Oxygen Transfer from Chromyl Chloride to Alkynes and Allene − IR-Spectroscopic Identification of η^1-Ketene and Cyclopropanone Complexes of $O{=}CrCl_2$

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Photolytically-induced reactions of chromyl chloride with acetylene and but-2-yne (dimethylacetylene) in low-temperature argon matrices yield *end-on* ketene and dimethylketene complexes of $O{=}CrCl_2$, respectively. The product formation probably results from an electrophilic attack of a Cr=O linkage on the C≡C triple bonds, leading to radical-like transition states or intermediates, which subsequently rearrange through 1,2-H or 1,2-methyl shifts. Consequently, allene is attacked at its central carbon and the allyl radical thus generated undergoes subsequent ring-closure to give a cyclopropanone complex of $O{=}CrCl_2$.

Introduction

The oxidation of olefins by chromyl chloride, which was established in the 19th century,[1] is still employed for the functionalization of C=C double bonds yielding epoxides, chlorohydrins, and dichlorides.[2] Although the associated mechanism has been the subject of extensive studies,[3] until recently the detailed course of these reactions remained speculative, and there was no evidence to support the intermediacy of the species that had been proposed to account for the experimental findings. Cook and Mayer wrote: "The nature and the chemistry of such intermediate chromium species is perhaps the most difficult aspect of these reactions to unravel",[4a] and indeed, this matter has received significant attention in the past.[2a,5] Substantial progress has, however, been made, especially within the last two years: Ziegler et al. have postulated, on the basis of exemplary DFT calculations in the case of ethylene,[6] that interactions with the $Cr(=O)_2$, $Cr(=O)Cl$, or $CrCl_2$ moieties represent the initial steps responsible for the formation of the three observed products (vide supra) when this olefin is oxidized. At the same time, we have been able to show that it is possible to photolytically induce olefin oxidations by chromyl chloride at 10 K in argon matrices. In this way, it has been possible to matrix-isolate complexes of ketones, aldehydes, and epoxides with the hitherto unknown oxometal halide $O{=}CrCl_2$, which represent the primary products of oxo-transfer reactions combined, in some cases, with 1,2-H migrations (cf. Scheme 1).[7] In fact $O{=}CrCl_2\cdots$epoxide complexes have been proposed as intermediates accounting for epoxide formation by others,[2a,6b] but the mechanism of the reactions occurring under photolytic matrix conditions is probably different from that which is operative under thermal conditions. The former most likely involves photoexcited chromyl chloride in its triplet state,[7b] which is not accessible under thermal conditions. Once in the excited state, chromyl chloride is capable of oxygenating olefins either via an epoxide-like or a radical-like transition state. The latter rearranges through a 1,2-H shift to generate a carbonyl complex, while the former yields epoxide complexes that have been postulated as being formed after a spin-crossover via glycolates in the thermal process (Scheme 1).[6b] Consequently, in spite of different initial transition states and intermediate geometries, the minima corresponding to the matrix-isolated species are common to the potential energy surfaces of both processes, making their identification, characterization, and investigation an important issue.

Results and Discussion

We have expanded our investigations concerning the photoreactions of chromyl chloride with unsaturated systems under matrix conditions from alkenes to alkynes and allene.

(a) CrO_2Cl_2/HCCH

Literature concerning the products of alkynes in oxidations with chromyl chloride under preparative conditions is scarce, but where reported diketones or α-C oxidation products have been obtained.[8] If the principles found for the matrix oxidations of olefins by chromyl chloride[7] also hold for alkynes, interesting products may be expected: an analogous route to path (i) in Scheme 1 would lead to an oxirene complex, while that corresponding to path (ii) would generate a η^1-ketene complex, as shown in Scheme 2 in the case of acetylene. Both are attractive targets:

(i) There have been many attempts to synthesize and characterize oxirenes. Such species have frequently been proposed as intermediates during the Wolff rearrangement or during oxidation reactions involving alkynes, and have

