Preparation of Purified $KHSO_5 \cdot H_2O$ and $n Bu_4NHSO_5$ from Oxone by Simple and Efficient Methods

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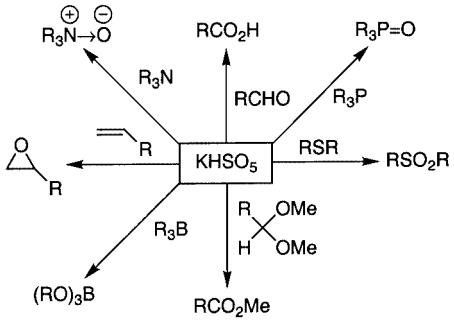
Keywords: Oxone / Oxidation / Synthetic methods / Potassium peroxymonosulfate / Tetrabutylammonium peroxymonosulfate

The chemistry of various salt forms of Oxone, an environmentally friendly oxidant, has been investigated. In addition to advances in the preparation of analytically pure $KHSO_5 \cdot H_2O$ and $n Bu_4NHSO_5$, a soluble form of this oxidant, we have also studied some of the known oxidative chemistry that utilizes Oxone as the oxidant. Our results indicate that utilizing purified reagents makes these reactions easier to workup and amenable to large scale synthesis because the amount of salt in the reaction has been greatly reduced.

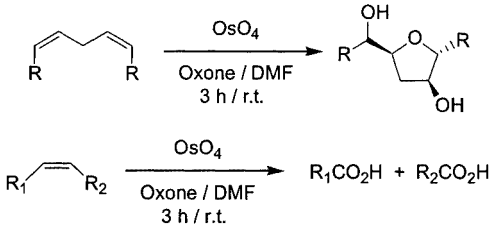
Introduction

Caro's acid (H_2SO_5) has had an intriguing history.[1,2] A potentially explosive substance that once proved difficult to isolate, purify, and identify now exists as a stable triple salt ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) sold under the trademark name of Oxone.[3–7] The active oxidant within the mixture, peroxymonosulfate (HSO_5^-), has been the subject of study in various fields ranging from atmospheric science to physical and computational chemistry. For example, HSO_5^- is proposed to be an intermediate in the atmospheric oxidation of sulfur and it is hypothesized that 35% of the total sulfur species in clouds exist as HSO_5^-.[8,9] The physical characteristics of peroxymonosulfate have also sparked debate. Two such examples include the standard electrochemical potential of HSO_5^- and the mode of HSO_5^- decomposition.[10–15] Organic chemists have also found peroxymonosulfate to be an intriguing molecule, especially since it has gained popularity in use for numerous organic transformations (Scheme 1).

Over the past twenty years, Oxone has become a popular oxidant for the preparation of dimethyl dioxirane in situ from acetone and buffered water to epoxidize olefins.[16] Other advances include oxidations of boron-, nitrogen-, phosphorous-, and sulfur-containing compounds, while it has also been shown to oxidize acetals to esters and aldehydes to acids (Scheme 1).[17–24] Recent work in our laboratory has further demonstrated Oxone's utility in oxidative cyclization and cleavage of olefins (Scheme 2).[25,26] Generally, these oxidations are performed in water, methanol, acetone, DMF, or a miscible mixture including one of the latter solvents. The need for aqueous and/or pH-controlled reactions is perhaps the most significant drawback in the use of Oxone for applications in organic chemistry.



Scheme 1



Scheme 2

To overcome the need for aqueous conditions, several tetraalkylammonium salts of Oxone have been reported. These include ammonium peroxymonosulfate, tetra-*n*-butylammonium peroxymonosulfate (TBA-OX), tetra-*n*-pentylammonium peroxymonosulfate, and tetra-*n*-hexylammonium peroxymonosulfate.[27,28] In 1985, Dehmlow et al. reported a methodology to prepare TBA-OX and other tetraalkylammonium salts of peroxymonosulfate by cat-

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ionic exchange from Oxone.[27] However, only in 1988 did Trost and co-workers popularize TBA-OX as an organic soluble form of Oxone that was capable of oxidizing sulfides to sulfones under anhydrous conditions.[28] This reagent was prepared from cationic exchange of the bulk potassium ions, and thus yielded a soluble version of the triple salt; i.e., tetra-*n*-butylammonium salts of sulfate and bisulfate were also formed. The oxidative activity of the nBu$_4$NHSO$_5$ was 37.5% of the actual weight.

