Carbonyl dihalides: synthesis and spectroscopic characterization

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New, or improved, syntheses of phosgene, carbonyl bromide chloride and carbonyl bromide fluoride have been elaborated. The NMR (^{13}C, ^{19}F and ^{17}O) and electron impact mass spectra were recorded for COX_2 (X = F, Cl or Br), COClF, COBrCl and COBrF; trends in the chemical shifts are analysed in terms of σ and π contributions to the bonding. Attempts to prepare carbonyl diiodide in solution were unsuccessful, and the reasons for this are analysed.

Whilst completing a monograph describing phosgene and the related carbonyl halides[1] we became aware of many lacunae in the literature. As part of our investigation into the electronic structure of the carbonyl halides, COX_2 (X = F, Cl or Br) and COXY (X = F, Y = Cl or Br; X = Cl, Y = Br),[2,3] it was necessary to develop safe, reproducible laboratory-scale syntheses for these materials, and these are described herein, along with previously unreported ^{17}O NMR chemical shifts for these simple materials.

Carbonyl diiodide has never been isolated, and (until very recently) the only report of its observation was as a possible (but improbable) component of the essential oil of a Hawaiian seaweed. In 1995, however, there was a report of the first observation of COI_2, formed in the gas phase by the reaction of 'heated' tetraiodomethane with dioxygen.[4] The evidence for its existence rests entirely upon the observation of two infrared bands, at 1812 [ν_1(C=O)] and at 760 cm^{-1} [ν_4(CI)]. The latter band occurs, somewhat disturbingly, at a frequency higher than that observed (at 747 cm^{-1}) for the analogous asymmetrical ν_4(CBr) band of the well characterized carbonyl dibromide, $COBr_2$.[5] We thus attempted to prepare this thermodynamically unstable material, with an unsurprising lack of success.

Experimental

CAUTION: No toxicological data have been recorded for carbonyl bromide fluoride or carbonyl bromide chloride, and no occupational exposure limits have been recommended. The physiological effects of all the carbonyl halides used here were assumed similar to those of phosgene, but clearly a modern detailed evaluation is required if they are to be used more widely. The following safety precautions were adopted on the assumption that the toxicity of these compounds was similar to that of phosgene.

Handling carbonyl dihalides

Phosgene is a toxic gas, with a permissible UK occupational exposure limit (OEL) of 0.08 mg m^{-3} of air (0.02 ppm v/v).[6] In the event of exposure the victim may experience chest pain, coughing and rapid breathing associated with pulmonary œdema, and it may take over 24 h for symptoms to appear. There is no antidote to phosgene poisoning,[1] and hence treatment is usually directed to the main symptom, toxic pulmonary œdema.[7] Hence, all manipulations involving carbonyl dihalides were carried out in a well ventilated fume cupboard with a face velocity of > 0.75 m s^{-1}, and in the presence of at least one other experienced research worker. The vacuum line was constructed within the fume cupboard. The atmosphere both inside and outside the fume cupboard was constantly checked using Dräger tubes[8] and detector tape (Rimon Laboratories Ltd). All glassware used greaseless taps, and joints were lubricated with Teflon sleeves. After use, the carbonyl dihalides were destroyed by passage through a column containing moist activated charcoal. The fume cupboard was fitted with an alarm system, which was activated automatically if the extractor mechanism failed, or manually in the event of an accident. After use, all equipment was washed with an aqueous solution of sodium hydroxide before removal from the fume cupboard. Samples for spectroscopic analysis were of such a volume that even catastrophic release of the entire sample would not raise the local concentration above the OEL.

These toxic materials, after being loaded into the appropriate spectrometer cells, should be transported to the instrument laboratory in a suitable closed, padded carrying case. Only the instrument operator and one other experienced worker should be in the laboratory when the samples are being studied. The mass spectrometer pumps should be vented to an exhaust system and not to the laboratory.

