



Nitrogen oxides/selenium dioxide-mediated benzylic oxidations

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Received 11 October 2002; accepted 12 February 2003

Abstract

The oxidation of benzylic groups to the corresponding carboxylic acid functionality by dioxygen is mediated by a combination of nitrogen oxides and selenium dioxide (SeO_2). Substrates examined include alkylnaphthalenes and alkyipyridines. The aldehyde appears to be an intermediate in the reaction. Mechanistic studies suggest that the rate-determining step is hydrogen atom abstraction by nitrogen dioxide (NO_2) to form the benzyl radical. Selenium dioxide subsequently oxidizes this radical to the desired product.

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Keywords: Benzylic oxidation; Selenium dioxide; Nitrogen oxides; Dioxygen

1. Introduction

Stoichiometric selenium dioxide (SeO_2) oxidations have long been known, but yields have often been low and purification difficult due to organoselenium side products and difficulty in removing selenium in its reduced form [1,2]. In some cases, it is possible to make the oxidation catalytic by the addition of a sacrificial reoxidant. For example, selenium dioxide-catalyzed oxidation of allylic compounds has been achieved in good yields using peroxides [3]. However, from an economic standpoint, dioxygen rather than the more expensive peroxide is desirable.

Interest in new methods for benzylic oxidation remains high due to the use of naphthoic and pyridyl acids in making pharmaceuticals, dyes, agricultural products, and polyester monomers. However, effective methods for the direct formation of these products are still few. One reason for this is that conventional

benzylic oxidation procedures, including the Amoco Mid-Century process, is unsatisfactory for methyl naphthalenes due to increased ring reactivity [4–6]. For example, the electron transfer mechanism, which operates in many benzylic oxidations involves the initial formation of an aromatic radical cation. While this species typically loses a proton from the benzylic position to form the radical species, in the case of species like 2-methylnaphthalene the proton alpha to the benzylic position is more reactive leading to ring-substituted products. For methylpyridines a likely explanation is that the electron withdrawing nitrogen hinders the formation of the radical cation. Thus, to effectively oxidize these substrates, catalysts must be found which operate via a different mechanism.

Here, we describe a procedure for benzylic oxidation that directly uses dioxygen and is mediated by a combination of nitric oxide (NO) and selenium dioxide. The mixture of nitric oxide and dioxygen also serves to keep the selenium in the catalytically active oxidized form. Thus, it is possible to start with either elemental selenium or selenium dioxide. Though alcohol is the usual product of allylic oxidation with

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selenium dioxide [1–3], carboxylic acids are invariably obtained in the present case. Similar systems have been described in the patent literature but there has been no systematic study and no mechanistic information is available [7–12].

2. Experimental

All chemicals were commercially available and purchased in their highest purity available. Solvents were purchased as anhydrous and used as received. NMR spectra were collected on a Bruker DPX-300 spectrometer and referenced to residual protonated solvent peak. Product identity was confirmed by NMR comparison to standard reference spectra and/or coinjection of standards. Purity of products after isolation was determined based on integration of residual NMR resonances. Melting points, Mel-Temp II apparatus (uncorrected), were also determined. Attempts to identify side products proved unsuccessful, as they were generally insoluble and soluble compounds failed to elute during liquid chromatography. GC/MS work was conducted at the Penn State MS facility on a HP-5972 instrument using a DB-5 column.

2.1. 2-Naphthoic acid from 2-alkylnaphthalenes

One of the 2-alkylnaphthalenes (10.0 mmol), Se (0.90 mmol, 71 mg), and *o*-dichlorobenzene (7 ml) were combined in a two-neck flask with condenser. Alternatively, selenium dioxide (0.64 mmol, 71 mg) was used with water added in the desired amount. The mixture was stirred in an oil bath at the desired temperature for 4 h. During this time, a 1:1 mixture of NO:O₂ (1 atm pressure) was slowly bubbled through a needle into the flask.

After 4 h, the reaction mixture was cooled to room temperature and could be purified via filtration of the *o*-dichlorobenzene mixture through a long plug of silica gel with methylene chloride. The acid was then washed from the silica using a mixture of methylene chloride and methanol. The resulting tan powder after solvent removal was found to be pure by NMR spectroscopy and melting point determination (mp = 185–187 °C, Lit = 186 °C [13]). The methyl, ethyl, and isopropyl substituted naphthalenes gave 80, 74,

and 25% yield of isolated acid product, respectively, for 160 °C reaction temperature.

