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Abstract: A four-armed tetra-l-imidazolyl ligand (Lig) equipped with the concave framework of diphenylglycoluril (tetrahydro-3a,6a-diphenylimidazole[4,5-d]imidazole-2,5,1(H,3H)-dione) has been designed to construct a host that contains a potentially catalytically active metal center in or close to a cavity. Reaction of Lig (arm = CH₂(OC₆H₄CH₂)₃Im) with Pd(CH₃CN)₂Cl₂ results in the formation of a complex with the general formula [Pd(Lig)]Cl₂. This complex has a cavity structure that is unstable and collapses. The collapsed structure has either a left or a right twisted conformation. These conformations interconvert rapidly, the activation free energy of the process being 30 ± 2 kJ·mol⁻¹. Ligands without oxygen atoms or only one oxygen atom per arm react with Pd(CH₃CN)₂Cl₂ to afford cage complexes with the molecular formula [Pd(Lig)]Cl₂. The cages of these complexes do not collapse. The imidazolyl groups and the chloride ions are involved in a scrambling process in such a way that at any moment the Pd²⁺ ion is surrounded by three imidazolyl groups and one chloride ion. Data are presented suggesting that intramolecular H bonding is a driving force for cage collapse.

Results and Discussion

Strategy. Cram realized that in the design of cavity-containing molecules it is preferable to start from a concave building block. Our design for a ligand, which has to supply the framework for a cavity-containing molecule, starts from such a block, viz. glycoluril (tetrahydro-3a,6a-diphenylimidazole-2,5,1(H,3H)-dione (1a); Chart 1) that has its convex side sterically shielded by two phenyl groups (1c). To the ureylene nitrogen atoms can then be attached four chains as spacer units (A), which are furnished with potential substrate-binding sites and terminated with metal-binding groups (L). In this way may be called a heterotopic tetrapodal ligand or simply a tetrapod and is formed. Coordination of the four ligating groups to a metal center M results in the creation of a metalloccage (Figure 2). Thus, in this design the metal center has a dual function. First, it acts as a template facilitating the formation of the desired cavity. Second, it is a potentially reactive site, e.g. a catalytic center.

We have chosen ethylene glycol ether chains, which are known to possess binding properties, as spacer units and imidazolyl groups, which are excellent ligands to a variety of metal ions, as the metal-binding groups. For comparative purposes, tetrapodands containing either 2-oxaalkyl chains or n-hexyl chains as spacer units have also been prepared.

Scheme I

Route A:

\[
\begin{align*}
\text{Ph}_2\text{GU}-\text{H}_4 & \quad \text{X-A-X} \quad \text{Ph}_2\text{GU}-(\text{A-X})_4 \\
1c & \quad \text{Ph}_2\text{GU}-(\text{CH}_2\text{OH})_4 \\
& \quad \text{X} = \text{Cl, Br}
\end{align*}
\]

Route B:

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{Ph}_2\text{GU}-\text{H}_4 \quad \text{OH}^- \quad 2 \quad \text{H}^+ \\
1c & \quad \text{H}_2\text{O} \\
3b & \quad \text{OH-A-X} \quad \text{Ph}_2\text{GU}-(\text{A-X})_4 \\
& \quad \text{p-TsOH} \\
& \quad \text{X} = \text{Cl, Br}
\end{align*}
\]

Scheme II

\[
\begin{align*}
\text{Ph}_2\text{GU}(\text{A-X})_4 & \quad \text{ImH} \quad \text{Ph}_2\text{GU}(\text{A-Im})_4 \\
& \quad \text{X} = \text{Cl, Br} \\
& \quad \text{NaH}
\end{align*}
\]

Synthesis of Tetrapodands. The general synthesis of the tetrapodands begins with the coupling to diphenylglycoluril of four spacer units, each of which is suitably terminated with a halogenide

(6) Part of this work has been described in a preliminary communication: Niele, F. G. M.; Zwikker, J. W.; Nolte, R. J. M. Tetrahedron Lett. 1986, 27, 243-246. In this paper it was erroneously concluded that the two twisted forms of [Pd(4d)]₉⁺ do not interconvert rapidly.
(8) We propose the general name dipteranes for compounds derived from the two-winged diphenylglycoluril unit (from the Greek sperane = two-winged).
Palladium(II) Cage Compounds

Figure 1. MSB concept.

Figure 2. Strategy for preparing a metallocage from diphenylglycoluril.

Figure 3. Crystal structure of compound 4a.

Figure 4. Results of gel permeation chromatography.

