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Isolation of a stable Cr(V) intermediate in the oxidation of aryl-substituted alkenes by chromylchloride

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Abstract

The isolation and characterization of a stable chromium(V) intermediate in the chromylchloride oxidation of aryl-substituted alkenes is reported. A 2:1 complex of CrO_2Cl_2 and alkene could be isolated in high yields. Based on spectroscopic evidence and density functional theory calculations (UBecke3LYP/6-31G*) we propose a structure for the elusive intermediate. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chromylchloride; Alkene oxidation; DFT calculations; EPR

1. Introduction

The mechanism of the oxidation of alkenes by d^0 metal-oxo compounds has been discussed intensively during the last years [1–3]. While permanganate and osmiumtetraoxide are known to *cis*-dihydroxylate alkenes in high yields, chromylchloride leads to a complex mixture of products. Early synthetic work by Sharpless et al. reported the formation of large amounts of chlorohydrine products [1] and the mechanistic question was raised how the alkene will coordinate to metalorganic compounds and how the differences between the various metal-oxo compounds capable of oxidizing alkenes can be explained. Matrix isolation studies at low temperature favor a direct interaction between the alkene and the oxo function of CrO_2Cl_2 [4].

Density functional theory calculations were recently successful in establishing the mechanism for osmiumtetraoxide [3] and permanganate [5], while in the case of chromylchloride [6] some questions arising from experimental results cannot be answered yet.

Chromium(V) species have also been identified to be biologically active compounds with regard to chromium-induced cancers [7–11] and X-ray structures show the stability of chromium(V) complexes [10,12].

Previous experimental studies revealed the existence of dioxodichlorochromates(V) as intermediates in the reduction of chromium(VI)dioxodichloride [13]. Evidence against a radical mechanism is the *cis*-stereospecificity of the chromylchloride addition to alkenes which was investigated using isotopically labeled alkenes [14].

For the chromylchloride oxidation of styrenes and cyclohexene the formation of an intermediate was reported, but its structure could not be fully elucidated [15–17]. Even the approximate composition was debated to be a 1:1 complex [15] or a 2:1 complex [17].

Recently it was shown that metal-oxo compounds are capable of abstracting hydrogen atoms from alkanes if the thermodynamic driving force is strong enough [18]. In the light of the ongoing discussion about the CH-abstraction ability of d^0 metal-oxo compounds and consequent formation of chromium(V) species we were interested in the characterization of those intermediates in the chromylchloride oxidation of alkenes. We therefore investigated the reaction of chromylchloride with different aryl-substituted alkenes.

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Table 1
Elementary analysis data of compounds **2a**–**2c**

	2a		**2b**		**2c**	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)
C	32.10	30.90	34.31	32.81	34.31	31.91
H	2.10	2.04	2.47	2.66	2.47	2.30
Cr	19.80	19.96	21.22	20.26	21.22	20.26
Cl	33.80	32.90	28.94	29.50	28.94	31.81

2. Results and discussion

2.1. Reactions of phenyl-substituted alkenes with CrO_2Cl_2

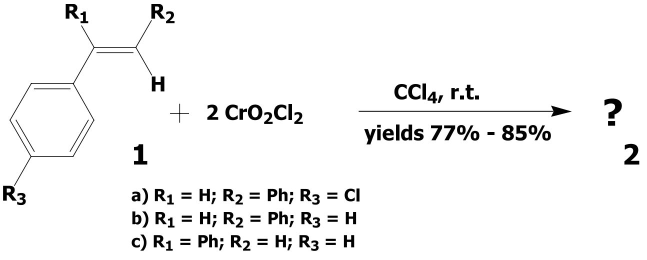
When 0.7 equivalents of CrO_2Cl_2 were reacted with one equivalent of 1-(4-chlorophenyl)-2-phenylethylene (**1a**) at room temperature, the elementary analysis of the resulting product **2a** (yield: 37.9%) shows approximately 2:1 molar ratio of CrO_2Cl_2–alkene. This was surprising due to an excess of alkene and the fact that besides a 2:1 adduct also a 1:1 adduct has already been reported in literature for the alkene oxidation with CrO_2Cl_2 [15]. The reaction was repeated with two equivalents of CrO_2Cl_2 per mole alkene and the same reaction product was received, but with a yield of 72.3%. Further reactions with *trans*-stilbene (**1b**) and 1,1-diphenylethylene (**1c**) using two equivalents of CrO_2Cl_2 (Scheme 1), also provided the corresponding 2:1 adducts **2b** and **2c** in high yields (77.1 and 84.7%, respectively). The results obtained from elementary analysis are given in Table 1.

