

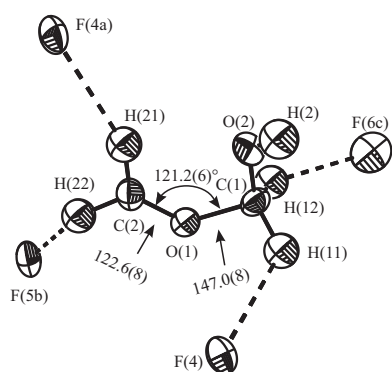


Figure 2. Structure of the cation **3** in the crystal with contacts, atom labels, and structural parameters for the central unit. Further distances [pm]: F4a⋯H21 236(8), F5b⋯H22 217(8), F6c⋯H12 244(8), F4⋯H11 240(9). Symmetry operations: $x-1, +y, +z$ (a), $-x+1, -y, -z+1$ (b), $x, -y-0.5, +z+0.5$ (c).

Table 2. Selected bond lengths [pm] and angles [°] for **3-AsF₆**. Not all the atoms of the anion are shown in Figure 2.^[a]

As(1)–F(2)	171.8(4)	C(2)–O(1)–C(1)	121.2(6)
As(1)–F(4)	171.0(4)	O(2)–C(1)–O(1)	108.8(5)
As(1)–F(6)	170.2(5)	F(1)–As(1)–F(4)	89.6(2)
O(1)–C(2)	122.6(8)	F(6)–As(1)–F(4)	90.4(3)
O(1)–C(1)	147.0(8)	F(1)–As(1)–F(2)	179.2(2)
O(2)–C(1)	132.5(8)		

[a] The standard deviations refer to the last digit.

Experimental Section

H₂CO was obtained and purified according to ref. [12]. AsF₅ was obtained by allowing the elements to reaction and purified by fractional condensation. SbF₅ was purified by fractional distillation, and HF was dried with fluorine.^[13]

In a KEL-F reactor MF₅ (3 mmol; M = As, Sb) was dissolved in HF (≈ 5 g). The solution was frozen at –196 °C, and then H₂CO (3 mmol) condensed onto the solution. The reaction mixture was allowed to warm slowly to –40 °C. The excess reactant was removed either at –78 °C or at –40 °C under a dynamic vacuum. Compound **3-MF₆** remained as a colorless solid.

Instruments: Raman: Jobin–Yvon T64000, Ar⁺ laser (λ = 514.5 nm) Spectra Physics; IR: Bruker IFS 133v; NMR: Bruker DPX300.

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measured reflections, 1199 independent reflections, 996 reflections used in the refinement, σ limit 2.0, Lp and absorption correction (ψ scans), μ(MoKα) = 5.035 mm^{–1}, min./max. transmission 0.78/0.91, structure solution: Patterson, difference-Fourier synthesis, SHELXS-86, SHELXL-93, PARST, PLATON, MISSYM, 114 free parameters; hydrogen atoms were experimentally determined and refined from Δ*F*, *R* = 0.0485, *wR* = 0.1194, *R* = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|, refinement method: full-matrix least squares on *F*², min./max. residual electron density = 0.787/–0.980 e Å^{–3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD – 407344.

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Matrix Isolation and Characterization of a Reactive Intermediate in Olefin Oxidation with Chromyl Chloride**

Christian Limberg,* Ralf Köppe, and Hansgeorg Schnöckel

Although the oxidation of organic substrates by Cr^{VI} compounds has always been a useful tool in the hands of chemists, the course of such reactions and the nature of the intermediates have remained for the most part unknown. For example, the mechanism of C–H activation in the Etard reaction,^[1] known since 1877, was only revealed in detail in 1995.^[2] In the past, complex mechanisms were put forward for the oxidation of olefins with chromyl chloride CrO₂Cl₂^[3, 4] that attempted to explain the great variety of products obtained on the basis of widely differing intermediates such as chromaoxetanes, chromium alkoxides, and epoxide complexes. None of these intermediates has ever been proven. The occurrence of carbonyl compounds among the products was explained by rearrangements of certain products during work-up,^[3, 5] whereas more recent work highlights the relevance of intermediate chromium complexes of these carbonyl compounds. For example, ethylene reacts with the CrO₂⁺ ion in the

