

A frontier orbital analysis of the oxidation of alkenes by thallium(III) salts*

M. STRAŠÁK and J. MAJER

Department of Analytical Chemistry, Faculty of Pharmacy,
Komenský University, 880 34 Bratislava

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Dedicated to Professor Dr. Ing. Jozef Tomko, DrSc., in honour of his 60th birthday

Application of the perturbation molecular orbital treatment based on frontier orbitals (FO's) is utilized to the interpretation of the Taft correlation in the oxidation of alkenes by thallium(III) salts. There is a good linear relationship between the logarithm of the reaction rate k and the inverse of the FMO gap. In order to elucidate the mechanistic similarities observed between the oxymetallation reactions and some other electrophilic additions to olefinic systems, comparative FMO analysis has been made and implications of these results to the reactivity-selectivity principle (RSP) are discussed. The model suggests that it is the differential HOMO—LUMO gap for a given substrate and reacting electrophiles that governs substrate selectivity.

Квантово-химическая теория возмущений на основании граничных орбиталей была использована для интерпретации корреляции Тафта при окислении алкенов солями Tl(III). Была обнаружена хорошая линейная зависимость логарифма значений констант скорости k и обратным значением энергетических различий граничных орбиталей (FMO gap). Для объяснения механистического подобия, наблюдаемого между реакциями оксиметаллирования и некоторыми другими реакциями электрофильного присоединения в олефинических системах, был использован анализ методом FMO и обсуждается вхождение этих результатов в рамки принципа реактивности селективности (RSP). Модель предполагает, что селективность субстрата обнаруживается в результате различного расстояния HOMO—LUMO энергетических орбиталей данного субстрата и электрофильных реагентов.

* Part X of the series Extrathermodynamic free energy relationships in the oxidation of alkenes by thallic salts.

For Part IX see Ref. [25].

It is well known that alkenes are oxidized to saturated carbonyl compounds by certain kinds of metal ions (Pd(II) [1], Hg(II) [2], Tl(III) [3], Rh(III) [4], and Pt(IV) [5]) in aqueous media. Many detailed mechanistic studies have been accumulated for Pd(II) [6], Hg(II) [7], and Tl(III) [8, 9], and it now seems to be established that three reactions are formed by similar sequential processes: (i) π complex formation of an alkene with the metal ion, (ii) conversion of the π complex into the β -hydroxyalkylmetal σ complex by a nucleophilic attack of an oxy-base, and (iii) redox decomposition of the σ complex accompanying an intramolecular 1,2-hydrogen shift. In the case of Hg(II) and Tl(III) this is to be expected on the grounds that Tl(III) is isoelectronic with the Hg(II) ion. However, one pronounced difference is in the type of product formed; Tl(III) gives glycols with aldehydes or ketones whereas Hg(II) produces only carbonyl compounds.

In mechanistic details, on the other hand, these metal ions show some interesting contrasts especially in the points concerning (1) the relative stability of the two types of intermediates involved, and (2) the steric course of the intramolecular hydrogen transfer during the redox decomposition. With respect to point (1), stability of the π complex decreases in the order Pd(II) > Hg(II) \gg Tl(III). As for point (2), metal-assisted *syn*-wise migration was postulated for Pd(II), although the *trans*-wise shift was ascertained for Hg(II) [10].

In a recent paper in this series [11] we showed that the rate constants for oxythallation (the rate-determining step for the overall reaction) of alkenes have been correlated with their ionization potentials (IP's). By use of the Koopman's theorem, the HOMO energies may be evaluated from the first IP values. Hence the significant role of the HOMO of alkene with respect to reaction path is obvious. The aim of this paper is to show that the FMO analysis may be helpful in understanding some of the mechanistic principles of electrophilic additions to olefinic systems, especially when it was shown how a physical explanation of the linear free energy relationship (LFER) may be proposed in the framework of a FMO method which has provided a basis for explaining several aspects of chemical reactivity [12].

