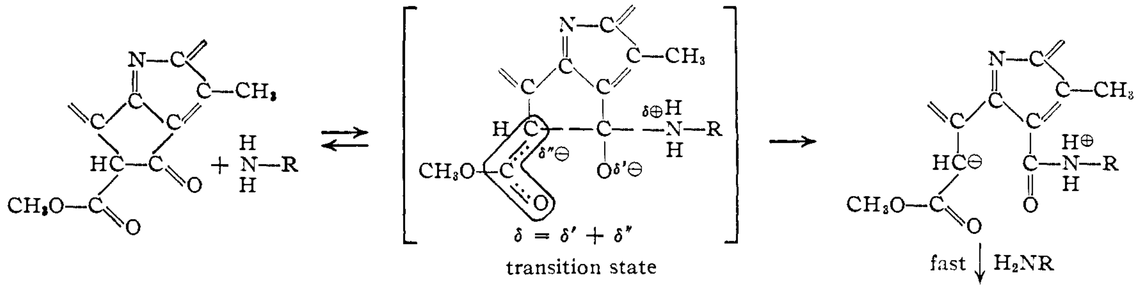

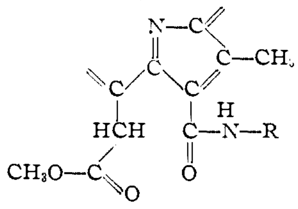

the amine as well as the ease of the attachment of the nitrogen to the electrophilic carbonyl carbon atom. It is also clear that steric effects must play some role in the orientation and attachment of the amine to carbon 9.

Bimolecular reactions involving complex molecules must have small frequency factors. Values for the entropy of activation as low as −30 e.u. can be accounted for in this manner. In this case an additional loss of entropy is imposed on the transition state, because of a considerable loss of mobility due to the partly double bond character of the ester side chain.

The increase of the reaction rate in going from chlorophyll-*a* to chlorophyll-*b* (*i.e.*, by substituting CHO for CH_3 on carbon 3, which is more than 10 Å. apart from the reacting carbon 9) must be ascribed mainly to a decrease of the energy of activation. This decrease, of about 0.8 kcal. may be due either to a reduction in the repulsion between carbon 9 and amino nitrogen and/or to an increase in the ionizability of the bond to be broken. The same holds for the increase of the reaction rate by going from pheophytin-*b* to chlorophyll-*b*, where the decrease of energy of activation is about 2.2 kcal. This is another illustration of the fact that the magnesium makes ring V more reactive.

OXFORD, ENGLAND

NOTES

A Proposed Approach to the Chelate Effect[1]

BY ARTHUR W. ADAMSON

RECEIVED SEPTEMBER 8, 1953

It has generally been observed that complex ions formed by the coördination of groups around a central metal ion tend to be more stable, *i.e.*, possess smaller dissociation constants, the larger the number of points of attachment of the central metal ion to each ligand. Thus bis-(ethylenediamine) complexes are more stable than the corresponding tetramines and tris-(ethylenediamine) ones more so than hexamines. Similarly with the tridentate diethylenetriamine complexes, and, finally, the hexadentate ligand ethylenediaminetetraacetic acid has become known for the unusually stable complexes which it forms with a large variety of ions. This increase in stability with dentate character has been termed the "chelate effect." It has been stated, in a general way, to be an entropy effect[2,3] while Schwarzenbach[4] has, in addition, presented a detailed kinetic treatment supposing a two-stage addition of a bidentate ligand with the rate of addition of the second functional group proportional to an effective concentration estimated from its free volume. This leads to a chain length effect roughly in accord with the meager existing data.

