J. Am. Chem. Soc. 1994, 116, 6271–6276 6271

Theoretical Studies of Thermal Syn Elimination Reactions. The Relative Rates of Ethyl Formate, Ethyl Xanthate, and Ethyl Phosphinate Eliminations

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Received August 2, 1993. Revised Manuscript Received March 7, 1994[●]

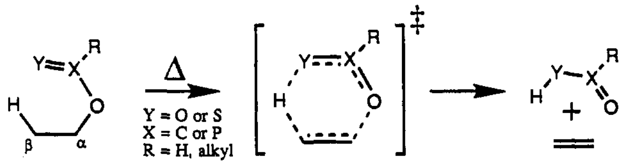
Abstract: The thermal elimination reactions of ethyl formate, ethyl xanthate, and ethyl phosphinate were examined in order to address the mechanistic details in this class of E_i reactions. The reactants, products, and transition structures were fully optimized at the RHF/6-31G* level with MP2/6-31G* single point energies calculated on the HF optimized structures. In addition, the electrostatic potential derived atomic charges were calculated for each reactant and transition structure. The results of this study show that the C_α–O bond is lengthened to a greater degree than the C_β–H bond in the transition structure and that the degree of the lengthening correlates with both calculated and experimental rate trends. It appears that the C_α–O bond dissociates in advance of the C_β–H bond in this asynchronous reaction and that the relative rates of these reactions depend primarily on the ease with which the C_α–O bond can dissociate.

Introduction

Many β-hydrogen-containing molecules are known to undergo decomposition upon heating to produce olefins. The mechanism for this transformation is generally believed to be a single-step process with a cyclic transition structure. This mechanism is known as the E_i mechanism or internal elimination mechanism and was first proposed by Hurd and Blunck.[1] One class of compounds believed to eliminate via an E_i mechanism involves a six-membered-ring transition structure, for example esters and xanthates[2] (see Scheme 1).

The concerted nature of these eliminations is supported both by first-order kinetics in the pyrolysis of esters and xanthates[2,3] and through observation of primary kinetic isotope effects that demonstrate C_β–H bond breakage in the rate-determining step in these reactions.[4] The cyclic nature of the transition structure is supported by observation of negative activation entropies[2,3] (typical ΔS values range from −5 to −10 eu) and also by the syn stereoselectivity of the reaction that has been rigorously demonstrated.[2,5] That radical inhibitors do not affect the reaction rates in ester and xanthate pyrolyses[2] argues against the involvement of free radicals in the mechanism.

Scheme 1. E_i Mechanism of 1,5 Thermal Elimination Reactions



A class of related molecules that has been shown to undergo pyrolytic decomposition to olefins includes alkyl phosphinates[6] and phosphates,[7] although the thermal eliminations of these molecules have not been examined to the same extent as ester and xanthate reactions. An interesting utilization of the phosphinate and phosphate thermal eliminations occurs in the shikimate biosynthetic pathway;[8] dehydroquinate synthase, the second enzyme in this pathway, catalyzes the transformation of D-*arabino*-heptulsonate-7-phosphate to dehydroquinate. In the second step of this transformation, inorganic phosphate is eliminated from an intermediate in a syn and intramolecular fashion.[8] This elimination, whose mechanism is reminiscent of the E_i mechanism, may be very similar to the pyrolytic reaction.

Two mechanisms have been proposed for the phosphoester eliminations, one of which is an E_i type, while the other is an E_1 mechanism involving a carbocation intermediate. The E_i process for the phosphoester thermal elimination would involve a six-membered-ring transition structure and has been included in the same class as the esters and xanthates. This class of thermal elimination has been termed 1,5 thermal elimination using the sigmatropic nomenclature.

