
Ab Initio Characterization of Ring-Opening H-Transfer In Ionized Cyclopentanone: Similarity to Ion-Neutral Complex-Mediated Alkane Eliminations

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Ab initio procedures were used to characterize the transition states for α -cleavage and subsequent H-transfer starting with ionized cyclopentanone (**1**). The objective was to determine whether the parts of the ion disconnected by the bond cleavage remain in close association through the H-transfer. The transition state for C-C bond cleavage is close in energy to the resulting distonic ion, which is a stable species, and far in geometry from any transition state involving H-transfer. We find no evidence for any concertedness or "quasi-concertedness" in this reaction. Ring-opening H-transfer in **1** and ion-neutral complex-mediated alkane eliminations are compared. © 1996 American Society for Mass Spectrometry (*J Am Soc Mass Spectrom* 1996, 7, 1251-1254)

In 1983 Hammerum and co-workers [1] suggested a similarity between the elimination of alkanes from small ionized alcohols, ketones, and amines (Scheme I) and the H-transfers preceding the loss of alkyl radicals from ionized cyclic compounds containing the same functional groups attached to the ring. Considerable evidence generated since indicates that most alkane eliminations by ions in the gas phase take place by bond cleavage to intermediate ion-neutral complexes followed by H-transfer between the partners [2]. In particular, ab initio studies indicate that bond cleavage and H-transfer are discrete steps in complex-mediated eliminations [2d, g, h].

Alkyl losses from cyclic ions with functional groups attached to the ring take place following α -cleavage H-transfer [3] (Scheme II). Whether the ring opening and H-transfer are somehow concerted or "quasi-concerted" [4] or take place in completely separate steps hitherto has not been addressed directly.

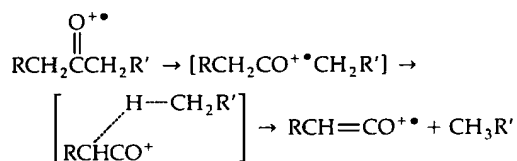
However, we have long been of the opinion that nearly all elementary reactions of ions in the gas phase take place in fully discrete steps [5, 6]. We previously interpreted the low energy reactions of ionized cyclopentanol assuming this viewpoint, depicting its initial reactions as being analogous to the first two steps in Scheme II [7]. The recent demonstration of Kenttämää and co-workers [8] that **2** is stable is consistent with the loss of ethyl from **1** taking place through

three successive steps. However, whether some association between the charge site and the radical site persists between the C-C bond cleavage and H-transfer cannot be resolved experimentally and has not been addressed by theory in **2** or any similar system. Therefore we used ab initio methods to explore whether or not alkyl losses from cyclic ions are linked by the reactant CH_2 remaining near the H it abstracts between the bond cleavage and H-transfer. We also wished further to characterize **2**, whose stability [8] is somewhat surprising because there would be relatively little angle strain in five-membered ring **1**, and such rings form more rapidly than those of any other size [9].

Results and Discussion

Ab initio energies [UHF/6-31G (d)//UHF/6-31G (d) level of theory] obtained using the *Gaussian 94* suite of programs [10] for equilibrium geometries and transition states for bond breaking and H-transfer in **1** are given in Table 1. According to those calculations, the C1-C5 bond stretches smoothly until it passes a transition state for bond breaking (Figure 1), with no concurrent interaction between C5 and an H on C2. The distance between C5 and H2 also increases steadily with the C1-C5 distance. The C1-C5 bond is shorter in the transition state [$R(\text{C1-C5}) = 2.28 \text{ \AA}$] than in the equilibrium ground state of **2** [$R(\text{C1-C5}) = 2.88 \text{ \AA}$], and the transition state is about 10 kJ mol^{-1} higher in energy than the fully ring-opened species (61.2 kJ mol^{-1} versus 50.8 kJ mol^{-1}), providing evidence that

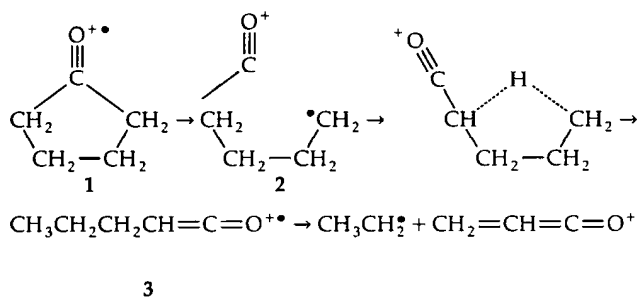
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Scheme I.