The brown powderous products are insoluble in most of the common solvents with the exception of acetone and acetonitrile. EPR spectra of the paramagnetic compounds therefore had to be measured in dry acetone. The EPR spectrum of **2a** is shown in Fig. 1. The g values are consistent with a chromium(V) species, the frozen solution (solvent acetone; 140 K) can be characterized by the anisotropic parameters $g_{\parallel} = 1.938$ and $g_{\perp} = 1.982$. The isotropic g value (for fluid solution) can be calculated by $g_0 = (g_{\parallel} + 2g_{\perp}) = 1.967$.

For **2b** a strong EPR signal for an axial symmetric chromium(V) species was observed (Fig. 2). From the anisotropic parameters $g_{\parallel} = 1.939$ and $g_{\perp} = 1.979$, an isotropic g value of 1.966 for a fluid solution can be calculated which is consistent with EPR data for chromium(V) compounds that have been reported in literature before [10,19].

It is accompanied by a signal which indicates the formation of an organic radical ($g = 2.0014$), marked by #. This could possibly be rationalized by a CH-abstraction reaction of chromylchloride, also leading to a chromium(V) intermediate $Cr(O)(OH)Cl_2$ and the corresponding radical.

The same is true for compound **2c**, where also an organic radical, indicated by # can be observed at



Scheme 1.

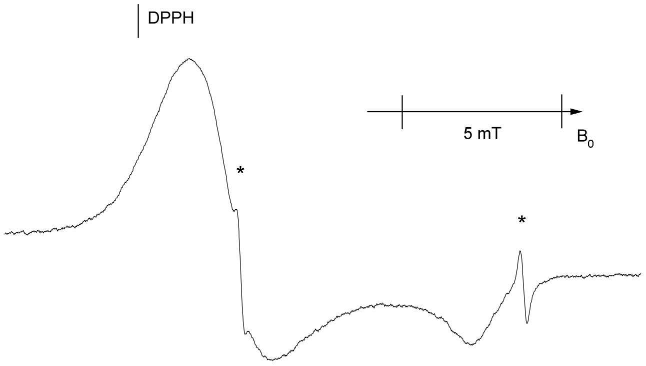


Fig. 1. EPR spectrum of **2a** with anisotropic parameters $g_{\parallel} = 1.938$ and $g_{\perp} = 1.982$. (*) Internal standard Mn^{2+}.

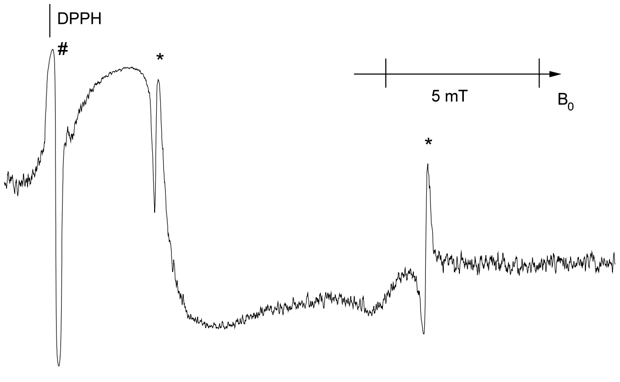


Fig. 2. EPR spectrum **2b** with anisotropic parameters $g_{\parallel} = 1.939$ and $g_{\perp} = 1.979$. An organic radical ($g = 2.0014$) is indicated by #, the internal standard Mn^{2+} by asterisks (*).

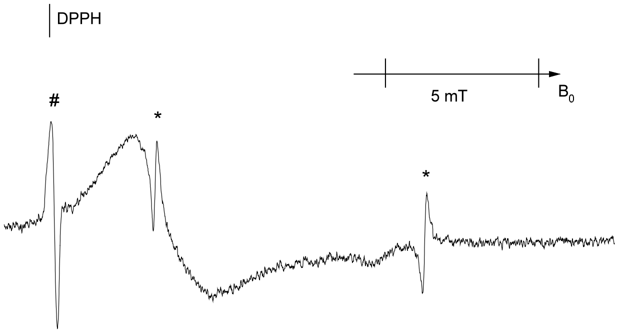


Fig. 3. EPR spectrum of **2c**, anisotropic parameters $g_{\parallel} = 1.939$, $g_{\perp} = 1.979$. An organic radical (#) with $g = 2.0014$ and the internal standard (*) are marked.

$g = 2.0014$ (Fig. 3). Similar anisotropic parameters $g_{\parallel} = 1.939$ and $g_{\perp} = 1.979$ lead to the corresponding isotropic g value (for fluid solution) of 1.966.

