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Contribution from the Dipartimento di Chimica Inorganica,
Universitá di Padova, via Marzolo 1, 35131 Padova, Italy

Selective Oxygenation of Aliphatic Ethers Catalyzed by Ruthenium(II) Complexes

Mario Bressan,* Antonino Morvillo, and Giorgio Romanello

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Selective and fast conversions of primary ethers to esters (or lactones) are achieved by using lithium hypochlorite in the presence of catalytic amounts of complexes of ruthenium(II) RuX_2L_4 [L = $(CH_3)_2SO$, $(L)_2$ = 1,3-bis(diphenylphosphino)propane]. Isopropyl ether undergoes oxidative cleavage to acetone, while secondary ethers bearing methylene groups in the β-position are converted into β-keto ethers. Methyl ethers are unaffected by the oxidation. The origin of the observed selectivity is investigated and discussed.

Introduction

Metal oxides in high oxidation states, such as chromium trioxide and permanganate, are among the few stoichiometric oxidants that are effective for the selective oxygenation of primary ethers to esters.[1a,b] Reactions with other conventional oxidizing agents, such as bromine, lead tetraacetate, or ozone,[1c–e] as well as anodic oxidation,[1f] lead to further oxidation of the esters to anhydrides and carboxylic acids. Ruthenium tetraoxide, early introduced as a useful stoichiometric reagent for the mild and selective oxidation of a variety of organic substrates, also promotes the oxidation of primary ethers to esters with moderate selectivity.[2a] Attempts to make the above oxidation catalytic by using simple salts of ruthenium in conjugation with periodate or hypochlorite ions as the stoichiometric oxidants are also reported.[2b,c] Other mild catalytic methods, based on heterogeneous platinum catalysts and dioxygen, which are able to unselectively convert cyclic ethers into lactones and products of oxidative cleavage are described.[3]

Following our previous communication,[4] dealing with the catalytic behavior of a representative choice of ruthenium(II) complexes in the oxygen-transfer reactions from single-oxygen donors to organic substrates, we delineate here some mechanistic features for the oxidation of ethers. The catalysts examined are five- and six-coordinate complexes of ruthenium(II), namely $[RuCl(DPP)_2]PF_6$, *trans*-$[RuCl_2(DPP)_2]$ [DPP = 1,3-bis(diphenylphosphino)propane], and *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$. *cis*-$[RuCl_2(1,10\text{-phenanthroline})_2]$ and the osmium(II) derivative $[OsCl(DPP)_2]PF_6$ were occasionally tested but exhibited lower activity. Lithium hypochlorite or sodium hypochlorite, which was successfully introduced for the oxidation of organic substrates catalyzed by metalloporphyrins,[5] and transition-metal salts[6] were used as alkaline aqueous solutions. In the presence of catalytic amounts of the ruthenium(II) complexes, hypochlorite exhibits good oxidizing properties, thus possibly making the present procedure a fast, mild, and chemioselective method for the oxygenation of ethers.

Experimental Section

Materials. $[RuCl(DPP)_2]PF_6$ was prepared by refluxing ethanolic suspensions of *trans*-$[RuCl_2(DPP)_2]$ in the presence of excess NH_4PF_6,[7] and *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$ by the standard procedure.[8] Commercial products were used for gas chromatographic standardization. Tetrahydrofuran-d_8 (98%) was purchased from Aldrich, while tetrahydrofuran-*3,3,4,4*-d_4 was prepared by acid-catalyzed (Nafion-H) condensation of 98% 1,4-butanediol-*2,2,3,3*-d_4, following the procedure described by Olah.[9] Isotopic purity of the product was checked by ^1H NMR and mass spectroscopy.

