Supplementary Material Available: Experimental procedures for preparation of the tungsten and rhenium enolates, including ^1H NMR, ^{13}C NMR, IR, and analytical data for **4a–d, 5–7, 8a,** and **9–11** (6 pages). Ordering information is given on any current masthead page.

## Selective Catalytic Oxidation of Organic Compounds by Nitrogen Dioxide

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New, catalyzed, gas-phase reduction/oxidation reactions that are highly selective and efficient are described in this paper. The reactions are based upon the surface-catalyzed reduction of nitrogen dioxide (NO_2) by organic compounds that can readily be dehydrogenated or oxidized. These reactions between certain organic compounds and NO_2, which are catalyzed by metals— most effectively by gold—constitute the basis not only for new selective approaches to synthesis but also for selective and sensitive chromatography detectors.[1] Oxidation of organic compounds by nitric acid and nitrogen oxides has been reviewed.[2] In one report[3] gold was used to catalyze the reaction of oxygen with alkenes, but gold catalysis of the oxidation of specific organic compounds by NO_2 is novel. The uncatalyzed gas-phase reaction of NO_2 with alcohols has been reported to give the corresponding nitrite,[4] in contrast to the aldehydes obtained in the present gold-catalyzed reactions. Copper oxide catalysts facilitate the conversion of alcohols to aldehydes by quite different processes in which hydrogen is a byproduct.[5,6]

At temperatures ranging from ambient to 400 °C, NO_2 can dehydrogenate or oxidize certain classes of organic compounds on the gold catalyst surface, while more inert classes of organic compounds are unreactive. We have examined several reactions to identify the oxidation products. Experiments have been performed using microgram quantities of starting materials which elute from a gas chromatograph and then transmit the catalyst bed within 1 s (calculated residence time is 0.16 s). For example, gas chromatography/mass spectrometry (GC/MS) analysis of the products resulting from reaction of 1-pentanol indicates complete oxidation at 200 °C; no unreacted starting material was detected and no reaction products other than pentanal, nitric oxide (NO), and water were observed under these conditions.

$$CH_3CH_2CH_2CH_2CH_2OH + NO_2 \xrightarrow[\text{Au catalyst}]{200\ °C}$$
$$CH_3CH_2CH_2CH_2CHO + NO + H_2O$$
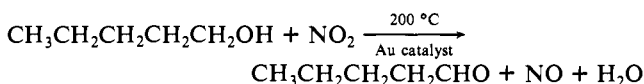
The limit of detection of volatile byproducts and unreacted starting material was estimated to be ≤1% of the pentanal formed. Identification of compounds was accomplished by comparison of mass spectral data and of chromatographic retention times with those of authentic standards.

Other primary alcohols have been catalytically converted to the corresponding aldehydes in a similar manner using NO_2. With the gold catalyst at 350–400 °C, 4-methyl-2-pentanol was rapidly oxidized to 4-methyl-2-pentanone. Again the conversion was virtually quantitative and proceeded without significant formation

of byproducts; no detectable starting alcohol remained in the product. Under similar reaction conditions, aliphatic ketones can undergo catalytic dehydrogenation to form α,β-unsaturated ketones, but in lower yield than obtained with alcohols. Olefins can also be dehydrogenated; for example, cyclohexene is oxidized by NO_2 on gold surfaces at 350–400 °C to benzene.

When uncoated borosilicate glass beads were substituted for the gold-coated catalyst beads none of these reactions occurred to a detectable extent under the same conditions used for the catalyzed experiments. However, a small amount of n-amyl nitrite was observed when no catalyst was present in the reaction of NO_2 with 1-pentanol, which is in agreement with previously reported work.[4] Likewise, with the catalyst present but with air instead of NO_2 substituted as a possible oxidizing agent, oxidation was not observed for any of these compounds.

Gold-catalyzed gas-phase oxidation with NO_2 offers an attractive new synthesis approach because it is selective, occurs rapidly, can be performed on small as well as large scales, and generates an easily removed gaseous byproduct, NO. The NO can be removed and easily oxidized back to NO_2 by air to allow for recycle processes with net consumption of only oxygen and the compound being oxidized.