A second type of soluble peroxymonosulfate has been described recently by Hajipour and co-workers.[29] The reported benzyltriphenylphosphonium peroxymonosulfate salt has the ability to perform some of the oxidative reactions that are well developed for Oxone. These include oxidation of alcohols to aldehydes and ketones and the deprotection of acetals, trimethylsilyl ethers and tetrahydropyranyl ethers to yield the corresponding alcohols.[29−32]

While Oxone is a convenient and cheap triple salt to purchase (approx. $10/Kg), there is only about 50% of active oxidant per mol of the triple salt. Several methods have been developed to prepare the pure potassium salt of peroxymonosulfate, yet these purified oxidants have not been used in synthesis, most probably due to the less than convenient procedures necessary to purify the oxidant. Appleman et al. isolated and characterized pure KHSO$_5$ and KHSO$_5$·H$_2$O by passage of sodium peroxydisulfate (Na$_2$S$_2$O$_8$) through a cationic ion-exchange resin, followed by hydrolysis of the peroxydisulfate at 50 °C to yield an equimolar mixture of peroxymonosulfate and bisulfate. Adjustment of the pH with KHCO$_3$ and lyophilization yielded the purified KHSO$_5$·H$_2$O.[33] This resulted in one of two reported crystal structures of KHSO$_5$·H$_2$O. Interestingly, both reports were published within months of each other.[34,35] The purification of KHSO$_5$·H$_2$O was revisited by Connick et al. in the early 90's along with a modified method for its preparation.[36] Essentially, a straightforward filtration protocol starting from Oxone, followed by evaporation and crystallization resulted in the isolation of analytically pure KHSO$_5$·H$_2$O. Again, this method received little attention from organic chemists perhaps due to its limitations upon scale-up where the removal of large volumes of water is required.

Herein, we describe a modified, straightforward, and stepwise procedure for the preparation of pure KHSO$_5$·H$_2$O (>99% activity) from Oxone. Additionally, the preparation of analytically pure tetra-*n*-butylammonium peroxymonosulfate (TBA-OX) from KHSO$_5$·H$_2$O is described. A procedure to not only purify but also obtain nBu$_4$NHSO$_5$ from the Oxone triple salt in one step is provided. Furthermore, the chemical reactivity of commercially available Oxone is compared with pure KHSO$_5$·H$_2$O and two soluble forms of the oxidant.

Results and Discussion

Preparation of pure KHSO$_5$·H$_2$O and KHSO$_5$

From a preparative point of view, a comparison of the two reported methods to obtain KHSO$_5$·H$_2$O in pure form favors the method described by Connick et al.[36] The procedure is easier since the starting material is Oxone, which contains the active oxidant and does not lose activity over time. This method provides the desired pure KHSO$_5$·H$_2$O, but requires a laborious removal of water, which is followed by crystallization of the product. This limits the scale on which the procedure can be performed easily. In order to satisfy our need for large amounts of KHSO$_5$·H$_2$O, we have devised a preparative scheme that is not only facile, and reproducible, but also amenable to large scale production (0.5 mol).

To prepare the purified oxidant, commercially available Oxone was added to deionized (DI) water (1:1 w/w) and swirled for 5 min until the noticeable fizzing subsided. Molecular oxygen is the gas evolved during the mixing of Oxone with water. This was shown by bubbling the gas through a suspension of CuI in aqueous NH$_4$OH. The solution turned blue immediately as Cu^{2+} was generated through oxidation of Cu^{+} with oxygen. The overall loss of oxidant is less than 2% (measured via iodometric titration of the solution after the evolution of gas had ceased), and is probably due to chemisorbed oxygen in the solid Oxone.

Potassium peroxymonosulfate is more soluble in H$_2$O than the corresponding sulfate salts and is dissolved preferentially. However, keeping the slurry for a prolonged time allows the salts to equilibrate and lower yields are obtained. The cold slurry (at about 10 °C) was filtered and washed with minimal amounts of cold DI H$_2$O. The initial pH of this clear solution was about 1.0. The pH of the filtrate was adjusted to 3.5 by addition of solid KHCO$_3$ while continuously stirring the solution. At the endpoint a noticeable pink color was observed along with the formation of some precipitate. We found that overshooting the endpoint resulted in a reduced yield of the purified material. If need be, the pH can be readjusted with a few drops of concentrated H$_2$SO$_4$. This pink slurry was filtered and the solid was washed with MeOH (2 volumes) and combined with the original water filtrate resulting in the formation of more precipitate. The precipitate was again filtered and washed with MeOH (1 volume). The slightly cloudy solution containing water and MeOH (1:3 v/v) was placed in a freezer overnight to crystallize the purified product. The thick slurry was filtered and washed with Et$_2$O to provide KHSO$_5$·H$_2$O in 45% yield (based on oxidative equivalence as compared to Oxone). The crop was found to be 99.1% pure after triplicate iodometric titration. A second crop (4%) could be obtained if the filtrate containing the water, methanol, and diethyl ether mixture was again placed in the freezer overnight. This material showed negligible loss of activity over a prolonged period of time (6 months) when stored on the bench top in an amber bottle.