Source and purity of carbonyl dihalides

Phosgene, $COCl_2$ (BDH), carbonyl difluoride (Fluorochem), and carbonyl chloride fluoride (Ozark-Mahoning) were all distilled in *vacuo* prior to use, and their purity monitored by gas-phase infrared spectroscopy. Both phosgene and carbonyl chloride fluoride revealed no impurity bands; a weak band due to CO_2 was observed in the infrared spectrum of COF_2, which corresponded to an impurity level of $\leqslant$2%. Carbonyl dibromide was prepared and purified by a method described in the following paper.[9]

Spectroscopic measurements

The ^{13}C and ^{17}O NMR spectra were recorded on a Bruker WM360 spectrometer operating at 90.55 and 48.82 MHz, respectively. The ^{13}C and ^{17}O chemical shifts were measured with respect to external tetramethylsilane and water, respectively. Mass spectra were recorded on a Kratos MS80RF mass spectrometer by the electron-impact method (ionizing voltage 70 eV, *ca.* 1.12×10^{-17} J), and infrared spectra on a Perkin-Elmer 598 spectrometer. Gas-phase infrared spectra were recorded using a 10 cm gas cell fitted with CsI windows, a typical pressure being *ca.* 0.5 kPa. All spectra were calibrated using

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polystyrene (1601 and 907 cm^{-1}) and indene (551.7 and 420.5 cm^{-1}). The band assignments for the unsymmetrical carbonyl dihalides, used here, are formally incorrect. The accepted convention for assigning fundamental modes of the same symmetry is to number them sequentially with the highest frequency first and the lowest last. However, the convention adopted here, as elsewhere,[1] uses the same assignments for COXY (C_s) as for COX_2 (C_{2v}), allowing easier comparison between the symmetrical and unsymmetrical carbonyl dihalides.

Preparations

Carbonyl bromide chloride. Tribromochloromethane (20 g, 70 mmol) was placed in a three-necked flask fitted with a dropping funnel containing concentrated sulfuric acid (22 cm^3), and two condensers (one positioned above the other and maintained at 10 and −78 °C respectively). The flask was gently warmed until the solid had melted, and the sulfuric acid was added dropwise. The reaction mixture was then heated under reflux at *ca.* 130 °C for 3 h. The two condensers were then quickly removed, and replaced with a fractional distillation unit. The products were fractionally distilled and the fraction boiling in the range 23–40 °C was collected. The deep red impure distillate was then transferred quickly onto the vacuum line. It was held at −95 °C and continuously evacuated for 1 h to remove SO_2 and $COCl_2$. To remove the considerable quantities of free dibromine, the product was condensed into an ampoule (fitted with a greaseless tap) containing mercury, and allowed to warm to room temperature. The ampoule was then closed and removed from the vacuum line, and vigorously (but carefully) agitated within the fume cupboard for 5 min. The ampoule was then reconnected to the vacuum line, and the liquid distilled into a storage bulb. The straw-coloured liquid was then distilled into an ampoule fitted with a greaseless tap, and stored at room temperature in the absence of light. The purity of the product was checked by gas-phase infrared spectroscopy. Yield (based on CBr_3Cl) 2.98 g (30%).

Carbonyl bromide fluoride. A three-necked flask was fitted with a dropping funnel containing tribromofluoromethane (50 g, 180 mmol), and two condensers (one positioned above the other and maintained at 10 and 0 °C respectively). Sulfur(VI) oxide (200 g, 2.5 mol), carefully warmed using a hot-air blower, was then poured into the flask under an atmosphere of dinitrogen. The CBr_3F was then added dropwise to the SO_3 over 45 min at 35–45 °C. The evolved gas was passed through trichloroethene (300 cm^3, 30 cm height) under UV light (supplied by a 100 W UV lamp) to remove dibromine, and then through concentrated sulfuric acid (300 cm^3, 30 cm height) to remove SO_2. The product was then collected at −196 °C, and rapidly transferred onto the vacuum line, where the small amount of CO_2 present was removed by trap-to-trap distillation. The colourless gas was then distilled into a glass bulb (2 l) fitted with a greaseless tap, and stored at room temperature. The purity of the final product was checked by gas-phase infrared spectroscopy and gas chromatography. Yield (based on CBr_3F) 13.59 g (58%).

Phosgene. In this novel preparation, hydrogen chloride (4.2 g, 115 mmol) was condensed onto *N*,*N*′-carbonyldiimidazole (2.5 g, 15 mmol) at −196 °C. The reaction vessel was warmed to −63 °C, and connected to a trap held at −196 °C. The vessel was opened and the excess of hydrogen chloride condensed into the −196 °C trap. The gas-phase infrared spectrum of the contents of the −63 °C trap showed strong bands at 1827 and 849 cm^{-1} due to phosgene, as well as a much weaker band at 2886 cm^{-1} due to hydrogen chloride. Yield (based on *N*,*N*′-carbonyldiimidazole) 0.74 g (49.8%).

Carbonyl diiodide. Four unsuccessful attempts to prepare COI_2 by halide-exchange reactions, under extremely mild conditions, are described.