Table I. Ruthenium-Catalyzed Oxidation of Ethers by LiClO[a]

substrate	products	catalytic activity[b] I	II	III
di-*n*-propyl ether	propyl propionate	51	66	24
diisopropyl ether	acetone	*c*	*c*	54
methyl *n*-butyl ether	methyl butyrate	24	24	15
tetrahydrofuran	γ-butyrolactone	42	54	21
2-methyltetrahydrofuran	2-methyldihydrofuran-3-one	12	12	6
	γ-valerolactone	9	6	6
2,5-dimethyltetrahydrofuran	2,5-dimethyldihydrofuran-3-one	177	93	52
2,5-dimethylfuran	2,5-dimethylfuran-3-one	*c*	*c*	4.4
2,3-dihydrofuran	γ-butyrolactone	*c*	*c*	0.1

[a] Catalyst, 2 mM, and substrate, 1 M, in CH_2Cl_2; LiClO, 0.7 M, in H_2O; 22 °C. [b] Units: turnovers/h. I = *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$; II = *trans*-$[RuCl_2(DPP)_2]$; III = $[RuCl(DPP)_2]PF_6$. [c] Not determined.

Instrumentation. NMR spectra were recorded on a JEOL FX 90 Q FT spectrometer. Organic analyses were made on a DANI 3800 gas chromatograph equipped with FID, using a 30-m SE-30 capillary column (0.25-mm i.d.). The identity of each product was confirmed by comparison of the fragmentation patterns in the mass spectra obtained with a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV.

Procedure for the Catalytic Oxidations. A 1-mL aliquot of a CH_2Cl_2 solution containing 1 mmol of the substrates, 2 μmol of the complexes, and a gas chromatographic standard (*n*-decane, 5 μmol) was stirred magnetically in a 2-mL vial together with 1 mL of an aqueous alkaline solution of lithium hypochlorite (between 0.5 and 1 M, as determined by iodometric titration). GLC analyses were performed on aliquots of the organic layer, withdrawn at appropriate times with a hypodermic microsyringe. Reaction rates were determined at 22 °C for early stages of the reaction (up to 10 turnovers) and were reproducible to within 15%.

Results

The catalytic oxygenation of a choice of secondary and primary ethers is investigated. In a typical experiment, the ethereal substrates (1 M) and the catalyst (2 mM) are dissolved in CH_2Cl_2 and the resulting solution is stirred vigorously with an equal amount of an aqueous alkaline (pH ca. 13) solution of LiClO, 0.7 M. Data reported in Table I refer to the initial rate of the conversions as measured from the amount of the products detected in the organic layer. Kinetic isotope effects were measured for the oxygenation of variously deuterated forms of tetrahydrofuran into the corresponding γ-butyrolactones, and the results are presented in Table II. A kinetic investigation was undertaken for the ruthenium(II)-catalyzed reaction between 2,5-dimethyltetrahydrofuran and hypochlorite, whose results are presented in Figure 2. The reaction mechanism of Scheme II is proposed, which will be discussed at appropriate places in the following section.

Discussion

The compounds listed in Table I are the only products detected in the reaction mixtures, apart from negligible amounts of chlorinated derivatives (ca. 1% or less), likely arising from the chlo-

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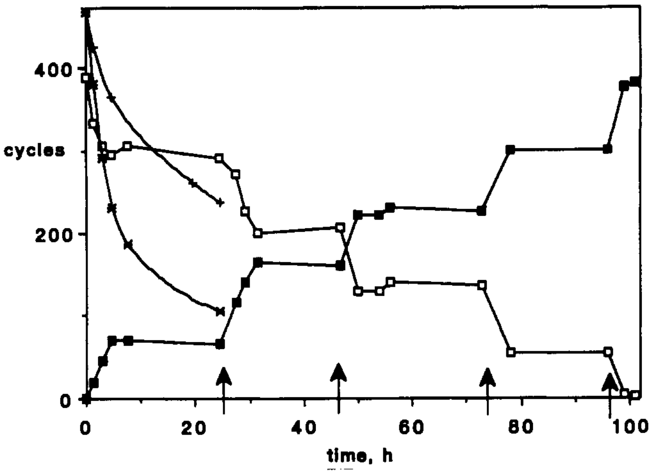


