitrobenzene (technical grade) [11, 12], nitromethane (*p.a.*) [13] and propylene carbonate (*p.a.*) [14]. Benzonitrile (*p.a.*) [15] was distilled at least three times from phosphorus pentoxide (*p.a.*). The residue then was slightly yellow, in contrast with earlier distillations when it became dark brown. The water content of the purified solvents was less than 2×10^{-4} *M*. The specific conductances of the purified solvents are between 2×10^{-8} and 7×10^{-8} Ω^{-1} cm^{-1} (acetone, benzonitrile, acetonitrile, nitrobenzene and propylene carbonate) and between 2×10^{-7} and 5×10^{-7} Ω^{-1} cm^{-1} (nitromethane).

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The preparation and recrystallisation of tetraethylammonium chloride, bromide and perchlorate, as well as the tetraethylammonium and tetraphenylarsonium tetrahaloferrates(III) have been described elsewhere [7]. Tetraphenylarsonium chloride (Fluka, *p.a.*) was used without further purification.

Kinetic Measurements

All kinetic measurements were performed with a stopped-flow apparatus using UV–Visible detection. Two observation cells were available, one of 2 mm optical pathlength [7] (Nortech Ltd.) and the other of 18 mm optical pathlength [8].

All the measurements were carried out under pseudo first-order conditions using excess halide. The ratio of the halide concentration to the iron(III) complex concentration ranged from at least 6 to about 40, employing at least six halide concentrations. It was checked that under these conditions contributions of the reverse reaction were negligible. The reactions were followed at 420 nm for all solvents except nitrobenzene, where 440 nm was used.

The reactions were followed to at least 90% completion. The rate constants were evaluated by means of a least-squares analysis. The temperature dependence of the reactions was studied between 298.1 and 278.6 K for all solvents except nitrobenzene: here a temperature interval from 303.1 to 284.1 K was used, because nitrobenzene freezes at 278.9 K. The temperature was kept constant within ±0.1 K.

Conductivity Measurements

The apparatus described earlier [7] was somewhat changed. The a-c signal was supplied by a Hewlett-Packard 241 A oscillator, and an EG and G Brookdeal Precision Lock-in Amplifier 9503 was used for detection. Kraus Erlenmeyer type cells of 250 ml were used with cell constants of 1.108, 1.052 and 0.041 ± 0.001 cm^{-1}. The solutions were prepared in two ways, depending on the rate at which the compounds dissolve. In the case of moderate to high dissolution rates, weighted quantities of solid compound were transferred into the cell. Otherwise weighted aliquots of a concentrated stock solution were transferred into the cell by means of a Hamilton syringe. Weigths were converted to molarities with the aid of solvent densities [16, 17]; At least fourteen concentrations were measured, with the highest concentration always well below the upper concentration limit of 3.2×10^{-7} D^3 *M*, set by Fuoss [18].

All measurements were carried out at a fixed frequency of 10,000 Hz because of the small frequency dependence of the conductivity and the uncertainties in the extrapolation procedure [19]. Literature values of the dielectric constant and the viscosity [16, 17, 20] of the solvents were used in the evaluation of the ion-pair association constants. The conductivity data were analyzed in terms of the conductance equations of Fuoss [21, 22], Pitts [23, 24] and Lee and Wheaton [25, 26, 27], as previously described [7].

Solubilities

Solubilities were determined as described earlier [28]. Iron(III) complex concentrations were determined spectrophotometrically. Tetraethylammonium chloride concentrations were determined by potentiometric titration with silver nitrate.

Results

Ion-Pair Association Constants from Conductivity Measurements

The conductance data were analyzed with the aid of three conductance equations, the Fuoss-1978 equation, the Pitts equation and the Lee–Wheaton equation. As far as standard deviations of the fit ($<0.06\%$) are concerned, no significant differences were found. The Lee–Wheaton equation fitted somewhat better to the data obtained in solvents with moderate to high dielectric constant, and the Fuoss-1978 equation fitted best to the data in solvents with a low dielectric constant. In contrast to this, a significantly different picture was obtained when the fitting parameters were compared. The values obtained for the ion-pair association constants vary by approximately 15%, increasing in the order Lee–Wheaton < Fuoss-1978 < Pitts.