While specific structural aspects are undoubtedly relevant, it is suggested here that the chelate effect is largely a consequence of the arbitrary asymmetry in the usual choice of standard states. Consider the general equation for the formation of a complex ion from a hydrated metal ion M and the ligand X.

$$M(H_2O)_n^a + pX^b = [M(H_2O)_{n-p}X_p]^{(a+pb)} + pH_2O \quad (1)$$

The hypothetical one molal state is employed for solutes while for the solvent the pure substance is chosen. In comparing a series of processes of type (1), of varying n and p values, not only are the magnitudes of ΔS^0 and ΔF^0 dependent upon the choice of standard state, but also their *relative* values or positions in a sequence. If the effect of standard state choice is regarded as primarily one of varying the translational entropy contributions, a brief can be made for the use of the hypothetical mole fraction unity state for the solutes. Such a state is one of minimum translational entropy for a solute retaining the properties it possesses in dilute solution. The conversion

---

[1] This work was carried out under contract N6onr23809 between the Office of Naval Research and the University of Southern California.

[2] A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., New York, N. Y., 1952, p. 149f.

[3] C. G. Spike and R. W. Parry, THIS JOURNAL, **75**, 2726, 3770 (1953).

[4] G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).

equations are

$$\Delta S^{0\prime} = \Delta S^0 - \Delta nR \ln 55.5 = \Delta S^0 -7.9\Delta n \text{ (at 25°)}$$

$$\Delta F^{0\prime} = \Delta F^0 + \Delta nRI \ln 55.5 = \Delta F^0 +2360\Delta n \text{ (at 25°)}$$

The primed quantities are based on the hypothetical mole fraction unity state, and Δn denotes the moles of products minus those of reactants, exclusive of solvent.

A restatement of the chelate effect would be that ΔF^0 values tend to be negative and ΔS^0 values positive for processes of the type (assuming for simplicity that X and Y are neutral species)

$$MX^a_p + p/2\,Y = MY^a{}_{p/2} + pX \qquad (2)$$

where Y denotes a bidentate group. If, as proposed here, it is true that the effect is primarily due to the unequal contributions of the large translational entropy terms for the usual standard state then $\Delta S^{0\prime}$ for (2) should be small. Also, if the functional groups on X and Y are similar so that the bond energy per functional group would be the same, then $\Delta F^{0\prime}$ values should also be small. It is seen from Table I that such is the case; the available data show that $\Delta S^{0\prime}$ and $\Delta F^{0\prime}$ values tend to be symmetrical around zero. Thus the apparent extra stability of chelate complexes disappears with the new choice of standard states.

TABLE I

INFLUENCE OF CHOICE OF STANDARD STATE ON THE "CHELATE" EFFECT[a]

M	p	ΔF^0, kcal.	$\Delta F^{0\prime}$, kcal.	ΔS^0, e.u.	$\Delta S^{0\prime}$, e.u.
I. $M(NH_3)_p + p/2\ en = M(en)_{p/2} + pNH_3$					
Co^{+2}	2	−3.2	−0.9		
Ni^{+2}		−3.7	−1.4		
Cu^{+2}		−4.3	−2.0	5.7	−2.2
		−3.3	−1.0[b]		
Zn^{+2}		−1.6	0.7	5.7	−2.2
Cd^{+2}		−1.3	1.0	4.4	−3.5
		−1.4	1.1	4.7	−3.2[c]
	Av.	−2.7	−0.4	5.1	−2.8
Co^{+2}	4	−7.7	−3.0		
Ni^{+2}		−8.6	−3.9		
Cu^{+2}		−10.4	−5.7	19.1	3.3
		−6.7	−2.0[b]		
Zn^{+2}		−2.3	2.4	13.4	−2.4
Cd^{+2}		−4.0	0.7	11.8	−4.0
		−5.6	−0.9	19.3	3.5[c]
	Av.	−6.4	−1.7	15.6	0.1
Co^{+2}	6	−12.7	−5.6		
Co^{+3}		−18.3	−11.2		
Ni^{+2}		−13.2	−6.1	24.0	0.3
II. $M(NH_3)_p + p/3\ den = M(den)_{p/3} + pNH_3$[d]					
Co^{+2}	3	−5.3	−0.5		
Ni^{+2}		−5.8	−1.0		
Cu^{+2}		−8.2	−3.4		
Zn^{+2}		−3.1	1.7		
Cd^{+2}		−3.5	1.3		
	Av.	−5.2	−0.4		
III. $M(NH_3)_p + p/4\ trien = M(trien)_{p/4} + pNH_3$[e]					
Co^{+2}	4	−8.2	−1.1		
Ni^{+2}		−9.1	−2.0		
Cu^{+2}		−11.6	−4.5		
Zn^{+2}		−4.6	2.5		
Cd^{+2}		−5.3	1.8		
	Av.	−7.8	−0.7		

