Table IX. Charge[a] over the Formaldehyde Fragment in Formaldehyde–$TiCl_4$ Complexes

complex	structure	q
H_2CO–$TiCl_4$	A1	0.170
$(H_2CO)_2$–$TiCl_4$[b]	C	0.182
	T2	0.213
$(H_2CO$–$TiCl_4)_2$[b]		0.212

[a] q, in atomic units, computed from the Mulliken population analysis of the 3-21G structures. [b] The charge has the same value in both formaldehyde ligands.

H_2CO–$TiCl_4$ and H_2CO seems to involve an important energy barrier due to the geometry distortion of the H_2CO–$TiCl_4$ moiety.

The trans isomer could also be formed from the cis isomer through a cis–trans interconversion process. Recently, Hansen and Marynick have suggested that cis–trans isomerization in octahedral ML_6 complexes takes place through a trigonal prism transition state.[40] The investigation of the isomerization in the $(H_2CO)_2$–$TiCl_4$ complex involves a huge computational effort. However, significative information can be obtained if the model complex $TiCl_6^{2-}$ is studied. For this system, a D_{3h} trigonal prism transition state has been located with the 3-21G basis set, the energy barrier being 32.3 kcal/mol. For $(H_2CO)_2$–$TiCl_4$, this barrier is expected to be greater, given the steric repulsion between both H_2CO ligands in the transition state. So, any cis–trans interconversion should take place through a dissociative mechanism, involving H_2CO–$TiCl_4$ as an intermediate.

Our pilot calculations have shown that the formation of the $(H_2CO$–$TiCl_4)_2$ complex from H_2CO–$TiCl_4$ (step 3 in Scheme I) can be a competitive process with the formation of $(H_2CO)_2$–$TiCl_4$ (step 2 in Scheme I). The experimental structures suggest that this dimerization is the most favorable process in the case of monodentate carbonyl compounds, while the formation of chelates (similar to cis 2:1 complexes) is favored for bidentate carbonylic compounds.

The interaction scheme discussed above shows that the interaction of formaldehyde with $TiCl_4$ increases in the order H_2CO–$TiCl_4 < (H_2CO)_2$–$TiCl_4 < (H_2CO$–$TiCl_4)_2$. In the cases in which geometry optimization has been carried out, this ordering can be related to the values of the Ti–O bond lengths and to the degree of distortion of the H_2CO molecules in the complexes (see Tables V and VIII). The same trends can be observed from the values of the charge over the H_2CO fragment in the complexes presented in Table IX. These results show that $TiCl_4$ is a stronger Lewis acid when it forms dimeric complexes with carbonyl compounds.

Concluding Remarks

The results obtained in this work show that formaldehyde forms 1:1 and 2:1 complexes with $TiCl_4$. In the first case, the complex has a trigonal bipyramidal structure with the H_2CO molecule in an axial position. The formation of 2:1 complexes is predicted to be energetically favorable. In this case, two different cis–trans isomers can be considered. However, the formation of the trans isomer seems to involve a greater energy barrier. The formation of a $(H_2CO$–$TiCl_4)_2$ complex through dimerization of H_2CO–$TiCl_4$ has also been discussed, and it has been shown that in such a complex the interaction between $TiCl_4$ and formaldehyde is stronger. These results agree with the experimental results, according to which monodentate carbonyl compounds form complexes with dimeric $TiCl_4$, while chelating esters or ketones can form octahedral 1:1 complexes in which two carbonyl groups are cis coordinated to the Ti atom of $TiCl_4$.

Acknowledgment. Parts of the calculations presented in this paper have been carried out in the CRAY XMP/14se supercomputer of Construcciones Aeronâuticas S.A. with a grant of computer time from the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT).

Registry No. H_2CO-$TiCl_4$ (A1), 140411-13-8; $(H_2CO)_2$-$TiCl_4$ (C), 140411-14-9; $(H_2CO)_2$-$TiCl_4$ (T1), 140629-70-5; $(H_2CO$-$TiCl_4)_2$, 140411-15-0; H_2CO, 50-00-0; $TiCl_4$, 7550-45-0.