Farrell and Lay [10] found that Cr(V) complexes tend to be five-coordinate species. All the EPR data on complexes **2a–2c** indicate that the geometry is distorted from a tetrahedral geometry, but still shows some symmetry elements. Especially the strong anisotropy indicates a change in geometry from the tetrahedral chromylchloride. To reach the penta-coordination it might add a donating solvent molecule (acetone or acetonitrile) which would also explain the solubility of these intermediates in donating solvents.

Valuable information on Cr(V) species is provided by UV/Vis spectroscopy. All Cr(V) complexes show a charge transfer transition between ~250 and 300 nm, irrespective of the geometry of the system [10]. This band can be found for compounds **2a–2c** at 238–241 nm.

Fig. 4 shows the IR spectrum of complex **2b** between 100 and 500 cm^{-1}. This low region allows the identification of metal–halogen bonds. The value of 277 cm^{-1} is a characteristic band for a Cr–Cl vibration. The regular IR spectrum up to 4000 cm^{-1} shows the expected bands, e.g. a signal at 1015 cm^{-1}, which can be assigned to a ν(Cr=O) vibration.

2.2. Hydrolyzation of the intermediates

Compounds **2a–2c** were hydrolyzed by adding water and stirring vigorously for 30 min. The products were isolated by extraction of the aqueous phase with chloroform. The organic layer was separated and dried over $MgSO_4$. The dry organic solutions were immediately subjected to GC–MS analysis. The corresponding benzophenones, resulting from a rearrangement of a phenyl group, and benzils were detected for all compounds. For **2a** and **2b**, benzaldehydes resulting from double bond cleavage were additionally observed, but no other products like e.g. chlorohydrines or diols were detected according to the GC–MS data.

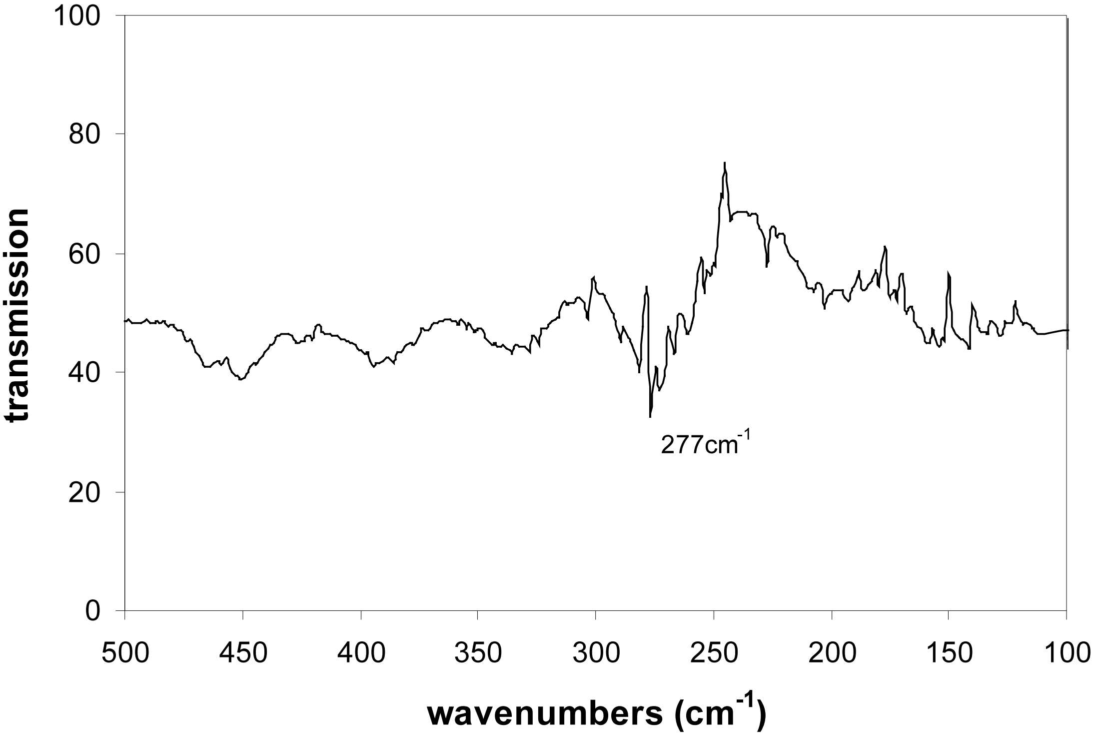


Fig. 4. IR spectrum of **2b**.