Plots of the standard deviation of the fit *versus* the distance parameter *a* yielded one minimum for the Lee–Wheaton equation and two minima for the Fuoss-1978 and Pitts equations. For solvents with moderate to high dielectric constant ($D > 30$) values of *a* were found near the Bjerrum critical distance. Serious deviations from this behaviour were found for solvents with low dielectric constant ($D \leqslant 25$). Because of the small variation of the ion-pair association constant, K_{ip}, with the distance parameter *a*, the ion-pair association constants were evaluated at the Bjerrum critical distance [29]. In view of a comparison of the results for different solvents, including those published for dichloromethane [7], only the Fuoss-1978 values of the ion-pair association constants are given in Table I. The standard deviation of K_{ip} is less than 5%.

Only ion-pair association constants larger than about 100 M^{-1} show a temperature dependence. This temperature dependence can be described by the empirical eqn. 1 [30]:

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

TABLE I. Ion-Pair Association Constants from the Analysis of Conductivity Data Using the Fuoss-1978 Theory.

Solvent	Compound	Ion-Pair Association Constant[a]						Λ_0[b]
		278.65 K	284.15 K	289.65 K	293.15 K	298.15 K	303.15 K	
Acetone	Et_4NCl	500	490	470	480	500		194
	Et_4NFeCl_4	90	88	82	89	94		194
	Et_4NFeBr_4	89	87	80	87	93		186
	$(C_6H_5)_4AsCl$	107	104	98	104	108		169
	$(C_6H_5)_4AsFeCl_4$	75	73	70	75	80		166
	$(C_6H_5)_4AsFeBr_4$	82	77	68	72	91		160
Nitrobenzene	Et_4NCl		55	54	59	62	66	36
	Et_4NFeCl_4		21	22	22	25	32	38
	Et_4NFeBr_4		18	19	18	19	27	34
Benzonitrile	Et_4NCl	230	240	240	230	250		52
	Et_4NFeCl_4	51	51	52	51	53		51
	Et_4NFeBr_4	44	45	46	45	45		48
Propylene Carbonate	Et_4NCl	1	1	2	2	2		29
	Et_4NFeCl_4	3	4	4	4	4		29
	Et_4NFeBr_4	4	5	4	4	5		28
	$(C_6H_5)_4AsCl$	–	–	–	–	–		–
	$(C_6H_5)_4AsFeCl_4$	7	6	6	5	5		24
	$(C_6H_5)_4AsFeBr_4$	8	10	9	10	9		23
Acetonitrile	Et_4NCl	23	23	18	23	24		174
	Et_4NFeCl_4	24	23	24	23	22		184
	Et_4NFeBr_4	20	23	23	21	19		176
	$(C_6H_5)_4AsCl$	8	9	12	10	9		146
	$(C_6H_5)_4AsFeCl_4$	24	24	26	21	22		155
	$(C_6H_5)_4AsFeBr_4$	23	24	27	21	19		146
Nitromethane	Et_4NCl	9	11	9	12	11		101
	Et_4NFeCl_4	12	13	13	12	14		108
	Et_4NFeBr_4	15	15	14	15	17		104
	$(C_6H_5)_4AsCl$	4	4	4	4	4		89
	$(C_6H_5)_4AsFeCl_4$	11	12	10	10	12		91
	$(C_6H_5)_4AsFeBr_4$	13	15	13	16	15		90

[a] In M^{-1}; standard deviation $\sigma(\Lambda)$ is better than 0.05%. [b] Equivalent conductance at zero concentration in units $cm^2\ \Omega^{-1}\ M^{-1}$ at 298.15 K.

