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Evidence for an Unstable Bi(II) Radical from Bi–O Bond Homolysis. Implications in the Rate-Determining Step of the SOHIO Process

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The reaction of $BiCl_3$ with the lithium salt of *o*-di-*tert*-butylphenol under nitrogen forms organic oxidation products rather than the expected $Bi(OAr)_3$ complex, and bismuth disproportionation products. Likewise, the decomposition of Bi(III) aryloxides $Bi(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)_3$ and $ClBi(O\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)_3$ leads to corresponding organic oxidation products. These reactions can be explained by Bi–O bond homolysis to form unstable Bi(II) radicals, analogous to a fundamental step suggested to intervene in the SOHIO process.

The SOHIO process is the selective oxidation and ammoxidation of propylene to make the commodity chemicals acrolein and acrylonitrile. In 1997, the worldwide production of acrylonitrile alone was over 5 billion kilograms.[3] The predominant commercial processes for acrylonitrile and acrolein production use multicomponent catalysts based on $Bi_2O_3 \cdot MoO_3$ catalysts developed by SOHIO (Standard Oil of Ohio Company) workers in 1959−1962.[4,5]

Bismuth is known to be necessary to both the rate-determining and later steps of the catalytic cycle.[3] The generally accepted mechanism for the SOHIO oxidation/ammoxidation of propene implicates the formation of an allyl radical as the rate-determining step of the process, occurring at a bismuth site.[3] The role of bismuth has been substantiated by several experiments in heterogeneous systems.[6−9] No homogeneous model systems, however, have been used to model the substrate activation to date. In contrast, the product-forming steps in the proposed mechanism have been largely substantiated by homogeneous model studies.[10−18] The Limberg group has reported the first few examples of homogeneous molybdenum/bismuth alkoxide complexes,[19,20] which have intriguing possibilities as bimolecular model compounds.

Three different mechanisms have been proposed to explain the role of bismuth in propene activation (Scheme 1, mechanisms A, B, and C).[21,22] Although it has not yet been possible to distinguish between these mechanisms, Rademann et al. have published a study of the reduction of mass-selected bismuth clusters by propene, with the conclusion that a terminal oxo group is not necessary for propene oxidation.[23] Later articles in the ammoxidation field favor version B,[3] but no experimental support has been reported that can distinguish between versions A and B.

We have now observed reactions in homogeneous solution that shed light on the chemical pathways available to the Bi−O bond. We have observed spontaneous Bi−O bond homolysis in solution to form unstable Bi^{II} radicals, analogous to the key step in propene activation, version B. In our system the bismuth(II) radicals are not stable and disproportionate to bismuth metal and insoluble Bi^{III} byproducts.

The addition of 3 equiv of Li(O-2,6-di-*tert*-butylphenyl)$_3$ (**1**) to BiX_3 (X = Cl, Br) in dry solvent (THF, C_6D_6, ether) under nitrogen atmosphere[24] leads to a transient yellow color, which quickly darkens to appear black, partly due to a

