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GASEOUS CATIONS (CARBONIUM IONS)

MINDO/3 CALCULATIONS ON SINGLY POSITIVELY CHARGED PROPYL IONS

SOLIMAN H. AL-KHOWAITER and C. ANTHONY WELLINGTON*
Department of Chemistry, University College of Swansea, Swansea, Wales

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Abstract—MINDO/3 calculations have been used to study processes involving n-propyl cations and sec-propyl cations. The calculations show that the former is interconverted into the more stable sec-$C_3H_7^+$ cations with no localised minima. The lowest energy process is shown to be the production of H_2 and $C_3H_5^+$ ions from sec-$C_3H_7^+$. The results of the calculations of the decomposition of n-$C_3H_7^+$ to $CH_3^+ + C_2H_4$ and methylene + $C_2H_5^+$ are given. The calculations are generally consistent with experimental studies.

There have been several experimental studies on the processes involving propyl cations (carbonium ions) and the conflicting evidence is discussed by McAdoo *et al.*(1) It seemed possible that n-$C_3H_7^+$ could be formed without rearrangement, but the general conclusion is that the latter can isomerise to a more stable structure. Ottinger[2] has considered the elimination of H_2 from $C_3H_7^+$ ions and concludes that scrambling of isotopic species is not complete and the minimum activation energy for this process is 38.6 kcal mol^{-1}.

As regards the complementary theoretical calculations Dewar[3] has shown MINDO/3 gives satisfactory structures for these species whereas the earlier ab-initio calculations of Pople *et al.*[4] indicate that a distorted n—$C_3H_7^+$ structure is more stable than any of the protonated cyclopropane structures. This contradicts the experimental evidence which is in favour of the sec-$C_3H_7^+$ and Pople *et al.*[5] have found it necessary to include d-functions on carbon in their basis set to obtain results consistent with the experimental observation. Thus we have used MINDO/3 since it appears to give satisfactory structures and heats of formation without the need to introduce any additional modifications.

RESULTS AND DISCUSSION

Calculation of ground state geometries of $C_3H_7^+$. The initial geometry parameters for n-$C_3H_7^+$ were based on the structure of propane[6] and are shown in Table 1. It was not possible to do a complete geometry optimization because of the isomerization which occured (see later). It was however possible to do a restricted optimization on the following basis, the $C_{(3)}$–$H_{(4,5,6)}$ bond lengths and $C_{(2)}$–$C_{(3)}$–$H_{(4,5,6)}$ bond angles were held to be the same during our calculations, the same restrictions have been applied on C–H bonds and HCC bond angles correspond to the hydrogen atoms connected to C_1 and C_2. The heat of formation obtained was 204.11 kcal mol^{-1} (experimental value is 208 kcal mol^{-1}).[7]

When the n-$C_3H_7^+$ structure **1** of Fig. 1 was subjected to full geometry optimization, it went to a form similar to that shown in structure **2** Fig. 1, the calculated heat of formation is 184.00 kcal mol^{-1}. The geometry optimization in MINDO/3 produces this substantial structure change and the resulting structure **2** is almost identical to **3** which is the optimized structure for sec-$C_3H_7^+$. This shows that there is no localised minima, that is no structure with any significant energy between **1** and **2**. This would seem to eliminate the possible stability of a hydrogen bridged structure.

The optimized structure of sec-$C_3H_7^+$ was established next, this is **3** of Fig. 1. The calculated heat of formation of sec-$C_3H_7^+$ was found to be 184.03 kcal mol^{-1} and this agrees quite well with experiment (191.7 kcal mol^{-1})[8] and with a previous theoretical calculation (184.3 kcal mol^{-1}).[3] This confirms that sec-$C_3H_7^+$ is the most stable form of propyl ions, and n-$C_3H_7^+$ ions isomerize to sec-$C_3H_7^+$ without activation, and with no structures intermediate between **1** and **3** with localised minima.

This indicates that n-$C_3H_7^+$ ions will isomerize into sec-$C_3H_7^+$ ions. This suggestion is inconsistent with the conclusion of McAdoo *et al.*[1] However, there have been

Table 1.

