

Peroxides and Chromium Compounds – The Ether Test for Identity

Götz Bucher^a, Michaela Kampe^b, and Julius F. Roelcke^b

^a Lehrstuhl für Organische Chemie II, Ruhr-Universität, D-44801 Bochum, Germany

^b Chemistry and Analysis of Pharmaceuticals, Lippe and Hoexter University of Applied Sciences, Georg-Weerth-Str. 20, D-32756 Detmold, Germany

Reprint requests to Prof. Dr. J. F. Roelcke. E-mail: julius.roelcke@fh-luh.de

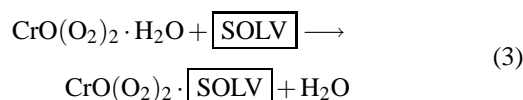
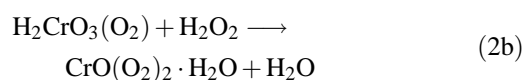
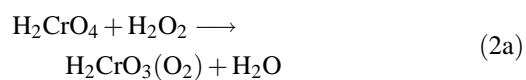
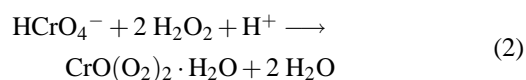
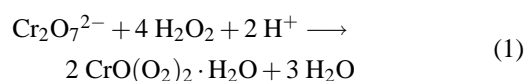
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Chromium compounds and hydrogen peroxide are usually identified by their reaction to form blue chromium oxide peroxide hydrate, which is extracted with diethyl ether as a co-ligand. Findings suggest that diethyl ether can be replaced without loss in analytical performance using solvents from the alcohol, arene, ester, ether, halogenated hydrocarbon, and ketone series. DFT calculations have been performed for several solvates. Results indicate that some of the solvates studied may exist as two rotamers.

Key words: Chromium, Electronic Spectra, Peroxides, Solvates of Chromium Oxide Peroxide, DFT Calculations

Introduction

For decades diethyl ether (Et₂O) has been commonly used for the identification of chromium compounds in undergraduate laboratory exercises [1, 2] and for the identification of peroxides in commercial laboratories [3, 4]. The blue reaction product is a diperoxo chromium oxide complex [5,6], which is subsequently extracted into ether. The overall reaction of chromates with hydrogen peroxide in acidic media is represented by equation (1) [7], the overall oxidation reaction by eq. (2) [7]. The oxidation reaction takes place in two steps. First, the monoperoxo compound is formed from chromic acid [6, 7, 21]; see eq. (2a). Secondly, diperoxo chromium oxide hydrate is then formed by the attack of a second H₂O₂ [6,7]; see eq. (2b). Subsequently, the water ligand is replaced by an appropriate organic solvent “SOLV” (3):



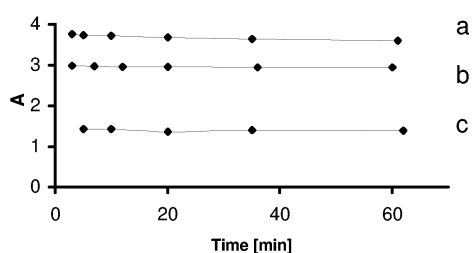
Et₂O has always been the preferred ligand [1–4]. Due to its volatility, its flammability, and a hydroperoxide formation in the presence of ubiquitous oxygen, Et₂O is classified as a dangerous substance [8, 9]. The entrepreneur represented by his laboratory manager is obliged to apply substitute material, if a significant risk reduction can be achieved. Guidance in risk management [10, 11] has been transferred into national legislations. In this study, Et₂O has been replaced by a choice of substitute solvents to be tested for applicability. DFT calculations have been performed for comparison with experimental results.

