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MINDO/3 CALCULATION OF THE POTENTIAL ENERGY SURFACE FOR $C_3H_5^* \rightarrow C_3H_3^* + H_2$ AS APPLIED TO UNDERSTANDING ENERGY PARTITIONING ACCOMPANYING FRAGMENTATION

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ABSTRACT

The semi-empirical molecular orbital method MINDO/3 was used to investigate the potential energy surface describing the loss of H_2 from the allyl cation $C_3H_5^2$. The two lowest energy processes found are the 1,2- and 1,3-eliminations and they commence by $2 \rightarrow 1$ and $3 \rightarrow 1$ hydrogen atom migrations, respectively. In the 1,2-elimination this involves isomerization to the 2-propenyl ion while in the 1,3-elimination, isomerization is to an intermediate corner-protonated cyclopropene. The reactions then proceed by H_2 elimination from the 2-propenyl ion and from protonated cyclopropene to yield the propargyl and cyclopropenyl ions, respectively. The results of the calculations are compared to previous experimental studies on metastable ions to examine the partitioning of reverse activation energy between kinetic energy of separation, and internal vibrational energy. In making such a comparison, the limitations of MINDO/3, in particular the overestimation of the stability of small ring compounds, are recognized. It is found that the reverse activation energy appears predominantly in the released kinetic energy, for both reactions. Such findings are in accord with qualitative expectations based on reaction dynamics and are discussed in relation to them. In particular, the activated complexes for both the 1,2- and 1,3- eliminations are "tight" and the potential energy surfaces are of the "repulsive" type for which it is predicted that a high percentage of the reverse activation energy will be partitioned as kinetic energy. The activated complexes are well described as species in which the daughter ion is solvated by the H₂ leaving. The incipient products are close to their equilibrium geometries, which is in accord with the observation that energy is partitioned predominantly into translation.

INTRODUCTION .

Background and concepts

Experimental information on energy partitioning in unimolecular reactions of metastable ions has been accumulated for several years [1] with the following major results.

(i) A variable fraction of the reverse activation energy of the reaction (ϵ_0^r) appears as kinetic energy of separation of the products (T). This fraction may vary considerably even for somewhat similar molecules. For example, eliminations of HF from CH₂=CHF⁺ and CH₂=CF⁺₂ are associated with large energy partitioning quotients T/ϵ_0^r , whereas a much smaller quo-

tient is observed for HF elimination from fluoroalkanes [2].

(ii) Woodward—Hoffmann rules [3] may be applied to estimate if the activation energy of a reaction will be large or small, corresponding to symmetry-forbidden or symmetry-allowed reactions, respectively. Although Woodward—Hoffmann rules do not yield detailed knowledge of reaction pathways and do not deal at all with energy partitioning, they at least provide a start. g point for characterizing the course of a chemical reaction.

(iii) For at least some reactions, the energy partitioning quotient is characteristic of the mechanism involved, in spite of variations in the ions studied. In the loss of formaldehyde from *para*-substituted anisoles via four-centered hydrogen transfer, an almost constant percentage (16%) of ϵ_0^r is partitioned as *T*. This is independent of the nature of the *para*-substituent [4]. Similarly, an energy partitioning coefficient of $25 \pm 5\%$ was measured for 1,2-elimination of HCl from various chloroalkanes [5].

(iv) A correlation appears to exist between the quotient T/ϵ_0^r and the "tightness" of the activated complex. It has been found for complex organic ions that if the activated complex forms a "tight" structure, such as a threeor four-membered ring, then T/ϵ_0^r will be larger [4,6]. As the ring size becomes larger and the activated complex assumes a "looser" structure (or the reaction occurs in a non-concerted manner), the translational energy comprises only a few percent of the energy available [7].

(v) The energy partitioning coefficient can be decreased by increasing the number of vibrational degrees of freedom in the fragmenting ion. This was observed in the secondary expulsion of a methyl group from dialkylketene ions [8]. Partitioning of excess internal energy between the fragments formed in the primary process results in decreasing energy available for secondary decomposition of the ketene ion with increasing size of the neutral lost.