(C–C)	1.533 A°	CCC	112.0°
(C–H) (CH$_3$)	1.097 A°	HCH (CH$_3$)	107.9°
(C–H) (CH$_2$)	1.096 A°	HCH (CH$_2$)	107.8°

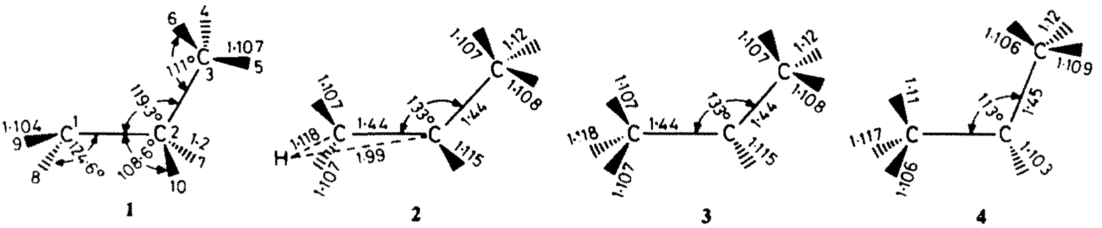

Fig. 1. The figure shows the ground state geometries for the n-propyl cation (**1**), fully optimized n-propyl cation (**2**); sec-propyl cation (**3**); and sec-propyl cation (**4**) with geometry restrictions.

suggestions that n-$C_3H_7^+$ ions can be formed at higher energies and since a simple bond breaking reaction is likely to occur at a substantial rate, we have investigated by MINDO/3 calculations the energies of the likely simple bond breaking process.

Since the ΔH_f of H^+ is very much larger than that of CH_3^+ and $C_2H_5^+$ it was considered improbable that a process producing $C_2H_6 + H^+$ would in any way compete with those producing CH_3^+ or $C_2H_5^+$. Thus no calculations were performed on the former process. If of course there were a substantial activation energy of the latter two processes then that producing H^+ and $C_3H_6^+$ could compete. Thus while ΔH for the latter processes can be estimated, no information is available as whether the processes involve activation energies, the following give the results of the calculations.

Decomposition of n-$C_3H_7^+$. Two possible reaction pathways of n-$C_3H_7^+$ have been considered, and these are given in eqn (1) along the activation energies (kcal mol^{-1}) that have been calculated using MINDO/3.

$$n\text{-}C_3H_7^+ \begin{array}{l} \xrightarrow{76.9} CH_3^+ + C_2H_4 \text{ (a)} \\ \xrightarrow{112.6} :CH_2 + C_2H_5^+ \text{ (b)} \end{array} \qquad \text{Eqn (1)}$$

The $C_{(2)}$–$C_{(3)}$ and $C_{(1)}$–$C_{(2)}$ distances were used as a reaction coordinates for (a) and (b) respectively. The energy profiles are shown in Figure 2 and plots of interesting geometries along the reaction coordinates are shown in Fig. 3.

At reaction coordinates values equal to 9A°, the products of reactions of 1a and 1b no longer interact and the corresponding heats of formation are 279.5 kcal mol^{-1} and 314.9 kcal mol^{-1} respectively. The heats of formation of all the products have been calculated separately using MINDO/3, the results are compared with experiment in Table 2.

From Table 2 the calculated heat of formation for CH_3^+ and C_2H_4 in reaction (1a) is equal to 279.5 kcal mol^{-1} which predicted successfully in this study, and agrees quite well with that calculated from the experimental data 272.49 kcal mol^{-1}. Similarly for reaction (1b) heats of formation are calculated to be 314.43 kcal

