

Determination of Reactivity by MO Theory (Part 50). MO Studies on the Gas Phase Pyrolysis of Esters

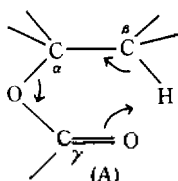
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The gas phase pyrolyses of eight esters have been studied by MNDO-MO method. In the ethylformate pyrolysis, α -methylation had a steric releasing effect whereas β -methylation had a steric crowding in the transition state; the latter, however, is over-compensated by a greater electronic repulsion resulting in a net steric releasing effect. Considerations of formal charges and geometrical changes involved in the activation led us to propose a pyrolysis mechanism in which a preequilibrium of acidic proton transfer is followed by the rate-limiting bond polarization of C_α -O bond in a cyclic transition state.

Introduction

The gas phase pyrolysis of esters is a typical example of the retroene reaction¹ and has been widely investigated experimentally.² Present status of the experimentally established mechanism of the ester pyrolysis can be summarized as follows: (i) The reaction is best described as a cyclic process that is not fully concerted, i.e., electron pairs in (A) do not move synchronously.

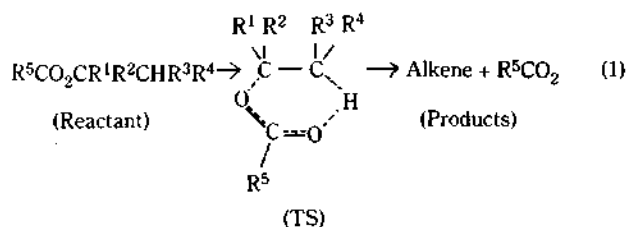


- (ii) The Hammett ρ values show that charge development in the TS is the greatest on the C_α and the least on the C_β atom.
 (iii) The C_α -O bond polarization is the rate-determining process.

In this work we have undertaken to elucidate the ester pyrolysis mechanism MO theoretically using the semiempirical MNDO method.³

Calculations

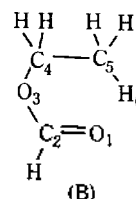
The MNDO method was used throughout in this work. Geometries of the reactants (ground states, GS) and products involved in eight ester pyrolysis, (1), were fully optimized. The transition state (TS) was located by the gradient norm minimization and was confirmed by the single negative eigenvalue in the Hessian matrix.⁴ Eight esters investigated are given in Table 1.



Heavy atom skeleton and a hydrogen atom involved in the cyclic TS are numbered as in (B) throughout in the present studies. Both cis, (B),

Table 1. Esters Studied in this Work

Designation	Non-Hydrogen substituent	Nomenclature
(I)		Ethylformate
(II)	$\text{R}^1 = \text{CH}_3$	<i>i</i> -Propylformate
(III)	$\text{R}^1 = \text{R}^2 = \text{CH}_3$	<i>t</i> -Butylformate
(IV)	$\text{R}^3 = \text{CH}_3$	<i>n</i> -Propylformate
(V)	$\text{R}^3 = \text{R}^4 = \text{CH}_3$	<i>i</i> -Butylformate
(VI)	$\text{R}^5 = \text{CH}_3$	Ethylacetate
(VII)	$\text{R}^1 = \text{F}$	1-Fluoroethylformate
(VIII)	$\text{R}^5 = \text{F}$	Ethylfluoroformate



and trans conformations of ethylformate, (I), were found to have planar structures for the heavy atom skeleton shown in (B), while the planarity was not strictly kept in the ground states of other esters studied.

Relevant formal charges and bond lengths are summarized in Table 2, and energetics are shown in Table 3 for all the compounds studied.

The Hartree-Fock energy changes in the activation, $\Delta E_{HF}^* = E_{(TS)} - E_{(GS)}$, can be expressed with changes in component energies, i.e., one-electron (orbital) energies, $\Delta(2\Sigma \epsilon_i)$, nuclear repulsion energies, ΔV_{nn} , and electron repulsion energies, ΔV_{ee} , eq(2).⁵

$$\begin{aligned}
 \Delta E_{HF}^* &= \Delta(2\Sigma \epsilon_i) + \Delta V_{nn} - \Delta V_{ee} \\
 &= \Delta(2\Sigma \epsilon_i) + \Delta(V_{nn} - V_{ee})
 \end{aligned} \quad (2)$$

Energy component analysis for the eight ester pyrolyses are summarized in Table 4.

