

Reactive Intermediates in Olefin Oxidations with Chromyl Chloride. IR-Spectroscopic Proof for O=CrCl₂–Epoxide Complexes

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After photolytic induction (411 nm) of the reaction between chromyl chloride and olefins in low-temperature matrixes, for the first time primary products of this system have been isolated and identified: the reaction of propylene yields O=CrCl₂···O=CHCH₂CH₃ and O=CrCl₂···OCH₂CHCH₃, while in the case of *trans*- and *cis*-2-butylene, OCrCl₂···O=C(CH₃)(CH₂CH₃) as well as OCrCl₂···(*trans*-2,3-butylene oxide) and OCrCl₂···(*cis*-2,3-butylene oxide) are obtained, respectively. Epoxide formation proceeds under complete retention of stereochemistry, and the regioselective reaction route leading to the carbonyl products can be suppressed if all hydrogen atoms at the olefinic bond are substituted: tetramethylethylene is selectively oxidized to tetramethylethylene oxide, which forms a complex with OCrCl₂. All products were characterized by IR spectroscopy, which was further supported by DFT calculations in certain cases. The mechanism leading to the formation of these products, their electronic states, and the implications of the matrix results on the thermal reactions of chromyl chloride are discussed.

Introduction

For quite some time the olefin oxidation with chromyl chloride (CrO₂Cl₂) seemed to proceed completely unspecifically, and reports with the most different product palettes accumulated.^{1–6} The first selective oxidation was reported in 1969 by F. Freeman et al. claiming that reductive workup of the reaction mixtures in the presence of zinc enables the isolation of carbonyl compounds in good yields.⁷ However, mainly disubstituted, electron-rich olefins had been employed in this investigation.^{7–11} In 1973 K. B. Sharpless et al. found that chloroketones are formed selectively if the reactions are carried out in acetone at –78 °C,¹² and they related the findings made on reductive

workup^{7–11} to the reduction of these oxychlorides by zinc. To study the influence of the solvent on the product distribution Sharpless et al. further investigated the CrO₂Cl₂/olefin system in CH₂Cl₂.¹³ Various types of olefins yielded chlorohydrins, epoxides, and dichlorides—formed by *cis*-additions in each case—as the three main products. These were claimed to generally occur in all CrO₂Cl₂ oxidations of olefins (being modified in cases by individual experimental conditions), so an attempt was made to fit them into a general reaction pattern:¹³ a hypothetical olefin complex of CrO₂Cl₂ was suggested to either undergo a Cr–Cl bond insertion reaction (generating a Cr(VI) chloroalkyl compound) or rearrange to a chromoxetane in the first step. The latter can decompose via the mechanism shown in Scheme 1 where the substrate as well as the reaction medium was proposed to determine the main reaction pathway. However, none of these intermediates postulated has ever been proved, and, moreover, they cannot account for all of the final products found^{1–11} by researchers.

Recently, the matrix isolation technique has been successfully employed to investigate the ethylene oxidation by CrO₂Cl₂ at an early stage: the species O=CrCl₂···O=CHCH₃, **1** (see eq 1), was identified by IR spectroscopy.¹⁴ The inorganic part of **1**, the O=CrCl₂ molecule, had often been mentioned in the literature^{7–11,13,15} as a potentially important species in such oxidation reactions. Its formation had even been predicted to

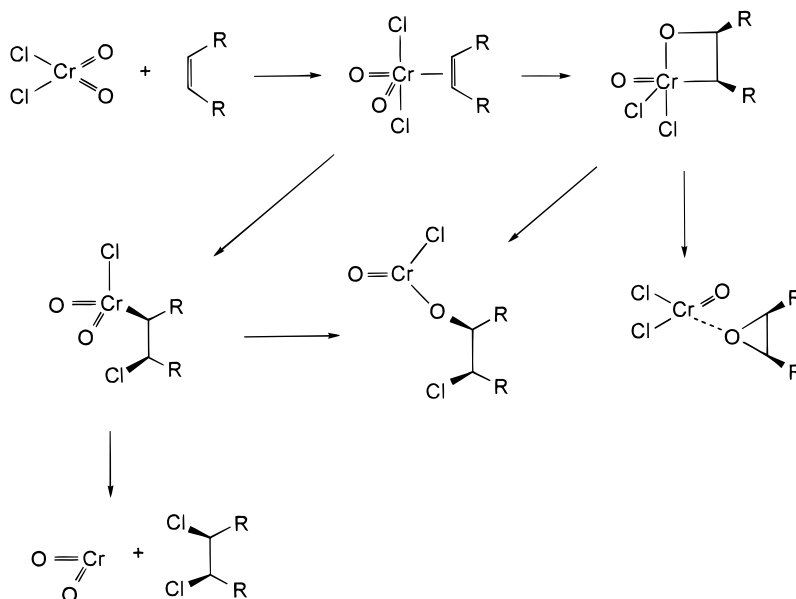
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Scheme 1. Postulated Mechanism for the Thermal Olefin Oxidation with CrO₂Cl₂¹³

represent the driving force of the latter¹⁵ although there had never been proof of its existence. Bearing this in mind, it seems surprising that, in spite of the frequent observation of carbonyl compounds as products in CrO₂Cl₂ olefin oxidations (vide supra), intermediates such as **1**, i.e. complexes of carbonyl compounds to O=CrCl₂, had never been proposed and are missing in Scheme 1. Instead, the carbonyl products were preferentially thought to be a result of the decomposition of chlorohydrins¹² or rearrangements of the free epoxides during workup.^{7–11}

However, after proving the intermediacy of **1**, at least under photolytic matrix conditions, the following three questions arise:

(1) Do other olefins show the same reactivity toward chromyl chloride under matrix conditions, so that the findings made can be generalized?

(2) Can regioselectivity be observed when unsymmetrical olefins are reacted?

(3) What happens if attempts are made to separate the two steps needed for the formation of **1**, i.e., oxygen transfer and hydrogen shift?

In the present contribution we address these questions with the aim of obtaining more detailed mechanistic insights.

Experimental Section

Computational Method. Density functional calculations were carried out with the Gaussian/DFT¹⁶ or Turbomole/DFT¹⁷ series of programs. The B3LYP formulation of density functional theory was used employing the basis set LANL2DZ¹⁶ or SV(P).¹⁷ For the purpose of comparison the structure of **8** was additionally optimized using BP/SV(P).¹⁷ Harmonic vibrational frequencies and infrared intensities were predicted at those levels by numerical second derivatives using analytically calculated first derivatives. No scaling was applied.

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Experimental Methods. A Leybold Displex closed-cycle helium refrigerator gave temperatures of ca. 10 K inside a shroud maintained at a pressure below 10⁻⁷ Torr. Mixtures were prepared in a vacuum line with use of standard manometric techniques and then deposited on the cold support. A copper block was used for all the IR experiments, and the slow spray-on deposition was favored for CrO₂Cl₂ with the sample held at -65 °C.

The photolysis source was a 200-W medium-pressure arc. The radiation was filtered with a Balzers interference filter (bandpass ca. 15 nm). IR spectra were recorded in reflection within the ranges of 4000–300 and 1000–200 cm⁻¹ and with a resolution of 1 cm⁻¹ on a Bruker IFS 66 v spectrophotometer, respectively.

CrO₂Cl₂ (99.99% pure) and tetramethylethylene (99% pure) were supplied by Aldrich and further purified by fractional condensation in high vacuum prior to use. Argon, propylene (99.999 and 99.95% pure, Messer Griesheim), and *cis*- and *trans*-2-butylene (99% pure, Aldrich) were used as received. The compounds 2-butanone, acetone, propanal, and *trans*-2,3-butylene oxide (99% pure, Aldrich), which were matrix isolated in order to obtain information concerning the intensity ratios of the bands displayed and to compare literature values, were distilled before dilution with argon.

¹⁸O-enrichment of CrO₂Cl₂ can be achieved by the following procedure: 100 mg (0.6 mmol) of CrCl₃ and a trace of Zn were placed into a flamed-out ampule provided with a stopcock in a glovebox. A 0.5 mL amount of H₂¹⁸O was co-condensed, and the mixture was stirred until all of the halide had dissolved (green color). Subsequently, the solution was frozen to -150 °C, and in a stream of argon 116 mg (5.0 mmol) of sodium, freshly cut in a glovebox, was added. Afterward the mixture was cooled with ice, initiating a vigorous reaction of sodium with the water and evolution of hydrogen. Stirring overnight yielded a bright green sludgy suspension of Na₃[Cr(¹⁸OH)₆] in water containing 1.4 mmol of Na¹⁸OH which was frozen to 77 K and treated with 1 mmol of chlorine gas. After it was annealed, the mixture was stirred for a period of 2 h during which it turned bright yellow. All volatiles were removed, and the resulting solid, consisting mainly of NaCl and Na₂Cr¹⁸O₄, was reacted with an excess of dry HCl gas. After 15 min of reaction, a subsequent flash distillation in high vacuum followed by a fractional condensation yielded 50 mg (0.3 mmol, 54% yield) of pure CrO₂Cl₂ containing 70–80% of ¹⁸O as judged by infrared. IR data: Cr¹⁸O₂Cl₂ (Cr¹⁸O¹⁶OCl₂): 960 (992) [$\nu_{as}(\text{CrO}_2)$], 943 (951) [$\nu_s(\text{CrO}_2)$], 502 [$\nu_{as}(\text{CrCl}_2)$], 461 [$\nu_s(\text{CrCl}_2)$] cm⁻¹.