Although the esters, xanthates, and phosphinates are believed to go through the same mechanism during thermal decomposition, their rates differ substantially. The rates of these reactions are difficult to compare due to lack of kinetic studies run under similar conditions; albeit, a qualitative measure of the reaction rates is the temperatures that are typically required to achieve decomposition to olefins in good yield. Esters react the most slowly of the three, typically requiring temperatures in excess of 500 °C.[2] Xanthates, on the other hand, can decompose to form olefins at 150 °C.[2] Phosphinates and phosphates typically require temperatures of 300–350 °C in order to form olefins.[7] Collectively the trend in rates is xanthates > phosphinates > esters, based on the typically required reaction temperatures; the causes determining these rate differences are the foci of this paper.

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[●] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

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0002-7863/94/1516-6271$04.50/0

A related question concerning these E_i reactions involves the order[9] of C_β–H and C_α–O bond dissociation in the activated complex. Evidence for an asynchronous mechanism is provided by experimental substituent effect studies that demonstrate that polar groups in the α- and β-positions affect reaction rate. For example, electron withdrawing groups placed in the β-position accelerate thermolysis rates suggesting that there is an increase of negative charge on C_β as the reaction proceeds.[10] Hammett studies on the pyrolysis of 2-arylethyl acetates indicate a ρ value of 0.2 supporting the notion that electron withdrawing groups accelerate the reaction rate.[10b] Furthermore, it appears that the α-carbon is positively charged in the transition structure, as indicated by negative Hammett ρ values (–0.66), suggesting rate acceleration by electron donation at this position.[11] The assymmetrical charges of the C–C bond in the transition structure (positively charged C_α and negatively charged C_β) imply an asynchronous reaction.[12]

Which bond breaks first in this asynchronous reaction? Taylor proposed that the C_α–O bond dissociates in advance of the C_β–H bond.[11] He based his proposal on the fact that the Hammett ρ values at the α-carbon were of larger magnitude than those observed for the β-carbon.[10] In addition, the elimination rates increase with the addition of electron withdrawing groups on the carbonyl carbon.[13] It is believed that this acceleration is due to assisted dissociation of the C_α–O bond by the electron withdrawing substituents at the carbonyl carbon.[2a] In contrast, a series of semiempirical studies utilizing the AM1 Hamiltonian[14] concluded that it was the C_β–H bond which dissociated first in the reaction.[15] In this work it was determined that the activation energies were lower for C_α–O bonds than C_α–S bonds (in thioesters) in agreement with experimental observations.[16] On the basis of bond strength (C–O bonds are stronger than C–S bonds[15]) it was concluded that compounds with the C_α–S bond would decompose at a faster rate, if the rate was determined by C_α–X (X = O or S) bond dissociation. The present study examines the question of synchronicity by looking at the E_i transition structures, wherein geometries and/or electronic properties of the transition structure can be correlated with the observed trend in rates.

Computational Methods

The thermodynamics of the 1,5 thermal elimination reactions of esters, xanthates, and phosphates were explored using Hartree–Fock molecular orbital methods. Ground state and transition structure geometries for the decomposition of ethyl formate, xanthate, and phosphinate were fully optimized with the 6-31G* basis set[17] utilizing the SPARTAN[18] or GAUSSIAN 90[19] programs. Minima and transition structures were verified via normal mode analysis. Electron correlation was considered using Møeller–Plesset perturbation theory truncated to the second order[20] (MP2) by calculation of single point energies at the RHF/6-31G* geometries. Only valence electrons were included in the correlation expansion (the so-called frozen core approximation).[21] The effects of basis set and electron correlation on the geometries obtained were explored on the ethyl formate system by re-optimizing all structures at the RHF/6-311G*[22] and the MP2/6-31G* levels, respectively. All electrons were included in the correlation calculations in the MP2 geometry optimizations and normal mode calculations.