Experimental

Chemicals

The oxidation solution of thallium(III) sulfate was prepared as described previously [13]. The thallium concentration was determined by titrating the iodine liberated by the reaction of Tl(III) with KI with a defined solution of Na₂S₂O₃ [14].

The alkenes were prepared and purified by methods described previously [15].

Kinetics

The kinetics of oxidation were followed by u.v. spectrophotometry in the region 200–240 nm [15, 16]. The reaction temperature was $25 \pm 0.1^\circ\text{C}$.

Method

The calculations of the HOMO (an olefin) and LUMO (an electrophile) energies were performed using the Klopman's perturbation theory. In the case of the donor-acceptor interaction the basic eqn (1) is valid. The right-hand side of this equation consists of two terms — an electrostatic and a covalent one [17–19].

$$\Delta E = -\frac{q_s q_t}{4\pi R_{st} \epsilon} + 2 \sum_m \sum_n \frac{(c_s^m c_t^n \Delta\beta_{st})^2}{E_m^* - E_n^*} \quad (1)$$

where ΔE is the change in energy produced during the interaction of two systems, e.g. an atom s of electron-donor molecule S and an atom t of electron-acceptor molecule T in a solvent with the permittivity ϵ ; q_s and q_t are the charges of atoms s and t in the separate molecules; R_{st} is the distance between two atoms s and t ; c_s^m are coefficients of the AO's of atom s in the occupied MO's m of molecule S ; c_t^n are coefficients of the AO's of atom t in the unoccupied MO's n of molecule T ; $\Delta\beta_{st}$ is the change in resonance integral produced during interaction of orbitals of atoms s and t at the distance R_{st} ; E_m^* and E_n^* are the values characterizing the energies of MO's m and n in the separate molecules S and T in reaction medium.

The results of the Klopman's perturbation theory agree with *Pearson's* concept [20, 21], according to which the hard base—hard acid interaction is characteristic of charge-controlled reactions, whereas the soft base—soft acid interaction is a result of covalent coordination of a donor with an acceptor. Since according to the HSAB classification [20, 21] olefins are soft bases and studied electrophiles are soft acids, the Klopman's method [19, 22] is suitable for calculation of the HOMO and LUMO energies. In accordance with the Klopman's method these energies may be calculated from values of the IP's, the electron affinities (EA's), and the effective radius R_{ion} of reacting atoms using eqns (2) and (3).

For acceptors

$$\frac{E_n^*}{\text{eV}} = -\frac{3 \text{ IP} + \text{EA}}{4 \text{ eV}} + \frac{14.388(q - 0.5\chi)\chi}{R_{\text{ion}} + 82 \text{ pm}} \left(1 - \frac{1}{\epsilon_t}\right) \text{ pm} \quad (2)$$

For donors

$$\frac{E_m^*}{\text{eV}} = -\frac{\text{IP} + 3 \text{ EA}}{4 \text{ eV}} + \frac{14.388(q + 0.5\chi)\chi}{R_{\text{ion}}} \left(1 - \frac{1}{\epsilon_t}\right) \text{ pm} \quad (3)$$

where q is the numerical value of initial charge of an ion, ϵ_t is the dielectric constant

of the medium, and χ is empirically set equal to $q - (q - 1) \sqrt{0.75}$ for $q \geq 1$. The first term of the right-hand side of these equations characterizes the orbital electronegativity in gaseous phase and the second term correction on the solvent influence.

The values of the effective energy of the LUMO of electrophiles, calculated according to Klopman's method, are illustrated in Table 1. Values of the rate

Table 1

Calculated softness character for some electrophiles

Electrophile	LUMO E_n/eV
Ag ⁺	-2.82 ^a
Tl ³⁺	-3.37 ^a
Hg ²⁺	-4.64 ^a
Br ⁻	-7.73
Cl ⁻	-8.62

a) Values from Ref. [22]. For all cases the value of $\epsilon_{\text{H}_2\text{O}}$ was taken. Values of IP and EA for Br⁺ and Cl⁺ extrapolated from data in Ref. [22].