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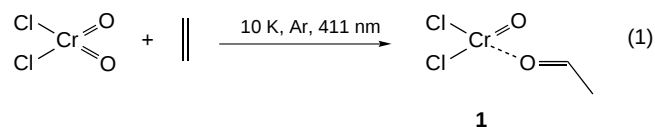
[**] C.L. is grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for scholarships and equipment, and to Professor G. Huttner for his generous support.

mass spectrometer to yield $\text{O}=\text{Cr}^+ \cdots \text{O}=\text{CHCH}_3$.^[6] The aim of the matrix studies presented here was to isolate intermediates in olefin oxidation with CrO_2Cl_2 in order to gain reliable information concerning the reaction mechanism. The investigations began with ethylene, the simplest olefin, and the first step was to identify the products formed on treatment with CrO_2Cl_2 under thermal conditions. The reaction of ethylene with CrO_2Cl_2 at -80°C in dichloromethane yields primarily 2-chloroethanol after isolation of the resulting Etard complex and work-up with wet acetonitrile. Therefore $\text{CrOCH}_2\text{CH}_2\text{Cl}$ fragments should be present in the Etard complex, and, consequently, **A** can be postulated as a possible intermediate.



In the next step, CrO_2Cl_2 was co-condensed with a mixture of ethylene and argon, the resulting matrix irradiated at 411 nm (activation of the $\text{Cl} \rightarrow \text{Cr}$ charge-transfer (CT) transition),^[7] and the reaction followed by IR spectroscopy.^[8] The spectra (Figure 1) show that a product has formed in good yield (approximately 40 %) which produces an intense new band in the $\text{Cr}=\text{O}$ region at 1009 cm^{-1} ; this indicates the presence of only *one* $\text{Cr}=\text{O}$ bond. In the $\text{Cr}-\text{Cl}$ region, two new bands at 452 and 385 cm^{-1} appear suggesting that the CrCl_2 fragment is preserved during the reaction. This excludes **A** as the product. These findings tend to point to the fragment $\text{O}=\text{CrCl}_2$ as the inorganic part of the reaction product, and, consequently, CrO_2Cl_2 must have transferred one oxygen atom to the organic substrate ethylene. A new band at 1669 cm^{-1} helps to clarify the composition of the resulting organic product. This must belong to a carbonyl compound whose $\nu(\text{C}=\text{O})$ band is shifted to lower wavenumber due to complexation with a Lewis acidic center (the formation of complexes, often only weakly bound, after photoreaction in

noble gas matrices is commonly observed^[9]). In addition, since investigations into the concentration dependence showed that only one equivalent of ethylene is involved in the reaction, the organic product must consist of a carbonyl compound with a C_2 unit ($\text{O}=\text{CH}_2$ can be excluded as the product^[10]). Only acetaldehyde meets these requirements, and the connectivity **1** shown in reaction (1) can be assigned to



the product of the matrix experiment. Further proof was obtained by using $[\text{D}_4]$ ethylene to synthesize the deuterated version of **1**, whose IR spectrum—when compared with that of the hydrogenated compound—showed all the changes expected in terms of the above interpretation: All bands assigned to the $\text{O}=\text{CrCl}_2$ fragment exactly maintained their previous positions, indicating that this fragment oscillates independently. The carbonyl band shows a slight shift ($\Delta\tilde{\nu} = 18\text{ cm}^{-1}$) due to weak coupling to $\text{C}-\text{H}$ modes (such as $\delta(\text{CH})$). All other bands show strong shifts due to the large contributions from $\text{C}-\text{H}$ vibrations. When $^{18}\text{O}_2\text{CrCl}_2$ ^[11] was used with the aim of synthesizing the ^{18}O isotopomer of **1**, significant shifts were only observed for three bands: the $\nu(\text{C}=\text{O})$ band ($\Delta\tilde{\nu} = 29\text{ cm}^{-1}$), the $\nu(\text{Cr}=\text{O})$ band (43 cm^{-1}), and a further band at 852 cm^{-1} (26 cm^{-1}), which can be assigned as having principally $\delta(\text{CCO})$ character. The remaining signals shift only marginally. Reaction of the mixed isotopomer $^{18}\text{O}^{16}\text{OCrCl}_2$ does not lead to new bands, which further proves the presence of only one $\text{Cr}=\text{O}$ bond in **1**.