Table 1. Calculated Energies of the Reactants, Transition Structures, and Products of the 1,5 Thermal Elimination Reactions[a]

molecule	RHF/ 6-31G*//6-31G*	MP2/ 6-31G*//RHF/6-31G*
(1) ethyl formate	–266.731 487	–267.465 671
(1a) ethyl formate TS	–266.627 305	–267.377 509
(2) ethyl xanthate	–986.871307	–987.679909
(2a) ethyl xanthate TS	–986.785435	–987.602947
(3) ethyl phosphinate	–570.173698	–570.896988
(3a) ethyl phosphinate TS	–570.080633	–570.814816
(4) ethylene	–77.976935	–78.229562
(5) formic acid	–188.725259	–189.201182
(6) dithiocarbonic acid	–908.979205	–909.424519
(7) phosphinic acid	–492.169458	–492.634238

[a] Energies in atomic units with zero point energy corrections included.

The electronic properties of the transition structures were probed by calculating molecular electrostatic potentials (MEPs). MEPs were derived at ~2000 points located on an equidensity surface enclosing ~96% of the total electron density calculated from the RHF/6-31G* wavefunction.[23] Potential derived monopoles (atomic charges) were subsequently derived from the MEPs using the fitting method of Cox and Williams;[24] this was carried out for each transition structure and reactant.

The basicity of the hydrogen accepting atom (O or S) was examined by calculating the proton affinities (PA) for each reactant[25] in the standard way.[21] PAs were calculated at the RHF/6-31G* level.

Results and Discussion

I. Activation Energies. The energies for the reactants, transition structures, and products of the 1,5 eliminations are summarized in Table 1. This approach to deriving activation energies (E_{ACT}) is sensitive to the energy of the reactants, which is potentially problematic given the flexibility of ethyl formate, xanthate, and phosphinate. Since typical reaction conditions[2] do not involve solvent, it is reasonable to use theory to locate the global minimum, which in turn has been used to calculate the reported E_{ACT} values. The conformational profile for each reactant was explored by a grid search, wherein each backbone torsion angle was driven in 15° increments, followed by optimization (RHF/6-31G*) of all internal coordinates exclusive of the driven torsion.[26] Upon locating the global minimum, the

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Table 2. MP2/6-31G*//RHF/6-31G* Relative Energies of the 1,5 Thermal Elimination Reactions[a–c]

reactant	$E_{Ts} - E_{reactant}$ (E_a)	$E_{product} - E_{reactant}$
(1) ethyl formate	55.3 (65.4)	21.9 (18.4)
(2) ethyl xanthate	48.3 (53.9)	16.2 (9.5)
(3) ethyl phosphinate	51.6 (58.4)	20.8 (17.1)

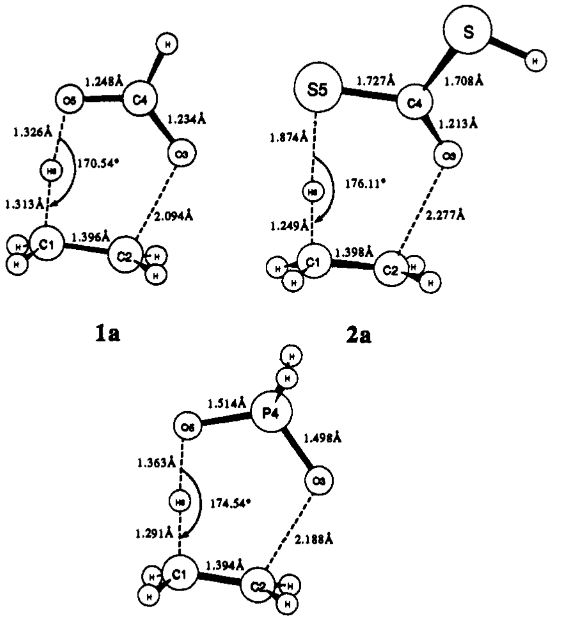
[a] Energies in kcal·mol⁻¹. [b] RHF/6-31G* energies in parentheses. [c] Zero point energy corrections included. Energy difference trends are not affected by inclusion of zero point energy corrections.

structure was allowed to fully relax; the energies for these structures are included in Table 1. Very good agreement was found between the angles predicted from the torsion analysis and the fully relaxed structures.