Results and Discussion

The analytical procedure

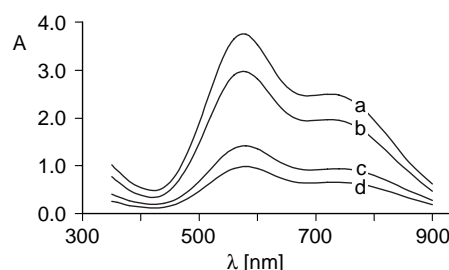
For each ligand, the procedure was performed as described for identity testing of 3% aqueous hydrogen peroxide [3]. Solvents from the alkane series were excluded: An extraction study with mixtures of tributylphosphate and cyclohexane has been performed previously [12]. Lacking appropriate ligand moieties, alkanes except halogenated ones have been shown to be inadequate for extractions of polar substrates from the aqueous phase. (For solvents chosen for this study see Table 1).

Solvents	Compounds	Absorptions; λ_{\max} [nm] (absorbance)
Hydroxylated compounds	pentanol	571 (0.5) ^a
	water	approx. 520 [11]
Ethers	diethylether	579 (1.4) ^a
	(<i>tert</i> -butyl)-methylether	580 (1.0) ^a
Esters	ethylacetate	576 (3.7) ^a
	butylacetate	577 (1.2) ^a
	medium chain triglyceride (Miglyol [®] 840)	not measured, insoluble
	glyceroltripentanoate (Miglyol [®] 812)	419 (0.48), 586 (0.44), 610 (0.39;sh) ^b
Ketones	4-methyl-2-pentanone (methyl-isobutyl-ketone)	577 (3.0) ^a
	toluene	431 (0.82), 595 (0.7;sh), 635 (0.9) ^b
Arenes	xylene	429 (0.36), 600 (0.3;sh), 633 (0.4) ^b
	chlorobenzene	422 (0.52), 590 (0.5), 610 (0.5;sh) ^b
Halogenated alkanes	dichloromethane	425 (0.70), 605 (0.6;sh), 631 (0.3) ^b

Table 1. Spectral data of $\text{CrO}(\text{O}_2)_2$ solvates.^a Blue solution; ^b green solution.Fig. 1. Stability in color of CrO_5 solvates with EtOAc, MIBK, and Et_2O . a EtOAc; b MIBK; c Et_2O .

Considering the well-known cytotoxic effects of the Cr(VI) reagent [13, 32], quenching was attempted. The blue color, however, is remarkably stable. The oxidation of xylenes or alcohols by diperoxo chromium oxide [14] requires 0.2–7 h refluxing in benzene – in contrary to the rapid oxidation by chromium trioxide [15] or chromium(VI) acetate [16] at or below 0°. In our reaction mixtures, shaking with 0.5 ml of 1M $\text{Na}_2\text{S}_2\text{O}_3$ or Na_2SO_3 was an appropriate quenching procedure.

With respect to regulations within the author's field of work [17], proof of the aptitude of substitute materials is obligatory. Within the ester, ether, and ketone series, for all solvents tested the color was stable for 1 h and maximum absorbances ranged within at least 90 per cent of the initial values, which is sufficient for transvalidation [17] of identity testing. As an example of stable coloration, the absorbance of the blue extract in Et_2O is compared with that in ethyl acetate (EtOAc) and 4-methyl-2-pentanone (MIBK) in Fig. 1. Extraction with pentanol led to a similar coloration, which, however, was not stable. Visible range spectral data for all solvents applied are given in Table 1.

Fig. 2. Electronic spectra of diperoxo chromium oxide solvates with ethylacetate, methylisobutylketone, diethyl ether, and *tert*-butyl-methyl-ether. a EtOAc; b MIBK; c Et_2O ; d BOM.