Kinetics of Chloride–Bromide Exchange

Previously we reported a study on the four consecutive chloride–bromide substitution reactions at tetrahedral tetrahaloferrates(III) [7]. The final bromide–chloride substitution in the formation of $FeCl_4^-$ from $FeBr_4^-$, according to eqn. 2,

$$FeCl_3Br^- + Cl^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FeCl_4^- + Br^- \qquad (2)$$

was chosen as a model reaction in the present study on solvent effects. Owing to the stability of the $FeCl_4^-$ complex this reaction can be followed to completion and data can be obtained easily.

The reaction rates in dichloromethane [7] proved to be markedly dependent on the nature of the counterion present in solution. An ion-pair, ion-pair mechanism according to Davies [31] accounted quantitatively for the effects. These medium effects

TABLE II. Statistical Regression Analysis on Rate Constant k_4 as a Function of the Chloride Concentration at 298.1 K.

Solvent	Cation	Reaction Route[a]	$k_{4,0}$ (s^{-1})	$k_{4,1}$ ($s^{-1}\ M^{-1}$)	F value
Acetone	Et_4N^+	A	1.5	4.5×10^4	13100
		B	−2.2	4.7×10^4	1420
	$(C_6H_5)_4As^+$	B	0.4	4.3×10^3	4860
		D	0.2	1.5×10^2	440
Nitrobenzene	Et_4N^+	B	6.0	4.6×10^5	4230
		B[b]	0.8	4.1×10^5	1360
		D	−12	2.7×10^4	440
Benzonitrile	Et_4N^+	A	10	4.9×10^5	340
		B	2.6	2.3×10^5	3960
Propylene Carbonate	Et_4N^+	B	27	3.3×10^7	1840
		D	−4.5	1.3×10^5	3550
	$(C_6H_5)_4As^+$	B	18	1.5×10^7	1420
		D	−3.1	1.1×10^5	4950
Acetonitrile	Et_4N^+	B	22	4.2×10^5	2980
		D	−43	4.7×10^4	220
	$(C_6H_5)_4As^+$	B	7.0	8.6×10^5	9760
		D	1.0	1.3×10^4	550
Nitromethane	Et_4N^+	B	26	3.7×10^6	8300
		D	−8.1	7.8×10^4	2450
	$(C_6H_5)_4As^+$	B	18	3.7×10^6	5930
		D	6.5	4.6×10^4	2400

[a] A = ion-pair, ion-pair; B = ion-pair, ion; D = ion, ion. [b] Results of experiments with 7.9×10^{-2} *M* Et_4NClO_4 added.

can be separated from solvent effects with the aid of the conductometrically determined ion-pair association constants and the use of different counterions. To this end tetraethylammonium and tetraphenylarsonium were used.

Presently, the reaction rates are interpreted in terms of four conceivable reaction routes, two of which – (B) and (C) – are mathematically equivalent:

(A) (i-p, i-p) $Cat^+ \cdot FeCl_3Br^- + Cat^+ \cdot Cl^- \longrightarrow$

$$k(obsd) = k_{4,0} + k_{4,1}\,(1-\alpha)(1-\beta)[Cl^-]_{tot} \qquad (3)$$

(B) (i-p, i) $Cat^+ \cdot FeCl_3Br^- + Cl^- \longrightarrow$

$$k(obsd) = k_{4,0} + k_{4,1}\,(1-\alpha)\beta[Cl^-]_{tot} \qquad (4a)$$

(C) (i, i-p) $FeCl_3Br^- + Cat^+ \cdot Cl^- \longrightarrow$

$$k(obsd) = k_{4,0} + k_{4,1}\,\alpha(1-\beta)[Cl^-]_{tot} \qquad (4b)$$

(D) (i, i) $FeCl_3Br^- + Cl^- \longrightarrow$

$$k(obsd) = k_{4,0} + k_{4,1}\exp\{-2A(I)^{1/2}\}\alpha\beta[Cl^-]_{tot} \qquad (5)$$