The energy barriers for both the forward and reverse elimination reactions are summarized in Table 2. Comparison of the calculated (55.3 kcal·mol^{-1})[27] and the experimental (44.1 kcal·mol^{-1}; gas phase)[28] E_{ACT} values of ethyl formate reveals that the calculated number is somewhat overestimated.

There are no experimentally determined E_{ACT} values for the simple ethyl xanthate and phosphinate eliminations although some have been measured for more complex systems. The E_{ACT} of 3β-cholestryl *S*-methyl xanthate was set at 33 kcal·mol^{-1} (liquid phase), or 11 kcal·mol^{-1} less than the corresponding acetate.[29] The value calculated herein is 48.3 kcal·mol^{-1} which is 7 kcal·mol^{-1} less than the calculated ethyl formate value. The sole E_{ACT} measured for the phosphinate type of thermal elimination was determined for tributyl phosphate (liquid phase) to be 40 kcal·mol^{-1} (4.1 kcal·mol^{-1} less than the formate),[30] which compares favorably with the calculated E_{ACT} for ethyl phosphinate (51.6 kcal·mol^{-1} or 3.7 kcal·mol^{-1} less than the formate).

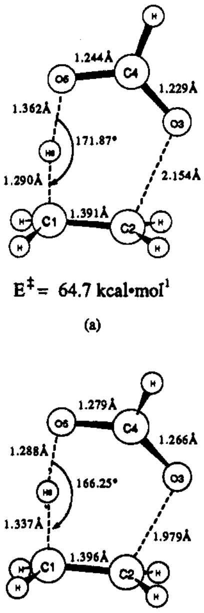
II. Transition Structures. The RHF/6-31G* transition structure geometries of the ethyl formate, xanthate, and phosphinate thermal elimination reactions are collected in Figure 1. The atoms comprising the ring in the cyclic transition structure are numbered one through six beginning with the β-carbon. Even though transition structures calculated at the HF/6-31G* level have been shown to be comparable to those calculated at the MP2/6-31G* level for similar reactions,[31] there are certain structural features of the ethyl formate elimination transition structure that vary with the level of theory and warrant mention. For example, the C_α–O bond lengths increase, and the C_β–H bond lengths decrease, as the level of theory is altered from MNDO to AM1 to RHF/3-21G.[32] These structural alterations have converged at the RHF/6-311G* level; albeit, inclusion of electron correlation during the optimization (MP2/6-31G*) results in some noteworthy structural differences. Figure 2 compares the RHF/6-311G* and the MP2/6-31G* transition structures for the ethyl formate elimination along with their respective activation energies. In contrast to the all-atom intramolecular atom–atom distance rms of 0.02 Å^2 for the 6-31G* and 6-311G* transition structures, the rms difference between the RHF/6-31G* and MP2/6-31G* transition structures is 0.08 Å^2. (For comparison, an rms difference of 0.02 Å^2 was obtained between the transition structure and itself with only a 7° rotation about the C_2–O_3 bond, while a value of 0.08 Å^2 is equivalent to the rms difference between the transition structure and itself with a 22°C rotation about the C_2–O_3 bond.) Due to the larger computational sizes of the xanthate and phosphinate, the whole series could not be examined at the higher level of theory. Nevertheless, the trends exhibited at the RHF/6-31G* level in the transition structure geometries should be illustrative given that these trends seem to persist at higher levels (i.e., for the ethyl formate example) in spite of the structural differences noted.



1a 2a

3a

Figure 1. RHF/6-31G* optimized transition structures of the thermal eliminations of ethyl formate (**1a**), ethyl xanthate (**2a**), and ethyl phosphinate (**3a**).



E‡ = 64.7 kcal·mol^1

(a)

E‡ = 55.5 kcal·mol^1

(b)

Figure 2. Optimized transition structures of the thermal elimination of ethyl formate at the (a) RHF/6-311G*//RHF/6-311G* and (b) MP2/6-31G*//MP2/6-31G* levels.

