Dichloroketen; Gas Phase Preparation and Characterisation by Photoelectron Spectroscopy

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Summary Dechlorination of trichloroacetyl chloride, CCl_3COCl, at low pressure, leads to the formation of dichloroketen, $Cl_2C{=}C{=}O$, which is studied by HeI photoelectron spectroscopy.

Although the parent keten molecule has been investigated by a wide range of physical and chemical techniques, the halogenated ketens are known only as transient intermediates in solution, undergoing 1,2-cycloaddition with olefins and other unsaturated compounds.[1] Thus, dichloroketen, $Cl_2C{=}C{=}O$, has been generated *in situ* by dehydrochlorination of $CHCl_2COCl$,[2,3] or by dehalogenation of CCl_3COBr.[4]

Continuing our studies of small unstable molecules by gas phase ultraviolet photoelectron spectroscopy (UPS), we now report that we have obtained relatively clean photoelectron spectra for a series of monosubstituted ketens ($XHC{=}C{=}O$, X = Me, Br, or Cl) and disubstituted ketens ($X_2C{=}C{=}O$, X = Me, Br, or Cl). The spectra are entirely consistent with those expected for a substituted keten molecule.

Direct pyrolysis of the parent monosubstituted acetyl halide at 700 °C and at low pressure (*ca.* 0·1 Torr) in a flow system, readily eliminates HCl giving $XHC{=}C{=}O$. However, direct pyrolysis of $CHCl_2COCl$ under similar conditions fails to yield $Cl_2C{=}C{=}O$; instead the final products are HCl, CO, and C_2Cl_4, presumably formed by decomposition of the transient keten, and coupling of the intermediate dichlorocarbene [see equation (1)]. A similar result was obtained

$$\begin{tikzcd} Cl_2HCCOCl \arrow[r, "700\ ^{\circ}\mathrm{C}", "ca.\ 0.1\ \mathrm{Torr}"'] & HCl + [Cl_2C{=}C{=}O] \arrow[d] \\ C_2Cl_4 & :CCl_2 + CO \arrow[l] \end{tikzcd} \qquad (1)$$

recently, where UPS was used to follow the pyrolysis of Cl_3CCHO.[5]

We now find that $Cl_2C{=}C{=}O$ can be obtained in good yield by dechlorination of CCl_3COCl vapour using Zn metal, and this occurs at a lower temperature than direct pyrolysis [equation (2)] the products being pumped directly into the

$$Cl_3CCOCl \xrightarrow[ca.\ 0.1\ \mathrm{Torr}]{\mathrm{Zn},\ 500\ ^{\circ}\mathrm{C}} Cl_2C{=}C{=}O + ZnCl_2 \qquad (2)$$

ionisation chamber of a photoelectron spectrometer.[6]

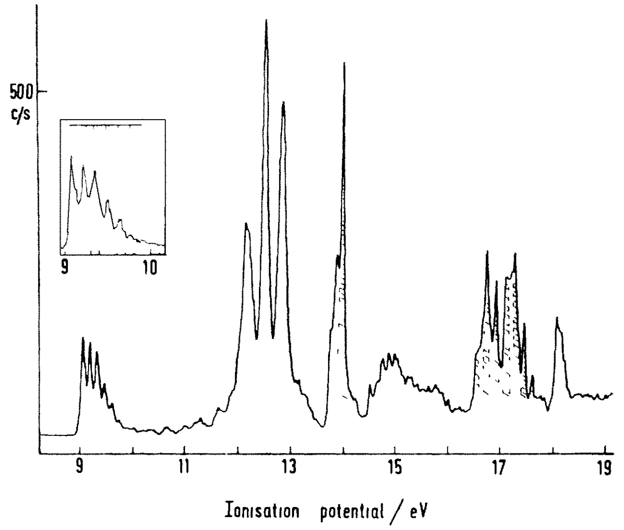

FIGURE. HeI photoelectron spectrum of $Cl_2C{=}C{=}O$; CO shaded. Inset: expansion of first ionisation potential.

