He¹ Photoelectron Spectra of Unstable Molecules: Mono- and Di-halogenoketenes

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He¹ Photoelectron spectra are reported for the mono- and di-chloro- and -bromo-ketenes (XHC=C=O and X₂C=C=O, X = Cl, Br) generated in high yield as unstable molecules from thermolysis of acid halides. The spectra are discussed and assigned by reference to the parent ketene molecule, orbital trends, and comparison with theoretical calculations.

Halogen-substituted ketenes are unstable molecules known primarily as reactive intermediates in solution where they undergo cycloaddition to olefins and other unsaturated products.[1,2] Identification thus rests mainly on *in situ* reactions, although limited i.r. data have been obtained on solutions that were believed to contain monomeric dihalogeno species;[3,4] subsequent work[1] has suggested that dimer species were involved. More recently, a matrix i.r. spectrum of dichloroketene produced by photolysis of a larger precursor has been reported.[5]

In preliminary work it has been demonstrated[6–8] that these molecules, including the methyl and dimethyl derivatives, can be prepared in high yield directly in the gas phase, thereby considerably expanding the possibilities for spectroscopic evaluation. Microwave spectra have been obtained for monochloro-[9] and monobromo-ketene,[10] and vibrational studies employing Fourier transform i.r. spectroscopy are in progress.[11] In the early investigation[6–8] of gas-phase halogenoketenes the technique of u.v. photoelectron spectroscopy (u.p.s.) was used to evaluate preparative routes, although full details of these and the resulting photoelectron (p.e.) spectra were not reported, and the bromoketenes were omitted. In this work we report preparative details and complete He¹ p.e. spectra for the chloro- and bromo-ketenes, both mono- and di-substituted. The analysis, which is assisted by reference to some recent calculations employing perturbation corrections to Koopmans' theorem,[12] provides an insight into the effect of halogen substitution upon the π system of the ketene moiety.
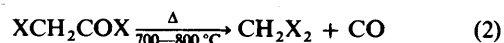
Experimental
The most direct route for preparing a halogenoketene involves dehydrohalogenation of a halogeno substituted acid halide at 700—800 °C in a low-pressure flow system. All pyrolyses were accomplished in a silica tube (25 cm × 0.7 cm i.d.) heated over *ca.* 12 cm by a non-inductively wound furnace.

The dehydrohalogenation reaction (1) was thus used

$$XCH_2COX \xrightarrow[700—800\ °C]{\Delta} XHCCO + HX \qquad (1)$$

to prepare monochloro- and monobromo-ketene. HX was removed by gas-phase titration with NH₃ before admission into the p.e. spectrometer. The more stable mono- and di-methyl-ketene have also been produced by this route.[7] The chloroketene is formed in high yield by this reaction; the bromoketene is less readily formed due to competing elimination of CO [reaction (2)].

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$$XCH_2COX \xrightarrow[700—800\ °C]{\Delta} CH_2X_2 + CO \qquad (2)$$

In principle a similar reaction employing a dihalogenoacetyl halide should provide a route to the dihalogenoketenes [reaction (3)], but in practice it was found that further decomposition took place according to equation (4).

$$X_2CHCOX \xrightarrow{\Delta} X_2CCO + HX \qquad (3)$$

$$X_2CCO \xrightarrow{\Delta} X_2C: + CO \qquad (4)$$
$$\downarrow$$
$$C_2X_4$$
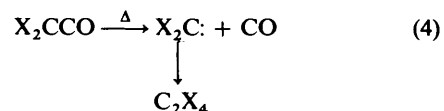
The limited stability of the dihalogenoketenes at the high (> 700 °C) temperature required for HX elimination thus precludes their observation in our direct pyrolysis experiments. However, they can be produced in high yield by a dehalogenation reaction involving metallic zinc.[6]

Reaction (5) occurs at lower temperatures (300—400 °C) and was therefore used to produce dichloro- and dibromo-ketene from the respective trihalogenoacetyl halides. This reaction is extremely efficient, as shown by the p.e. spectra, and eliminates the problem of gaseous HX. We have demonstrated its generality by also producing the parent ketene (from monochloroacetyl chloride) and monochloroketene (from dichloroacetyl chloride). We would add that attempted production of fluoroketenes *via* these routes leads to the formation of products other than the intended fluoroketenes. These reactions are at present under investigation.

$$X_3CCOX \xrightarrow{\Delta}{Zn} X_2CCO + ZnX_2 \qquad (5)$$

All halogenoacetyl halides except CBr₃COBr were commercial samples (Eastman; B.D.H.) and were used without further purification. CBr₃COBr was synthesised by treatment of CBr₃COOH with PBr₃ in toluene. After refluxing for 2 h the bulk of the toluene was distilled off, the remaining solvent being pumped off *in vacuo*.

