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Effect of Substituents on the Structure of Reaction Complexes

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Abstract: Ab initio molecular orbital calculations with the 4-31G basis set have been used to examine the structures and stabilities of a set of model hydrogen-bonded complexes, $XFHFX'^+$, with X, X′ = H, Li, Me, and F. The results indicate that in all cases the structure of the complex resembles the structure of the more stable of the two possible ion–molecule pairs ($XF + HFX'^+$ and $XFH^+ + FX'$) from which the complex may be formed. However, the results do not support a differential analogue of this principle, i.e., we find that stabilization of one set of reactants, e.g., $XF + HFX'^+$, does not necessarily result in increasing resemblance of the complex structure to these reactants. Extension of these conclusions to the question of transition-state structure suggests that while the Hammond postulate is likely to be of wide applicability, its differential analogue may not necessarily be valid in all cases. These results are interpreted in terms of both valence-bond and potential-energy surface models.

Introduction

The question of how substituents affect the structure of the transition state of a chemical reaction is yet largely unresolved. This is true despite the large number of theoretical models which have been developed over recent years. Most prominent are the models proposed by Bell,[2] Evans and Polanyi,[3,4] Hammond,[5] Thornton,[6] More O'Ferrall,[7] Harris and Kurz,[8] and Critchlow.[9] Much of the difficulty stems from the fact that over recent years a number of experimental papers on S_N2 transition states have appeared which are in at least partial disagreement with most of the existing models.[10] A molecular orbital–valence bond model which attempts to overcome these difficulties has recently been presented.[11]

Unfortunately, the explicit structure of a transition state cannot be experimentally determined. At best, qualitative aspects of the structure can be inferred from experimental information. In contrast, recent advances have allowed the detailed structures of transition states to be rigorously determined theoretically, and a number of ab initio studies of this type have been reported.[12] As a preliminary to a study of the effect of substituents on transition-state structure, we report in this paper the results of a study of the effect of substituents on the structure of reaction complexes (i.e., local minima in the reaction profile) in potential-energy surfaces. In particular, we examine the effect of substituents on the structure and stability of the reaction complex involved in proton-transfer reactions of the type 1.[13]

$$A{-}H^+ + B \rightarrow [A{\cdots}H{\cdots}B]^+ \rightarrow A + H{-}B^+ \qquad (1)$$

Table I. Calculated Total Energies (4-31G, hartree) for Parent Ions (XFH^+), Parent Neutral Molecules (FX'), and Complexes ($XFHFX'^+$)

system	energy	system	energy
HFH^+	−100.06512	$HFHFH^+$	−200.02054
$MeFH^+$	−139.08427	$MeFHFMe^+$	−278.00545
FFH^+	−198.55570	$FFHFF^+$	−397.03147
$LiFH^+$	−107.17588	$LiFHFLi^+$	−214.10044
FH	−99.88729	$HFHFMe^+$	−239.01854
FMe	−138.85804	$HFHFF^+$	−298.53438
FF	−198.45843	$HFHFLi^+$	−207.09626
FLi	−106.82409	$MeFHFF^+$	−337.54745
		$MeFHFLi^+$	−246.07422
		$FFHFLi^+$	−305.63687

Table II. Calculated Heats of Complex Formation (kJ mol^{-1}) for Complexes ($XFHFX'^+$) Formed from Ions (XFH^+) and Neutrals (FX')

	FX′			
XFH^+	FH	FMe	FF	FLi
HFH^+	179	250	28	544
$MeFH^+$	123	166	12	435
FFH^+	240	351	46	675
$LiFH^+$	87	106	7	264

We seek in this study answers to the following questions:

(i) How is the structure of a reaction complex related to that of the reactant or product moieties?

(ii) Do our results support an analogue[14] of the "Hammond postulate"[5] for minima on a potential surface?

(iii) How do substituents affect the structure of the reaction complex?

