A Non-empirical Molecular Orbital Study of the Wolff Rearrangement

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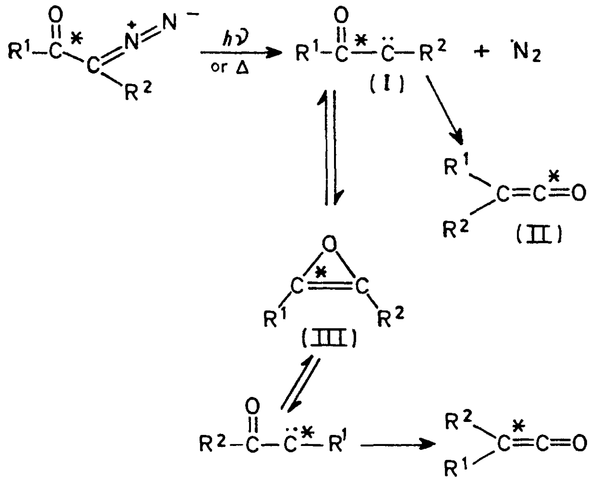
Oxiren and formylcarbene, postulated intermediates in the Wolff rearrangement, are shown to have almost identical energies and both are less stable than keten by 70 kcal mol^{-1}. Reactivities of the isomers are explicible in terms of computed charge densities.

DIAZO-KETONES[1,2] and α-diazo-esters[3] undergo the Wolff rearrangement to form ketens. The initial step in the gas-phase photolysis is decomposition into a singlet carbene (I)[3,4] and molecular nitrogen.



The α-keto-carbene then forms a keten (II), either directly or *via* an oxiren (III) intermediate and a different carbene. The product is the same in both mechanisms but the level of radioactivity in the carbon monoxide obtained from subsequent decomposition of the keten requires equilibration of the two keto-carbenes through an oxiren intermediate. The reaction has been shown to follow the same mechanism in anhydrous ether solution, with the carbene again being in the singlet state.[4]

Earlier evidence for the existence of oxiren intermediates comes from the reaction of peracetic and perbenzoic acids with acetylenes.[5,6] The ready oxidation to diketones by the electrophilic peracid was interpreted as evidence that the intermediates are oxirens with highly reactive 4π electron systems, rather than carbenes, which would have to be attacked at an electron-deficient carbon atom.

The objective of the present investigation was to use non-empirical LCAO–MO–SCF calculations to further probe the equilibrium between the parent oxiren ($R^1 = R^2 = H$) and its isomer formylcarbene. The calculations used an 8^s, 3^p (C and O), and 3^s (H) Gaussian basis set, with contraction to 3^s, 1^p, and 1^s, respectively,[7] and employed the IBMOL–IV program.[8] Experimental geometries were used for keten[9] and carbon monoxide;[10] those of the remaining species were estimated from average values in the literature,[11] and are listed in Table 1.

TABLE 1

Estimated geometries

Oxiren	C–C	1·30 Å
	C–O	1·41 Å
	C–H	1·07 Å
	$\widehat{\text{H–C–C}}$	120°
Formylcarbene	C–O	1·230 Å
	C–C	1·460 Å
	C–H (aldehyde)	1·115 Å
	C–H (carbene)	1·07 Å
	$\widehat{\text{C–C–O}} = \widehat{\text{C–C–H}} =$	120°
Methylene	C–H	1·07 Å

Only the position of the hydrogen on the carbenoid carbon of formylcarbene was optimised. This was found to be in a plane at right angles to the remainder of the molecule with a C–C–H bond angle of 110°, comparing favourably with the optimum bond angle of 105° found for the $^1A_1$ ground state of methylene. Finally, throughout the study only the ground-state closed-shell singlets of all species were considered.

The computed total energies for all species in their optimum conformations are given in Table 2 and the energy differences are given in the Figure. Keten is found to be more stable than both oxiren and formylcarbene by slightly more than 70 kcal mol^{-1}, explaining why neither of the latter are physically observable. However, unlike the extended Hückel calculations[3] which predict that ethoxycarbonylcarbenes are much

TABLE 2

Computed total energies (hartree)

Keten	−151·0276
Oxiren	−150·9128
Formylcarbene	−150·9121
Carbon monoxide	−112·2118
Methylene ($^1A_1$)	−38·7346

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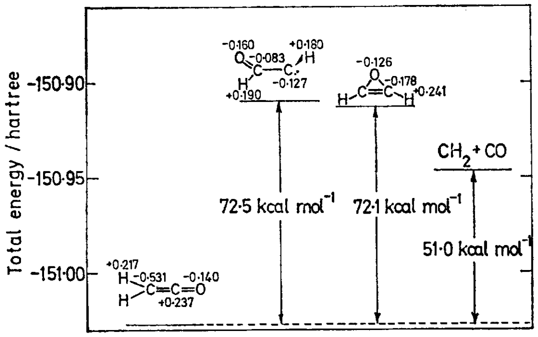
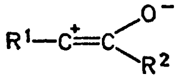
more stable than the corresponding oxirens, the more reliable *ab initio* calculations predict oxiren and formylcarbene to have almost the same energy, with the former being slightly more stable (by 0·39 kcal mol^{-1}).

The early failure to observe oxirens [1,12] as intermediates in solution reactions may be explained either by unreliable data [13] or by the high instability of the keto-carbene relative to that of the isomeric ketene.



Relative energies and charge densities of isomers of C_2H_2O

From the computed charge distribution in formylcarbene (see Figure) it is apparent that the dipolar structure (IV) is an incorrect description of keto-carbenes.[5] [Calculations using bond lengths appropriate to structure (IV) were not carried out.] The surprisingly large negative charge computed for the formally electron-deficient carbon atom suggests that protonation on this carbon atom, followed by loss of the acidic proton from the formyl group will very quickly result in keten in any solvent which is capable of accepting and donating protons.



(IV)

Rapid oxidation in the reaction of acetylenes with perbenzoic acids [5,6] is indeed best explained by oxiren being the reactive intermediate. The computed electron densities on the carbon atoms and on the oxygen are all large and negative indicating that protonation or electrophilic attack by the peracid will both be energetically favourable reactions.

Finally the energies of carbon monoxide and methylene, photochemical decomposition products of keten, are included in the Figure. This dissociation was not investigated further as it has been the subject of a recent molecular orbital treatment.[14]

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