The gaseous effluent from the pyrolysis reactions was pumped directly into a p.e. spectrometer specifically designed for the study of unstable molecules.[13] Resolution was typically 30 meV under the conditions of the experiments. Spectra were calibrated using the known ionisation potentials (IPs) of CH₃I, CO, HCl, HBr, N₂, and Ar.
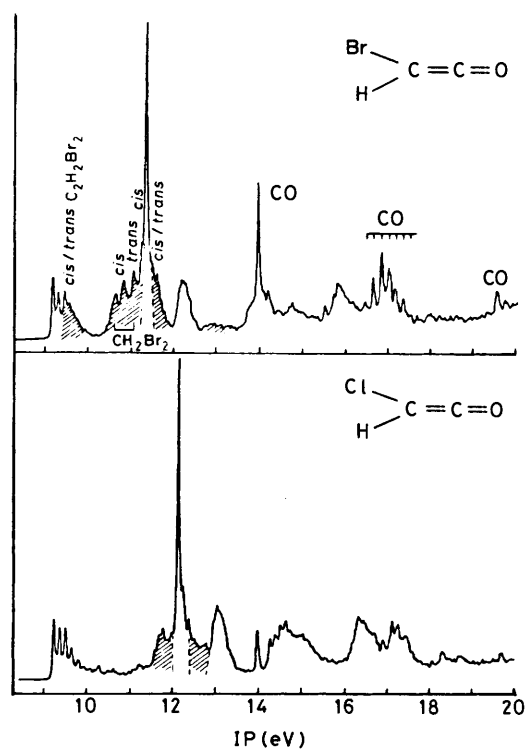
Results
The p.e. spectra of monochloro- and monobromo-ketene produced by direct pyrolysis at 700 °C of, respectively, monochloroacetyl chloride and monobromoacetyl bromide are

Table 1. Experimental vertical IPs, vibrational structure, and assignments for the monohalogenoketenes

| Band | BrHCCO | | ClHCCO | | Assignment[a] | Calc.[b] Ave. GA (eV) |
	IP(eV)[c]	v' cm^{-1} [d]	IP(eV)[c]	v' cm^{-1} [d]		
1	9.14	420 1 060 2 200	9.25	1 080 2 220	3a″	9.11
2	11.37		12.15	1 000 2 150	8a′	12.05
3	12.24		13.10		2a″	13.09
4	14.0		14.54	950	7a′	14.80
5	14.82		15.06		1a″	15.69
6	15.95		16.39		6a′	16.69
7	17.09		17.20		5a′	17.62
8	18.03		18.30		4a′	18.91

[a] Valence orbital numbering. [b] From ref. 12, for monochloroketene. [c] First four IPs ± 0.02 eV; the remainder, ± 0.05 eV. [d] Ionic vibrational frequencies, ± 50 cm^{-1}; ground-state molecular frequencies,[11] C=C stretch, ca. 1 260 cm^{-1}, and C=O stretch, ca. 2 150 cm^{-1}.

Figure 1. He[I] photoelectron spectra of monochloroketene and monobromoketene produced by pyrolysis of chloroacetyl chloride and bromoacetyl bromide respectively. HCl and HBr have been removed by titration with NH$_3$

Figure 2. He[I] photoelectron spectra of dichloroketene and dibromo-ketene produced by pyrolysis of trichloroacetyl chloride and tribro-moacetyl bromide respectively over zinc metal. Shaded area is monobromoketene (see text)

shown in Figure 1 and affirm the efficiency of these reactions. HX produced in the reaction has been eliminated by gas-phase titration with NH$_3$. The p.e. spectrum of the starting acid chloride has been previously reported,[14] and only a small trace (shaded) remains in the spectrum of chloroketene. The sharp peak at 14.01 eV is a trace of CO produced as a decomposition product. The p.e. spectrum of bromoketene shows substantially more CO (labelled) together with additional bands (shaded), which under expansion and careful analysis can be ascribed to cis- and trans-dibromoethylene (p.e. spectra in refs. 15 and 16) and dibromomethane (in ref. 17). The dibromoethylenes result from decomposition of the bromoketene according to equation (4); CH$_2$Br$_2$ is produced in the competing reaction (2),

accompanied by an increase in the CO. This observation is supported by recent microwave work.[10]