Table I. Molar Conductivities of Palladium Complexes

<table>
<thead>
<tr>
<th>compd</th>
<th>$\Lambda_m, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$</th>
<th>compd</th>
<th>$\Lambda_m, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pd}(4d)\text{Cl}_2])</td>
<td>170</td>
<td>([\text{Pd}(6b)\text{Cl}_2])</td>
<td>94</td>
</tr>
<tr>
<td>([\text{Pd}(5b)\text{Cl}_2])</td>
<td>106</td>
<td>TEBA</td>
<td>101</td>
</tr>
<tr>
<td>([\text{Pd}(5d)\text{Cl}_2])</td>
<td>110</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In methanol at 25 °C. $^b$ TEBA = triethylbenzylammonium chloride.

affords the tetrahalogenides 4a, 4c, and 5a (see the Experimental Part). In the final stage the resulting tetrahalogenides from these two routes are then reacted with sodium imidazolate to afford the tetrapodands 4b and 4d (containing ethylene glycol spacers), 5b and 5d (containing 2-oxaalkyl spacers), and 6b (containing n-hexyl spacers); see Scheme II.

During these investigations X-ray structural characterization of a tetracyclic ether (3a) and of a tetrahalogenide (4a) has been carried out. The crystal structure of 3a shows a compound with two cis-tied imidazolidon rings and two six-membered ether rings. The latter rings are in the chair conformation. The structure determination of the short-armed tetrabromide 4a not only confirms the primary structure of the compound but also shows the steric shielding by the two phenyl groups on the convex side of the glycoluril unit (see Figure 3).

Palladium Complexes. Reaction of tetrapodand 4d (containing the ethylene glycol spacers) with \(\text{Pd}\)(CH$_3$CN)$_2$Cl$_2$ in methanol as a solvent yields a product which, according to elemental analysis, has the molecular formula \(\text{Pd}(4d)\text{Cl}_2\). In the FAB mass spectrum the ion \([\text{Pd}(4d)]^+\) was detected with an isotope pattern that perfectly matches the one simulated for C$_{48}$H$_{62}$N$_2$O$_{10}$Pd.

To check that no oligomeric or polymeric networks had been formed, we determined the molecular weight of this new product. The ebulliometric value (in methanol MW 1125 ± 75; calcd 1143)

is in agreement with a monomeric palladium-tetrapodand system. In addition, gel permeation chromatography was applied to obtain information on relative molecular sizes. The results (Figure 4) show clearly that Pd(4d)Cl₂ has a molecular size of the same order of magnitude as that of the free tetrapodand 4d. This supports the molecular weight determination, and it is therefore concluded that the complex Pd(4d)Cl₂ is monomeric in solution.

The following step was to identify the ligands comprising the coordination sphere within the Pd(4d)Cl₂ complex. The molar conductivity of this complex determined in methanol solution (Table I) is in the range expected for 2:1 electrolytes¹¹ and suggests that the Cl⁻ anions are not bonded to the palladium center, i.e. [Pd(4d)]Cl₂. Furthermore, the ¹H NMR data for this compound (methanol-d₄, 200 MHz) point to all four imidazolyl groups being coordinated to the palladium; compared to the free tetrapodand 4d, the resonances of the NCHN imidazole protons in the complex show a large downfield chemical shift (0.55 ppm). The white color of [Pd(4d)]Cl₂ that is typical of complexes with four (substituted) imidazolyl ligands coordinated to Pd(II)¹² is a third indication for the proposed formulation. These results indicate for [Pd(4d)]²⁺ a metallocage structure as depicted in Figure 2. However, this picture is too simple. Whereas the CH₃Im protons H² and H⁰ (Figure 5a) would be expected to be equivalent, the ¹H NMR spectrum shows them not to be so since they give rise to four triplets in the region 4.0–4.15 ppm (Figure 5c). Spin decoupling by irradiation of their vicinal H² protons converted the four triplets into an AB quartet, indicating the protons E and D to be chemically nonequivalent. To obtain more detailed information, NOE difference spectroscopy was employed (Table II). Irradiation of the olefinic imidazole proton H⁰ caused a NOE enhancement of the Hc signal, which implies the presence of a spatial connection between Hc and H'/H* near the coordinated (1-substituted) imidazolyl groups, which all make the same angle with the xy metal coordination plane.¹³

In a second NOE experiment, the NC₄H₄O methylene protons H¹ and H² were irradiated. The NOE difference spectrum shows a very remarkable NOE enhancement of the H² signal, which implies the presence of a spatial connection between H² and H¹/H² (Figure 5b). A CPK model of [Pd(4d)]²⁺ shows that this spatial connection can arise from a collapse of the metallocage via a twisting motion along the z axis (see Figure 6a). The orientation of the CH₃H⁺ methylene protons must be outward since their irradiation also induced NOE effects on their neighboring methylene protons H¹ and some (most likely ortho) phenyl protons H₅.