(iv) Having established the effect of substituents on the structure of minima on a potential surface, what can we anticipate regarding the behavior of transition states, taking into account, of course, their different characteristics?

The system we have examined is a relatively simple one involving complex formation and subsequent proton transfer between a series of conjugate acids XFH^+ and parent fluorides FX' as shown in equation 2. Analysis of a possible structure–stability

$$X{-}F{-}H^+ + F{-}X' \rightarrow [X{-}F{\cdots}H{\cdots}F{-}X']^+ \rightarrow X{-}F + H{-}F{-}X'^+ \qquad (2)$$

relationship for these hydrogen-bonded complexes may contribute

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(1) (a) Ben Gurion University. (b) Australian National University.

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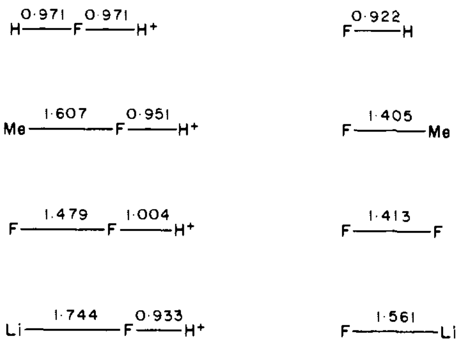

Figure 1. 4-31G optimized structural parameters for ions XFH^+ (constrained to linearity) and neutrals FX′.

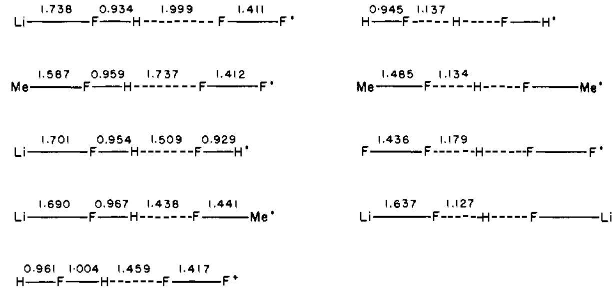

Figure 2. 4-31G optimized structural parameters for complexes XFHFX′ (constrained to linearity).

to answering the questions posed above.

Computational Method and Results

Standard ab initio molecular orbital calculations were carried out by using a modified version[15a] of the Gaussian 70 system of programs[15b] and the 4-31G[16] (for H, C and F) and 5-21G[17] (for Li) basis sets.[18] Structures were fully optimized by using a gradient technique,[19] except that the XFH^+ and $XFHFX'^+$ systems were constrained to linearity along the XFH and XFHFX′ axes, respectively, and for X = Me, standard[20] C–H bond lengths (1.09 Å) and angles (109.47°) were utilized throughout. The constraint of linearity is artificial but simplifies the analysis of the structure–stability relationship, the main objective of this paper.

Calculated total energies for the neutral molecules FX′, the protonated species XFH^+, and the complexes $XFHFX'^+$ are listed in Table I. Optimized structures of the molecules XF and ions XFH^+ are displayed in Figure 1. Optimized structures for the complexes $XFHFX'^+$ are displayed in Figure 2. Calculated heats of complex formation for complexes $XFHFX'^+$ formed from ions XFH^+ and neutrals FX′ are presented in Table II.

Discussion

The data in Table II indicate that for all X and X′ studied, a stable complex is formed between XFH^+ and FX′. Theoretical heats of complex formation range from 7 kJ mol^{-1} for the reaction between $LiFH^+$ and FF to 675 kJ mol^{-1} for the reaction between FFH^+ and FLi.

Key trends in the table are evident. Complex stability for different neutral fluorides increases in the order FF < FH < FMe < FLi for any given cation, while for different cations (with any neutral fluoride) the stability increases in the opposite order, $LiFH^+ < MeFH^+ < HFH^+ < FFH^+$. This behavior is clearly governed by the electron-donating properties of the substituents which increase in the order F < H < Me < Li. Thus the Li substituent causes FLi to be an effective proton acceptor relative to the other substrates, while making $LiFH^+$ a poor proton donor. Not surprisingly the most stable complex is formed between the strongest proton donor FFH^+ and the strongest proton acceptor FLi while the weakest complex is formed between the poorest proton donor $LiFH^+$ and the poorest proton acceptor FF.