KHSO$_5$·H$_2$O can be dried under vacuum at room temperature to yield pure anhydrous KHSO$_5$. Although we have not had any incidents of rapid decomposition or explosion with Oxone (triple salt or purified) when heated, the oxidizing activity is lost at 70 °C, and thus drying the sample should be carried out at room temperature. Also noteworthy is that dry KHSO$_5$ does not seem to be a con-

tact explosive. This was tested by repeatedly hammering a sample on a smooth flat surface. The two major advantages of the latter procedure are the immediate crystallization of $KHSO_5 \cdot H_2O$ that provides analytically pure product, and the fact that large volumes of water need not be removed via evaporation. The only limit to perform this procedure effectively on a large scale is the need for several large flasks.

There is a significant advantage for converting the commercially available Oxone to purified $KHSO_5 \cdot H_2O$ since less weight of salt is required. Oxone's ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) molecular weight of 615 g/mol is equivalent to 307 g/mol of oxidizing equivalence. This is significantly more than $KHSO_5 \cdot H_2O$ (170 g/mol). Thus, the use of purified Oxone results in more oxidant per mol of salt. This significantly reduces the amount of oxidant needed, which could be a major factor when doing large-scale chemistry.

Preparation of Soluble Oxone

As mentioned previously nBu$_4$NHSO$_5$ (TBA-OX) has been prepared by both the Dehmlow and Trost groups with 61% and 37.5% activity, respectively. While the preparative methods are similar, it is necessary to explain the differences to better understand how it has led us to obtain >98% active TBA-OX with only minor modifications. Dehmlow's procedure requires the preparation of two solutions, a concentrated aqueous solution of Oxone and a solution of nBu$_4$NHSO$_4$. The two solutions were mixed together overnight and the TBA-OX was isolated by extraction with CH_2Cl_2. In contrast, Trost's procedure utilizes five equivalents of nBu$_4$NHSO$_4$ per equivalent of Oxone. The two reagents are mixed for 30 min in water, followed by extraction with CH_2Cl_2 to provide 37.5% active TBA-OX. The two examples above yield products with different activities, probably due to two factors: time of mixing prior to extraction and the ratio of nBu$_4$NHSO$_4$ and Oxone used for preparation of soluble Oxone. Optimization of both factors should lead to the isolation of a more pure product with higher activity.

We have found that the solubility of nBu$_4$NHSO$_5$ in CH_2Cl_2 (352 mg/mL) is higher than the solubility of nBu$_4$NHSO$_4$ in the same solvent (168 mg/mL). Thus, it should be possible to preferentially extract nBu$_4$NHSO$_5$ over nBu$_4$NHSO$_4$. It is plausible that the excess amount of nBu$_4$NHSO$_4$ used in Trost's extraction procedure counterbalances the higher solubility of TBA-OX and leads to the extraction of nBu$_4$NHSO$_4$ along with TBA-OX. To illustrate this point Oxone (1 equiv.) and varying amounts of nBu$_4$NHSO$_4$ were used to extract TBA-OX into CH_2Cl_2. As can be seen from Figure 1, lowering the amount of nBu$_4$NHSO$_4$ used in the extraction greatly enhances the purity of the extracted TBA-OX (range of 35% to 91%), presumably due to the higher solubility of nBu$_4$NHSO$_5$ in CH_2Cl_2. Therefore, by utilizing one equivalent of nBu$_4$NHSO$_4$ in a single extraction, 88% of the oxidative equivalence is obtained in soluble form (TBA-OX). Additionally we do not find it necessary to mix the solids for an extended amount of time, but instead simply mixing both solids in water followed by an immediate extraction provided reproducible results. We attribute the success of this procedure to the fact that $KHSO_5$ dissolves preferentially over $KHSO_4$ and K_2SO_4, and that nBu$_4$NHSO$_5$ is more soluble in CH_2Cl_2 than nBu$_4$NHSO$_4$ in the same solvent.

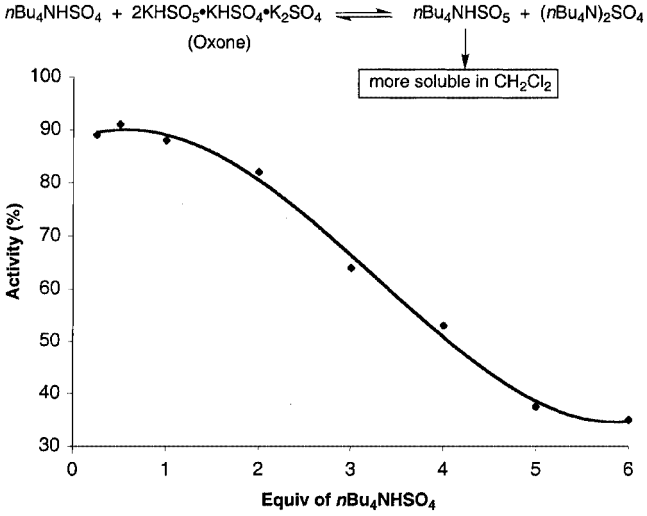


Figure 1. Extraction of TBA-OX from Oxone into CH_2Cl_2 with various equiv. of nBu$_4$NHSO$_4$; higher extraction efficiencies are realized with less nBu$_4$NHSO$_4$