Discussion

Changes in geometries involved in the ethylformate pyrolysis are shown in eq(3).

Two bonds that are breaking, i.e., C_4 - O_3 and C_5 - H_6 , are seen to stretch to 0.115 and 0.615 Å respectively from the GS

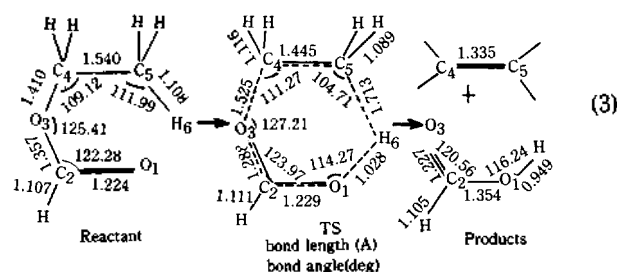
Table 2. Formal Charges of Atoms (electronic charge unit) and Bond Lengths (d in Å) for Reactants (RE) and Transition State (TS)

Molecule	Atom	Formal Charges Bond Lengths						
		RE	TS	Δq	Bond	RE	TS	Δd
I	C ₂	0.382	0.461	+0.079	O ₃ -C ₄	1.410	1.525	+0.115
	C ₄	0.174	0.295	+0.121	C ₅ -H ₆	1.108	1.713	+0.605
	C ₅	0.020	-0.685	-0.705	C ₂ -O ₃	1.357	1.288	-0.069
	H ₆	0.008	0.316	+0.308	C ₄ -C ₅	1.540	1.445	-0.095
II	C ₂	0.385	0.461	+0.076	O ₃ -C ₄	1.416	1.534	+0.118
	C ₄	0.128	0.252	+0.124	C ₅ -H ₆	1.109	1.716	+0.607
	C ₅	0.019	-0.671	-0.670	C ₂ -O ₃	1.355	1.287	-0.068
	H ₆	0.005	0.315	+0.310	C ₄ -C ₅	1.552	1.454	-0.098
III	C ₂	0.392	0.457	+0.065	O ₃ -C ₄	1.422	1.543	+0.121
	C ₄	0.103	0.211	+0.108	C ₅ -H ₆	1.107	1.703	+0.596
	C ₅	0.014	-0.652	-0.666	C ₂ -O ₃	1.353	1.287	-0.066
	H ₆	0.017	0.313	+0.296	C ₄ -C ₅	1.562	1.466	-0.096
IV	C ₂	0.382	0.466	+0.084	O ₃ -C ₄	1.411	1.500	+0.089
	C ₄	0.188	0.303	+0.115	C ₅ -H ₆	1.114	1.729	+0.613
	C ₅	-0.033	-0.729	-0.696	C ₂ -O ₃	1.357	1.293	-0.064
	H ₆	0.018	0.320	+0.302	C ₄ -C ₅	1.551	1.463	-0.088
V	C ₂	0.381	0.465	+0.084	O ₃ -C ₄	1.408	1.478	+0.070
	C ₄	0.198	0.299	+0.101	C ₅ -H ₆	1.121	1.686	+0.565
	C ₅	-0.072	-0.744	-0.672	C ₂ -O ₃	1.357	1.300	-0.057
	H ₆	0.017	0.323	+0.306	C ₄ -C ₅	1.562	1.488	-0.074
VI	C ₂	0.348	0.427	+0.079	O ₃ -C ₄	1.410	1.529	+0.119
	C ₄	0.178	0.300	+0.122	C ₅ -H ₆	1.108	1.711	+0.603
	C ₅	0.020	-0.683	-0.703	C ₂ -O ₃	1.361	1.291	-0.070
	H ₆	0.008	0.315	+0.216	C ₄ -C ₅	1.540	1.442	-0.098
VII	C ₂	0.393	0.478	+0.085	O ₃ -C ₄	1.414	1.542	+0.128
	C ₄	0.361	0.474	+0.113	C ₅ -H ₆	1.107	1.706	+0.599
	C ₅	0.011	-0.689	-0.700	C ₂ -O ₃	1.363	1.289	-0.074
	H ₆	0.017	0.318	+0.216	C ₄ -C ₅	1.564	1.463	-0.101
VIII	C ₂	0.555	0.631	+0.076	O ₃ -C ₄	1.416	1.549	+0.133
	C ₄	0.180	0.288	+0.108	C ₅ -H ₆	1.108	1.699	+0.591
	C ₅	0.018	-0.636	-0.654	C ₂ -O ₃	1.351	1.287	-0.064
	H ₆	0.015	0.317	+0.302	C ₄ -C ₅	1.540	1.441	-0.099