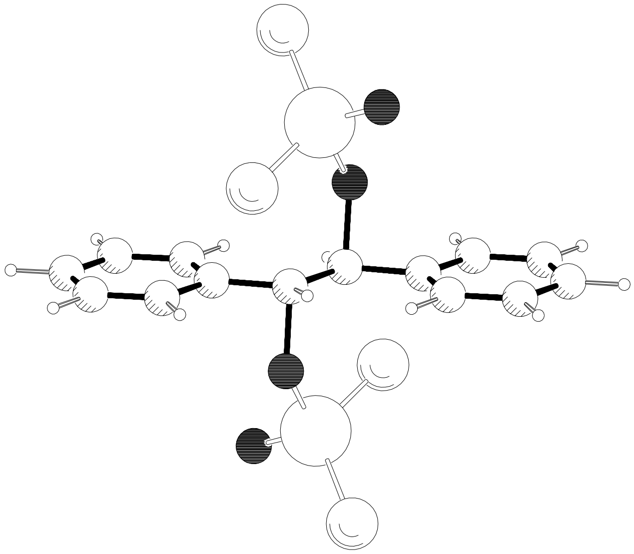


Fig. 5. Proposed structure of the Cr(V) intermediate **2b**.

3. Conclusion

We propose a three-dimensional structure (Fig. 5) for the elusive intermediate of the styrene oxidation by chromylchloride with a 2:1 stoichiometry, where two molecules CrO_2Cl_2 react with the double bond leading to a complex with two Cr(V) centers on opposite sides of the former double bond.

This proposal is supported by density functional theory calculations, which predict the product shown in Fig. 5 to be stabilized by 39.6 kcal mol^{-1}.

4. Experimental

4.1. General remarks

CrO_2Cl_2 (99.99%) and 1,1-diphenylethylene (97%) (**1c**) were purchased from Aldrich. *trans*-Stilbene (97%) (**1b**) and CCl_4 (uvasol grade, 99.7%) were supplied by Merck, while 4-chloro-*trans*-stilbene (**1a**) was synthesized [20]. Reagents were degassed and stored under an atmosphere of nitrogen. CCl_4 was chosen as the reaction medium to avoid side reactions.

Elementary analyses were performed in the microanalytical laboratory of the Technical University Munich.

UV/Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrometer. The acetone solution was measured in the range of 190–600 nm.

Infrared spectra were measured on a BIO RAD IR-FT spectrometer FTS575C. The pellets were prepared directly from the substance without addition of KBr to avoid hydrolyzation. To measure below 500 cm^{-1} polyethylene windows were used.

For the separation and identification of reaction products a Hewlett–Packard gas chromatograph HP5890 with a mass selective detector HP5890B was used.

EPR spectra were recorded in a JEOL JES-Re2X system using X-band frequency in a frozen solution (solvent acetone) at a temperature of 140 K. The spectra were measured at a microwave frequency of ca. 9.05 GHz with a microwave power of 5 mW. The modulation amplitude was 0.2 or 0.4 mT with a modulation frequency of 100 kHz. The g values were determined using Mn^{2+} (nuclear spin $I = 5/2$) embedded in MgO as internal standard (indicated by asterisks * in the figures) and DPPH (2,2-diphenyl-1-picryl-hydrazyl; $g = 2.0036$) as an external standard. Experimental error: $\Delta g \pm 0.003$.

4.2. General procedures

All reactions were carried out under an atmosphere of dry nitrogen. The reactions of chromylchloride with alkenes **1a**–**1c** (Scheme 1) were performed according to the following general procedure: 10 mmol of alkene were dissolved in 10 ml CCl_4 at room temperature. A solution of 1.63 ml CrO_2Cl_2 (20 mmol) in 10 ml CCl_4 was added dropwise under vigorous stirring at room temperature. The solution slightly warms during addition, while a brown solid precipitates. The mixture was stirred for another 2 h. Filtration yielded the precipitate, which was washed with CCl_4 until no more red color originating from CrO_2Cl_2 was observed. The products were dried under high vacuum, providing brown powders.

4.3. Computational details

All calculations were run in the VPP supercomputer of the Leibniz-Rechenzentrum Muenchen. The density functional/Hartree–Fock hybrid model UBecke3LYP [21] implemented in GAUSSIAN 98 [21] has been used. The split valence double-ζ (DZ) basis set 6-31G(d) has been employed in the DFT calculations. All geometries have been fully optimized, the energies listed are in kcal mol^{-1} relative to the reactants unless noted otherwise.

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References

[1] K.B. Sharpless, A.Y. Teranishi, J.E. Backvall, J. Am. Chem. Soc. 99 (1977) 3120.