Figure 1. Time course of the oxygenation of methyl *n*-butyl ether (□) to methyl butyrate (■) by aqueous LiClO (✱) catalyzed by $[RuCl(DPP)_2]PF_6$, 2 mM, in CH_2Cl_2 at 22 °C. + refers to the concentration of residual LiClO in an experiment of dismutation in the same conditions and in the absence of the substrate. Arrows indicate the addition of fresh solid LiClO.

rinating action of small amounts of HClO: they were not formed when other single-oxygen oxidants, such as PhIO or $KHSO_5$, were used. Rigorous degassing of the solutions, to remove oxygen prior to the reactions, has no effect on both the composition and the rate of formation of the products. Conversions may be somewhat larger than those reported in Table I, since some oxidation products are moderately soluble in the aqueous saline phase. The latter, previously acidified with H_2SO_4, was carefully examined to check for the presence of carboxylic and hydroxy carboxylic acids, which are among the possible products of the oxidation or the alkaline hydrolysis of the formed esters and lactones. In fact, although some of the esters and lactones produced by the reactions under investigation are reported to undergo fairly rapid hydrolysis in alkaline media,[10] we never detected significant amounts of hydrolysis products within the short reaction times examined.

The present catalytic system generally maintains the initial activities for an extended period of time, and over 1000 cycles have been achieved, provided that an excess of hypochlorite, calculated on the basis of the stoichiometric requirement, is periodically added to the reaction mixtures (Figure 1). The losses of oxidant can be explained by noting that the ruthenium complexes also catalyze the dismutation of hypochlorite to chloride and oxygen, which is a well-known process, commonly triggered by a variety of metal ions.[11] Test experiments showed that 2 mM CH_2Cl_2 solutions of $[RuCl(DPP)_2]PF_6$ promoted the dismutation of 1 M aqueous solutions of LiClO at an initial rate of ca. 30 turnovers/h. Dismutation is favored by the presence of small amounts of ethers, less than 0.1 M, which likely act as phase-transfer agents with respect to hypochlorite: indeed, addition of conventional phase-transfer agents, i.e. crown ethers and quaternary ammonium salts, does not significantly improve yields and conversion rates.

Analysis of the oxidation mixtures of primary ethers RCH_2OCH_2R revealed the presence of esters (or lactones) only (eq 1). No products of further oxidation, such as anhydrides (eq 2) or carboxylic acids, derived from their hydrolysis, were detected.

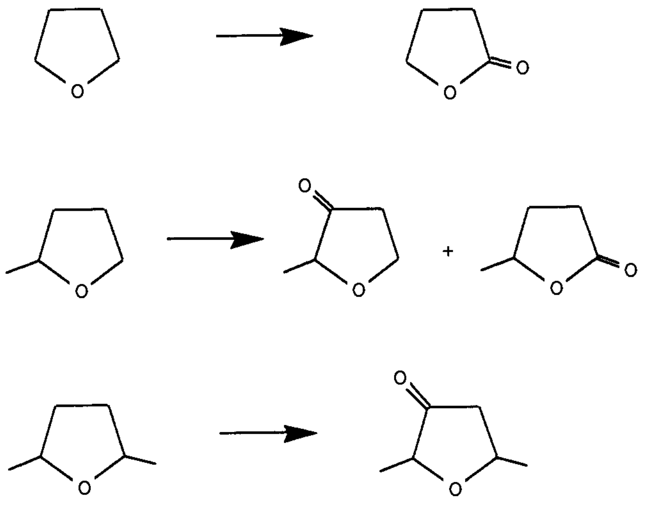
$$RCH_2OCH_2R + 2[O] \rightarrow RCH_2OCOR + H_2O \quad (1)$$

$$RCH_2OCOR + 2[O] \rightarrow RCOOCOR + H_2O \quad (2)$$

We independently verified that esters and lactones are recovered unchanged, if reacted with the ruthenium(II)–hypochlorite system under identical conditions.