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Charge Oscillation in the Homolysis of MeX Derivatives

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Abstract: Ab initio electronic structure methods are used to show that, in the (barrierless) homolytic dissociation of the CH_3X system (X = an atom or group more electronegative than CH_3) going from equilibrium geometry to products ($CH_3^\bullet + X^\bullet$), the charge on CH_3 first increases and then decreases to zero. This result, which can be rationalized on the basis of simple models, violates the common assumption that the character of intermediates along a reaction path is bound by the properties of reactants and products. The implications of this new conclusion to kinetic/thermodynamic data relationships in chemical reactions are discussed.

A basic assumption in the field of reaction mechanisms is that the electronic structure description of the system anywhere along the reaction coordinate varies monotonically from reactants to products and is bound by their property values. Therefore, the transition state (TS), regardless of its location (early or late), has a structure intermediate between that of reactants and products. This assumption also provides the foundation for the mechanistic significance of linear free energy relationships (LFER).[1]

In this work, changes in ionicity which occur during the homolysis of MeX (Me = CH_3, X = an atom or a group which is more electronegative than Me) from equilibrium geometry to radical fragments were investigated. Since MeX in its ground-state (GS) equilibrium geometry is polarized $Me^{\delta+} + X^{\delta-}$, it is expected on the basis of the above binding assumption that, upon dissociation, the charge on X (= −charge on the Me group) will be gradually reduced from $\delta-$ to zero as the system approaches the neutral dissociation products $Me^\bullet + X^\bullet$.

The dissociation energy curve of MeX as a function of the C–X distance for a series of nine methyl derivatives was calculated using the ab initio multiconfiguration self-consistent field (MCSCF)

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[1] Leffler, J. E.; Grunwald, E. *Rates and Equilibrium of Organic Reactions*; Wiley: New York, 1963; p 157.

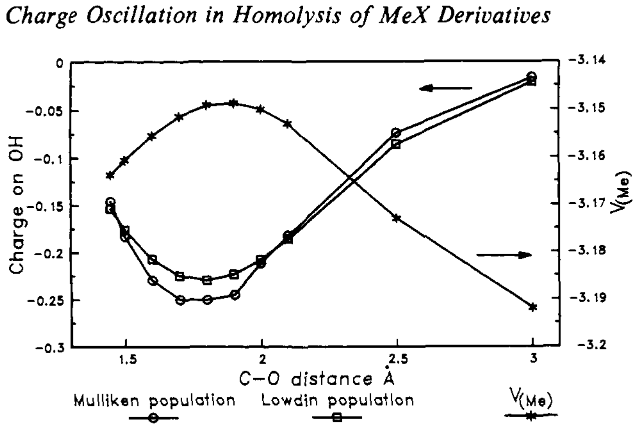

Figure 1. Charge variations as a function of the C–O distance in the homolytic dissociation of MeOH.

Table I. Calculated Parameters for MeX Derivatives

X	BDE[a]	r_e[b]	r_{max}/r_e Mulliken	Lowdin	$V_{(Me)}$
CN	120.30	1.51	1.56	1.65	1.65
CCH	115.40	1.51	1.45	1.52	1.58
C_2H_3	90.70	1.56	1.40	1.35	1.48
F	89.80	1.41	1.25	1.28	1.34
OH	76.20	1.45	1.22	1.24	1.29
NH_2	72.80	1.50	1.21	1.20	1.35
NO_2	65.67	1.52	1.24	1.32	1.24
N_3	65.52	1.51	1.25	1.32	1.30
NO	34.60	1.52	1.13	1.00	1.02

[a] In kilocalories/mole; not corrected for zero-point energy differences in the MeX → Me• + X• process. [b] In angstroms.