[2] (a) M.A. Pietsch, T.V. Russo, R.B. Murphy, R.L. Martin, A.K. Rappe, Organometallics 17 (1998) 2716;
(b) D.V. Deubel, G. Frenking, J. Am. Chem. Soc. 121 (1999) 2021;
(c) K.P. Gable, T.N. Phan, J. Am. Chem. Soc. 116 (1994) 833;
(d) P. Gisdakis, N. Roesch, J. Am. Chem. Soc. 123 (2001) 697.

[3] (a) U. Pidun, C. Boehme, G. Frenking, Angew. Chem. Int. Ed. Engl. 35 (1997) 2817;
(b) A.J. DelMonte, J. Haller, K.N. Houk, K.B. Sharpless, D.A. Singleton, T. Strassner, A.A. Thomas, J. Am. Chem. Soc. 119 (1997) 9907;
(c) S. Dapprich, G. Ujaque, F. Maseras, A. Lledos, D.G. Musaev, K. Morokuma, J. Am. Chem. Soc. 118 (1996) 11660;
(d) M. Torrent, L. Deng, M. Duran, M. Sola, T. Ziegler, Organometallics 16 (1997) 13.

[4] (a) C. Limberg, R. Koeppe, Inorg. Chem. 38 (1999) 2106;
(b) C. Limberg, R. Koppe, H. Schnockel, Angew. Chem. Int. Ed. Engl. 37 (1998) 496.

[5] (a) K.N. Houk, T. Strassner, J. Org. Chem. 64 (1999) 800;
(b) T. Strassner, M. Busold, J. Org. Chem. 66 (2001) 672.

[6] (a) M. Torrent, L. Deng, M. Duran, M. Sola, T. Ziegler, Can. J. Chem. 77 (1999) 1476;
(b) M. Torrent, L. Deng, T. Ziegler, Inorg. Chem. 37 (1998) 1307.

[7] R. Codd, C.T. Dillon, A. Levina, P.A. Lay, Los Alamos Natl. Lab. Prepr. Arch. Condens. Matter (2001) 537.

[8] D.I. Pattison, P.A. Lay, M. Davies, J. Inorg. Chem. 39 (2000) 2729.

[9] A. Levina, P.A. Lay, N.E. Dixon, Inorg. Chem. 39 (2000) 385.

[10] R.P. Farrell, P.A. Lay, Comments Inorg. Chem. 13 (1992) 133.

[11] R.P. Farrell, R.J. Judd, P.A. Lay, N.E. Dixon, R.S.U. Baker, A.M. Bonin, Chem. Res. Toxicol. 2 (1989) 227.

[12] (a) T. Wistuba, C. Limberg, P. Kircher, Angew. Chem. Int. Ed. Engl. 38 (1999) 3037;
(b) M. Miteva, P.R. Bontchev, V. Vozhinov, Inorg. Nucl. Chem. Lett. 8 (1972) 51;
(c) W.H. Leung, A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1991) 2051.

[13] E.K. Mooney, K.R. Seddon, Transition Met. Chem. (Weinheim, Ger.) 2 (1977) 215.

[14] J.E. Baeckvall, M.W. Young, K.B. Sharpless, Tetrahedron Lett. (1977) 3523.

[15] F. Freeman, N.J. Yamachika, J. Am. Chem. Soc. 92 (1970) 3730.

[16] F. Freeman, N.J. Yamachika, J. Am. Chem. Soc. 94 (1972) 1214.

[17] S.J. Cristol, K.R. Eilar, J. Am. Chem. Soc. 72 (1950) 4353.

[18] (a) T. Strassner, K.N. Houk, J. Am. Chem. Soc. 122 (2000) 7821;
(b) G.K. Cook, J.M. Mayer, J. Am. Chem. Soc. 117 (1995) 7139;
(c) G.K. Cook, J.M. Mayer, J. Am. Chem. Soc. 116 (1994) 8859;
(d) G.K. Cook, J.M. Mayer, J. Am. Chem. Soc. 116 (1994) 1855.

[19] G. Barr-David, M. Charara, R. Codd, R.P. Farrell, J.A. Irwin, P.A. Lay, R. Bramley, S. Brumby, J.-Y. Ji, G.R. Hanson, J. Chem. Soc. Faraday Trans. 91 (1995) 1207.

[20] S.A. Lebedev, V.S. Lopatina, E.S. Petrov, I.P. Beletskaya, J. Organomet. Chem. 344 (1988) 253.

[21] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(b) A.D. Becke, J. Chem. Phys. 97 (1992) 9173;
(c) A.D. Becke, J. Chem. Phys. 98 (1993) 1372;
(d) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(e) M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.