**I**). An oven-heated 100-mL three-necked flask containing a magnetic stirring bar was fitted with gas inlet and outlet tubes (the outlet connected to a gas bubbler containing silicon oil) and then was swept with nitrogen. After the apparatus cooled, 40 mL of THF per gram of protected aldehyde along with 2–8 mol % of catalyst (≃40 mg per gram of substrate) was added. The flask was then fitted with a neoprene septum, and the Grignard reagent (1.4 equiv) was added at 0 °C (73 °C for Fe(AcAc)$_3$-catalyzed examples). The reaction mixture was stirred at ambient temperature under nitrogen for 16 h and then poured onto 50 mL of 10% hydrochloric acid. If isolation of the imine is desired, the reaction should be poured onto water only. The organic layer was removed, and the aqueous layer was extracted several times with ether. The combined and dried (MgSO$_4$) ether layers were concentrated to an oil, which may be further purified by radial or flash chromatography.

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**Registry No.** **2a**, 115765-22-5; **3a**, 81522-28-3; **3b**, 1203-68-5; **3c**, 32832-95-4; **3d**, 529-20-4; **3e**, 59059-42-6; **3f**, 28272-96-0; **3i**, 119183-52-7; **3j**, 40137-29-9; **4**, 119183-53-8; **5**, 4383-25-9; **6**, 119183-54-9; benzaldehyde, 100-52-7.

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# Mediated Electrochemical Synthesis of Aromatic Aldehydes, Ketones, and Quinones Using Ceric Methanesulfonate

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Cerium(IV) in aqueous methanesulfonic acid is an excellent reagent for the oxidation of alkyl aromatics and polycyclic aromatics to aldehydes, ketones, and quinones. The benefits of methanesulfonic acid include low cost, low nucleophilicity, stability to anodic and electrochemical oxidation, and high solubility of Ce(III) and Ce(IV) in aqueous solutions of this acid. The properties of this medium are ideal for electrochemical regeneration, giving current efficiencies up to 89% at 500 mA/cm$^2$. With this system, enhanced yields of menadione were obtained by adding Cr(VI). A new solid oxidant, Ce(CH$_3$SO$_3$)$_2$(OH)$_2$·H$_2$O, was produced electrochemically, providing a convenient starting material for these oxidations. Improved selectivity was obtained in the synthesis of *m*-phenoxybenzaldehyde by using this solid material in place of soluble Ce(IV).

Aromatic aldehydes, ketones, and quinones are important chemicals, with applications such as chemical intermediates, pharmaceuticals, agricultural chemicals, pulp and paper chemicals, dyestuffs, and flavor and fragrance materials. The preparation of these partially oxidized chemicals has generally relied on the high selectivity of transition metal oxidants such as chromium(VI),[1] manganese(III),[2] cobalt(III),[3] and cerium(IV).[4,5] The stoichiometric use and disposal of these reagents is undesirable from economic and environmental viewpoints. As a result, there has been much recent interest in the electrochemical recycle of these oxidants.[6]

Mediated, or indirect, electrosynthesis is a cyclic process involving electrochemical generation of a redox agent and use of that agent to effect a chemical reaction. Figure 1 shows the general scheme. A redox agent such as Ce(IV), generated in an electrochemical cell, is contacted with reactant in a conventional chemical reactor to form a product. The spent redox agent is separated from the product and returned to the electrochemical cells. Carrying out the chemical reaction and electrochemical reaction in separate vessels allows each reaction to be independently optimized. Pichaichanarong et al. have recently reviewed engineering aspects of mediated electrosynthesis.[7]

Of the above metal oxidants, chromium(VI) is the most soluble and has the lowest reduction potential and is thus the easiest to regenerate electrochemically. On the other hand, Cr(VI) generally gives the lowest selectivities in the organic oxidations of interest.[8-11] The manganic ion gives good selectivities but is unstable toward disproportionation, except at very high acid concentrations where both Mn(III) and Mn(II) have low solubilities.[10,12] The powerful Co(III) ion is also unstable, due to water oxidation.[3] Cerium(IV) is generally the reagent of choice due to its higher stability and solubility at acid concentrations, which yield excellent selectivities to aromatic carbonyl products.[4-11]