The reaction of propylene with CrO₂Cl₂ under photolytic conditions was performed as follows: 100 mg (0.6 mmol) of CrO₂Cl₂ was condensed into a high-pressure tube provided with a stirring bar and sealed with a greaseless valve. An excess of liquid propylene (ca. 3

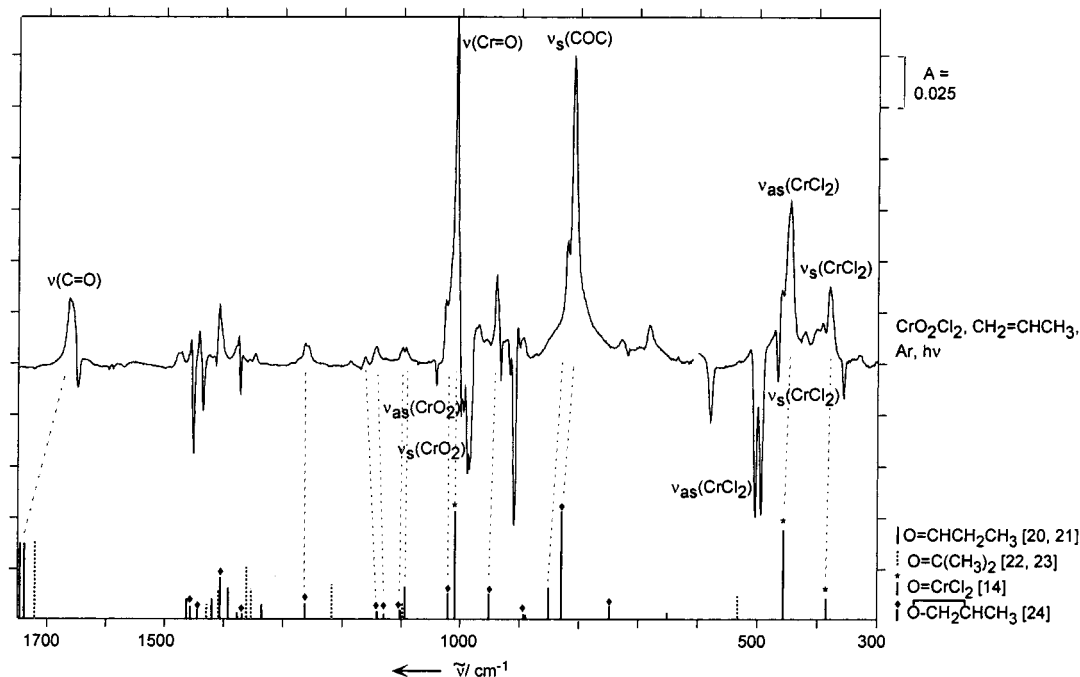


Figure 1. Upper trace: Difference between the IR spectrum of CrO_2Cl_2 isolated in an argon matrix doped with 8 mol % of propylene at 10 K and the spectrum recorded of the same matrix after photolysis at 411 nm for 20 min. Lower trace: The line diagrams for the IR spectra of propanal, acetone, propylene oxide, and $\text{O}=\text{CrCl}_2$.

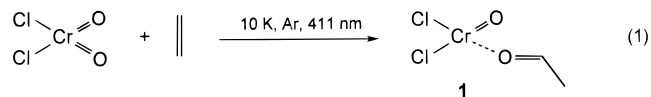
mL) was co-condensed, and the CrO_2Cl_2 dissolved at 100 K. The red solution was cooled to 77 K again and stirred at that temperature. A photolysis lamp (Hg, medium arc pressure) was placed directly beside the solution in the dewar with liquid nitrogen, and the mixture was irradiated for 30 min. Afterward the propylene was pumped off with the sample held at -100°C , and unreacted CrO_2Cl_2 was removed at a temperature of -60°C . Subsequently the sample was annealed and all other volatiles were removed, leaving behind a brown powder. A 0.5 mL amount of wet $[\text{D}_3]$ acetonitrile was co-condensed, in which the solid was dissolved, and all volatile compounds delivered by this process were distilled together with the solvent into an NMR tube which was flame-sealed. The product distribution was determined NMR spectroscopically by comparison with the spectra of authentic samples. To compare the result with the nonphotolytic reaction the experiment was performed as above, the only difference being that the sample was slowly annealed to room temperature without prior photolysis.

The reactions of TME and 2,4,4-trimethyl-1-pentene were performed in CH_2Cl_2 solutions, which were slowly annealed to room temperature. After workup as above an NMR sample containing a pinacolone/TMEO/acetone mixture (45/30/25% yield) was obtained in the case of TME, while 2,4,4-trimethyl-1-pentanal (65% yield) was essentially pure. The yields were determined by means of a standard.

Results

Product Identification. Concentrations were chosen so that statistically¹⁸ ca. 30% of the CrO_2Cl_2 molecules had one olefin molecule as nearest neighbor (i.e., $\text{Ar}/\text{olefin} = 96/4$) or higher. Since molecules do not undergo diffusion in the resulting solid matrixes at 10 K, the reservoir of collisional reactant pairs formed upon deposition is depleted as the photolytically induced reaction proceeds. The resulting new bands observed in the IR spectra reported below were occasionally somewhat broader than usually found in matrix isolation experiments, but the line widths proved to be independent of the CrO_2Cl_2 concentration, which excludes aggregation processes as a possible reason. They rather seemed to be correlated with the size of the molecules generated, probably due to conformational isomers.

Reaction of Chromyl Chloride with Propylene. Co-condensation of a mixture of propylene in Ar (8%) with CrO_2Cl_2 (-65°C) at 10 K yielded an IR spectrum of the isolated starting materials, which was subtracted from a spectrum recorded after subsequent photolysis at 411 nm. The result is shown in Figure 1 (the negative bands belong to consumed starting material). As in the case of ethylene¹⁴ the conversion is relatively high (30%), i.e., all collisional pairs must have reacted. The bands at 1009, 447, and 380 cm^{-1} in Figure 1 can be assigned to $\text{O}=\text{CrCl}_2$ by analogy with the $\text{CrO}_2\text{Cl}_2/\text{ethylene}$ case (1009 cm^{-1} $\nu(\text{Cr}=\text{O})$, 452 cm^{-1} $\nu_{\text{as}}(\text{CrCl}_2)$, and 385 cm^{-1} $\nu_{\text{s}}(\text{CrCl}_2)$). The satellites/shoulders beside some of these bands and those in spectra which will be discussed later are due to matrix splitting caused by the residence of trapped species in different matrix sites.¹⁹ Additionally, the formation of a new $\nu(\text{C}=\text{O})$ band at 1662 cm^{-1} can be observed (1669 cm^{-1} in the ethylene reaction for $\text{O}=\text{CHCH}_3$ (eq 1)), which could belong to propanal, acetone,



or both: free matrix-isolated acetone^{20,21} shows a $\nu(\text{C}=\text{O})$ band at 1721 cm^{-1} , while propanal^{22,23} causes a matrix-split band at $1746/1738\text{ cm}^{-1}$, but an exact prediction of the shifts resulting from their complexation to $\text{O}=\text{CrCl}_2$ cannot be made.²⁴ Therefore it is necessary to get an idea of the complete band

(19) This effect is also responsible for the splitting of the bands belonging to consumed CrO_2Cl_2 (compare for instance the negative bands at $447/460\text{ cm}^{-1}$ in Figure 1) and has been observed in some of our experiments mainly for the bands belonging to chromyl chloride or the $\text{O}=\text{CrCl}_2$ unit and independently of type and concentration of the olefins.