2.2. Kinetic studies of 2-naphthoic acid from 2-methylnaphthalene

2-Methylnaphthalene (20.0 mmol, 2.84 g), Se (1.80 mmol, 142 mg) or SeO₂ (1.28, 142 mg), and dimethyl sulfoxide (14 ml) were reacted under the conditions described above at 150 °C. Every half-an-hour an NMR sample (0.5 ml) was removed for analysis until the reaction was complete to about 80%. At this point side products began forming. Yields were calculated via integration of the proton in the 1-position of the naphthalene ring of the products (aldehyde: s, 8.48 ppm, 1H; acid: s, 8.67 ppm, 1H) relative to the proton in the 3-position of the ring of the starting material (d, 7.28 ppm, 1H).

2.3. 2,6-Naphthalenedicarboxylic acid and 6-methyl-2-naphthalene carboxylic acid from 2,6-dimethylnaphthalene

2,6-Dimethylnaphthalene (5.00 mmol, 0.781 g), Se or SeO₂ (0.45 mmol), and dimethyl sulfoxide (4 ml) were combined and set up as above. The reaction was run at 150 °C for the indicated time period, then cooled to room temperature. An excess of water was added to precipitate a creamy white solid. After collection and aqueous washing by suction filtration, the solid was dried under high vacuum. The mixture contained only 2,6-naphthalenedicarboxylic acid and 6-methyl-2-naphthalene carboxylic acid by NMR. Relative yields of the two acids were calculated by NMR integrations of the proton(s) in the 1 (s, 8.51 ppm, 1H) or 1,5-positions (s, 8.67 ppm, 2H) of the naphthalene ring for the mono and diacid products, respectively. The amount of 6-methyl-2-naphthalene carboxylic acid ranged from 5 to 50% while the amount of 2,6-naphthalenedicarboxylic acid varied between 10 and 57%. A total yield of 60–65% was obtained in each experiment.

2.4. 2,6-Naphthalenedicarboxylic acid from 6-methyl-2-naphthalene carboxylic acid

The reaction and workup were performed as described above for 2,6-dimethylnaphthalene. The

resultant bright yellow solid consisted of a mixture of only 2,6-naphthalenedicarboxylic acid and 6-methyl-2-naphthalene carboxylic acid by NMR.

2.5. 6-Methyl-2-naphthoic acid from 2,6-dimethylnaphthalene

Bromination and conversion to aldehyde were adapted from previously reported methods [14,15]. 2,6-Dimethylnaphthalene (100.0 mmol, 15.62 g) was dissolved in 500 ml carbon tetrachloride. *N*-bromosuccinimide (110.0 mmol, 19.58 g) was then added followed by another 1000 ml carbon tetrachloride. The mixture was irradiated with a 500 W glass filtered halogen lamp for 3 h. During this time a precipitate of white succinimide was observed in the reaction. The reaction mixture was filtered and evaporated to dryness in vacuo leaving a pink/white solid. The solid was dissolved in approximately 250 ml of methylene chloride and insoluble material was filtered out leaving a deep red solution. The solution was added dropwise to 120.0 mmol, 16.82 g of hexamethylenetetramine in 30 ml methylene chloride and refluxed gently for 2 h. The solution was cooled and filtered washing with 3 ml \times 25 ml of hexanes. The resulting tan solid was dissolved in 150 ml of 50% acetic acid and refluxed for 2 h. At this point 30 ml of concentrated HCl was added to the mixture and refluxed for an additional 10 min. The resulting mixture was then extracted with ethyl ether and solvent removed in vacuo. The resulting mixture of aldehydes was separated via column chromatography using a 3:1 mixture of methylene chloride/hexanes. This yielded 33.9 mmol, 5.77 g (34% yield) of 6-methyl-2-naphthaldehyde as a white, flaky solid (mp = 128–130 °C, Lit = 123–124 °C [16]) and 4.03 mmol, 0.742 g (4% yield) of 2,6-dinaphthaldehyde as a white, flaky solid (mp = 174–176 °C, Lit = 174–176 °C [17]).

The conversion of 6-methyl-2-naphthaldehyde to 6-methyl-2-naphthoic acid was adapted from a previously reported method [18]. 6-Methyl-2-naphthaldehyde (10.0 mmol, 1.70 g) was dissolved in 40 ml of a 1:1 mixture of ethanol/acetic acid. Sodium perborate tetrahydrate (12 mmol, 1.85 g) was added in portions over about 30 min. The solution was stirred for 8 h at 50 °C. At this time another 12 mmol of sodium perborate tetrahydrate was added and stirring was continued at 50 °C for another 5 h. The resulting solution with

white precipitate was evaporated to dryness in vacuo and then washed with an excess of water. Recrystallization from ethanol/water afforded 64.0 mmol, 1.19 g (64% yield) of 6-methyl-2-naphthoic acid (mp = 245–246 °C, Lit = 229 °C [19]).

