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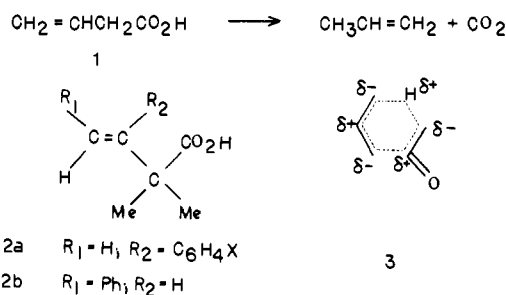
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Thermal Decarboxylation of But-3-enoic Acid. MINDO/3 Calculations of Activation Parameters and Primary Kinetic Isotope Effects

Sir:

While typical pericyclic reactions have traditionally been considered^{1,2} to take place in a synchronous manner,³ recent MINDO/3⁴ molecular orbital calculations suggest that this is rarely so. Thus the Diels-Alder reactions of ethylene with butadiene, and of acetylene or ethylene with cyclobutadiene, are predicted to involve highly unsymmetrical transition states in which one of the new bonds is essentially formed while the other is barely formed at all.^{5,6} A similar situation was found for the "allowed" conversion of benzvalene to benzene⁷ and in several chelotropic reactions.⁸ The "allowed" thermal ring opening of bicyclobutane to butadiene⁹ and the degenerate Cope rearrangement of bicyclo[2.2.0]hexane¹⁰ were predicted by MINDO/3 to be not only nonsynchronous³ but two-step³ reactions involving stable biradical intermediates. It was therefore with interest that we discovered that according to our MINDO/3 calculations the retro-ene decarboxylation of but-3-enoic acid (**1**) proceeded via a six-center transition state in a synchronous manner.

The kinetics of decomposition of **1** have been reported sev-



eral times.¹¹⁻¹³ Most of the mechanistic studies, however, owing largely to Bigley and coworkers,^{12,14-18} have been concerned with the analogous 2,2-dimethylbut-3-enoic acid derivatives **2** since these are free of complications arising from isomerization to the α,β -unsaturated acids and show a lower tendency to lactone formation.¹⁹ These studies²⁰ pointed to a synchronous reaction via a six-membered transition state for the gas phase thermal decomposition of **1** and related acids. Thus the reaction is homogeneous and first order,^{13,17} has a

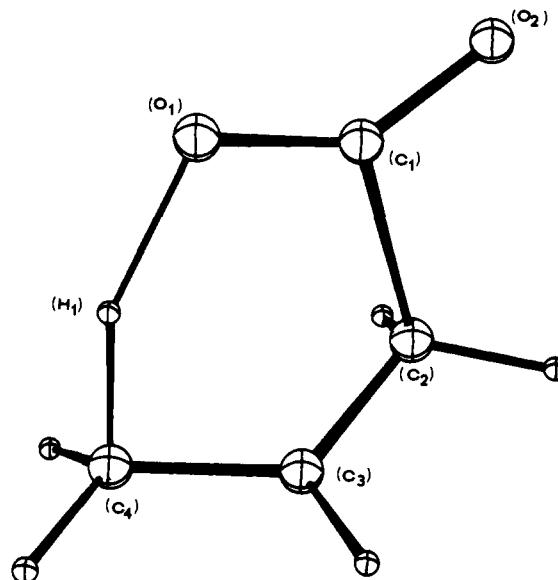


Figure 1. ORTEP plot of the calculated transition state for thermal decomposition of but-3-enoic acid.

negative entropy of activation,^{12,16,17} proceeds at the same rate in the gas as in the liquid phase,¹⁷ and shows significant deuterium^{11,15} and ¹⁴C¹⁶ kinetic isotope effects (see below). Substituent effects in a series of substituted 2,2-dimethyl-3-phenylbut-3-enoic acids **2a** have been reported,¹⁴ and, on the basis of a Hammett σ^+ correlation, suggest approximately a 20% positive charge development at C₃ in the transition state.