The spectra of dichloro- and dibromo-ketene are shown in Figure 2. That of dichloroketene is relatively pure apart from the presence of some CO (labelled). Confirmation of the identity of this species is provided by an in situ quadrupole mass analyser[18] which, under the same conditions as these experiments, and with a He[I] light source (21.2 eV) gives a parent ion peak, Cl$_2$CCO$^+$, at m/z 114, 112, and 110 and fragment ions, CCl$_2$$^+$ (m/z 86, 84, and 82), CCl$^+$ (m/z 49 and 47) and CO$^+$ (m/z 28). With HL$_\alpha$ radiation (10.2 eV) there is an enhanced parent ion peak, and weaker CCl$_2$$^+$ and CCl$^+$ fragments. The only major impurity observed in the p.e. spectrum of dibromoketene

Table 2. Experimental vertical IPs, vibrational structure, and assignments for the dihalogenoketenes

| Band	Br$_2$CCO IP(eV)[c]	Br$_2$CCO v'/cm^{-1}[d]	Cl$_2$CCO IP(eV)[c]	Cl$_2$CCO v'/cm^{-1}[d]	Assignment[a]	Calc.[b] Ave. GA (eV)
1	8.89	380	9.07	320	3b_1	8.89
		1 120		1 100		
		2 100		2 200		
2	11.20		12.18		4b_2	11.58
3	11.58		12.52		1a_2	12.01
4	11.87		12.84		6a_1	12.36
5	12.98		13.90		2b_1	13.72
6	14.0		14.90	950	3b_2	14.82
7	15.07		15.62		1b_1	16.14
8	16.05		16.75		2b_2	16.83
9	16.46		17.18		5a_1	17.20
10	17.69		18.13		4a_1	18.37

[a] Valence orbital numbering. [b] From ref. 12, for dichloroketene. [c] First six IPs $\pm$ 0.02 eV; the remainder, $\pm$ 0.05 eV. [d] Ionic vibrational frequencies, $\pm$ 50 cm^{-1}; ground-state molecular frequencies,[11] C=C stretch, 1 291 cm^{-1}, and C=O stretch, 2 160 cm^{-1}.

is monobromoketene (shaded). Since CBr$_3$COBr was synthesised from a commercial sample of CBr$_3$COOH it was assumed that the final sample contained either unchanged CBr$_3$COOH, or some dibromoacetyl bromide, which upon reaction with Zn gave monobromoketene. Fortunately the presence of the monobromoketene does not severely hinder determination of the IPs of dibromoketene. Weak sharp peaks at 13.8 and 18.1 eV are assigned to traces of CO$_2$.

The experimental IPs for the monochloro- and monobromoketene are shown in Table 1, and those for the dihalogenoketenes in Table 2. In both instances the assignments are also given, together with the calculated values and these will be discussed in the next section.

Assignments.—The starting point for an assignment of the p.e. spectra of the halogenoketenes is the parent ketene molecule, where p.e. spectra and assignments[19] are supported by calculations using the pseudonatural orbital coupled electron-pair approach,[19] and independently by calculations employing perturbation corrections to Koopmans' theorem.[20] The first and second IPs are assigned to the non-bonding out-of-plane (π_{nb}'') and in-plane (π_{nb}') type orbitals respectively, which derive from the $2\pi(\pi_g)$ orbital of the isoelectronic linear CO$_2$ molecule. The third and fourth IPs are assigned to the bonding pair of orbitals, out-of-plane (π_b'') and in-plane (π_b') respectively, which derive from the $1\pi(\pi_u)$ orbital of CO$_2$. The fifth IP of ketene is a $p\sigma$ orbital located primarily on the terminal oxygen atom. The terms π_{nb}'', π_{nb}', π_b'', and π_b' will subsequently be used to describe orbitals of similar character in the PE spectra of the halogenoketenes. There is a large gap (*ca.* 4.4 eV) between the first (π_{nb}'') and second (π_{nb}') IPs of ketene, and it is in this region that ionisation from the halogen *p*-type orbitals of the halogeno substituted ketenes is expected to occur.