The HeI photoelectron spectrum of $Cl_2C{=}C{=}O$ is shown in the Figure. Essentially all of the major peaks are attributable to $Cl_2C{=}C{=}O$, with the sharp peak at 14·01 eV and the vibrational series around 17 eV (shaded) belonging to CO, the decomposition product. The starting material, CCl_3COCl,[7] has been almost entirely consumed, most of the weak peaks in the 10—12 eV region being due to the HeI_β 'shadow' lines of the intense bands in the 12—13 eV region.

The first ionisation potential (I.P.) at 9·07 eV shows resolved vibrational frequencies of 330 and 1100 cm^{-1}. Comparison with the other halogenated ketens indicates that two main frequencies, 1100 and 2200 cm^{-1}, are present here. Keten itself shows a similarly structured band at 9·60 eV[5] (9·63 eV),[8] with resolved frequencies of 1080 and 2220 cm^{-1}, corresponding to the ionic CC and CO stretching modes. The additional mode weakly excited in $Cl_2C{=}C{=}O$ probably corresponds to a CCl_2 bending mode. In the parent keten there is an appreciable gap (*ca.* 4 eV) between the first two I.P.'s which correspond to the degenerate 2π orbitals of the isoelectronic linear CO_2 molecule. The 1π orbitals of CO_2 form the third and fourth I.P.'s of keten, with higher I.P.'s being of σ type. The proposed assignment[8] is supported by ionisation energies calculated using the correlated PNO–CEPA approach,[8] and perturbation corrections to Koopmans' theorem.[9]

In $Cl_2C{=}C{=}O$, the gap in the 10—14 eV region is accommodated by the four chlorine $3p$ type orbitals which are assigned as indicated in the Table. This ordering takes into account the resonance interaction between orbitals of the same symmetry, and the uniqueness of the a_2 orbital (sharpest band at 12·52 eV). Above 14 eV there are five additional I.P.'s which are also assigned as shown in the Table.

TABLE. Vertical ionisation potentials, cation states and *ab initio* orbital energies, ϵ_j, of $Cl_2C{=}C{=}O$.

Cation state	I.P./eV[a]	Molecular orbital	ϵ_j/eV[b]
$\tilde{X}\ ^2B_1$	9·07[c]	$4b_1$	−8·07
$\tilde{A}\ ^2B_2$	12·18	$8b_2$	−11·18
$\tilde{B}\ ^2A_2$	12·52	$2a_2$	−11·79
$\tilde{C}\ ^2A_1$	12·84	$13a_1$	−12·06
$\tilde{D}\ ^2B_1$	13·90	$7b_2$	−13·71
$\tilde{E}\ ^2B_2$	14·90[d]	$3b_1$	−13·75
$\tilde{F}\ ^2B_1$	15·62	$6b_2$	−16·52
$\tilde{G}\ ^2A_1$	16·75	$12a_1$	−16·92
$\tilde{H}\ ^2B_2$	17·18	$2b_1$	−17·43
$\tilde{I}\ ^2A_1$	18·13	$11a_1$	−18·75

[a] First six I P 's, ± 0·02 eV, the rest, ± 0·05 eV. [b] STO-3G minimal basis set [c] Vibrational structure, 330, 1100 and 2200 ± 40 cm^{-1}. [d] Vibrational structure 930 ± 60 cm^{-1}

In addition to the experimentally determined values and the proposed assignments, the Table also includes the results of a minimal basis (STO-3G) *ab initio* calculation.[10] Since no structural data are, as yet, available for this molecule, the geometry used for this calculation was based on the structures of methylketen[11] and 1,1-dichloroethylene,[12] *viz.* CC = 1·306, CO = 1·171, CCl = 1·727 Å and ClCCl = 113·6°. The agreement is only fair, with the $^2B_2$ ionic states being consistently destabilized. At this level of calculation it is not yet possible to say if this is due to a failure of Koopmans' theorem.

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