The transition state predicted by our MINDO/3 calculations is shown in Figure 1 and Table I and is completely consistent with these experimental data and the pictorial representation **3** of this transition state assumed by workers in this field.²⁰ Several features may be noted with respect to the "synchronicity" of this reaction. Thus the C₂C₃ and C₃C₄ bonds are of equal length (cf. 1.34 and 1.49 Å in **1**) in the transition state. The breaking bonds C₁C₂ and H₁O₁ are both substantially extended. The hydrogen atom H₁ is approximately midway between C₄ and O₁ and the OCO angle is intermediate between that in **1** (121.9) and the incipient CO₂ molecule. The geometry of Figure 1 corresponds approximately to a rather flattened boat. Consequently we assumed at first that there must be an alternative reaction path via an analogous chair conformer, but despite our most diligent efforts we were unable to locate such a transition state. In agreement with the studies¹⁴ of substituent effects, the calculations imply development of a sizable positive charge at C₃ (column 4, Table I). The calculations also bear out the "intuitive" transition state model **3** in predicting development of negative charge at C₂ and C₄. The only available data concerning substituent effects at these positions are for various methylated and phenylated^{12,16} derivatives in which it is not possible to distinguish the electronic and steric influences.

In view of our recent success in calculating molecular vibrational frequencies,²¹ isotopic shifts,²² and absolute en-

Table I. Structural Parameters and Formal Charge Distribution for But-3-enoic Acid Retro-ene Transition State (Figure 1)

Bond lengths, Å	Bond angles, degrees	Formal charges	δ^a
C ₁ C ₂ , 1.680	C ₁ C ₂ C ₃ , 106.58	C ₁ , 0.8926	0.0737
C ₂ C ₃ , 1.420	C ₂ C ₃ C ₄ , 125.24	C ₂ , 0.1640	-0.1051
C ₃ C ₄ , 1.420	C ₃ C ₄ H ₁ , 90.25	C ₃ , 0.2469	0.2255
O ₁ C ₁ , 1.248	C ₄ H ₁ O ₁ , 150.21	C ₄ , -0.1210	-0.0877
O ₂ C ₁ , 1.218	H ₁ O ₁ C ₁ , 114.01	O ₁ , -0.6143	-0.1018
H ₁ O ₁ , 1.419	O ₁ C ₁ C ₂ , 111.39	O ₂ , -0.5716	-0.0400
H ₁ C ₄ , 1.218	O ₁ C ₁ O ₂ , 139.80	H ₁ , 0.1987	-0.0591

^a Charge development; i.e., $\delta = q$ (transition state) - q (reactant).

Table II. Calculated and Experimental Activation Parameters for the Decarboxylation of But-3-enoic Acid at 650 K

	Obsd	MINDO/3	Error
$\Delta H^{a,b} (\Delta S^a)$	-6.8 ^{a,b}	-6.8 ^b (28.3) ^c	0.0 ^b
$\Delta H^{\ddagger b}$	39.3 ± 1.6 ^c	46.3 ^d	-7.0
$\Delta S^{\ddagger e}$	-10.2 ± 2.5 ^c	-13.9	3.7
k_H/k_D	2.7 ^f	2.1	0.6
k_{12}/k_{14}	1.035 ± 0.010 ^g	1.031 ^h	0.004

^a Heat of reaction (entropy of reaction) at 25 °C. The "experimental" value is derived from the known heats of formation of butanoic acid (-112.4), propene (4.9), and carbon dioxide (-94.1) by assuming that the difference in heat of formation between butanoic acid and but-3-enoic acid is equal to the mean for a number of similar pairs, CH₃CH₂X and CH₂=CHX. Thermochemical data were from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970. The entropy of reaction was calculated using the rigid rotator approximation and may therefore be in error owing to neglect of internal rotation. However, since such errors should be present in both but-3-enoic acid and propene, they should tend to cancel in the calculation of ΔS . Indeed our value agrees closely with that estimated (30.5) from group addivities: S. W. Benson and H. E. O'Neal "Kinetic Data on Gas Phase Unimolecular Reactions", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., 1970. ^b Units in kcal mol⁻¹. ^c Reference 13. ^d Corrected for zero point energy and $\Delta H^{\ddagger}_{\text{vib}}$ at 650 K: 46.3 = 51.4 - (2.66 + 2.44). ^e Units in cal mol⁻¹ deg⁻¹. ^f Reference 11. ^g Data were for PhCH=C(CH₃)CO₂H at 550 K; cf ref 15. ^h At 550 K.