From sodium iodide and carbonyl dibromide. Carbonyl dibromide (0.2 g, 1.1 mmol) was condensed onto sodium iodide (0.13 g, 0.87 mmol) at −196 °C and the reaction mixture allowed to warm to −78 °C, whence a purple coloration was observed. The gas-phase infrared spectrum of the reaction mixture at this temperature showed a strong band at 2143 cm^{-1} due to carbon monoxide, along with strong bands at 1828, 788 and 747 cm^{-1} indicative of carbonyl dibromide. No bands which could have been attributed to carbonyl diiodide or carbonyl bromide iodide were observed.

From sodium iodide and phosgene. Phosgene (0.38 g, 3.8 mmol) was condensed onto sodium iodide (0.7 g, 4.6 mmol) at −196 °C and the reaction mixture allowed to warm to −78 °C, whence a purple coloration was observed. The gas-phase infrared spectrum of the reaction mixture at this temperature showed a strong band at 2143 cm^{-1} due to carbon monoxide, together with strong bands at 1827 and 849 cm^{-1} due to phosgene. No bands which could have been attributed to carbonyl diiodide or carbonyl chloride iodide were observed.

From tetraethylammonium iodide and phosgene. Phosgene (0.25 g, 2.5 mmol) was condensed onto tetraethylammonium iodide (0.8 g, 3 mmol) at −196 °C, and the reaction mixture allowed to warm to room temperature. No colour change was observed, and the gas-phase infrared spectrum of the reaction mixture showed only strong bands at 1827 and 849 cm^{-1} (due to phosgene). No bands which could have been attributed to carbon monoxide, carbonyl diiodide or carbonyl chloride iodide were observed.

From tetrabutylammonium iodide and phosgene. Tetrabutylammonium iodide (0.95 g, 2.6 mmol) was dissolved in dichloromethane (2 cm^3). Phosgene (0.28 g, 2.8 mmol) was condensed onto this solution at −196 °C, and the subsequent reaction mixture allowed to warm to −78 °C, whence a purple coloration was observed. The gas-phase infrared spectrum of the reaction mixture at this temperature showed a strong band at 2143 cm^{-1} due to carbon monoxide, together with strong bands at 1827 and 849 cm^{-1} due to phosgene.

Results and Discussion

Carbonyl bromide chloride

Two methods are described in the literature for the synthesis of COBrCl. The first, from phosgene and aluminium(III) bromide,[10] involves the use of high pressure and was therefore not adopted. The other method, described by Overend and Evans,[5] involves the reaction of bromotrichloromethane with concentrated sulfuric acid. However the use of CCl_3Br is more likely to generate $COCl_2$ rather than the desired COBrCl, and so a more logical choice of starting material would be CBr_3Cl.

Although the basis of the reaction is the same as that described by Overend and Evans,[5] the method employed here used CBr_3Cl: as well as the products shown in equations (1) and (2),

$$CBr_3Cl + H_2SO_4 \longrightarrow COBrCl + 2HBr + SO_3 \quad (1)$$

$$2HBr + SO_3 \longrightarrow SO_2 + H_2O + Br_2 \quad (2)$$

there were also considerable quantities of phosgene in the product mixture. Conventional trap-to-trap distillation was ineffective at completely separating the $COCl_2$ from the COBrCl ($COCl_2$, b.p. = 7.48 °C; COBrCl, b.p. = 25 °C). However, keeping the product mixture at −95 °C, and continuous evacuation for 1 h, gave a purity of ⩾ 95% (determined from the solution ^{13}C NMR and gas-phase IR spectra of the gaseous product). The gas-phase infrared spectrum of the vapour above the liquid COBrCl showed the impurities to be $COCl_2$ (*ca.* 6%)

and $COBr_2$ (*ca.* 3%). The concentration of the more volatile phosgene is exaggerated using this technique, and shows that care must be taken when using gas-phase infrared spectroscopy as an assessment of the purity of a liquid. The exaggerated concentration of phosgene was also observed in the mass spectrum of the COBrCl (since here, again, it is the vapour which is being analysed). However, in the photoelectron studies described elsewhere,[3] where continuous evacuation is occurring, no such problem was encountered. The synthesis of COBrCl was performed twice, giving an average yield of 30%.