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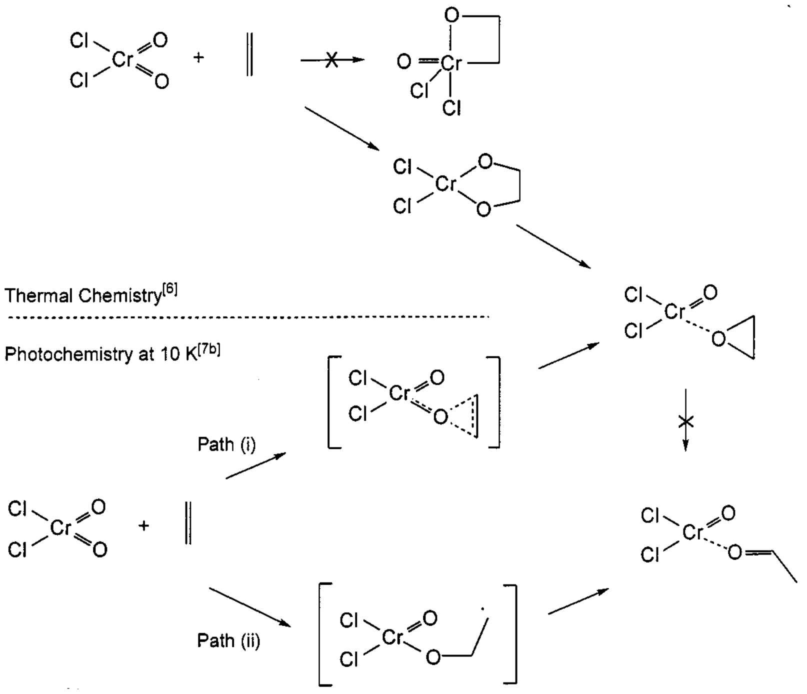


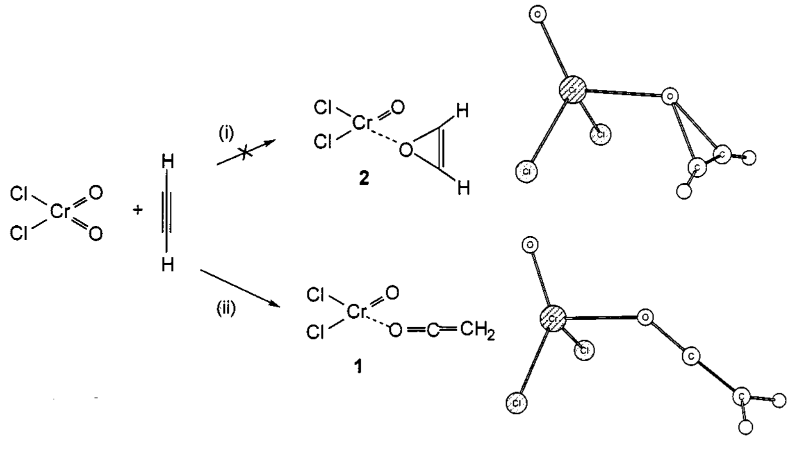
Scheme 1. Mechanistic possibilities for the photolytic olefin oxidation with CrO_2Cl_2 under matrix conditions[7b] vs. calculated intermediates[6]

been the subject of numerous theoretical investigations.[9] To date, only one successful oxirene synthesis (photodecomposition of α-diazo ketones in Ar matrices[10]) has been reported, but as a stabilization can be expected from its coordination to a transition metal (cf. the case of cyclobutadiene[11]), the complex **2** shown in Scheme 2 seemed to be a reasonable product.

(ii) Although various complexes of ketenes have been analysed structurally,[12–15] none of these shows an *end-on* coordination mode.

DFT calculations (B3LYP/LANL2DZ) proved that for both complexes of the type $O{=}CrCl_2{\cdots}O{=}C{=}CH_2$, **1**, and $O{=}CrCl_2{\cdots}O(CH)_2$, **2**, minima can be found on the potential energy surface (triplet state structures of C_1 symmetry were optimized as shown in Scheme 2) but that, not surprisingly, **1** is more stable than **2** by 258.6 kJ/mol.

Our investigation of the reaction of chromyl chloride with alkynes in low-temperature matrices started with the simplest alkyne, i.e. acetylene, under conditions[7] that had already enabled the characterization of intermediates such as those depicted in Scheme 1. Since molecules do not undergo diffusion in the solid low-temperature matrices, the reservoir of collisional reactant pairs formed upon deposition is depleted as the photolytically-induced chemical reaction proceeds. The line-widths of the new bands observed were found to be independent of the chromyl chloride concentration and the relatively broad appearance of some of them is probably due to conformational isomers.



Scheme 2. Possible routes for a photolytically-induced reaction of chromyl chloride with acetylene at 7 K; optimized structures of **1** and **2** (B3LYP/LANL2DZ)