Table 2

Values of the rate constants for hydroxythallation of alkenes at 25°C and LUMO—HOMO gap^a

No.	Alkene	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\delta E/\text{eV}$
1	Ethylene	0.335 ^b	7.145
2	Propylene	9.423 ^b	6.374
3	1-Butene	18.80 ^b	6.255
4	1-Pentene	20.85	6.154
5	1-Hexene	25.72	6.108
6	1-Heptene	14.91	6.072
7	1-Octene	8.40	6.190
8	Allyl alcohol	0.25	7.25 ^c
9	3-Methyl-1-butene	35.01	6.163
10	4-Methyl-1-pentene	19.80	6.082
11	Methyl allyl ether	0.26	7.20 ^c
12	4-Chloro-1-butene	0.66	6.76 ^c
13	Styrene	1.16	6.98 ^c

a) Values of IP used for calculations are taken from Ref. [23]; b) values from Ref. [8, 9]; c) values of IP for calculation from Ref. [11].

constants of the second order for hydroxythallation of alkenes together with values of difference of the HOMO—LUMO energies are listed in Table 2.

Discussion

Frontier orbital theory [22, 24] shows how the interaction of the molecular orbitals of the starting materials influences the transition state of an organic reaction. The energy of interaction is composed of two main contributions — a charge component and an orbital component. The former is a simple coulombic contribution to the overall energy of interaction. The latter component consists of all the two-electron stabilizing interactions between occupied and unoccupied orbitals in the reacting moieties. However, due to the dominance of the HOMO—LUMO interactions in many systems, these are often the only ones that are explicitly considered.

The magnitude of stabilizing interaction, SE, between an occupied and unoccupied orbital is given approximately by eqn (4), which is the simplification of the second term of eqn (1).

$$SE = \frac{\beta^2}{E_{\text{LUMO}} - E_{\text{HOMO}}} \quad (4)$$

The stronger the interaction energy, SE, the smaller the activation energy [12].

From earlier studies [1, 2, 11, 15] it is obvious that the rate-determining step of the oxidation of alkenes by thallium(III) salts is the electrophilic addition of TI^{3+} which proceeds through bridged transition states and intermediates (at least in the case of $\text{RCH}=\text{CH}_2$ and $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$ alkenes [25]). In the case of this reaction the relevant orbitals are the π orbital of alkene (the HOMO) and σ^* orbital of TI^{3+} (the LUMO). In addition, accordingly with Pearson's HSAB concept [20, 21], an alkene is a very soft nucleophile, at least partly because it is uncharged and has a high-energy HOMO and TI^{3+} is a soft electrophile because it has a low-energy LUMO. Thus their reaction is fast. Quantitative support for the importance of frontier orbitals comes from our study [11] of a reaction in which the coulombic term was kept small and relatively constant. The rate of the hydroxythallation of alkenes correlated well with the IP of the π orbital of alkenes.

Fig. 1 shows that there is a good linear relationship between the logarithm of the rate constant of hydroxythallation of $\text{RCH}=\text{CH}_2$ alkenes and the inverse of the FMO gap. For alkenes branched on the C=C bond the correlation is not very good. In this case both steric and resonance effects are important but these are ignored in FMO analysis. If the gap between the HOMO of alkene and the LUMO of the thallic ion decreases, the rate of hydroxythallation is enhanced. From Fig. 1 it is obvious that there is a good linear relationship

$$\log k = \frac{A}{E_{\text{LUMO}} - E_{\text{HOMO}}} + B \quad (5)$$

where A (in eV) and B are experimental constants. For hydroxythallation of $\text{RCH}=\text{CH}_2$ alkenes eqn (5) may be rewritten into the form