(vi) Some of the experimental results are sensible in terms of simple dynamics. The energy partitioning behavior of HF elimination from the fluoroalkenes and fluoroalkanes can be considered in terms of the structures of the activated complexes [2]. The reverse reaction involves HF addition to an alkyne and an alkene, respectively. The shorter C—C bond distance in the alkyne suggests that the distance between the H and F atoms in the complex is expected to be closer to the HF equilibrium bond length in the fluoroalkenes. This qualitative description of the activated complex explains the more effective manner in which the potential energy (PE) is converted into translational energy rather than into vibrational excitation of the products for the fluoroalkene as compared to the fluoroalkane reaction.

Although concepts of the type just noted may be used as the basis for simple generalizations for understanding energy partitioning, a more complete description is the goal of PE surface calculations. A chemical reaction may be thought of as taking place on a potential energy surface which possesses certain characteristics. Working on bimolecular reactions, Polanyi has done extensive investigations in this field of reaction dynamics to see which features of these surfaces govern the partitioning of ϵ_0° into kinetic and vibrational energy [9,10]. From this work an extremely useful concept, which deals with the location of the energy barrier along the reaction path, has been developed. Potential energy surfaces which have the downhill slope situated primarily in the entry valley are commonly referred to as "attractive" and those with the downhill slope in the exit valley are denoted "repulsive". (These designations correspond in configuration to reactant-like and product-like activated complexes, respectively.) It is predicted that attractive surfaces favor vibrational excitation of the products, whereas repulsive ones result in most of the excess energy being released as kinetic energy. Many calculations have, in general terms, confirmed this statement [10].

In this work, the calculation of the PE surface for unimolecular ionic dissociations was done by the MINDO/3 method [11a]. This was chosen because it is an economical alternative to minimal basis set ab initio molecular orbital calculations, and it has provided reasonable results for the rearrangements of other carbocations in the past [11b]. MINDO/3 is specifically parameterized to reproduce experimental heats of formation, which is what is needed to characterize the thermochemistry of these reactions. Because much can be learned about energy partitioning from the qualitative nature of PE surfaces, we are more interested in sketching important features than in calculating energies and geometries to the highest possible accuracy.

The reaction $C_3H_5^{+} \rightarrow C_3H_3^{+} + H_2$

Calculations of the PE surface for this reaction are our first attempt to investigate mass spectrometric fragmentations theoretically. This reaction was chosen for several reasons.

(i) It yields a composite metastable peak [12,13]. Such peaks are widespread and have been particularly useful for ion structure and thermochemical studies.

(ii) It is a closed shell system, which facilitates the MINDO/3 calculations, especially the geometry optimizations.

(iii) Its thermochemistry is quite well known [12,13]. Tabulated values of these quantities will be given later in this report, alongside the corresponding calculated values.

On the basis of these experimental results, it is generally accepted [12-14] that the most stable form of the parent $C_3H_5^*$ ion is allyl, and that the narrower component of the metastable peak corresponds to the 1,2-elimination of H_2 to form the propargyl ion, while the wider one corresponds to the 1,3-elimination to yield the cyclopropenyl ion. Both reactions are Woodward-Hoffmann forbidden. In addition, mechanisms have been proposed for both reactions [13]. The 1,3-elimination is thought to proceed by conrotatory closure of allyl to cyclopropyl, followed by a 1,2-elimination of H_2 . The 1,2-elimination is postulated to proceed by a straightforward loss of H_2 to yield the propargyl ion. This study of the PE surface refines and extends these earlier conjectures.

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TABLE 1

Previously determined heats of formation *

	Ab initio	MINDO/3	Experiment
C ₁ H ⁺ ₅ allyl	218 [15]	222 [19]	226 [21]
$C_3H_{5}^4$, 2-propenyl	233 [15]	214	237 [22]
C₃H ⁺ ₅ , cyclopropyl	257 [15]	238	238 [22]
$C_2H_3^+$, cyclopropenyl	0 [20] **	240	257 [21]
$C_3H_3^+$, propargyl	15.3 [20] **	257	281 [21]

* All data in kcal mol⁻¹, this work unless otherwise noted. ** The relative stabilities of the $C_3H_3^+$ isomers are given.

