A COMPUTATIONAL STUDY OF ADDUCTS BETWEEN ATOMIC CHLORINE AND CARBON DIOXIDE,
CARBONYL SULFIDE AND CARBON DISULFIDE

Paul Marshall

Department of Chemistry

University of North Texas

PO Box 5068, Denton, Texas 76203

ABSTRACT

The geometries and vibrational frequencies of the adducts ClCO_2 , ClCOS and ClCS_2 are derived at the HF/3-21G(*) level. The C_s structure of ClCO_2 corresponds to one C-O bond and one C=O bond. Similarly, C_s ClCS_2 has one C-S and one C=S bond, and ClCOS has one C-S and one C=O bond. Single-point spin-projected MP4/3-21G(*) calculations at these geometries are used in bond separation reactions to derive ΔH°_0 for adduct formation, which is calculated to be about 39 kJ mol^{-1} exothermic for ClCOS and ClCS_2 , but about 39 kJ mol^{-1} endothermic for ClCO_2 . C_{2v} structures for ClCO_2 and ClCS_2 are also characterized. The geometry of ClCS_2 has not been determined experimentally; comparison with an available measured entropy for ClCS_2 suggests that the C_{2v} structure is the one formed by addition of Cl to CS_2 , although the energy relative to the C_s form is not reliably calculated because of instability in the HF wavefunction.

1. INTRODUCTION

A recent study of the elementary reaction of atomic aluminum with carbon dioxide suggests that a stable adduct can be formed [1], a conclusion which is supported by a computational investigation of the $\text{Al} + \text{CO}_2$ potential energy surface [2]. Such adducts may be invoked as intermediates for reactions which show strong deviations from simple Arrhenius behavior [3]. As part of a general investigation of this type of reaction, and to test one approach to the calculation of thermochemical properties, a computational study of adduct formation between a *non-metal*, atomic chlorine, and CO_2 and the valence isoelectronic molecules COS and CS_2 is presented here.

Nicovich et al. have demonstrated that $\text{Cl}(^2\text{P}_j)$ reversibly forms a stable adduct with CS_2 , and measured the kinetics and thermochemistry of the process

by monitoring the time-resolved decay of Cl in the presence of excess CS_2 [4].

One aim of the present study is to obtain the geometry and vibrational frequencies of this ClCS_2 adduct computationally, information which is not available from experiments. Analogous complexes of Cl with CO_2 and COS are also investigated,

and likely Cl-C bond strengths predicted. The vibrational frequencies of these species are predicted, to guide future direct observation of these adducts by IR spectroscopy.

2. COMPUTATIONAL APPROACH

Geometries of CXY (X and Y = O and/or S) and ClCXY are optimized at the self-consistent field (Hartree-Fock) level [5] with the 3-21G and 3-21G(*) split-valence basis sets of atomic orbitals (the latter set includes d-type polarization functions on S and Cl) [6] using analytical gradients [7]. Spin-restricted HF is used for closed-shell species [8], and unrestricted HF for open-shell species [9]. Harmonic frequencies are calculated at these geometries to verify that true energy minima are located. These frequencies are scaled by a factor of 0.9 to approximate ν_0 before calculation of zero-point vibrational energies (ZPE) [10]. Total electronic energies at each HF/3-21G(*) geometry are then calculated by means of fourth order Møller-Plesset perturbation theory with contributions from single, double, triple and quadruple substitutions to account for electron correlation, with frozen core electrons [11], applied using the 3-21G(*) basis set. Combination of MP theory with this basis set has been employed previously e.g. by Gordon and co-workers [12]. For open-shell species there is a possibility of spin-contamination which affects the calculated energies: this is accounted for by spin-projection [13] and the results are denoted as PMP4/3-21G(*)//HF/3-21G(*) energies. All calculations are carried out using the Gaussian 88 program [14] on a VAX 6310 computer.

3. RESULTS AND DISCUSSION

Structures and frequencies of CXY molecules

A necessary condition for the calculational method is that it reproduce the known properties of the parent CXY molecules. The linear geometries calculated for $^1\Sigma$ CO₂, COS and CS₂ are summarized in Table I. It may be seen

that the bond lengths agree satisfactorily with experiment. The C-S distances calculated at the HF/3-21G(*) level are about 5 pm shorter than at the HF/3-21G level, and are closer to the experimental values. Also, use of an atomic basis set with polarization functions yields a slightly improved C-O distance in COS. The mean absolute error in bond length for the CXY molecules is 0.9 pm with the 3-21G(*) basis set. In the rest of this study attention is therefore mainly focused on data obtained with this larger set. The structure of CO₂ is also calculated using a correlated wavefunction, at the MP2/3-21G level, which yields $r(\text{C-O}) = 119.6$ pm. This is about 4 pm too large, and together with the HF result brackets the experimental value. Similarly, MP2/3-21G(*) calculations on COS yield $r(\text{C-O}) = 119.4$ pm, again about 4 pm too large, and $r(\text{C-S}) = 157.1$ pm, which is about 1 pm greater than the experimental distance. Inclusion of electron correlation therefore appears to have little effect on the calculated C-S distance.