2 is indeed a stable species. The equilibrium geometry of 2 is given in Figure 2. To confirm that we had actually found the transition state (TS) for 1 → 2, we also located this transition state at the UHF/6-31G + (d) and UHF/6-311G(d) levels of theory. The C1-C5 distance in TS(1 → 2) changed by only about 0.02 Å at these higher levels of theory.

A separate transition state for transfer of a H from C2 to C5 (Figure 3) was found at a substantially higher energy (161.8 kJ mol⁻¹) than that for bond breaking. Although we did not attempt to find a transition state for a concerted bond cleavage H-transfer, given that the C5-H2 distance in TS(1 → 2) is 3.26 Å and is 1.37 Å in TS(2 → 3), a concerted transition state would probably be at much higher energy than either of the ones characterized [11]. Thus we conclude that ring



Scheme II.

opening and H-transfer are completely separate steps. However, the intermediate 2 is "C-shaped" in its equilibrium geometry (Figure 2), rather than being fully extended, suggesting some tendency for the charge to attract the free end of the open chain, as occurs between the partners in an ion-neutral complex. However, this effect would probably be insignificant at the energy of TS(2 → 3), since the energy of the latter is well above that of extended 2 (Table 1).

According to our results, 2 is a stable species 50.8 kJ mol⁻¹ higher in energy (previous MP2/6-31G(d)/6-31G(d) results = 33 kJ mol⁻¹ [8]) than 1 and isolated from it by a barrier only about 10.4 kJ mol⁻¹ in height. This is not inconsistent with the conclusion of Kenttämää and co-workers [8] that 2 formed by the addition of ketene to ·CH₂CH₂CH₂CO⁺ with subsequent loss of CO is a stable species that maintains its identity in the gas phase. However, the well depth we find is surprisingly shallow for the whole population of 2 to be isolated from the more stable 1. This suggests either that our relative energies are somewhat in error or that there is very little excess energy in the ions created by ion-molecule reactions. It is also possible that the geometry we found for 2 is not a global minimum, although a partially extended (not given) and the fully extended (Table 1) forms were higher in energy than our most stable geometry.

The ion-dipole and ion-induced dipole forces holding the partners in an ion-neutral complex together have been described by Morton as a "leash" [12]. In 2 and other ring-opened ions in the gas phase, the carbon chain plays the same role. Thus, as previously suggested [1], there is indeed a strong similarity between the two processes with the reactive sites being "leashed" together. However, we find no evidence for preservation of a more specific association between the sites of C-C bond breaking and the H-transfer in 2 at

Table 1. Ab initio characterization of α-cleavage H-transfer in ionized cyclopentanone^a

Species	R(C1-C5) (Å)	R _{min} (C5-H2) (Å)	E (hartrees)	ZPE ^b (kJ mol ⁻¹)	ΔE (kJ mol ⁻¹)	ΔE ZPE ^c (kJ mol ⁻¹)
CH ₂ CH ₂ CH ₂ CH ₂ C=O ⁺ (opt 1)	1.5123	3.0796	-268.572039	301.0	0.0	0.0
	1.7000	3.1598	-268.563161		23.3	
	1.9000	3.2341	-268.551997		52.6	
	2.1000	3.2598	-268.547479		64.5	
	2.3000	3.2528	-268.546180		67.9	
·CH ₂ CH ₂ CH ₂ CH ₂ C=O ⁺ (2)	2.877	3.3739	-268.549379	292.6	59.2	50.8
Extended 2	4.999	4.212	-268.545263		70.3	
CH ₃ CH ₂ CH ₂ CH=C=O ⁺ (3) ^d	4.909	1.084	-268.555631	294.5	43.1	36.6
TS(1 → 2)	2.281	3.2561	-268.546167	294.3	67.9	61.2
TS(2 → 3)	3.505	1.3744	-268.504043	284.3	178.5	161.8

^a Geometries and energies were all calculated at the UHF/6-31G(d) level of theory. ZPE = zero point energy.