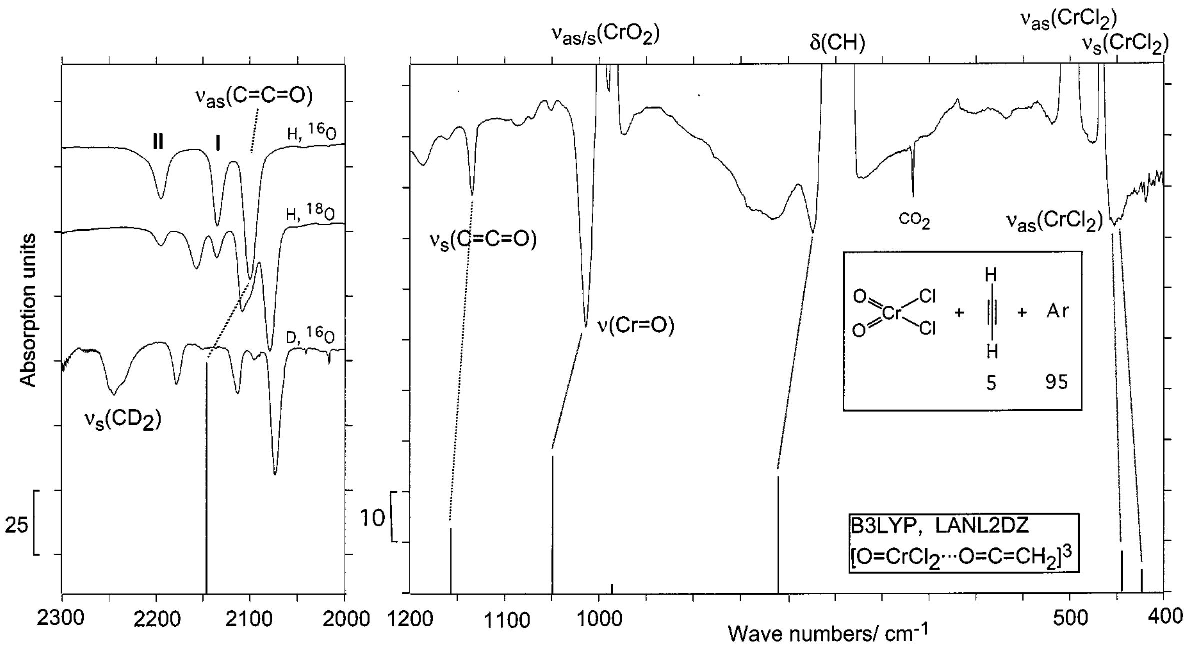
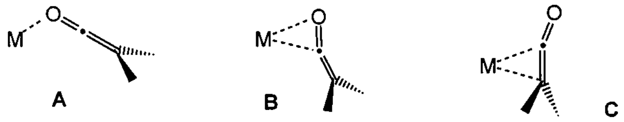


Figure 1. Upper trace: Difference between the IR spectrum (1800−350 cm^{-1}) of CrO_2Cl_2 isolated in an argon matrix doped with 5 mol-% acetylene at 7 K and the spectrum recorded of the same matrix after photolysis at 411 nm for 20 min. Lower trace: Line diagrams for the IR spectrum calculated for **1**; the upper trace of the offset shows the 2000−2200 cm^{-1} region of the spectrum, the middle trace the effects of the ^{18}O enrichment on this region, and the lower trace the effects of complete deuteriation

Identification of 1: Co-condensation of a mixture of acetylene in argon (5%) with chromyl chloride at 7 K yielded an IR spectrum of the unperturbed starting materials, which was subtracted from a spectrum recorded after subsequent photolysis (15 min at 411 nm). The result is shown in Figure 1 (the negative bands are attributable to consumed starting material). The band at 1014 cm^{-1} can be assigned to ν(Cr=O) of an $O{=}CrCl_2$ fragment, by analogy with the CrO_2Cl_2/ethylene case (1009 cm^{-1}).[7a] The band due to $\nu_{as}(CrCl_2)$, which had previously been observed at 452 cm^{-1}, can be discerned as a broad feature at 424 cm^{-1}, while the corresponding $\nu_s(CrCl_2)$ band, expected to appear around 380 cm^{-1}, is probably broadened into the base line (not shown in Figure 1).

In addition, a new intense band can be seen at 2095 cm^{-1}, which is accompanied by two less intense bands at 2132 and 2195 cm^{-1}. These are discussed separately below. The findings point to ketene as the oxidation product, since free ketene shows a ν_{as}(C=C=O) band at 2142 cm^{-1},[16] which can be expected to be red-shifted upon coordination to $O{=}CrCl_2$. The observed shift of 47 cm^{-1} is of the same order as that found for acetaldehyde[7a] (60 cm^{-1}). Since the absorption cross-section of ν_{as}(CCO) found for free ketene exceeds that of any other IR absorption by at least one order of magnitude (and can even be expected to be enhanced on complexation), all other IR absorptions due to the ketene ligand should have very low intensities in Figure 1. Indeed, apart from the absorptions mentioned so far, only two other definite bands − namely a weak but sharp band at 1135 cm^{-1} and a broad, low-intensity band at 773 cm^{-1} − can be detected. These show the same growth behaviour as the 2095 cm^{-1} band. All these observations thus provide further support for the formation of an $O{=}CrCl_2{\cdots}O{=}C{=}CH_2$ complex.

