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Quantifying the Hammond Postulate: Intramolecular Proton Transfer in Substituted Hydrogen Catecholate Anions

Jerzy Cioslowski

Contribution from the Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006. *Received January 28, 1991*

Abstract: A rigorous formulation of the Hammond postulate is presented. The concepts of the reaction exothermicity (γ) and the structural proximity between the transition state and the reactants (β) are quantified. Another quantity, called the isosynchronicity parameter (α), is introduced. The structural proximity and the isosynchronicity parameter are defined by using structural distances calculated with the help of the recently introduced NOEL similarity indices. The new indices α, β, and γ, which can serve as theoretical tools for systematizing mechanisms of chemical reactions, are calculated at the HF/6-31++G** level for a series of 10 intramolecular proton transfers between both unsubstituted and (poly)fluorosubstituted hydrogen catecholate anions. A positive correlation, as implied by the Hammond postulate, is found between the calculated values of β and γ.

Introduction

In their efforts to understand and systematize the mechanisms of chemical reactions, chemists often resort to various correlations involving structures and energies of reactants, products, and transition states. The Hammett[1] and Brønsted[2] relationships serve as examples of correlations in which well-defined quantities such as free energies and dissociation constants are used. In contrast, the widely used correlations based on the intuitively appealing Hammond postulate[3] are of a qualitative nature. This partially stems from the vaguely defined concepts of the early and late transition states. The corollary due to Melander[4] which states that, for a given type of reaction, increased exothermicities imply earlier transition states is usually invoked (and often incorrectly called the Hammond postulate) in the chemical literature instead of the original postulate.[3] It is obvious that, in order to derive a more quantitative formulation of the Hammond postulate, one must first define rigorously the concepts of exothermicity and the progress along the reaction coordinate determining whether the transition state in question is of the early or the late character.

First, we quantify the concept of exothermicity. Let E_A, E_B, and E_{TS} stand for the energies of reactants (A), products (B), and the relevant transition state (TS), respectively. Let

$$\gamma = (E_B - E_A)/(2E_{TS} - E_A - E_B) \qquad (1)$$

The so-defined exothermicity γ, which assumes values between -1 and $+1$, is given as the ratio of the difference and the sum of the activation energies, $E_{TS} - E_A$ and $E_{TS} - E_B$, for the forward and reverse reactions, respectively. Exothermic reactions are characterized by negative values of γ, while the endothermic reactions have positive γs.

The progress along the reaction path can in principle be measured in many different ways. There are several reasons for which the intuitively obvious choice of the reaction path arc length between reactants and the structure in question cannot be used for this purpose. Besides the rather high computational cost of calculations involving reaction path following,[5] such measure is not invariant to the isotope substitution of nuclei and, even more importantly, to the choice of internal coordinates. The commonly used approach[6-11] that involves monitoring the bond orders that are most affected by the reaction also has several disadvantages. First, it requires identification of the "most important" bonds, which is always an arbitrary exercise. The semiempirical formalisms that are used in the description of chemical reactions, such as the BEBO method,[12] tacitly assume that the structural changes accompanying chemical reactions are limited to a few (usually two) bonds. This assumption may be reasonable for simple atom-transfer processes, but it is certainly invalid for many rearrangement reactions. Moreover, the various definitions of bond orders available in the chemical literature suffer from an explicit dependence on the basis functions used in molecular structure calculations. Only very recently a new definition that is free from these limitations has been proposed.[13]

Taking the above observations into account, the need for a new rigorous measure of the progress along the reaction path is obvious. For this reason, we introduce the concept of structural proximity. Let $d(X, Y)$ be a measure of the structural distance between two chemical systems X and Y. We require $d(X, Y)$ to have all the classical properties of distance, namely

$$d(X, Y) = 0 \text{ only if } X = Y; \text{ otherwise } d(X, Y) > 0 \qquad (2)$$

$$d(X, Y) = d(Y, X) \text{ for any X and Y} \qquad (3)$$

$$|d(X, Z) - d(X, Y)| \le d(Y, Z) \le d(X, Z) + d(X, Y) \quad \text{for any X, Y, and Z} \qquad (4)$$