Utilizing the same extraction technique, the preparation of analytically pure TBA-OX is feasible simply by extracting pure $KHSO_5 \cdot H_2O$ (1 equiv.) with nBu$_4$NHSO$_4$ (1.2 equiv.). In fact, single extraction with purified $KHSO_5 \cdot H_2O$ yields >98% active TBA-OX. The two methods described above use stoichiometric amounts of nBuNHSO$_4$ to easily prepare pure TBA-OX. The highly purified TBA-OX (>98%) is stable for more than six months at room temperature in an amber vial. Moreover, removal of residual water from the purified TBA-OX under vacuum causes no problems. This should allow for the use of TBA-OX in an anhydrous form for oxidations in organic solvents without the necessity for using a great excess of oxidant or mixed tetrabutylammonium salts. It should be noted that heating of TBA-OX at 70 °C in order to speed up the drying leads to the decomposition of the oxidant (complete loss of activity).

The latter experiments strongly suggest that solubility plays a major role in obtaining pure nBu$_4$NHSO$_5$. To demonstrate this further we have compared the solubility of $KHSO_5 \cdot H_2O$ and TBA-OX. $KHSO_5 \cdot H_2O$ possesses very poor solubility in CH_2Cl_2 such that a 1:6 (w/w) mixture of $KHSO_5 \cdot H_2O$ and TBA-OX resulted in 99% recovery of the $KHSO_5 \cdot H_2O$ after filtration. To ensure that the oxidative equivalence measured by iodometric titrations of the organic phase are not a result of $KHSO_5 \cdot H_2O$'s partial solubility in CH_2Cl_2, $KHSO_5 \cdot H_2O$ was vigorously stirred with CH_2Cl_2 and the filtrate was titrated for oxidizing activity. The iodometric titrations showed less than 1% activity present in the organic filtrate based on the starting amount of $KHSO_5 \cdot H_2O$.

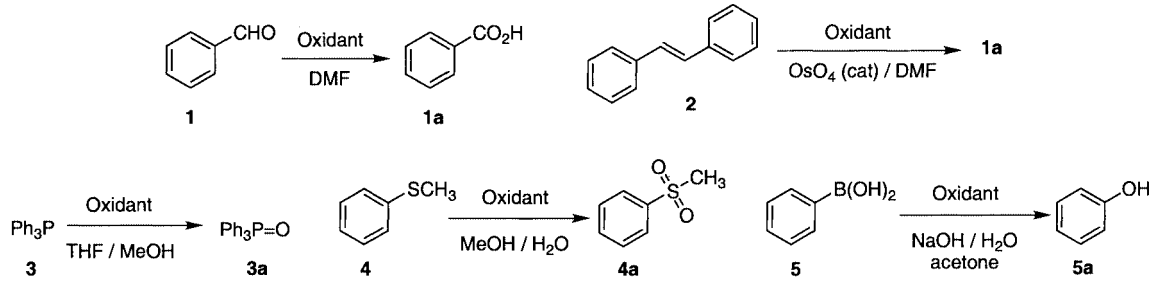
The soluble salt forms of Oxone have a good solubility profile with various organic solvents, thus making it possible to use a large number of organic solvents for the oxidations. This is clearly an advantage over traditional Oxone chemistry, which uses water in a large number of the reported reactions. Oxone (triple salt) is practically insoluble in all solvents except water, although the $KHSO_5$ portion of Oxone does have some solubility in other solvents such as DMF. $KHSO_5 \cdot H_2O$ is also soluble in water, however, it exhibits notable solubility in DMF (100 mg/mL) and slight solubility in MeOH. TBA-OX is completely soluble in DMF, acetone, water, $CHCl_3$, CH_2Cl_2, CH_3NO_2, CH_3CN, and MeOH at 100 mg/mL (this is not to say the solutions are saturated). Other solvents such as EtOAc, hexanes, CCl_4, benzene, THF, and Et_2O are not able to dissolve TBA-OX. Comparably, $Ph_3BnPHSO_5$ is soluble only in MeOH, $CHCl_3$, CH_2Cl_2, and DMF and insoluble in all other solvents tested. Interestingly, none of the soluble salt forms of Oxone are soluble in diethyl ether. This could perhaps be beneficial since it can provide an easy route to remove the oxidant and its by-products (usually $n Bu_4NHSO_4$) by simple precipitation from the reaction mixture upon addition of diethyl ether.