Several catalysts were prepared and investigated, including copper, silver, and gold supported on silica, different forms of silica support, and different forms of solid gold and gold alloys. Under the conditions tested the highest NO production, oxidation efficiency, and stability was achieved with pure gold supported on borosilicate glass beads. Less specificity was observed with gold alloys. The supported catalyst was prepared by precipitating auric chloride onto glass beads (0.5-mm diameter).[7–9] After air drying, the gold was reduced by flowing hydrogen over the beads at 400 °C for 2 h, then washing the beads well with water, and finally treating them again under hydrogen at 400 °C for 6 h.

The apparatus consisted of a heated catalyst bed, a means of introducing sufficient NO_2 into the catalyst bed, a means of introducing the organic reducing agent, and a sorbent for collecting and analyzing the reaction products. The catalyst bed, a gas-phase, single-pass, packed bed reactor, consisted of a 4-mm i.d. by 8-cm length of quartz tubing, filled with 1 g of gold-coated beads, maintaining at the desired temperature (200–400 °C). A thermostated Teflon permeation tube produced a constant 11 $\mu g/min$ emission of NO_2 in a helium carrier gas stream flowing at 30 mL/min. A gas chromatograph was used to introduce selected reducing agents into this NO_2 doped carrier gas as it passed over the catalyst. The effluent of the catalyst bed was directed to a NO chemiluminescence detector through a polymeric sorbent trap of Tenax GC. In this manner any NO produced was detected[10] immediately upon reaction of the reducing agent with NO_2. Subsequently, the sorbent cartridge was removed, and the reaction products were thermally desorbed and cryogenically focused[11,12] for analysis using GC/MS.

The following classes of compounds, when allowed to react with NO_2 in a catalyst bed at 350–400 °C, produced NO and corresponding oxidation products: alcohols, aldehydes, phenols, ketones, olefins, carboxylic acids and amines. Hundreds of compounds that produce nitric oxide have been studied.[13] The following are representatives of the different compound classes: 2-octanol, benzyl alcohol, benzaldehyde, nonanal, 5-nonanone, 2,6-dimethylaniline, 2,6-dimethylphenol, 2-hexene, 1-nitropropane, tert-butyl disulfide, 1-octanethiol, naphthalene, indole, diethylethyl phosphonate, triethyl phosphite, and triethyl phosphate. Yields of NO vary from compound to compound according to ease of oxidation and reaction conditions but are reproducible under fixed

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conditions. By contrast, no NO could be detected in the effluent when NO$_2$ in the heated Au catalyst bed (400 °C) was mixed with alkanes, chlorinated alkanes, or water.

This redox process, which produces NO, has been coupled with a second redox reaction to allow for selective detection of the previously mentioned classes of reducing compounds with or without prior chromatographic separation.[13] In such detectors the NO formed is subsequently allowed to react with ozone in the well-known redox reaction accompanied by chemiluminescence.[10] Several inorganic compounds can also be oxidized by NO$_2$ in the presence of a catalyst. A different method of analysis in which carbon monoxide (rather than NO$_2$) is fed continuously in excess to a flowing gas stream, to allow the measurement of NO$_2$, has been reported by Bollinger, Sievers, Fahey, and Fehsenfeld.[14] In the present study we have learned that, in the presence of NO$_2$ on gold catalysts, ammonia, hydrogen peroxide, carbon disulfide, sulfur dioxide, hydrogen sulfide, and hydrogen react to produce NO and thereby can also be detected by the redox chemiluminescence process.