Putting the explicit definition of $d(X, Y)$ aside until the next section of this paper, we define the structural proximity of the transition state to the reactants as

$$\beta = [d(A, TS) - d(B, TS)]/d(A,B) \qquad (5)$$

Due to the left side of the triangle inequality (eq 4), β always assumes values between -1 and $+1$. Between the limits of -1 and $+1$ that correspond to the transition states identical with the reactants and products, respectively, lie negative (positive) values of β that characterize early (late) transition states.

To complete the quantitative characterization of chemical reactions, we also define a parameter given by

$$\alpha = [d(A, TS) + d(B, TS)]/d(A, B) \qquad (6)$$

Due to the right side of the inequality (eq 4), α is never smaller than 1. The meaning of α can be understood by considering a hypothetical reaction in which the structures along the reaction path (the transition state in particular) lose their similarity to the reactants at exactly the same rate as they gain their similarity to the products. This implies not only synchronicity of the reaction,

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but also the absence of structural changes outside the reaction center. The parameter α assumes the limiting value of 1 for such a perfectly *isosynchronous* (which means both synchronous and with localized structural changes) reaction. Thus, α can be regarded as the isosynchronicity parameter.

Having the relevant quantities rigorously defined, we focus on the assumptions behind the Hammond postulate. Strictly speaking, the postulate is limited to the reactions in which the nuclei are displaced by finite distances. The dissociation reactions often do not possess barriers. The atom- and group-transfer reactions often violate the predictions of Hammond postulate due to so-called perpendicular effects[14-16] that give rise to "anti-Hammond" behavior.[17] On the other hand, processes with limited (although not necessarily localized) motions of nuclei, such as rearrangement reactions, are expected to follow the Hammond postulate.

Justification of the Hammond postulate has been attempted in the chemical literature by considering general mathematical properties of the reaction profile curves.[18,19] Such justification relies heavily on the assumption that the reaction profiles describing the same type of chemical reaction belong to the same family of curves. Obviously, one has to clarify the meaning of "the same type of reaction". Strictly speaking, this implies changes (such as substitution) at locations outside the reaction centers. In practice, however, the Hammond postulate in often invoked to describe broader families of reactions.

We propose here the following quantitative reformulation of the Hammond postulate: *For a series of similar reactions with finite nuclear motions, and a definition of the structural distance that satisfies the conditions 2–4, there is a positive correlation between the exothermicity γ, eq 1, and the structural proximity of the transition state to reactants β, eq 5.* Such a rigorous formulation necessarily limits somehow the scope of applicability of the original postulate, but at the same time enhances its predictive power by allowing quantitative correlations. This means that, once validity of the Hammond postulate for a series of similar reactions is established, one can predict quantitatively (or semiquantitatively) the position of the reaction barrier from knowledge of the activation energies for the foward and reverse reactions.

In the subsequent sections of this paper, we introduce a practical definition of the structural distance and discuss possible applications of the indices α, β, and γ. Next, we apply the developed formalism to a series of 10 reactions involving intramolecular proton transfer in unsubstituted and (poly)fluorosubstituted hydrogen catecholate anions.

