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The Activation Parameters in Thermolysis of Norbornyl Acetates and Their Significance for Reaction Mechanisms with Cyclic Transition States.

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The transition state in the thermolysis of esters[1] has been shown[2] to involve development of cationic carbon with rupture of its bond to oxygen. In the normal case, also, the evidence[1] amply supports the six-membered cyclic structure of the transition state through which the elimination is effected. A considerable amount of rate data has been reported in consonance with these conclusions. They demonstrate[3] a continuous increase in $\underline{\Delta S^{\ddagger}}$ accompanying a structurally increased tolerance for ionic character in the $[-\overset{|}{\underset{|}{C}} - O]^{\ddagger}$ bond; that is, as we go from primary

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[1] C. H. Depuy and R. W. King, Chem. Revs., 60, 442 (1960).

[2] (a) G. G. Smith, D. A. K. Jones and D. F. Brown, J. Org. Chem., 28, 403 (1963).
(b) R. Taylor, G. G. Smith and W. H. Wetzel, J. Am. Chem. Soc., 84, 4817 (1962).

[3] J. C. Scheer, Ph.D. Thesis, University of Amsterdam, June 7, 1961.

to tertiary ester substrates. This small increase, in keeping with the small reaction (ρ) constant[2], is nonetheless regular, unlike the case of the solvolysis reaction where solvent striction effects in the transition state manifest themselves in the form of almost unpredictable oscillations in the $\underline{\Delta S}^{\ddagger}$ value[4]. Similar circumstances apparently also determine the $\underline{\Delta H}^{\ddagger}$ factor in the thermolysis reaction. Scheer[3], who has examined the rates for a very large number and variety of acetates, has demonstrated linear interdependence of $\underline{\Delta H}^{\ddagger}$ and $\underline{\Delta S}^{\ddagger}$ terms within a given class; primary, secondary and tertiary acetates, representing a wide variety of structures (in such plots), each constitute a line of slope nearly parallel to those of the other two classes. On this basis alone we should have anticipated that the activation parameters of the epimeric norbornyl acetates would adhere to the line of the secondary acetates, as indeed, substituted cyclohexyl esters do; (see Table).

While the _exo_ epimer does not strikingly depart from expectation in this regard, the _endo_ exhibits activation properties which are completely out of range of any plots described by presently known data[1,3]. Moreover, its _activation enthalpy is about 10 Kcal lower and entropy some 20 e.u. smaller (more negative)_ than the corresponding lowest values ever reported[3]. Particular significance (here) also attaches to the

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(4) A. H. Fainberg and S. Winstein, _J. Am. Chem. Soc._, _79_, 1597 (1957).

fact that, amongst the reported $\Delta H^{\ddagger}$ data in the literature of the acetate thermolysis, there is only a spread of less than 10 Kcals (at 400° ca. 37.9 → 46.9 Kcals)[3] and, amongst all the $\Delta S^{\ddagger}$ data, a spread of only about 20 e.μ. (+6.5 → -13.8 e.μ.)[3].

Furthermore, the compositions of *endo* and *exo* products are quite similar. The *exo* thermolysis product, collected at temperatures (of our rate studies) ranging from 300-360°, consisted of approximately 30 → 50% cyclopentadiene and 70 → 50% of a bicyclic hydrocarbon mixture comprised of norbornene and nortricyclene (in the approximate ratio of 8:1 at 300°). The *endo* products obtained from thermolyses in the temperature range 360-410° consisted of approximately 50 → 97% cyclopentadiene and a variable amount of the same bicyclic hydrocarbon mixture. It was also observed that both norbornene and nortricyclene subjected to increasing temperatures (from 300-360°) were increasingly converted to cyclopentadiene and a non-condensable gas, presumably ethylene; norbornene undergoes this thermolytic cleavage somewhat more readily than nortricyclene. Clearly, our results support the conclusion that both *exo* and *endo* norbornyl acetates thermolyze by the normal reaction course familiar to that of other acetates (Table) but possesses considerably different transition state (activation) parameters. It is unlikely, at the temperatures used in this study, that the course of reaction of the bicyclic esters involved prior carbon-carbon bond cleavages analogous to the retrograde Diels Alder[5]. The product compositions can only be reconciled with the occurrence of such side reactions (leading to cyclopentadiene) after the elimination of acetic acid and the formation of the elimination products, norbornene and nortricyclene.