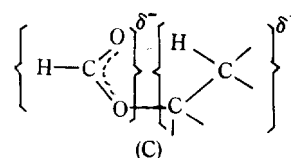
to the TS. The later bond in the TS is actually more product-like. In the activation, polarization of the C₄-O₃ and C₅-H₆ bonds causes positive charges of the carbon atoms C₄ and C₂ to increase and the C₅ atom to become more negative (Table 2), the increase in the negative charge of the C₅ being much

Table 3. Heats of formation for Reactants, Transition State (TS) and Products, and Derived Energetics, ΔE^* and ΔE_0 (Kcal/mol)

Compounds	Reactant	TS	Product	ΔE^*	ΔE_0
I	-90.969	-10.975	-77.316	79.994	13.653
II	-92.680	-14.019	-87.735	78.561	4.945
III	-88.969	-13.583	-94.713	75.113	-6.017
IV	-95.709	-22.670	-87.735	73.039	7.974
V	-96.737	-30.040	-94.713	66.697	2.024
VI	-99.033	-19.709	-86.699	79.324	12.334
VII	-139.453	-62.339	-127.234	77.114	12.219
VIII	-141.774	-61.517	-127.831	80.257	13.943



greater. Much greater bond polarization of the C₅-H₆ bond places considerable positive charge on the H₆ atom, so that the positive charge is delocalized over the entire O₃-C₂-O₁ frame in the TS. Originally in the TS, the C₄-C₅-H₆ frame was somewhat electron-deficient and the O₃-C₂-O₁ frame electron-rich, (C), since HCO₂ group is an electron attracting (-) and C₂H₅ group an electron donating (+) substituents.



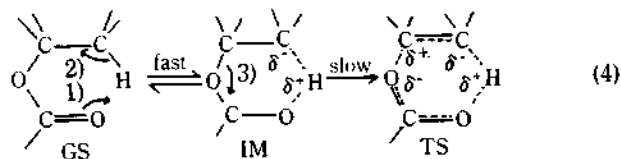
These trends of changes in geometries and formal charges in the activation are found to be general for all the compounds studied as can be seen in Table 2.

Experimentally, the Hammett ρ values indicated that the charge development on the C₄ is the greatest and that on the C₅ is the least in the TS.^{2b} This is in contrast with the formal charges found theoretically in this work (Table 2). This apparent discrepancies can be rationalized as follows: As a result of the electron demand and supply within the GS of the esters, the carbonyl oxygen, O₁, becomes highly negative and β -hydrogen, H₆, becomes quite acidic, so that a fast equilibrium, reminiscent of a fast proton transfer equilibrium,

Table 4. Decomposition of the Hartree-Fock Energy Changes, $\Delta E_{HF}^{\ddagger} = E_{TS} - E_{GS}$, (Kcal/mol)

E	Compounds							
	I	II	III	IV	V	VI	VII	VIII
$(2\Sigma f)$	-49.040	-8.659	9.659	-3.196	21.706	-51.516	-36.279	-134.799
ΔV_{nn}	2354.571	1855.106	872.369	3864.983	4148.676	2406.618	1536.949	2635.398
ΔV_{ee}	2225.540	1767.890	806.953	3788.751	4103.688	2275.948	1423.560	2420.346
$\Delta(V_{nn}-V_{ee})$	129.031	87.215	65.416	76.232	44.988	130.670	113.389	215.052
ΔE_{HF}^{\ddagger}	79.991	78.556	75.111	73.036	66.674	79.153	77.110	80.253

take place (eq 4).