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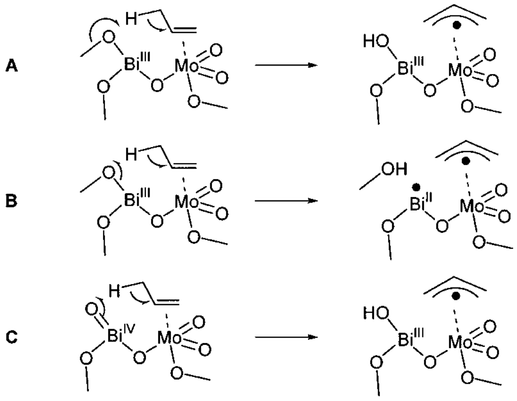
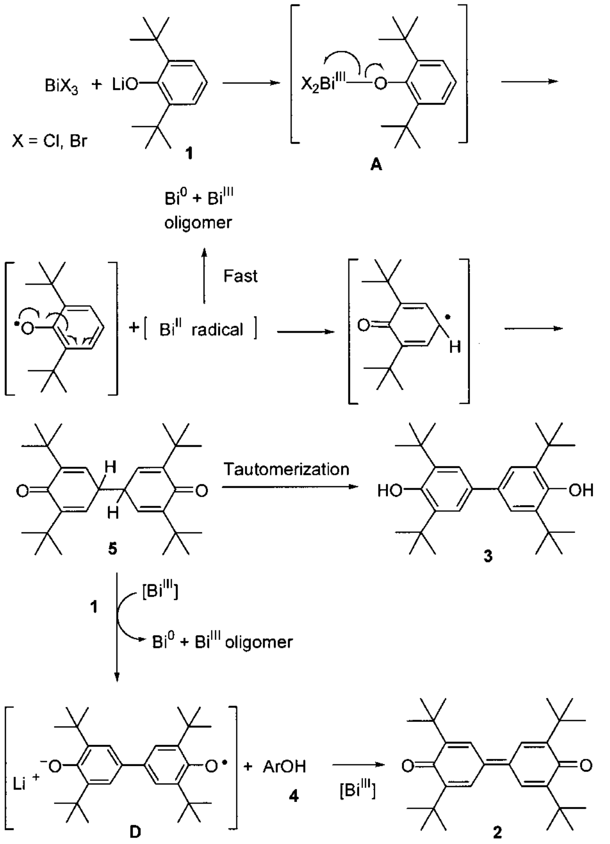
Scheme 1. Possible Mechanisms for Propene Activation on the SOHIO Catalyst[21,22]



Scheme 2. Proposed Mechanism for the Reaction of $BiCl_3$ with LiO-2,6-$^tBu_2C_6H_3$



mirrorlike coating on the inside walls of the reaction vessel. The product mixture is 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**2**), 3,3′,5,5′-tetra-*tert*-butylphenol (**3**), 2,6-di-*tert*-butylphenol (**4**), bismuth metal, and uncharacterized insoluble byproducts, presumably oligomeric bismuth(III) species.[25] The reaction, together with the proposed mechanism, is shown in Scheme 2. If the aryloxide substituent is introduced to bismuth by the addition of **4** to $Bi[N(SiMe_3)_2]_3$,[26] the products **2**−**4** are similarly observed, in addition to $HN(SiMe_3)_2$ and black solid.

The initial step is a simple substitution reaction of the aryloxide anion for the bismuth halide to form intermediate complex **A**. If the ortho groups on the aryloxide salt are less bulky, the substitution proceeds to completion to form a stable yellow bismuth alkoxide. We have thus formed $Bi(OAr)_3$ for the complexes with ortho substituents of Me (**6**)[27] and ^{i}Pr (**7**),[28] and the resulting complexes are stable for indefinite periods in the absence of air.[29] When $Bi(OAr)_3$ **7** is heated at 75 °C over 24 h, however, a mixture of **7**, the corresponding diphenoquinone,[30] diol,[30] and alcohol are observed in the reaction mixture by proton NMR.

A transient yellow color is observed upon addition of ArOLi **1** to $BiCl_3$, and a ^{1}H NMR spectrum of **A** at low temperature is consistent with the proposed formulation. We have not yet determined whether this initial substitution forms a mono-, di-, or trialkoxide.[31]

Intermediate **A** is unstable even at low temperature, and the reaction mixture quickly darkens to green/black. Although no radical species is seen by proton NMR, 3,3′,5,5′-tetra-*tert*-butyl-1,1′-dihydro-2,2′,5,5′-bis-cyclohexadiene-4,4′-one (**5**)[32] can be observed.[30] Tautomerization forms the diphenol **3**[30,32] in differing ratios depending on the polarity of the medium. Further oxidation of dihydrodiphenoquinone **5** with excess lithium aryloxide (a proton acceptor) by Bi(III) complexes (either starting material or formed by disproportionation) proceeds in a stepwise manner to form the anion radical **D**, followed by a second one-electron oxidation to lead to the remaining major products, phenol **4** and diphenoquinone **2**.