In principle, there are three possible coordination modes for ketene at a metal centre, which are depicted in Scheme 3: *end-on* **A**, *side-on* (O=C) **B**, and *side-on* (C=C) **C**. A few compounds are known where type **B** or **C** structures have been established by X-ray crystal structure analysis. Not surprisingly, ketene complexes of early, very oxophilic transition metals all display mode **B**,[12][13] while type **C** has mainly been observed by X-ray diffraction analysis of some structurally closely related complexes of Mn.[14] However, only recently, the first bond isomerism of a ketene metal complex has been demonstrated.[15] In order to permit assignment of the coordination mode of the ketene ligand in $O{=}CrCl_2{\cdots}O{=}C{=}CH_2$ as **A**, **B**, or **C**, DFT calculations (B3LYP, LANL2DZ), which have previously been shown to provide reliable information concerning the IR spectra and the corresponding isotopic shifts of such species,[7] were performed for individual complexes. Bearing in mind the results presented in Scheme 1, the theoretical investigation was started with a frequency calculation for complex **1** based on the structure shown in Scheme 2, which is, of course, only one of several possible conformations for type **A** coordination. The result has been included in Figure 1 in the form of a line diagram. As can be seen, the band pattern and the intensity ratios of the experimental spectrum are nicely reproduced. Additional support for the assignment of the experimental spectrum to **1** with an *end-on*-coordinated ketene ligand was provided by experiments employing ^{18}O-enriched CrO_2Cl_2: apart from ν(Cr=O), which is shifted by 43 cm^{-1} as ν(Cr=O) of $O{=}CrCl_2{\cdots}O{=}CHCH_3$,[7a] and ν_{as}(CCO) (21 cm^{-1}), the band at 1135 cm^{-1} also shows a significant shift (22 $\mathrm{cm^{-1}}$) and hence it can confidently be assigned to ν_s(CCO). Moreover, the ^{18}O shifts observed are in excellent agreement with those predicted by the calculation (cf. Table 1). Additional experiments employing C_2D_2 were performed, and the resulting shifts are also compared with the calculated values in Table 1. Naturally, these shifts are larger than those obtained upon ^{18}O enrichment, and hence the deviations between the experimental and calculated values are correspondingly higher. However, such deviations can arise from very small differences between the theoretical and actual structures.[17] Deuteriation additionally allows the observation of $\nu_{as}(CD_2)$ at 2260 $\mathrm{cm^{-1}}$, which was the only other observable band besides ν_{as}(CCO) when free deuteriated ketene was generated by NO_2 oxidation of [D_2]acetylene in an Ar matrix.[18] Further calculations ruled out the two possible η^2-coordination modes **B** and **C** (vide infra). Taken together, the aforementioned results strongly support the assignment of all new bands below 2100 $\mathrm{cm^{-1}}$ to compound **1**, a metal complex with a ketene ligand in the *end-on* coordination mode **A**. The underlying reasons for the preference of $O{=}CrCl_2{\cdots}O{=}C{=}CH_2$ to adopt coordination mode **A** can be traced to the oxophilic nature of the *hard* d^2 Cr centre, which is electron-poor and therefore not suitable for efficient back-bonding.



Scheme 3. Possible coordination modes for ketenes at metal centres

The Additional Bands: The above assignments leave only the two bands at 2132 $\mathrm{cm^{-1}}$ (**I**) and 2194 $\mathrm{cm^{-1}}$ (**II**) unaccounted for. The left-hand part of Figure 1 shows their positions and intensities, as well as their behaviour on isotopic enrichment in comparison to ν_{as}(CCO) of **1**. While the upper trace corresponds to the right-hand part of Figure 1, the middle trace is the result of an $^{18}O_2CrCl_2$ reaction (note that the satellites beside the shifted bands are due to the ^{16}O isotopomers, which formed simultaneously due to incomplete ^{18}O enrichment). D_2C_2 gave rise to the lower trace. The wavenumbers of **I** and **II** are rather high, and their ^{18}O shifts indicate that the corresponding vibrations should involve a significant motion of the oxygen. On the other hand, there must also be a contribution from the C−H vibrations, as indicated by the D shifts observed for these bands, although these are smaller than the shift found for ν_{as}(CCO) of **1**. The fact that the bands still appear in the same region after isotopic enrichment proves that they are *not* the result of a Fermi resonance or an overtone. Their characteristics are therefore also indicative of ν_{as}(CCO) vibrations, but as they show markedly different isotopic shifts and positions in comparison to ν_{as}(CCO) of **1**, they have to be assigned to ν_{as}(CCO) vibrations of two independent species that are related to, but are nevertheless significantly different from **1**. Interestingly, it proved possible to decrease the intensity of the ν_{as}(CCO) band of **1** in favour of the bands **I** and **II** by irradiation with light of the wavelengths 313 and 545 nm.