Among the large number of ligands, EtOAc shows the highest intensity in coloration. The extraction of $\text{CrO}(\text{O}_2)_2 \cdot \text{[SOLV]}$ into EtOAc has also been applied for quantitation of chromium in alloys [18]. For quantitative commercial or forensic analyses the required stability and reproducibility of test solutions, however, might be a limiting property. Shaking must be started immediately to obtain reproducible results. Therefore, automated processing will be necessary to avoid inter-operator unprecision. Within the period of 1 h the ratio of maximum absorbances between 570–600 and 720–750 nm remained unchanged, except in pentanol. Example absorbance curves of *tert*-butyl-methyl-ether (BOM), MIBK, and EtOAc are given in Fig. 2, proving that the tested substitute materials are appropriate for the identification reaction. Hence, diethyl ether can be replaced successfully.

Structures of complexes

Constitutions of pyridine and bipyridyl complexes have been investigated [5, 19, 26, 31], elucidated [26],

Solvent	Calcd. λ_{\max} (rel. absorbances $\cdot 10^4$)	Measured λ_{\max} (absorbance)
Et ₂ O	667 (31), 587 (31), 533 (28), 515 (7), 510 (1), 491 (9)	740 (0.9), 579 (1.4) [5]
BOM (1)	671 (29), 603 (12), 541 (25), 529 (9), 514 (3), 499 (6)	(not prevailing)
BOM (2)	649 (27), 588 (11), 537 (12), 530 (19), 519 (9), 495 (10)	740 (0.67), 580 (0.98)
EtOAc (1)	646 (28), 571 (14), 527 (1), 522 (26), 520 (2), 485 (12)	724 (2.5), 576 (3.7) [18]
EtOAc (2)	643 (24), 579 (12), 535 (3), 528 (4), 523 (23), 492 (10)	(prevalence not assigned)

Table 2. CrO(O₂)₂ Solvates; comparison of calculated and measured absorbance maxima in the visible range of electronic spectra (wavelengths: 400 nm < λ < 800 nm, rounded to integers).

and confirmed for a series of N ligands and pyridine N-oxide [31].

Kinetics of CrO₅ formation have been elucidated within a wide pH range [5–7, 13, 21, 22, 33, 34]. It is widely agreed [6, 7, 22–24, 33, 34] that chromium in its oxide diperoxide solvate is usually hexacoordinated in oxidation state +VI (as shown by combustion analyses of the pyridine and the 2,2'-bipyridyl solvates [25]). The CrO₅ units form pentagonal pyramids (X-ray structural analysis of the pyridine complex [26]). Hence, reaction (3) has been confirmed for the N ligand series with pyridine and bipyridyl solvates. The configuration of CrO₅ · [SOLV] differs from the geometry of unsolvated CrO₅. According to a photoelectron spectroscopy study [39], free CrO₅ contains one cyclic and one open-chain peroxide moiety. For H₂O as a ligand the hitherto “belief” of CrO(O₂)₂ · H₂O being blue perchromic acid [33], has been accepted generally [34] owing to [31]. For this complex, formal replacement of pyridine by a water ligand produced an accurate prediction of a Raman spectrum in an earlier study [38].

For organic oxygen-coordinated ligands used in analytical chemistry and chromium speciation, however, evidence for the proposed [24] geometry of a pentagonal pyramid has not been provided. For solvents with one plane of symmetry only, like BOM or EtOAc, two different orientations within the complex can be formulated. In an attempt to assign a prevailing orientation of the ligand, some structures and the resulting spectra were calculated using time-dependent density functional theory (TD-DFT) [27, 28] as implemented in Gaussian 98 [29]. A LANL2DZ (5D, 7F) basis set in combination with the standard B3LYP [30] hybrid DFT method was applied for both geometry optimization and calculation of electronic spectra. The calculated electronic spectra are compared with the experimental spectra of the colored extracts (Table 2). The absorptions in the yellow spectral range at 570–600 nm match well for Et₂O with an error of 8 nm.