All diamagnetic species in the proposed mechanism have been observed by ^{1}H NMR spectroscopy; however, EPR

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(24) Although it is impossible to completely disprove the possibility of trace oxygen being available in this reaction, thus Bi(III) acting as a catalyst rather than an oxidant, we believe it can be discounted. We have tested the reaction solvents immediately before use with a drop of sodium benzophenone ketyl to ensure that oxygen is absent. We have also performed the reaction in the presence of air with no observable rate difference. The same products were observed in the air reaction as in under nitrogen, with, however, a relatively high ratio of aryl alcohol. In addition to these indications, the formation of bismuth metal implicates the noncatalytic participation of bismuth in the reaction.

(25) In a nitrogen-filled glovebox at room temperature, 16.0 mg of $BiCl_3$ (50.7 mmol) was suspended in 0.25 mL of dry C_6D_6, 32.5 mg of **1** (153 mmol) was partially dissolved in 0.25 mL of dry C_6D_6, and the mixtures were combined. The reaction mixture immediately turned clear yellow, then darkened to orange, then brown/red, and then opaque green/black during mixing. The mixture was transferred to an NMR tube, where flocculent black precipitate slowly settled to reveal yellow/green solution. A ^{1}H NMR spectrum showed the presence of dione **5** and unreacted **1**, and then the tube was frozen, evacuated, and flame-sealed. A ^{1}H NMR spectrum taken after 2 days at room temperature showed solely ArOH **4**, diol **3**, and diphenoquinone **2**. Ratios of these three products varied according to polarity of the reaction mixture; however, a typical ratio determined after 8 days by integration against an internal standard Ph_3CH was 22:9:11 **4**:**3**:**2**. In a larger-scale run, qualitative analysis (dissolution in nitric acid, addition of NH_4OH to precipitate $Bi(OH)_3$, and reduction with $Na_2Sn(OH)_4$) confirmed the presence of bismuth in a mirrorlike coating of the inside of the reaction vial and in the black solid, while the soluble materials tested negatively for bismuth.

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(29) Heating complex **6** causes the formation of black precipitate; however, no decomposition products were observed by ^{1}H NMR.

(30) ^{1}H NMR identification was confirmed by comparison to spectra of an authentic sample.

(31) The Bi−O bond homolysis reaction may occur irrespective of *n*, as diphenoquinone **2** formation is observed in reactions with a stoichiometry of 1:1, 1:2, or 1:3 BiX_3:LiOAr.

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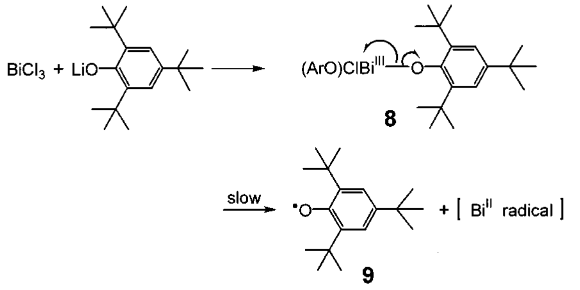
spectroscopy showed only one well-defined species, a relatively stable organic radical. The short lifetime and resulting low concentration of the putative Bi^{II} radical makes it difficult to refine the spectra to identify its ESR signal (a previous ESR study of Ph$_2$Bi^{II} radical formed by photolysis in the EPR probe was also forced to rely on the identification of the organic phenyl radical rather than the bismuth one).[33] An EPR signal, shown in Figure 1, of a long-lived organic radical (consistent with the ion-paired semiquinone **D**,[34] Scheme 2) does indicate, however, that the reaction goes through a radical pathway.