2.6. 4-Pyridinecarboxylic acid from 4-methylpyridine

4-Methylpyridine (10.0 mmol, 0.931 g), Se (0.61 mmol, 48 mg), and *o*-dichlorobenzene (7 ml) were combined and reacted as described above at 160 °C for 4 h. After cooling and precipitation with hexanes, the light yellow precipitate was collected with suction filtration. The solid was then washed with portions of cold, dry isopropanol until the melting point matched that of 4-pyridinecarboxylic acid. The resulting acid (94% yield) was found to be pure by NMR spectroscopy (mp = 316–322 °C, Lit = 315 °C [13]).

2.7. 2-Pyridinecarboxylic acid from 2-methylpyridine

2-Methylpyridine (10.0 mmol, 0.931 g), Se (0.61 mmol, 48 mg), and *o*-dichlorobenzene (7 ml) were combined and reacted as described above at 150 °C for 4 h. The resulting solution was evaporated to dryness in vacuo, washed with ether and methylene chloride. The resulting brown solid was dissolved in ethanol and decolorized with activated carbon. Filtration and evaporation gave 38% yield of a pure creamy white solid by NMR spectroscopy (mp = 169–172 °C, Lit = 137 °C [13]).

2.8. Kinetic isotope effect for toluene substrates

Toluene (5.00 mmol, 0.461 g), *d*₈-toluene (5.00 mmol, 0.501 g), Se (0.61 mmol, 48 mg), and *o*-dichlorobenzene (7 ml) were combined and reacted as described above at 150 °C for 4 h. The solvent was removed in vacuo, dissolved in methylene chloride, and filtered to collect the soluble material. The volume of the solute was reduced and separated via liquid chromatography (methylene chloride/1% acetic acid) to yield pure benzoic acids as an off-white powder (2.9% yield, molecular weight adjusted for kinetic isotope effect). The acids were derivatized to their respective methyl esters using methanol/acetyl chloride and analyzed using GC/MS.

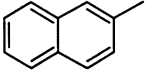
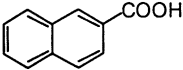
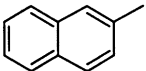
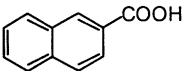
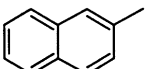
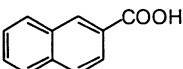
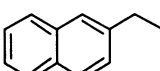
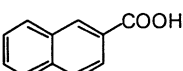
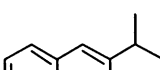
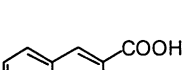

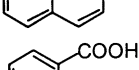

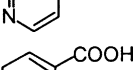
3. Results and discussion

Table 1 summarizes our results. The described oxidation occurred with varying degrees of completion depending on the substrate used. As shown for 2-methylnaphthalene, reduction of reaction temperature causes a decrease in acid yield (entries 1, 2, and 3). At 160 °C, complete conversion of the starting material was seen. Apart from the desired acid, some side products were also observed. Lowering the reaction temperature results in both lower total conversion and the amount of acid obtained. Thus, it seems that the overall reaction is substantially slowed at lower temperature. It is also interesting that under these conditions much of the Se remained unoxidized, as evidenced by the black Se particles persisting during the course of the reaction. An Arrhenius plot of the reaction as a function of the temperatures shown in Table 1 gave a value of 23 kcal/mol for 2-methylnaphthalene. In general, the temperature trends observed for 2-methylnaphthalene were observed for the other substrates.

2-Ethynaphthalene, entry 4, also yielded 2-naphthoic acid in similar yield to that of 2-methylnaphthalene. It is proposed that the methyl ketone is formed first and is then converted to glyoxal, a known reaction for selenium dioxide [20]. Under the conditions employed, this would quickly be oxidized to the resultant acid and carbon dioxide. 2-Isopropynaphthalene, entry 5, resulted in a poor yield of the acid product with the majority of the starting material going to unknown products. This may be attributed to the difficulty in forming a ketone intermediate with this substrate and not to the difficulty in forming a benzylic radical from hydrogen abstraction. The latter process should actually be more facile for these substrates.