There is good accord between the experimental and calculated vibrational frequencies of CXY molecules, summarized in Table I. Slightly better agreement is again obtained with the larger basis set: the data at the HF/3-21G and 3-21G(*) levels have mean absolute errors of 73 and 52 cm⁻¹, respectively.

C_s structures of ClCXY adducts

Minima located in the potential energy surfaces for the ClCXY adducts show C_s symmetry. The HF wavefunction at each apparent minimum is checked to ensure that it is stable with respect to perturbations in the orbital symmetries, and is the lowest energy wavefunction at this geometry [15]. The stability with respect to small changes in the nuclear geometry is also tested, to ensure that a true energy minimum is located. Geometries for these

planar $^2A'$ adducts calculated at the HF/3-21G and HF/3-21G(*) levels are shown in Figure 1. The main differences are in the C-Cl distances which are ≈ 10 pm shorter upon inclusion of d-functions in the basis set. This is similar to the changes found by Hehre *et al.* for chloromethane, where $r(\text{C-Cl})$ at the HF/3-21G level is too large by 11 pm, and too large by only 2.5 pm at the HF/3-21G(*) level [10]. The C_s geometry of ClCO_2 is also optimized using correlated wavefunctions at the MP2/3-21G(*) level: the two C-O distances are 137.5 pm and 121.0 pm, and the C-Cl distance is 181.0 pm. Based on the effects of correlation on the calculated CO_2 structure noted above, the HF and MP2 calculations probably bracket the true values of $r(\text{C-O})$, and suggest a likely uncertainty of around 4 pm or less in the HF/3-21G(*) bond lengths.

The average C-Cl distance of ≈ 176 pm calculated for the three adducts is similar to that found in CH_3Cl (178 pm) [16], which suggests that the C-Cl bond is a normal σ bond. Compared to the parent CXY molecules, the main feature of the adducts is that the C-X distance remains almost unchanged from the separation in the multiply bonded parent, while the C-Y distance is increased and approaches that for a single C-Y bond. In ClCO_2 the two C-O separations are calculated to be 136 and 118 pm, values which are similar to the C-O distances measured in CH_3OH (142 pm) [10] and CO_2 (116 pm) [16], respectively. A plausible description of the bonding is therefore

with the unpaired electron on an oxygen atom. This idea is also consistent with the distortions of the bond angles away from 120° on simple VSEPR arguments. In ClCOS the C-O distance of 119 pm is close to that in CO_2 , while the C-S distance has increased to 175 pm, comparable to that observed for

CH₃SH (182 pm) [10]. A consistent bonding picture is

In ClCS₂ the C-S separations of 162 and 173 pm are again approximately consistent with one singly and one doubly bonded S atom:

No evidence was found for any minima where Cl bonded directly to O or S, by contrast to e.g. the experimentally known adduct between H and CO₂ which can be represented as HOCO [18].

C_{2v} structures of ClCO₂ and ClCS₂

Minima have also been located at C_{2v} geometries for the Cl-atom adducts to CO₂ and CS₂, with equivalent pairs of C-O and C-S bond lengths. The HF/3-21G(*) geometries were verified to be stable with respect to perturbations in the nuclear positions. The results are summarized in Table II. The C-Cl distances are strongly dependent on the inclusion of d-functions in the atomic basis set: the more reliable 3-21G(*) values of ≈173 pm are typical for Cl bonded to an aromatic or olefinic C atom [19]. The C-X distances are intermediate between single and doubly bonded X, as given above. The structure predicted for ClCS₂ differs from that considered by Nicovich et al., who assumed that r(C-S) is 155 pm, r(C-Cl) is 200 pm and the S-C-S angle is 150° [4]. The C_{2v} structure for ClCO₂ is also optimized at the MP2/3-21G(*) level, to yield r(C-O) = 127.4 pm, r(C-Cl) = 175.1 pm and an O-C-O angle of 117.3°. Thus, as in the case of the C_s structure, the bonds are slightly lengthened when correlation is taken into account.

The HF wavefunctions are found to be internally unstable[15], which means that the apparent energy differences between the two forms of the ClCO_2 and ClCS_2 adducts (see Table II) do not reliably indicate that the C_s forms are indeed the lowest energy configurations. Such "symmetry breaking" effects which artificially destabilize the C_{2v} structures have been discussed by McLean *et al.* who analyzed the C_s and C_{2v} forms of HCO_2 [20]. In the case of ClCS_2 experimental data, discussed below, are used to resolve the issue of the lowest energy geometry.