The synthesis employed by Overend and Evans[5] is very poorly described, and no account is given of the scale or yield of their reaction. It is, however, apparent from their gas-phase infrared spectrum that the COBrCl contains $COCl_2$ (*ca.* 25%) and $COBr_2$ (*ca.* 10%). Even allowing for the fact that the gas-phase infrared spectrum will exaggerate the concentration of phosgene, their sample of COBrCl is significantly less pure than that prepared here. The synthesis described here is therefore a significant improvement, both in yield and purity, to that described by Overend and Evans.[5]

The gas-phase infrared spectrum of COBrCl showed the following bands: ν_1, 1828; ν_2, 517; ν_4, 806; ν_5, 372; and ν_6, 547 cm^{-1}; ν_3 was too weak to observe, even at 46.6 kPa. The frequencies observed here are in excellent agreement (±2 cm^{-1}) with the only values in the literature.[5]

Carbonyl bromide fluoride

Three syntheses of COBrF are reported in the literature. Two require the use of special equipment, since they use difluorine[11] or bromine(III) fluoride[11,12] as fluorinating agents. The other method, which was used here, equation (3), was similar to that

$$CBr_3F + SO_3 \longrightarrow COBrF + Br_2 + SO_2 \qquad (3)$$

described by Siegemund[13,14] and could be performed using conventional glassware. However, the purification of the COBrF employed here was significantly different to that used by Siegemund,[13,14] who made no attempt to remove the SO_2 formed in the reaction, and consequently reported that 29.5% of his product was SO_2. Here, the majority of SO_2 was removed by passing the product mixture through concentrated sulfuric acid, which achieved a purity of *ca.* 93% (as determined by gas-phase infrared spectroscopy). The impurities present were SO_2 (*ca.* 4%) and CO_2 (*ca.* 3%), and this was confirmed by gas chromatography. The results from these independent gas chromatography studies help to justify the use of infrared spectroscopy as a reliable means of assessing purity. As a result of the more extensive purification procedure employed here, a lower yield of a purer product was obtained, *viz.* 58%, compared with 64% reported in the literature.[13,14] The alternative syntheses of COBrF using difluorine[11] and bromine(III) fluoride[11,12] give reported yields of *ca.* 30 and *ca.* 90% respectively. Although the latter synthesis affords an excellent yield, the reported method of purification was complex, and unsuccessful in removing the large amounts of COF_2 present. The method described here thus gives the highest-purity sample of COBrF ever prepared.

The purified COBrF was stored in a glass bulb (2 l), since it was found that storage in a steel cylinder caused a yellow-brown discoloration of the product after 1 month. The gas-phase infrared spectrum of this yellow-brown product showed strong bands due to COF_2 and $COBr_2$, and indicated a complete absence of COBrF. It was therefore apparent that storage in a steel cylinder was unsuitable and caused disproportionation, according to equation (4). Disproportionation is also reported

$$2COBrF \rightarrow COF_2 + COBr_2 \qquad (4)$$

to occur if COBrF is stored in a glass bulb at room temperature for several weeks.[12] However it should be noted that the sample prepared here showed no sign of disproportionation, even after 10 months of storage in a glass bulb at room temperature in normal light. The use of brass needle valves also caused yellow-brown discoloration of the COBrF, presumably also due to reaction (4). It is therefore critical that all manipulations of COBrF use either glass or stainless-steel apparatus, neither of which was observed to induce disproportionation.

The gas-phase infrared spectrum of COBrF showed the following bands: ν_1, 1868; ν_2, 721; ν_3, 398; ν_4, 1068; ν_5, 335; and ν_6, 620 cm^{-1}. The frequencies observed here are in excellent agreement (±1 cm^{-1}) with the recent values of Zhao and Francisco,[15] except for the value for ν_3, a weak, poorly resolved band, which agrees with the observation of Patty and Lagemann.[16] Our value for ν_1, however, exactly corresponds to that of Zhao and Francisco,[15] being 6 cm^{-1} lower than the earlier value.[16]

A novel route to phosgene

The rapid reaction of *N*,*N*′-carbonyldiimidazole with carboxylic acids to generate *N*-acylimidazoles is well documented.[17,18] It was decided, in the hope of synthesizing $COCl_2$, to perform the analogous reaction, substituting hydrogen chloride for the carboxylic acid. Although this method affords a new and very straightforward synthesis of $COCl_2$, the low yield of the reaction (50%) together with a purity of only *ca.* 94% (*ca.* 6% HCl impurity determined from the gas-phase infrared spectrum) indicates that it is unlikely to provide an alternative source of phosgene. Moreover, phosgene is available very cheaply from commercial suppliers (synthesis from carbon monoxide and dichlorine affords a yield of *ca.* 100%).