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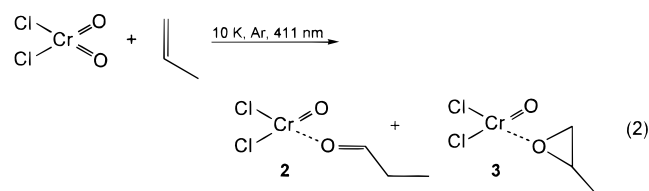
Table 1. Frequencies Obtained Experimentally by the Photolysis of CrO₂Cl₂ Isolated in a Propylene/Ar (8%) and *trans*-2-Butylene/Ar (4%) Matrix, Respectively, as Well as the Frequencies Displayed by Propanal,^{22,23} Acetone,^{20,21} Propylene Oxide,²⁵ 2-Butanone, and *trans*-2,3-Dimethyloxirane When Isolated in Argon Matrixes in cm⁻¹ ^a Together with Those Calculated for **2** and OCrCl₂···O=C(CH₃)₂ (B3LYP/LANL2DZ)

CrO ₂ Cl ₂ / propylene	<i>cis</i> - propanal ^{22,23}	acetone ^{20,21}	propylene oxide ²⁵	calcd 2	calcd O=CrCl ₂ ···acetone	CrO ₂ Cl ₂ / <i>trans</i> - 2-butylene	2-butanone	<i>trans</i> - 2,3-butylene oxide	assignment (refs 20, 21, and 25–27)
1662 (0.18)	1746/1738 (1)	1721 (1)		1684 (1)	1644 (1)	1662/1650 (0.08)	1731/1710 (0.5/1)		$\nu(\text{C}=\text{O})$
1476 (0.02)	1462 (0.41)		1456 (0.12)	1527 (0.07)	1500 (0.14)	1483 (0.06)	1455 sh		$\delta(\text{CH}_3)$
1456 (0.04)			1444 (0.10)	1524 (0.08)	1486 (0.25)	1461 (0.04)	1439 (0.21)	1491 (0.70)	$\delta(\text{CH}_3)$
1443 (0.06)	1420 (0.40)	1429 (0.20)		1460 (0.18)	1480 (0.09)	1449 (0.14)	1420 (0.30)		$\delta(\text{CH}_3)$
1409 (0.15)	1392 (0.50)	1408 (0.35)	1406 (0.4)	1457 (0.17)	1434 (0.36)	1432 (0.04)	1394 (0.15)	1415 (0.70)	$\delta(\text{CH}_3)$
1376 (0.04)	1378 (0.12)	1362 (0.66)	1369 (0.06)	1428 (0.02)	1430 (0.22)	1389 (0.42)	1367 (0.50)	1386 (0.85)	$\delta(\text{CH}_3)$
1349 (0.01)	1336 (0.25)	1354 (0.4)		1383 (0.04)		1348 (0.02)	1350 (0.25)	1336 (0.12)	$\omega(\text{CH}_2)$
1262 (0.03)			1264 (0.18)			1252 (0.01)		1258 (0.08)	$\delta(\text{CH})$
		1217 (0.5)			1316 (0.20)				$\nu_{\text{as}}(\text{CCC})$
1163 (0.05)			1143 (0.06)			1179 br (0.02)	1181 (0.20)	1157 (0.10)	$\rho(\text{CH}_3)$ i.p.
1146 (0.01)			1130 (0.03)			1122 (0.06)		1115 (0.70)	C–H bend
1101 (0.02)	1120 (0.05)		1103 (0.12)			1111 (0.06)	1094 (0.15)		$\rho(\text{CH}_3)$ i.p.
1094 (0.02)	1094 (0.49)	1092 (0.25)		1129 (0.06)	1143 (0.03)				CH ₃ rock (oop)
1026 (0.15)			1022 (0.27)			1027 (0.46)		1027 (0.90)	CH ₃ rock
	1005 (0.01)					1016 sh		1012 (0.70)	CH ₃ rock
1009 (1)				1046 (0.34)	1050 (0.70)	1007 (1)			$\nu(\text{Cr}=\text{O})$
				1040 (0.22)			997 (0.03)	960 (0.25)	$\nu(\text{CCC})$
941 (0.18)			951 (0.25)						$\delta(\text{CH}_3)/\nu(\text{CO})$
906 (0.04)			893 (0.03)			916 (0.06)	941 (0.06)		$\nu(\text{CC})$
896 (0.03)	892 (0.05)	882 (0.02)				876 (0.14)	897 (0.02)	886 (1)	CH ₃ rock (i.p.)
821/810 (0.89)	851 (0.50)		829 (1)	867 (0.06)		798 (0.66)	853 (0.11)	810 (1)	$\rho_{\text{s}}(\text{CH}_3)/\nu_{\text{s}}(\text{COC})$
729 (0.03)			748 (0.15)			727 (0.03)		719 (0.5)	$\nu(\text{CO})$
		781 (0.01)				668 (0.06)	587 (0.05)	470 (0.7)	CO i.p. bend
683 (0.06)				683 (0.05)					$\delta(\text{CCC})$
	651 (0.10)	529 (0.25)		668 (0.03)	563 (0.10)	653 (0.06)	409 (0.02)		$\delta(\text{CCO})$
447/460 (0.47)				435 (0.29)	422 (0.28)	446 (0.86)			$\nu_{\text{as}}(\text{CrCl}_2)$
395 (0.03)									
380 (0.22)				367 (0.21)	361 (0.10)	380 (0.20)			$\nu_{\text{s}}(\text{CrCl}_2)$

^a Intensities are given in parentheses and were mostly determined by us.

pattern expected for both molecules OCrCl₂···O=CHCH₂CH₃ and OCrCl₂···O=C(CH₃)₂. In Figure 1 line diagrams of the spectra of free matrix-isolated *cis*-propanal^{22,23} and acetone^{20,21} are shown.

As can be seen, acetone exhibits medium intense bands at 1217 and 529 cm⁻¹ ($\nu_{\text{as}}(\text{CCC})$ and $\delta(\text{CCO})$, respectively) which cannot be found in our experimental spectrum, so acetone is excluded as a product at the outset. On the other hand, a strong band (810 cm⁻¹) and a band of medium intensity (821 cm⁻¹) can be found in the region between 1000 and 600 cm⁻¹, where acetone displays only one band of negligible intensity. Propanal, however, shows a mode at 851 cm⁻¹, whose intensity would fit to the one of the 821 cm⁻¹ band. The intensity of the 810 cm⁻¹ band is far too high for such an assignment and consequently it finds no match in the spectrum expected for OCrCl₂···O=CHCH₂CH₃, **2**. It should therefore have its origin in a second species generated by photolysis of the starting materials. The only possible product, which could be anticipated to show such a band, is a propylene oxide adduct OCrCl₂···OCH₂CHCH₃, **3** (eq 2): free propylene oxide shows a strong



band at 829 cm⁻¹ [$\nu_{\text{s}}(\text{COC})$]²⁵ and its intensity will be further

enhanced on complexation of the epoxide by OCrCl₂ (the bands of the latter fragment are expected to coincide with the corresponding ones of **2**). This assignment is further supported by experiments employing ¹⁸O₂CrCl₂: the 810 cm⁻¹ band shifts by 23 cm⁻¹ which is characteristic for $\nu_{\text{s}}(\text{COC})$ modes (compare the experimental and calculated spectra of **7** and **8** discussed below). Accordingly, a line diagram for the IR spectrum of free matrix-isolated propylene oxide²⁵ has been included in Figure 1, too. Apart from the $\nu_{\text{s}}(\text{COC})$ band two modes of medium intensity at 951 (CH₃ bend/CO stretch) and 1022 cm⁻¹ (CH₃ rock) as well as a weak band at 1264 cm⁻¹ (CH def) can be noticed in the region between 800 and 1300 cm⁻¹ for free propylene oxide, and these are indeed observed in the spectrum in Figure 1 at 941, 1026, and 1262 cm⁻¹. It would be tentative to compare the residual very weak features of the experimental spectrum to weak bands displayed by free propanal or propylene oxide and to thereby assign them as belonging to either **2** or **3**. However, as can be seen, even on this level the match is more than agreeable, and concludingly the band pattern found in the experimental spectrum fits nicely to the one a mixture of *free* propylene oxide and propanal would display. Complexation naturally weakens the bonds of the coordinating functional groups leading to a red shift of $\nu(\text{C}=\text{O})$ and $\nu_{\text{s}}(\text{COC})$ (84/76 and 19 cm⁻¹, respectively). The bands at 951 cm⁻¹ (propylene oxide) and 851 cm⁻¹ (propanal) both show red shifts on complexation (compare Figure 1 and Table 1), too, as the first band has a partly $\nu(\text{C}-\text{O})$ character,²⁵ while the second one is expected to involve a $\nu(\text{C}=\text{O})$ motion.

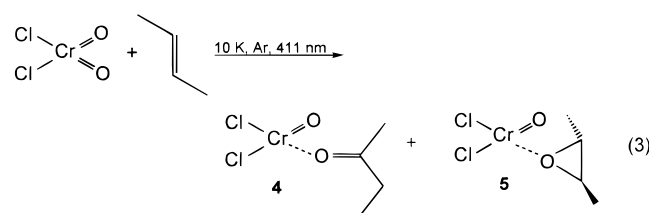
The identification of propanal as the organic oxidation product of the matrix experiment could additionally be supported by

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preparative experiments simulating the matrix conditions. Propylene "contaminated" by CrO_2Cl_2 is still fluid at 77 K and can be stirred. After slow annealing of such a mixture to room temperature and isolation of the precipitated Etard complex¹⁻⁷ by removal of the volatiles, the hydrolytic decomplexation of the latter yields propanal, dichloropropane, chloroacetone, acrolein, 2-chloropropanal and allyl alcohol besides the main product 1-chloro-2-propanol. However, if the propylene/ CrO_2Cl_2 mixture is photolyzed at 77 K while stirring and the volatiles are removed at low temperatures, a similar work up yields a product distribution in which the propanal proportion is significantly enhanced.

