Table II. Calculated and Experimental Activation Parameters for the Decarboxylation of But-3-enoic Acid at 650 K

	Obsd	MINDO/3	Error
$\Delta H^{a,b}$ (ΔS^{a})	$-6.8^{a,b}$	-6.8^{b} $(28.3)^{c}$	0.0^{b}
$\Delta H^{\ddagger\ b}$	39.3 ± 1.6^{c}	46.3^{d}	-7.0
$\Delta S^{\ddagger\ e}$	-10.2 ± 2.5^{c}	-13.9	3.7
k_H/k_D	2.7^{f}	2.1	0.6
k_{12}/k_{14}	1.035 ± 0.010^{g}	1.031^{h}	0.004

[a] Heat of reaction (entropy of reaction) at 25 °C. The "experimental" value is derived from the known heats of formation of butanoic acid (−112.4), propene (4.9), and carbon dioxide (−94.1) by assuming that the difference in heat of formation between butanoic acid and but-3-enoic acid is equal to the mean for a number of similar pairs, CH_3CH_2X and $CH_2{=}CHX$. Thermochemical data were from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970. The entropy of reaction was calculated using the rigid rotator approximation and may therefore be in error owing to neglect of internal rotation. However, since such errors should be present in both but-3-enoic acid and propene, they should tend to cancel in the calculation of ΔS. Indeed our value agrees closely with that estimated (30.5) from group additivities: S. W. Benson and H. E. O'Neal "Kinetic Data on Gas Phase Unimolecular Reactions", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., 1970. [b] Units in kcal mol^{-1}. [c] Reference 13. [d] Corrected for zero point energy and $\Delta H^{\ddagger}_{vib}$ at 650 K: $46.3 = 51.4 - (2.66 + 2.44)$. [e] Units in cal mol^{-1} deg^{-1}. [f] Reference 11. [g] Data were for PhCH=CHCMe$_2{}^{14}$CO$_2$H at 550 K; cf ref 15. [h] At 550 K.

tropies[23] of a number of stable molecules, we decided to apply these techniques to this transition state and derive both the entropy of activation[24] and the primary kinetic isotope effect, this being the first time that such an isotope effect has been calculated entirely from the molecular orbital theory. The entropy of the transition state was calculated from the MINDO/3 vibrational frequencies as it was previously,[23] except that the vibration corresponding to translation along the reaction coordinate was not included. The kinetic isotope effect was calculated[25] from eq 1 where $u = hc\omega/kT$ and u_{1i}

$$\frac{k_1}{k_2} = \frac{\nu^{\ddagger}{}_1}{\nu^{\ddagger}{}_2} \cdot \frac{\prod^{3n-6} \dfrac{u_{2i}}{u_{1i}}}{\prod^{3n-7} \dfrac{u^{\ddagger}{}_{2i}}{u^{\ddagger}{}_{1i}}} \cdot \frac{\prod^{3n-6} \dfrac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}}{\prod^{3n-7} \dfrac{1 - e^{-u^{\ddagger}{}_{1i}}}{1 - e^{-u^{\ddagger}{}_{2i}}}} \times \frac{\exp\left[\sum^{3n-6} (u_{1i} - u_{2i})/2\right]}{\exp\left[\sum^{3n-7} (u^{\ddagger}{}_{1i} - u^{\ddagger}{}_{2i})/2\right]} \quad (1)$$

and u_{2i} refer to the light and heavy isotopically substituted reactant molecules while $u^{\ddagger}{}_{1i}$ and $u^{\ddagger}{}_{2i}$ refer to the corresponding transition states. $\nu^{\ddagger}{}_1$ and $\nu^{\ddagger}{}_2$ refer to the frequencies of the vibration corresponding to the reaction coordinate in the two transition states. The results are given in Table II together with the calculated activation enthalpy, which was overestimated somewhat. The values of $\Delta S^{\ddagger}$ and k_H/k_D were well calculated. Unfortunately the only value of k_{12}/k_{14} available[15] refers to **2b** (^{14}C at C-1) which, however, decomposes at almost the same rate as **1** at 550 K and so is likely to have similar isotope effects. The value observed for **2b** agreed with our calculated one for **1**. These results were particularly gratifying because the procedure we used is strictly valid only for the rigid-rotor-harmonic-oscillator case. Apparently the errors due to nonrigidity cancelled, as we had indeed expected.

The heat and entropy of reaction for conversion of **1** to propene and carbon dioxide are also listed in Table II. The value for ΔH agrees with an estimate from experimental data and that for ΔS with one by Benson (see Table II).