Vibrational frequencies of ClCXY adducts

Table III summarizes the scaled vibrational frequencies calculated for the ClCXY adducts, and their intensities [21]. For ClCO_2 the most intense bands are predicted to be at 1775 cm^{-1} or 1890 cm^{-1} , depending on the symmetry. These are separated from CO_2 modes by more than 300 cm^{-1} and are the most promising for IR detection. Potential detection frequencies for ClCOS and ClCS_2 are similarly well-separated from frequencies of COS and CS_2 . For ClCS_2 Nicovich *et al.* estimated frequencies of 350, 400, 500, 500, 650 and 1530 cm^{-1} [4]. The major differences from the *ab initio* values are in the highest frequency mode, which is predicted here to lie about 400 or 500 cm^{-1} (depending on the symmetry) lower than their estimate [4], and in the lowest frequency modes, where the *ab initio* values are 100 cm^{-1} or more smaller than their estimates [4].

Thermochemistry

The HF/3-21G(*) structures and geometries for CS_2 and ClCS_2 yield a calculated [23] ΔS° for reaction 1 at 221 K of $-93\text{ J K}^{-1}\text{ mol}^{-1}$ for the C_s

adduct, and $-101 \text{ J K}^{-1} \text{ mol}^{-1}$ for formation of the C_{2v} adduct. The experimental value of $\Delta S^\circ = -109 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$ [4] therefore favors the existence of the C_{2v} form. The main contribution to the difference in entropy between the alternative structures arises from the rotational symmetry factor. The entropy of the C_{2v} adduct may still be somewhat overestimated, suggesting that the lowest derived vibrational frequencies are perhaps too small. The symmetry assignment demonstrates that the energy differences between C_s and C_{2v} forms (ΔE of Table II), calculated at the HF/3-21G(*) level, are inadequate because of symmetry breaking. At the MP2/3-21G(*) level the C_{2v} form of ClCO_2 is calculated to be only 7 kJ mol^{-1} above the C_s form, so it appears that inclusion of correlation at the MP2 level considerably reduces ΔE . McLean *et al.* indicate that for reliable estimation a more sophisticated MCSCF approach is required [20]. However, it is possible to estimate energy changes involving the C_s adducts and, based on the small energy differences between C_s and C_{2v} HCO_2 [20], the derived bond energies may approximate the bond energies in the C_{2v} adducts also.

To obtain *ab initio* estimates of enthalpy changes for reactions 1-3, bond separation processes which lead to simple products but which conserve the number and type of formal bond between the atoms are analyzed [24]. The C_s adducts have straightforward bond assignments presented earlier. For example, to investigate reaction 1, ΔH°_0 for the process

which conserves the number of C=S, C-S and C-Cl bonds is calculated at the PMP4/3-21G(*)//HF/3-21G(*) level including ZPE. *Ab initio* energy data are summarized in Table IV. Similarly, reactions 2 and 3 are investigated by means of ΔH°_0 for the processes

respectively. Experimental values of ΔH_f° for CH_4 [16], CH_3Cl [16], HCHO [16], HCHS [25], CH_3OH [26] and CH_3SH [26] are then employed to derive the ΔH_f° of the adducts, tabulated in Table V. These ΔH_f° are combined with experimental values [16] of ΔH_f° for Cl and the parent CXY molecules to yield D_0 , the bond dissociation energies for the adducts at 0 K, also tabulated in Table V. The largest uncertainties quoted for the experimental ΔH_f° values employed are about ± 2 and $\pm 6 \text{ kJ mol}^{-1}$ in the quantities for CH_3Cl and HCHO [16], respectively. The uncertainty in ΔH_f° for HCHS is estimated to be about 15 kJ mol^{-1} here [25]. The calculated D_0 values for ClCO_2 and ClCOS are therefore uncertain by approximately $\pm 8 \text{ kJ mol}^{-1}$, and the D_0 values for ClCS_2 are uncertain by about $\pm 17 \text{ kJ mol}^{-1}$. Table V shows good agreement between experiment and theory for reaction 1, which suggests that bond energies predicted for reactions 2 and 3 may also be reliable.

4. CONCLUSIONS

Both C_{2v} and C_s forms of ClCO_2 and ClCS_2 have been investigated, and vibrational frequencies predicted. Hartree-Fock instability prevents reliable calculation of the more stable structure, but entropy measurements for $\text{Cl} + \text{CS}_2$ indicate that C_{2v} ClCS_2 is formed in experiments. The C-Cl bond energy calculated for this molecule agrees with experiment, and predictions are made for reactions 2 and 3 which may aid the design of experiments to study these processes. In particular reaction 2, calculated here to be endothermic, will be difficult to monitor.