TABLE 2

Structures of the ions discussed



Previous quantum mechanical calculations have been reported for the $C_3H_5^+$ surface [15], but none have studied H_2 elimination. However, calculations of the heats of formation of systems relevant to this work are available and are listed in Table 1; the ab initio values are included for comparison with our MINDO/3 results. A listing of the structures discussed in this paper is provided, for convenience, in Table 2.

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EXPERIMENTAL

- The MINDO/3 program was used in the same form as developed by Dewar and co-workers. The portions of the $C_3H_5^+$ PE surface describing H_2 loss were searched by means of a two-dimensional grid, for which the H-H distance (R_{H-H}) and the C-H distance (R_{C-H}) associated with one of the breaking bonds were chosen as reaction coordinates. The total energy was then minimized by optimizing the molecular geometry with respect to all other variables, no symmetry constraints being imposed. Some parts of the PE surface are not single-valued in energy for a given choice of R_{H-H} and R_{C-H} . However, by proper selection of starting geometry, it is possible to map continuous regions of interest on the PE surface using this grid search. The transition states were located approximately, using a grid mesh size of 0.1 Å for R_{C-H} and 0.05 Å for R_{H-H} . The second derivative test of McIver and Komornicki [16], a procedure used to establish that a point on a PE surface is indeed a bona fide transition state, was not used. Because both activated complexes were easily seen to be the highest energy points (within the grid mesh size) in "valleys" leading from the allyl reactant to the desired products, omission of this test was felt to be justified in obtaining approximate transition state geometries.

Because of the large number of possible pathways on the PE surface and the limitations to the usefulness of MINDO/3 for certain types of structure [11,17], the corresponding experimental results were used as a guide when the calculations were performed. The mass spectral data provided a standard by which the validity of the calculations was measured. In particular, the isomeric form of the reactant was chosen with regard to the experimental results.

RESULTS

The two lowest energy processes found on the calculated PE surface correspond to a 1,2-elimination and to a 1,3-elimination. The 1,3-elimination starts with a $3 \rightarrow 1$ hydrogen atom transfer, which is coupled with a cyclization of the three carbon atoms. The resulting ion, corner-protonated cyclopropene, may be thought of as the product of a Lewis acid—base reaction between CH₃ and acetylene. It represents a local minimum on the C₃H₅ surface. In the next portion of the mechanism, the system is forced to move "uphill" away from this minimum. Without this, however, the system would never leave the vicinity of this minimum. Such behavior can be understood because we have chosen to examine systems with sufficient internal energy to pass through such a configuration which corresponds to an isomerized form of the reactant ion and to go on to give dissociation products: The next part of the 1,3-elimination process is the formal 1,1-elimination of H₂ from the corner-protonated cyclopropene ion. This mechanism is very different from the preliminary conjecture proposed earlier for the 1,3-elimination, especially in the isomerized form of the $C_3H_5^+$ reactant.

Both the isomerization and the subsequent elimination steps can be followed along one valley in the potential energy surface leading continuously from reactants to products. The pathway is sketched semi-quantitatively in the R_{C-H} , R_{H-H} plane of the surface in Fig. 1. Figure 2 shows the approximate structure and geometry of the activated complex for the elimination. The structure is seen to resemble the product cyclopropenyl ion closely, with the eliminated H₂ being near carbon atom 1. The calculated thermochemical quantities of interest in the 1,3-elimination are given in Table 3.

The MINDO/3 results indicate that the 1,2-elimination is, in several respects, analogous to the 1,3-elimination. It occurs by isomerization of the allyl ion to 2-propenyl followed by a formal 1,1-elimination of H_2 . The pathway is sketched in two dimensions in Fig. 3 which separately shows the isomerization (a) and the elimination (b). The activated complex for both the isomerization (a) and for the elimination (b) are shown in Fig. 4. The latter is thus essentially the daughter propargyl ion, with the leaving H_2 group near carbon atom 1. The activated complex thus includes a three-membered ring



Fig. 1. Partial heat of formation grid and reaction path for the 1,3-elimination of H_2 from $C_3H_5^+$, in the R_{H-H} , R_{C-H} plane. R_{C-H} refers to that carbon-hydrogen bond of allyl which involves the end carbon from which H atom migration occurs.