tropies²³ of a number of stable molecules, we decided to apply these techniques to this transition state and derive both the entropy of activation²⁴ and the primary kinetic isotope effect, this being the first time that such an isotope effect has been calculated entirely from the molecular orbital theory. The entropy of the transition state was calculated from the MINDO/3 vibrational frequencies as it was previously,²³ except that the vibration corresponding to translation along the reaction coordinate was not included. The kinetic isotope effect was calculated²⁵ from eq 1 where $u = hc\omega/kT$ and u_{1i}

$$\frac{k_1}{k_2} = \frac{\nu^{\ddagger}_1}{\nu^{\ddagger}_2} \cdot \frac{\prod_{i=1}^{3n-6} \frac{u_{2i}}{u_{1i}}}{\prod_{i=1}^{3n-7} \frac{u^{\ddagger}_{2i}}{u^{\ddagger}_{1i}}} \cdot \frac{\prod_{i=1}^{3n-6} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}}{\prod_{i=1}^{3n-7} \frac{1 - e^{-u^{\ddagger}_{1i}}}{1 - e^{-u^{\ddagger}_{2i}}}} \times \frac{\exp\left[\frac{\sum_{i=1}^{3n-6} (u_{1i} - u_{2i})/2}{\sum_{i=1}^{3n-7} (u^{\ddagger}_{1i} - u^{\ddagger}_{2i})/2}\right]}{\exp\left[\frac{\sum_{i=1}^{3n-7} (u^{\ddagger}_{1i} - u^{\ddagger}_{2i})/2}{\sum_{i=1}^{3n-6} (u_{1i} - u_{2i})/2}\right]} \quad (1)$$

and u_{2i} refer to the light and heavy isotopically substituted reactant molecules while u^{\ddagger}_{1i} and u^{\ddagger}_{2i} refer to the corresponding transition states. ν^{\ddagger}_1 and ν^{\ddagger}_2 refer to the frequencies of the vibration corresponding to the reaction coordinate in the two transition states. The results are given in Table II together with the calculated activation enthalpy, which was overestimated somewhat. The values of ΔS^{\ddagger} and k_H/k_D were well calculated. Unfortunately the only value of k_{12}/k_{14} available¹⁵ refers to **2b** (¹⁴C at C-1) which, however, decomposes at almost the same rate as **1** at 550 K and so is likely to have similar isotope effects. The value observed for **2b** agreed with our calculated one for **1**. These results were particularly gratifying because the procedure we used is strictly valid only for the rigid-rotor-harmonic-oscillator case. Apparently the errors due to nonrigidity cancelled, as we had indeed expected.

The heat and entropy of reaction for conversion of **1** to propene and carbon dioxide are also listed in Table II. The value for ΔH agrees with an estimate from experimental data and that for ΔS with one by Benson (see Table II).

We are currently calculating several further reactions of this type to see if entropies of activation and kinetic isotope effects can be generally calculated with accuracy comparable with that achieved here. If, as we expect, this proves to be the case, such calculations will prove a powerful aid in the study of reaction mechanisms.

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Anomalous Stability Sequence of Lanthanide(III) Chloride Complexes with 18-Crown-6 in Methanol. Abrupt Decrease to Zero from Gd³⁺ to Tb³⁺

Sir:

Although the preparation of solid complexes of lanthanide(III) metal cations with cyclic polyethers has been reported,^{1,2} thermodynamic data describing these reactions in solution are not available. Furthermore, contradictory results have been presented^{1,2} as to whether or not complexes are formed between the latter members of the lanthanide series