All these results already confirm **1** unequivocally as the product of the matrix experiments, but additional calcula-

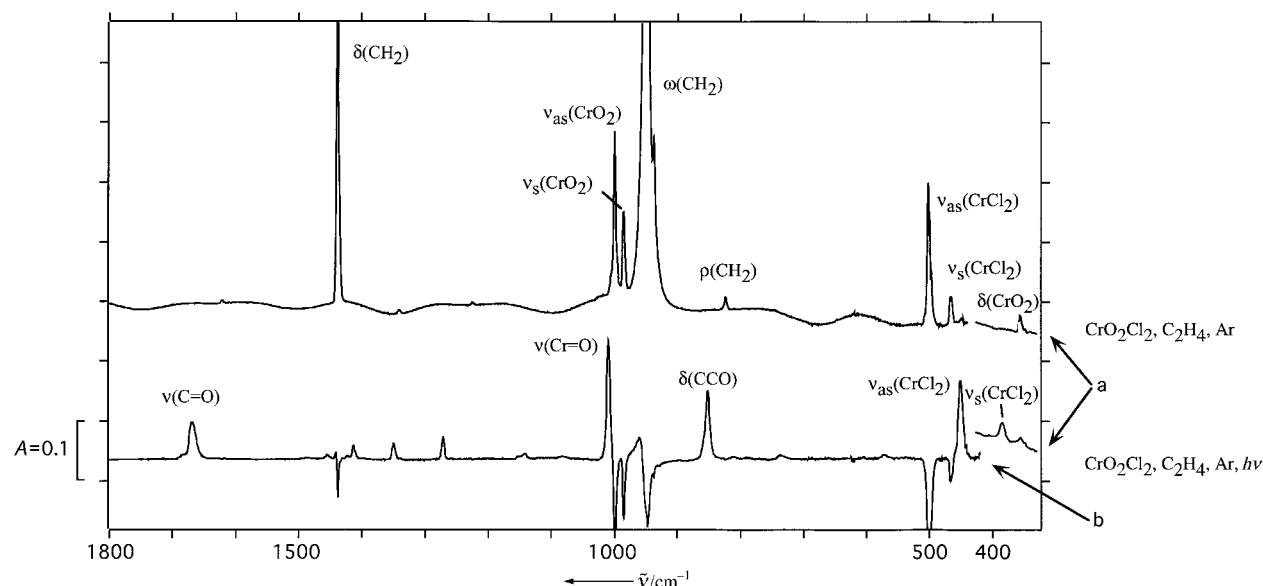
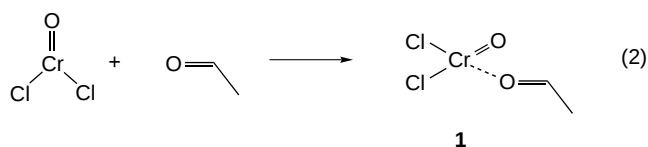


Figure 1. IR spectra of CrO_2Cl_2 in an ethylene/argon matrix (4/96) at 10 K in the region of $1800\text{--}330\text{ cm}^{-1}$; upper trace: absolute spectrum (a) after deposition of the starting materials for 15 min; lower trace: difference spectrum (b) after irradiation at $\lambda = 411\text{ nm}$ for 10 min. and the absolute spectrum (a) for the region below 400 cm^{-1} to give an impression of the conversion in the reaction. When the bands of the initial spectrum overlap with newly formed bands, the intensity ratios can be slightly perturbed upon spectrum subtraction.

tions—with respect to the structure of **1** on the one hand and in order to obtain information on the theoretically expected frequencies on the other—were of interest. Since DFT calculations (B3LYP, LanL2DZ, G94)^[12] yielded good results for the structure of CrO₂Cl₂ (the maximum deviations in bond lengths and angles from those of the gas-phase structure^[13] amounted to 0.03 Å and 2°, respectively), this method was employed for calculating the structure of **1**. The most stable *syn* conformation is energetically only 5.1 kJ mol^{−1} less stable than the most stable *anti* conformation. It is therefore the most likely structure of the product originating from a chromaoxetane^[4] potentially generated in the primary step. However, because the latter intermediate step has never been proved and because conformers are photochemically interconvertible in matrices, a decision in favor of one structure or another cannot be made. Both show the features expected from the experimental IR spectra: the Cr=O bond is shorter than in CrO₂Cl₂, and the bond to the acetaldehyde oxygen atom is very strong (almost in the region of a Cr–O single bond^[14]). This explains the significant shift of ν(C=O) to lower wavenumbers (observed: Δν̄ = 52 cm^{−1} in comparison to free acetaldehyde^[15]). The enthalpy of reaction (1) was calculated as −157.5 kJ mol^{−1}, whereas reaction (2) already proceeds exothermically with −144.4 kJ mol^{−1}. Therefore, product formation is also accounted for on energetic grounds.