Table III. Correlation of Complex Structures (As Measured by α_G) and Reaction Energies ($\Delta E°$)

complex	α_G[a]	$\Delta E°$[b]
Li-F-H···F-F$^+$	1.00	668
Me-F-H···F-F$^+$	0.99	339
Li-F-H···F-H$^+$	0.96	457
Li-F-H···F-Me$^+$	0.93	330
H-F-H···F-F$^+$	0.93	212
Me-F-H···F-H$^+$	0.82	127
X-F··H··F-X^{+c}	0.50	0

[a] α_G is defined by eq 3. [b] $\Delta E°$ is the calculated energy change (in kJ mol^{-1}) for reaction 2. A positive value indicates that reactants are more stable than products. [c] $XFHFX^+$ represents all the symmetrically substituted complexes (i.e., X = H, Li, Me, or F).

Structure–Stability Relationship. In a recent communication,[14] it was suggested by Bouma and Radom that the structures of complexes might be governed by a postulate analogous to the Hammond postulate[5] for transition states, viz., *when two sets of reactants [(AB + C) or (A + BC)] interact to form a common stable complex (A···B···C), the complex will generally resemble the set of reactants of lower energy.*

Such a postulate is found to hold for all the systems examined in the present study. This may be confirmed by defining a structural parameter, α_G, which compares the structural similarity of the complex to the reactants and products, and relating α_G to $\Delta E°$, the energy difference between reactants and products (i.e., the energy change for reaction 2). It is convenient for the purpose of this discussion to define $XFH^+ + FX'$ as the reactants and XF + HFX'^+ as the products although either pair, of course, gives rise to the same complex $XFHFX'^+$. α_G is given by[21]

$$\alpha_G = (\Delta r_2/r_2)/[(\Delta r_1/r_1) + (\Delta r_2/r_2)] \qquad (3)$$

where r_1 and r_2 are the F–H bond lengths in XFH^+ ("reactant") and HFX'^+ ("product"), respectively, and Δr_1 and Δr_2 are the respective differences between r_1 and r_2 and the corresponding bond lengths in the complex $XFHFX'^+$. Thus α_G may take values within the range 0–1.0: a value close to 1.0 indicates high resemblance to the reactants, a value of 0.5 indicates a structure which resembles reactants and products equally, while a value close to 0 indicates a high resemblance to products.

Examination of the α_G values for the complexes studied (Table III) shows that there is, in fact, a clear correlation between complex structure and stability. Thus, the complex is always more closely related structurally to the more stable of its two possible ion–molecule component pairs (reflected in α_G values ≥0.5), in agreement with the postulate proposed by Bouma and Radom.[14] For example, the α_G value of 1.00 for $LiFHFF^+$ indicates that the species resembles a loose complex between $LiFH^+$ and FF rather than a complex between LiF and HFF^+. Thus, the bond lengths in the species are very close to corresponding values in the isolated components $LiFH^+$ and FF. In addition, the LiF-H···FF distance is a substantial 1.999 Å, reflecting the weak interaction between the two species. This is confirmed by the low heat of complex formation, 7 kJ mol^{-1} for $LiFHFF^+$ when formed from $LiFH^+$ + FF compared to the enormous 675 kJ mol^{-1} released when the same complex is generated from the LiF and