Fig. 2. The activated complex for the 1,3-elimination of H_2 from allyl to give the cyclopropenyl ion.

and is very tight; the surface is predominantly of the repulsive type. The calculated thermochemical quantities characterizing this reaction are summarized in Table 3. The corresponding experimental values are included for comparison.



Fig. 3. (left) Partial heat of formation grid and reaction path for the 1,2-elimination in the $R_{\rm H-H}$, $R_{\rm C-H}$ plane. The minimum energy profile shown leads from the vicinity of the reactant toward that of the products. Part (a) shows the allyl \rightarrow 2-propenyl isomerization. $R_{\rm C-H}$ refers to the carbon-hydrogen bond from the methyl carbon in 2-propenyl; (b) shows the subsequent H₂ elimination to yield propargyl. $R_{\rm C-H}$ refers to the distance from the second (middle) carbon atom to one of the hydrogens leaving.

Fig. 4. (right) The activated complexes for (a) the isomerization ally \rightarrow 2-propenyl, and (b) for the elimination of H₂ to give the propargyl ion.

	1,2-Elimination (ally) \rightarrow propargyl)		1,3-Elimination (ally) \rightarrow cyclopropenyl)	
	MINDO/3	Experiment	MINDO/3	Experiment
Y			· · · · · · · · · · · · · · · · · · ·	
ΔH_{f} , reactant	222.0	226 [21]	222.0	226 [21]
ΔH_{f} , products	256.8	281 [21]	240.4	257 [21]
ΔH reaction	34.8	55.0 [13]	18.4	31,30.1 [13]
€o	39.2	67 ± 3.7 [12],	36.7	58 ± 1 [12],
		65.0 [13]		65.0 [13]
ε	4.4	12.0 ± 3.7 [12].	18.3	26.8 ± 1 [12].
		10.0 [13]		34.9 [13]
Т	_	6.2 ± 0.5 [12],	—	$23.9 \pm 2[12]$
		5.8 [23]		23.5 [23]

ical quantities for $C_3H_5^+ \rightarrow C_3H_3^+ + H_2^+$ MI

* All values in kcal mol^{-1} .

DISCUSSION

Thermochemistry and energy partitioning

When the calculated thermochemical quantities are compared to the experimental ones, they reproduce the qualitative aspects (such as competitive 1,2- and 1,3-elimination) properly, but the absolute agreement can be called only fair. The activation energies of the two processes are calculated to be nearly equal, as required by the experimental observation that in metastable transitions they compete in the same ratio over a wide range of electron beam energies, even down to values near the thresholds for the two reactions [13]. The MINDO/3 heat of formation of allyl agrees very closely with the mass spectral value, but this theoretical method overestimates the stabilities of the activated complexes and products. This is in accord with the known tendency of MINDO/3 calculations to overestimate the stabilities of small ring compounds [11]. A consequence of this shortcoming of MINDO/3 is that the reverse activation energy $\epsilon_0^{\rm r}$ is considerably underestimated. The calculations overestimate the stability of both the intermediate (2-propenyl) and the product (propargyl) in the 1,2-elimination so that ϵ_0^r is again uncertain and 2-properly must be considered as an intermediate in the reaction rather than as the stable form of $C_3H_5^*$. Pople and co-workers [15] calculated a 17 kcal mol⁻¹ barrier between allyl and 2-propenyl. However, MINDO/3 predicts 2-propenyl to have a lower heat of formation (214 kcal mol⁻¹) than allyl, which is contradictory to the experimental conclusions. This emphasizes the point that such calculations must always be done with reference to experimental results.