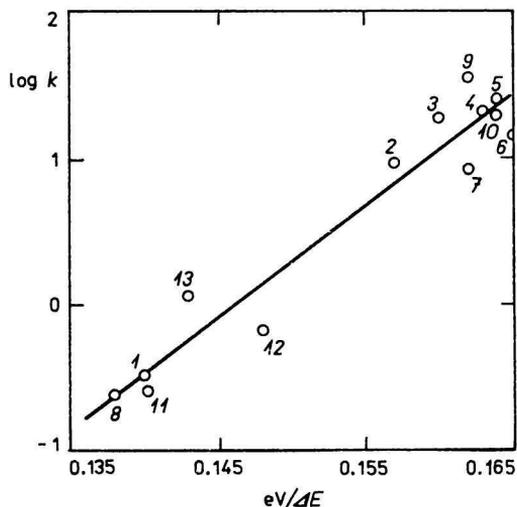


Fig. 1. Relationship between the logarithm of value of the rate constants for hydroxythallation of alkenes by $Tl_2(SO_4)_3$ in aqueous H_2SO_4 at $25^\circ C$ and the inverse of the FMO gap.

$r = 0.967$; $r^2 = 0.935$. The notation of alkenes is the same as in Table 2.

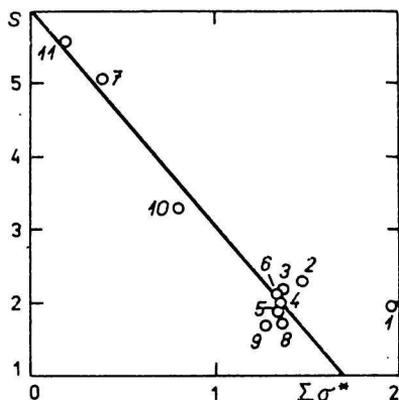


Fig. 2. Substituent effects on selectivity of Ad_E reactions at $25^\circ C$.

$$S = \log(k_{Br}/k_{Ti}) = (\rho_{Br}^* - \rho_{Ti}^*) \Sigma\sigma^* + \log(k_{Br}^0/k_{Ti}^0);$$

$r = 0.970$; $r^2 = 0.9402$. Point 1 excluded from correlation. The notation of alkenes is the same as in Table 3.

$$\log k = \frac{0.760 \text{ eV}}{E_{LUMO} - E_{HOMO}} - 0.475 \quad (6)$$

We noted recently [26] that structure effects in the oxidation of alkenes by thallic salts play a similar role as in the bromination of alkenes. This conclusion is further supported by the observation that a plot of selectivity, S , against $\Sigma\sigma^*$ for these two reactions gives a significant correlation (Fig. 2).

Using a linear regression analysis we found that

$$S = 6.00 - 2.95 \Sigma\sigma^* \quad (7)$$

Substituents capable of stabilizing the species of carbocationic character formed during reaction bring about greater selectivity in these species in accord with the RSP [27]. Since $2.303 RT S = \Delta\Delta G^\ddagger = \Delta G_{ATl}^\ddagger - \Delta G_{ABr}^\ddagger$ (the difference in the free energies of activation for the reaction of alkene with thallium(III) ion and bromine, respectively) is linearly related to $\log(k_{Br}/k_{Ti})$, the selectivity of a species will be proportional to $\Delta\Delta G^\ddagger$. The selectivity data for these two reactions at $25^\circ C$ are listed in Table 3.

From Fig. 2 and Table 3 it is evident that more substituted C=C bonds (with electron-releasing substituents) exhibit greater $\Delta\Delta G^\ddagger$. This fact is in accord with

the RSP. In line with *Leffler—Hammond* postulate [30, 31], the stabilization of a particular species will result in a corresponding increase in its selectivity. Table 3 indicates that reactive species of n-alkenes exhibit lower $\Delta\Delta G^\ddagger$ values compared to reactive species of substituted internal alkenes, which are more stable. Since the interaction between n-alkene and bromine or thallium(III) ion in the transition state is weak, because it occurs early along the reaction coordinate, n-alkene will exhibit low preference for Tl^{3+} over Br_2 . The corresponding transition state for substituted internal alkene, however, is more advanced along the reaction coordinate, which results in greater interaction between substituted internal alkene and Br_2 or Tl^{3+} , and as a consequence a substituted one will exhibit higher selectivity.

