The spectroscopic identification and characterisation of carbonyl telluride (OCTe)†

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Photolysis of H_2Te in CO or 1% CO/Ar matrices at *ca.* 10 K results in the formation of carbonyl telluride; the assignment of the ν_{CO} modes of OCTe (1965.3 cm^{-1}), O^{13}CTe (1920.0 cm^{-1}) and ^{18}OCTe (1921.3 cm^{-1}) in neat CO matrices is confirmed by DFT calculations.

Carbonyl telluride (OCTe) is the only member of the carbonyl chalcogenides (apart from carbonyl polonide) that has not been spectroscopically identified or characterised, either in the solid, vapour or in cryogenic matrices. Reference to it in the chemical literature is very fleeting, including the first report of its preparation in 1944 which contained no experimental or characterisation details, but which did indicate that it was less stable than the analogous carbonyl selenide.[1] In 1993 Sonoda[2] reported that carbonyl telluride had not yet been identified, and we cannot find any subsequent reports. There are however, a couple of earlier papers containing predictions of its vibrational modes,[3] and calculations of its proton affinity and structural parameters.[4] As carbonyl selenide has been identified as the catalytic intermediate in the selenium assisted carbonylation of amines,[2] and it is also known that tellurium catalyses this reaction[5] we have initiated a study of the interaction of tellurium atoms with carbon monoxide to spectroscopically identify and characterise carbonyl telluride so that its presence in tellurium mediated organic transformations can be identified. One of the most common ways of stabilising reactive species is matrix isolation, but there is a distinct paucity of tellurium atom cryochemistry because the predominant vapour phase species above heated elemental tellurium are dimers, tetramers, *etc.*, and even when the vapour is superheated, the fraction of tellurium atoms remains low.[6] In this work we report the photolysis of H_2Te as an alternative source of tellurium atoms, and whilst this has been used previously to obtain tellurium atoms in argon matrices for Mössbauer experiments,[7] it has not been exploited as a cryochemical synthetic tool. In addition to being a source of atomic tellurium, Donovan *et al.*[8] have shown that when H_2Te is photolysed by UV light, some of the resultant Te atoms are in a $^1D_2$ excited state rather than the $^3P_2$ ground state expected from thermal evaporation, and this may result in lower activation barriers for subsequent reactions.

When H_2Te was matrix isolated in solid N_2 and photolysed with UV radiation,[9] the intensities of the three IR active bands at 2085.2 cm^{-1} (ν_1), 865.1 cm^{-1} (ν_2) and 2092.0 cm^{-1} (ν_3), (in good agreement with the previous high resolution[10] and nitrogen matrix[11] IR data) were reduced considerably, with no sign of the growth of any other bands. We have noted that this photobleaching is much more efficient using UV rather than visible irradiation, and that photolysis during deposition also increased the photobleaching of the H_2Te bands. In a neat CO ($^{12}C^{16}O$) matrix, the H_2Te stretching modes were obscured by the bands due to the various CO isotopomers. On UV photolysis in neat CO the ν_2 mode of H_2Te at 863.0 cm^{-1} decreased, and a new band (in the ν_{CO} region associated with carbonyl complexes) grew in at 1965.3 cm^{-1}, as well as features[12] due to

HCO (*ca.* 1860 cm^{-1}) and H_2CO (*ca.* 1740 cm^{-1}) [Fig. 1(a)]. When ^{13}CO was used [Fig. 1(b)] the 1965.3 cm^{-1} band shifted to 1920.0 cm^{-1} and the use of ^{12}CO:^{13}CO ($\approx$1:1) mixed matrices [Fig. 1(c)] confirmed the presence of only one CO group in the moiety giving rise to these bands. With the use of $C^{18}O$ [Fig. 1(d)], the shift from a CO (1965.3 cm^{-1}) to a $C^{18}O$ matrix (1921.3 cm^{-1}) was less than that for a ^{13}CO matrix (1920.0 cm^{-1}). When H_2Te was trapped in a 1% CO/Ar matrix, the only band observed after photolysis in the 2000–1680 cm^{-1} region was at 1970.7 cm^{-1}, which is the counterpart of the 1965.3 cm^{-1} feature in the neat CO matrices, with no evidence of any HCO or H_2CO. When D_2Te was isolated and photolysed in a 1% CO/Ar matrix, the band at 1970.7 cm^{-1} was also present with no sign of any deuterated analogue, and photolysis of H_2Te in 1% ^{13}CO/Ar yielded a new feature at 1924.7 cm^{-1}.