For both of the EtOAc [18, 20] solvates the calculated differences of Table 2 are small, rendering a de-

cision on a structural proposal difficult (for calculated structures see Fig. 3d and 3e). A slight preference for EtOAc(2) can be based on very weak C-H \cdots O interactions, which are slightly stronger in isomer 2. Here, the distance between the methylene protons and the closest peroxy oxygen atoms of the CrO₅-moiety is calculated as 2.42 Å, as compared to the H \cdots O distance of 2.71 Å for the interaction of two acyl CH₃ protons of isomer 1 with the proximal peroxy oxygen atoms. Electrostatic arguments also favor isomer 2. Its dipole moment is calculated as 7.4 D, as compared to 8.5 D in case of isomer 1. As calculated by the DFT algorithm, the oxo group is the O ligand instead of the alkoxy group.

Similarly, for the asymmetric ether BOM, two isomeric complexes had to be taken into account. One of them matches with the measured spectrum within an experimental error of 8 nm – an error comparable with the Et₂O solvate. So for the two BOM complexes, the *exo*-orientation of the voluminous alkyl group seems to be the prevailing one (for structure see Fig. 3c). A significant C-H \cdots O interaction is only predicted for isomer 2, where the distance between one of the methoxy protons and a peroxy oxygen atom of the CrO₅ moiety is calculated as 2.17 Å. The most likely factor disfavoring isomer 1 is steric interaction between the bulky *tert*-butyl substituent of the ligand and the peroxy ligands of the CrO₅ moiety, which results in a smaller distance between the chromium atom and the plane described by the four peroxy oxygen atoms. In both isomers, the C_{tert}–O bond of the ether moiety is predicted to be elongated ($r = 1.53$ Å (isomer 1) and 1.55 Å (isomer 2); *c.f.* $r = 1.48$ Å (free ligand)). According to our calculations, complexation to the CrO(O₂)₂ fragment results in polarization of the BOM ligand, with increased positive charge density (atomic charges: 0.43 in the complexes *vs.* 0.41 in free BOM) at the tertiary carbon, and with increased negative charge at the ether oxygen atom (atomic charges: –0.46 in the complexes *vs.* –0.34 in free BOM).

The discrepancy between the calculated and experimental positions of the longest-wavelength (red range) absorption bands of the adducts is probably due to the