From the experiments performed, it is clear that this redox reaction process can be used in either a continuous manner or in batch-type reactions to accomplish selective oxidation. The catalyzed redox reactions can be coupled with chemiluminescence detection in either continuous on-line sensors or as chromatographic detectors.[13,15] Sensitivities of detection comparable to those of flame ionization detectors have been shown for the selected classes of compounds that can undergo catalyzed oxidation.[13,16]

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Identification of Rb⁻ and Complexed Rb⁺ in Alkalides and Electrides by X-ray Absorption Spectroscopy (XANES and EXAFS)

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We recently synthesized a variety of novel salts that contain alkali-metal anions[2-4] (alkalides) or trapped electrons (electrides).[5,6] The counterions are alkali cations complexed with 18-crown-6, 15-crown-5, or [2.2.2]cryptand. Species identification and structural information, which are essential for understanding these new materials, are severely hampered by their thermal instability and poor crystal quality. In some cases, but not for complexed Rb⁺, alkali-metal NMR can be used to identify species.[7,8] We

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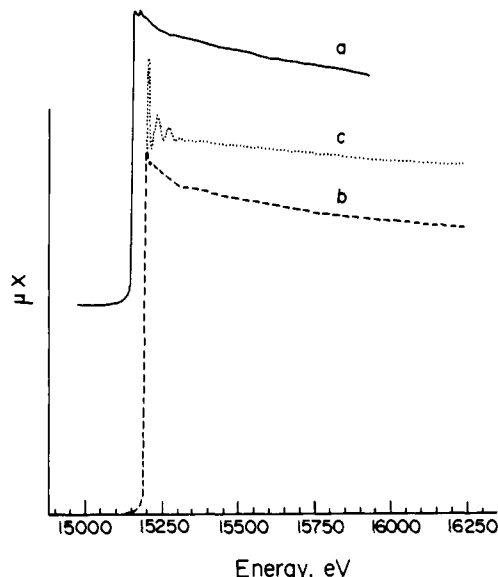(3) Van Eck, B.; Le, L. D.; Issa, D.; Dye, J. L. *Inorg. Chem.* **1982**, *21*, 1966–1970.
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Figure 1. K-edge X-ray absorption spectra of (a) krypton gas,[14] (b) Cs(18C6)$_2$·Rb⁻, and (c) Rb⁺(18C6)·Br⁻·2H$_2$O. Note that the Kr spectrum has been shifted horizontally. All three spectra have also been shifted vertically.

Table I. Relative Areas^a (A) of Rubidium K-Edge Absorption Threshold Resonances (Normalized to Edge Jump)

compound	A(pristine)	A(oxided)
Rb⁺(18C6)·Br⁻·2H$_2$O	25	
Rb⁺(18C6)·SCN⁻	27	
Rb⁺(18C6)·Na⁻	19	29
Cs⁺(18C6)$_2$·Rb⁻	1	30
Rb⁺(18C6)·Rb⁻	12	29
Rb⁺(18C6)·e⁻ or Rb⁺(18C6)$_2$·Rb⁻	14	27
Rb⁺(15C5)$_2$·Na⁻	29	34
Rb⁺(15C5)$_2$·Rb⁻	18	29
Rb⁺(18C6)·K⁻ and/or K⁺(18C6)·Rb⁻	10	29
Rb⁺(15C5)$_2$·K⁻ and/or K⁺(15C5)$_2$·Rb⁻	16	34
Rb⁺C222·e⁻	21	
K⁺C222·Rb⁻	3	26

^{a} Estimated accuracy: ±4 units.

report here the first X-ray absorption study of alkalides and electrides. Rubidium XANES and EXAFS with appropriate studies of model salts of known structure[9,10] provide unequivocal identification of Rb⁻ and/or complexed Rb⁺.

Transmission measurements[11] at −50 °C were performed at CHESS[12] under strictly anaerobic conditions. After each measurement the alkalide or electride[13] was allowed to react with air and the resulting oxide/hydroxide (decomposed sample) was measured again.

The X-ray absorption spectra of Cs⁺(18C6)$_2$·Rb⁻ and Rb⁺(18C6)·Br⁻·2H$_2$O are depicted in Figure 1. The energy of the K-edge absorption threshold of Rb⁻ is only 2 eV lower than that of complexed Rb⁺ salts (which have the same edge position as the decomposition product). Thus, as for some noble metal compounds,[14] the relative rubidium edge positions are not good indicators of the formal oxidation states. However, the absorption threshold resonance ("white line"); which results from transitions to vacant bound excited states and is a measure of the density

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