(A) *Monohalogenoketenes.* Ketene, with C_{2v} symmetry, has six observable IPs within the He^1 range. Substitution with a single halogen reduces the symmetry to C_s and introduces two additional IPs. All orbitals then transform as either a'' (out-of-plane) or a' (in-plane) with subsequent mixing of orbitals of the same symmetry. Nevertheless the π_{nb} and π_b orbitals retain their essential C=C=O π character, and the interaction of the halogen X$_p$ orbitals with these levels can be investigated (compare the isoelectronic XNCO, XN$_3$ molecules[21]). Since the p.e. spectrum of bromoketene parallels that for chloroketene the assignments will be discussed together. Despite some overlap from decomposition products (*cis*- and *trans*-C$_2$H$_2$Br$_2$ and CO) and
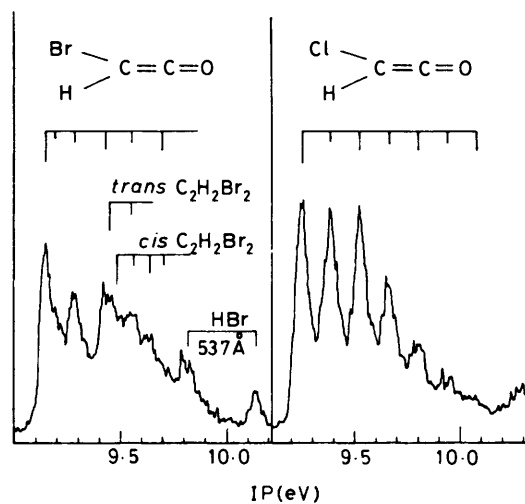
Figure 3. Expansion of the first IPs of monochloro- and monobromoketene

the competing reaction (2) giving some CH$_2$Br$_2$, all eight IPs of bromoketene can be observed.

Chloroketene and bromoketene. The first IPs of both chloro- and bromo-ketene, typical of those for all ketenes, are structured bands, well separated from the rest of the spectrum. With coincident adiabatic and vertical IPs at 9.25 (Cl) and 9.14 eV (Br), these bands are assigned to the π_{nb}'' orbital (3a''), and follow similar values for the isoelectronic halogenoallene molecules.[22] Substitution of hydrogen by Cl or Br thus destabilises the HOMO of ketene from 9.63 eV, indicating that the antibonding resonance interaction of the ketene CCO π system with the halogen *np* orbital is greater than the inductive effect of X. In both cases, the dominant vibrational structure (Figure 3 and Table 1) is very similar, and is analogous to that in the ground ionic state of the parent ketene molecule. The two main progressions can therefore be assigned to excitation of the C=C and C=O stretching frequencies; Fourier transform i.r. results[11] on chloroketene indicate that the corresponding molecular ground-state frequencies occur at *ca.* 1 260 and 2 150 cm^{-1}. The ionic frequencies are therefore consistent with ejection of electrons from an orbital that is CO antibonding and
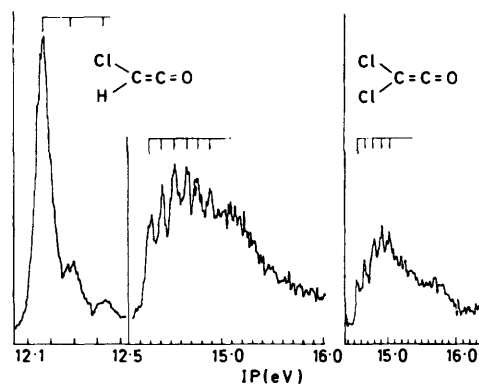
Figure 4. Expansion of the second and fourth/fifth IPs of monochloroketene, and the sixth/seventh IPs of dichloroketene

Figure 5. Expansion of the first IPs of dichloro- and dibromo-ketene

CC bonding. For bromoketene there is evidence for a weaker progression of 420 cm^{-1}, probably arising from a BrCH bending mode.