Even the analogous reaction with hydrogen bromide, which in theory should yield $COBr_2$, is unlikely to replace the conventional synthesis described elsewhere.[9] However, *N*,*N*′-carbonyldiimidazole may be potentially useful in the synthesis of unsymmetrical carbonyl dihalides, COXY, by successive reactions with stoichiometric quantities of HX and HY, and may offer a route to COXI.

Attempted syntheses of carbonyl diiodide

Of the four possible carbonyl iodides, only COFI has been synthesized [by the reaction of iodine(V) fluoride and carbon monoxide in an autoclave].[11,19] It is a low-boiling liquid, which is reported to decompose at −20 °C.[20]

Limu kohu (*Asparagopsis taxiformis*) is an edible red seaweed which is highly appreciated, for both its taste and smell, in the American state of Hawaii. This alga, whose Hawaiian name means ‘supreme seaweed’, contains a wealth of halogenated compounds in its essential oil, many of which are normally regarded as acutely or chronically toxic. The volatile oil of *A. taxiformis* (obtained by condensing onto a −78 °C finger *in vacuo*) contains iodine compounds. Separation of the oil using chromatography (on silica gel at 5 °C) and analysis by gas chromatography–mass spectrometry reveals a trace of material (< 0.1%) the mass spectrum of which is not inconsistent with that expected for carbonyl diiodide.[21] Although CHI_3, and several other iodinated compounds, were readily identified by both NMR and mass spectral analysis of the crude oil obtained from *A. taxiformis*, many of the original iodine-containing compounds were found not to survive the chromatographic separation. Carbonyl diiodide was therefore postulated as an artefact that results from the decomposition of CHI_3 during the chromatographic process.[21] Recently, there was another report[4] of the ‘first’ observation of COI_2, formed in the gas phase by the reaction of ‘heated’ tetraiodomethane with dioxygen: here, the only evidence offered was the gas-phase infrared spectrum of the reaction mixture.

The reactions described here, all performed at −78 °C, were

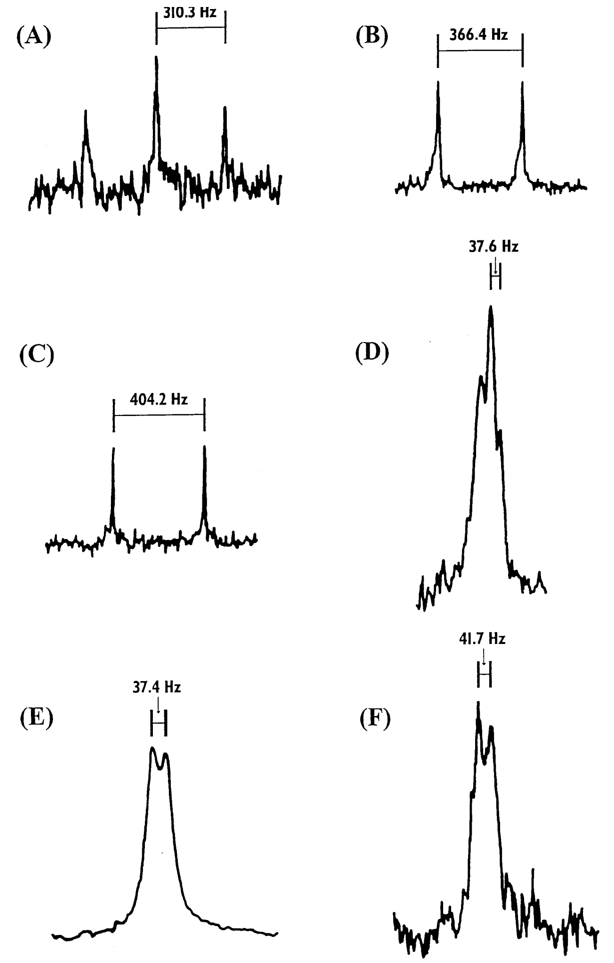

Fig. 1 The ^{13}C NMR spectra for (A) COF_2, (B) COClF and (C) COBrF, and the ^{17}O NMR spectra for (D) COF_2, (E) COClF and (F) COBrF

designed to see if the carbonyl iodides could be prepared under mild conditions. The reactions of sodium iodide with either $COCl_2$ or $COBr_2$, or of $[NBu_4]I$ with $COCl_2$ (in CH_2Cl_2), produced free I_2, with evolution of carbon monoxide; treatment of $[NEt_4]I$ with phosgene produced no observable reaction. Thus, in none of the reactions was there any evidence for the formation of COI_2, or the more probable COClI and COBrI, despite the temperature of reaction being −78 °C. There was no reaction between tetraethylammonium iodide and phosgene, due to the insolubility of the former in the latter. Earlier attempts to prepare COI_2 from phosgene and either hydrogen iodide[22] or aluminium(III) iodide[23] had also been unsuccessful, yielding only CO and iodine. The apparent instability of COI_2 is supported by thermodynamic calculations, *viz*. equations (5) and (6), calculated from the JANAF Thermochemical Tables[24]