It is noteworthy that traditional ruthenium tetraoxide oxidations are, on the contrary, rather unselective, giving rise to extensive oxidation of esters,[2a,b] whereas a similar high chemioselectivity was achieved by Sharpless by adding acetonitrile to a conventional $RuCl_3$–periodate system.[2c] A simple explanation apparently points to a specific role played by well-defined complexes of the metal in medium-low oxidation states, likely to be stabilized by good ligands or, at least, by good-coordinating solvents.

Scheme I



Contrary to α-methylene groups, α-methyl groups of ethers are not affected by the oxidation: thus, the asymmetric methyl *n*-butyl ether is selectively converted into methyl butyrate (eq 3) and no *n*-butyl formate could be detected. Isopropyl ether was rapidly oxidized to acetone, suggesting a mechanism that involves an initial insertion of the oxygen into the tertiary C–H bond with formation of an hemiketal (eq 4), likely in equilibrium with the corresponding ketone and alcohol (acetone and 2-propanol, eq 5). Most likely,

$$CH_3OCH_2CH_2CH_2CH_3 + 2[O] \rightarrow CH_3OCOCH_2CH_2CH_3 + H_2O \quad (3)$$

$$Me_2CHOCHMe_2 + [O] \rightarrow Me_2C(OH)OCHMe_2 \quad (4)$$

$$Me_2C(OH)OCHMe_2 = Me_2CO + Me_2CHOH \quad (5)$$

acetone also derives from further oxidation of 2-propanol, as evidenced by the fact that under identical conditions the present catalytic system is capable of effectively converting alcohols into the corresponding carbonyl compounds.[4]

Quite unexpectedly, secondary ethers bearing methylene groups in β-positions, such as 2,5-dimethyl- and 2-methyltetrahydrofuran, behave differently and do not undergo oxidation at the tertiary carbon atom. The only product detected upon oxygenation of 2,5-dimethyltetrahydrofuran is the β-keto ether 2,5-dimethyldihydrofuran-3-one, whereas 2-methyltetrahydrofuran yields comparable amounts of γ-valerolactone, which is the product of the "normal" oxidation of the α-methylene group, and of 2-methyldihydrofuran-3-one. No 2-methyldihydrofuran-4-one, the other possible β-keto ether, could be detected (Scheme I).

The anomalous and intriguing reactivity of this class of secondary ethers deserves further consideration, since a reactivity order tertiary > secondary > primary is expected in the oxidation of saturated C–H moieties, where loss of hydrogen is the rate-limiting step and substitution at the carbon atom might increase the rate of oxidation. Indeed, this argument, while accounting for the observed lack of reactivity of methyl ethers, does not explain both the poor reactivity of the α-CH groups in 2,5-dimethyl- and 2-methyltetrahydrofuran and the facile oxidation of the β-CH_2 groups close to the tertiary carbon atoms. The fact that oxidation at the β-position is preferred to the attack at the tertiary α-carbon atom strongly suggests that these β-positions are also in some way "activated" by the presence of the heteroatom. Indeed, β-ketonization of 2,5-dimethyl- and 2-methyltetrhydrofuran occurs with remarkably high rates, up to ca. 3 turnovers/min (see Table I), thus comparable to the conversions of primary ethers to esters, but much larger than the oxygenation rates of unactivated alkanes,

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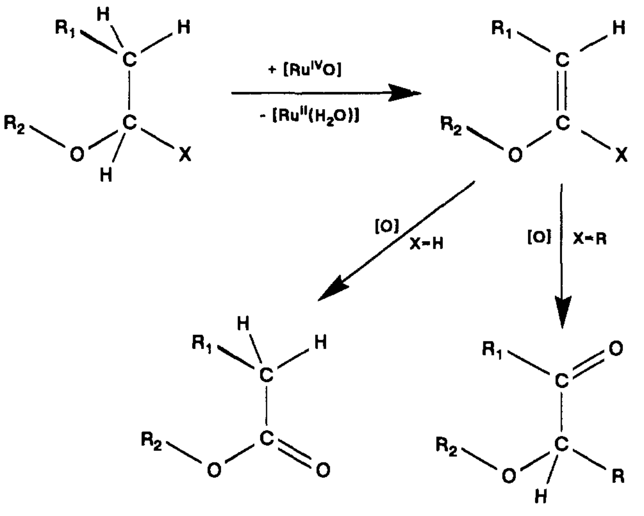
Table II. Kinetic Isotope Effects in Ruthenium-Catalyzed Oxidation of Tetrahydrofuran to γ-Butyrolactone[a]