5. ACKNOWLEDGMENTS

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- lies midway between a mass spectrometric estimate of $90 \pm 8 \text{ kJ mol}^{-1}$ [M. Roy and T.B. McMahon, *J. Organic Mass Spectrosc.* 17 (1982) 392] and an *ab initio* estimate of 123 kJ mol^{-1} [L.A. Curtiss, C. Jones, G.W. Trucks, K. Raghavachari and J.A. Pople, *J. Chem. Phys.* 93 (1990) 2537].
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TABLE I

Comparison of *ab initio* geometries and frequencies for CXY molecules with experiment.^a

molecule		r(C-O)/pm	r(C-S)/pm	ν_o/cm^{-1} ^b
CO ₂	HF/3-21G	115.6	-	593, 593, 1285, 2217
	Experiment	116.0	-	667, 667, 1385, 2349
COS	HF/3-21G	114.0	162.7	513, 513, 691, 2018
	HF/3-21G(*)	114.7	156.5	527, 527, 799, 2000
	Experiment	116.0 ^c	156.0 ^c	524, 524, 859, 2064
CS ₂	HF/3-21G	-	157.9	390, 390, 588, 1354
	HF/3-21G(*)	-	154.1	410, 410, 653, 1454
	Experiment	-	155.3	396, 396, 658, 1535

(a) Unless noted otherwise, experimental data are taken from ref. [16].

(b) *Ab initio* harmonic frequencies have been scaled by 0.9 (see text).

(c) Data from ref. [17].

TABLE II

Geometries of HF minima for C_{2v} forms of $ClCX_2$ molecules

Species	Basis set	r(C-Cl)/pm	r(C-X)/pm	angle X-C-X	$\Delta E/kJ\ mol^{-1}\ ^a$
$^2B_2\ ClCO_2$	3-21G	188.2	122.8	122.2°	105
	3-21G(*)	173.2	124.1	117.2	
$^2B_2\ ClCS_2$	3-21G	180.1	168.7	116.0°	37
	3-21G(*)	172.5	164.8	113.7	

(a) Electronic energy above $C_s\ ^2A'$ state at the HF/3-21G(*) level.

TABLE III

Scaled HF/3-21G(*) vibrational frequencies for ClCXY adducts^a

² A' ClCO ₂	ν_o/cm^{-1}	357	452	638	659	1008	1775
	ϵ^b	5	1	37	142	217	417
² B ₂ ClCO ₂	ν_o/cm^{-1}	394	443	621	657	1329	1890
	ϵ^b	7	0.5	243	45	484	1844
² A' ClCOS	ν_o/cm^{-1}	243	398	486	563	775	1719
	ϵ^b	2	1	86	13	326	343
² A' ClCS ₂	ν_o/cm^{-1}	230	278	435	448	776	998
	ϵ^b	1	0.4	2	31	125	45
² B ₂ ClCS ₂	ν_o/cm^{-1}	270	275	477	505	909	1135
	ϵ^b	1	0.1	29	1	286	2185

(a) *Ab initio* harmonic frequencies have been scaled by 0.9 (see text).(b) IR absorption coefficient in units of 10³ m mol⁻¹ [22].

TABLE IV

Energies calculated at the PMP4/3-21G(*)//HF/3-21G(*) level and zero-point energies calculated from scaled HF/3-21G(*) frequencies.

Species	energy/hartrees	ZPE/kJ mol ⁻¹
CO ₂	-186.919693	28.0
² A' ClCO ₂	-644.361575	29.2
COS	-508.150938	23.0
² A' ClCOS	-965.621941	25.0
CS ₂	-829.371907	17.6
² A' ClCS ₂	-1286.846570	18.9
CH ₄	-40.093895	113.4 ^a
H ₂	-1.146946	25.1 ^a
HCHO	-113.454402	68.5 ^a
CH ₃ Cl	-497.051911	95.9 ^a
HCHS	-434.691561	63.3 ^a
CH ₃ OH	-114.630063	128.8 ^a
CH ₃ SH	-435.887704	117.3 ^a

(a) ZPE taken from ref. [10].

TABLE V

Thermochemistry of ClCXY adducts at 0 K.

Species	Calculated $\Delta H_f^\circ/\text{kJ mol}^{-1}$	$D_0(\text{CXY-Cl})/\text{kJ mol}^{-1}$
$\text{C}_s \text{ ClCO}_2$	-234	$-39 \pm 8 \text{ calc.}$
$\text{C}_s \text{ ClCOS}$	-57	$38 \pm 8 \text{ calc.}$
$\text{C}_s \text{ ClCS}_2$	+197	$39 \pm 17 \text{ calc.}$
Expt. ClCS_2		$40 \pm 3 \text{ expt. [4]}$

Figure 1

Scale diagrams of the planar C_s geometries calculated for $ClCO_2$, $ClCOS$ and $ClCS_2$ adducts at the HF/3-21G(*) level (upper numbers) and HF/3-21G level (lower numbers).

Figure 1