The usefulness of cerium(IV), particularly in indirect electrochemical oxidations, has been limited by the counteranions. Problems include instability toward oxidation (e.g., benzenesulfonate[13] and chloride[14]), reactivity with organic substrates (e.g., nitrate,[15] chloride,[14] and perchlorate[16]), or marginal solubility (e.g., sulfate,[17] acetate,[18]

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**Table I. Electrochemical Generation of Ce(IV) in Aqueous Methanesulfonic Acid**

| run no. | solution composition | anode material | current density, mA/cm$^{2a}$ | final Ce(III), M | overall current efficiency, % |
|---|---|---|---|---|---|
| 1 | 1.5 M Ce(III), 2 M $CH_3SO_3H$ | platinum sheet | 100 | 0.60 | 96 |
| 2 | 1.5 M Ce(III), 2 M $CH_3SO_3H$ | platinum sheet | 200 | 0.44 | 88 |
| 3 | 1.5 M Ce(III), 2 M $CH_3SO_3H$ | $IrO_x$/Ti sheet | 200 | 0.44 | 69 |
| 4 | 0.6 M Ce(III), 6 M $CH_3SO_3H$ | platinum sheet | 200 | 0.48 | 38 |
| 5 | 0.6 M Ce(III), 6 M $CH_3SO_3H$ | platinum sheet + 2 platinum-clad niobium screens | 200 | 0.48 | 97 |
| 6 | 0.88 M Ce(III), 4 M $CH_3SO_3H$ | reticulated $IrO_x$/Ti | 500 | 0.83 | 89 |

[a] Across the membrane.

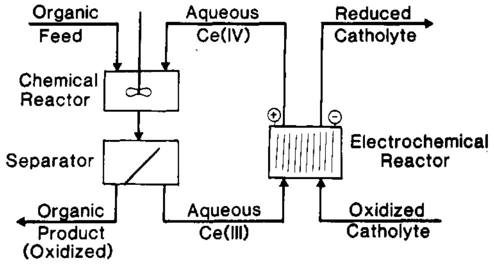

**Figure 1.** General scheme for mediated electrosynthesis.

trifluoroacetate,[19] fluoride, $BF_4^-$, $SF_6^{2-}$, and $PF_3^-$).[13] We have found that cerium salts of methanesulfonate and trifluoromethanesulfonate obviate the above problems and provide a system capable of Ce(IV) regeneration via electrochemical oxidation. A preliminary account of this work has been communicated.[20] In addition, we have isolated a solid ceric material, $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$, which is a very useful laboratory reagent for the preparation of aromatic aldehydes, ketones, and quinones.

These aromatic carbonyl products can also be prepared by direct oxidation of organic substrates at an anode, but this method generally suffers from low selectivity, especially at practical current densities (>50 mA/cm$^2$), poorly conductive electrolytes, and difficult product separations.[21,22] To minimize electrode fouling, it is best to limit the contact of the electrodes with the organic materials.[16] This can be accomplished by performing the organic oxidations with a mediator in a reactor that is separated from the electrochemical cells. Cerium(IV) in aqueous methanesulfonic acid provides an excellent mediator for this purpose.

## Results and Discussion

**Preparation of Ceric Methanesulfonate.** Solutions of cerium(III) in aqueous methanesulfonic acid are easily prepared by the addition of the acid to a suspension of cerous carbonate in water.[23] One of the major advantages of using aqueous methanesulfonic acid is the good solubility of Ce(III), and this is compared in Figure 2 to the solubility of Ce(III) in sulfuric acid.[17] The solubility of Ce(III) is critical since it determines the concentration of oxidant that can be used in each cycle of an indirect electrochemical oxidation. The current efficiency (and, thus, the maximum current density) is also determined by the concentration of cerium(III).

