We conclude that the degree of association of carbanion ion pairs in nonpolar solvents is highly dependent upon the extent of charge delocalization; the anionic charge in benzylic carbanion ion pairs is sufficiently delocalized that the electrostatic stabilization provided by aggregate formation is insufficient to overcome the resultant unfavorable entropy of association. It is notable that the substitution of a strongly electron donating *p*-methoxy group into phenylacetonitrile has the expected acid-weakening effect but did not lessen the degree of charge delocalization to an extent where aggregate formation could be observed.[9]

Standard enthalpies and entropies of reactions obtained by studying eq 1 as a function of temperature are summarized in Table II. The indicator used in this study was 2,3:6,7-dibenzofluorene (DBF). DBF was chosen because its lithium and cesium salts are known to exist exclusively as solvent-separated and contact ion pairs, respectively, in THF.[4,5] Table II shows that the formation of the lithium salts is generally accompanied by a net entropy increase of 9–15 eu, whereas for the cesium benzylates an entropy decrease of ca. 4 eu is usually observed; exceptions to this generalization are exhibited by the lithium enolate of *tert*-butyl phenylacetate and the cesium salt of benzyl phenyl sulfone. The data for the remaining compounds are consistent with both the lithium and cesium salts existing as contact ion pairs. The large positive entropy changes exhibited by the lithium salts are then a consequence of the releasing of solvating THF molecules as the solvent-separated indicator anion is protonated and the carbanion contact ion pair is formed.[10] Highly delocalized carbanions tend to form solvent-separated ion pairs with lithium as gegenion in THF.[11] Thus, the formation of monomeric contact lithium benzylate ion pairs demonstrates that *contact–solvent separated and monomer–aggregate equilibria have different dependencies on the degree of carbanion delocalization.*

The reactions with cesium cation involve only contact ion pairs and are expected to show entropy changes near zero. However, formation of a benzylic carbanion is accompanied by the restricted rotation of a conjugating aryl group, resulting in a small net decrease in entropy.[12] Note that this factor also makes the lithium $\Delta S°$ values less positive than they would otherwise be. The small negative entropy change observed in the reaction of *tert*-butyl lithiophenylacetate probably results from additional restrictions on the motions of the conjugating ester group in the carbanion. The large positive entropy change for the formation of the cesium salt of benzyl phenyl sulfone is particularly striking and suggests a reduced solvation of the cation because of the chelating effect of the negative sulfone oxygen atoms. Note that the same effect seems manifest with the lithium salt and is also suggested by recent molecular orbital calculations.[13]

Finally, note that the THF ion pair pK_a values are relative values based for convenience on an assigned value of 18.49 to 9-phenylfluorene. With this assignment, the cesium ion pair pK_a values are numerically in close agreement with acidity measurements under free ion conditions in dimethyl sulfoxide solution:[2] phenylacetonitrile, 22.2; *tert*-butyl phenylacetate, 23.9; benzyl phenyl sulfone, 23.4. However, contact ion pairs with lithium cation are less dissociating than those with the larger cesium cation, and, accordingly, lithium ion pair p*K*'s of these benzylic systems are 3–5 pK_a units more acidic (relative to the 9-phenylfluorenyllithium solvent-separated ion pair standard) than the cesium pK_a or ionic pK_a values.

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Variable-Pressure Study of a Molybdenum(III) Reaction: First Definitive Evidence for the Associative Nature of Complex Formation on Hexaaquamolybdenum(III)

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Kinetic studies of substitution reactions on transition-metal aqua cations have been subject to a renewed interest especially since kinetic evidence was found for a changeover in the mechanisms of water exchange along the first-row transition-metal series.[3] This gradual trend was also subsequently seen for monocomplex formation reactions of divalent cations of the same series.[4] For the second-row transition-metal series, Mo^{3+} (d^3) is, at present, the only monomeric aqua ion of an early element available for such a kinetic study. Unfortunately, the water exchange rate on $Mo(H_2O)_6{}^{3+}$ is not accessible (it appears too slow to be followed using the Swift–Connick ^{17}O NMR line-broadening approach and too fast for isotopic labeling techniques) and one is forced to turn toward complex formation reactions.