Cat^+ symbolizes the cation; i-p = ion-pair; i = ion; k(obsd) is the observed pseudo first-order rate constant; $k_{4,0}$ takes into account the possibility of a solvent path, comparable to the solvent route in the two-term rate law for substitution reactions at square-planar complexes [32, 33]; α and β are the degrees of dissociation of the iron(III) complex ion-pair and the chloride ion-pair respectively. Values of α and β were calculated from the conductometrically determined ion-pair association constants. For the temperature-independent constants the averaged values were used in the calculations. The values of the ion-pair association constants of the mixed iron(III) complexes can be obtained by linear interpolation, as shown by Balt *et al.* [3]. Rate constants $k_{4,1}$ for route D, the ion, ion route, were evaluated taking into account the expected primary kinetic salt effect [34, 35].

As outlined previously [7], a statistical regression analysis can be used to decide on the reaction route. For all possible reaction routes and combinations thereof, a regression analysis was carried out and F-values were computed. A null hypothesis was used to test the significance of the differences in F-values. Table II contains the results of the statistical regres-

TABLE III. Activation Parameters and Reaction Routes for Chloride–Bromide Exchange at Tetrahedral Tetrahaloferrates(III).

Solvent	Cation	Reaction Route[a]	$\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\ K^{-1}\ mol^{-1}$)
Acetone	Et_4N^+	A	27 ± 2	−66 ± 5
	$(C_6H_5)_4As^+$	B	27 ± 2	−83 ± 7
Nitrobenzene	Et_4N^+	B	26 ± 2	−49 ± 5
Benzonitrile	Et_4N^+	B	22 ± 2	−69 ± 5
Propylene Carbonate	Et_4N^+	D	36 ± 2	−26 ± 5
	$(C_6H_5)_4As^+$	D	34 ± 2	−35 ± 4
Acetonitrile	Et_4N^+	B	17 ± 1	−81 ± 3
	$(C_6H_5)_4As^+$	B	26 ± 3	−43 ± 9
Dichloromethane[b]	Et_4N^+	A	9 ± 1	−114 ± 5
	$(C_6H_5)_4As^+$	A	18 ± 1	−113 ± 4
	PNP^+	A	19 ± 1	−118 ± 3
Nitromethane	Et_4N^+	B	27 ± 1	−27 ± 3
	$(C_6H_5)_4As^+$	B	16 ± 2	−66 ± 7

[a]A = ion-pair, ion-pair; B = ion-pair, ion; D = ion, ion. [b]From our previous work, ref. [7].

sion analysis for data at 298.1 K for those two routes yielding the best fit to the data*.

In previous cases the value of the intercept $k_{4,0}$, obtained from the regression analysis, could be used as a criterion in deciding the reaction route. Although negative values are sometimes found [36], these are physically meaningless for simple substitution reactions like the present ones. Positive values of $k_{4,0}$ are possible for a solvent route in the mechanism. However, a solvent route is unlikely in view of the fact that positive as well as negative intercepts are found. The deviations from the expected values for the intercepts, *i.e.* zero within experimental error, can be explained by the high velocity of the reactions. Only a small concentration range could be employed in order to keep the reactions within the stopped-flow time-scale. The steep slopes and the small range of the concentration function account for the spread of the intercepts around zero. To verify the foregoing an experiment with added perchlorate, by which a larger range of the concentration function was achieved, was carried out in nitrobenzene. From the results in Table II it can be seen that the intercept $k_{4,0}$ becomes zero within the experimental error. The rate constants $k_{4,1}$ for the experiments with and without added perchlorate differ by about 10%. Previous results on the accuracy of the analysis [7] show a 10% variation in the rate constants with a 20% change in the values of the ion-pair association constants. In view of the approximate value of the tetraethylammonium perchlorate ion-pair association constant used in the calculations, the observed difference in rate constants seems to be reasonable.