Reaction of Chromyl Chloride with *trans*-2-Butylene. After the reaction of *trans*-2-butylene, yet again the bands characteristic for the $\text{O}=\text{CrCl}_2$ core were observed (1007 $\nu(\text{Cr}=\text{O})$, 446 $\nu_{\text{as}}(\text{CrCl}_2)$ and 380 $\nu_{\text{s}}(\text{CrCl}_2)$ cm^{-1} , compare Table 1). By analogy with the propylene case a likely assignment for a matrix split band at 1662/1650 cm^{-1} is a 2-butanone complex **4** as shown in eq 3, while an intense band at 798 cm^{-1} suggests the



formation of a *trans*-2,3-butylene oxide complex **5** (the free epoxide isolated in an argon matrix shows a strong $\nu_{\text{s}}(\text{COC})$ band at 810 cm^{-1} (see Table 1)). *trans*-2,3-Butylene oxide further shows two strong bands at 1027 and 886 cm^{-1} (identified as medium intense bands at 1027 and 876 cm^{-1} in case of **5**), two bands of medium intensity at 1012 and 719 cm^{-1} (observed as a shoulder at 1016 and a weak absorption at 727 cm^{-1} in the product spectrum) as well as a medium intense band around 470 cm^{-1} (the corresponding mode of **5** probably gets perturbed by the subtraction of $\nu_{\text{s}}(\text{CrCl}_2)$ of CrO_2Cl_2 at 467 cm^{-1}). Medium intense bands of free *trans*-2,3-butylene oxide and 2-butanone at 1115 and 1094 cm^{-1} , respectively, appear for their complexed versions at 1122 and 1111 cm^{-1} with decreased intensities. The remaining bands of free 2-butanone, shown within the region of 500–1300 cm^{-1} , are only weak and are easily masked by more intense bands in the experimental spectrum.

Reaction of Chromyl Chloride with *cis*-2-Butylene. As expected, bands which had previously been assigned to **4** also appeared in this case after photolysis. However, none of the intense bands of **5** could be detected. Instead the most intense and therefore characteristic band of **5** at 798 cm^{-1} seemed to have been shifted to 766 cm^{-1} ($\Delta = 34$ cm^{-1}), which corresponds well to the wavenumber difference between the $\nu_{\text{s}}(\text{COC})$ bands of free *trans*- and *cis*-2,3-butylene oxide ($\Delta = 32$ cm^{-1}). A pendant for the second predominant band of **5** at 1027 cm^{-1} was not observed when *cis*-2-butylene was employed, probably due to masking: when the positions of the corresponding bands displayed by the free molecules are compared, again a shift ($\Delta = 33$ cm^{-1}) to lower wavenumbers can be observed on going from *trans*- to *cis*-2,3-butylene oxide; if it is assumed that this is characteristic for the $\text{O}=\text{CrCl}_2$ complexes, too, the band would be placed in a region where intense bands of the starting materials appear. As a consequence, it is reasonable to suggest the formation of a complex $\text{O}=\text{CrCl}_2 \cdots (\textit{cis}\text{-}2,3\text{-butylene oxide})$, **6**, showing a spectrum significantly different from the one that **5** displays.

Reaction of Chromyl Chloride with Tetramethylethylene (TME). After the photolytic reaction of this olefin with CrO_2Cl_2 at 10 K no band in the carbonyl region of the difference infrared spectrum can be found (see Figure 2), while the intense, matrix-split bands of the $\text{O}=\text{CrCl}_2$ fragment (1009, 451, and 383 cm^{-1}) are present as in the spectra discussed above. An additional intense band at 816 cm^{-1} gives a first hint to a complexation of this $\text{O}=\text{CrCl}_2$ core by tetramethylethylene oxide (TMEO) (free matrix-isolated TMEO shows an intense $\nu(\text{COC})$ absorption at 847 cm^{-1}).²⁸ Additional support for an assignment to $\text{O}=\text{CrCl}_2 \cdots \text{TMEO}$, **7** (eq 4) comes from experiments with ¹⁸O-enriched CrO_2Cl_2 (compare Figure 2, upper trace): apart from $\nu(\text{Cr}=\text{O})$, which is shifted by 44 cm^{-1} (43 cm^{-1} in the case of **1**) only the band at 816 cm^{-1} shows a significant shift (28 cm^{-1}) and can therefore confidently be assigned to the ring stretch vibration (the satellites observed beside $\nu(\text{Cr}=\text{O})$ and $\nu_{\text{s}}(\text{COC})$ belong to the ¹⁶O isotopomer which simultaneously formed due to incomplete enrichment). Furthermore, as can be seen in Table 2, the 1500–1100 cm^{-1} region of the spectrum of **7**, where mainly bands of the TMEO ligand appear, fits nicely to the one in the spectrum of free TMEO.²⁹

DFT Calculations. In support of the assignments DFT calculations were carried out, which had already helped the identification of **1**.¹⁴ Calculations concerning CrO_2Cl_2 itself had previously established that at the B3LYP/LANL2DZ level of theory^{14,30} deviations of 100 cm^{-1} are nothing unusual and have their origins in very small differences between the theoretical and real structures.^{14,31,32} It has further been shown,³⁰ that—although in comparison to ab initio studies DFT calculations are more suitable for frequency calculations concerning species of this type—the sign of the errors made is not constant, making the application of a scaling factor unreasonable. However, in the case of **1** the general band pattern was found to be in accordance with the experimental one.

(a) $\text{CrO}_2\text{Cl}_2/\text{CH}_3\text{CH}=\text{CH}_2$. According to qualitative arguments, the pattern of those bands remaining in the experimental spectrum of Figure 1, if the bands assigned to **3** are *not* considered, fits to the one which would be expected for a propanal complex **2**, while an acetone complex should give rise to a different spectrum. Structures of **2** and $\text{O}=\text{CrCl}_2 \cdots \text{O}=\text{C}(\text{CH}_3)_2$ were optimized³³ (LANL2DZ) in form of their singlet and triplet states with C_1 symmetry. The triplet states proved to be much more stable (vide infra), and the results of the subsequent frequency calculations for those are shown in Table 1. It becomes obvious that all of above statements and assumptions concerning both frequencies and intensities are correct, so that the outcome of the matrix experiment can definitely be summarized by eq 2. However, it cannot be excluded that minor amounts of $\text{O}=\text{CrCl}_2 \cdots \text{O}=\text{C}(\text{CH}_3)_2$ have been formed simultaneously and are just not detected due to masking.

(26) Durig, J. R.; Feng, F. S.; Wang, A.; Phan, H. V. *Can. J. Chem.* **1991**, *69*, 1827–1844.

(27) Durig, J. R.; Nease, A. B.; Rizzolo, J. J. *J. Mol. Struct.* **1982**, *95*, 59–84.

(28) Nakata, M. *Spectrochim. Acta A* **1994**, *50*, 1455–1465.

(29) Note that the intensity ratios shift in advance to $\nu_{\text{s}}(\text{COC})$ due to complexation (compare for instance the ratios calculated for **7** (vide infra) with those calculated for and displayed by free TMEO in Table 2).

(30) Torrent, M.; Gili, P.; Duran, M.; Solà, M. *J. Chem. Phys.* **1996**, *104*, 9499–9510.

(31) Bérces, A.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 11417.

(32) Bérces, A. *J. Phys. Chem.* **1996**, *100*, 16538.

(33) The flexible C_3 backbone of the propanal ligand in **2** opens up many possibilities for structural arrangements, which all show slightly different IR spectra. We have optimized four of them, and the frequencies of the one with propanal in a *cis* conformation (the most stable conformation of *free* propanal) are given in Table 1.