Finally, we examined the temperature dependence of the normal ¹H NMR 200-MHz spectrum of [Pd(4d)]Cl₂ in the region 7.5–9.0 ppm. In the range 32–60 °C, the spectrum does not alter noticeably, but lowering the temperature to −95 °C leads to a splitting of the H⁵ signals (Figure 5d). CPK models show that in the twisted compressed conformation two of the imidazolyl groups are situated close to the ureylene carbonyls (Figure 6b, site S), indicating the possibility of a significant anisotropy effect

---

**Table II. NOEDS Results for [Pd(4d)]Cl₂**

<table>
<thead>
<tr>
<th>irradiated proton</th>
<th>NOE effect (intensity, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Pd(4d)]Cl₂</td>
</tr>
<tr>
<td>D(E)</td>
<td>A (3.5)</td>
</tr>
<tr>
<td>E(D)</td>
<td>C (2.6)</td>
</tr>
<tr>
<td>I(J)</td>
<td>C (1.0)</td>
</tr>
<tr>
<td></td>
<td>K (1.2)</td>
</tr>
<tr>
<td></td>
<td>A (7)</td>
</tr>
<tr>
<td></td>
<td>C (2.3)</td>
</tr>
</tbody>
</table>

---

on the $^{11}$C chemical shift. The other two imidazolyl groups are in a different chemical environment (Figure 6b, site T). These variable-temperature $^1$H NMR experiments imply that at room temperature the two sets of imidazolyl protons are involved in a fast exchange process in which the metallogate alternates between the left and right twisted conformations (Figure 6a). The free energy of activation of this conformational change is 30 ± 2 \text{kJ/mol}.

A second phenomenon noted in the $^1$H NMR spectra on lowering the temperature was the downfield shift of the weighted average of the signals of the NCHN protons. This suggests that these protons are participating in a hydrogen bond; a CPK model of the twisted cage conformation does show that a NCHN hydrogen atom can approach both oxygen atoms of its own spacer unit (Figure 6c).

To discover what would happen when one or both oxygen atoms in the spacer units were omitted, the tetrapodands 5b, 5d, and 6b were reacted with Pd(CH$_3$CN)$_2$Cl$_2$. In all three cases, the elemental analysis of the product corresponded to the molecular formula Pd(tetrapodand)Cl$_2$. The molar conductivities of solutions of the three Pd(tetrapodand)Cl$_2$ compounds fall in the range for dianions, whereas an increase in temperature (to 60 °C) caused a little sharpening, but no fine structure came up. The NCHN imidazole case of [Pd(6b)Cl]Cl resulted in an even greater broadening, indicating the temperature was the downfield shift of the weighted average of the signals of the NCHN protons. This suggests that these protons are participating in a hydrogen bond; a CPK model of the twisted cage conformation.

In the case of [Pd(4d)]$^{2+}$, the metallocage is unstable and collapses via a twisted motion, most likely as a consequence of intramolecular H bonding between the polar C(2)H bond of the imidazolyl groups and the CH$_2$OCH$_2$ functions in the spacers. However, in the three [Pd(tetrapodand)]$^{2+}$ cage compounds, where there are fewer ether functions, metal coordination fluxionality is observed.

**Experimental Part**

**General Procedures.** $^1$H NMR spectra were recorded on Varian EM-360, Bruker AW-80, and Bruker WP-200 instruments. Chemical shifts (δ) are reported downfield from internal (CH$_3$)$_2$Si. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared and UV-vis/spectra were taken on Perkin-Elmer 283 and Perkin-Elmer 555 spectrophotometers, respectively. FAB mass spectra were recorded on a VG ZAB 2F spectrometer (matrix: glycerol, thioglycerol). Conductivity measurements were carried out at 25.0 °C with a Philips WS 9501 conductivity meter. Molecular weights were determined with a modified Galloway ebuliometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry (Utrecht). Drying of the solvents was performed at 35 °C and 0.01 mm Hg. Gel permeation chromatography was performed on a Sephadex LH-60 column (length 21.5 cm, diameter 1 cm) with methanol as eluent at a flow rate of 31 mL/h.