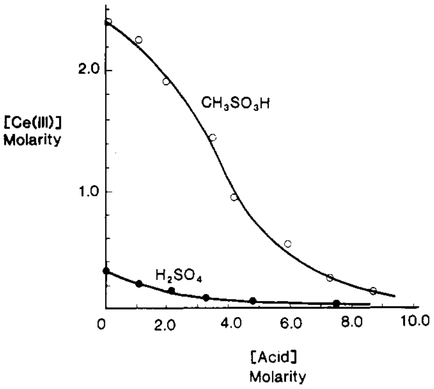

**Figure 2.** Solubility of Ce(III) in aqueous methanesulfonic acid and aqueous sulfuric acid.[16]

Table I shows results of electrolysis with cerium(III) in aqueous methanesulfonic acid at various solution compositions, conversions, and anode materials. The high solubility of the cerous ion in 2 M methanesulfonic acid permits the generation of high concentrations of ceric ion with excellent current efficiencies at high current densities (runs 1 and 2). Titanium sheet coated with $PbO_2$ can be used as an anode material, giving the same results as with a platinum sheet. Titanium sheet coated with iridium oxide (run 3) or with ruthenium oxide (not shown) gives slightly lower current efficiencies than Pt or $PbO_2$ as anode materials.

The solubility of cerium(III) is lower in 6 M $CH_3SO_3H$, thus the electrolysis must be carried to a high degree of conversion to obtain the same ceric concentration. This results in lower current efficiency as shown in run 4 of Table I (compare to run 2). Excellent current efficiency can be maintained at high conversion by employing a high-surface-area anode. This is accomplished in run 5 by simply adding two platinum-clad niobium screens to the anode compartment. These screens make electrical contact with the platinum sheet, increasing the effective surface area by a factor of 3. This can also be accomplished with an anode comprised of reticulated titanium coated with iridium oxide (run 6). The current densities obtained here are substantially higher than those typically obtained with direct anodic oxidations of organic substrates.[29]

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**Table II. Oxidations Performed with Ceric Methanesulfonate**

| line no. | oxidation | conversion,[a] % | selectivity,[a] % | concn $CH_3SO_3H$, M |
|---|---|---|---|---|
| (1) | toluene → benzaldehyde | 98 | 93 | 5.5 |
| (2) | toluene → benzaldehyde + benzyl alcohol | 10 | 57 + 37 | 5.5 |
| (3) | *p*-chlorotoluene → *p*-chlorobenzaldehyde | 99 | 87 | 5 |
| (4) | *o*-chlorotoluene → *o*-chlorobenzaldehyde | 92 | 73 | 8 |
| (5) | *p*-xylene → *p*-tolualdehyde | 98 | 80 | 5 |
| (6) | *o*-xylene → *o*-tolualdehyde | 98 | 81 | 5 |
| (7) | *m*-xylene → *m*-tolualdehyde | 91 | 77 | 5 |
| (8) | 1,2,3,5-tetramethylbenzene → 2,4,6-trimethylbenzaldehyde | 26 | 63 | 4 |
| (9) | *p*-*tert*-butyltoluene → *p*-*tert*-butylbenzaldehyde | 31 | 88 | 4 |
| (10) | *p*-ethyltoluene → *p*-methylacetophenone, *p*-ethylbenzaldehyde | 32 | 70, 10 | 4 |
| (11) | *p*-isopropyltoluene → *p*-methylacetophenone, *p*-isopropylbenzaldehyde | 20 | 53, 19 | 4 |
| (12) | ethylbenzene → acetophenone | 92 | 48 | 5 |
| (13) | 1,2,3,4-tetrahydronaphthalene → 1-tetralone | 16 | 62 | 5 |
| (14) | *p*-methylanisole → *p*-anisaldehyde[b,c] | 93 | 84 | 0.8 |
| (15) | styrene → benzaldehyde | 98 | 89 | 5 |
| (16) | anthracene → 9,10-anthraquinone[b] | 98 | 95 | 5 |
| (17) | naphthalene → 1,4-naphthoquinone[b] | 92 | 98 | 3 |
| (18) | 2-methylnaphthalene → 2-methyl-1,4-naphthoquinone, 6-methyl-1,4-naphthoquinone[b–d] | 94 | 67, 17 | 2 |
| (19) | 1-nitronaphthalene → 5-nitro-1,4-naphthoquinone[b] | 92 | 90 | 5 |
| (20) | 2-*tert*-butylnaphthalene → 6-*tert*-butyl-1,4-naphthoquinone, 2-*tert*-butyl-1,4-naphthoquinone[b,c] | 100 | 65, 26 | 1.5 |