Attempts to oxidize 2,6-dimethyl naphthalene resulted in mixtures of the di- and monoacids. The combined yield was typically around 60–65%. For reasons that are not clear, the ratio of the two compounds varied markedly between experiments; however, the total yield was always about the same. One possible reason for the incomplete conversion to the diacid is the deactivating effect of the electron-withdrawing carboxylic

Table 1
Carboxylic acid yields for various substrates (10 mmol) using Se (5 wt.%) and a 1:1 NO:O₂ mixture bubbled through the reaction

Entry	Substrate	Time (h)/temperature (°C)	Product	Yield (%)
1		4/160		80
2		4/150		54
3		4/140		22
4		4/160		74
5		4/160		25
6		4/160		94
7		4/150		38

Reactions were run in *o*-dichlorobenzene (7 ml). Yield reported is that of isolated product.

acid group of the monoacid [21,22]. Consistent with this, the use of 6-methyl-2-naphthoic acid under the standard reaction conditions resulted in the formation of the diacid in amounts similar to those obtained starting with 2,6-dimethylnaphthalene.

The results from the methyl pyridine reactions, entries 6 and 7, yielded interesting results. The reaction with 4-methylpyridine resulted in nearly quantitative yield of the acid; however, the yield dropped substantially for 2-methylpyridine. A lower reaction temperature was employed in this case to minimize the formation of side products. A reaction employing 3-methylpyridine resulted in only a trace of the acid product. In a similar oxidation, the rate of 4-methylpyridine oxidation was found to be greater than that obtained for 3- or 2-methylpyridine [12].

As shown in Fig. 1, a selenium species is required for the benzylic oxidation to proceed. In its absence, low yields (ca. 10%) of the acid were observed with the primary reaction products being unidentified side products. However, beyond this minimum amount, the amount of selenium in the reaction mixture does not make a significant difference.

As mentioned earlier, either selenium or selenium dioxide can be employed in the reaction mixture. Control experiments under typical reaction conditions but in the absence of substrate showed that elemental selenium is oxidized within 15 min to soluble selenium dioxide (identified by isolation and melting point determination) in the presence of nitric oxide

Table 2

Results for the addition of water to the oxidation reaction employing selenium dioxide (5 wt.%)

Entry	Water added (μl)	2-Naphthoic acid yield (%)
1 ^a	0	–
2	10	35
3	25	65
4	100	62
5	150	–
6	250	–

Reactions were run with 2-methylnaphthalene (10 mmol), *o*-dichlorobenzene (7 ml), and a 1:1 mixture of NO:O₂ bubbled through at 150 °C for 4 h.

^a Reaction was run at 160 °C.

and oxygen. Curiously, while no water is necessary when elemental selenium is employed, a trace of water is required for reactions employing selenium dioxide (Table 2). However, once a certain threshold is achieved, water is clearly detrimental to the reaction. While the origin of the water effect remains unclear, there is some indication that it is related to particle size: water apparently aids in the break up and dissolution of the large commercially available selenium dioxide particles that were employed (note that selenious acid is formed by the reaction of selenium dioxide with water). The added water may only be necessary to get the reaction started since the oxidations produce water as a side product.

Studies were undertaken to elucidate the reaction pathway. Initial experiments, with 2-methylnaphthalene

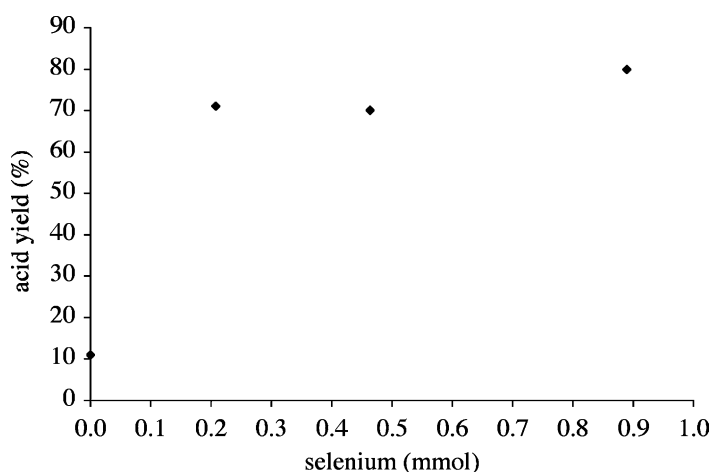


Fig. 1. Effect of catalyst loading on 2-naphthoic acid yield. Reactions were run with 2-methylnaphthalene (10 mmol) in 7 ml of *o*-dichlorobenzene for 4 h at 160 °C. A 1:1 mixture of NO:O₂ was bubbled through the reaction mixture.