^b Scaled by multiplying by 0.89

^c Corrected for zero point energy (Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem.* 1981, 15, 269).

^d A second stable configuration was found for 3 at a 1.4 kJ mol⁻¹ higher energy.

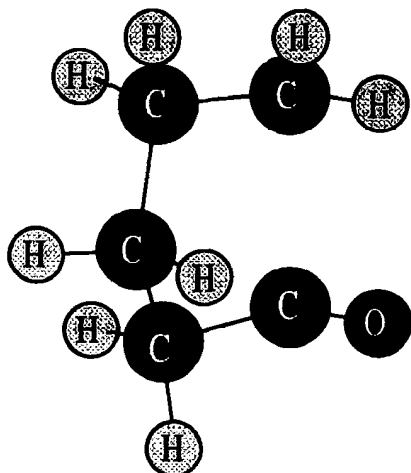


Figure 1. Transition state obtained at the UHF/6-31G(d) level of theory for the opening of the ring in 1 to form 2. Note the lengthened C-C bond.

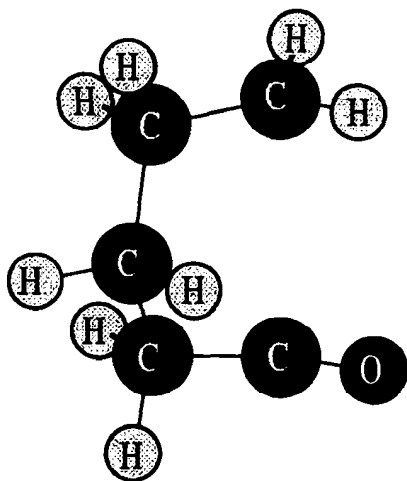


Figure 2. The equilibrium geometry found for 2 at the UHF/6-31G(d) level of theory. This geometry is somewhat more stable than more extended ones in which the CO and terminal CH₂ are away from each other.

the energy at which H-transfer occurs. Ab initio geometries for transition states for alkane eliminations [2d, g, h] suggest that the partners "reorient" fairly freely between bond cleavage and H-transfer in those reactions.

Computations

All computations were carried out using the Gaussian 94 suite of programs [10] on a Cobra Carrera computer. All structures and vibrational frequencies were optimized with the opt = tight criterion.

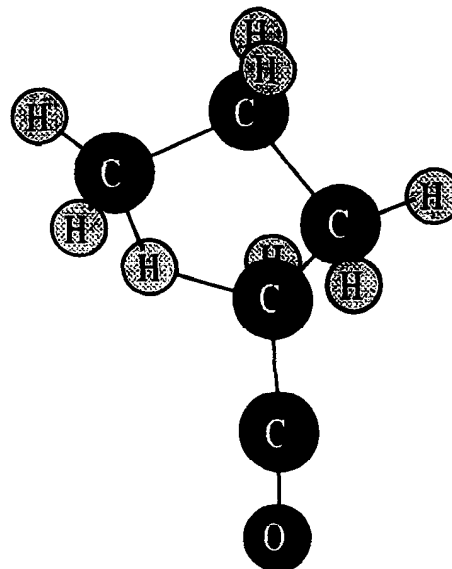


Figure 3. UHF/6-31G(d) transition state geometry for the H-transfer converting 2 to 3. The substantial distance between C1 and C5 is consistent with the bond between them being fully broken before the initiation of H-transfer.

Acknowledgment

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