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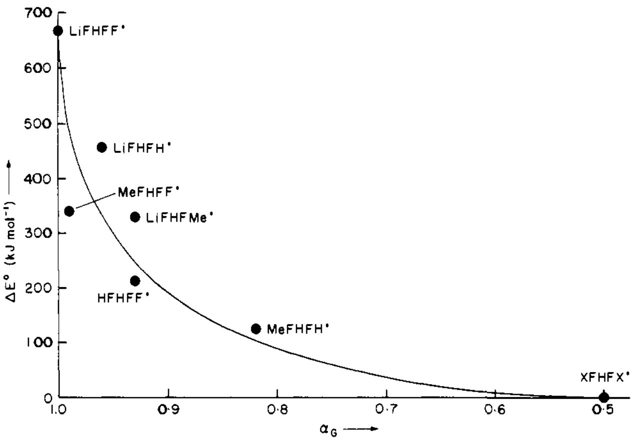

Figure 3. Structure–stability relationship for complexes. α_G is the structural parameter defined by eq 3; $\Delta E°$ is the endothermicity of reaction 2.

HFF^+ pair. Symmetrically substituted complexes ($\Delta E° = 0$) of course have α_G values of 0.5.

A plot of α_G vs. $\Delta E°$ (Figure 3) suggests that the extent to which the complex resembles reactants (where we have considered the reaction in each case in the endothermic direction) does appear to be related in a general way to the energy difference between reactants and products. Thus, as the overall reaction (reactants → products) becomes more endothermic, the resemblance of the complex to the reactants tends to increase also. However, the relationship is not a smooth one. For example, both $HFHFF^+$ and $LiFHFMe^+$ possess identical α_G values (0.93) while exhibiting quite different $\Delta E°$ values (212 and 330 kJ mol^{-1}, respectively), and there is even one case where a complex with a smaller $\Delta E°$ value ($MeFHFF^+$; $\Delta E° = 339$ kJ mol^{-1}) has a more reactant-like structure ($\alpha_G = 0.99$) than has a complex with a larger $\Delta E°$ value ($LiFHFH^+$; $\Delta E° = 457$ kJ mol^{-1}; $\alpha_G = 0.96$).

We conclude therefore on the basis of these calculations that one cannot extend the structural postulate for complexes to a more explicit differential form. In other words, if a substituent has a stabilizing effect on the reactants leading to complex formation, it does not always follow that the complex will be more reactant-like.

We now relate our results to two models which may be utilized to rationalize and predict the effect of substituents on the structure of the complex.

Analysis Using a Valence-Bond Formalism. In a recent paper, Shaik[22] has defined S_N2 transition states in terms of linear combinations of reactant configurations, and this approach has subsequently been utilized by Pross and Shaik[11] to analyze the effect of substituents on transition-state structure.

Here we apply similar reasoning to the problem of relating the structure of a complex to the nature of the reactants, viewing the wave function which describes the complex as a linear combination of reactant wave functions. A suitable basis set may be built up from three basic reactant configurations. These are $XF{-}H^+ :FX'$, $XF: H{-}FX'^+$, and $XF: H^+ :FX'$. Hence the wave function describing the complex may be written as

$$(XFHFX'^+) = c_1(XF{-}H^+ :FX') + c_2(XF: H{-}FX'^+) + c_3(XF: H^+ :FX') \quad (4)$$

or in more simple valence bond (VB) language

$$XFHFX'^+ \equiv (XF{-}H^+ :FX') \leftrightarrow (XF: H{-}FX'^+) \leftrightarrow (XF: H^+ :FX') \quad (5)$$

The effect of substituent changes on the structure and stability of the complex will be governed by the effect of the substituents on each reactant configuration. Stabilization of a given configuration will result in that configuration mixing into the wave function of the complex to a greater extent. As a result, the complex will resemble that configuration more closely, both structurally and energetically.

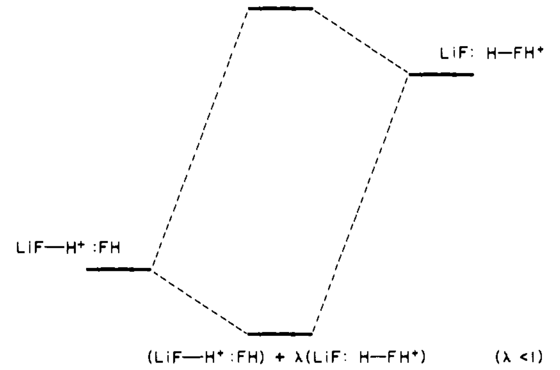

Figure 4. Interaction of configurations $LiF{-}H^+ :FH$ and $LiF: H{-}FH^+$.