$$2NaI(s) + COCl_2(g) \longrightarrow 2NaCl(s) + CO(g) + I_2(g); \quad \Delta G_{298} = -107.4 \text{ kJ mol}^{-1} \quad (5)$$

$$2NaI(s) + COCl_2(g) \longrightarrow 2NaCl(s) + COI_2(g); \quad \Delta G_{298} = -39.1 \text{ kJ mol}^{-1} \quad (6)$$

and estimates of the thermodynamic stability of COI_2.[25]

Reaction (5) is so facile at room temperature that it has been used in the quantitative determination of phosgene.[26,27] The driving force for these reactions is the formation of NaCl; thus substitution of tetrabutylammonium iodide for sodium iodide would be expected to increase their free energy and therefore possibly encourage the formation of COClI or COI_2. However, even in this reaction, carbon monoxide and iodine are formed, thus implying that COI_2 is unstable above −78 °C. This conclusion is supported by Staudinger and Anthes,[27] whose attempts to prepare ethanedioyl diiodide at −78 °C resulted in its decomposition to carbon monoxide and iodine (presumably *via* COI_2).

It would appear, on the basis of the evidence presented and discussed here, that COI_2 is unstable in solution, not surprising given that the estimated standard change of free energy associated with dissociation (7) is −68.3 kJ mol^{-1}, corresponding to a

$$COI_2(g) \rightleftharpoons CO(g) + I_2(g) \qquad (7)$$

standard dissociation constant, $K^{\ominus}$, of 9.2×10^{11}.[25]

The observations that COI_2 is detected in the mass spectrum of the oil extracted from the alga *Asparagosis taxiformis*[21] and in the gas-phase infrared spectrum of the reaction mixture produced by oxidizing CI_4 with O_2[4] must be regarded as unproven. It is unsound scientific practice to base identification of a newly claimed molecule upon a single spectroscopic technique, and neither mass spectrometry nor infrared spectroscopy is capable, alone, of producing definitive evidence of the existence of COI_2, especially under the conditions reported. As in law, proof should be established beyond reasonable doubt. To quote the Duke of Venice, 'To vouch this is no proof, without more wider and more overt test than these thin habits and poor likelihoods of modern seeming do prefer against him' (Shakespeare, *Othello*, Act I, Scene III). That is not to say that, under conditions of low pressure in the gas phase, COI_2 may not exist, simply that convincing evidence is still lacking.

NMR studies

The ^{13}C and ^{17}O NMR spectra (and ^{19}F when relevant) were recorded for all the known carbonyl dihalides, except COFI. The chemical shifts, coupling constants (where appropriate) and solvents are listed in Table 1. The ^{13}C and ^{17}O NMR spectra of the three fluorinated carbonyl dihalides studied are shown in Fig. 1. The chemical shifts and coupling constants recorded here are in good agreement with the more restricted set of values reported in the literature,[28–32] the exception being the ^{19}F chemical shift for COBrF. The value reported here is δ 84.7, compared with a value of δ −83.7 obtained by Krannich and Sundermeyer,[32] both shifts being measured with respect to CCl_3F. It is clear that Krannich and Sundermeyer were not following the IUPAC recommendations of sign convention, and moreover they did not state which sign convention they were using. A similar problem exists for some of the data for COF_2 amongst extant literature.

As is apparent from Fig. 2, there is no simple correlation between ^{13}C chemical shift and Pauling electronegativity (confirming Gombler)[28] or π(CO) bond order.†,[33] Clearly, the σ and π effects are working against each other, and to different extents, in each compound, the result being to nullify any correlation that might exist between the chemical shift and either σ or π effects. As noted by Gombler,[28] the pattern revealed in Fig. 2(*a*) is indicative of the presence of strong CF π bonding, and this is supported by the reflection of this pattern in Fig. 2(*b*). The $^{1}J(CF)$ coupling constant should increase as the amount of C–F π bonding increases: COF_2 has the lowest π(C–F) bond order (0.172 *versus* 0.199 and 0.192 for COClF and COBrF respectively), and hence it has the smallest $^{1}J(CF)$ coupling constant (310.3 Hz). The difference in coupling constants between