Peroxysulfate Salts as Oxidizing Reagents

As discussed above, Oxone is an effective oxidant in many types of transformations. Having at hand a simple method to synthesize both the $KHSO_5 \cdot H_2O$ and $n Bu_4NHSO_5$ forms, a comparison of their reactivity was pursued. Through a set of simple experiments Oxone, $KHSO_5 \cdot H_2O$, TBA-OX, and $Ph_3PBnHSO_5$ (TPPB-OX) were compared directly in five different reaction types. The results are summarized in Table 1. Essentially, Oxone and $KHSO_5 \cdot H_2O$ show no significant differences in reactivity or yield of isolated products in the reactions studied, namely, oxidation of benzaldehyde to benzoic acid, oxidative cleavage of *trans*-stilbene to benzoic acid, oxidation of triphenylphosphane to triphenylphosphane oxide, oxidation of thioanisol to methylphenylsulfone, and oxidative cleavage of phenylboronic acid to phenol. On the other hand, TBA-OX is ineffective in oxidizing benzaldehyde to benzoic acid and not very effective in cleaving the C−B bond of phenylboronic acid, providing phenol in only 40% yield. However, as reported by others for the less pure TBA-OX, it is efficient for the oxidation of both phosphorous and sulfur. Use of TBA-OX for oxidative cleavage of olefins was attempted with *trans*-stilbene. Although both Oxone and $KHSO_5 \cdot H_2O$ yield benzoic acid as the oxidation product, TBA-OX leads to the isolation of benzaldehyde as the sole product in 88% yield. Clearly, the soluble form of Oxone has attenuated activity. This is a beneficial outcome since selectivity can be exercised based on the oxidant utilized for the reaction. TPPB-OX is a rather poor oxidant for the reactions illustrated here except for the oxidation of triphenylphosphane, giving a 98% yield of triphenylphosphane oxide.

During the course of our study we found that using purified reagents show only minor reactivity differences, and that the workup is facile for all substrates on a 1 mmol scale. However, extraction and chromatography are more tedious upon scale-up. To investigate this further we evaluated the oxidation of triphenylphosphane with Oxone, $KHSO_5 \cdot H_2O$, $n Bu_4NHSO_5$ (30%, containing other $n Bu_4N$ sulfate salts) and $n Bu_4NHSO_5$ (98%) on a 10 mmol scale. Not surprisingly, the starting material was cleanly converted into the corresponding triphenylphosphane oxide over a 2 h period with all the oxidants utilized. In a typical experiment, removal of the organic solvent under reduced pressure by 50% was followed by precipitation of the salts with Et_2O. The precipitation was completed upon storing of the

Table 1. Oxidation of various functionalities with Oxone and soluble Oxone[a]



Substrate	Product	Oxone[b]	$KHSO_5$	TBA-OX	TPPB-OX
Benzaldehyde (**1**)	benzoic acid (**1a**)	97%	94%	N.R.[b]	N.R.[b]
trans-Stilbene (**2**)	(**1a**)	95%	97%	88%[c]	25% [c]
Triphenylphosphane (**3**)	triphenylphosphane oxide (**3a**)	98%[d]	99%	97%	98%
Thioanisol (**4**)	methylphenylsulfone (**4a**)	95%[d]	90%	91%	52%
Phenylboronic acid (**5**)	phenol (**5a**)	86%[d]	80%	40%	30%

[a] See Exp. Sect. for reaction details. [b] Starting material was recovered (90% for TBA-OX, 85% for TPPB-OX). [c] Yield of **1**. [d] Yield reported in the literature.

filtrate in the freezer for 3 h, and the salts were removed by filtration to provide excellent yields of the product (>95% in all cases after removal of solvent). Oxidation with pure nBu_4NHSO_5 led to only 3% of the tetrabutylammonium salts remaining in the final product. However, when 30% active nBu_4NHSO_5 was used the product was contaminated with 35% of tetrabutylammonium salt. Both Oxone and $KHSO_5 \cdot H_2O$ yield clean products, but less Et_2O is required for precipitation and washing using the purified $KHSO_5 \cdot H_2O$. Thus, for large-scale reactions it is advantageous to use purified oxidant to reduce the amount of solvent needed for purification. Also, use of pure soluble oxidants yields products of higher purity after a simple filtration of the tetrabutylammonium salts.

Conclusion

Oxone is a cheap commercially available oxidant that easily oxidizes numerous functional groups. It is also an environmentally friendly oxidant with no toxic by-products, and thus is an attractive green reagent. In this study, we have developed a facile procedure for the preparation of pure $KHSO_5 \cdot H_2O$ in a straightforward and efficient manner, which is amenable to large scale production. An improved procedure for the preparation of nBu_4NHSO_5 has also been developed that requires much less nBu_4NHSO_4 and delivers high purity in a single extraction from either Oxone or $KHSO_5 \cdot H_2O$. The purified $KHSO_5 \cdot H_2O$ is as effective as Oxone, but requires only half the mass of oxidant, thus making the reaction workups more facile. Column chromatography was generally not necessary with either Oxone or $KHSO_5 \cdot H_2O$ reactions. The high purity of TBA-OX leads to easier purification since less tetrabutylammonium ions are present. TBA-OX is also unique in that it does not oxidize aromatic aldehydes, but remains as effective as Oxone in the oxidative cleavage reaction, thus providing an alternate oxidant for procuring aldehydes instead of carboxylic acids.