Let us treat, for example, the complex $MeFHFH^+$. The Me substituent has a greater stabilizing effect in the $MeFH^+ + FH$ ion–molecule pair than in $MeF + HFH^+$ (as indicated by the $\Delta E°$ value in Table III), a result which is compatible with the observation that substituent effects in charged species are significantly greater than in neutral ones.[23] As a result, the contribution of the VB form $MeF{-}H^+ :FH$ to the structure of the complex will increase at the expense of $MeF: H{-}FH^+$ and $MeF: H^+ :FH$. The complex should therefore resemble more closely the VB form $MeF{-}H^+ :FH$ in both structure and energy, as is found. Thus this simple VB model provides a theoretical basis for the postulate governing the structure of complexes. The complex will invariably resemble the more stable ion–molecule pair, since the VB form represented by that ion–molecule pair will make a larger contribution to the wave function describing the complex.

Why is the relationship between $\Delta E°$ and α_G an approximate one? Since the structural postulate for complexes is substantiated by the VB analysis, it might seem surprising at first glance that its differential analogue does not appear to be invariably true. Let us analyze this point.

For the case in which two configurations of widely differing stability interact (e.g., the stable configuration $LiF{-}H^+ :FH$ with the less stable one $LiF: H{-}FH^+$), one can use a simple perturbation formalism[24] to analyze the resultant wave function. Thus, using the example of $LiFHFH^+$,

$$(LiFHFH^+) = (LiF{-}H^+ :FH) + \lambda(LiF: H{-}FH^+) \quad (6)$$

where $\lambda \ll 1$. The coefficient λ represents the extent to which the less stable configuration mixes into the more stable one. This is depicted schematically in Figure 4 and is directly analogous to an orbital interaction diagram. Thus, the magnitude of the mixing coefficient, λ, is, according to perturbation theory, given by

$$\lambda = H/\Delta E \quad (7)$$

where H is the resonance integral (which is closely related to overlap) and ΔE is the energy difference between the two configurations.

From eq 7, it is apparent that while the extent of mixing of the less stable configuration into the overall wave function of the complex is indeed inversely proportional to the energy separation, this is not the only factor. The degree of overlap, reflected in the H parameter, influences the extent of mixing as well. Thus, at the outset, one should not anticipate a smooth correlation between α_G and $\Delta E°$ because of the additional (and less predictable) involvement of H. Significantly, the relationship between $\Delta E°$ and α_G appears more satisfactory when only one substituent in the complex $XFHFX'^+$ is varied. Thus, within a limited family of complexes $XFHFX'^+$ where only X is varied, the $\Delta E°$ vs. α_G relationship holds quite well (cf. Figure 3). It is only for cases in which both substituents, X and X′, are varied that the $\Delta E°$

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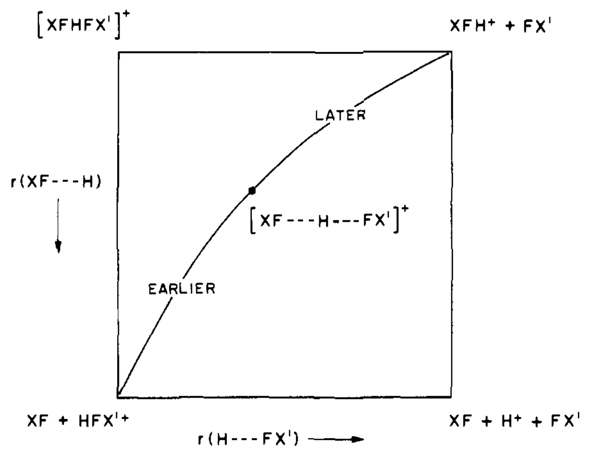

Figure 5. Schematic representation of potential-energy surface related to reaction 2.

vs. α_G relationship becomes less satisfactory.