	rate[b]		k_H/k_D	
substrate	I	III	I	III
tetrahydrofuran	42	21		
tetrahydrofuran-d_8	6.8	4.2	6.2	5.0
tetrahydrofuran-*3,3,4,4*-d_4	20	10.7	2.1	1.95
tetrahydrofuran-*2,2,5,5*-d_4			2.95[c]	2.55[c]

[a] Catalyst: 2 mM I (*cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$) or 2 mM III ($[RuCl(DPP)_2]PF_6$). Conditions: substrate, 1 M, in CH_2Cl_2; LiClO, 0.7 M, in H_2O; 22 °C. [b] From the amount of γ-butyrolactone formed. Units: turnovers/h. [c] Values calculated from the ratios between total isotope effects (tetrahydrofuran-d_8) and the data obtained with tetrahydrofuran-*3,3,4,4*-d_4.

Scheme II



by the same catalytic system (e.g., cyclohexane is converted to cyclohexanol and cyclohexanone at a rate of ca. 1 turnover/h under identical conditions).[4]

The observed "total" isotope effect for perdeuteriotetrahydrofuran is rather large, $k_H/k_D > 5$ (Table II), as expected for a hydrogen radical abstraction from an sp^3-hybridized C–H bond.[12] The most striking feature is the sizable isotope effect resulting from the deuteration of the 3- and 4-positions only of tetrahydrofuran, $k_H/k_D \approx 2$, which can be hardly attributable to (possibly weak) secondary isotope effects, usually ranging as high as 1.5.[13] On the contrary, these values are very close to those calculated for the 2- and 5-positions, $k_H/k_D = 2.5$–3, thus suggesting a peculiar mechanism for the oxidation of ethers, likely to proceed by a hydrogen atom transfer, *involving both α- and β-carbon atoms*.

The overall mechanistic pathway is depicted in Scheme II, where oxoruthenium(IV) intermediates are proposed as the species responsible for the oxygen transfer. Although direct evidence of these species has not been obtained in the present investigation, a variety of monooxo derivatives of ruthenium have been reported to oxygenate organic substrates, among which are ethers.[14] On the basis of the information derived from product distribution and kinetic isotope effects, a simultaneous hydrogen abstraction from both α- and β-positions could be envisaged, similar to a mechanism recently proposed by Meyer for the stoichiometric oxidation of alcohols by oxoruthenium complexes.[15] The resulting unsaturated ethers may undergo further oxidation, leading to the formation of a carbonyl group located in either the α- or β-position, depending on the availability of hydrogen atoms on each position. Within this reaction scheme not only might the oxidation of ethers exhibit sizable and comparable α- and β-deuterium kinetic effects, but also, as observed, oxygenation of α-tertiary groups should become unviable. In the case of secondary ethers bearing methyl groups at the β-position, such as isopropyl ether, the classical mechanism should be operating, with hydrogen abstraction at the α-position only, in view of the larger C–H bond energy of methyl with respect to methylene groups.

