

## Dichloroketen; Gas Phase Preparation and Characterisation by Photoelectron Spectroscopy

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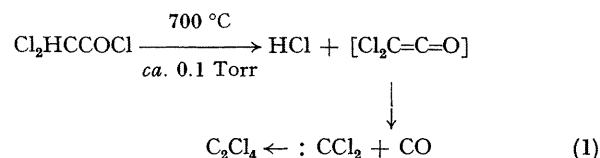
**Summary** Dechlorination of trichloroacetyl chloride,  $\text{CCl}_3\text{COCl}$ , at low pressure, leads to the formation of dichloroketen,  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ , which is studied by HeI photoelectron spectroscopy.

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.<sup>1</sup> Thus, dichloroketen,  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ , has been generated *in situ* by dehydrochlorination of  $\text{CHCl}_2\text{COCl}$ ,<sup>2,3</sup> or by dehalogenation of  $\text{CCl}_3\text{COBr}$ .<sup>4</sup>

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 ( $\text{XHC}=\text{C}=\text{O}$ ,  $\text{X} = \text{Me}$ ,  $\text{Br}$ , or  $\text{Cl}$ ) and disubstituted ketens ( $\text{X}_2\text{C}=\text{C}=\text{O}$ ,  $\text{X} = \text{Me}$ ,  $\text{Br}$ , or  $\text{Cl}$ ). The spectra are entirely consistent with those expected for a substituted keten molecule.

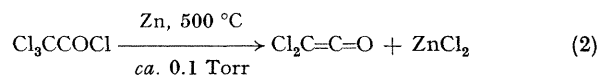
Direct pyrolysis of the parent monosubstituted acetyl halide at 700 °C and at low pressure (*ca.* 0.1 Torr) in a flow system, readily eliminates HCl giving  $\text{XHC}=\text{C}=\text{O}$ . However,

direct pyrolysis of  $\text{CHCl}_2\text{COCl}$  under similar conditions fails to yield  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ ; instead the final products are HCl, CO, and  $\text{C}_2\text{Cl}_4$ , presumably formed by decomposition of the transient keten, and coupling of the intermediate dichlorocarbene [see equation (1)]. A similar result was obtained



recently, where UPS was used to follow the pyrolysis of  $\text{Cl}_3\text{CCHO}$ .<sup>5</sup>

We now find that  $\text{Cl}_2\text{C}=\text{C}=\text{O}$  can be obtained in good yield by dechlorination of  $\text{CCl}_3\text{COCl}$  vapour using Zn metal, and this occurs at a lower temperature than direct pyrolysis [equation (2)] the products being pumped directly into the



ionisation chamber of a photoelectron spectrometer.<sup>6</sup>

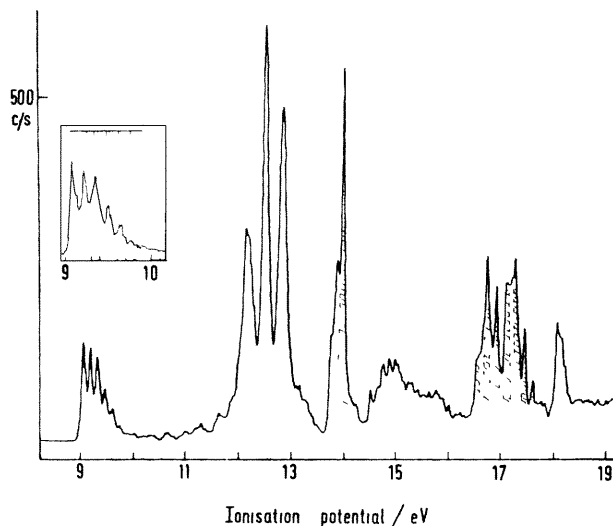


FIGURE. HeI photoelectron spectrum of  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ ; CO shaded. Inset: expansion of first ionisation potential.

The HeI photoelectron spectrum of  $\text{Cl}_2\text{C}=\text{C}=\text{O}$  is shown in the Figure. Essentially all of the major peaks are attributable to  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ , 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,  $\text{CCl}_3\text{COCl}$ ,<sup>7</sup> has been almost entirely consumed, most of the weak peaks in the 10–12 eV region being due to the HeI<sub>β</sub> '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  $\text{cm}^{-1}$ . Comparison with the other halogenated ketens indicates that two main frequencies, 1100 and 2200  $\text{cm}^{-1}$ , are present here. Keten itself shows a similarly structured band at 9.60 eV<sup>5</sup> (9.63 eV),<sup>8</sup> with resolved frequencies of 1080 and 2220  $\text{cm}^{-1}$ , corresponding to the ionic CC and CO stretching modes. The additional mode weakly excited in  $\text{Cl}_2\text{C}=\text{C}=\text{O}$  probably corresponds to a  $\text{CCl}_2$  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  $2\pi$  orbitals of the isoelectronic linear  $\text{CO}_2$  molecule. The  $1\pi$  orbitals of  $\text{CO}_2$  form the third and fourth I.P.'s of keten, with higher I.P.'s being of  $\sigma$  type. The proposed assign-

ment<sup>8</sup> is supported by ionisation energies calculated using the correlated PNO-CEPA approach,<sup>8</sup> and perturbation corrections to Koopmans' theorem.<sup>9</sup>

In  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ , 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,  $\epsilon_i$ , of  $\text{Cl}_2\text{C}=\text{C}=\text{O}$ .

Cation state	I.P./eV <sup>a</sup>	Molecular orbital	$\epsilon_i/\text{eV}^b$
$\tilde{X}^2B_1$	9.07 <sup>c</sup>	$4b_1$	-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 <sup>d</sup>	$3b_1$	-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

<sup>a</sup> First six I.P.'s,  $\pm 0.02$  eV, the rest,  $\pm 0.05$  eV. <sup>b</sup> STO-3G minimal basis set. <sup>c</sup> Vibrational structure, 330, 1100 and 2200  $\pm 40$   $\text{cm}^{-1}$ . <sup>d</sup> Vibrational structure 930  $\pm 60$   $\text{cm}^{-1}$ .

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.<sup>10</sup> Since no structural data are, as yet, available for this molecule, the geometry used for this calculation was based on the structures of methylketen<sup>11</sup> and 1,1-dichloroethylene,<sup>12</sup> 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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