Symmetrical Complexes. It is of interest to observe the tightness of the symmetrically substituted complexes $XFHFX^+$ as a function of the substituent. One might have anticipated large variations in the H···F bond length in $XFHFX^+$ for different substituents X. In fact, there is a very small variation in the theoretical H···F lengths, which lie within the range 1.13–1.18 Å for the four symmetrical complexes.

This behavior may also be understood within the framework of the configuration VB model. Clearly the two configurations ($XF–H^+$:FX) and (XF: $H–FX^+$) contribute equally to the wave function of the complex, for all substituents X, due to symmetry considerations. Thus, the tightness–looseness of symmetrical complexes will be governed by the third configuration (XF: H^+ :FX). The more this configuration mixes into the complex wave function, the looser the complex will become. So the question that arises is to what extent this configuration mixes into the complex wave function and how this mixing will be modified by substituents.

The first point which should be made is that the energy of this configuration is substantially higher than that of the other two configurations (by the proton affinity of XF, which is ca. 450 kJ mol^{-1}). On this basis alone a small contribution is anticipated. This point, however, gains additional support when we consider the changes brought about by substituents on the degree of mixing. We have already noted that substituent effects in the neutral molecule XF are substantially smaller than in the ion XFH^+. As a result, the effect of substituents on the configuration (XF: H^+ :XF) will also be small. Clearly slight variations in a quantity which is, a priori, small in itself are not expected to bring about significant changes in the structure of the complex. Thus, the nearly constant tightness predicted by the quantitative calculations for the symmetrical complexes is readily rationalized in terms of the VB model.

Analysis Using Potential-Energy Surface Model. We now wish to analyze the results in terms of the so-called potential-energy surface model and compare the predictions with those of the VB model. While potential-energy surfaces have been utilized in different ways in various theoretical models,[6–9] we will utilize here the method of More O'Ferrall.[7] This approach is characterized by its simplicity and ready application to a variety of questions relating to the effect of substituents on both molecular structure and reaction pathways. Numerous applications of such surfaces to problems of reactivity have recently appeared.[25]

A potential-energy surface for the complex formation and proton-transfer reaction 2 is illustrated in Figure 5. Bottom left-hand and top right-hand corners indicate reactants and products, respectively. The complex lies at a minimum along the reaction profile.

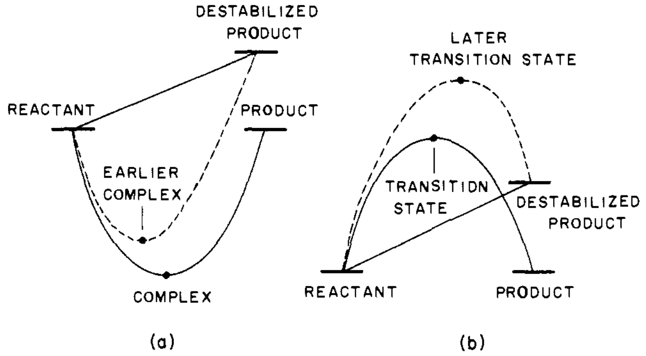

Figure 6.