[a] Based on substrate. [b] Substrate dissolved in 1,2-dichloroethane (4% by weight). [c] Anolyte contains 25% by volume of acetonitrile. [d] Contains Cr(VI) additive.

Komatsu et al. have shown that the current efficiency for Ce(IV) generation in 10% aqueous sulfuric acid drops rapidly at Ce(III) concentrations below 0.2 M (60% at 0.1 M, 40% at 0.05 M with a current density of 163 mA/cm$^2$ using a net-type platinum anode).[24] Thus, the current efficiency for oxidizing a (saturated) 0.2 M Ce(III) in 1 M $H_2SO_4$ will be low, even at low conversions.[24,25] This problem has been overcome somewhat by using slurries of cerous sulfate, such that the concentration of cerium(III) remained at the level of saturation during the electrolysis.[26] However, this resulted in Ce(III) solids following the oxidation of the organic material, creating a difficult, three-phase separation.[27,28] The solubility of cerous sulfate has been enhanced somewhat by the presence of excess ceric sulfate, but the amount of usable Ce(IV) per cycle was still only 0.12 M, even though 0.74 M of total cerium was carried in the aqueous solution.[24,28]

The solubility of cerium(IV) is limited at lower concentrations of methanesulfonic acid (Figure 3). Thus, electrochemical generation of cerium(IV) at low acid concentrations can produce slurries, but these slurries are effective in oxidizing organic substrates (vide infra). Note in this case, the use of solid ceric methanesulfonate in organic oxidations generates soluble cerous methanesulfonate, allowing for facile separation of products and efficient electrochemical regeneration of the ceric material. The solid ceric material has been identified by elemental analysis as $Ce(CH_3SO_3)_2(OH)_2 \cdot H_2O$ or $Ce(CH_3SO_3)_2O \cdot 2H_2O$. The first formulation is most likely since the IR spectrum is devoid of significant peaks between 800 and 1000 cm$^{-1}$, indicating the absence of a Ce=O bond. This solid material is a convenient oxidant since it is very soluble in water (up to 1.7 M), and solutions of Ce(IV) in aqueous methanesulfonic acid are easily prepared from aqueous solutions of $Ce(CH_3SO_3)_2(OH)_2 \cdot H_2O$.

**Organic Oxidations with Ceric Methanesulfonate.** Ceric methanesulfonate is a selective oxidant for the synthesis of a wide range of aldehydes, ketones, and quinones from alkyl aromatic and polycyclic precursors (Table II).

