A Non-empirical LCAO–MO–SCF Study on the Site of Protonation of Keten

By **Alan C. Hopkinson,** Department of Chemistry, York University, Downsview, Ontario, Canada

β-Carbon-protonated keten (the methyloxocarbenium or acetyl ion) is computed to be more stable than its α-carbon- or oxygen-protonated isomers. The proton affinities of C_2O^{2-}, HC_2O^-, and H_2C_2O are computed to be 651·7, 448·4, and 216·8 kcal mol^{-1} respectively.

THE addition of alcohols,[1] amines,[2] and some carboxylic acids [3] to ketens occurs through nucleophilic attack at the α-carbon atom with synchronous addition of a proton to the β-carbon atom. Addition of the stronger carboxylic acids follows a different mechanism, being initiated by a rapid proton transfer either to the oxygen or β-carbon atom, followed by a rate-determining reaction between the resulting carbonium ion and the carboxylate anion.[3] In this mechanism isotope effects again favour addition of the proton to the β-carbon atom.[3] Finally, in the addition of hydrogen halides to dimethylketen the reaction is found to be second order in acid and thus is interpreted as initial oxygen protonation, followed by an acid catalysed rearrangement which essentially transfers the proton to the β-carbon atom.[4] More recently it has been shown that the acetyl ion is the sole product of the protonation of keten in superacid, although the oxygen-protonated isomer is considered a possible intermediate in its formation.[5]

In an attempt to resolve the problem of the site of protonation of ketens non-empirical LCAO–MO–SCF calculations have been carried out on the parent keten molecule and on the three possible isomers of protonated keten (I)—(III)

The calculations used an 8^s3^p (C and O) and 3^s (H)

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[1] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 889.

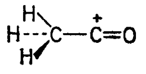
[2] J. M. Briody and D. P. N. Satchell, *Tetrahedron*, 1966, **22**, 2649.

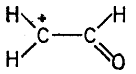
[3] J. M. Briody, P. J. Lillford, and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 885.

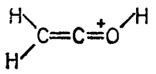
[4] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1968, 897.

[5] G. A. Olah, K. Dunne, Y. K. Mo, and P. Szilagyi, *J. Amer. Chem. Soc.*, 1972, **94**, 4200.

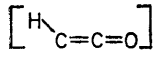
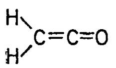
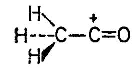
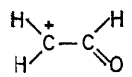
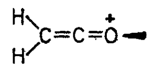
basis set of Gaussian-type functions, contracted to 3^s, 1^p, and 1^s respectively.[6] They were carried out on an IBM 360/65 computer, using the IBMOL–IV program.[7] The geometry of the acetyl ion (I) was taken from the literature.[8] The bond lengths of the α-carbon protonated isomer (II) were estimated from average values given in the literature [9] and all bond angles were taken to be 120°. A conformational study showed the ion to be planar. The geometry of the oxygen-protonated keten (III) was taken partly from a study on the vinyl cation [10] and the C–O–H angle and the O–H bond length were taken to be 120° and 0·96 Å respectively. A rotational study on the hydroxy-proton gave the most stable conformation to have the hydrogen at 90° to the plane of the remainder of the ion (as in the isoelectronic molecule allene) with a rotational barrier of 23·2 kcal mol^{-1}. Finally the C–O bond length was found to have an optimum value of 1·28 Å.