On the basis of the statistical regression analysis a choice between different reaction routes is straightforward. Combinations of reaction routes did not improve the fits. The reproducibility of the rate constants is within 3% for the correct reaction route. Activation parameters determined by means of a weighted least-squares Eyring analysis [37] are given in Table III.

Solubilities

Solubilities of the compounds were determined in the solvents in which i-p, i-p or i-p, i routes are operative. The results are given in Table IV. With the aid of the ion-pair association constants, equilibrium fractions of the associated species present in the saturated solutions were calculated. Transfer chemical potentials for initial and transition states of the reactions were calculated as described earlier [38]. The results are given in Table V, together with transfer functions for chloride obtained from a comprehensive literature review [39]. The molar Gibbs energy of transfer of chloride from acetonitrile to nitrobenzene was interpolated from the relation of the chloride transfer function with the acceptor number of the solvent [40].

Discussion

Although a thorough discussion of the conductivity data is beyond the scope of this study, a few

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*Data at four other temperatures are available on request.

TABLE IV. Solubilities in M.[a]

Solvent	Compound	Temperature		
		298.1 K	293.6 K	278.6 K
Dichloromethane	Et_4NCl	2.6	2.5	2.1
	Et_4NFeCl_4	5.3×10^{-2}	4.7×10^{-2}	2.6×10^{-2}
	Et_4NFeBr_4	1.2×10^{-2}	1.1×10^{-2}	6.5×10^{-3}
Acetone	Et_4NCl	4.7×10^{-2}	4.2×10^{-2}	3.0×10^{-2}
	Et_4NFeCl_4	0.85	0.79	0.64
	Et_4NFeBr_4	0.40	0.38	0.29
Nitrobenzene	Et_4NFeCl_4		0.27	
Benzonitrile	Et_4NFeCl_4		0.33	
Acetonitrile	Et_4NFeCl_4		0.80	
Nitromethane	Et_4NFeCl_4		0.63	

[a] Accuracy within 3%.

TABLE V. Transfer Functions[a] for Initial and Transition State in Ion-Pair, Ion-Pair and Ion-Pair, Ion Route at 293.6 K.

Solvent	Reaction Route[b]		Initial State			Transition State
			Et_4NFeCl_3Br[c]	Et_4NCl	Cl^-	
Acetone	A	$\delta_m\Delta H$	−13	10		15
		$-\delta_m\Delta S$	6	1		−7
		$\delta_m\Delta G$	−7	11		8
Nitrobenzene	B	$\delta_m\Delta G$	3		12	15
Benzonitrile	B	$\delta_m\Delta G$	2		10	13
Nitromethane	B	$\delta_m\Delta G$	1		−3	−8

[a] Reference: dichloromethane for A-route solvents and acetonitrile for B-route solvents; units kJ mol^{-1}. [b] A = ion-pair, ion-pair; B = ion-pair, ion. [c] For route A values obtained by linear interpolation between Et_4NFeCl_4 and Et_4NFeBr_4. For route B Et_4NFeCl_4 is used as a model for Et_4NFeCl_3Br.

points should be noted. First, tetraphenylarsonium chloride is found to be ion-paired in nitromethane, in contradiction to earlier reports [41]. The much higher accuracy of our data (standard deviation $\sigma\Lambda$ of 0.05% *versus* 0.19% for the reported data) and the fact that in our analysis terms of $(c)^{3/2}$ have been included in the conductance equation, account for the difference. Justice [42] and Carman [43] have shown that omission of these higher terms in c leads to seriously miscalculated ion-pair association constants.

Second, Walden products, $\Lambda_0\eta$, were calculated. The products are constant within 3% for any solvent and about constant (within 10%) among all solvents except propylene carbonate. This implies that the extent of ionic solvation is comparable in all solvents. The larger Walden products found for propylene carbonate seem to indicate a lesser solvation.