By optimizing the structures of over a dozen different complexes and calculating their IR spectra (plus isotopic shifts), the following facts could be established:

(i) Neither different matrix sites nor different conformations are responsible for these bands, as these could not explain the significantly different positions and isotopic shifts of **I** and **II**.

(ii) The change of spin state from triplet to singlet has a large effect on the IR properties of the $O{=}CrCl_2$ fragment, but the effects on the $O{=}C{=}CH_2$ unit are negligible.

(iii) A coordination mode of type **B** would not be expected to cause a shift of $\nu_{as}(C{=}C{=}O)$ to higher wavenumbers compared to that in **1**. Moreover, a structure with a corresponding starting geometry changed its mode to **A** during the optimization.

(iv) A mode of type **C** would, in fact, cause a shift of $\nu_{as}(C{=}C{=}O)$ to higher wavenumbers, but a corresponding complex would additionally show a band half as intense as $\nu_{as}(C{=}C{=}O)$ at ca. 890 $\mathrm{cm^{-1}}$. No band can be seen in this region of the experimental spectrum (Figure 1).

(v) Oxirene or formyl carbene complexes do not show bands of significant intensity in the region 2000−2200 $\mathrm{cm^{-1}}$, nor does oxiranylidene, which has recently been identified in low-temperature matrices.[19]

Consequently, a reaction of **1** with an excess of acetylene was then considered as a possible explanation for bands **I**

Table 1. Frequencies obtained experimentally on photolysis of $Cr^{16}O_2Cl_2$ and $Cr^{18}O_2Cl_2$ isolated in HCCH (or DCCD)/Ar matrices (5%), as well as calculated frequencies for **1** (B3LYP/LANL2DZ) in $\mathrm{cm^{-1}}$ (intensities given in parentheses); the assignments are based on the spectrum of free ketene,[16] as well as on the results of the calculation

Bands [$\mathrm{cm^{-1}}$]	calculated [$\mathrm{cm^{-1}}$]	Δ^{18}O found [$\mathrm{cm^{-1}}$]	Δ^{18}O calcd. [$\mathrm{cm^{-1}}$]	ΔD found [$\mathrm{cm^{-1}}$]	ΔD calcd. [$\mathrm{cm^{-1}}$]	Assignment
2195 (0.47)		37		17		**II**
2132 (0.55)		27		19		**I**
2095 (1.00)	2146 (1.00)	21	20	22	35	$\nu_{as}(C{=}C{=}O)$
	1405 (0.02)	−	0	−	186	$\delta(CH_2)$
1135 (0.25)	1157 (0.14)	22	27	242	216	$\nu_s(C{=}C{=}O)$
1014 (0.85)	1049 (0.30)	43	45	0	0	$\nu(Cr{=}O)$
	986 (0.02)	−	1	−	154	$\delta_s(CH_2)$
773 (0.19)	818 (0.25)	0	2	216	172	$\delta_s(CH_2)$
450 (0.31)	445 (0.09)	3	2	5	7	$\nu_{as}(CrCl_2)$
	424 (0.05)		3		61	$\nu(CrO)/\delta(CH_2)$

and **II**, even though the concentrations and conditions chosen do not usually permit reactions with significantly more than one equivalent of a substrate. However, acetylene is a very special case in that it forms aggregates even at very low pressures in the gas phase.[20a] A real matrix *isolation* of acetylene can therefore only be achieved by diluting it with argon to such a low concentration that would preclude study of its reaction with chromyl chloride as the number of collisional pairs formed upon co-condensation would become too low. The concentration amounted to 5% in the experiment described above, and consequently oligomers of acetylene were also isolated in the matrices, as indicated by their characteristic bands.[20] As a result, the structures of the matrices could not, of course, be treated statistically: the ratio of chromyl chloride molecules with just *one* acetylene molecule as a nearest neighbour to those with more than one such neighbour was significantly decreased compared to the situation under standard conditions. Thus, the bands **I** and **II** may well result from species incorporating more than one equivalent of acetylene, and indeed, a decrease of the acetylene concentration down to the lowest possible level of 2% (where the signal-to-noise ratio is still acceptable in the difference spectrum following irradiation) led to a significant decrease in the intensities of these bands in relation to the intensity of ν_{as}(CCO) attributable to **1**. Bearing in mind the effects observed upon photolysis at 313 and 545 nm, respectively, the corresponding species must be accessible by direct reaction of **1** with acetylene. A reaction of the ketene moiety can be excluded as no product can be envisaged that would still exhibit a band at a higher wavenumber than 2100 cm^{-1} (with a significant ^{18}O shift). The most likely reaction at the metal centre is a complex formation (i.e. a weak or even strong binding of acetylene). Unfortunately, DFT calculations are not adequate for describing the simultaneous complexation of acetylene and ketene at an $O{=}CrCl_2$ fragment (at least not with the B3LYP functional),[21] hence it was not possible to unequivocally assign the bands **I** and **II** to alkyne complexes of **1**.