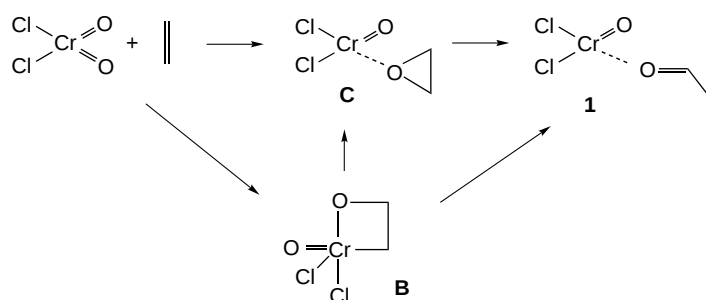
Calculations of the vibrational frequencies showed that the IR spectra of the two conformers differ only slightly^[16] with respect to the error present in the calculations, thus preventing the assignment of one conformer to the experimental spectrum. However, as can be seen for the example of the most stable *syn* conformer in Table 1, the band pattern obtained experimentally could be reproduced qualitatively. The calculated shifts of the bands resulting from replacement of ¹⁶O by ¹⁸O agree very well with the experimental spectrum; any errors made previously cancel each other. In only one case (852 cm^{−1}) was the calculated shift too low.

Table 1. Experimental frequencies ν̄ in cm^{−1} measured after photolysis of an ethylene/argon (4/96) matrix doped with Cr¹⁶O₂Cl₂ or Cr¹⁸O₂Cl₂, and frequencies calculated with a combination of B3LYP/LanL2DZ for the most stable *syn* conformer of **1** (¹⁶O and ¹⁸O isotopomer, respectively) (the values in parentheses refer to relative intensities *I*; no scaling). The last column gives a qualitative assignment based on the calculations and the isotopic shifts.

Cr ¹⁶ O ₂ Cl ₂	Cr ¹⁸ O ₂ Cl ₂	Δν̄(¹⁶ O – ¹⁸ O)	calcd 1 (¹⁶ O) (<i>I</i>)	calcd Δν̄(¹⁶ O – ¹⁸ O)	Assignment
1669	1640	29	1651 (0.58)	26	ν(C=O)/ν(CC)/δ(CH)
1453	1453	0	1492 (0.15)	0	δ _{as} (CH ₃)
1413	1408	5	1483 (0.26)	4	δ _{as} (CH ₃)
1349	1349	0	1434 (0.37)	1	δ _s (CH ₃)/δ(CH)
1271	1266	5	1418 (0.09)	7	δ _s (CH ₃)/δ(CH)
1141	1141	0	1166 (0.18)	1	ν(CC)/δ(CCO)
1009	966	43	1104 (1.00)	47	ν(Cr=O)
852	826	26	932 (0.12)	6	δ(CCO)
			809 (0.08)	0	τ _r (CH ₃), δ(CH)
			535 (0.12)	11	δ(CrOC)
452	451	1	425 (0.85)	0	ν _{as} (CrCl ₂)
385	379	6	362 (0.15)	7	ν _s (CrCl ₂)

The oxo chromium dichloride molecule in **1**, with chromium in the rare oxidation state of +IV, is particularly significant. This species was often mentioned as an important intermediate in oxidations with CrO₂Cl₂.^[3, 4, 17] The experiments presented here describe for the first time the isolation and characterization of this fragment as complexed with acetaldehyde.

The fact that a primary product must exist between the substrate and **1**, which rearranges to **1** by a hydrogen shift, raises the question of the mechanism for the formation of **1**. In principle, the primary product could be a chromaoxetane **B**, which could then be the source of a photochemically generated diradical 'OCH₂CH₂' for which experimental data and MO calculations favor isomerization to acetaldehyde.^[18] However, a more likely alternative is the intermediate formation of the oxirane adduct **C** in Scheme 1, either directly



Scheme 1. Possible mechanism for the formation of **1**.