We are currently calculating several further reactions of this type to see if entropies of activation and kinetic isotope effects can be generally calculated with accuracy comparable with that achieved here. If, as we expect, this proves to be the case, such calculations will prove a powerful aid in the study of reaction mechanisms.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

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Michael J. S. Dewar,* George P. Ford
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received May 6, 1977

Anomalous Stability Sequence of Lanthanide(III) Chloride Complexes with 18-Crown-6 in Methanol. Abrupt Decrease to Zero from Gd^{3+} to Tb^{3+}

Sir:

Although the preparation of solid complexes of lanthanide(III) metal cations with cyclic polyethers has been reported,[1,2] thermodynamic data describing these reactions in solution are not available. Furthermore, contradictory results have been presented[1,2] as to whether or not complexes are formed between the latter members of the lanthanide series

Table I. Log K, ΔH,[a] and $T\Delta S$[a] Values for the Interaction of 18-Crown-6 with Several Trivalent Rare Earth Chlorides in Methanol at 25 °C and $\mu = 0.005$

	Log K^b	ΔH^b	$T\Delta S$
La^{3+}	3.29 ± 0.03	2.81 ± 0.04	7.30
Ce^{3+}	3.57 ± 0.20	2.54 ± 0.13	7.41
Pr^{3+}	2.63 ± 0.28	4.46 ± 0.40	8.05
Nd^{3+}	2.44 ± 0.16	4.77 ± 0.26	8.10
Sm^{3+}	2.03 ± 0.07	3.67 ± 0.04	6.44
Eu^{3+}	1.84 ± 0.14	3.06 ± 0.14	5.57
Gd^{3+}	1.32 ± 0.12	3.73 ± 0.15	5.53
(Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}, UO_2			

[a] Kilocalories/mole. [b] Values represent average and standard deviation, respectively of three–six calorimetric determinations. [c] No measurable heat other than heat of dilution was found for the mixing of these cations with the ligand.

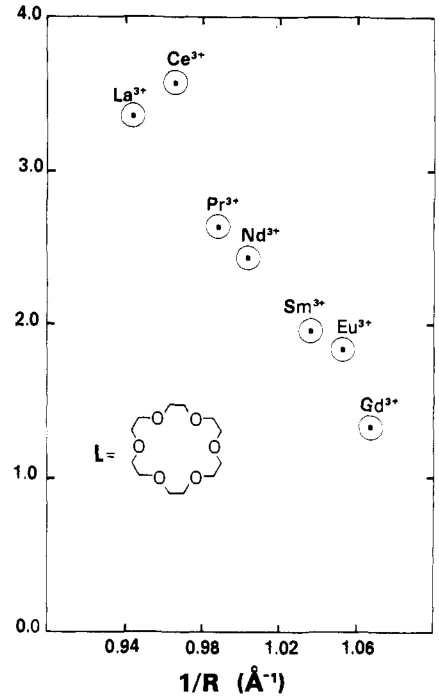

Figure 1. Log K for the reaction $M^{3+} + L = ML^{3+}$ (L = 18-crown-6) in methanol at 25 °C in presence of Cl^- vs. reciprocal of cation radius.[10] No heat of reaction was observed with Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, or Lu^{3+}. (See text.)

and the crown-6 members of the cyclic polyether family. It has been suggested[1] that trivalent rare earth–cyclic polyether interactions could be useful in the separation and purification of lanthanides. Similar application might also be made to the series of actinides, some elements of which form stable tripositive ions of comparable chemical behavior. In addition, isotopic separation of elements from either series by cyclic polyethers may be feasible. Isotopes of Ca^{2+} have already been separated by a solvent extraction technique employing dicyclohexo-18-crown-6.[3] We have therefore embarked on a study of the thermodynamics of interaction of the hydrated lanthanide(III) chlorides with cyclic polyethers using a titration calorimetric technique previously described.[4]

Log K, ΔH, and $T\Delta S$ values for the reaction in methanol of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+} with 18-crown-6 are given in Table I. Identical calorimetric titrations with Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}, UO_2^{2+}, and Th^{4+} produced no measurable heat other than heat of dilution. Three features of these results are particularly significant. (i) No heat of reaction is observed with the post-Gd^{3+} lanthanide cations. (ii) All reaction enthalpies in Table I are positive and, thus, observed stabilities are entropic in origin. (iii) With increasing atomic number, the stabilities of the complex formed decrease, rather than increase as is the case with the trivalent lanthanide complexes of most other ligands.