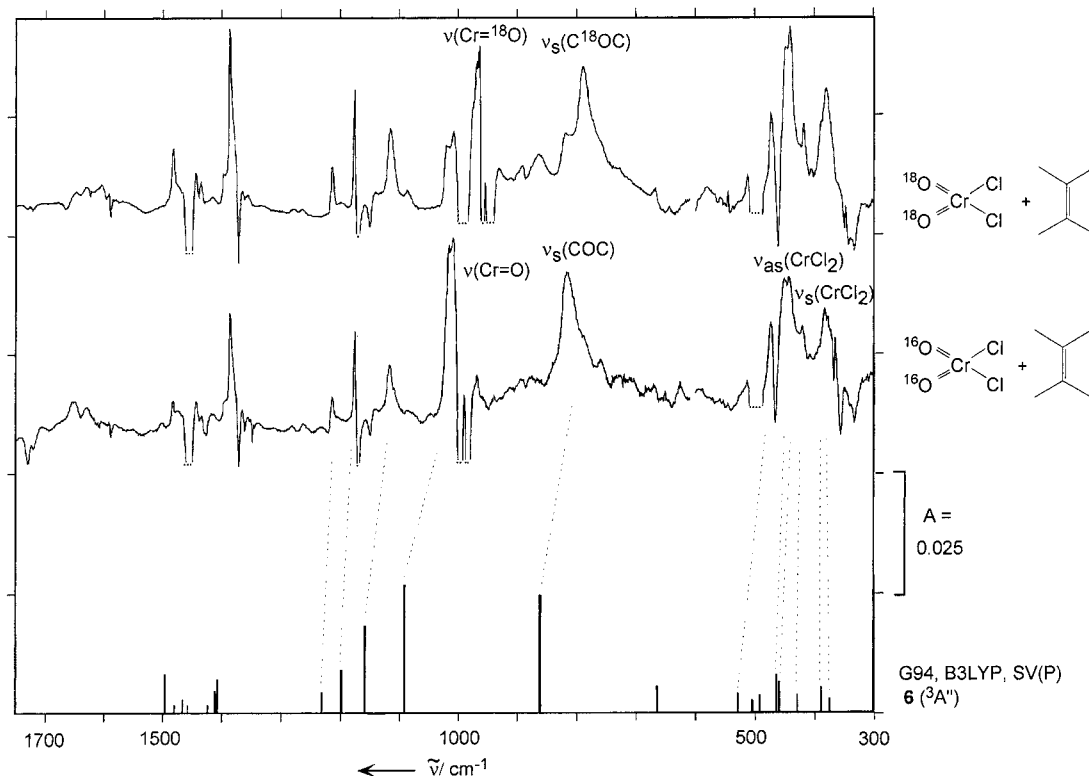


Figure 2. Middle trace: Difference between the spectrum of CrO_2Cl_2 isolated in an argon matrix doped with 4 mol % of tetramethylethylene at 10 K and the spectrum recorded of the same matrix after photolysis at 411 nm for 20 min. Upper trace: Difference spectrum obtained via the same procedure as described above but using ^{18}O -enriched CrO_2Cl_2 . Lower trace: The line diagram calculated for the IR spectrum of $\text{OCrCl}_2\cdots\text{TMEO}$, **7**, shown in Figure 3 by means of DFT calculations using SV(P) basis sets (B3LYP).

Table 2. Frequencies Obtained Experimentally by the Photolysis of $\text{Cr}^{16}\text{O}_2\text{Cl}_2$ and $\text{Cr}^{18}\text{O}_2\text{Cl}_2$ Isolated in a Tetramethylethylene/Ar (4%) Matrix, as Well as Calculated Frequencies (B3LYP, SV(P)) for $\text{OCrCl}_2\cdots\text{TMEO}$, **7**, and Free TMEO in cm^{-1} ^a

$^{16}\text{O}_2\text{CrCl}_2/\text{TME}$	expt $\Delta(^{16}\text{O}-^{18}\text{O})$	calcd $^{16}\text{O}-7$	calcd $\Delta(^{16}\text{O}-^{18}\text{O})$	expt ²⁸ TMEO	calcd TMEO	assignment
1483 (0.12)	0	1502 (0.29)	0	1484 (0.2)	1501 (0.43)	CH_3 bend
1444 (0.09)	0	1484 (0.05)	1	1471 (0.1)	1482 (0.13)	CH_3 bend
1434 (0.12)	0	1469 (0.09)	0	1438 (0.1)	1437 (0.13)	CH_3 bend
1396 (0.05)	0	1461 (0.06)	0	1406 (0.1)	1421 (0.10)	CH_3 bend
1386 (0.50)	0	1410 (0.25)/1414 (0.15)	1/0	1381 (0.7)	1409 (0.40)	CH_3 bend
1214 (0.16)	0	1232 (0.15)	0	1205 (0.3)	1220 (0.58)	$\nu_{\text{as}}(\text{CCC})$
1176 (0.37)	0	1200 (0.33)	0	1173 (1.0)	1199 (1)	$\delta(\text{CCC})$
1117 (0.25)	2	1160 (0.67)	2	1142 (0.3)	1180 (0.50)	$\rho(\text{CH}_3)$
1087 (0.06)	0					
1016/1009 (1)	44	1091 (1)	54			$\nu(\text{Cr}=\text{O})$
816 (0.60)	28	860 (0.93)	28	847 (0.2)	881 (0.40)	$\nu_s(\text{COC})$
		662 (0.19)	14			$\nu_{\text{as}}(\text{COC})$
474 (0.60)	0	525 (0.14)	19			$\delta(\text{CrOC})$
451 (0.43)	2	459 (0.29)	0			$\delta(\text{CrOC}), \rho(\text{CCC})$
441 (0.50)	0	455 (0.14)	1			$\nu_{\text{as}}(\text{CrCl}_2)$
421 (0.43)	3	423 (0.13)	0			$\omega(\text{CCC})$
383 (0.50)	3	385 (0.19)	2			$\rho(\text{CCC})$
373 (0.40)	2	370 (0.14)	1			$\nu_s(\text{CrCl}_2)$

^a Intensities are given in parentheses. The assignments are based on the spectrum of free TMEO²⁸ whose experimental and calculated frequencies are given for comparison, too, as well as the results of the calculation.

(b) $\text{CrO}_2\text{Cl}_2/(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$. Calculations were also performed in the case of **7**, where the spectrum is complicated by the relatively large organic moiety making a straightforward interpretation difficult. During the structure optimization (SV(P))³⁴ for a $\text{OCrCl}_2\cdots\text{TMEO}$ complex with C_s symmetry, the small HOMO–LUMO gap indicated that the triplet state $^3A''$ is significantly favored over the singlet state. Accordingly, the $^3A''$ structure was optimized, and the result is shown in Figure 3. The structure shows qualitatively all features which could have been expected considering the experimental spectrum: the $\text{Cr}=\text{O}$ bond is shorter (1.552 Å) than in CrO_2Cl_2 and the bond to TMEO is very strong (2.000 Å), explaining the significant

red shift of $\nu_s(\text{COC})$ (31 cm^{-1}). Only few crystal structures of metal epoxide complexes are known,^{35–37} and these display $\text{M}\cdots\text{O}$ distances of 2.2–2.4 Å. The angles between the $\text{M}\cdots\text{O}$

- (34) SV(P) basis sets were used in this case, as the results of geometry optimizations¹⁴ were very good when they were used in combination with the BP functional of the *Turbomole* program,¹⁷ which, however, is not suitable to determine the corresponding IR spectra.
- (35) Groves, J. T.; Han, Y.; Van Eugen, D. *J. Chem. Soc., Chem. Commun.* **1990**, 436–437.
- (36) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 538–539.
- (37) Harder, S.; Boersma, J.; Brandsma, L.; Katers, J. A.; Duisenberg, A. J. M.; van Lenthe, J. H. *Organometallics* **1990**, *9*, 511.

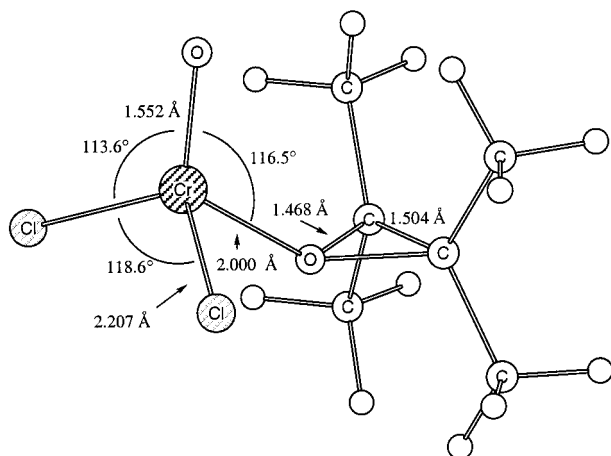


Figure 3. Optimized C_s ($^3A'$) structure calculated for $\text{OCrCl}_2 \cdots \text{TMEO}$, **7**, by means of DFT calculations using SV(P) basis sets (B3LYP). Selected bond lengths and angles are given in angstroms and degrees, respectively.

vectors and the epoxide planes found there are in good agreement with the angle found for **7** (125.8°). The calculated IR spectrum based upon this geometry further confirmed the assignment of the experimental IR spectrum to **7**. As can be seen in Figure 2 and Table 2, its band pattern and intensity ratios could be reproduced nicely, especially if the general comments made above and the fact that no scaling factor has been applied are considered. The calculation predicted the position of the $\nu(\text{COC})$ band at 860 cm^{-1} with a theoretical ^{18}O shift of 28 cm^{-1} , the latter being in exact agreement with the experimental result. To obtain information about the errors made in the calculation of the theoretical IR spectrum of **7**, additional calculations concerning the vibrational frequencies of free TMEO were performed. It is evident from Table 2 that the deviations of the calculated frequencies from the experimental ones are in excellent agreement with those obtained for **7**.