In general, the thermal syn-elimination transition structures (Figure 1) consist of a planar six-membered ring, in which the hydrogen transfer is close to linear (i.e. C_1–H_6–O_5 angles of 170-175°), in agreement with primary kinetic isotope effect measurements.[2a] Each of the transition structures is consistent with respect to the degree of lengthening of the two bonds that are dissociating in the reaction. These are compared by taking

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[32] See ref 26, pp 17–18, for a complete comparison.

Table 3. RHF/6-31G* Percent Bond Lengthening in the 1,5 Thermal Elimination Reactions[a]

	bond	
	C_α–O	C_β–H
ethyl formate	47	21
ethyl xanthate	59	15
ethyl phosphinate	53	19

[a] Percent bond lengthening = (TS bond length − reactant bond length)/reactant bond length.

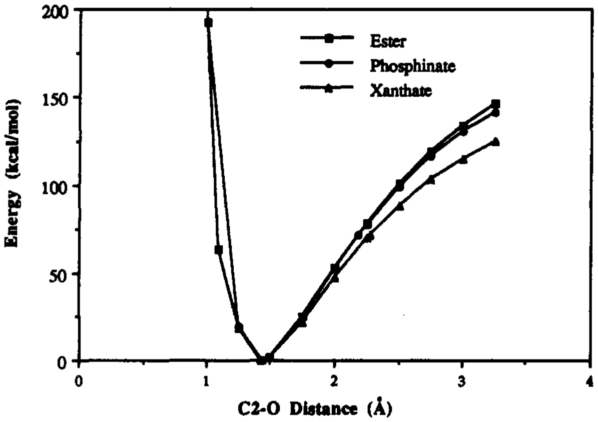

Figure 3. RHF/6-31G* C_α–O bond stretching potential energy curves for ethyl formate, ethyl xanthate, and ethyl phosphinate.

the percent lengthening relative to the reactant bond length as shown in Table 3. To put these relative bond lengthening values in perspective, it is useful to compare the lengthenings obtained in the ester decomposition reactions with those of similar concerted reactions. For example, in the retroene reaction of 1-pentene, the degree of C–H and C–C bond lengthening is 33.4% and 36.5%, respectively.[33] That the two bonds are lengthened to approximately the same degree is expected for a synchronous reaction. Additionally, the degree of lengthening is also ~35% in other concerted reactions such as the retroene of 4-hydroxy-1-butene[33] (C–H and C–C bond lengthenings are 35.7% and 34.6%, respectively) and the Cope rearrangement of 1,5-hexadiene[34] (32.9%). In contrast, the C_α–O bond is lengthened by approximately 50% while the C_β–H bond is only lengthened by ~20% in each of the 1,5 thermal eliminations examined here. This result suggests that C_α–O bond breakage precedes that of the C_β–H bond, if the lengthening of the respective bonds can indeed be related to their dissociation. This relationship was further explored by calculating the HF/6-31G* energies of the reactants at increasing C_α–O bond lengths (to 3.25 Å with 0.25-Å steps). The same procedure was carried out for the C_β–H bond and the resulting bond stretching potentials were plotted against displacement in Figures 3 and 4. This analysis permits a direct comparison of the energy–bond length relationship between the three reactants and the two bonds.[35] The C_β–H bond stretching potentials are qualitatively deeper than the C_α–O curves, in agreement with infrared spectra data.[36] Additionally, the C_α–O and C_β–H curves vary little from one another (especially at the transition structure bond lengths), suggesting that direct comparison of the degree of lengthening of each bond within the series of reactions is possible. It is important to note that the energy required to stretch the C_α–O bond to the transition structure length is ~40 kcal·mol^{-1} higher than the energy needed to stretch the C_β–H bond to its transition structure length.