From the fact that no heat of reaction was measured for the latter members of the lanthanide(III) chloride series, we may conclude that (i) ΔH is immeasurable close to 0 and/or (ii) log K is very small. However, although reaction may occur even when no heat is measured, five factors lead us to conclude that no reaction occurs with the tripositive ions of the elements Tb through Lu. (i) Log K steadily decreases through the series Ce^{3+} to Gd^{3+} (Figure 1). (ii) Abrupt changes in slope of curves describing the variation of log K with atomic number have been noted to occur around Gd^{3+} with acetylacetone, carboxylic acids, and EDTA.[5] These irregularities have been explained in terms of a proposed change in coordination number at or near Gd^{3+}.[5,6] A sudden drop in stability at Tb^{3+} is therefore not without related precedent. (iii) The probability that all seven of the heavier lanthanide cations would react with 18-crown-6 with ΔH being 0 in every case is small especially since ΔH changes very little from a value of +3 kcal/mol along the first part of the series. (iv) King and Heckley[1] isolated some solid lanthanide(III) nitrate complexes with the polyether dibenzo-18-crown-6 from acetonitrile but found that heavier lanthanides from Sm onward failed to yield product. Furthermore, these same investigators were successful in separating a mixture of Pr^{3+} and Er^{3+} by passing the solution through a chromatography column loaded with this polyether, Pr^{3+} alone being retained on the column. (v) Mixtures of Sm^{3+} and Tb^{3+} and of Eu^{3+} and Yb^{3+} were titrated with 18-crown-6. The calculated log K values for these mixtures were 2.10 and 1.81, respectively. These log K values are within the error limits for Sm^{3+} and Eu^{3+}, respectively, indicating that complexes between Tb^{3+} or Yb^{3+} and 18-crown-6 do not form.

The observation by King and Heckley[1] combined with the results of our investigation suggest a novel method of lanthanide separation. We report little or no reaction of 18-crown-6 with any post-Gd^{3+} lanthanides. They report little or no reaction of dibenzo-18-crown-6 with any post-Nd^{3+} ions. Where subtle ligand structural variations such as substitution with benzene rings can alter the list of lanthanides which react with crown ethers, then simple solvent extraction, column chromatographic, or liquid membrane techniques could be employed to very effectively separate different sets of elements in the lanthanide series.

While formation enthalpies of lanthanide cation complexes are in general exothermic, endothermic heats of formation other than those reported here are not unknown.[7] For instance, the heats of formation of lanthanide complexes of simple carboxylic acids, amino acids, and sulfate ion are positive. However, while formation enthalpies vary in sign, formation entropies of rare earth complexes are almost invariably positive, as are those reported in this study.

Our 18-crown-6 solution was standardized by calorimetric titration with KCl. The methanolic MCl_3 (99.9%) solutions were standardized by EDTA titration using xylenol orange to indicate the end point. These latter standardizations made it possible to compute accurately the extent to which the chloride salts of the cations were hydrated. The values all fell within the range 7–9 mol of H_2O/mol of salt. It has been shown[8,9] that in methanol solution the chloride ion associates with these cations to some degree. Thus the reaction under consideration is

$$M(H_2O)_x(CH_3OH)_yCl_z{}^{3-z} + \text{crown} \rightarrow M(\text{crown})(H_2O)_{x'}(CH_3OH)_{y'}Cl_{z'}{}^{3-z'} + (x - x')H_2O + (y - y')CH_3OH + (z - z')Cl^-$$

To check for a possible anion effect, the calorimetric reaction of 18-crown-6 with La^{3+} and Ce^{3+} was repeated using the nitrate salts of both cations and the perchlorate salt of the latter. The nitrates both produced precipitated complex, while the reaction results (both log K and ΔH) of 18-crown-6 with $Ce(ClO_4)_3$ were well within the range of values found for that with $CeCl_3$.

Although the lighter lanthanides are similar in size to Na^+, and although the stability constant of Ce^{3+} (log K = 3.57, radius = 1.03[10]) approaches that of Na^+ (log K = 4.36,[11] radius = 1.02[10]), entirely different thermodynamic factors are responsible for the stabilities of the complexes of these two cations. While alkali and alkaline earth metal ion complexes of 18-crown-6 are enthalpy stabilized and entropy destabilized,[12] the opposite is true of the rare earth complexes. In addition, the stability decrease along the series of lanthanides is enthalpic in origin for the cations up to Nd^{3+} and then entropic in origin for those from Sm^{3+} to Gd^{3+}. This fact reflects the delicate balance among ligand–cation binding, solvation, and ligand conformation which exists in these systems,[12] each of which will be discussed briefly in the following paragraphs.