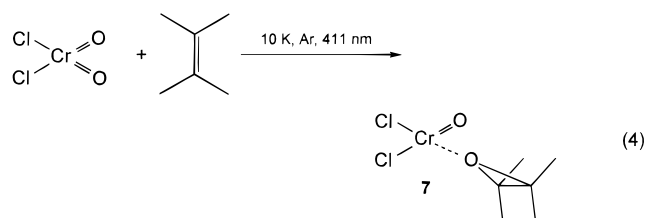
Discussion

Mechanistic Inferences. To find answers to the questions 1 and 2 of the Introduction, propylene, which combines asymmetry with simplicity, had been chosen as an appropriate substrate first to be reacted with CrO_2Cl_2 . The results show that, in agreement with the observations¹³ made in thermal oxidations of terminal olefins by CrO_2Cl_2 , the *carbonylation* proceeds regioselectively at the carbon with a lower degree of substitution, yielding complex **2** as the thermodynamically less stable product (the acetone complex was calculated to be energetically favored by ca. 50 kJ/mol). This makes the existence of a transition state likely which discriminates between the two possible products, either by way of its formation or via a selective decomposition pathway. Furthermore, an *epoxidation* of propylene by CrO_2Cl_2 producing **3** was observed, and in order to obtain information about the stereochemistry of this reaction, *trans*- and *cis*-2-butylene were employed as further reactants. The bands for **5** could not be detected in the *cis*-butylene experiment, and those of **6** were not present in the spectrum when *trans*-butylene was reacted. This observation of complete stereochemistry retention in the epoxides (which again fits to the findings made by Sharpless¹³ in the thermal oxidations with CrO_2Cl_2) implies that if the reaction proceeds via an intermediate, internal rotation around the central C–C bond is either not possible in principle or is slow on the scale of the intermediates lifetime.

These results further clarify that H shift coupled oxygenation and epoxidation of olefins by CrO_2Cl_2 are in fact *typical*

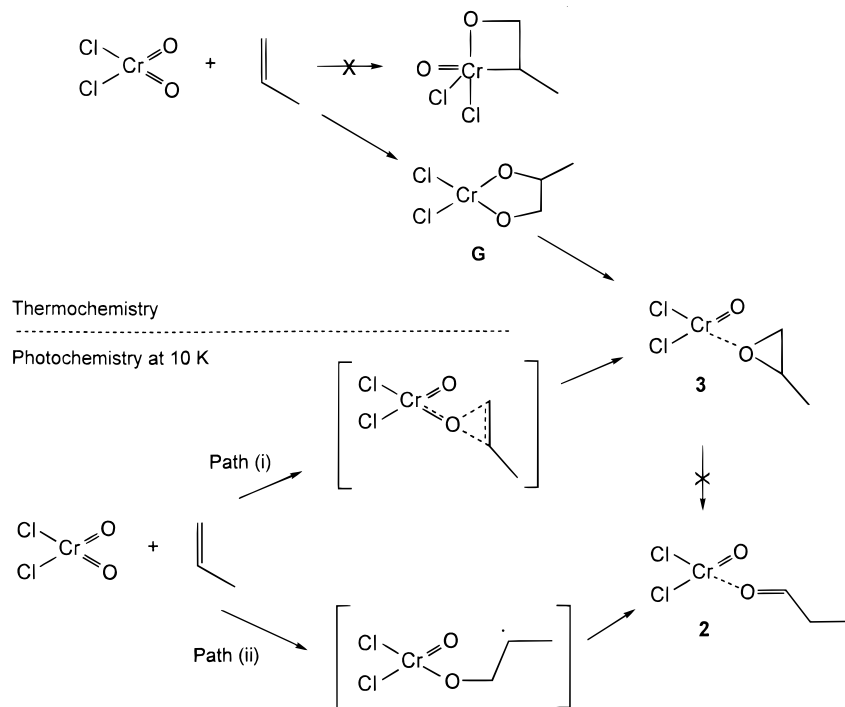
reactions observed in low-temperature matrixes, when they are induced photochemically. In light of these findings a band³⁸ of medium intensity at 852 cm^{-1} in the spectrum,¹⁴ which had been obtained after photolysis of the ethylene/ CrO_2Cl_2 system may also be interpreted in terms of an epoxide adduct $\text{O}=\text{CrCl}_2 \cdot$

$\cdots \text{OCH}_2\text{CH}_2$, **8**. A calculation (B3LYP/LANL2DZ) proved³⁹ that indeed, besides the bands of the OCrCl_2 fragment, which are masked by those of **1**, **8** should show just one intense band (calculated at 835 cm^{-1}) with the ^{18}O shift found almost exactly.³⁸ Comparison to the corresponding band position of the free epoxide²⁵ yields a shift of 25 cm^{-1} as a result of complexation, fitting nicely to the shifts found for **3** and **7** and confirming finally the simultaneous formation of **8** with **1**. A comparison of the $\nu(\text{C}=\text{O})/\nu_s(\text{COC})$ ratios of the pairs **1/8**, **2/3**, and **4/5** reveals a steady decrease of these values within the series of experiments involving ethylene/propylene/2-butylene. This suggests that epoxide products are becoming more and more important when the degree of methyl substitution at the olefin is increased, although a quantitative statement is not possible due to the unknown extinction coefficients of the corresponding bands. This finding is in agreement with the results of H. Frei et al. who studied the photooxidation of matrix-isolated olefins by NO_2 .⁴⁰ Our results obtained on employment of $\text{CD}_2=\text{CD}_2$ further prove, that the H migration step during *carbonylation* is not rate determining, as the product ratio of $\mathbf{8^D}/\mathbf{1^D}$ is not higher than the one of $\mathbf{8}/\mathbf{1}$,⁵ as judged by the $\nu(\text{COC})/\nu(\text{C}=\text{O})$ intensity ratios. All original bonds at the olefin should therefore still be mainly intact in the transition state leading to the carbonyl products, so that the influence of methyl substitution on this barrier should be confined to electrical and steric factors becoming effective on approximation of the two reactants. This suggested the further experiment employing TME to test whether the aforementioned trend would lead to exclusive epoxidation in this case. As described in the Results, the selective formation of **7** could be confirmed. A methyl shift, which would have yielded a pinakolon adduct, did indeed not occur and the fact that no other product has been isolated instead mean that the barrier leading to the carbonyl compounds can no longer compete successfully with epoxide formation anymore if the olefins are peralkylated. Our calculation (B3LYP/SV(P)) yielded a reaction enthalpy of $\Delta H = -150 \text{ kJ/mol}$ for eq 4 and



for purposes of comparison the one for the oxidation of ethylene to yield **8** was calculated, too, employing two different func-

- (38) This band, which shows an ^{18}O shift of 26 cm^{-1} (compare 23 cm^{-1} for **3** and 28 cm^{-1} for **7**) and which had not been in agreement¹⁴ with the frequencies calculated for **1** with respect to its isotopic shift and its intensity, had only tentatively been assigned to a $\delta(\text{CCO})$ vibration of **1**, as seemingly there were not enough bands in the spectrum to accommodate a second product and also since it proved impossible (vide infra) to alter its intensity ratio with respect to $\nu(\text{C}=\text{O})$ in various photolytic cycles. In addition, all bands exhibited an identical growth behavior which normally suggests an assignment to a single species.
- (39) Calculated frequencies (intensities) for **8**: 375 (0.34, $\nu_s(\text{CrCl}_2)$), 426 (0.39, $\nu_{\text{as}}(\text{CrCl}_2)$), 680 (0.09), 830 (0.13), 835 (1, $\nu_s(\text{COC})$), $\Delta\delta$ 117 and $\Delta^{18}\text{O}$ 29), 1051 (0.91, $\nu(\text{Cr}=\text{O})$, $\Delta^{18}\text{O}$ 45), 1281 (0.24), 1501 (0.06).
- (40) Frei, H. *Chimia* **1991**, *45*, 175–190.

Scheme 2. Mechanistic Possibilities for the Photolytic Olefin Oxidation with CrO_2Cl_2 under Matrix Conditions vs Relevant Intermediates for the Thermal Process According to Calculations^{42,43}

tionals and basis sets: B3LYP yielded -113.2 (SV(P)) and -115.4 kJ/mol (LANL2DZ), while BP gave $+6.5$ kJ/mol (SV(P)) (compare $+36.8$ kJ/mol as found by T. Ziegler et al. in an NL-P approach/STO, *vide infra*). The considerable differences within these values stimulated further calculations concerning the enthalpy of the reaction of CrO_2Cl_2 with ethylene to yield *free* oxirane and ${}^3[\text{O}=\text{CrCl}_2]$, as a value of $+104.4$ kJ/mol can be deduced from experimental data⁴¹ which allowed a validation of the theoretical data in this case. B3LYP yielded $+9.0$ (SV(P)) and $+120.2$ kJ/mol (LANL2DZ), while BP gave $+97.8$ kJ/mol (SV(P)). All three calculated energies therefore agree concerning the endothermic nature of this reaction, and two of them are even close to the experimental value. Their comparison with the data calculated for the formation of **8** provides an idea about the energy, which is released on complexation of organic O donors by OCrCl_2 and which compensates the loss of energy for the “pure oxidation process” (of course the oxidation product is never really separated from the Cr center in the *real* experiment). However, different functionals and basis sets seem to give quite different values for these complexation energies (-91.2 to -235.6 kJ/mol). Accordingly, it is difficult to judge how exothermic these reactions really are, but, in any case, the reactions proceed in the matrix due to selective excitation of CrO_2Cl_2 (*vide infra*) and thermally due further exothermic aggregation processes (formation of the Etard complex), through which the species are constantly removed from any potential equilibrium.