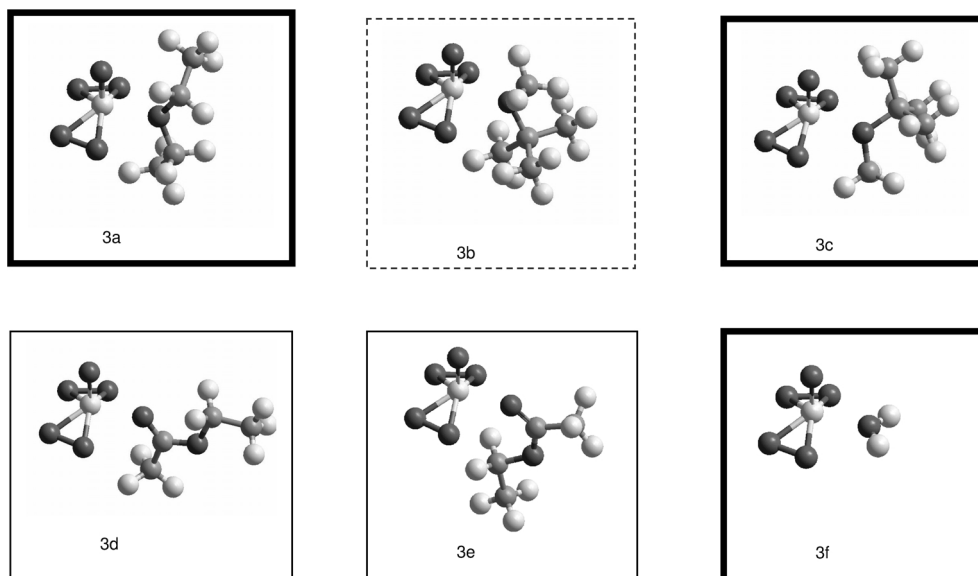


Fig. 3. Calculated conformations of CrO_5 complexes (probable conformers in bold frames). 3a $\text{CrO}_5 \cdot \text{Et}_2\text{O}$; 3b $\text{CrO}_5 \cdot \text{BOM}(1)$; 3c $\text{CrO}_5 \cdot \text{BOM}(2)$; 3d $\text{CrO}_5 \cdot \text{EtOAc}(1)$; 3e $\text{CrO}_5 \cdot \text{EtOAc}(2)$; 3f $\text{CrO}_5 \cdot \text{H}_2\text{O}$.

significant charge transfer character of these bands, which results in preferential solvation of the (more polar) excited states and thus in bathochromic solvatochromism. We also calculated the visible electronic spectrum of the geometry-optimised intermediate compound $\text{CrO}(\text{O}_2)_2 \cdot \text{H}_2\text{O}$ with the same DFT algorithm [29] to have a maximum at 527 nm. The geometry obtained is similar to the geometry published by Gili and co-workers, using a different basis set [31]. Coordinative bond lengths are similar to those measured by an X-ray absorption fine structure experiment [35–37]. A rapid scan electronic spectrum of this compound recorded by Grampp and co-workers [7] shows a maximum at approximately 520 nm, whereas an absorbance maximum at 580 nm, which had been assigned to the aquo complex previously [33], can be explained by a solvent ligand exchange (usually by Et_2O , see Tables 1 and 2, Fig. 3a).

Conclusion

From the present work we conclude that a large number of ligands is appropriate for H_2O_2 and chromium analysis. Appropriate solvents with respect to occupational health are alkyl acetate, short chain triglycerides, BOM, and MIBK. The use of pentanol as solvent and ligand should not be discarded at present, because both decoloration and turbidity are indicat-

ing an oxidation reaction. For the far future the complete ban of chromates, however, should be pursued. In this work, a procedure for disposal of carcinogenic chromium oxide diperoxide is suggested. The presented work comprises a commitment to establish state of the art variations of a widely used procedure and evidence for the structure of some reaction products. For BOM and Et_2O as ligands, there seems to be a relationship between the calculated structures and the observed visible electronic spectra. Calculated spectra of both $\text{CrO}_5 \cdot \text{EtOAc}$ rotamers are similar to the experimental one. $\text{CrO}_5 \cdot \text{EtOAc}(2)$ may slightly prevail owing to weak $\text{C-H}\cdots\text{O}$ interactions and electrostatic effects.

Experimental Section

Spectra were measured in a Pharmacia Biotech Ultrospec 3000 UV Visible Spectrophotometer within the range of 350–900 nm with a resolution of 0.5 nm. All reagents used were of analytical grade. All solvents used for spectroscopic measurements were of spectroscopic grade except for glyceryltrivalerate (Miglyol[®] 812, Sasol GmbH, D-58453 Witten; approx. 90% pentanoyl, approx. 10% hexanoyl moieties, used without further purification). In a typical run the amounts of the pharmacopoeial procedure [3] were doubled: 2.0 ml of 1 M sulfuric acid, 4.0 ml of the appropriate solvent, and 1.0 ml of 3% aqueous hydrogen peroxide solution were placed in a separating funnel. The mixture was shaken for

30 s with 0.2 ml of a 5% aqueous potassium chromate solution. Blanks were produced by shaking 3 ml of water with the same amount of the identical solvent. Mixtures were decontaminated by shaking with 0.5 ml of a 1M Na₂S₂O₃ solution. Modifications: 1) Ethyl acetate and 4-methyl-2-pentanone: The procedure was performed with a double amount of solvent (8.0 ml) to allow absorbance measurements within the range of ≤ 3 ; 2) Pentanol: The organic phase became turbid

immediately after extraction. Turbidity returned some 5 min after Na₂SO₄ desiccation, and decoloration was complete after 40 min.

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