method.[2,3] The homolytic C–X bond dissociation products were obtained by correlating the $\sigma_{C-X}(\sigma)$ bond only by including the three possible configurations, σ^2, $\sigma^1(\sigma^*)$, and $(\sigma^*)^2$ in the MCSCF calculations. After the MeX equilibrium geometry had been gradient optimized for a given X, calculations were carried out for a series of fixed C–X distances where, at each value of r_{C-X}, all the other geometric parameters were gradient optimized. The basis set used was of valence double zeta + d polarization function quality, and a compact effective potential (CEP) was used for the core electrons.[4] This CEP-31G* is analogous to the Pople group's standard 6-31G* basis set.[5] In all cases, the dissociation curve showed monotonically increasing energy as R_{C-X} was stepped toward larger r_{C-X} from equilibrium.

The ionicity was gauged by three different methods: atomic charges using the Mulliken and Lowdin population analyses and the total electrostatic potential ($V_{(Me)}$) at the nucleus of the carbon atom of the Me group. $V_{(Me)}$ is a sensitive function of the valence electron charge density in the immediate vicinity of the atom and is therefore a good measure of the net charge on that atom.[6] In all of the cases studied, it is found that, upon going from reactants (MeX at equilibrium geometry) to products (Me• + X•), the ionicity first increases and then decreases to zero. A typical plot of the variation of the ionicity as a function of the C–X distance using MeOH as an example is given in Figure 1.

In Table I, the C–X distance of maximum ionicity (r_{max}) for each of the three methods, normalized for comparative purposes by dividing it by the calculated r_e (the C–X distance at the equilibrium geometry), is given for each derivative. Examination of the data in this table reveals an interesting correlation between r_{max}/r_e and the calculated bond dissociation energy (BDE). In Figure 2, r_{max}/r_e for $V_{(Me)}$ is plotted against BDE. The two other methods of gauging ionicity give similar plots. Thus for example, for $V_{(Me)}$, a reasonably linear correlation ($r = 0.972$) exists between r_{max}/r_e and the BDE. However, it is not our intention to claim that the correlation has to be linear.

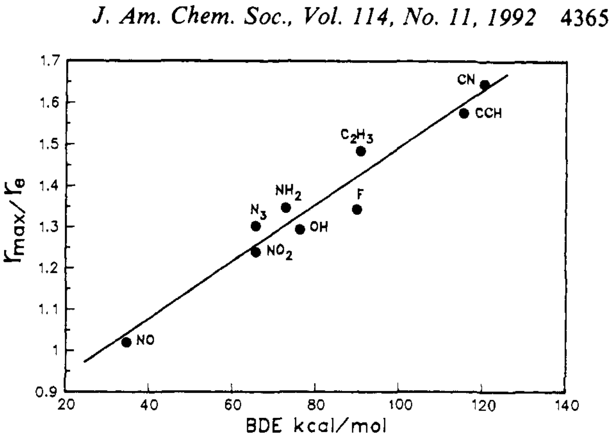

Figure 2. Plot of r_{max}/r_e vs the calculated bond dissociation energy for all of the CH_3X.

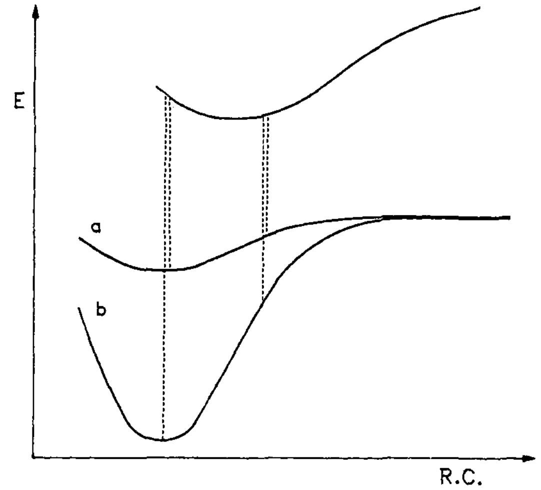

Figure 3. Schematic representation of the energy gap (Δ) variation as a function of r for CH_3X systems having (a) small or (b) large values of their BDE.