Unlesst otherwise indicated, commercial chemicals were used as received. DMSO, DMF, and methanol were dried over 3-Å sieves prior to use. Diethyl ether and chloroform were distilled from benzophenone ketyl and CaCl$_2$, respectively.

**Conclusion**

The above results concerning the palladium compounds clearly show the great importance of the spacer composition of the tetrapod in determining the type of palladium--tetrapodand complex that is formed. In the case of [Pd(4d)]$^{2+}$, the metallocage is unstable and collapses via a twisted motion, most likely as a consequence of intramolecular H bonding between the polar C(2)H bond of the imidazolyl groups and the CH$_2$OCH$_2$ functions in the spacers. However, in the three [Pd(tetrapodand)]$^{2+}$ cage compounds, where there are fewer ether functions, metal coordination fluxionality is observed.

**Palladium(II) Cage Compounds**

- **Figure 7.** Fluxional behavior of the Pd(II) compounds derived from 5b, 5d, and 6b.
Niele and Nolte

water, and dried (P₂O₅) under vacuum: yield 514 mg (40%) of white 3b; mp >300 °C dec; FABMS (M + H)⁺/m/e 784; IR (KBr) 1728 (C = O), 1122, 1027 (CO) cm⁻¹; 1. H NMR (CDCl₃) δ 7.20 (s, 10 H, ArH), 5.70 and 4.60 (AB q, J = 12 Hz, 4 H, C. 1, 7, 10, 14). 1.3.4,6-Tetakis(4-bromo-2-oxaethyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4a). Compound 2 (20.8 g, 50 mmol), 2-bromoethanol (250 g, 2 mol), and p-toluenesulfonyl acid monohydrate (0.51 g, 2.7 mmol) were dissolved in 400 mL of toluene, and 50 mmol), 2-bromochloroethanol (250 g, 2 mol), and p-toluenesulfonyl acid monohydrate (0.51 g, 2.7 mmol) were dissolved in 400 mL of toluene, and the solution was refluxed under N₂ for 48 h with a Soxhlet extraction apparatus.

The residue was dissolved in a minimum of CHCl₃ and added dropwise, with vigorous stirring, to 500 mL of diethyl ether. The precipitate was filtered and dried under vacuum; yield 38.7 g (92%) of white 4a. A sample was recrystallized from 2-bromoethanol-water: mp 125 °C; mp 176 °C; IR (KBr) 1720 (C = O), 1110-1000 (COC) cm⁻¹; 'H NMR (CDCl₃) δ 7.12 (m, 10 H, ArH), 4.93 (AB q, J = 9 Hz, 8 H, NCH₂0), 3.6 (m, 16 H, OC₂H₄CH₂Cl). Anal. Calcd for C₃₆H₄₀Br₂N₁₂O₈: C, 49.43; H, 5.12; Br, 6.29; N, 14.10. Found: C, 49.41; H, 5.08; Br, 6.32; N, 14.12.

1.3.4,6-Tetakis(7-chloro-2,5-dioxoheptyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4b). mp >100 °C dec; mp >130 °C dec; 'H NMR (CD3OD) as for 4a. 1.3.4,6-Tetakis(8-chloro-2-oxaoctyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4c): mp >90 °C dec; FABMS (M - Cl)⁺/m/e 1107; IR (KBr) 1720 (C = O), 1110-1000 (COC) cm⁻¹; 'H NMR (CD3OD) 6.19; 'H, NMR (CD3OD) 7.08 (br, 4 H, ArH). The mixture was refluxed for 16 h, filtered and evaporated under vacuum; yield 80-90% of a glossy yellow compound. Attempts to take FAB mass spectra of the complexes were unsuccessful. The UV–vis spectra (methanol) show intensive bands of the tetrapodands masking the ligand.

1.3.4,6-Tetakis(6-chlorohexyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4d). In a nitrogen atmosphere complex 1c (5.9 g, 20 mmol) and NaH (from a 80% dispersion in mineral oil, washed with hexane; 49.4 mg, 2.0 mmol) were mixed with 100 mL of DMF, and the solution was stirred at 80 °C for 16 h. The reaction mixture was treated with 20% methanol in toluene and evaporated under vacuum pressure (65 °C). The residue was dissolved in 8 mL of CHCl₃, washed (4X) with 8 mL of basic water (adjusted to pH 12 with Na₂CO₃) and with 8 mL of water (2X), dried (MgSO₄), and evaporated under vacuum; yield 100% of the tetraimidazolyl compound.