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† The π(CO) bond orders, calculated on a simple overlap basis from *ab initio* calculations using an STO-3G basis set within the Gaussian 82 package, are: COF_2, 0.742; COClF, 0.750; COBrF, 0.751; $COCl_2$, 0.780; COBrCl, 0.775; $COBr_2$, 0.772. The π(CF) bond orders are: COF_2, 0.172; COC1F, 0.199; COBrF, 0.192.[33]

Table 1 Carbon-13, ^{19}F and ^{17}O NMR spectroscopic data for the carbonyl halides[a]

	δ(^{13}C)[b]	δ(^{19}F)[c]	δ(^{17}O)[d]	^1J(CF)[e]/Hz	^2J(OF)[f]/Hz	Ref.
COF_2	134.2	−23.0		309		28
	134.1	−20.4	259.5	310.3	37.6	This work
			+21.54[g,h]		308.4[i]	29
		+23.4[h,j]				30
		+22.5[h,k]				30
COClF	140.5	59.7		366		28
	139.9	60.0	375.1	366.4	37.4	This work
$COCl_2$	141.8[p]					28
	142.1[l,m]					31
	142.8[n]		483.6[n]			This work
COBrCl	125.0					28
	127.2[n]		526.5[n]			This work
COBrF		−83.7[h,m]				32
	127.6	+84.7	401.9	404.2	41.7	This work
$COBr_2$	103.4[l]					28
	106.9[n]		549.2[n]			This work

[a] Dissolved in trichlorofluoromethane, and measured at −50 °C, unless otherwise stated. [b] Measured with respect to $SiMe_4$. [c] Measured with respect to CCl_3F. [d] Measured with respect to external water. [e] Measured from the ^{13}C NMR spectra. [f] Measured from the ^{17}O NMR spectra. [g] Value extrapolated to infinite dilution, temperature not quoted. [h] Presumably measured with a reversed (and unstated) sign convention. [i] Measured in the neat liquid. [j] Measured in diethyl ether. [k] Measured in fluorobenzene. [l] Measured at room temperature. [m] Measured in tetrachloromethane. [n] Measured in dichloromethane.

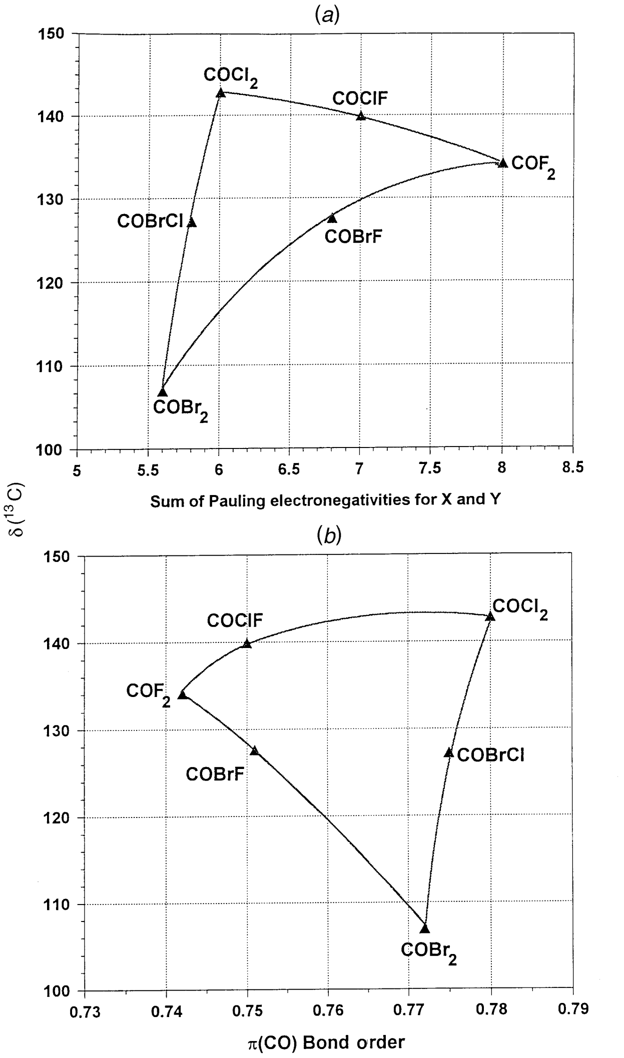

Fig. 2 Carbon-13 chemical shifts of COXY as a function of (*a*) the sum of the Pauling electronegativities of X and Y,[28] and (*b*) the π(CO) bond order

COClF (366.4 Hz) and COBrF (404.2 Hz) must be due to electronegativity effects, since the π(C−F) bond orders predict COClF would have the larger coupling constant.