The general charge oscillation phenomenon as well as the above correlation between r_{max}/r_e and BDE can be qualitatively explained using a valence bond (VB) model. The Me–X bond description in the electronic GS can be considered as resulting from the variational mixing of two VB configurations: the lower energy purely covalent Me•X• and the higher energy purely ionic Me^+X^-.[7] The polarity of MeX at a given r_{C-X} results from the degree of mixing of the higher energy ionic configuration into the nonpolar covalent configuration at that r_{C-X}. However, there is no reason to assume that the maximal extent of this mixing (maximum ionicity) occurs at the minimum energy point on the GS dissociation curve (r_e).

Explicitly, the electronic GS in such a model[8a] is described as the lower energy result of mixing two VB configurations: $\psi(GS) = c_1\psi_1 + c_2\psi_2$ at each r_{C-X}, where $\psi_1 = (Me^\bullet)(X^\bullet)$ and $\psi_2 = (Me^+)(X^-)$. Using the resulting 2 × 2 secular equation to analytically construct $T = c_2/c_1$ shows that T can have an extremum

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(7) For the electronegative groups described here, the Me^-X^+ configuration is at even higher energy and therefore is expected to contribute to the GS wave function to only a small extent.

(8) (a) See, for example: Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: New York, 1960. Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 1129. (b) $r_{min}(\psi_2) > r_e$ for MeX systems where X is fluorine or chlorine can also be deduced from the ionic radii of F^- (1.33 Å) and Cl^- (1.81 Å) being larger than the equilibrium bond lengths of 1.34 (C–F) and 1.78 Å (C–Cl) (*CRC Handbook of Chemistry and Physics*, 69th Ed.; CRC Press: Boca Raton, FL, 1988).

value at $r_{max} > r_e$ if $r_{min}(\psi_2) > r_e$, where $r_{min}(\psi_2)$ is the energy minimum C–X distance of the ionic configuration ψ_2. Since we show by ab initio calculations that $r_{max} > r_e$ for a number of MeX systems, it can be concluded that $r_{min}(\psi_2)$ is greater than r_e for those systems.[8a] This situation arises from a subtle interplay between the energy gap (Δ) between ψ_1 and ψ_2, and the exchange matrix element (U_{12}) which couples ψ_1 and ψ_2, in separately determining r_e and r_{max}.

The r_{max}/r_e vs BDE correlation can also be explained by the VB model. To a crude approximation it can be assumed that (on a normalized r_{C-X}/r_e scale), for a given rightward displacement (to larger r_{C-X}) from the equilibrium geometry, the U_{12} term for configuration mixing, which is similar to the Me–X overlap term, will be nearly the same regardless of the identity of X. Therefore, the contribution of U_{12} to the configuration mixing and the resulting ionicity will be roughly independent of X at a given r_{C-X}/r_e. On the other hand, because the energy gap (Δ) in the bonding region roughly parallels the BDE value as a function of X, it will tend to induce relatively more configuration mixing for a MeX system with a greater BDE at larger r_{C-X}/r_e values where Δ is smaller. In contrast, for a MeX system with a weaker bond (smaller BDE), the energy gap will vary less steeply with r_{C-X}/r_e (see Figure 3). Consequently, the maximum ionicity for large BDE methyl derivatives will be shifted more to the right, thus approximately giving the dependence of r_{max}/r_e on the BDE shown in Figure 2.