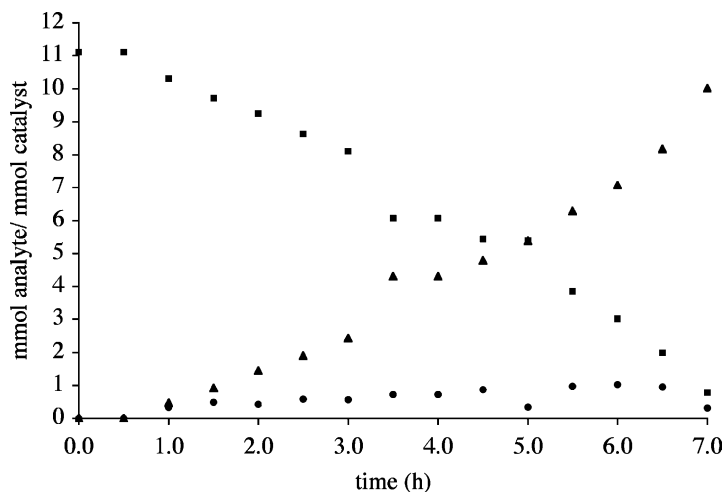


Fig. 2. Kinetics for the oxidation of 2-methylnaphthalene (20 mmol) using selenium (1.80 mmol) in 14 ml of dimethyl sulfoxide with a 1:1 mixture of NO:O₂ bubbled through. Reactions were run at 150 °C. ■, 2-methylnaphthalene; ●, 2-naphthaldehyde; ▲, 2-naphthoic acid.

showed that the aldehyde could be produced in preference to the acid if only a trace of nitric oxide was used. Under these conditions 2-naphthaldehyde and 2-naphthoic acid were obtained in 37 and 3% isolated yields, respectively (both isolated by liquid chromatography and confirmed by NMR spectroscopy). Here, the remaining yield was only unreacted starting material. Conclusive evidence that the alde-

hyde is an intermediate even under the standard reaction conditions came from kinetic experiments. 2-Naphthaldehyde was present in steady-state concentrations in reactions using either elemental selenium (Fig. 2) or selenium dioxide (Fig. 3). These figures also indicate similar oxidation rates for both selenium and selenium dioxide. Indeed, turnover rates of 1.4 and 1.3 mmol substrate/mmol catalyst h are obtained

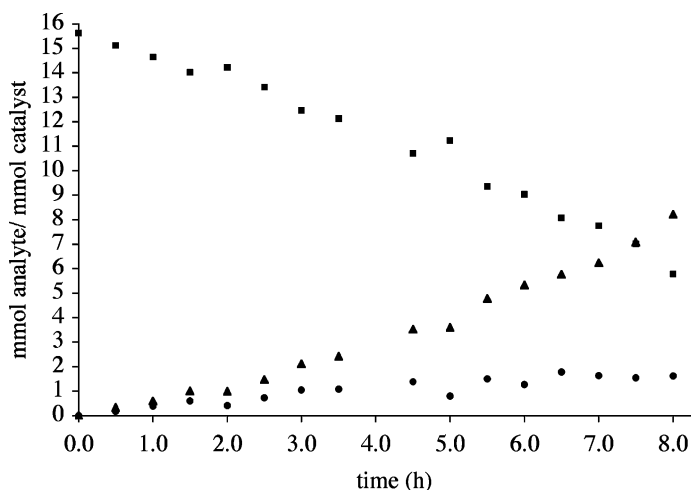
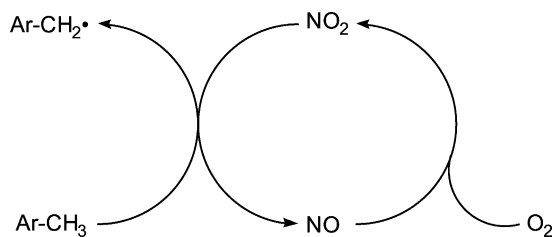


Fig. 3. Kinetics for the oxidation of 2-methylnaphthalene (20 mmol) using selenium dioxide (1.28 mmol) in 14 ml of dimethyl sulfoxide with a 1:1 mixture of NO:O₂ bubbled through. Reactions were run at 150 °C. ■, 2-methylnaphthalene; ●, 2-naphthaldehyde; ▲, 2-naphthoic acid.