Let us first assess the effect of a substituent X on the location of the reaction complex in the set of reactions labeled 8. When

$$XF + HFH^+ \rightarrow [XFHFH]^+ \rightarrow XFH^+ + FH \quad (8)$$

X = H, this represents a degenerate proton-transfer reaction. If the substituent X = H is replaced by X = F, this corresponds to a *destabilization* of the top right-hand corner since the electron-withdrawing F substituent has a destabilizing effect on XFH^+. Reaction 8 is then endothermic. The prediction of the potential-energy surface model is that the position of the complex, located at a minimum on the reaction pathway, will be shifted by this substituent from midway along this pathway to a position *earlier* on the reaction profile. A mechanism for predicting the direction of change has been presented by Thornton[6] using a simple geometric model (cf. Figure 6a). The minimum is represented by a parabola and the perturbation by a straight line representing an endothermic reaction. Summing the two leads to a new parabola, whose minimum lies at higher energy, and whose position has been shifted toward the *reactant* side. This contrasts with the direction of the structural change observed for the same perturbation on a transition state, which is of course located at a maximum on the reaction profile (Figure 6b). In this case the position of the maximum is shifted toward the *product* side of the reaction. For this reason the effect of a perturbation on the position of a minimum is often termed an "anti-Hammond" effect,[25] reflecting the contrast between the behavior pattern of minima compared to the more widely recognized behavior of maxima and which is associated with the Hammond postulate.[5]

The effect of substituents on the position of a transition state and a stable complex differ in other respects as well. In addition to representing a maximum along the reaction coordinate, the transition state is located at a minimum perpendicular to the reaction coordinate. A complex, however, constitutes a minimum both parallel *and* perpendicular to the reaction coordinate. Thus a transition state is expected to exhibit "Hammond behavior" parallel to the reaction coordinate and anti-Hammond behavior perpendicular to the reaction profile. A complex on the other hand is expected to exhibit anti-Hammond behavior both parallel *and* perpendicular to the reaction profile. Thus stabilization of any one corner of the potential-energy surface will tend to draw the structure of the complex toward that corner.

Referring back to our quantitative results, we conclude that the predictions of the potential-energy surface model are indeed borne out, but only in a general way. The complexes studied do resemble in structure the more stable of the two possible reactant pairs. However, as discussed earlier, the differential extension of this rule, i.e., that an additional stabilization of a reactant pair will tend to make the particular complex structurally more similar to that particular reactant pair, is *not* found to be invariably true. In this respect, therefore, the quantum mechanical model appears to be superior to the potential-energy surface model. The potential-energy surface model does not appear to be capable of rationalizing the failure of the differential extension of the postulate

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governing complexes, whereas the VB approach does contain within it additional features which allow deviations from a smooth relationship.

What comments may we make on the question of transition-state structure on the basis of our results and analysis? Arguing by analogy with our results for reaction complexes, it would appear that the Hammond postulate, which strictly speaking only refers to transition-state structure in highly exothermic or endothermic reactions, is substantiated. On the other hand, the differential extension of the Hammond postulate, sometimes termed the Leffler-Hammond postulate[25c] (but often erroneously also termed the Hammond postulate), may not be universally valid. Stabilization of reactants in a given reaction may not necessarily mean that the transition state will be more product-like.

Conclusions

The results presented in this paper provide further support for a structural postulate for complexes[14] analogous to the Hammond postulate[5] for transition states, namely, when two sets of reactants [(AB + C) or (A + BC)] interact to form a common stable complex (A-B-C), the complex will generally resemble the set of reactants of lower energy. The differential analogue of this postulate is not invariably true, i.e., stabilization of one set of reactants does not necessarily result in increasing resemblance of the complex structure to these reactants. Both of these results are readily rationalized in terms of a configuration valence bond model.

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Why UO_2^{2+} Is Linear and Isoelectronic ThO_2 Is Bent