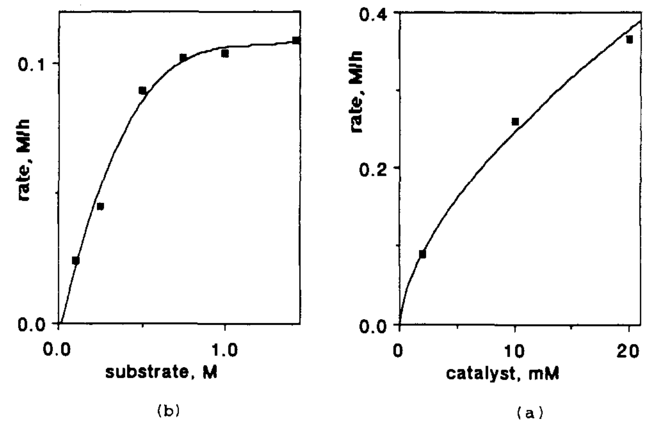


Figure 2. Conversion rate of 2,5-dimethyltetrahydrofuran to 2,5-dimethyldihydrofuran-3-one with aqueous LiClO (ca. 0.7 M) catalyzed by $[RuCl(DPP)_2]PF_6$, 2 mM, in CH_2Cl_2 at 22 °C; (a) effect of substrate concentration (catalyst, 2 mM); (b) effect of catalyst concentration (substrate, 1 M).

That primary ethers are selectively oxidized to esters and β-keto ethers are never formed can find an explanation, although sibylline, in the general behavior of enol ethers (the putative reaction intermediates), which seem to undergo ketonization exclusively at the position nearest to the heteroatom, at least with conventional oxometal reagents.[16] In agreement with the above statement, γ-butyrolactone was the only oxygenated product found during the oxidation of 2,3-dihydrofuran with the present catalytic system, whereas, significantly, 2,5-dimethylfuran was converted into the corresponding 3-keto ether 2,5-dimethylfuran-3-one. However, the oxidations of the above unsaturated ethers are definitely slow (Table I), if compared to the oxygenation rates of the saturated ethers, and this is not fully consistent with the fact that we never observed the expected accumulation of detectable amounts of enol ethers during ether oxidations.

Indeed, we also found that the ruthenium-catalyzed reaction between ethers and hypochlorite, which is substantially first-order in the catalyst, shows an unexpected zero-order dependence on the concentration of the substrate at a saturated level (Figure 2), thus possibly suggesting that a relatively stable reaction intermediate between the substrate and the catalyst is formed. The fact that each examined substrate is oxidized at a different rate reasonably rules out the possibility that the rate-determining step is the formation of the active oxometal derivative (in this case the rate should be completely indifferent to the concentration of the substrate). A possible mechanism could be a two-step process involving a prior fast equilibrium between the ruthenium complexes, or their oxo derivatives, and the ethers, followed by the rate-determining hydrogen abstraction from the substrates. Therefore, one can speculate that the ether is never leaving the coordination sphere of the catalyst, by undergoing *all* the required transformations always coordinated to the metal, likely through the oxygen atom.

No evidence for this intermediate could be obtained, since measurements on the reacting mixtures were intrinsically difficult to perform. Thus, whereas the rapid mixing of aqueous hypochlorite with the CH_2Cl_2 solutions of the catalysts does not result in any substantial change of the initial characteristic colors of the complexes, i.e. pale yellow for *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$, yellow

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for *trans*-$[RuCl_2(DPP)_2]$, and red for $[RuCl(DPP)_2]PF_6$, quantitative spectral measurements of the organic phases were prevented by the fact that, as soon as stirring was stopped, the CH_2Cl_2 solutions turned dark green the change being particularly sharp and fast for *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$. On stirring, the organic phases revert again to the initial colors. In some cases, green products could be isolated in the solid state and satisfactorily characterized as oxo-bridged binuclear complexes of ruthenium(III).[17] The green solutions can be therefore considered a sort of "resting" situation, and indeed, they do not exhibit any absorption in the 780–900-cm^{-1} region, where $\nu(Ru{=}O)$ are expected to fall.[18] It is concluded that the following reactions (eqs 6–9)