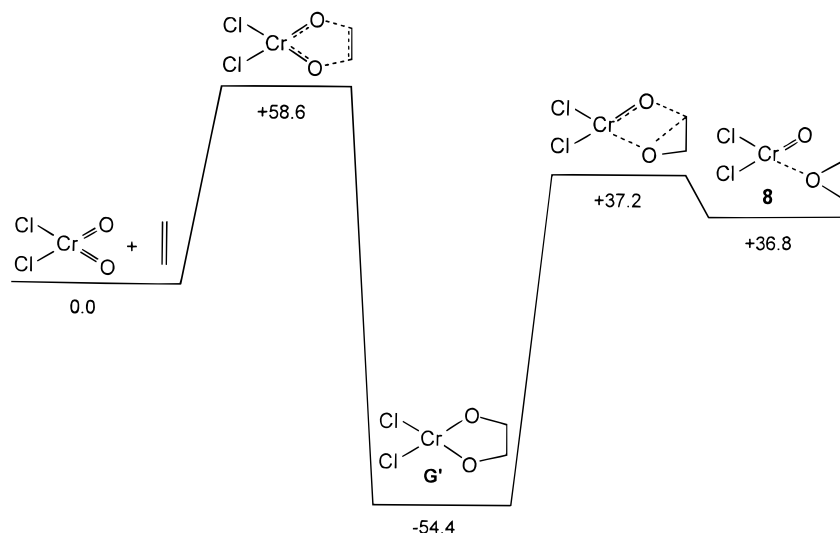
The $\nu(\text{C}=\text{O})/\nu_s(\text{COC})$ ratios within the pairs **1/6**, **2/3**, and **4/5** were not found to vary significantly with changes concerning the external conditions (matrix apparatus and photolysis lamp). This means that the two different products—complexes of carbonyl compounds and epoxides—form within these systems always roughly in the same relative yields (not overall yields!), which additionally proved to be independent of the irradiation wavelength used to generate the products. Furthermore, no

isomerization between them could be induced (it was impossible to significantly change the ratios by photolysis at any wavelength; photolysis with UV light decomposed both products). Especially the latter finding is important, since it means that the epoxides and carbonyl compounds are formed via independent routes, i.e., the complexes of the carbonyl compounds were *not* generated by rearrangement of the epoxide complexes. The reaction paths shown in Scheme 2 for propylene could account for all findings made so far. A species such as **3** had already previously been suggested as one of the intermediates formed in reactions of alkenes with CrO_2Cl_2 .¹³ There it was proposed to have its origin in a chromaoxetane (see Scheme 1), which reductively eliminates the epoxide. However, recent DFT calculations by T. Ziegler et al.⁴² have shown that a [2+3] addition of ethylene to the $\text{Cr}=\text{O}$ bonds in CrO_2Cl_2 (which would yield a glycolate **G** in the propylene case) is favored over the [2+2] addition to one $\text{Cr}=\text{O}$ linkage both kinetically and thermodynamically [on the singlet as well as the triplet potential energy surface (PES)]. These DFT results suggest exclusion of chromaoxetanes as the intermediates responsible for product formation during our matrix experiment, too. Very recently Ziegler et al.⁴³ calculated the potential energy surface for the thermal epoxidation of ethylene by CrO_2Cl_2 assuming that **8**, the species we have isolated and identified not only as such but also in form of its methylated derivatives **3**, **5**, **6**, and **7** as part of the present work, is an intermediate product. They found that the kinetically and thermodynamically most favored reaction route leads from the singlet starting materials via a singlet transition state (see Scheme 3) to a triplet [2+3] cycloadduct. The resulting five-membered ring **G'** is sufficiently flexible to allow for a facile rearrangement route to yield **8** via a modest activation barrier. In principle the products **1–8** isolated in the present study could therefore have their origins

(42) Torrent, M.; Deng, L.; Ziegler, T. *Inorg. Chem.* **1998**, *37*, 1307–1314.

(43) Torrent, M.; Deng, L.; Duran, M.; Solá, M.; Ziegler, T. *Can. J. Chem.*, submitted.

(41) Ebbinghaus, B. B. *Combust. Flame* **1995**, *101*, 311–338.

Scheme 3. Thermal Epoxidation Mechanism According to DFT Calculations⁴³ (Enthalpies Given in kJ/mol)

in such glycolates, which would have to decompose photolytically via two independent routes. However, this does not seem very likely as the reaction to \mathbf{G}' has been calculated to be exothermic by -54.4 kJ/mol. Therefore such intermediates should have been observable at some stage during our experiments, as long as their lifetimes under photolytic matrix conditions are not too short to prevent detection. Their UV/vis absorption properties are not expected to be markedly different from those displayed by the OCrCl_2 complexes, meaning that if a photolytic conversion of \mathbf{G}' to $\mathbf{8}$ is possible, the reverse reaction should be possible, too. Consequently, such short lifetimes would require very exothermic reactions of the glycolates to those complexes (in all cases!) combined with very low activation barriers for these processes. As can be seen in Scheme 3, this is not at all the case according to the calculations⁴³ for ethylene and the same is expected for propylene, so it should have been possible to observe the glycolates at least in these reactions if they had been the intermediates responsible for epoxide formation. Their presence would have become most obvious through $\nu(\text{Cr}-\text{O})$ bands⁴⁴ in the region between 750 and 500 cm^{-1} ; in our experiments, however, only in the case of propylene a weak band has been observed.

How are the compounds $\mathbf{1-8}$ produced if not via glycolates or chromaoxetanes? The starting situation in the matrix experiments is different from the one under thermal conditions: at the outset there are weak collisional $\text{CrO}_2\text{Cl}_2/\text{olefin}$ complexes formed upon deposition (neither in photolytical nor annealing experiments were we able to observe classical olefin complexes as suggested previously¹³ (compare Scheme 1) at any stage) and only those react on photolysis as indicated by the yields obtained. Formation of the epoxide complex $\text{OCrCl}_2\cdots\text{OCH}_2\text{CHCH}_3$, $\mathbf{3}$, can then be imagined via a direct interaction between one $\text{Cr}=\text{O}$ group and the olefin. This would account for the retention of stereochemistry during epoxide formation in our experiments, and there are already precedent cases in the literature where intermediates/transition states with the characteristics of the species in path i (Scheme 2) are discussed.⁴⁵⁻⁴⁷ As pointed out above, we have found no

evidence for isomerization of $\mathbf{3}$ to $\mathbf{2}$ under matrix conditions, so there should be an alternative route to $\mathbf{2}$. J. M. Mayer et al. found a small loss of stereochemistry in an oxo transfer reaction from an epoxide to a tungsten center, which they explained by a ring-opened radical species containing the fragment $\text{W}-\text{OCH}_2\text{CH}_2\cdot$.⁴⁵ An analogous species $\text{Cl}_2(\text{O})\text{CrOCH}_2(\text{CH}_3)\text{CH}\cdot$ as shown in Scheme 2 (path ii) should be considered as a transition state or even intermediate, too: it has been established that the $\text{Cr}=\text{O}$ double bond of CrO_2Cl_2 in its ground state—although having no principle radical character—can abstract a hydrogen atom from organic substrates.⁴⁸ If it attacked olefins in a similar manner, this would produce the species mentioned above with the necessary condition that the resulting $\text{C}-\text{O}$ bond (whose bonding energy is not known) is strong enough to represent the driving force of the reaction. Addition of an organic radical to CrO_2Cl_2 is likely to be very exothermic,⁴⁸ so that the loss of π -bonding energy could be compensated. The regioselectivity found would then be explained by generation of the most stable radical and a subsequent 1,2-H migration should yield $\mathbf{2}$. According to DFT results⁴³ a radical-like transition state as shown in Scheme 2 should show a ring closure to a glycolate, but the carbon carrying the unpaired electron would have to come close to the $\text{Cr}=\text{O}$ bond, which might not be possible within the rigid Ar lattice at 10 K, so that 1,2-hydrogen migration becomes faster.