Experimental Section

General Remarks: All commercially available starting materials were obtained from Aldrich and used without further purification except for benzaldehyde, which was distilled prior to use. ^1H and ^{13}C spectra were recorded on a 300 MHz NMR spectrometer (VARIAN INOVA) in $CDCl_3$. Column chromatography was performed using Silicycle (40−60 μm) silica gel. Analytical TLC was done using pre-coated silica gel 60 F_{254} plates. GC analysis was performed using a HP (6890 series) GC system equipped with a capillary column (AltechSE-54, 30 m × 320 μm × 0.25 μm).

Preparation of $KHSO_5 \cdot H_2O$: Commercially available Oxone (307 g, 0.5 mol) was placed into a 2 L Erlenmeyer flask. DI H_2O (307 mL) was added and swirled for 5 min until the noticeable fizzing subsided (internal temperature 10 °C). The slurry was filtered (Buchner funnel with Whatman filter paper) and washed with cold DI H_2O (30 mL). With the aid of a pH meter, the pH of the filtrate was adjusted to 3.5 by addition of solid $KHCO_3$ (approx. 75 g) with stirring. The initial pH of this clear solution was about 1.0 and at the endpoint a pink color was observed. We found that overshooting the endpoint resulted in a reduced yield of the purified material. If need be, the pH can be readjusted with a few drops of concentrated H_2SO_4. The pink slurry was filtered (Buchner funnel with Whatman filter paper) and the solid was washed with MeOH (2 × 307 mL) into the original water filtrate resulting in the formation of more precipitate in the filtrate. This precipitate was again filtered (Buchner funnel with Whatman filter paper) and washed with MeOH (307 mL). The slightly cloudy solution containing water (337 mL) and MeOH (921 mL) was placed in the freezer overnight to crystallize the purified product. The thick slurry was filtered and washed with Et_2O (4 × 200 mL) to yield 76.88 g, 45% yield of $KHSO_5 \cdot H_2O$ and found to be 99.1% pure after triplicate iodometric titration. A second crop (6.52 g, 4% yield) could be obtained if the filtrate containing the water, methanol, and diethyl ether mixture was again placed in the freezer overnight. The second crop was found to be 98.9% pure after iodometric titration.

Iodometric Titration of $KHSO_5 \cdot H_2O$: The iodometric titrations for purified $KHSO_5 \cdot H_2O$ were all performed in triplicate. $KHSO_5 \cdot H_2O$ (250.6 mg) was dissolved in DI H_2O (75 mL), 25% (w/w) KI (10 mL), and 10% (v/v) H_2SO_4 (15 mL). The dark brown solution was immediately titrated with 0.1003 M $Na_2S_2O_3$ to a slightly yellow endpoint. This method was adopted from the procedures developed by DuPont, Inc., and can be found at the following website: http://www.dupont.com/oxone/techinfo/index.html.

Preparation of nBu_4NHSO_5. Method A, using $KHSO_5 \cdot H_2O$: Pure $KHSO_5 \cdot H_2O$ (15 g, 88.2 mmol) was dissolved in DI H_2O (50 mL) and placed into a separating funnel. A slight excess of nBu_4NHSO_4 (31.4 g, 92.6 mmol) was added to the separating funnel and the slurry was extracted with CH_2Cl_2 (4 × 100 mL). The combined organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure providing nBu_4NHSO_5 (31.5 g, 96% yield based on nBu_4NHSO_4, 98.6% activity) as a white solid.
Method B, using Oxone: Oxone (2 g, 3.25 mmol) was dissolved in DI H_2O (20 mL) and placed into a separating funnel. nBu_4NHSO_4 (0.25 → 6 equiv.) was added to the funnel and the slurry was extracted with CH_2Cl_2 (6 × 50 mL). The combined organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure to provide nBu_4NHSO_5 in 90 → 99% yield based on nBu_4NHSO_4 and ranged in activity from 35 → 91% activity based on triplicate iodometric titration.

Iodometric Titration of nBu_4NHSO_5:[28] The assay was performed in triplicate using the following procedure. nBu_4NHSO_5 (200.3 mg) was dissolved in glacial acetic acid (2 mL), 10% (w/w) NaI (4 mL), and diluted with distilled THF (14 mL). The dark brown solution was immediately titrated with 0.1276 M $Na_2S_2O_3$ to reach the slightly yellow endpoint.