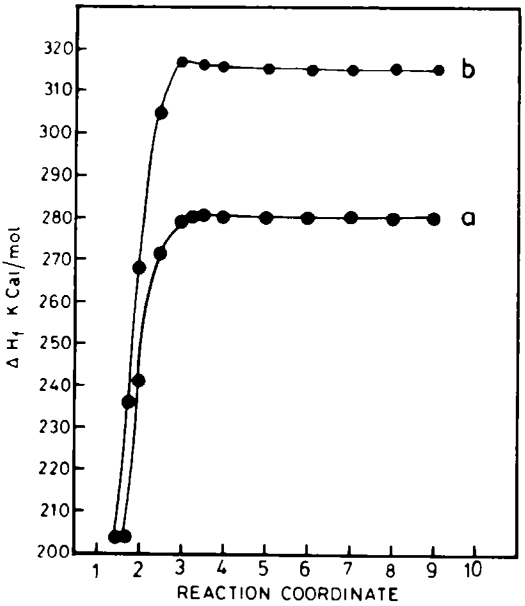

Fig. 2. Plot of heat of formation against reaction co-ordinate, (a) for the decomposition of n-propyl cation to CH_3^+ and C_2H_4; (b) for the decomposition of n-propyl cation to: CH_2 and $C_2H_5^+$.

Table 2.

Compound	MINDO/3	Experiment
CH_3^+	260.3	260.0
C_2H_4	19.2(9)	12.49(11)
CH_2	100.2(10)	101(12)
$C_2H_5^+$	214.23	219.0(6)
n-$C_3H_7^+$	204.11	208.0
sec-$C_3H_7^+$	184.05	191.7

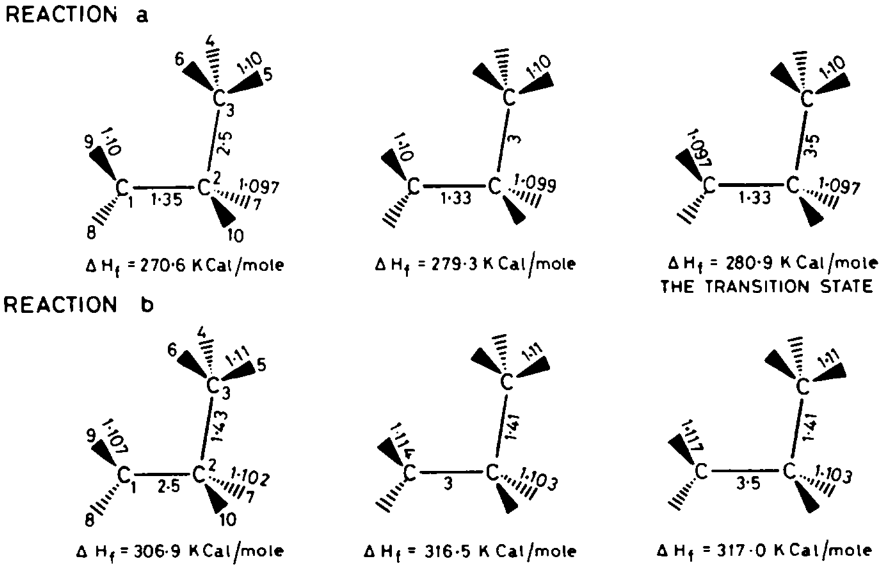

Fig. 3. Intermediate structures for the energy profile (a) for the decomposition of n-propyl cation to CH_3^+ and C_2H_4, (b) for the decomposition of n-propyl cation to: CH_2 and $C_2H_5^+$. The figure shows the reaction co-ordinates, interatomic distances (Å) and heats of formation calculated by MINDO/3.

mol^{-1} and 320 kcal mol^{-1} in this study and from the experimental data respectively.

MINDO/3 calculations for ions are very reasonable and are likely to be less discrepant than that for ethylene. For the formation of CH_3^+ and C_2H_4 the largest discrepancy is due to the high MINDO/3 value for ethylene. The n-$C_3H_7^+$ calculated value is a little different from the experimental value but is satisfactory within the uncertainties in the structure of the ion. Due to some compensation of discrepancies the ΔH calculated value for process (b) is in a good agreement with the thermochemical values from the lieterature. It is clear that the enthalpy changes for (a) and (b) are equal or nearly equal to the activation energies for the processes and that in order for the processes to occur the n-$C_3H_7^+$ ions would have to have substantial amounts of excess energy, to decompose to CH_3^+ and $C_2H_5^+$. These ions are thus only likely to be formed at high mass spectrometric energies.