Although the di-*tert*-butylphenoxy radical was not sufficiently stable to be observed directly, mixture of BiCl$_3$ with LiO-2,4,6-^{t}Bu$_3$C$_6$H$_2$ formed the complex ClBi(O-2,4,6-^{t}Bu$_3$-C$_6$H$_2$)$_2$ **8**,[35] which slowly decomposes at room temperature to form the long-lived tri-*tert*-butylphenoxy radical **9** (eq 1). The experimental and simulated ESR spectra of **9** are shown in Figure 2. These spectra are consistent with those previously reported for **9**,[36−39] with coupling to two aryl protons and nine *tert*-butyl protons. There is a 9.51 G coupling to two ^{13}C's, which we have assigned to the meta carbons, consistent with Karplus/Fraenkel theory.[40]



(1)

Radical trapping agents (CCl$_4$, (CH$_3$)$_4$C$_2$) have failed to stop the reaction shown in Scheme 2, although they did appear to slow its progress. It is likely that the Bi(II) radical undergoes rapid disproportionation to nonradical products before escape from the radical cage; thus radical traps would be ineffective.

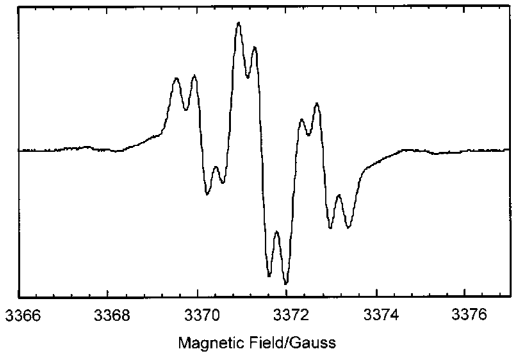


Figure 1. Room temperature EPR spectrum of anion radical salt **D** in THF. The spectrum is a triplet of triplets with $g = 2.005 \pm 0.001$, $a_1 = 1.38 \pm 0.01$ G, $a_2 = 0.40 \pm 0.03$ G. Asymmetry is due to tight ion-pairing of the lithium, similar to that reported by Prokof'ev et al.[34]

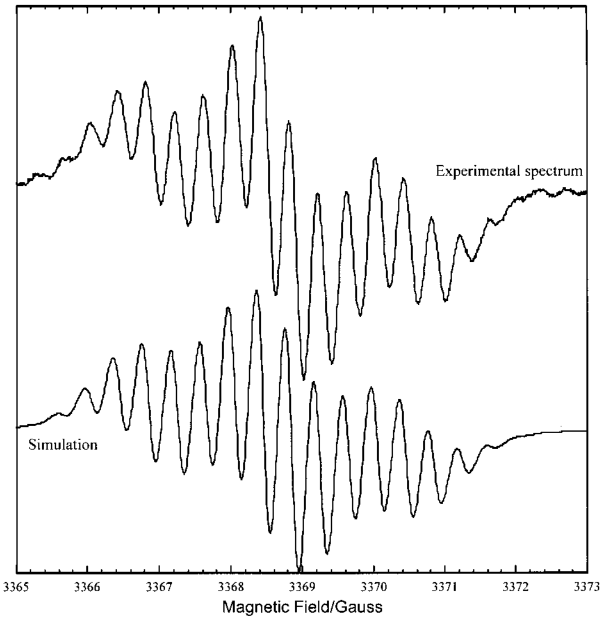


Figure 2. EPR experimental and simulated spectra at 210 K of tri-*tert*-butylphenoxy radical **9**. The spectrum shows coupling to two aryl protons and nine *tert*-butyl protons with $g = 2.0050 \pm 0.001$, $a_1 = 1.597 \pm 0.003$ G (2 protons), $a_2 = 0.396 \pm 0.001$ G (9 protons).

The work presented here demonstrates for the first time that homogeneous bismuth(III) aryloxides can act as one-electron oxidizing agents to form bismuth(II) radicals, in the same way as solid bismuth molybdate is postulated to react during propene oxidation. We have described homogeneous reactions that model version B (Scheme 1) of the proposed rate-determining step of the SOHIO process. The fundamental step in both cases is the homolysis of a Bi−O bond to form a Bi^{II} radical. Bismuth aryloxides may therefore provide suitable homogeneous model complexes for the activation of propene on SOHIO catalysts.

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Supporting Information Available: Experimental details for low-temperature and ESR reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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