Consequently, a mechanism as in Scheme 2 could explain all experimental findings but the electronic states of the products still deserve some comments: in the case of $\mathbf{1}$ and $\mathbf{2}$ the energy differences between triplet and singlet states $\Delta H(\text{T}-\text{S})$ were calculated (B3LYP/LANL2DZ) to amount to ca. -70 kJ/mol (with slight deviations dependent on individual conformers), while -118 kJ/mol was found for $\mathbf{8}$, in agreement with the findings made for $\mathbf{7}$. This is what should be expected for d^2 complexes with distorted tetrahedral geometries on grounds of simple ligand field considerations: in the ground state the two d orbitals of lowest energy are occupied with one electron each and to reach a singlet state the spin pairing energy has to be overcome, which is far higher than ΔE_{d-d} . Without calculating the structures of products $\mathbf{3-6}$, it is therefore reasonable to assume that in general the triplet states are energetically favored

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over the singlet states. Further, the π^* character of both SOMOs in such complexes is not distinct, so that the rather strong Cr=O bond (compare $\nu(\text{Cr}=\text{O})$ of 1009 cm^{-1}) is only slightly weakened by the partial occupation of these orbitals. This destabilizing effect is even less pronounced, if the orbital of lower energy, which is less antibonding in comparison to the one of higher energy, accommodates both electrons (i.e., in a singlet state). This manifests in the IR spectra of **11** and **31**, for which, as an example, a $\Delta\nu(\text{Cr}=\text{O})$ value of 70 cm^{-1} was calculated. It was found that the deviations of the band positions in the spectrum calculated for **31** from those in the experimental spectrum are much smaller than in the case of **11**, thereby supporting the assignment of all spectra to the triplet molecules. Reaction in the matrix occurs on photoexcitation at 411 nm (mainly a Cl→Cr CT transition⁴⁹), yielding an excited singlet state initially, which may well be the state showing the reaction with the olefins. However, as ethylene is a singlet molecule, too, somewhere along the reaction coordinate certain transient configurations have to change their spin state to yield the triplet complexes. Although the selection rule forbids such intersystem crossings, spin-orbit coupling occurring in transition metal complexes can enhance the probability that a change of spin state occurs at or near the crossover point of the two different energy surfaces⁵⁰ (note that the thermal oxidation of olefins by CrO_2Cl_2 resulting in paramagnetic Cr(III/IV) species⁴⁸ is forbidden, too). Absorption, emission, and excitation spectra have further shown that CrO_2Cl_2 possesses a low-lying triplet state^{51–53} and that it shows phosphorescence from this state on excitation at 436 nm.⁵⁴ Consequently, this state is accessible in our experiments, too, and if this was responsible for product formation a forbidden spin crossover would not even have to be considered. In any case, after excitation the reactions appear to be very fast, so that there must be two low-barrier reaction paths (probably involving intermediate geometries such as the ones depicted in Scheme 2) producing either complexes of epoxides or carbonyl compounds. The probability of the excited collisional complexes reacting via one route or the other should depend on the electronic conditions of the olefins employed, explaining the effects of methylation. The possibility that the two different products are formed due to a “two-state reactivity” cannot be excluded, but such an explanation seems to be inconsistent with the relative product yields observed in the series of olefins from ethylene to TME and the constancy of these yields, implying that both paths have a common outset.

In our opinion, therefore, the results obtained in the present matrix study are explained best by a reaction of triplet CrO_2Cl_2 with olefins in close proximity producing either epoxides via route i or carbonyl compounds via path ii. Besides being reasonable chemically as outlined above, this mechanism accounts for retention of stereochemistry in epoxide formation, the regioselectivity found for the generation of the carbonyl compounds, and does not require a forbidden change of spin to yield the most stable products.

Implications on the Thermal Oxidation of Olefins by Chromyl Chloride. According to arguments above the PES investigated in the matrix experiments under photolytic condi-

tions is probably different from the one the system moves on when the reactions are induced thermally. Light of the wavelength 411 nm is far below the Cr=O dissociation threshold so that CrO_2Cl_2 , which shows a visible absorption band nearby, takes up energy via this transition to reach an excited state capable of reacting with olefins under matrix conditions. Consequently the first transition states and intermediate geometries which have to be passed will be different from the thermal ones. However, as outlined above, in order to account for the products of the thermal reactions a spin crossover has to occur somewhere along the reaction coordinate, so that the thermal and photochemical PES's will meet at some stage. We consider it as being very likely that the products isolated in the present matrix study represent such touching points. This conclusion can be deduced from our experimental study in combination with the theoretical investigation by Ziegler et al., both of which, for the case of ethylene, yielded the same intermediate species **8**. This finding in turn suggests that the $\text{O}=\text{CrCl}_2\cdots\text{O}=\text{CRR}'$ complexes we have identified are in fact intermediates during thermal reactions, too. At least their incorporation into the Etard complex would explain the frequent observation of carbonyl compounds as products of such oxidations more nicely than subsequent reactions of certain endproducts during workup. Furthermore this statement is supported by the results of H. Schwarz et al., who were able to show that, analogously to CrO_2Cl_2 in low-temperature matrixes, CrO_2^+ reacts with ethylene in the gas phase⁵⁵ (i.e., under thermal conditions) in a metal-assisted oxidation linked to a 1,2-hydrogen migration to yield acetaldehyde ($\text{O}=\text{Cr}^+\cdots\text{O}=\text{CHCH}_3$ has been identified among the products in the gas phase, while **1** was the matrix product). After the formation of the aforementioned intermediates, of course, other barriers, which are too high for matrix experiments, can be crossed thermally, as for instance the one for the isomerization of epoxides to carbonyl compounds catalyzed by Lewis acidic centers.

In summary, the characterization of species isolated in such matrix experiments is instructive for revealing the mechanism of oxidation reactions with chromyl chloride, even if allowance is made for different formation paths under photolytical and thermal conditions. Proving the existence and intermediate stability of compounds such as **1–8** provides strong evidence that they are likely intermediates also in the “real” oxidation processes. A very recent investigation⁴⁴ by B. S. Ault concerning the reaction of chromyl chloride with MeOH has proved, that indeed the products generated via photolytic reaction in the matrix are identical with those formed in the primary steps thermally. Further support also comes from the fact that the main features observed in the thermal reactions do correspond quite well to the matrix results: as mentioned in the Introduction, previous reports had claimed that olefin oxidation by CrO_2Cl_2 can be directed toward selective formation of carbonyl compounds by reductive workup, for instance, in the cases of TME and 2,4,4-trimethyl-1-pentene which are oxidized to pinakolon and 2,4,4-trimethyl-1-pentanal in 50 and 78% yields, respectively.^{7–11} However, in our hands these carbonyl compounds were obtained in good yields *without* reductive workup. In the case of TME the main side product was TMEO (eq 5) and it follows, that oxidation of TME, as just one example, can in principle yield both epoxide and ketone, the latter being favored under the typical preparative conditions, but this might be different for other olefins. This is exactly what we have found studying the intermediates in our matrix experiments. It can

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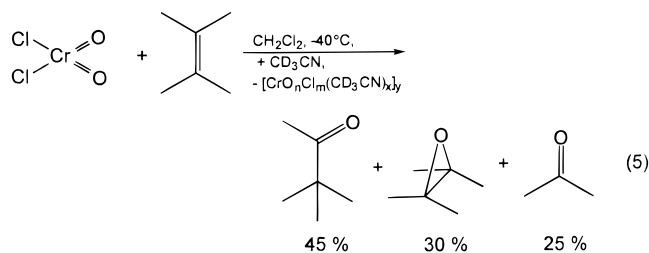
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therefore be concluded in accordance with previous reports^{1-6,12} that carbonyl compounds can represent typical products of olefin oxidations by CrO_2Cl_2 even without special workup procedures. They form in concurrence to epoxides and can analogously be found coordinated to Cr centers in the Etard complex after the reaction. We have recently shown that complexation of epoxides by CrO_2Cl_2 itself at -50°C can induce a rearrangement to chromium chloroalkoxides,⁵⁶ yielding chlorohydrins on hydrolysis. From the spectroscopic investigation of this system at low temperatures, therefore, a picture emerges which can explain the variety of products resulting from such oxidations.

Conclusions

Cryogenic matrix studies concerning the olefin/ CrO_2Cl_2 system have allowed for the first time the isolation and

characterization of complexes $\text{O}=\text{CrCl}_2\cdots\text{O}=\text{CRR}'$, whose coexistence with other aggregated intermediates in the Etard complex generated in olefin oxidations with CrO_2Cl_2 could explain the frequent observation of carbonyl compounds among the products after hydrolysis. It could be excluded that they were generated in the matrix by isomerization of epoxide complexes and on permethylation of the olefinic bond (i.e., employment of TME) their formation route was completely suppressed. Moreover, first representatives for $\text{OCrCl}_2\cdots\text{epoxide}$ complexes, often proposed as intermediates in the literature,^{1-11,13,15,43} have been isolated and characterized. Both types of complexes should be considered as respectable intermediates also under thermal conditions. The stereo- and regiochemistry observed in the common products of the thermal and photochemical processes are in agreement and other characteristic principles are comparable, too, even if the initializations of the reactions are different.

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