Since n-$C_3H_7^+$ ions appear to isomerise without activation energy to the more stable sec-$C_3H_7^+$ ions, we considered some of the processes which are likely to occur with this ion. Processes (a) and (b) above will involve rearrangement and possibly extra energy and sec-$C_3H_7^+$ has a lower (by 20 kcal mol^{-1}) ΔH_f. These processes are less favourable by at least this amount. These are thus unlikely to be important, and the more likely process would be the elimination of a molecule such as H_2 or CH_4.

Decomposition of sec-$C_3H_7^+$. Since most of the latest experimental[1,2] and theoretical studies[3] have reported that n-$C_3H_7^+$ ions isomerize to sec-$C_3H_7^+$ ions without activation and they predicted sec-$C_3H_7^+$ is the most stable form in propyl ions. Ottinger supported by McLafferty *et al.* have reported that the decomposition of labelled sec-$C_3H_7^+$ ions in the metastable drift region occurs according to reaction (2) to yield hydrogen molecule and $C_3H_5^+$ ions.

$$\text{sec-}C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \qquad (2)$$

In this investigation of this reaction, $C_{(1)}$–$H_{(9)}$ and $C_{(3)}$–$H_{(6)}$ bond lengths were used as reaction coordinates (see Fig. 1 structure 3). At initial attempt sec-$C_3H_7^+$ structure was restricted so that the CCC angle was kept constant at 113°, nearly the same as in propane ($<CCC = 112 \pm 1°$).[6] This restriction brought the heat of formation up to 191.2 kcal mol^{-1} which is nearly the same as that found by experiment (191.7 kcal mol^{-1}).[8]

An endothermic pathway to H_2 and $C_3H_5^+$ is found as the reaction coordinates distances are systematically increased. When the reaction coordinates reached 1.55 Å the CCC angle was allowed to optimize along with the other geometry parameters, to determine the best transition state. The transition state geometry with several points along the reaction coordinates are shown in Fig. 4 and the energy profile is shown in Fig. 5. By reaction coordinates 1.65 Å, the transition-states have been achieved, the $H_{(6)}C_{(3)}C_{(2)}$ and $H_{(9)}C_{(1)}C_{(2)}$ bond angles have decreased to 73.7° and 102° respectively as shown in Fig. 4. In particular the hydrogen atoms $H_{(9)}$ and $H_{(6)}$ moved close to each other and they were 0.74 Å apart, where this distance corresponds to the bond distance for the hydrogen molecule. In other words the hydrogen atoms start to combine forming hydrogen molecule, while C–H bonds dissociate to form $C_3H_5^+$ cations. Once the transition-state is passed the sec-$C_3H_7^+$ decomposition to H_2 and $C_3H_5^+$ occurs.

At the final point of this reaction the hydrogen and $C_3H_5^+$ cation are separated by 4.0 Å, and the final heat of formation is 226 kcal mol^{-1}. Experimental work estimated that the heats for formation of $C_3H_5^+$ and H_2 are respectively 226[13] and zero[11] kcal mol^{-1}, which sum to 226 kcal mol^{-1}, agrees very well with that predicted sucessfully in this work.

Activation energy for H_2 *loss from* sec-$C_3H_7^+$. Figure 5 shows the reaction profile for the complete reaction. On the basis of this profile the activation energy is 61 kcal mol^{-1}, on the basis of the sec-$C_3H_7^+$ ground state with the geometry restriction on the CCC angle of 113°. On the basis of the sec-$C_3H_7^+$ calculation with no restriction the activation energy will be 7 kcal mol^{-1} higher. There is no experimental value for this minimum for H_2 elimination. However, McAdoo *et al.*[1] have concluded that the minimum activation energy for the elimination of H_2 is 38.6 kcal mol^{-1}. This based on the measurement of 0.2 eV[14] for the kinetic energy of the metastable ion produced during the elimination of H_2 from sec-$C_3H_7^+$