(b) CrO_2Cl_2/CH_3CCCH_3

Next, but-2-yne was employed as a reactant in order to find out whether the corresponding dimethylketene derivative $O{=}CrCl_2{\cdots}O{=}C{=}C(CH_3)_2$, **3**, is formed, or whether the methyl groups prevent rearrangement by 1,2-migration (no methyl shift has ever been observed for any analogous olefin reactions[7b]). Provided that the above arguments in the case of acetylene are correct, formation of **3** should also be accompanied by the generation of two additional species. The concentrations of the latter, however, should be much lower: in contrast to acetylene, but-2-yne does not show a pronounced tendency to aggregate, so that a reaction of chromyl chloride molecules with *two* equivalents of alkyne should, on statistical grounds, only be possible for the small fraction of molecules that have two alkyne neighbours in the solid matrix (ca. 10% for a 5:95 ratio of butyne/Ar vs. 34% with just *one* neighbour[22]).

Following the reaction of but-2-yne with chromyl chloride, the bands for the $O{=}CrCl_2$ fragment could be found as before. In addition, a band at 2072 cm^{-1} was observed, suggesting that a dimethylketene complex **3** had indeed been formed. This was further corroborated by repeating the experiment with $^{18}O_2CrCl_2$ (leading to shifts comparable to those found previously for **1**), as well as by calculations (B3LYP/LANL2DZ) concerning the structure and frequencies of such a complex, the latter being in good agreement with the experimental frequencies (cf. Table 2). As anticipated (vide supra), two additional bands could be observed at higher wavenumbers beside the ν_{as}(C=C=O) band of **3**, albeit with only minor intensities.

The fact that **3** was formed by a 1,2-methyl migration suggests that such a shift should, in principle, also be possible in the case of olefins. However, in the latter case, a low degree of methylation leaves open too many alternative 1,2-H migration routes, while permethylation makes path (i) in Scheme 1 more favourable. The transition state associated with the analogous path (i) in Scheme 2 is of course very high in energy (**2** itself was calculated to form in an *endothermic* reaction, while formation of **1** is exothermic by −246 kJ/mol). The transition state energy will be lowered only slightly if H is substituted by Me. Consequently, there is only one low-energy path open for alkynes, which probably involves attack of a Cr=O bond at the triple bond in a fashion analogous to path (ii) in Scheme 1. After passing through the corresponding radical-like transition state, a methyl shift yields **3**. The postulation of such a transition state prompted a further experiment that might support its existence: thus, allene was employed as the unsaturated component.

(c) $CrO_2Cl_2/CH_2{=}C{=}CH_2$

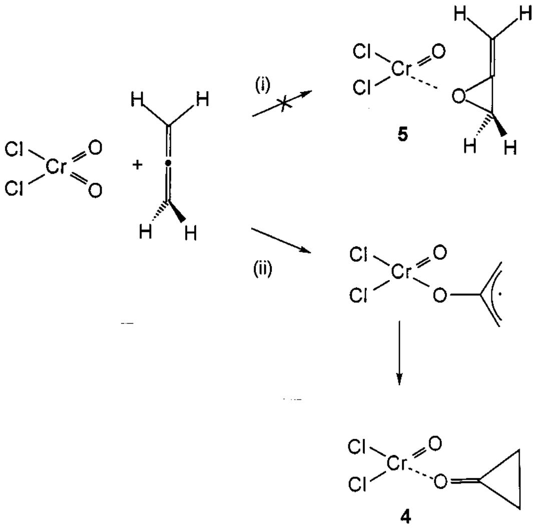
If radical-like transition states, produced by attack of the Cr=O function at the unsaturated bonds, do indeed govern product formation in the reactions of alkenes and alkynes, allene can be expected to be attacked at the central carbon, as this would lead to a resonance stabilized allyl radical as shown in Scheme 4. A downhill route involving a 1,2-H or 1,2-Me shift would then not be accessible, but the reaction could proceed through a subsequent ring-closure to yield a cyclopropanone complex (NO_2 oxidation of allene in low-temperature matrices leads to cyclopropanone).[24]

A terminal attack at the allene followed by a 1,2-H shift would yield acrolein, or, alternatively, an epoxidation of one olefinic bond may be envisaged [compare path (i) in Scheme 4].