Rate constants for 1:1 anation on $Mo(H_2O)_6{}^{3+}$ highly depend upon the incoming ligand.[5-7] The values, including recent results on an inner sphere reaction with molecular oxygen,[8] cover almost 5 orders of magnitude (Table I), implying an associative mode of activation. The preparation of several seven-coordinate Mo^{3+} complexes has been reported.[9-11]

We now report the results from a variable-temperature and pressure study of the 1:1 NCS^- anation reaction on $Mo(H_2O)_6{}^{3+}$, a well-characterized reaction, proceeding to completion.[5] Solutions of $Mo(H_2O)_6{}^{3+}$ in triflic (trifluoromethanesulfonic) acid were prepared and characterized as described previously.[7] A 10-fold excess of Mo^{3+} over NCS^- concentration ensured pseudo-first-order conditions and monocomplex formation. The acid concentration was fixed at 0.98 M with triflic acid (no acid dependence is observed) and the ionic strength at 1.00 M (lithium triflate). The UV spectrum of the 1:1 thiocyanato complex shows a well-resolved charge-transfer band at 303 nm (ϵ 2170 $M^{-1}\ cm^{-1}$). This band suggests N bonding of the NCS^- group.[5] The reaction was studied at 320 nm. The temperature range covered in the previously reported study (298.1–313.5 K)[5] was extended downward to 283.0 K, to include the temperature at which the variable-pressure experiments would be performed. A double-beam Perkin-Elmer 340 spectrophotometer equipped with thermostated cells was used. The variable-pressure work was carried out up to 140 MPa at 285 K, a temperature at which the time required for the preparation of samples, their introduction into the pressure vessel, and thermostating at the desired pressure (ca. 15 min) limited the loss to only one-half of the starting material at most. The high-pressure optical cell was designed and built in Lausanne.[12] It is small enough to fit into the sample compartment

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Table I. Second-Order Rate Constants for Monocomplex Formation on $Mo(H_2O)_6^{3+}$ at 298 K

incoming group	k_f^{298}, M^{-1} s^{-1}	ref	incoming group	k_f^{298}, M^{-1} s^{-1}	ref
Cl^-	$4.6 \times 10^{-3\,a}$	5	$Co(C_2O_4)_3^{3-}$	0.340^b	7
NCS^-	0.268^a	5	$MoO_2(H_2O)_5^{3+}$	42.0^b	8
	0.317^a	this work	O_2	180.0^b	8
$HC_2O_4^-$	0.490^a	6			

$^a\mu = 1.00$ M. $^b\mu = 2.00$ M. The presence of an accompanying redox reaction in these studies is noted.

Table II. Kinetic Parameters for NCS^- Anation on $Mo(H_2O)_6^{3+\,a}$

	this work	ref 5
k_f^{298}, M^{-1} s^{-1}	0.317 ± 0.014	0.268 ± 0.013
$\Delta H^\ddagger$, kJ mol^{-1}	67.2 ± 2.7	68.1 ± 1.7
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	-29.2 ± 9.4	-26.7 ± 5.4
$\Delta V^\ddagger$, cm^3 mol^{-1}	-11.4 ± 0.5^b	

$^a\mu = 1.00$ M. ^{b}At 285 K.

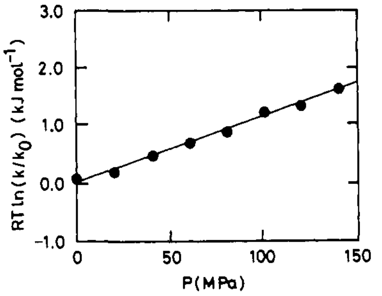

Figure 1. Pressure dependence of the rate constant for the formation of $Mo(H_2O)_5NCS^{2+}$ at 285 K in normalized logarithmic scale.

of most commercial spectrophotometers and was used in the same instrument as for the temperature work.

Plots of $\ln(A_\infty - A_t)$ vs. time, linear over more than four half-lives, yielded pseudo-first-order rate constants k_{obsd} at eight pressures (Figure 1). The k_f values obtained from $k_{obsd} = k_f[Mo^{3+}]$ were fitted as $\ln k_f = \ln k_0 - \Delta V_f^\ddagger P/RT$ with $\ln k_0$ and $\Delta V_f^\ddagger$ as adjustable parameters. The resulting volume of activation, $\Delta V_f^\ddagger = -11.4 \pm 0.5$ cm^3 mol^{-1}, is given in Table II with the other kinetic parameters for the reaction.