from the starting materials or via **B**. The adduct **C** was mentioned previously as a possible intermediate^[4] and could isomerize to form **1**. Such rearrangements of oxiranes to carbonyl compounds catalyzed by Lewis acids are widely known in synthetic chemistry,^[19] and it is possible that in the present case the required activation energy is supplied photochemically and not thermally.^[20] To compare the role of **1** in the reaction under inert conditions and irradiation with that under thermal conditions, a transfer of the results of the matrix experiments to preparative chemistry was attempted. As already mentioned, the reaction of ethylene with CrO₂Cl₂ at −50°C in the dark followed by decomplexation of the Etard complex yields mainly chloroethanol. However, acetaldehyde (5%) was also present among the products, which

could, in principle, originate in **1** incorporated in the Etard complex. When the matrix conditions are simulated by dissolving the two reactants in a Freon mixture at -80°C and quenching the resulting solution at 77 K to form a glass, the amount of acetaldehyde among the oxidation products increases to 35 % after subsequent photolysis at 77 K and usual work-up; this is then comparable to the yield in the matrix experiment.^[21] Therefore, **1** should also occur immediately in the thermal reaction of ethylene with CrO_2Cl_2 . Since other olefins are quantitatively oxidized to carbonyl compounds by CrO_2Cl_2 in thermal reactions,^[3] intermediates analogous to **1** could play a more important role in these cases, although, of course, other mechanisms for the formation of carbonyl compounds are imaginable.^[5]

The isolation of an intermediate in an olefin oxidation by CrO_2Cl_2 was achieved for the first time. The presence of this intermediate could explain the occurrence of carbonyl compounds in the product spectrum of such reactions.

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- [16] The fact that some of the calculated bands deviate by approximately 100 cm^{-1} from the experimental values is not unusual for such calculations and presumably has its origin in slight deviations of the calculated structure from the real one. The structure of CrO_2Cl_2 calculated with the B-P functional and SV(P) basis sets (TurboMol [R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169]) represents the real structure almost ideally ($\Delta r < 0.01$ Å, $\Delta(\text{angle}) < 1^{\circ}$), and therefore shows that this combination of functional and basis sets has to be considered more suitable for structure determination (the calculation of the frequencies is not possible) than the combination of B3LYP/LanL2DZ. The more reliable B-P/SV(P) structure of **1** differs slightly ($\Delta r < 0.05$ Å, $\Delta(\text{angle}) < 4^{\circ}$) from the B3LYP/LanL2DZ structure which forms the basis for the calculation of the spectrum. These differences can have drastic effects on the calculation. Accordingly, the deviations of the experimental IR spectrum calculated for chromyl chloride with the combination of B3LYP/LanL2DZ from the experimental spectrum were of the same magnitude. For DFT structure and frequency calculations for CrO_2Cl_2 , see M. Torrent, P. Gili, M. Duran, M. Solà *J. Chem. Phys.* **1996**, *104*, 9499–9510. Differences in frequencies of the two most stable *syn* and *anti* conformations: $\nu_s(\text{CrCl}_2)$: 10, $\nu_{\text{as}}(\text{CrCl}_2)$: 6, $\delta(\text{CCO})$: 18, $\nu(\text{Cr}=\text{O})$: 20, $\nu(\text{C}=\text{O})$: 1 cm^{-1} . The maximum deviation was obtained for a band that should be at 535 cm^{-1} for *syn*-**1** and at 576 cm^{-1} for *anti*-**1**, but which does not appear in the experimental spectrum due to low intensity; the calculated intensity ratios do not differ significantly.
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- [21] Whereas residual amounts of CrO_2Cl_2 do not react in the matrix experiment, free CrO_2Cl_2 reacts further thermally when the Freon mixture is warmed to temperatures that allow volatile components to be pumped off. The compounds produced by this route are also among the products.

Si₆, Si₁₄, and Si₂₂ Rings in Iodide Silicides of Rare Earth Metals**

Hansjürgen Mattausch and Arndt Simon*

Numerous metal-rich halides MX_nA ($n \leq 2$) of rare earth metals M with interstitial atoms A = H, C, N, O have been prepared.^[1–3] Recently we reported on boride and boride carbide halides.^[4–6] Owing to the electropositive character of the rare earth metals, the interstitial atoms are present as anions, and in the case of carbon C_2^{6-} and C_2^{4-} units are found besides discrete C^{4-} ions.^[1] In $\text{M}_4\text{X}_5\text{B}_4$ the boron atoms form rhomboids which are linked into chains.^[6] Several factors influence the nature of the interstitial species: the number of

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