Structural Distance

Let $\Gamma_X(\vec{x},\vec{x}')$ and $\Gamma_Y(\vec{x},\vec{x}')$ stand for the reduced first-order density matrices[20] that describe the chemical systems X and Y, respectively. By the chemical system, we mean a molecule or a set of molecules in a specific electronic state and in a specific relation (such an orientation in a descriptive sense) to the other chemical system in comparison. Therefore, identical molecules can represent distinct chemical systems depending on their orientations and/or electronic states. Let Ω_{XY} denote the mutual orientation (three translations and three Euler angles) of X and Y. We prove that the following quantity

$$d(\mathrm{X},\mathrm{Y}) = \min_{\Omega_{XY}}\left[\int\int|\Gamma_X(\vec{x},\vec{x}') - \Gamma_Y(\vec{x},\vec{x}')|^2\,\mathrm{d}\vec{x}\,\mathrm{d}\vec{x}'\right]^{1/2} \qquad (7)$$

has the properties 2–4 described in the preceding section of this paper. The min sign in eq 7 does not necessarily mean the global minimum. Instead, it stands for a local minimum that describes a particular chemical situation.

The properties 2 and 3 can be verified by inspection of eq 7. The property 4 is just the triangle inequality in the Hilbert space spanned by the reduced first-order density matrices with the norm defined by eq 7. The calculation of the so-defined structural distance, which is sensitive to both the structural (the positions of nuclei) and electronic (the electron density) dissimilarities, is greatly simplified by noting that

$$d(\mathrm{X},\mathrm{Y}) = [(\mathrm{X},\mathrm{X}) + (\mathrm{Y},\mathrm{Y}) - 2(\mathrm{X},\mathrm{Y})]^{1/2} \qquad (8)$$

where

$$(\mathrm{X},\mathrm{Y}) = \max_{\Omega_{XY}}\int\int\Gamma_X^*(\vec{x},\vec{x}')\Gamma_Y(\vec{x},\vec{x}')\,\mathrm{d}\vec{x}\,\mathrm{d}\vec{x}' \qquad (9)$$

is the recently introduced NOEL (the number of overlapping electrons) similarity index.[21] Referring the reader to the original paper,[21] we mention that the NOEL index can be calculated very rapidly at a cost that scales proportionally to the third power of the size of the systems in question. NOEL lends itself to a transparent interpretation since, for the density matrices derived from the Hartree–Fock (HF) wave functions, (X, Y) is equal to the number of the electrons in the molecular fragment(s) common to X and Y. As a corollary, one should note that, for the system X described at the HF level, (X, X) is equal to the number of electrons in X.

The definition of structural distance introduced here bears some resemblance to the similarity index (SI) of Polansky et al.[22] However, since SI is defined with the elements of the charge–bond order matrix instead of the reduced first-order density matrix, its validity is limited to comparisons between chemical structures with the same geometry, such as two different electronic states of the same molecule. This means that SI cannot be used for assessing the structural distances between products, reactants, and the transition state. Moreover, because the definition of SI relies on the charge–bond order matrices, the computed values of SI are expected to depend strongly on the basis sets used in calculation of the wave functions in question (as, for example, Mulliken atomic charges do). On the other hand, the structural distance defined here is guaranteed to converge smoothly to a well-defined limit with the improving quality of basis sets. This means that one can expect only a weak dependence of the computed reaction parameters on the basis sets and the electron correlation method provided that some minimal requirements for the theoretical level of calculations are met.

For a particular reaction, one may depict the structural relations between the reactants (A), and products (B), and the transition state (TS) by drawing a triangle with vertices representing A, B, and TS, and the edges having lengths proportional to the respective structural distances. Examples of such structural relations graphs are given in Figure 5 (which is discussed in the next section of this paper). The structural relations graph allows one to assess at a glance the character of the chemical reaction in question. A broad base between A and B indicates significant structural changes accompanying the reaction. The opposite is true for narrow triangles. Tall triangles represent reactions that are either asynchronous and/or are accompanied by large structural changes outside the reaction center. Triangles with the apex tilted to the left (right) indicate early (late) transition states.