In spite of these difficulties, the calculations reproduce the experimental

observation [12,13] (Table 3) that the 1,2-elimination has by far the smaller ϵ_0^{t} . They also indicate when compared to the experimental energy release that virtually the entire reverse activation energy is partitioned as kinetic energy, for both reactions. Contributions to T from the non-fixed energy ϵ^{*} of the activated complex are expected to be small and will not change this basic conclusion [18]. The calculations relating to energy partitioning are extremely useful and entirely consistent with the observation that both activated complexes are very tight and resemble the products closely. The potential energy surfaces for both reactions are thus of the repulsive type, for which a large percentage of ϵ_0^{r} is expected to be partitioned as kinetic energy of separation of the products. As is shown below, the value of these calculations lies chiefly in the insights they provide regarding the details of the reactions.

Reaction mechanisms

Holmes et al. [12] raised the possibility that the allyl ion may isomerize to 2-propenyl before fragmentation. Our results support this suggestion with regard to the 1,2-elimination, although the competitive 1,3-elimination occurs via a different intermediate (corner-protonated cyclopropene). Other earlier suggestions [13] regarding the mechanism are not consistent with our results for either reaction channel.

A 1,1-elimination of H_2 from allyl was also investigated. The loss of two hydrogen atoms the same carbon in the allyl ion will yield $H_2C^--CH=C^{2+} \Leftrightarrow H_2C^+-CH\equiv C^+$, or else $C^+\equiv C--CH_3$, as the product ion. MINDO/3 indicates that the portions of the PE surface leading to these ions are at extremely high energies, as expected. Such instability may be reduced by the concomitant migration of a hydrogen atom to carbon atom 1. This would represent, though, either the 1,2- or 1,3-elimination mechanism, which have been examined previously in this paper.

The possible occurrence of a 1,3-elimination of H_2 from the 2-propenyl ion to yield the cyclopropenyl product was considered in detail. A continuous path was found, but the region near the activated complex (which included a five-membered ring) was of such high energy that this mechanism is not competitive with the 1,2- and 1,3-eliminations from allyl. In addition, the possible intermediacy of the 1-propenyl ion in this pathway was considered. However, MINDO/3 failed to achieve self-consistency for 1-propenyl. This primary carbonium ion does not correspond to a minimum on the C₃H₅ surface and is therefore calculated to be unstable. From ab initio calculations, 1-propenyl should rearrange to 2-propenyl with little or no activation energy [15].

An interesting detail of mechanism concerns the difference in the C–H bond lengths in the C_{H}^{H} system for the 1,2- and the 1,3-eliminations. The hydrogen molecule solvates the carbonium ion in an end-on fashion in the 1,2-case and in a side-on fashion in the 1,3-case. Dewar and Rzepa [24] have

reported an analogous end-on transition state in the 1,1-elimination of H_2 from $C_2H_5^*$. It is of some interest that as the H_2 separates further in the 1,3-reaction, it rotates away from the side-on configuration. Some of the reverse activation energy must be consumed as rotational energy in this process.

CONCLUSIONS

Four of our main findings for this reaction are as follows.

(i) The transition states for both reaction channels are described as having the incipient H_2 , with almost equilibrium bond length, close to the daughter ion moiety, also in a near-equilibrium configuration. Hence the reverse activation energy must be partitioned predominantly as translational energy. This is in accord with observed large partitioning quotients.

(ii) Both reaction profiles are extreme examples of the repulsive type. This is consistent with the expectations offered in the Introduction.

(iii) The calculated activated complexes are found to be tight rather than loose. The energy partitioning pattern is thus consistent with that expected from previous experimentally based generalizations on tight complexes.

(iv) These activated complexes can be thought of as representing the result obtained by solvating the daughter $C_3H_3^+$ ion with an H_2 molecule. Thus, polarization forces appear to be dominant in bonding the two moieties of the $C_3H_5^+$ system together. The unimolecular decomposition may be thought of as a desolvation reaction. Further work is in progress to see if these concepts can be extended to other metastable ion fragmentations with large energy partitioning quotients, and to determine if they too can be characterized as desolvation reactions of the neutral product from the daughter ion.

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