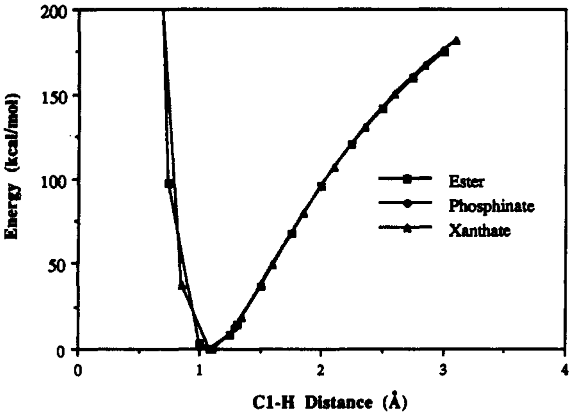

Figure 4. RHF/6-31G* C_β–H bond stretching potential energy curves for ethyl formate, ethyl xanthate, and ethyl phosphinate.

Table 4. RHF/6-31G* Electrostatic Potential Derived Atomic Charges (Q) and Transition Structure–Reactant Charge Differences (Δq) of the 1,5 Thermal Elimination Transition Structures[a]

	reaction					
atom	ethyl formate		ethyl xanthate		ethyl phosphinate	
no.	q	Δq	q	Δq	q	Δq
1	−0.65	−0.19	−0.43	−0.11	−0.58	−0.12
2	0.23	−0.28	0.11	−0.17	0.22	−0.28
3	−0.74	−0.10	−0.65	−0.36	−0.86	−0.18
4	0.91	0.03	0.80	0.28	1.35	0.06
5	−0.80	−0.14	−0.52	−0.08	−0.89	0.08
6	0.48	0.34	0.23	0.13	0.44	0.29

[a] $\Delta q = q_{TS} - q_{reactant}$.

Another structural similarity existing in each transition structure is the planar geometry of the α-carbon. This is reminiscent of the sp^2 carbon that exists in the product, ethylene. The product-like nature of the transition structure is in accord with the endothermic nature of these reactions (see Table 2).[37] The planarity of the α-carbon may also indicate carbocation-like character in the transition structure. To distinguish these two possibilities (i.e. sp^2 vs carbocation) electrostatic potential derived atomic charges of each of the transition structures and the transition structure–reactant atomic charge differences (Table 4) were examined. The results indicate that the α-carbon does indeed possess a significant positive charge in each of the transition structures and that the β-carbon is negatively charged. These findings indicate that the transition structures most resemble E_1-like intermediates.

Although the transition structures of the three elimination reactions are similar, the subtle differences in the geometries and electronic properties of each reinforces the notion that C_α–O bond dissociation occurs first in the reaction. Comparison of the percent C_α–O lengthening in each of the reactions reveals the trend of xanthate (59%) > phosphinate (53%) > formate (47%). That the trend in the degree of C_α–O bond lengthening corresponds to the trend in rates implies that the more the C_α–O bond is lengthened in the transition structure, the faster the rate of reaction. This trend implies that the C=S group stretches the C_α–O bond to a greater extent than the C=O group. A similar phenomenon was observed when electron withdrawing groups were placed on the ester carbonyl carbon.[2a,27b] Interestingly, the opposite trend is seen in the percent lengthening of the C_β–H bond, with the trend here being formate > phosphinate > xanthate. These data indicate that the more the C_β–H bond is lengthened (dissociated) the slower the reaction.

The trends in bond lengthening are mirrored in the atomic charges (Table 4). There is a buildup of negative charge (i.e. $\Delta q = q_{TS} - q_{reactant}$) on O_3 in each transition structure, consistent

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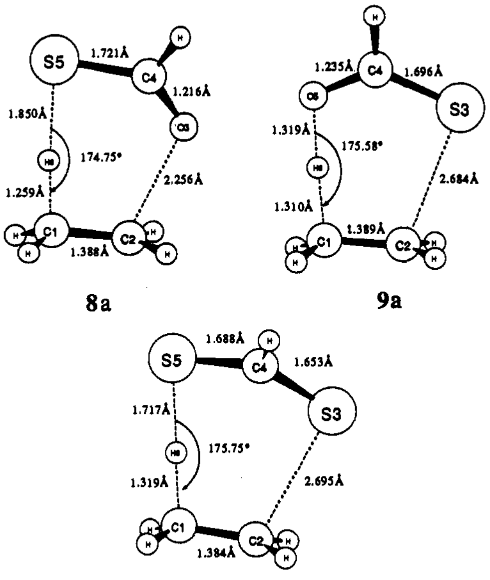
(33) Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6947–6952.