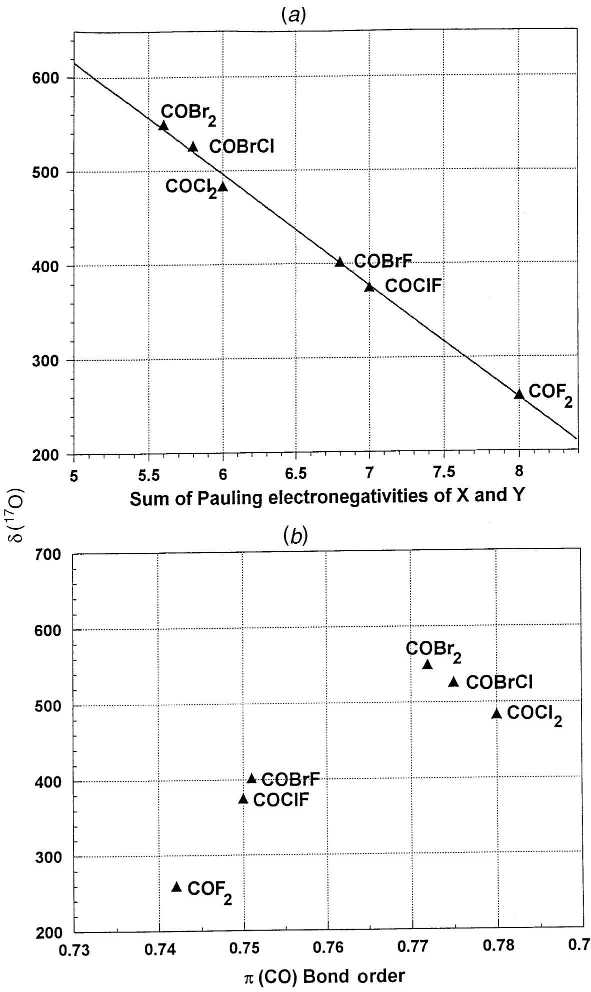

Fig. 3 Oxygen-17 chemical shifts of COXY as a function of (*a*) the sum of the Pauling electronegativities of X and Y, and (*b*) the π(CO) bond order

Examination of Fig. 3 shows there to be no meaningful correlation between ^{17}O chemical shift and π(CO) bond order, yet a very good correlation ($r = -0.998$, $n = 6$) exists between the ^{17}O chemical shift and the sum of the Pauling electronegativities of the halogens. This suggests that the inductive effect dominates

Table 2 The El mass spectrometric data for the carbonyl halides COXY[a]

	[COXY]$^+$	[COX]$^+$	[COY]$^+$	[CO]$^+$	[XY]$^+$	[CX]$^+$	[CY]$^+$	X$^+$	Y$^+$
COF_2[b]	73	100	—	30		5	—		
$COCl_2$	22	100	—	24	23	17	—	46	—
$COBr_2$		100	—	4	37	12	—	86	—
COClF	64	57	100	7				16	
COBrCl	14	92	100	8		18	12	90	23
COBrF	37	100	13	4		10		34	

[a] The relative % intensities are listed, normalized to the strongest peak in each spectrum. [b] Data taken from ref. 35.

the determination of terminal oxygen chemical shift (as appears also to be the case with the restricted data set from the ^{19}F chemical shifts),[28] whereas the chemical shift of the central carbon atom is determined by a balance of opposing σ and π effects. The ^{2}J(OF) coupling constants listed in Table 1 are so similar that it would be redundant to attempt to account for their differences.

Mass spectrometric studies

The mass spectrum of COF_2 is well documented,[34–36] and was therefore not recorded. The mass spectra of $COCl_2$,[35,37] COClF[35] and COBrF[32] have been reported in the literature previously, and these results are in reasonable agreement with those obtained here. The mass spectra of $COBr_2$ and COBrCl are previously unreported. As is apparent from Table 2, with the exception of $COBr_2$, all the carbonyl dihalides give well defined molecular ions and show similar fragmentation patterns. The absence of a molecular ion for $COBr_2$ is not too surprising, since it is the least stable of the isolated carbonyl dihalides, and readily dissociates to CO and Br_2, with a dissociation constant of 12.[38] There was no evidence of any associated species in any of the mass spectra, this being particularly relevant to $COCl_2$, the dimer and trimer of which are well known.[1]

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