Following co-condensation of a 5% allene/argon mixture with chromyl chloride, the usual photolysis at 411 nm led to the bands of $O{=}CrCl_2$, which were seen at 1012 and 447 cm^{-1}. Additionally, an intense matrix-split band was observed at 1800 cm^{-1}, which must be attributable to a ν(C=O) vibration in view of the marked ^{18}O-shift and the negligible D-shift observed when experiments were performed with $^{18}O_2CrCl_2$ and $D_2C{=}C{=}CD_2$, respectively. All

Table 2. Frequencies obtained experimentally on photolysis of $Cr^{16}O_2Cl_2$ and $Cr^{18}O_2Cl_2$ isolated in CH_3CCCH_3/Ar matrices (5%), as well as calculated frequencies for **3** (B3LYP/LANL2DZ) in cm^{-1} (intensities given in parentheses); the assignments are based on the spectrum of free dimethylketene,[23] as well as on the results of the calculation

Bands [cm^{-1}]	calculated [cm^{-1}]	$\Delta^{18}O$ found [cm^{-1}]	$\Delta^{18}O$ calcd. [cm^{-1}]	Assignment
2126 (0.08)				
2089 (0.14)				
2072 (0.47)	2114 (1)	18	16	$\nu_{as}(C{=}C{=}O)$
1453 (0.33)	1513 (0.07)	0	0	CH_3 bend
1436 (0.43)	1505 (0.04)	0	0	CH_3 bend
1369 (0.20)	1450 (0.03)	0	0	CH_3 bend
1360 (0.18)	1436 (0.02)	0	0	CH_3 bend
1339 (0.15)		0		CH_3 bend
1254 (0.52)	1361 (0.21)	11	16	$\delta(CH_2)$, wag
1157 (0.13)	1196 (0.01)	0	0	$\rho(CH_3)/\delta(CCC)$
1145 (0.13)		5		
1082 (0.14)		–		$\rho(CH_3)/\delta(CCC)$
1061 (0.15)	1107 (0.01)	0	1	$\rho(CH_3)/\delta(CCC)$
1009 (1)	1045/1050 (0.44)	41	41	$\nu(Cr{=}O)$
451 (0.50)	431 (0.16)	3	0	$\nu_{as}(CrCl_2)$



Scheme 4. Proposed mechanism of the photolytically-induced reaction of chromyl chloride with allene at 7 K

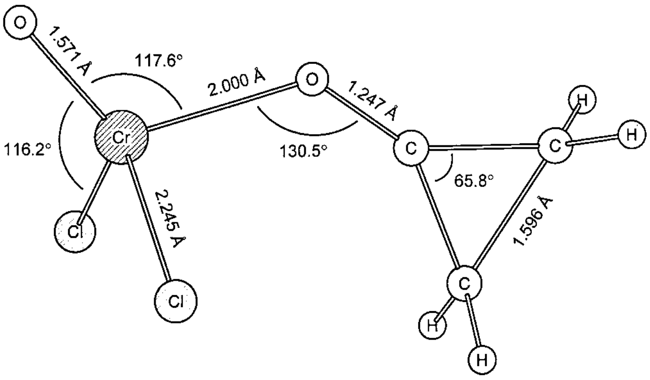


Figure 2. The optimized structure calculated for $OCrCl_2$···cyclopropanone, **4**, by means of DFT using LANL2DZ basis sets (B3LYP); selected bond lengths and angles are given in Å and°

bands and their isotopic shifts are shown in Table 3, along with the theoretical frequencies and the calculated isotopic shifts for an optimized structure of the cyclopropanone···$Cr(O)Cl_2$ complex **4** (Figure 2). As can be seen, the agreement is very good, hence it can safely be concluded that **4** was indeed formed. This supports the hypothesis of a radical-like transition state in carbonylations with chromyl chloride under matrix conditions. The simultaneous formation of the allene oxide complex **5** in Scheme 4 can be ruled out on the basis of further calculations concerning its frequencies.[26] This finding is not surprising as the barrier leading to **5** is probably much higher than that associated with the conversion of the allyl radical to **4**. Moreover, **5** itself is less stable than **4** by 59 kJ/mol.

Conclusions

We have shown herein that the reactions of chromyl chloride with acetylene and but-2-yne (dimethylacetylene) under matrix conditions yield η^1-ketene and -dimethylketene complexes of $O{=}CrCl_2$, respectively. The oxidation of allene leads exclusively to a cyclopropanone complex, probably through an initial radical-like attack of a Cr=O functionality at the central carbon, with subsequent ring-closure. The formation of all products is consistent with the general reactivity pattern observed previously for chromyl chloride in reactions with olefins,[7] and supports the idea that radical-like transition states are involved in the corresponding carbonylation reactions.