Oxidations of Benzaldehyde: Benzaldehyde (100 mg, 0.94 mmol, 1 equiv.) was dissolved in DMF (0.1 M). The appropriate HSO_5^- salt (1.1 equiv.) was added in one portion and the reaction was stirred at room temp. for 18 h. 1 N HCl (25 mL) was then added to dissolve the salts and Et_2O (25 mL) was added to extract the products. The organic extract was washed three times with 1 N HCl and brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The reaction with Oxone and $KHSO_5 \cdot H_2O$ yielded benzoic acid in yields of 97% (111 mg) and 94% (108 mg), respectively. The products were analytically pure and did not require additional purification. Oxidation with TBA-OX and $Ph_3PBnHSO_5$ led to the isolation of starting material. The products of the latter two reactions were purified by column chromatography with CH_2Cl_2 as the eluent.

Oxidations of *trans*-Stilbene: *trans*-Stilbene (100 mg, 0.55 mmol, 1 equiv.) was dissolved in DMF (0.1 M), and OsO_4 (0.01 equiv., 2.5% in *t*BuOH) was added and stirred for 5 min. The appropriate HSO_5^- salt (4.4 equiv.) was added in one portion and the reaction was stirred at room temp. for 18 h. Na_2SO_3 (2 equiv.) was added and stirred for an hour or until the solution became dark brown/black to reduce the remaining Os(VIII) species. 1 N HCl was added to dissolve the salts and EtOAc was added to extract the products. The organic extract was washed three times with 1 N HCl and brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Oxidation with Oxone and $KHSO_5{\cdot}H_2O$ yielded benzoic acid in 95% (128 mg), and 97% (131 mg) yield, respectively. The products were analytically pure and did not require additional purification. TBA-OX and $Ph_3PBnHSO_5$ oxidation of *trans*-stilbene provided benzaldehyde in yields of 88% (104 mg) and 25% (29 mg), respectively. The products of the latter two reactions were purified by column chromatography with CH_2Cl_2 as the eluent.

Oxidations of Triphenylphosphane: Triphenylphosphane (300 mg, 1.14 mmol, 1 equiv.) was dissolved in THF/MeOH (1:1, 0.1 M). The appropriate HSO_5^- salt (1.1 equiv.) was added in one portion and the reaction was stirred at room temp. for 1 h. The solvent was removed under reduced pressure and the products were purified by column chromatography with CH_2Cl_2 as the eluent. Oxidation of triphenylphosphane with $KHSO_5{\cdot}H_2O$, TBA-OX, and $Ph_3PBnHSO_5$ led to the isolation of triphenylphosphane oxide in yields of 99% (325 mg), 97% (318 mg), and 98% (107 mg), respectively.

Oxidations of Thioanisol with $KHSO_5{\cdot}H_2O$: Thioanisol (347 mg, 2.8 mmol, 1 equiv.) was dissolved in MeOH/H_2O (1:1, 0.1 M). $KHSO_5{\cdot}H_2O$ (524 mg, 3.1 mmol, 1.1 equiv.) was added in one portion and the reaction was stirred at room temp. for 4 h. The solvent was diluted with CH_2Cl_2 and water. The aqueous fraction was washed with CH_2Cl_2 (3 × 40 mL) and the combined organic extract was washed with brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain methylphenylsulfone (90%, 393 mg).

Oxidation of Thioanisol with TBA-OX: Thioanisol (347 mg, 2.8 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (0.1 M). TBA-OX (1.1 g, 3.1 mmol, 1.1 equiv.) was added in one portion and the reaction was stirred at room temp. for 3 days. The reaction was absorbed onto silica gel and was purified by column chromatography with CH_2Cl_2 to obtain methylphenylsulfone (91%, 398 mg). Oxidation of thioanisol with $Ph_3PBnHSO_5$ followed the same procedure outlined above for TBA-OX and led to the isolation of methylphenylsulfone (52%, 75 mg).

Oxidations of Phenylboronic Acid: Phenylboronic acid (100 mg, 0.82 mmol, 1 equiv.) and NaOH (50 mg) were stirred for 5 min in H_2O (3 mL). $NaHCO_3$ (8.2 mmol, 10 equiv.), the appropriate HSO_5^- salt (1.1 equiv.), 400 μM EDTA (4 mL), and acetone (1 mL) were added at 0 °C and stirred for 15 min. The reaction was quenched with sodium bisulfite and extracted with EtOAc. The organic extract was washed twice with 1 N HCl, H_2O, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product, which was purified by column chromatography with CH_2Cl_2. Oxidation with $KHSO_5{\cdot}H_2O$, TBA-OX, and $Ph_3PBnHSO_5$ yielded phenol in yields of 80% (62 mg), 40% (31 mg), and 30% (23 mg), respectively.