1.3,4,6-Tetakis(4-1-imidazolyl-2-oxaethyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4b): white solid; mp 87 °C; FABMS (M + H)⁺/m/e 791; IR (KBr) 1728 (C = O), 1110-1000 (COC) cm⁻¹; 'H NMR (CD3OD) 8 (br, 4 H, ArH), 7.08 (br, 4 H, N(1’)-CH(CN)(3)), and 6.92 (dd, 4 H, N(1’)-CH(3)/N(3)) resp. (10.8 g, 26 mmol) and 4-chloro-1-butanol (56.5 g, 520 mmol)) in 50 mL of methanol. The mixture was refluxed for 16 h and filtered over infusorial earth, and evaporated under vacuum; yield 9.14 g (35%); mp 56 °C; dec; FABMS (M + H)⁺/m/e 484; IR (KBr) 1730 (C = O), 1130-1000 (COC), 725 (CCl) cm⁻¹; 1. H NMR (CDCl₃) δ 6.7-6.8 (m, 10 H, ArH), 4.8 (AB q, J = 11 Hz, 8 H, OCH₂), 3.6 (m, 16 H, OCH₂CH₂CH₂Cl). Anal. Calcd for C₃₂H₄₀Cl₂N₁₂O₆Pd: C, 52.94; H, 5.55; Cl, 6.2; N, 15.05; O, 10.03. Found: C, 52.85; H, 5.43; Cl, 15.99; N, 6.31; O, 10.81. 1.3.4,6-Tetakis(8-chloro-2-oxaoctyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4c): mp >90 °C dec; FABMS (M + Cl)⁺/m/e 1107; IR (KBr) 1720 (C = O), 1110-1000 (COC) cm⁻¹; 'H NMR (CD3OD) 8 (br, 4 H, ArH), 7.05 (d, J = 8 Hz, 4 H, N(1’)-CH(CN)(3)), 6.99 (4 J = 11 Hz, 8 H, OCH₂), 4.95 (t of (AB q, J = 17 Hz, 8 H, N(1’)-CH(3)/N(3)). 3.72 (s, 16 H, OCH₂CH₂CH₂Cl). Anal. Calcd for C₃₆H₄₄Cl₂N₁₂O₆Pd: C, 56.82; H, 5.76; Cl, 6.8; N, 14.75; O, 15.39. Found: C, 56.82; H, 5.75; Cl, 6.81; N, 14.75; O, 15.39. 1.3.4,6-Tetakis(4-1-imidazolyl-2-oxabutyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (4d): mp >100 °C dec; 1. H NMR (CD3OD) 8 (br, 4 H, ArH), 7.4-6.5 (br, 18 H, CH₃-NCHCN), 5.5-3 (br, 24 H, N(CH₂CH₂CH₂)(3)/N(3)). Anal. Calcd for C₃₆H₄₄Cl₂N₁₂O₆Pd: C, 52.75; H, 6.71; N, 12.96; O, 13.37. Found: C, 52.95; H, 6.94; N, 13.15; O, 13.86. 1.3.4,6-Tetakis(7-1-imidazolyl-2,5-dioxoheptyl)tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (5b): mp >100 °C dec; IR (KBr) 1730 (C = O), 1110-1000 (COC) cm⁻¹; 'H NMR (CDCl₃) 8.1-7.3 (m, 10 H, ArH). The mixture was refluxed for 16 h, filtered and evaporated under vacuum; yield 80-90% of a glossy yellow compound. Attempts to take FAB mass spectra of the complexes were unsuccessful. The UV–vis spectra (methanol) show intensive bands of the tetrapodands masking the ligand.

Acknowledgment. We thank R. H. Fokkens and Prof. N. M. Nibbering for measuring the FAB mass spectra, R. P. Sybesma for carrying out the NOE experiments, C. J. Witmans and Dr. J. W. Zwicker for synthesizing compounds 5, and Dr. M. Grove.
Selective Molecular Oxygen Oxidation of Thioethers to Sulfoxides Catalyzed by Ce(IV)

D. P. Riley,*† M. R. Smith,*‡ and P. E. Correa‡

Contribution from the Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, and The Procter and Gamble Company, Miami Valley Laboratories, P.O. Box 39175, Cincinnati, Ohio 45247. Received June 15, 1987