In the past, H-atom transfers by metal-oxo species have been rationalized in terms of intuitions based on analogy with organic radical chemistry, i.e. unpaired electron density was thought to be transferred to the oxygen of the metal compounds, which then determined its propensity to take part in radical reactions. In the meantime, it has been established that chromyl chloride – a d^0 system having no unpaired spin density – can in fact abstract hydrogen atoms from saturated organic systems. This has led to progress in current thinking, from considerations of radicals and spin density to a new approach based on the thermochemistry of the H-atom transfer step and, therefore, on the bond strengths.[27]

Table 3. Frequencies obtained experimentally on photolysis of $Cr^{16}O_2Cl_2$ and $Cr^{18}O_2Cl_2$ isolated in $H_2C{=}C{=}CH_2$ (or $D_2C{=}C{=}CD_2$)/Ar matrices (5%), as well as calculated frequencies for **4** (B3LYP/LANL2DZ) in cm^{-1} (intensities given in parentheses); the assignments are based on the spectrum of free cyclopropanone,[25] as well as on the results of the calculation

Bands [cm^{-1}]	calculated [cm^{-1}]	$\Delta^{18}O$ found [cm^{-1}]	$\Delta^{18}O$ calcd. [cm^{-1}]	ΔD found [cm^{-1}]	ΔD calcd. [cm^{-1}]	Assignment
1807/1800 (0.81)	1830 (1)	20	24	3	7	$\nu_{as}(C{=}O)$
1392 (0.05)	1434 (0.07)	0	0	222	292	$\delta(CH_2)$
1107 (0.07)	1080 (0.27)	2	1	10	23	ν(CC)
1107 (0.07)	1075 (0.11)	2	1	60	47	ring wag
1012 (1)	1053 (0.52)	47	46	1	0	$\nu(Cr{=}O)$
703 (0.13)	705 (0.09)	8	11	–	148	ring
447 (0.44)	428 (0.24)	1	0	0	0	$\nu_{as}(CrCl_2)$

These fundamental discoveries made for the *C−H activation* by chromyl chloride naturally raise questions concerning the initial steps of its reactions with *unsaturated systems.* It could be envisaged that in these oxidations chromyl chloride might also follow one reaction route (among others) where it behaves akin to a fleeting main group oxygen radical, giving rise to a radical intermediate or transition state, which finally undergoes rearrangement to produce the isolated carbonyl products. This is exactly what we seem to have found for the matrix reactions of chromyl chloride under photolytic conditions as outlined in the above. However, under thermal conditions (−80°C), an analogous reactivity can only be postulated provided that a necessary condition holds, i.e. that the thermochemistry is favourable or at least only slightly unfavourable,[27] in other words that the CrO−C bond formed in the course of the Cr=O attack at the carbon of an unsaturated bond must be sufficiently strong to drive the reaction in the direction of carbonylation. Addition of an organic radical to a Cr=O function is indeed likely to be very exothermic,[4b] and the CrO−C bond energy released can therefore easily overcompensate the loss of π-bonding energy if a similar addition is considered for an unsaturated bond. This has certainly been the case in our experiments, which have, however, started from chromyl chloride in an excited state.[7b] Therefore, it is not yet certain as to whether CrO−C bond formation is sufficiently exothermic to make a corresponding attack energetically favourable under thermal conditions as well. This subtle problem will only be resolved following an experimental determination of the Cr(V)O−C bond energy

Experimental Section

Computational Methods: Density functional calculations were carried out using the Gaussian-94/DFT[28] series of programs. The structures of **1−3** were optimized with the LANL2DZ basis set using in each case the B3LYP formulation of density functional theory, i.e. Becke's three-parameter exchange functional and the Lee−Yang−Parr correlation functional. Harmonic vibrational frequencies and infrared intensities were predicted at these levels by numerical second derivatives using analytically calculated first derivatives. No scaling was applied and no negative frequencies were obtained.

Experimental: Liquid helium cooling gave temperatures of ca. 7 K inside a shroud maintained at a pressure below 10^{-7} Torr. Mixtures were prepared in a vacuum line using standard manometric techniques and were then deposited on the cold support. A CsI window was used for all the IR experiments; the slow spray-on deposition was favoured for CrO_2Cl_2 with the sample maintained at −65°C.

The photolysis source was a 200 W medium-pressure arc. The radiation was filtered with a Balzers interference filter (band-pass ca. 15 nm). IR spectra were recorded in transmission mode over the ranges 4000−300 and 1000−200 cm^{-1}, with a resolution of 1 cm^{-1}, on a Bruker IFS 88 spectrophotometer.

CrO_2Cl_2 (99.99% pure), but-2-yne, and acetylene (99% pure) were supplied by Aldrich and further purified by fractional condensation in high vacuum prior to use. Argon (99.999% pure, Messer Griesheim), [D_2]acetylene (99% pure, Campro Scientific), and [D_4]allene (98% pure, Campro Scientific) were used as received.

^{18}O-enrichment of CrO_2Cl_2 can be achieved according to a published procedure. Allene was synthesized according to ref.[7b]

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