(34) Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565–8572.

(35) Single determinant methods always overestimate homolytic bond dissociation. See ref 19.

(36) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Introduction to Organic Spectroscopy*; Macmillan: New York, 1987; p 160.

(37) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.



8a **9a**

10a

Figure 5. RHF/6-31G* optimized transition structures of the thermal eliminations of ethyl thionformate (**8a**), ethyl thiolformate (**9a**), and ethyl dithioformate (**10a**).

with C_α–O bond dissociation that increases with increasing rate. This is in accord with the earlier observation that the C_α–O bond is dissociated to a larger degree in the faster reactions. As before, the opposite trend is apparent in the buildup of positive charge on the transferred hydrogen; the positive charge buildup decreases as the rate increases, in agreement with the trend in C_β–H bond lengthening.

Both charge distribution and percent bond lengthening data suggest asynchronous character in the 1,5 thermal elimination reaction. It is striking that there are many similarities between the transition structures of the 1,5 eliminations and putative E_1 intermediates that occur in a stepwise process. For the 1,5 elimination it appears that the C_α–O bond dissociates first, forming a partial positive charge on C_α, and this is then followed by abstraction of a β-hydrogen. In the series studied herein, there is a spectrum of transition structures ranging from the xanthate (the most E_1-like and the most facile) to the formate (the least asynchronous reaction and the least facile). This result is typical of reactions taking place in polar solvent; however, it is important to emphasize that the 1,5 eliminations are carried out in the absence of solvent. The gas-phase results here show an inherent bias in these systems toward being asynchronous.

The present conclusions are at odds with those reached by Lee and co-workers, who examined the thermal eliminations of ethyl formate and some thio derivatives with semi/empirical methods.[15] Lee calculated 1,5 elimination transition structures for ethyl formate, ethyl thionformate, ethyl thiolformate, and ethyl dithioformate using the AM1 Hamiltonian[15b] and found that the activation energies increased in the order ethyl thionformate > ethyl dithioformate > ethyl formate > ethyl thiolformate. These calculated E_{ACT} values are in agreement with experimental activation energy trends.[16] Because one might expect the molecules with the weaker C_α–S linkages to react faster than those with C_α–O bonds, it was concluded that the C_β–H bond dissociates first and is largely rate determining in the reaction. While the Lee study seems to contradict the present one, it is interesting that their AM1 transition structures exhibit the same trends of significant C_α–O bond lengthening relative to the reactant.[15b]

To further scrutinize the work of Lee, transition structures for the sulfur analogs of ethyl formate were repeated at the RHF/6-31G* level. The transition structures are shown in Figure 5 with their activation energies (calculated via MP2/6-31G*//RHF/6-31G*) and percent C_α–O bond lengthenings listed in Table 5. In general, these results follow the same trends as the experimental and AM1 results; however, some important differences arise between the 1,5 elimination reactions of molecules with C_α–O linkages and those with C_α–S bonds.[38] For example, comparison of the transition structures of ethyl formate and thionformate reveals the same trend as that seen with ethyl formate and xanthate, that is, the C_α–O bond is lengthened to a greater extent in the thion compound and consequently has a faster rate. On the other hand, this trend is not observed in the reactions of molecules with the C–S linkages, for instance the C_α–S bond is lengthened to the same extent in both the dithio- and thiolformate transition structures. Clearly, the 1,5 elimination transition structures involving thiol esters are not as sensitive to C_α–X bond lengthening as were their C_α–O analogs. The insensitivity may arise from the greater length of the C–S bond which places the carbonyl or thion group closer to the β-hydrogen making drastic bond deformation unnecessary or to the increased polarizability of sulfur vs oxygen. These subtle differences make it difficult to compare the 1,5 eliminations of molecules with C–O and C–S linkages. Nevertheless, both studies indicate that molecules with thion groups react faster than those with carbonyl groups and molecules with C–O linkages react faster than thiol molecules, in agreement with experimental rate trends. Again it appears that the more asynchronous reactions are more facile even in the absence of solvent.