The sharp second (12.15 and 11.37 eV) and broader third IPs (13.10 and 12.24 eV) of both chloro- and bromo-ketene are, respectively, the in-plane halogen lone pair ($8a'$) and the out-of-plane ($2a''$) halogen-based p orbitals. From chloro- to bromo-ketene the shift of these bands is the largest of any IP, confirming their identity to primarily X np. The second IP of chloroketene (Figure 4), which shows some weak vibrational coupling (Table 1), is calculated (unpublished results) to arise from an orbital almost 100% localised on the Cl atom; the same presumably follows for the Br species since it, too, is extremely non-bonding. The third IP ($2a''$) in both cases is significantly broader than the in-plane halogen lone pair ($8a'$) in accord with its bonding character.

The fourth and fifth bands of chloroketene (vertical IPs, 14.54 and 15.06 eV, respectively), partially overlap (Figure 4) as do the second and third bands of ketene (14.2 and 15.0 eV)[19] to which they correspond. The analogous bands in bromoketene occur at 14.0 and 14.82 eV, the former overlapped by the $^2\Sigma_g{}^+$ state of CO$^+$ at 14.01 eV. In ketene these bands are assigned to the π'_{nb} and π''_b orbitals respectively, and so, following this ordering, the fourth and fifth bands of the halogenoketenes are assigned to the $7a'$ and $1a''$ orbitals. For chloro- and bromo-ketene this gives separations of 5.29 and 4.86 eV for the π_{nb}-based orbitals (first and fourth IPs) compared with 4.4 eV for ketene; this is as expected for a resonance interaction with the intervening X non-bonding levels of the same symmetry. The fourth IP of chloroketene exhibits a progression of 950 cm^{-1}, possibly a reduced C=C stretching frequency, although there are indications that it is more complex than a simple progression. Structure on the corresponding band of ketene was also complex, indicating predissociation, and an analysis was not attempted.[19]

Following the ordering in ketene, the remaining three bands in the halogenosubstituted molecules can then be assigned to the π'_b orbital ($6a'$) and two σ orbitals ($5a'$ and $4a'$) as shown in Table 1. The difference between the values for the fifth and sixth IPs gives the separation of the ketene-based π_b orbitals, 1.33 and 1.13 eV for chloro-and bromo-ketene, respectively. The seventh IP in both molecules (partially overlapped by the $^2\Pi_u$ state of CO$^+$) is assigned to the $p\sigma$ type orbital ($5a'$) with localisation on the terminal oxygen atom. The very weak band at 18.30 and 18.03 eV in the chloro and bromo molecules is then assigned to the $4a'$ orbital which is of primarily C and O 2s plus H 1s character.

(B) *Dihalogenoketenes.* Addition of a second halogen atom introduces a further two IPs into the He^I region for a total of ten
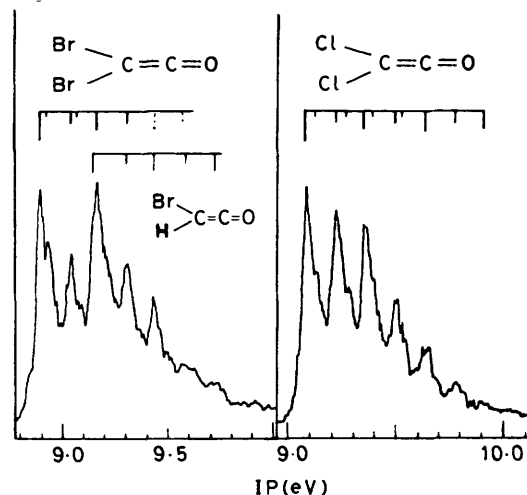
IPs. The symmetry of the molecule increases to C_{2v}, and so orbital symmetries are directly comparable with those of ketene. Although the He^I p.e. spectrum of dibromoketene is partially overlapped by that of monobromoketene (shaded, Figure 2) all ten IPs can be identified and correlated with those of dichloroketene.

Dichloroketene and dibromoketene. The first vertical IP [9.07 (Cl) and 8.89 eV (Br)] is again distinctly structured (Figure 5), and well separated from the rest of the spectrum (Figure 2). Relative to the monohalogenoketenes it is further destabilised by the introduction of additional antibonding X$_p$ character, and is assigned to the π''_{nb} orbital ($3b_1$). The predominant vibrational structure (Table 2) is assigned to the C=C and C=O stretching frequencies; Fourier transform i.r. results[11] give molecular ground-state frequencies of 1 291 and 2 160 cm^{-1}, respectively, again indicating that this orbital is C=C bonding and C=O antibonding.