Computational Methods

All the electronic structure calculations were performed on a CRAY Y-MP supercomputer with the GAUSSIAN 90 suite of programs.[23] The structures of the minima and transition states were optimized at the HF/6-31++G** level. The resulting total HF energies are given in

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Table I. Calculated 6-31++G** Total Hartree–Fock Energies

substituents[a]				E_{HF} (au)		
X_1	X_2	X_3	X_4	reactant (A)	transition state (TS)	product (B)
H	H	H	H	−379.879 932 3	−379.860 031 5	−379.879 932 2
H	H	H	F	−478.735 856 4	−478.716 394 3	−478.737 780 7
H	H	F	H	−478.742 929 6	−478.720 187 4	−478.736 785 9
H	H	F	F	−577.590 786 2	−577.568 594 7	−577.586 742 0
H	F	H	F	−577.591 529 8	−577.575 348 6	−577.599 519 6
H	F	F	H	−577.591 622 4	−577.572 111 6	−577.591 622 4
F	H	H	F	−577.591 738 5	−577.570 663 3	−577.591 738 5
F	F	H	F	−676.439 529 9	−676.421 815 9	−676.445 550 4
F	F	F	H	−676.440 582 6	−676.419 572 4	−676.438 503 8
F	F	F	F	−775.285 595 8	−775.265 195 9	−775.285 595 8

[a] The number of atoms is as follows: in reactants, 5–O^-, 6-OH, 1,2,3,4-substituents; in products, 5-OH, 6-O^-, 1,2,3,4-substituents.

Table II. HF/6-31++G** Calculated Values of the NOEL Similarity Indices

substituents[a]				NOEL			
X_1	X_2	X_3	X_4	(A,A) = (B,B) = (TS,TS)	(A,B)	(A,TS)	(B,TS)
H	H	H	H	58.000 00	56.375 39	53.560 19	53.560 19
H	H	H	F	66.000 00	63.848 05	61.396 38	61.423 25
H	H	F	H	66.000 00	64.252 99	61.401 16	61.729 29
H	H	F	F	74.000 00	71.769 12	69.193 44	69.536 56
H	F	H	F	74.000 00	71.803 21	69.594 33	69.246 82
H	F	F	H	74.000 00	72.213 64	69.493 47	69.493 47
F	H	H	F	74.000 00	71.371 44	69.147 06	69.147 06
F	F	H	F	82.000 00	79.305 86	77.266 00	77.004 95
F	F	F	H	82.000 00	79.760 58	77.260 83	77.338 47
F	F	F	F	90.000 00	87.256 05	85.048 72	85.048 72

[a] The numbering of atoms is as follows: in reactants, 5–O^-, 6-OH, 1,2,3,4-substituents; in products, 5-OH, 6-O^-, 1,2,3,4-substituents.

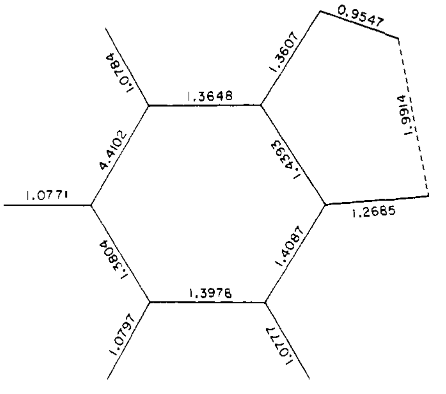

Figure 1. HF/6-31++G** optimized bond lengths (Å) in the equilibrium structure of the hydrogen catecholate anion.

Table I. The corresponding density matrices were used in computations of the NOEL indices, structural distances, and the optimal mutual orientations of molecules with the aid of the NOEL program.[24] The computed values of NOEL are presented in Table II.