Comparison of this activation volume with the values reported for water exchange or substitution reactions with uncharged ligands on trivalent cations is not directly possible, since substitution of water by an anionic ligand like NCS^- induces a large reduction in solvent electrostriction due to charge neutralization. The overall reaction can be described by eq 1. It appears second

$$M(H_2O)_6^{n+} + L^{n-} \overset{K_{os}}{\rightleftharpoons} [M(H_2O)_6,L]^{(n-m)+} \xrightarrow{k_I} M(H_2O)_5L^{(n-m)+} + H_2O \quad (1)$$

order with rate constant $k_f = K_{os}k_I$. The volume of activation is accordingly given by $\Delta V_f^\ddagger = \Delta V_{os}^0 + \Delta V_I$. The formation constant K_{os} and volume ΔV_{os}^0 of the outer-sphere reaction can be estimated from purely electrostatic models.[14,15] For uncharged ligands, ΔV_{os}^0 is assumed to be zero. For the anation of a monovalent anion with a trivalent cation, a positive contribution of about +5.3 cm^3 mol^{-1} is expected. The volume of activation for the interchange step in the formation of $Mo(H_2O)_5NCS^{2+}$, $\Delta V_I^\ddagger$, is therefore likely to be about -17 cm^3 mol^{-1}. This is far more negative than the values reported for the volumes of activation for water exchange $\Delta V_{ex}^\ddagger$ on the early trivalent elements of the first-row transition series, -12.1 cm^3 mol^{-1} for Ti^{3+}, -8.9 cm^3 mol^{-1} for V^{3+}, and -9.6 cm^3 mol^{-1} for Cr^{3+}.[3] It is also much larger than the extreme value of -13.5 cm^3 mol^{-1} proposed by Swaddle[16] for a limiting associative mechanism in the case of the simple, perfectly symmetrical, solvent exchange reaction. The overall volume change involved in this asymmetrical substitution process is not known. Nevertheless, large positive volumes of reaction have been obtained for NCS^- anation on V^{2+} (ΔV^0 = +9.4 cm^3 mol^{-1})[17] and Fe^{3+} (ΔV^0 = +7.5, +8.3, +8.9, and +17.5 cm^3 mol^{-1}),[4] and although an exact figure cannot be extrapolated, one can safely assume that the volume of reaction will also be positive for Mo^{3+}. It means that the volume of activation, $\Delta V_r^\ddagger$, for the reverse aquation reaction (not measurable) must be even more negative than $\Delta V_f^\ddagger$. The character of the reaction under study is thus undoubtedly associative. For such an associative mode of activation, the $\Delta V_I^\ddagger$ value is not expected to match the value of the activation volume for the corresponding water exchange, $\Delta V_{ex}^\ddagger$, in the same way that k_I values are not supposed to be equal to k_{ex}, but the $\Delta V_{ex}^\ddagger$ can be used as a reference value to define the degree of associativeness of the reaction. Following this idea, we can conclude that, in comparison with the $\Delta V_{ex}^\ddagger$ values mentioned above, the value of $\Delta V_I^\ddagger \simeq -17$ cm^3 mol^{-1} is characteristic of a very strong associative interchange mechanism, if not even of a limiting A mechanism.

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(12) It consists of a beryllium-copper pressure-tight cylinder (80 mm in length and 45-mm o.d.) with a sapphire window inbedded at one end and a closing beryllium-copper assembly at the other end, in which a second sapphire window is enclosed. The sample is contained in a 2-cm "pill box" quartz cell,[13] immersed in the pressure vessel. A 100-Ω platinum resistance is introduced sideways along the internal face of the cylinder to measure the temperature in the vicinity of the sample. A capillary connector transmits the applied pressure through the side wall. The cell is thermostated by circulation of a fluid in a helical groove carved in the outer surface of the cylinder, covered by a beryllium-copper envelope and thermally insulated from the outside by a cylindrical vacuumed quartz Dewar.

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Synthesis and Electron-Transfer Rates of Coplanar Diporphyrins: Models for (Heme) Protein-Protein Electron-Transfer Reactions

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Despite the crucial biological role of protein electron-transfer reactions, the factors which control this reactivity remain poorly understood.[1,2] One simple approach to developing such understanding is to develop "small" molecule model systems to mimic intramolecular electron transfer in the protein systems. Appropriate models require that the donor and acceptor be held at a fixed distance and orientation which correspond to those in the protein-protein complex. Current information[3] suggests that in the reactive heme protein-protein complexes, the heme centers are constrained at relatively long distances. For example in the cyt *c*/cyt b_5 complex, the Fe-Fe distance is ca. 16 Å, and in the cyt *c*/cyt *c* peroxidase complex, the Fe-Fe distance is ca. 24 Å. It is believed that the mean heme planes are held parallel in these complexes. In the models described herein, however, the protein

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