The presence of HCO and H_2CO in the neat CO matrices confirms that the photolysis of H_2Te yields hydrogen and tellurium. The assignment of the features at 1965.3, 1920.0 and 1921.3 cm^{-1} in neat CO matrices to the ν_{CO} modes of the isotopomers of a monocarbonyl species is straightforward on the basis of the mixed CO:^{13}CO experiments, and the fact that in 1% CO/Ar matrices the 1970.7 cm^{-1} band is not affected by deuteration confirms the lack of hydrogen in the species giving rise to these features. As OCS is one of the products formed when H_2S is photolysed in solid CO,[12] it is reasonable to assign the features at 1965.3, 1920.0 and 1921.3 cm^{-1} to the ν_{CO} modes of OCTe, O^{13}CTe and ^{18}OCTe, respectively. The lack of bands other than these in the 1% CO/Ar matrices confirms this assignment as it has been noted previously that HCO is only observed in dilute CO/Ar matrices when vac-UV photolysis rather than UV–VIS photolysis is employed.[13] The isotopic ratios, in conjunction with the experimental data for the ν_{CO} modes of OCSe (OC^{80}Se, 2023.525064 cm^{-1}; O^{13}C^{80}Se,
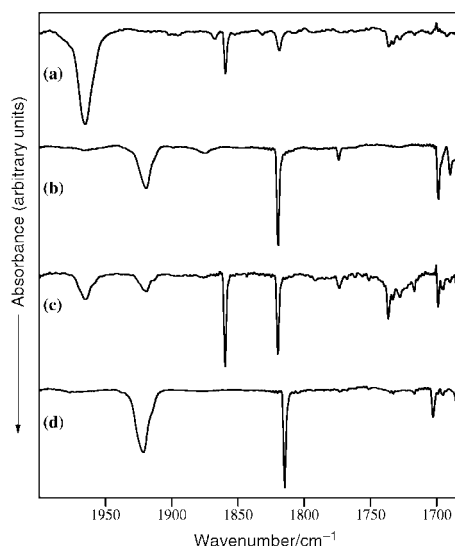

Fig. 1 Matrix isolation IR spectra of the photolysis products of H_2Te in neat CO matrices at *ca.* 10 K: (a) $^{12}C^{16}O$ (CO); (b) ^{13}CO; (c) CO:^{13}CO (~ 1:1); (d) $C^{18}O$.

1973.82425 cm^{-1}; $^{18}OC^{80}Se$, 1983.54657 cm^{-1})[14] and our DFT calculated[15] frequencies of the ν_{CO} modes of OCTe (OCTe, 1981 cm^{-1}; O^{13}CTe, 1933 cm^{-1}; ^{18}OCTe, 1939 cm^{-1}), all reinforce the conclusion that these bands are the ν_{CO} modes of carbonyl telluride. The DFT calculations also indicated that the intensity of the ν_{CTe} and δ_{OCTe} modes would be too low to be observed in the experimental spectra.[16]

Our previous DFT calculations[17] have shown that the bonding between a main group metal and CO can be described in an analogous way to the synergic mechanism used for conventional transition metal carbonyls. In the case of OCTe the DFT calculations predict that the Te σ-accepts *ca.* 0.6 e$^-$ and π-backdonates *ca.* 0.7 e$^-$ to CO, resulting in a lengthening of the CO bond and a reduction of the CO bond order and ν_{CO} frequency. The Te–CO bond energy for OCTe with respect to Te(^{3}P) and CO($^1\Sigma^+$) was calculated to be −187 kJ mol^{-1}, and OCTe was favoured over the COTe isomer by 152 kJ mol^{-1} with markedly different values for ν_{CO} of 1981 and 1835 cm^{-1}, respectively. The linear dicarbonyl telluride [(OC)$_2$Te] was found to be 36 kJ mol^{-1} less stable than OCTe, and (OC)$_3$Te was unstable with respect to decomposition.

Therefore, using the first spectroscopic identification and characterisation of carbonyl telluride, this work has demonstrated that the photolysis of hydrogen telluride is an excellent source of both hydrogen and tellurium atoms for use in cryochemical synthesis. The identification of the ν_{CO} modes of OCTe will be useful in identifying whether this is an intermediate in organic transformations.

Notes and references

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