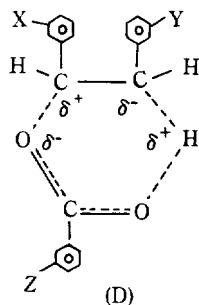


The processes (1) and (2) take place readily in a fast step forming an intermediate (IM), followed by the rate-determining process (3).^{2b}

In the IM, the negative charge builds up on the C₅ atom, since double bond formation between C₄ and C₅ is delayed until the leading event, the C₄-C₅ polarization, takes place in the rate-determining step; the processes (1) and (2) are concerted but the process (3) is not synchronous but is delayed. Since the negative charge is already built upon C₅, further increase on the process (3) will be small. The process (3) being the leading event in the activation, the charge development will be largely reflected on C₄ (positive) and O₃ (negative). These are in accord with the experimentally found relatively large negative $\rho_a(-0.66)^{2a,b}$ and positive $\rho_r(+0.26)^{2d}$ but small positive $\rho_s(+0.15)$ for the pyrolysis of ethylacetate derivatives at 600 K.

The above model (4), tacitly assumes that the interaction and hence charge transmission between C₄ and C₅ is rather inefficient so that sizable charge on C₅ is not efficiently transmitted to the electron deficient C₄ and consequently double bond formation between C₄ and C₅ takes place rather slowly in a later stage.

One way of testing the applicability of this model is to determine cross interaction constants, ρ_{ij} , between substituents X, Y and Z in (D).⁶ According to our mechanistic criteria based on the magnitude of cross interaction constants, $^{6c-e}|\rho_{XY}|$ and $|\rho_{YZ}|$ should be negligibly small,



since the two fragments with the substituents involved, i.e., X and Y, and Y and Z respectively, are not directly taking part in the rate-limiting step. The ρ_{XZ} should be the only one which will have a significant size, the two fragments with substituents X and Z being the partners involved in the rate-limiting polarization of the bond O₃-C₄.

Table 3 shows that methylations on C₄ and C₅ decrease the activation energies in agreement with the rate increases found experimentally.^{2a,g} However, reference to Table 2 reveals that progressive α -methylation, i.e., (I)→(II)→(III), leads to greater O₃-C₄ bond stretch in the TS, whereas the opposite is true for the progressive β -methylation, (I)→(IV)→(V). On the other hand, Table 4 shows that α -methylation is seen to cause steric release, i.e., $\delta\Delta V_{nn}<0$ and $\delta\Delta V_{ee}<0$, whereas β -methylation is causing steric hindrance, i.e., $\delta\Delta V_{nn}>0$ and $\delta\Delta V_{ee}>0$. This means that α -methylation will

result in the rate acceleration due to steric releasing effect in the TS, whereas β -methylation is expected to cause the steric rate retardation effect. However, in the latter, the increase in the electronic repulsion, $\delta\Delta V_{ee}$, is greater than that in the nuclear repulsion, $\delta\Delta V_{nn}$, so that the net effect is the favorable steric effect;⁵ $\delta\Delta V_{nn}>0$ and $\delta\Delta V_{ee}>0$, but $\delta\Delta(V_{nn}-V_{ee})<0$ since $|\delta\Delta V_{nn}|<|\delta\Delta V_{ee}|$ in eq(2). The lowering of the activation barrier accompanied by the α - and β -methylations is evident from these energy component changes in Table 4. We therefore conclude that although both α - and β -methylations lead to steric acceleration of the rate, the real origin in the latter is due to over-compensation of the steric crowding by a greater increase in the electronic repulsion. This is again consistent with our proposed model (4), since the temporary electronic charge built upon C₅ acts like a lone-pair,⁷ which interacts strongly with the C₅-R³ and C₅-R⁴ (eq (1)) bond-pairs; electron deficient center formed in the rate determining step on C₄ will naturally release steric repulsions of C₄-R¹ and C₄-R² bond pairs. Thus, the two carbon centers, C₄ and C₅, have quite opposite steric and electronic charge effects; momentarily C₄ is electron-deficient and releases steric crowding, while C₅ is electron-rich and steric hindrance increases in the TS.