Abstract: The selective molecular oxygen conversion of thioethers to sulfoxides is catalyzed by ceric ammonium nitrate (CAN) with rate enhancements that are at least three orders of magnitude greater than the uncatalyzed autoxidation of thioethers. Mechanistic studies (including spectroscopic, labeling, uptake, mixture, and analysis) of this novel reaction reveal that both atoms of dioxygen are incorporated into product sulfoxide, that a novel oxygen-driven Ce(IV)/Ce(III) redox cycle gives rise to the catalysis, and that molecular oxygen efficiently traps a sulfur-centered radical cation of the thioether (produced by Ce(IV) oxidation of thioether) to yield the oxygenated radical cation R₂S⁺O₂-. While this is proposed, reoxidizes Ce(III) to Ce(IV). The zwitterionic R₂S⁺OO⁻ intermediate (persulfide) reacts with thioether to yield two sulfoxide product molecules.

The ability to selectively convert a particular molecule via an oxidation utilizing the abundant and cheap oxidant oxygen often represents a desirable low-cost method for upgrading the value of a raw material. The goal of much of our research in recent years has been directed toward the utilization of oxygen as a cheap and selective oxidant. During our research into better methods of selectively oxidizing waste thioethers (e.g., Me₂S) to their more valuable sulfoxides, we discovered that thioethers are subject to a novel autoxidation process that under high oxygen concentrations, elevated temps., and polar solvents yields almost exclusively the sulfoxide product. The mechanism of this unusual autoxidation most likely involves an initial unfavorable electron transfer step (eq 1), followed by triplet oxygen (high concentration) trapping of the resultant radical cation (eq 2).

\[
\begin{align*}
R₂S + 3O₂ & \rightarrow R₂S' + O₂⁻ \quad (1) \\
R₂S' + 3O₂ & \rightarrow R₂S⁺O₂⁻ \quad (2)
\end{align*}
\]

Donation of an electron from superoxide to the oxygenated radical cation yields the zwitterionic species (eq 3) whose chemistry is known to yield sulfoxide upon exposure to additional thioether (eq 4).

\[
\begin{align*}
R₂S⁺O₂⁻ + O₂⁻ & \rightarrow R₂S⁻O⁻ + O₂ \quad (3) \\
R₂S⁻O⁻ + R₂S & \rightarrow 2R₂S⁻ \quad (4)
\end{align*}
\]

Given that the initial unfavorable electron-transfer step is rate-determining in this slow autoxidation reaction, we believed that the use of a suitable one-electron oxidant would possibly be capable of catalyzing or initiating the desired oxidation oxygen of R₂S to sulfoxide. We have communicated our preliminary successful attempts to catalyze this reaction using Ce(IV), and in this paper we present additional examples and mechanistic studies of the novel Ce(IV)-catalyzed molecular oxygen oxidation of thioethers to sulfoxides.

Experimental Section

All of the thioethers used in these studies were purchased from Aldrich Chemical Co. and distilled before use. Sulfoxide standards were prepared by standard procedures with H₂O₂ and (NH₄)₂Ce(NO₃)₆ and Ce(N₃)₂·6H₂O and purchased from Alfa-Ventron. HPLC grade acetonitrile was distilled before use and distilled, de-ionized water was used in all cases.

Electronic spectra were monitored by using matched quartz cells in a Hitachi 110A UV-VIS spectrophotometer over the range 200–500 nm. All high-pressure catalytic runs used an apparatus analogous to that reported previously. In general reactions were carried out with a reaction volume of 10 mL in an all glass/Teflon reactor. This small volume also minimized the potential risks inherent in running reactions with oxygen in an explosive regime. Caution must be exercised in such studies. In our system the reactor head-space (or gas) volume was kept very small; thus, only a small amount of O₂ is present in the reactor at any time. This reduces the possibility of extensive deflagration. Gas uptake measurements were made by utilizing a pressurized external calibrated steel tube connected directly to the reactor. Pressure drop in this calibrated external tube could be correlated to moles of O₂ consumed during the reaction. Reactions were monitored by gas chromatography on a Varian Model 3400 GC with a flame ionization detector and analyzed on a 15 m OV101 capillary column. Yields were determined by utilizing dodecane as an internal standard and by comparison to calibrated solutions. Electrochemical studies were performed on a Bioanalytical Systems CV-1B cyclic voltammograph, and voltammograms were recorded on a Houston Instruments 100 XY recorder. All cyclics were recorded in dry methylene chloride with 0.5 M tetra-n-butylammonium tetrafluoroborate.

†Monsanto Company.
‡The Procter and Gamble Company.

() Riley, D. P.; Correa, P. E.; Hardy, G. J. Org. Chem., accepted for publication.

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