Intramolecular Proton Transfer in Substituted Hydrogen Catecholate Anions

The intramolecular transfer reactions are important to many chemical, biochemical, and photochemical processes. An interesting practical application of these reactions is a proton-transer laser.[25] In this paper, we test the proposed quantitative reformulation of the Hammond postulate on the proton-transfer reactions involving both unsubstituted and (poly)fluorosubstituted hydrogen catecholate anions, $C_6H_{4-n}F_n(OH)O^-$. There are 16 such anions giving rise to 10 pairs of the foward and reverse reactions, 4 of them corresponding to degenerate rearrangements. In the case of the unsubstituted anion, the equilibrium geometry is characterized by distinctly different C–O and O–H distances (Figure 1) In the corresponding transition state, these distances become equal (Figure 2). To confirm the character of the transition state, the reaction coordinate was calculated from the HF/6-31G** force constants matrix and found to correspond to an in-plane proton shift. The GAPT atomic charges,[26] calculated at the same level of theory, show a characteristic pattern of alternation. The shifting hydrogen bears a positive charge of 0.593, whereas the oxygen atoms are negatively charged (−1.124). The carbon atoms linked to the oxygens have positive charges of 0.579, whereas their first neighbors have negative charges of −0.124, with the linked hydrogen atoms bearing charges of −0.015. The remaining two carbon and two hydrogen atoms are negatively charged (−0.074 and −0.039, respectively).

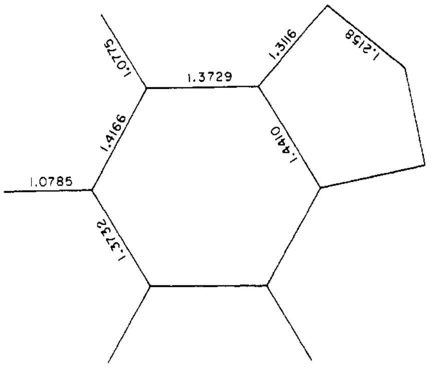

Figure 2. HF/6-31++G** optimized bond lengths (Å) in the transition-state structure of the hydrogen catecholate anion.

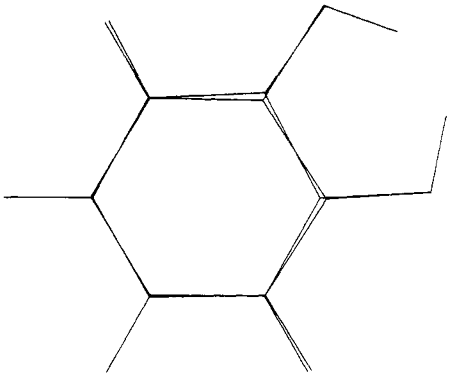

Figure 3. Optimized mutual orientation of the reactant and the product of the proton-transfer reaction of the hydrogen catecholate anion.

Table III. HF/6-31++G** Calculated Activation Energies[a] and Structural Distances

substituents[b]				E_{act} (kcal/mol)		structural distances		
X_1	X_2	X_3	X_4	A → TS	B → TS	*d*(A,B)	*d*(A,TS)	*d*(B,TS)
H	H	H	H	12.49	12.49	1.802 56	2.979 87	2.979 87
H	H	H	F	12.21	13.42	2.074 58	3.034 34	3.025 48
H	H	F	H	14.27	10.42	1.869 23	3.032 77	2.922 57
H	H	F	F	13.93	11.39	2.112 29	3.100 50	2.987 79
H	F	H	F	10.15	15.17	2.096 09	2.968 39	3.083 24
H	F	F	H	12.24	12.24	1.890 16	3.002 18	3.002 18
F	H	H	F	13.22	13.22	2.292 84	3.115 43	3.115 43
F	F	H	F	11.12	14.89	2.321 27	3.077 01	3.160 71
F	F	F	H	13.18	11.88	2.116 33	3.078 69	3.053 37
F	F	F	F	12.80	12.80	2.342 63	3.146 83	3.146 83

[a] At 0 K, zero-point vibrational energies not included. [b] The numbering of atoms is as follows: in reactants, 5-O^-, 6-OH, 1,2,3,4-substituents; in products, 5-OH, 6-O^-, 1,2,3,4-substituents.