$$Ru^{II} + ClO^- \rightarrow Ru^{IV}{=}O + Cl^- \qquad (6)$$

$$Ru^{IV}{=}O + Ru^{II} \rightarrow Ru^{III}{-}O{-}Ru^{III} \qquad (7)$$

$$Ru^{IV}{=}O + ClO^- \rightarrow Ru^{II} + O_2 + Cl^- \qquad (8)$$

$$Ru^{IV}{=}O + S \rightarrow Ru^{II} + SO \qquad (9)$$

are likely to take place when aqueous hypochlorite is allowed to be in contact with the organic phase containing the substrate S and the ruthenium(II) complexes. When the contact between the two phases is interrupted, the putative oxoruthenium(IV) intermediate is consumed with final formation of oxo-bridged species, likely catalytically inactive. With excess hypochlorite, the oxo terminal species is re-formed and, as a consequence, oxidations of both the substrate and the oxidant are allowed to continue.

All the catalysts examined in this investigation exhibit closely related activities and very similar chemioselectivities, despite the significant differences in the chemical environment and stereochemistry. It is therefore possible that a common and very active species is formed in small amounts by the action of hypochlorite on the various complexes since the onset of the reaction. We believe, however, that the active catalysts should be definite complexes of the metal, since the only common species reasonably deriving from the oxidation of the starting complexes are in fact simple "naked" ruthenium oxides, such as RuO_2, and for the latter very different selectivities in the oxygenations of ethers have been reported.[2a,b] The somewhat higher reactivity exhibited by *cis*-$\{RuCl_2[(CH_3)_2SO]_4\}$ can be attributed to its solubility in water, where it is present as the aquo derivative $\{RuCl_2[(CH_3)_2SO]_3(H_2O)\}$.[19]

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Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506-3701

Molecular Vapor Synthesis: The Use of Titanium Monoxide and Vanadium Monoxide Vapors as Reagents

Thomas J. Groshens and Kenneth J. Klabunde*

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The production and reactivity of titanium monoxide (TiO) and vanadium monoxide (VO) on a synthetically useful scale were studied by using the techniques and apparatus previously developed for reactions of metal atoms. Cocondensation reactions with chlorine showed that greater amounts of metal atoms were produced as impurities in the vapor when stoichiometric metal monoxides were used as vapor sources than when metal sesquioxides were used. It was found that evaporation of MO and M_2O_3 solids from open tungsten boats yielded vapor compositions of M, MO, and MO_2 similar to those reported earlier from Knudsen cells in the case of vanadium but somewhat different in the case of titanium. The monoxide molecules reacted with chlorine to produce oxometal chlorides in high yields. They reacted with 2,4-pentanedione and other organics containing relatively acidic hydrogen, to form water as a byproduct via protonation of the oxo moiety; coordination compounds of titanium and vanadium were isolated as acac complexes in high yields.

Introduction

In recent years, metal vapor chemistry investigators have explored the use of atomic vapors as synthetic reagents.[1,2] The same basic techniques and apparatus have been applied to the study of other highly reactive short-lived molecular species including CS,[3] BF,[4] SiX_2,[5] SiF_3,[6] SiO,[7] and others.[1] In an attempt to further expand the number of reactive molecular vapor reagents available, this work was undertaken as a systematic investigation of the generation and synthetic usefulness of titanium monoxide (TiO) and vanadium monoxide (VO) molecular vapor.

Only two reports have appeared that are concerned with transition-metal oxide vapors as synthetic chemical reagents in low-temperature matrices. Cook and Timms[8] studied the reactivity of molybdenum and tungsten trioxide vapors, which consist mainly of cyclic trimers along with lesser amounts of dimers, tetramers, and pentamers.[1] Cocondensation of 2,4-pentanedione with MoO_3 vapor followed by warming to room temperature produced a green solid that analyzed as $MoO_2(O_2C_5H_7)_2$. Presumably 1 molar equiv of water was also formed as a byproduct although no mention was made of its presence. With WO_3 vapor, no reactions occurred with pentanedione if care to avoid ligand pyrolysis was taken. Reactions with methanol, boron trichloride, and other reagents were also described. In general, Cook and Timms concluded that

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