Table 3

Selectivity data for hydroxythallation [15] and bromination [28] of alkenes at 28°C

No.	Alkene	$S = \log(k_{Br}/k_T)$	$\Sigma\sigma^{**}$	$\Delta\Delta G^\ddagger/kJ$
1	Ethylene	1.956	1.960	11.14
2	Propylene	2.291	1.470	13.06
3	1-Butene	2.188	1.370	12.43
4	1-Pentene	2.001	1.355	11.39
5	1-Hexene	1.889	1.340	10.76
6	1-Heptene	2.121	1.340	12.10
7	2-Methyl-2-pentene	5.083	0.390	28.93
8	4-Methyl-1-pentene	1.700	1.345	9.67
9	3-Methyl-1-butene	1.686	1.280	9.59
10	cis-4-Methyl-2-pentene	3.290	0.790	18.71
11	2,4,4-Trimethyl-2-pentene	5.585	0.190	31.78

a) Values were calculated from the data in Ref. [29].

Perturbation molecular orbital theory may be utilized to rationalize the above behaviour. An energy diagram showing the relevant orbitals involved in the electrophilic addition is shown in Fig. 3.

The energies of the π orbitals are considered to increase in the order n-alkene < internal alkene. This is because with increase in the number of substituents the HOMO energies are enhanced. For the competitive reaction of the two nucleophiles with a given electrophile, a differential stabilization will result as follows

$$SE_{\text{int.alk.}} - SE_{\text{n-alk.}} = \frac{\beta^2}{\delta E_{\text{int.alk.}}} - \frac{\beta^2}{\delta E_{\text{n-alk.}}} \quad (8)$$

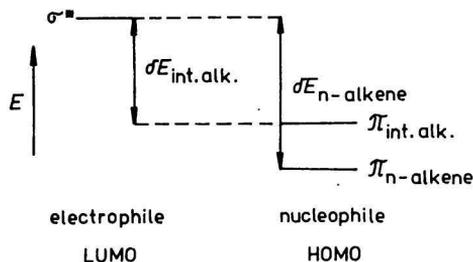


Fig. 3. Schematic energy diagram for the interaction of the nucleophile HOMO for an alkene with the electrophile LUMO.

The greater this differential stabilization, the greater the selectivity of the substrate toward the two nucleophiles. If the orbital interaction is dominated by the energy difference δE rather than the resonance integral β , then it is clear that the difference between the interaction of the $\pi_{n-alk.}$ orbital with $\sigma_{electrophile}^*$ will be larger than with $\pi_{int.alk.}$. This means that regardless of any change in the position of the transition state along the reaction coordinate, the intrinsic selectivity of substituted internal alkene toward electrophile is expected to be larger than that of the *n*-alkene. If two similar reactions (Fig. 3) have to be compared, that involving the smallest FMO gap (internal alkenes) will invoke the greatest charge transfer at the onset of the reaction, and the strongest bond-making in the transition state, and this will be the most product-like.

In order to elucidate the mechanistic similarities observed between the hydroxythallation reaction and some other electrophilic additions, comparative FMO analysis has been made. From the known ionization potentials and electron affinities, and correcting for the effect of solvation, values (E_n^* , Table 1) of the effective energy of the LUMO of the electrophiles were calculated. The results agree with Pearson's empirically derived order of softness. The appropriate energy diagram is shown in Fig. 4.

If the orbital interaction effects were to be dominant then the substrate selectivity would be expected to increase in the order $Ag^+ < Tl^{3+} < Hg^{2+} < Br^+ < Cl^+$. This order can be observed experimentally (Table 4) and it suggests that any change in the position of the transition state along the reaction coordinate brings about a minor change in selectivity.