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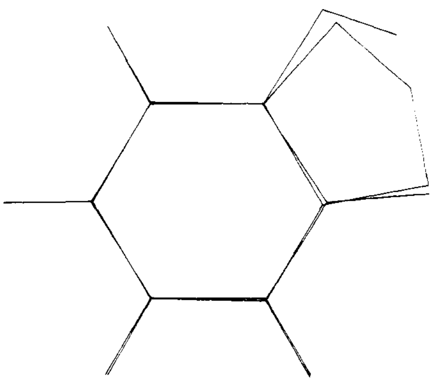

Figure 4. Optimized mutual orientation of the reactant and the transition state of the proton-transfer reaction of the hydrogen catecholate anion.

Table IV. Calculated HF/6-31++G** Parameters of the Transition States

substituents[a]				TS parameters		
X_1	X_2	X_3	X_4	α	β	γ
H	H	H	H	3.30626	0.00000	0.00000
H	H	H	F	2.92098	0.00427	−0.04711
H	H	F	H	3.18599	0.05895	0.15617
H	H	F	F	2.88232	0.05336	0.10026
H	F	H	F	2.88711	−0.05479	−0.19800
H	F	F	H	3.17663	0.00000	0.00000
F	H	H	F	2.71752	0.00000	0.00000
F	F	H	F	2.68721	−0.03606	−0.14525
F	F	F	H	2.89750	0.01197	0.05205
F	F	F	F	2.68659	0.00000	0.00000

[a] The numbering of atoms is as follows: in reactants, 5-O^-, 6-OH, 1,2,3,4-substituents; in products, 5-OH, 6-O^-, 1,2,3,4-substituents.

As one may conclude from inspection of Figure 3, the proton shift results in a product that has the geometrical structure remarkably similar to that of the reactant, the obvious difference being the position of the hydrogen atom. This is also reflected by the calculated values of (A, B) (Table II), which differ from the respective values of (A, A) and (B, B) by 1.7–2.8, the contribution of 1.0 coming directly from the altered position of the proton. This results in rather small values of the structural distances *d*(A, B) (Table III). On the other hand, the structure of the transition state is markedly different from that of either reactant or product. Besides the position of the shifting proton, the angles between the oxygen atoms and the C–C bonds of the benzene ring are significantly altered in the transition state (Figure 4). This gives rise to the decreased values of (A, TS) and (B, TS) (Table II) and increased structural distances *d*(A, TS) and *d*(B, TS) (Table III).

The calculated activation energies range between 10 and 15 kcal/mol and, due to the presence of diffuse functions in the basis set used, are expected to be close to the experimental ones. The differences between the energies of the reactants and products range between 0 and 5 kcal/mol. This corresponds to values of γ between −0.20 and 0.16, whereas the β index spans the range of −0.055 to +0.059 (Table IV).

As discussed above, the transition states have structures that are substantially different from those of both reactants and products. This is reflected in the large values of the isosynchronicity parameters α (Table IV). The fact that the reactions studied are far from being isosynchronous is also evident from the tall shapes of the structural relations graphs (Figure 5). The late and the early characters of the transition states for the "HHFH" and "HFHF" reactions, respectively, are also easily recognizable.

An alternative way of displaying the same information is the α–β plot, which is given in Figure 6. The points describing reactions involving early (late) transition states lie within the lower (upper) half-plane of the plot. Both half-planes are bordered by horizontal lines corresponding to $\beta = \pm 1$. The vertical axis, which corresponds to $\alpha = 1$, separates the forbidden left half-plane from the allowed right one. If one defines the parameters α and β with respect to a current point on the reaction path (rather than with respect to the TS as in eqs 5 and 6), the reaction path can be envisioned as originating from the $\beta = -1$ point on the vertical axis, stretching over the right half-plane, passing through the (α, β) point describing the transition state and terminating at the $\beta = 1$ point on the vertical axis. Depending on the isosynchronicity of the reaction, the reaction path may be very close to a straight vertical line or may be considerably bent to the right. Inspection