Table 5. MP2/6-31G*//RHF/6-31G* Relative Energies and Percent C_α–X Bond Lengthening of the 1,5 Thermal Elimination Reactions of the Sulfur Analogs of Ethyl Formate

reactant	$E_{TS} - E_{reactant}$ $(E_a)^{a,b}$	C_α–X bond lengthening[c]
(8) ethyl thionformate	52.1 (58.1)	58
(9) ethyl thiolformate	60.2 (66.7)	47
(10) ethyl dithioformate	51.4 (62.5)	48

[a] Energies in kcal·mol^{-1}. For energies and structures of the reactants see ref 24, pp 36 and 39. [b] RHF/6-31G* energies in parentheses. Zero point energy corrections included. [c] Percent bond lengthening = (TS bond length − reactant bond length)/reactant bond length. X = O or S.

III. Basicities. Another possible explanation[2] for the trend in rates in the three reactions (ethyl formate, phosphinate, and xanthate) is the relative ability of C═O, P═O, or C═S groups to abstract the hydrogen, in contrast to their ability to lengthen or weaken the C–O bond in the transition structure. In the above results, it was shown that molecules with a thion group eliminated faster than those with a carbonyl and exhibited a longer C_α–O bond in the transition structure. It is also known that electron withdrawing groups on the carbonyl group accelerate the rates of reaction and lengthen the transition structure C_α–O bond.[13,27b,39] To examine the relative basicities of the three molecules' hydrogen abstracting atoms, the proton affinities of ethyl formate, phosphinate, and xanthate were calculated. The results show that the proton affinities decrease in the order phosphinate (207.9 kcal·mol^{-1}) > xanthate (201.4 kcal·mol^{-1}) > formate (192.1 kcal·mol^{-1}). This trend disfavors the proposal that the proton abstracting ability of the molecule is the overriding reason for the rate difference in these reactions.

Conclusion

The results reported herein agree with the early proposals made by Taylor[11] concerning the order of bond dissociation in thermal 1,5 elimination reactions. Taylor postulated that the C_α–O bond breaks before the C_β–H bond based on Hammett studies,[10] in

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(38) One discrepancy lies in the fact that the activation energy is slightly higher for ethyl thionformate than for ethyl dithioformate (0.7 kcal·mol^{-1}) in contrast to the experimental results; however, the experimental activation energy difference between ethyl dithioacetate and ethyl thionacetate is only 2.4 kcal·mol^{-1}.

(39) Erickson, J. A.; Kahn, S. D., manuscript in preparation.

that larger magnitude ρ values were obtained for substituents on C_α than for those on C_β. Subsequently substituent effect studies have shown that electron withdrawing groups at the carbonyl carbon accelerated the rate of elimination presumably by weakening the C_α–O bond.[13] The dramatic effects of substituents on the E_1 transition structures have been investigated further elsewhere, particularly with respect to the dehydroquinate synthase catalyzed reaction.[39] This study has shown that the C_α–O bond is lengthened to a much greater degree in the transition structure than the C_β–H bond and that there is a correlation between the degree of this bond lengthening and the rates of the reaction. On the other hand, calculated proton affinities do not correlate with rate trends. These results, taken together with data on charge distributions in the transition structure, indicate that the C_α–O bond dissociates in advance of the C_β–H bond in the elimination reaction and that the rate of the reaction is accelerated by lengthening the C_α–O bond.

Acknowledgment. This work was partially supported by a grant from the National Center for Supercomputing Applications at the University of Illinois at Urbana—Champaign in the form of a generous allocation of supercomputer time. The authors also would like to thank Dr. David Hartsough for an implementation of the electrostatic fitting procedure.