It is indicated (Table 4) that the values of ρ^* decrease in the order chlorination $>$ bromination $>$ hydroxymercuration $>$ hydroxythallation. (In the classic and the new treatment of the reactivity there are differences between the two explanations of the Taft relationships concerning the significance of ρ^* values and the influence of substituents on the charge separation in transition state. In the old explanation ρ^* is a measure of the susceptibility of a reaction set to polar effects,

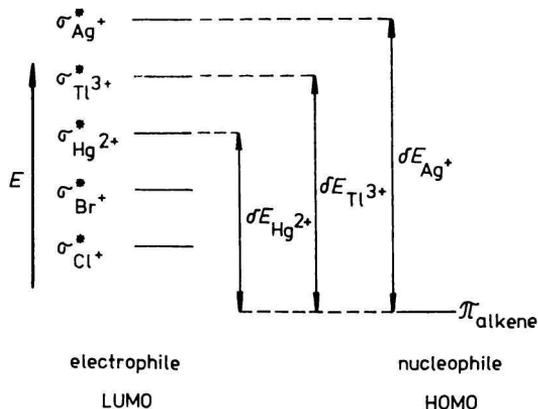


Fig. 4. Energy diagram for the interaction of orbitals of dissimilar electrophiles with an alkene.

Table 4

Summary of data for A_{dE} reactions

Reactions	Conditions	ρ^*	δ	Intrinsic selectivity	Ref.
Chlorination	Hydrocarbons, 25°C	-6.67	0.95	10 ⁷	[32]
Bromination of <i>cis</i>	CH ₃ OH, 25°C	-5.43	1.48	924 000	[28]
Bromination of <i>trans</i>	CH ₃ OH, 25°C	-5.43	0.99	924 000	[33]
Hydroxythallation	Tl ₂ (SO ₄) ₃ , H ₂ SO ₄ (aq), 25°C	-2.75	0.97	200	[15]
Hydroxymercuration	Hg(ClO ₄) ₂ , HClO ₄ (aq) 25°C	-3.3		250	[34]

whereas in the new one it reflects the sensitivity of the charge transfer [12]. Another difference between the two explanations is that in the classic approach the discussions of the influence of substituents in the transition state concern only the reaction sites, whereas, in the FMO treatment, the substrate and reagent are globally considered.) These values are reflected in the intrinsic selectivity of these substrates. This decrease in selectivity may be explained by assuming that the neighbouring group participation by the electrophilic atom becomes increasingly important in the transition state for the rate-determining step along this series. This will lead to a decreasing degree of carbonium ion character and thus to a relatively lower response to electron-releasing substituents at the double bond.

The value of 0.97 for the steric reaction constant for hydroxythallation, δ , is comparable with that obtained for bromination of *trans*-alkenes, 0.99, and chlorination, 0.95. The relative magnitudes of the $\delta \Sigma E_s$ and $\rho^* \Sigma \sigma^*$ terms for these

reactions indicate that steric factors become more important in determining the relative reactivities as participation by the electrophilic atom increases, and this further decreases the selectivity.

For Table 4 and Fig. 4 it is obvious, if we compare similar sets of reactions, that the chlorination involving the greatest absolute value of ρ^* corresponds to the smallest mean gap in FMO's. Hence the evolution of the ρ^* magnitude from one reaction series to another similar set may be regarded as a manifestation of the evolution of the transition state when the reaction set is changed; the stronger and the more product-like is the activated complex.

For a charge-controlled reaction the selectivity order, we anticipate, is identical to that based on an orbital-controlled reaction. While both these factors are likely to influence the selectivity we believe the orbital effect is dominant. This is because for the reaction of neutral molecules (Br_2 , Cl_2) charge effects are likely to be small.

In conclusion we state, while earlier MO theories of reactivity concentrated on the product-like character of transition states, the PMO theory concentrates instead on the other side of the reaction coordinate. It is concerned with how the interaction of the MO's of the starting materials influences the transition state. Both influences on the transition state are obviously important, and it is therefore important to know about both of them, not just about the one, for a better understanding of transition states, and hence of chemical reactivity. Although the problem of heavy metal ions interacting with unsaturated systems in solution has a sufficient complexity we believe the PMO theory will contribute at least partly to its study.

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