The next four bands appear in the gap between the ketene based π''_{nb} and π'_{nb} orbitals and can be assigned to essentially X lone pairs. In C_{2v} symmetry these transform as a_1, a_2, b_1, and b_2. The unique a_2 representation will give rise to the most non-bonding orbital, and this is evident by the sharpest peak at 12.52 eV in dichloroketene and 11.58 eV in dibromoketene. Similarly the broadest of the four bands is assigned to the $2b_1$ ionisation [13.90 (Cl) and 12.98 eV (Br)]; this is the C–X bonding counterpart of the first IP. In order to maximise the separation of orbitals of the same symmetry, the first and third bands of this group are then assigned to the $4b_2$ and $6a_1$ orbitals respectively. Overall, the dibromoketene bands show a decrease of just under 1 eV from the corresponding dichloroketene values.

The sixth band in each molecule [14.90 (Cl) and 14.0 eV (Br)] is assigned to the π'_{nb} ($3b_2$) orbital, and in the chloro case exhibits a progression of 950 cm^{-1} (Figure 4), assigned to the ionic C=C stretching frequency. The π_{nb} separation in the order ketene, dibromoketene, and dichloroketene is now 4.4, 5.11, and 5.83 eV.

The next two bands can then be assigned to the π''_b ($1b_1$) and π'_b ($2b_2$) pairs of orbitals which occur at 15.62 and 16.75 eV in dichloroketene and 15.07 and 16.05 eV in dibromoketene. This leaves two further bands, assigned to σ orbitals, $5a_1$ and $4a_1$ (Table 2), the former having appreciable C–X bonding character, and the latter somewhat more intense than the corresponding band in the monohalogenoketenes; this is a reflection of the incorporation of X$_{ns}$ and X$_{np}$ character instead of H$_{1s}$.
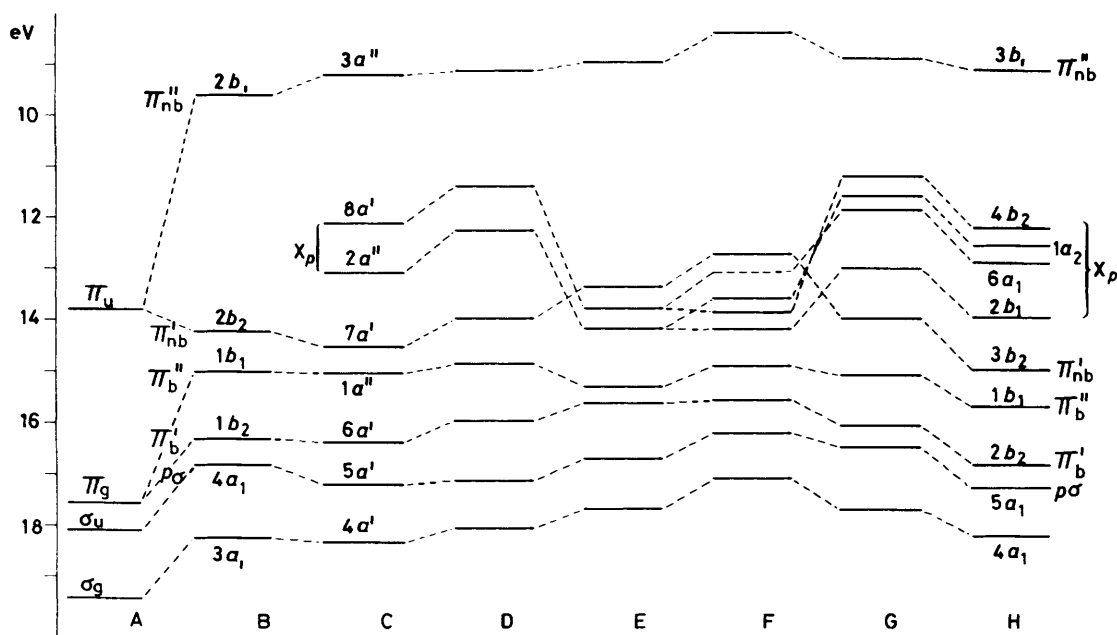
Figure 6. Correlation of the valence ionisation potentials of : A, carbon dioxide; B, ketene; C, chloroketene; D, bromoketene; E, methylketene; F, dimethylketene; G, dibromoketene; and H, dichloroketene