Acknowledgments

Generous support was provided in part by Michigan State University Startup funds to B. B. and a grant from the Michigan Economic Development Corporation (GR-183).

[1] M. Renz, B. Meunier, *Eur. J. Org. Chem.* **1999**, 737−750.
[2] H. Caro, *Angew. Chem.* **1898**, 845−846.
[3] J. O. Edwards, *Chem. Eng. News* **1955**, *33*, 3336−3337.
[4] R. Willstatter, E. Hauenstein, *Ber.* **1909**, *42*, 1839−1850.
[5] T. S. Price, *J. Chem. Soc.* **1906**, 53−59.
[6] H. Ahrle, *Z. Angew. Chem.* **1910**, *22*, 1713−1715.
[7] J. D′Ans, W. Friedrich, *Ber.* **1910**, *43*, 1880−1882.
[8] D. J. Jacob, *J. Geophys. Res.* **1984**, *89*, 1429−1433.
[9] D. J. Jacob, *J. Geophys. Res.-Atmos.* **1986**, *91*, 9807−9826.
[10] R. C. Thompson, *Inorg. Chem.* **1981**, *20*, 1005−1010.
[11] P. A. G. O′Hare, L. Basile, E. H. Appelman, *J. Chem. Thermodyn.* **1985**, *17*, 473−480.
[12] J. S. Price, I. R. Tasker, E. H. Appelman, P. A. G. O′Hare, *J. Chem. Thermodyn.* **1986**, *18*, 923−930.
[13] D. L. Ball, J. O. Edwards, *J. Am. Chem. Soc.* **1956**, *78*, 1125−1129.
[14] W. V. Steele, E. H. Appelman, *J. Chem. Thermodyn.* **1982**, *14*, 337−344.
[15] D. A. Horner, R. E. Connick, *Inorg. Chem.* **1986**, *25*, 2414−2417.
[16] S. E. Denmark, D. C. Forbes, D. S. Hays, J. S. DePue, R. G. Wilde, *J. Org. Chem.* **1995**, *60*, 1391−1407.
[17] L. A. Wozniak, W. J. Stec, *Tetrahedron Lett.* **1999**, *40*, 2637−2640.
[18] K. S. Webb, S. J. Ruszkay, *Tetrahedron* **1998**, *54*, 401−410.
[19] K. S. Webb, D. Levy, *Tetrahedron Lett.* **1995**, *36*, 5117−5118.
[20] B. M. Trost, D. P. Curran, *Tetrahedron Lett.* **1981**, *22*, 1287−1290.
[21] A. L. Baumstark, M. Beeson, P. C. Vasquez, *Tetrahedron Lett.* **1989**, *30*, 5567−5570.
[22] M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, *Synlett* **1999**, 777−779.
[23] F. A. Davis, S. G. Sal, *J. Org. Chem.* **1988**, *53*, 5004−5007.
[24] F. A. Davis, S. Chattopadhyay, J. C. Towson, S. Lal, T. Reddy, *J. Org. Chem.* **1988**, *53*, 2087−2089.
[25] B. R. Travis, R. S. Narayan, B. Borhan, *J. Am. Chem. Soc.* **2002**, *124*, 3824−3825.
[26] B. R. Travis, B. Borhan, *Tetrahedron Lett.* **2001**, *42*, 7741−7745.
[27] E. V. Dehmlow, B. Vehre, J. K. Makrandi, *Z. Naturforsch., Teil B* **1985**, *40*, 1583−1585.
[28] B. M. Trost, R. Braslau, *J. Org. Chem.* **1988**, *53*, 532−537.
[29] A. R. Hajipour, S. E. Mallakpour, H. Adibi, *Chem. Lett.* **2000**, 460−461.
[30] A. R. Hajipour, S. E. Mallakpour, H. Adibi, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *167*, 71−79.
[31] A. R. Hajipour, S. E. Mallakpour, I. M. Baltork, H. Adibi, *Synth. Commun.* **2001**, *31*, 1625−1631.
[32] I. Mohammadpoor-Baltork, M. K. Amini, S. Farshidipoor, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2775−2778.
[33] E. H. Appelman, L. J. Basile, H. Kim, J. R. Ferraro, *Spectroc. Acta Pt. A* **1985**, *41*, 1295−1300.
[34] E. O. Schlemper, R. C. Thompson, C. K. Fair, F. K. Ross, E. H. Appelman, L. J. Basile, *Acta Crystallogr., Sect. C* **1984**, *40*, 1781−1785.
[35] J. Flanagan, W. P. Griffith, A. C. Skapski, *J. Chem. Soc., Chem. Commun.* **1984**, 1574−1575.
[36] R. E. Connick, S. Y. Lee, R. Adamic, *Inorg. Chem.* **1993**, *32*, 565−571.

Received May 25, 2002
[O02283]