In general, marked differences in ion-pair association behaviour are observed between protic and dipolar aprotic solvents [44]. From Table I it can be seen that for solvents with low dielectric constant ion-pair association constants are larger for chloride than for the iron(III) complexes. The order becomes reversed in solvents with high dielectric constants. The cross-over occurs at D = 36 (acetonitrile) for the tetraethylammonium salts and at $20 < D < 36$ for the tetraphenylarsonium salts. For the present case the chloride and iron(III) complex ion-pair association constants follow the same order in dichloromethane (protic) [7] and acetone (dipolar aprotic). In view of the behaviour of the ion-pair association constants described above, this may be interpreted as follows. The difference between the chloride and complex ion-pair association constants is determined by electrostatic interactions in solvents with low dielectric constant. Apparently, more specific interactions with the solvent determine the differences in ion-pair association constants in solvents with moderate to high dielectric constant.

With the aid of the ion-pair association constants the reaction routes were established. From Table III it can be seen that all three routes occur. Which route is operative depends on the dielectric constant of the solvent: an i-p, i-p mechanism is found for dichloromethane ($D = 8.9$) and acetone ($D = 20.7$) an i-p, i mechanism for solvents with a moderate dielectric constant ($25 \leqslant D \leqslant 41$) and an i, i mechanism for propylene carbonate with a high dielectric constant ($D = 65.0$).

In agreement with the reaction in dichloromethane [7] an associative mode of activation can be deduced from the form of the rate law and values of the activation parameters (small $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$).

In order to obtain detailed information on solvent effects on the chloride–bromide exchange, an initial-state transition-state dissection [38] was worked out for the i-p, i-p and the i-p, i route with Et_4N^+ as the counterion. The results are given in Table V. As only two solvents are available for a comparison of transfer functions for the i-p, i-p route, additional information was obtained from the temperature dependence of the solubilities. With dichloromethane as the reference solvent it can be seen that the tetraethylammonium chloride ion-pair is destabilized in acetone, in agreement with the smaller acceptor properties of this solvent. In contrast, the iron(III) complex ion-pair is stabilized in this solvent, following the better donor properties of acetone. Both the effects noted above are primarily due to changes in $\delta_m \Delta H$, indicating considerable differences in the interaction of the solvent with the ion-pair in acetone relative to dichloromethane. In addition, the stabilization of the iron(III) complex ion-pair in acetone is accompanied by a substantial increase in $-\delta_m \Delta S$, thus partly compensating the effect in $\delta_m \Delta H$. This behaviour is commonly observed for solvational changes [45].

On going to the transition state the stabilization of the iron(III) complex ion-pair in acetone is completely lost and the transition state becomes strongly destabilized, but not so much as the chloride ion-pair in the initial state. The large increase in $\delta_m \Delta H$ (and decrease in $-\delta_m T\Delta S$) on going to the transition state, corresponds to changes in solvation of the transition state relative to the initial state. In the overall picture the destabilization of the transition state parallels the behaviour of the tetraethylammonium chloride ion-pair. In conclusion, it seems that donor and acceptor properties determine the initial state, whereas acceptor properties dominate the transition state.

Transfer Gibbs energies for initial and transition states for solvents in which an i-p, i mechanism is operative present a different picture (see Table V). The Gibbs free energy of the iron(III) complex ion-pair is approximately constant in all solvents. As expected the Gibbs energy of the chloride ion is proportional to the acceptor properties of the solvent. In addition, the Gibbs energy of the transition state shows the same dependence (correlation coefficient $r = 0.99$). From this relationship the importance of the charge of the complex in the transition state can be inferred.

The large variation of the transfer Gibbs energy of the transition state for both the i-p, i-p and i-p, i route parallels the results obtained for substitution reactions at square-planar palladium(II) and platinum(II) complexes [1, 46], but contrasts with the results of substitution reactions at saturated tetrahedral carbon [2]. For the latter reactions the transition state is considered to be desolvated in all solvents. As a consequence of compensating effects and the much smaller variation in reaction rates, the simple picture that substitutions at saturated carbon present becomes much more complicated on going to substitutions at four-coordinate transition metal complexes.

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