To the best of our knowledge, this is the first rigorous study which demonstrates that the electronic structure on the reaction path leading from reactants to products may not have features intermediate between the species at the two ends of the reaction profile. This also seems to be the first observation of the ionicity oscillation phenomenon for a reaction of such general nature as the homolysis of C–X bonds. The implications of these results to the interpretation of LFER are rather straightforward. Let us assume that a hypothetical reaction of this nature has a TS which can be probed by substituents on the methyl group.[9] If these substituents are designed to measure atom or group charges (via rho values or any equivalent reaction parameter), the traditional expectation would be that, since in the course of the reaction the methyl group monotonically loses its positive charge, the measured rho value will be larger as the TS comes later, reflecting the larger charge loss from the Me group. However, using the example in Figure 2 for MeOH and assuming that in this hypothetical reaction a TS is located around $r = 2.3$ Å, the measured rho value will be small because the polarity at this r_{C-O} value is about the same as that of the reactant at its equilibrium geometry. The inferred conclusion would then be that the TS resembles the reactants, i.e., is achieved early. In the absence of other evidence to the contrary, this erroneous conclusion would be widely accepted, since the experimental results do not contradict the assumption that the TS is of intermediate nature between (i.e., bound by) the reactants and products. The error in this assumption will be recognized only if the TS has an ionicity *larger* than that of the GS (e.g., around $r = 1.8$ Å in Figure 1). In this case, the unusual behavior of the system will be recognized as such due to the "wrong" sign of the measured rho value. It should be noted that when the reaction is viewed from the reverse direction the rho value will always have the "right" sign. However, as in the specific example of Figure 1 at $r = 1.8$ Å, its absolute value will exceed the equilibrium value somewhere along the association reaction path. This latter phenomenon has recently been discussed[10] in terms of a three VB configuration model.

The observation that along the reaction path for such an elementary reaction as a single-step homolytic dissociation the property value boundaries set by reactants and products can be exceeded suggests that the observed phenomenon is of a general nature. The traditional interpretation of rho values in terms of an early or late location of the TS should therefore be checked by independent experimental evidence for consistency.

Registry No. CH_3CN, 75-05-8; $CH_3C{\equiv}CH$, 74-99-7; $CH_3CH{=}CH_2$, 115-07-1; CH_3F, 593-53-3; CH_3OH, 67-56-1; CH_3NH_2, 74-89-5; CH_3NO_2, 75-52-5; CH_3N_3, 624-90-8; CH_3NO, 865-40-7.

Supplementary Material Available: Figure showing variations of energy and dipole moment as a function of r_{C-O} and a table of the related data for the dissociation of MeOH (2 pages). Ordering information is given on any current masthead page.

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(9) An actual TS can be found in homolytic dissociations of this type in cases where the odd electron in the bonding σ orbital on X relaxes during the dissociation process to a lower energy orbital (i.e., $CH_3{:}NC \rightarrow CH_3^{\bullet} + NC^{\bullet}$).

(10) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1129.

Stacked or T-Shaped Benzene Dimer in Aqueous Solution? A Molecular Dynamics Study

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Abstract: An aqueous solution of a benzene dimer has been investigated by means of molecular dynamics simulations. The potential of mean force as a function of the benzene separation for stacked and T-shaped configurations has been calculated. The close-contact T-shaped dimer was found to possess the lowest free energy. The more favorable benzene–benzene and benzene–water interaction present for the T-shaped geometry exceeds the increase in the hydrophobic surface free energy as compared to the close-contact stacked dimer. Moreover, a well-defined solvent-separated stacked minimum with a similar potential of mean force as the close-contact stacked minimum was obtained. The hydration of the benzene dimer is very similar to that of a single benzene molecule. The main exception occurs for the solvent-separated stacked dimer where water molecules located between the benzene dimer display a weaker preferential orientation with respect to the benzene molecules and a moderately enhanced water structure.

Introduction

There is experimental evidence that a small fraction of the benzene molecules dissolved in water occurs as dimers,[1] but information on the dimer structure is lacking. However, there are experimental data indicating that the planes of benzene in the dimer are not parallel in the gas phase,[2-4] and similar perpendicular

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(1) Tucker, E. E.; Lane, E. H.; Christian, S. D. *J. Solution Chem.* **1981**, *10*, 1.

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