(I)


(II)


(III)

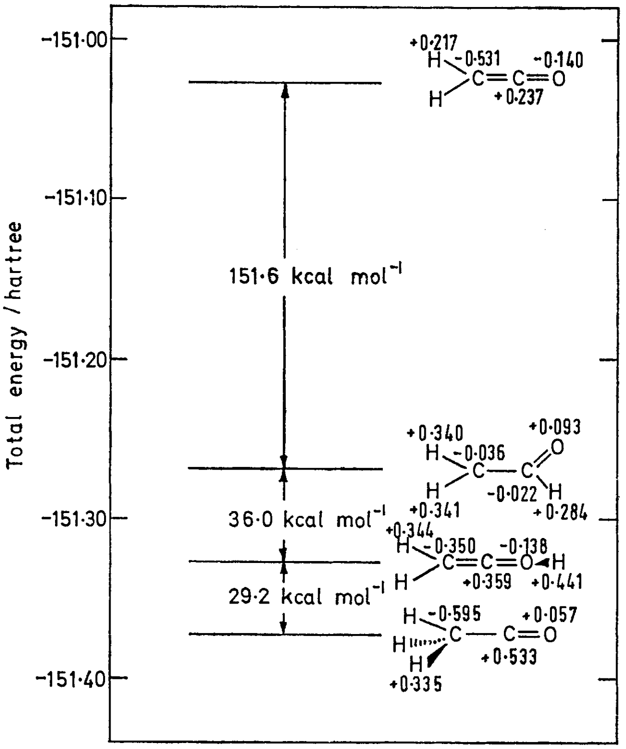
Computed total energies (hartree) and proton affinities (kcal mol^{-1})

Species	Computed total energy	Previous calculations	Computed proton affinity [a]
$[C{=}C{=}O]^{2-}$	−149·2750		651·7
	−150·3133		448·4
	−151·0276	−151·5077 [b]	216·8 [d]
	−151·3730	−151·8263 [c]	
	−151·2466		
	−151·3270		

[a] No correction is made for zero-point energy. [b] J. H. Ketcher, M. L. Unland, and J. R. Van Wazer, *J. Chem. Phys.*, 1969, **50**, 2185. [c] B. Rees, A. Veillard, and R. Weiss, *Theor. Chim. Acta*, 1972, **23**, 266. [d] Assumes β-carbon protonation.

The computed total energies for the cations along with those for keten and the anions formed by removal of the protons, are given in the Table. The geometries of the anions were taken to be the same as that of keten.[11] As usual the computed proton affinities are largest for the dinegative ion and smallest for the neutral molecule, and all probably overestimate the experimental value due to inadequancies in the size of the basis set.[12]

The energy differences between the isomers of protonated keten (see Figure) are found to be quite large, with the experimentally observed [5] acetyl ion being the most stable. The computed energy difference of 29·2 kcal mol^{-1} between the acetyl ion and the oxygen-protonated ketene would be easily sufficient to preclude the existence of detectable amounts of the latter at equilibrium conditions. However, the hydroxy-proton of the carbonyl-protonated keten is calculated to carry a large amount of positive charge, thereby making it a species capable of strong hydrogen bonding and probably stabilising it relative to the acetyl ion in solution. The α-carbon-protonated isomer would not be stabilised by solvation in this manner and the calculations can therefore be concluded to indicate β-carbon-protonation of keten, with



Computed energies and charge distributions for keten and the three isomers of protonated keten

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[6] M. Klessinger, *Theor. Chim. Acta*, 1969, **15**, 353.

[7] A. Veillard, 'IBMOL: Computation of Wave Functions for Molecules of General Geometry, Version 4,' IBM Research Laboratory, San Jose.

[8] F. P. Boer, *J. Amer. Chem. Soc.*, 1968, **90**, 6706.

[9] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1968, **90**, 7360.

[10] A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, 1971, **55**, 3835.

[11] H. R. Johnson and W. P. Strandberg, *J. Chem. Phys.*, 1952, **20**, 687.

[12] A. C. Hopkinson, N. K. Holbrook, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, 1968, **49**, 3596.

possibly traces of the oxygen-protonated isomer in strongly hydrogen-bonding solvents.

Finally, the calculated charge distribution on the keten molecule again favours attraction of the proton to the β-carbon atom, followed by attraction to the oxygen atom. The α-carbon atom carries a positive charge and would therefore repel any incoming proton.

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