Stability sequences of cyclic polyether complexes with nonpolarizable cations have been related to the relative sizes of cation and ligand cavity.[4,12] Like Na^+, the lanthanide(III) cations are too small for an ideal fit into the cavity of the 18-crown-6 ring. For this reason it is not surprising that complex stability decreases as cation size diminishes while proceeding across the series. This stability trend is opposite to that found for most ligands, whose complexes are generally more stable with the lanthanides of higher atomic number.[5]

Evidence exists that solvation number of the rare earth cations decreases with higher atomic number and that a sudden drop in solvation number occurs around Gd^{3+}.[6] It is possible, therefore, that the entropy contribution from loss of solvent (CH_3OH and/or H_2O) molecules which favors complexation is smaller for the lanthanides of higher atomic number. This factor may contribute significantly to the lack of formation of complexes with any of the rare earth cations beyond Gd^{3+}.

An x-ray crystal structure of the dicyclohexo-18-crown-6 complex of $La(NO_3)_3$ has been reported[13] showing La^{3+} to be situated in the crown ring cavity, and further coordinated to six oxygen atoms of three bidentate nitrate ions. The crown oxygens are not quite coplanar, two opposite atoms being displaced below the plane of the other four. This distortion from planarity is reminiscent of the bent ligand conformation of the 18-crown-6 complex of Na^+.[12] Further ordering of the ligand may also be responsible for a loss of entropic stabilization with the higher lanthanides.

Since 18-crown-6 exhibits unusual and potentially useful complexation characteristics with the lanthanides and since there is considerable interest in developing methods of separating actinides, we have investigated the possibility of interaction of this ligand with UO_2Cl_2 and $Th(NO_3)_4$ in methanol. Previous reports of the synthesis of solid uranyl complexes with 18-crown-6 have since been discounted as an example of cocrystallization.[14-16] Likewise no interaction has been reported between the uranyl cation and dibenzo-18-crown-6 or benzo-15-crown-5 in the solid phase[17] or with the cis-syn-cis isomer of dicyclohexo-18-crown-6 in aqueous solution.[4] We find no measurable heat of interaction of UO_2^{2+} or Th^{4+} with 18-crown-6 in methanol. This observation in the case of uranyl ion for which other data are available is supportive not only of the hypothesis that there is no complex formation between these two species under these conditions, but also of the usefulness of titration calorimetry in detecting the presence or absence of complexation in general.

Acknowledgments. Financial support of this study from the National Science Foundation (Grant CHE 76-10991) and the U.S. Public Health Service (GM18811-04) is acknowledged.

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R. M. Izatt,* J. D. Lamb, J. J. Christensen
Departments of Chemistry and Chemical Engineering and
Contribution No. 122 from the Thermochemical Institute
Brigham Young University, Provo, Utah 84602

Barry L. Haymore
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

Received August 8, 1977

Asymmetric Hydrogenation of α,β-Dehydroamino Acid Residue in Cyclic Dipeptides

Sir:

AM-Toxin I is a host specific phytotoxin, its structure being determined as c(L-Amp^1-Dha^2-L-Ala^3-L-Hmb^4) (c = cyclo, Amp = 2-amino-5-(*p*-methoxyphenyl)pentanoic acid, Dha = dehydroalanine, Hmb = 2-hydroxy-3-methylbutanoic acid).[1] To elucidate the role of a double bond in Dha^2 residue, we planned to prepare [L-Ala^2]- and [D-Ala^2]-AM-toxin I by hydrogenation of natural or synthetic[2] AM-toxin I. As a preliminary study we hydrogenated c(L-Leu-Dha) and observed unexpectedly high asymmetric induction affording pure c(L-Leu-L-Ala). This paper reports asymmetric hydrogenation of Dha residue in several cyclic dipeptides, preparation of pure L-alanine from c(L-Lys(ϵ-Ac)-Dha), preparation and hydrogenation of c(L-Leu-Dhb) (Dhb = dehydrobutyrine), and preparation of c(NMe-L-Trp-Dhb) (NMe = *N*-methyl) corresponding to natural cyclic dipeptide.[3] Poisel and Schmidt reported the efficient asymmetric induction forming L-Phe residue in some 90% on hydrogenation of c(L-Pro-NH-C(=CHC_6H_5)-CO) or c(L-Pro-$NCOCH_3$-C(=CHC_6H_5)-CO); there was however, almost no asymmetric induction isolating DL-phenylalanine in the case of c(L-Leu-$NCOCH_3$-C(=CHC_6H_5)-CO).[4] Akabori et al. observed low asymmetric induction isolating phenylalanine with 15% L form