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Abstract: The isoelectronic species UO_2^{2+} and ThO_2 possess very different geometries, namely, UO_2^{2+} is linear while ThO_2 is strongly bent ($\theta_{\mathrm{exptl}} = 122 \pm 2°$). Relativistic effective core potential (RECP) calculations using Hartree–Fock wave functions and double-zeta-plus-polarization quality basis sets were performed to determine the origin of this difference. The RECP calculations correctly predict the linear and bent geometries of UO_2^{2+} and ThO_2 ($\theta_{\mathrm{calcd}} = 118°$). The Th–O bond length, which is not known experimentally, is calculated to be 1.91 Å. Analysis of the results shows that the difference in geometries for UO_2^{2+} and ThO_2 has its origin in the relative ordering of the 5f and 6d levels. For uranium the 5f levels are lower and dominate the back-bonding from the oxygen in UO_2^{2+}, while for thorium the 6d levels are lower and dominate the back-bonding in ThO_2. Finally, the 5f levels prefer linear geometries, while the 6d prefer bent geometries, hence, the difference between UO_2^{2+} and ThO_2. The relative ordering of the 5f and 6d levels has a profound effect.

The uranyl cation (UO_2^{2+}) is very familiar and well-studied moiety in actinide chemistry. It always appears in a trans, i.e., linear, configuration in uranyl complexes. Given the linearity of UO_2^{2+} it is surprising that matrix isolation studies[1] indicate that the isoelectronic species ThO_2 possesses a bent geometry ($\theta = 122 \pm 2°$). It is natural to ask whether the significant difference in geometry indicates a significant difference in the bonding of UO_2^{2+} and ThO_2. To shed light on this question we have performed calculations on UO_2^{2+} and ThO_2 using ab initio Hartree–Fock wave functions based on relativistic effective potentials.[2] Finally, the results on UO_2^{2+} will be useful for comparison to the extended Hückel calculations of Tatsumi and Hoffmann.[3] The latter indicate that the nonvalence 6p orbitals of uranium play a key role in determining the linear geometry of UO_2^{2+}.

Calculational Details

The relativistic effective core potential (RECP) method has been discussed in detail elsewhere.[2] Briefly, the core electrons are replaced with a one-electron effective potential based on numerical relativistic Hartree–Fock atomic wave functions,[4] which include effects arising from the Darwin and mass–velocity terms. For uranium we employed the RECP previously used in calculations on UF_6[5] and UF_5.[6] It is based on U^{3+} atomic wave functions and replaces all but the outer 11 electrons, i.e., $6s^26p^65f^3$. For thorium we determined an RECP based on Th^0 atomic wave functions, which replaced all but the outer 10 electrons, i.e., $6p^66d^27s^2$. The f and g components of the RECP were determined from the $6p^65f^16d^17s^2$ and $5g^1$ configurations, respectively, by using core orbitals frozen from the $6p^66d^27s^2$ configuration. The parameters for the Gaussian fit to the RECP are given in Table I. The only deviation from past derivations of RECP's is that the procedure proposed by Christiansen et al.[7] and modified by Hay[8]

Table I. Representation of the Relativistic Th^0 Effective Core Potential in Terms of Gaussian Functions of the Form $d_k r^{n_k} e^{-\zeta_k r^2}$ ($N_c = 80$, the Number of Core Electrons)

n_k	ζ_k	d_k	n_k	ζ_k	d_k
	$(U_g - N_c/r)r^2$			$(U_s - U_g)g^2$	
0	39.7460	−0.215583	0	102.2215	2.631316
1	120.8967	−24.125688	1	32.1822	36.168565
1	17.1550	−37.429045	1	7.6879	40.379434
2	6.5275	−46.429080	2	2.6445	40.337168
2	2.3245	−14.403078	2	0.4673	11.401892
2	0.7593	−1.156695			
	$(U_d - U_g)r^2$			$(U_d - U_g)r^2$	
0	133.8067	4.697283	0	300.1223	2.912226
1	72.6419	69.214991	1	132.6264	73.921541
2	33.2173	401.032676	2	66.9945	464.679400
2	9.2374	158.353053	2	22.0007	264.072748
2	1.2414	93.227065	2	5.9121	84.016104
2	1.0867	−61.096221	2	1.1499	18.143108
	$(U_f - U_g)r^2$				
0	92.3245	3.937853			
1	28.3994	62.024430			
2	9.9343	132.317163			
2	2.0660	13.093309			
2	1.6609	−7.882653			

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