Discussion

The validity of the proposed assignments which follow smoothly from those of ketene is supported by recent calculations[12] on mono- and di-chloroketene which employ perturbation corrections to Koopmans' theorem; the average deviation from the experimental values is 0.3 eV in both cases. These calculations are shown in Tables 1 and 2 under the heading Ave. GA (average geometric approximation). Other workers[8] have obtained spectra of monochloroketene overlapped by HCl and CO, consequently placing the $6a'$, $5a'$, and $4a'$ orbitals all within the two IPs at 16.39 and 17.20 eV and ignoring the weak band at ca. 18.3 eV. For dichloroketene a switch of the closely spaced $2b_2$ (16.75 eV) and $5a_1$ (17.18 eV) orbitals is now preferred over the previous work.[6] Other workers[8] have mislocated the seventh to ninth IPs, mainly because of overlapping CO bands and MNDO calculations that give incorrect bunching of IPs. We do note, however, that the MNDO calculations give the correct qualitative ordering for both mono- and di-chloroketene.

Although no molecular orbital calculations have been performed on the bromoketenes it is evident that the assignments follow those for the chloroketenes; thus bands have similar Franck–Condon envelopes and shifts are as expected for replacement of Cl by Br. Only the first two IPs of monobromoketene produced by a different route have been previously quoted,[8] but the second, which we find to be sharp and distinctive, is in disagreement with that reported here, and the remainder of the pyrolysis spectrum was not assignable.[8] Dibromoketene has not been reported previously.

The evolution of the parent ketene IPs from those of the linear isoelectronic CO_2 molecule is shown in Figure 6, and demonstrates the orbital correspondence with mono- and di-substitution. Also included are the data for the methylketenes,[7] where the orbital ordering follows that for the halogenoketenes except for the $CH_3 p$ type orbitals. Thus, for all halogenoketenes, both mono- and di-substituted, the predominantly halogen X_p-type orbitals lie between the π''_{nb} and π'_{nb} levels. The $CH_3 p$-type orbitals, however, lie deeper, ca. 13—14 eV, and consequently push the π_{nb} levels together. The result of this is that the separation of the π_{nb} levels is greater for the halogenoketenes than for the parent ketene molecule, and decreases from Cl to Br. A similar effect obtains for the isoelectronic XNCO and XN_3 molecules.[21] The π_{nb} separation is larger for the dihalogenoketenes; the π_b separation is equal to or slightly less than that in ketene. This also follows the results for the $XNCO/XN_3$ molecules[21] after a minor revision of the assignments.[23]

Of some interest is the question of the electrophilic nature of ketenes, and the fact that dichloroketene is a far better electrophile than ketene, undergoing ready 1,2-cycloaddition to olefins. The orbital of relevance to this reactivity is the π^* C=O LUMO. This orbital is not accessible by one-electron p.e. spectroscopy, but we note that both ab initio and CNDO calculations performed during the course of this work consistently show a considerable lowering of the LUMO upon substitution by Cl, coupled with the, albeit smaller, resonance destabilisation of the HOMO. The net result is enhanced reactivity of dichloroketene.

Conclusions.—We have demonstrated how direct gas-phase thermolysis of halogenoacetyl halides in a flow system, with and without the use of zinc metal, leads to the formation of halogenoketenes in high yield. This has permitted full evaluation of the He[1] p.e. spectra of these molecules, and an assignment of the valence IPs to molecular orbitals. A comparison with calculations employing perturbation corrections to Koopmans' theorem substantiates these assignments, and once again demonstrates the unique symbiosis between experiment and theory. Although in the p.e. experiments the samples are pumped directly through the spectrometer, we have evidence from microwave experiments[9] that monochloroketene has a lifetime of several minutes at low pressure in a metal waveguide after which time there is complete disappearance and replacement by an, as yet, unidentified species. Reactions of such ketenes, including the fluoro derivatives, are at present under investigation.

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