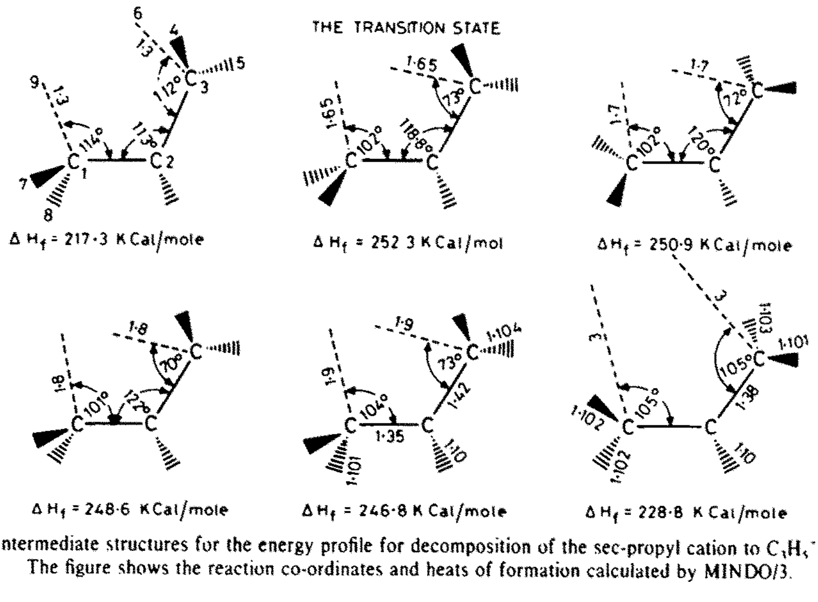

Fig. 4. Intermediate structures for the energy profile for decomposition of the sec-propyl cation to $C_3H_5^+$ and H_2. The figure shows the reaction co-ordinates and heats of formation calculated by MINDO/3.

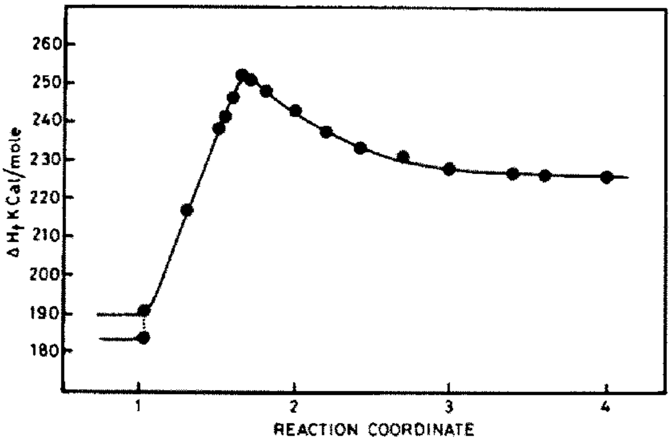

Fig. 5. Plot of the heat of formation against reaction co-ordinate for decomposition of the sec-propyl cation to $C_3H_5^+$ and H_2.

and the experimental thermochemical data for sec-$C_3H_7^+$ and $C_3H_5^+$. It is however unlikely that MINDO/3 calculations are in serious error, since in the previous calculations the errors were considerably lower than the difference between the present calculated and experimental values. It is possible that in the experimental work of McAdoo *et al.* the $C_3H_5^+$ ions were not formed in their ground states and that the measure kinetic energies of the products are lower than those which would be observed for the formation of H_2 and $C_3H_5^+$ in their ground states. It is to be noted that the calculated value for ΔH_f for $C_3H_5^+ + H_2$ at 4 Å separation (226.0 kcal mol^{-1}) is in excellent agreement with observed value (226 kcal mol^{-1})[13] for the formation of $C_3H_5^+$. Moreover it would be surprising if the reaction of $C_3H_5^+$ with H_2 had no activation energy. McAdoo *et al.* do quote their activation energy for H_2 elimination from sec-$C_3H_7^+$ of 38.6 as a minimum value and perhaps these differences may be resolved with further experimental work on sec-$C_3H_7^+$.

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