Scheme 1.

for selenium and selenium dioxide, respectively. The similarity between the two rates and the near identical curve shape suggests that initial oxidation of elemental selenium is fast.

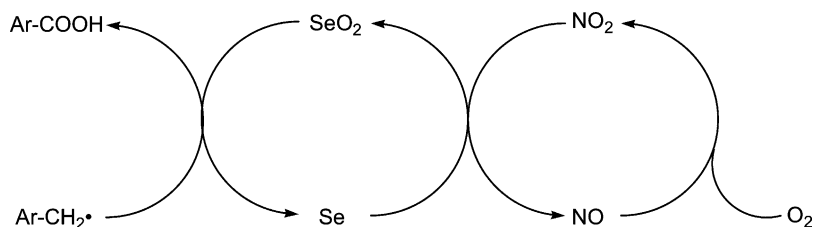
Schemes 1 and 2 summarize our proposed mechanism based on the observed reaction characteristics. Nitric oxide is known to oxidize rapidly and spontaneously to nitrogen dioxide (NO_2) with dioxygen [23] (N_2O_3 has been proposed as an intermediate in this reaction [24]). Nitrogen dioxide, thus generated, has two functions. First, it abstracts one of the weak benzylic hydrogen atoms from the substrate to form the corresponding benzyl radical, nitric oxide, and water (Scheme 1). Because of weaker C–H bonds, this is a more facile process for methyl groups on naphthalene (BDE = 86 kcal/mol) compared to those on benzene (BDE = 89 kcal/mol). Indeed, lower yields of acids were obtained from toluene and *p*-xylene than from 2-methylnaphthalene. Note that control experiments with selenium dioxide and 2-methylnaphthalene indicate that very little oxidation occurs in the absence of NO_x (NO_2/NO). While nitric oxide and nitrogen dioxide are both odd-electron species and are, in principle, capable of hydrogen atom abstraction; theoretical calculations suggest that the activation energy for hydrogen-atom abstraction is significantly lower with NO_2 than NO [25].

The second role of nitrogen dioxide is to oxidize selenium to selenium dioxide. This oxidation did not occur in the absence of NO_x . As described above, selenium dioxide was isolated from the reaction of selenium with the NO_x/O_2 mixture. Thus, NO_x serves as a catalyst for the oxidation of selenium by oxygen (Scheme 2). The selenium dioxide (or H_2SeO_3 , formed in the presence of water), then selectively oxidizes the benzyl radical to the corresponding aldehyde (Scheme 2). Experiments show that 2-naphthaldehyde is quickly converted to the acid even in the absence of selenium or selenium dioxide. Thus, either a parallel pathway operates where the selenium catalyst and NO_x are responsible for the formation of the acid from the aldehyde, or the NO_x acts exclusively to form acid from aldehyde. In the absence of selenium dioxide (or H_2SeO_3), the benzyl radical reacts further with NO_x and O_2 to form a host of unidentifiable products. Thus, nitrogen dioxide is required to form the benzyl radical and selenium dioxide is required for the selective oxidation of this radical.

The rate-determining step in the proposed multi-step reaction appears to be the initial hydrogen-atom abstraction. This is supported by the observation of a large kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 8.5$) in a competition reaction involving h_8 -toluene/ d_8 -toluene. High values for $k_{\text{H}}/k_{\text{D}}$ have been attributed to a linear transition state associated with homolytic C–H bond breaking [26,27], and is inconsistent with the pericyclic mechanism commonly invoked for the somewhat analogous allylic oxidations by selenium dioxide.

4. Conclusion

An unusual nitric oxide/selenium dioxide-mediated procedure for benzylic oxidations by dioxygen is described. The aldehyde is the initial product but it is



Scheme 2.

rapidly converted to the corresponding acid. Good to excellent yields were obtained for a series of alkyl-naphthalenes and alkyipyridines. It is possible to start with either elemental selenium or selenium dioxide since the former is rapidly oxidized to the latter under the reaction conditions. Mechanistic studies suggest that the rate-determining step is hydrogen atom abstraction by nitrogen dioxide forming the benzyl radical. Selenium dioxide subsequently oxidizes this radical to the desired product. Nitrogen dioxide also serves to oxidize selenium to selenium dioxide.

Acknowledgements

JER thanks the NCER STAR/EPA fellowship for financial support. This work was funded by Dow Chemical and the National Science Foundation.

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