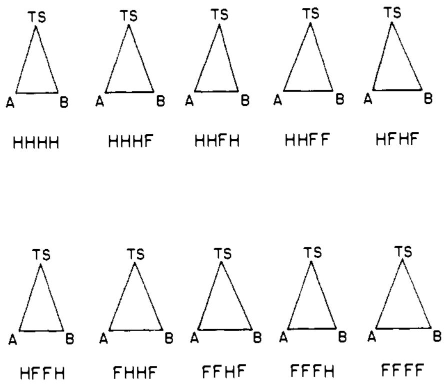

Figure 5. Structural relations graphs of the proton-transfer reactions of the unsubstituted and (poly)substituted hydrogen catecholate anions. See the footnote to Table I for the description of substituents.

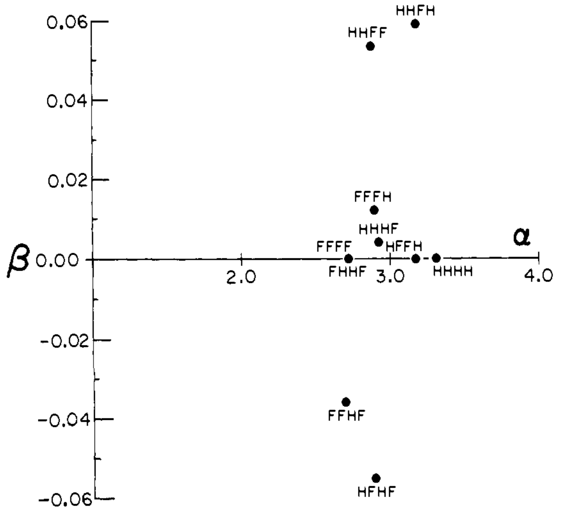

Figure 6. α–β plot for the proton-transfer reactions of the unsubstituted and (poly)substituted hydrogen catecholate anions. See the footnote to Table I for the description of substituents.

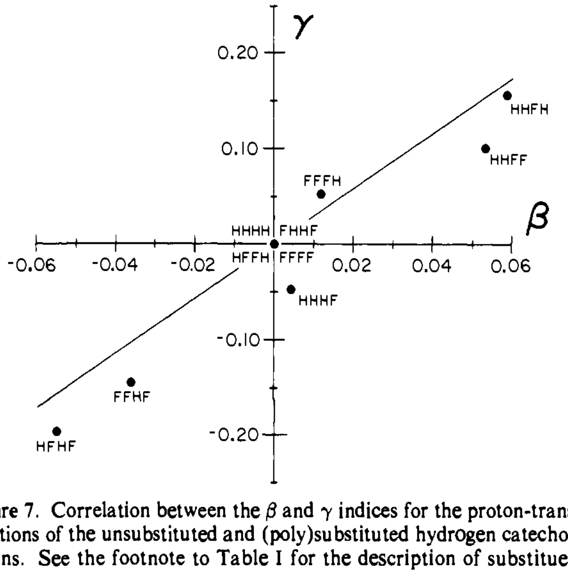

Figure 7. Correlation between the β and γ indices for the proton-transfer reactions of the unsubstituted and (poly)substituted hydrogen catecholate anions. See the footnote to Table I for the description of substituents.

of the α–β plot for the reaction series under study reveals little variability in α within the series.

The correlation between β and γ, implied by the Hammond postulate, is of central interest. As one may conclude from the inspection of Figure 7, the presence of such correlation is confirmed for the series of chemical reactions in question, although there is a considerable scatter of points. In particular, the fact that one of the reactions ("HHHF") is both exothermic and possesses a late transition state cannot be overlooked.

Conclusions

The ability to quantify the parameters of empirical relationships is of a great importance. It not only allows for establishing quantitative correlations, but also aids in understanding their limits of validity. Once numerical values are available, the quality of correlations can be readily assessed with statistical methods.