[a] Values from ref. 4, 5 and 7, for *ca.* 25°. [b] Propylenediamine instead of en. [c] NH_2CH_3 instead of NH_3. [d] Diethylenetriamine. [e] Triethylenetetramine.

It is suggested therefore that $\Delta F^{0\prime}$ and $\Delta S^{0\prime}$ values be employed as a more logical starting point from which to consider specific structural effects. Thus, as has been pointed out by Bjerrum[5] and by Schwarzenbach,[4] *a priori* or statistical factors enter also into the entropy change for processes (1) or (2). For a fully coördinated complex, *i.e.*, of the type MX_n, the statistical factor is unity, however, while for complexes such as $MX_2(H_2O)_{n-2}$, an assumption is required as to the equivalence of the various possible isomers. In addition, steric and chain length effects should cause variations in $\Delta S^{0\prime}$ values.

The entropy change for processes of type (1) must also include contributions due to the changes in charge and hydration that are occurring. However, for reactions of a similar charge type, the use of the hypothetical mole fraction unity standard state tends to minimize the translational entropy effect due to differing Δn values. Thus the average ΔS^0 for the formation in aqueous solution of $Cu(NH_3)_4{}^2$ and $Zn(NH_3)_4{}^2$ is -15 ± 1.2, while for $Ni(NH_3)_6{}^2$ and $Co(NH_3)_6{}^2$ it is -27 ± 0.3, a difference of 12 e.u. The corresponding $\Delta S^{0\prime}$ values are 17 and 21, and a large measure of the difference in entropy of formation has been accounted for.

The treatment of the entropy change for a single process of type (1) is more difficult. If the entropy of an aqueous species be regarded as a sum of translational, internal and charge (hydration) terms, then $\Delta S^{\circ\prime}$ might be considered as involving only the last two. The charge contribution may be estimated for monatomic ions by use of the Powell and Latimer equation,[6] and various ways have been suggested for estimating the internal or structural terms.[6-10] One difficulty lies in the estimation of the charge contribution for polyatomic ions. Considering a specific example, from the data of Latimer and Jolly,[8] $\Delta S^{\circ\prime} = -51$ for $AlF_2^+ + 2F^- = AlF_4^{-2}$; assuming the charge terms for AlF_2^+ and AlF_4^- cancel, the entropy change due to structural terms would be *ca.* −25 per F added. From this, a charge entropy of −87 may be calculated for AlF_6^{-3}, which, on the basis of the Powell and Latimer equation, corresponds to a radius of 1.8 Å. which is about the sum of the crystal radii for Al^{+3} and F^-. Actually, since such a calculated radius is an empirical quantity, it is difficult to decide what a reasonable value would be.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIF.

---

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[6] R. E. Powell and W. M. Latimer. *J. Chem. Phys.*, **19**, 1139 (1951).

[7] W. S. Fyfe, *J. Chem. Soc.*, 2018, 2023 (1952).

[8] W. F. Latimer and W. J. Jolly, THIS JOURNAL, **75**, 1548 (1953).

[9] J. W. Cobble, *J. Chem. Phys.*, **21**, 1451, 1448 (1953).

[10] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1952).