While a slightly greater degree of transition state ionization might be indicated for the _exo_ epimer on the basis of its activation parameters, as compared to those of substituted cyclohexyl esters (see Table), the full significance of this observation is yet to be established. On the other hand, the unusual rate characteristics of the _endo_ isomer are clearly indicative of a phenomenon in the mechanism of ester thermolysis and similar processes which hasn't been recognized before. The following appears to be an attractive explanation of the origin of this conformational factor in the thermolysis reaction.

In both epimeric esters we find the acetate group and its _cis alpha_ hydrogen perfectly eclipsed. The attainment of

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(5) As a matter of fact, the greater ease of the retrograde Diels Alder, (an example of _β_ scission reactions), can be correlated with the existence of an olefin center as, for examples, is present in the dehydronorbornyl acetates and in norbornene itself. Saturated hydrocarbons, such as norbornane and its derivatives, do not commonly undergo such cleavages at the temperatures we employed in our investigations.

coplanarity of the four pertinent centers of the cyclic transition state involved in formation of the coplanar pi orbitals of the incipient double bond is a requirement which is already fulfilled in the ground state of the bicyclic esters but not in the alicyclic or acyclic comparison cases. In addition to this, however, the endo acetate has experienced great restriction in rotations about the ring carbon-oxygen bond due to the transannular endo hydrogen at C_5 and the projected hydrogen at C_4. The loss of these degrees of freedom in the ground state makes possible a more than usually well structured transition state for cyclic elimination, as characterized by $\Delta S^{\ddagger} = -33.7$ e.μ. In fact, the organization is sufficiently high to permit a degree of concertedness in bond making and bond breaking that results in a $>$ 10 Kcal lowering of the enthalpy requirements. Conversely, the exo acetate group is not as rotationally restricted in the ground state. It is even possible that anchimeric assistance to ionization[6a,b] of the $\angle{-}\overset{\prime}{\underset{|}{C}} - \underline{O}/^{\ddagger}$ bond is reflected in the somewhat more positive value of $\Delta S^{\ddagger}$, (c.f. the comparable cyclic, cholesteryl acetate in the Table). The resulting distortion of the ring in the transition state may thus have reduced the facility for cyclic abstraction of

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(6) (a) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, J. Am. Chem. Soc., 75, 147 (1953).
(b) See, however, H. C. Brown, "Strained Transition States", Special Publication No. 16 The Chemical Society, London (1962).

the *cis alpha* proton by the departing acetate anion, thereby increasing somewhat the $\Delta H^{\ddagger}$ value (as observed). Experiments presently in progress are directed toward evaluating this possible explanation of the much greater rate of thermolysis of the *exo* isomer in the region of 400°C. At this point in our work, however, one inference may clearly be drawn. The great difference in the ease of thermolytic ionization of the epimeric acetates obviously parallels behavior observed in the analogous solvolytic reaction[7,6b].

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(7) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, *71*, 2953 (1949). *ibid.*, *74*, 1147, 1154 (1952).

See Next Page for Data Table

Table of Data

Comparison of Activation Parameters on the Thermolysis of Selected Acetates at 400°

Acetate	$\Delta H^{\ddagger}$ (Kcal/Mol.)[a,b]	$\Delta S^{\ddagger}$ (e.μ.)[a,b]	References
Ethyl	46.7	-5.4	This work[a,b],8,3
Cholesteryl	42.8	-3.6	10
t-Butyl	39.1	-1.0	11
exo-Norbornyl	45.9	+1.0	This work[a,b]
endo-Norbornyl	27.8	-33.7	" "

(a) Based upon kinetic runs carried out with an apparatus similar to that described in ref. (8). The activation parameters were computed from data taken in the temp. range 300-360° at five (5) different temperatures and three runs made at each temperature. In other words, each value of the activation parameters reported as this work in the Table of Data is based on 15 rate determinations.

(b) The precision of these results may be realized by reference to the statistical parameters of both sets of determinations, (which turned out to be identical): (variance) σ^2 = 0.0007 and (multiple correlation coefficient) r = 0.996.

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(8) J. de Graaf and H. Kwart, J. Phys. Chem., 67, 1458 (1963)

(9) A. T. Blades and P. W. Gilderson, Can. J. Chem., 38, 1407 (1960).

(10) G. L. O'Connor and H. R. Nace, J. Am. Chem. Soc., 75, 2120 (1953).

(11) C. E. Rudy, Jr., P. Fugassi, J. Phys. and Colloid Chem., 52, 359 (1948).