Fluoro-substituents on C₄ and C₂ increase bond stretch of C₄-O₃ bond (Table 2) by different mechanisms; in the former, (VII), n_F-C₄O^{*} interaction, (E),^{5b,d} cause lone pair electrons of F atom to transfer into the antibonding orbital of the C-O σ^* bond as $\angle FC_4O_3$ angle decreases from $\sim 109^\circ$ to near 90° , whereas in the latter, (VIII), F atom on C₂ acts as a strong inductive electron withdrawing group (-I effect) so that the negative charge developed in the rate-limiting step on O₃ is effectively delocalized

In the case of ethylacetate, (VI), methyl group on C₂ seems to have little effect on the energetics and bond stretch of O₃-C₄ bond.

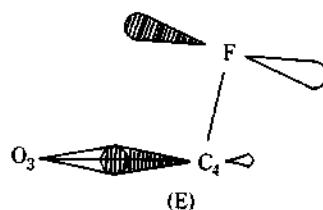


Table 3 shows that both activation energies, ΔE^\ddagger , and energy changes of reactions, ΔE_p , decrease with α and β -methylation. Lowering of activation energies by the methylation is consistent with the experimentally found faster rate of ester pyrolysis upon methylation on C₄ and C₅ atoms. The parallel decrease of ΔE^\ddagger with ΔE_p is, however, a manifestation of the Bell-Evans-Polanyi (BEP) principle.⁹ On the other hand, the decrease in ΔE_p with more product-like TS in the α -methylation series, (I)→(II)→(III), constitute a violation of the Hammond postulate; β -methylation series, (I)→(IV)→(V), is in accord with the Hammond postulate¹⁰ since the decrease in ΔE_p is accompanied by the shift to more reactant-like TS,¹⁰ i.e., less C₄-O₃ bond stretch at the TS with the decrease in ΔE_p as the β carbon is successively methylated.

Conclusion. We can conclude that both α - and β -methylations cause depression of activation barriers due to steric releasing in the TS but in the latter it owes to an over-compensation of steric crowding by a greater electron repul-

sion between the relatively large electronic charge and bond pairs at the β -carbon. The MNDO results are consistent with the TS where C_{α} -O bond polarization is the rate-determining step, which follows the pre-equilibrium involving the acidic hydrogen shift towards the carbonyl oxygen.

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A Nonlinear Theory of Diffusion-Driven Instability in the Oregonator

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A nonlinear theory presented previously is applied to the Oregonator, which is a model for the Belousov-Zhabotinskii reaction, to study instability near the critical point driven by diffusions. The result shows that the theory may be applied to an actual system.

Introduction

Theoretical and experimental studies of instability in chemically reacting systems date back at least to the early part of this century.^{1,2} Lotka¹ proposed in 1920 a simple model of autocatalytic chemical reactions which shows sustained oscillations in the concentration of the autocatalytic species when open to a flow of matter through the system. Bray² discovered this kind of sustained oscillation in an inorganic redox reaction. In 1952 Turing³ showed that stable spatial patterns can be obtained when chemical reactions are coupled to the process of diffusion. Thus, he laid the foundation for a biochemical theory of morphogenesis. Much attention has been given to that subject in the past 20 years since the dramatic phenomena in the Belousov-Zhabotinskii (B-Z) reaction sparked the interest of experimentalists and

theoreticians in chemistry and other fields.^{4,7}

Recently Lee and his coworkers⁸ have proposed a nonlinear theory for the fluctuations of intermediates in the Brusselator near the critical point caused by diffusion. The method used⁹⁻¹² is the two time scaling method which is one of the most widely used methods. In the conventional two time scaling method the whole range of time is divided into three regions of time. The initial region of time is the range of time where the linear approximation is valid. The second region is the region in which the nonlinear effect becomes important and the system approaches a steady state (or equilibrium state). The two time scaling method used⁸ is different from the conventional method in the sense that a slight nonlinear effect is included in the initial time region where the linear approximation is valid. Their nonlinear theory shows that fluctuations close to the critical point approach