The proposed indices make it possible to describe the characters of the transition states in a quantitative, yet concise, manner. They also provide the means for visualizing the structural relations between the reactants, the products, and the transition state. Series of similar reactions are expected to occupy distinct portions of the α–β graph, allowing for a general classification of chemical reactions.

The present definitions of exothermicity, structural proximity to reactants, and the isosynchronicity parameter use well-defined quantities that have transparent physical and chemical interpretations. The indices are readily calculated with the data available from the electronic structure calculations. As a side product, the optimized mutual orientations of the reactants, products, and transition states are obtained. A new concept of isosynchronicity, which describes the "straightforwardness" of the reaction path, is quantified with the aid of the parameter α.

The Hammond postulate, like any other empirical correlation, should be applied with caution. The relative proximities between the reactants, the products, and the transition state are only one of the several factors that determine the energetics of the forward and reverse reactions. In general, the larger the distance between the reaction center and the substituents that vary within the reaction series, the better correlation between β and γ can be expected.

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Covalent vs Ionic Bonding in Hexasubstituted "Push–Pull" Ethanes

Stacey T. Mixon and Jerzy Cioslowski*

Contribution from the Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006.

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Abstract: HF/6-31G* electronic structure calculations reveal the presence of a covalent central C–C bond in the $C(NH_2)_3CF_3$ molecule, whereas the $C(NH_2)_3C(NO_2)_3$ species is found to be best described as an ionic pair. The $C(NH_2)_3C(CN)_3$ molecule exists as either a covalent or an ionic isomer. These observations are derived from the optimized geometries of various rotamers of the "push–pull" hexasubstituted ethanes $C(NH_2)_3CX_3$, where X = F, CN, or NO_2, which are characterized as either minima or transition states according to the calculated vibrational frequencies. Additional confirmation of the presence of either covalent or ionic bonding is provided by the calculated GAPT charges and charge transfers, and by Bader atomic charges. The molecular graphs of the push–pull ethanes, as defined within the topological theory of atoms in molecules, exhibit very complicated patterns of bonding rich in weak bonds and unexpected ring and cage points.

Introduction

The effects of substituents on chemical properties of molecules are well known and understood by organic chemists. Phenomena such as the increase in acidity upon substitution by fluorine atoms, or the weakening of basicity upon phenyl substitution in amines, are textbook examples. In some molecules, the substituent effects are quite dramatic. For example, tricyanomethane and trinitromethane are strong acids in water, whereas methane itself manifests acidity under only very extreme conditions. Similarly, the triaminomethyl cation is one of the most stable carbocations known in organic chemistry.[1] Even such strong effects, however, do not usually result in a total alteration of the electronic structure.

The ethane molecule possesses a covalent central bond that requires about 88 kcal/mol to be cleaved homolytically. One may inquire how the C–C bonding in ethane could be influenced by the presence of several substituents on the carbon atoms. In particular, an arrangement where the electron-withdrawing substituents, X, are attached to one atom and the electron-donating substituents, Y, are attached to the other atom is of great interest. In an extreme situation, the resulting polarization of the C–C bond might bring about an ionic dissociation of the molecule, yielding an ionic pair. One could also contemplate the possibility of the existence of two isomers, the covalent one best described as CY_3CX_3 and the ionic one best formulated as $CY_3^+\ CX_3^-$.

Let us review the possible factors influencing the relative stabilities of the covalent and ionic isomers of this kind. The covalent molecule is stabilized by the presence of a strong single C–C bond, which must be at least partially dissociated in the ionic isomer. On the other hand, the ionic species may lower its energy through either inductive or mesomeric stabilization of the CX_3^- and CY_3^+ ions. Moreover, if the substituents X and Y are bulky, the steric destabilization is relieved in the ionic form due to the fact that the distance between X and Y is expected to be much larger in the ionic species than in the covalent one. Finally, should either CX_3^- or CY_3^+ be stabilized through Y resonance,[1,2] the preferable sp^2 hybridization of the central carbon atom is feasible only in

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* To whom correspondence should be addressed.

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