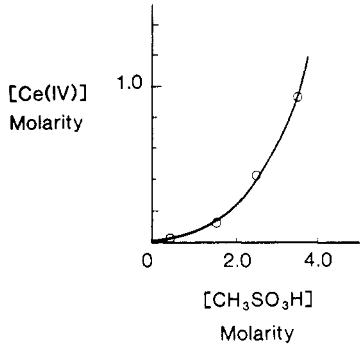

**Figure 3.** Solubility of Ce(IV) in aqueous methanesulfonic acid.

The reactions are fast, with an average time of 30 min and at most 120 min. In general, aromatic rings with electron-withdrawing substituents are less reactive and require higher acid concentration to effect reaction (e.g., *o*-chlorotoluene). Polycyclic compounds and aromatic rings with electron-donating substituents require lower acid concentrations and organic solvents to obtain high selectivities (e.g., naphthalene and *p*-methylanisole). Otherwise, highly colored products are obtained and polynuclear products such as binaphthyl are observed. Presumably, the slower reaction at lower acid concentrations and the dilution of substrate by organic solvent help to minimize dimerizations between radical cations.[19,30] Also, dilution of the starting material may limit its nucleophilic attack on the radical cation that is generated by electron transfer to Ce(IV).[30-32]

In oxidations that require very low concentrations of methanesulfonic acid, it is beneficial to add a cosolvent, such as acetonitrile, which is soluble in the aqueous phase.[9] This results in higher selectivities of *p*-anisaldehyde, 2-methyl-1,4-naphthoquinone, and 2-*tert*-butyl-1,4-naphthoquinone (Table II). With aqueous methane-

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**Table III. Effect of Organic Solvents on Ce(IV) Oxidation[a] of NA[b] to NQ[c]**

| line no. | organic solvent[d] | organic cosolvent | NA conv, % | NA select. to NQ, % | NA select. to PA, %[e] | Ce(IV) select. to NQ, % | Ce(IV) select. to PA, % | rxn time, min |
|---|---|---|---|---|---|---|---|---|
| (1)[f] | 1,2-dichloroethane | | 92 | 98 | 2 | 94 | 6 | 20 |
| (2) | 1,2-dichloroethane | | 80 | 84 | 13 | 68 | 32 | 60 |
| (3) | 1,2-dichloroethane | acetonitrile[g] | 94 | 97 | 3 | 91 | 8 | 10 |
| (4) | nitromethane | | 88 | 94 | 2 | 84 | 6 | 15 |
| (5) | nitroethane | | 96 | 97 | 1 | 94 | 4 | 60 |
| (6) | 1-nitropropane | | 86 | 94 | 6 | 81 | 16 | 60 |
| (7) | 2-nitropropane | | 83 | 93 | 8 | 78 | 19 | 60 |

[a] 0.6 "$Ce(CH_3SO_3)_4$"; 0.8 M $CH_3SO_3H$. [b] NA = naphthalene. [c] NQ = 1,4-naphthoquinone. [d] NA concn. = 0.33 M. [e] PA = phthalic acid. [f] 2.4 M $CH_3SO_3H$. [g] Equivalent in volume to the amount of 1,2-dichloroethane.

sulfonic acid, the addition of acetonitrile does not precipitate Ce(IV) or Ce(III), in contrast to aqueous sulfuric acid, where the cerium(III) sulfate is precipitated by added acetonitrile.[8,12] Maintaining cerium(III) in solution is important for product separation and electrochemical regeneration of cerium(IV) (vide supra).

The effect of acetonitrile addition is shown in Table III for the oxidation of naphthalene (NA). While this oxidation works well at 2.4 M $CH_3SO_3H$ (line 1), the selectivity to 1,4-naphthoquinone (NQ), is much lower at 0.8M $CH_3SO_3H$ (line 2). The selectivity to NQ is increased dramatically by the addition of acetonitrile. Approximately 50% of the added acetonitrile goes into the aqueous phase. This probably increases the solubility of naphthalene in the aqueous phase, making it more available for oxidation by Ce(IV), rather than the overoxidation of NA to phthalic anhydride (PA). Note that NQ is much more soluble than NA in the aqueous phase.

A single organic solvent can be used in place of 1,2-dichloroethane/acetonitrile provided that the solvent is immiscible with the aqueous phase and also has appreciable solubility in the aqueous phase. Thus, nitromethane and nitroethane are good solvents (lines 4 and 5), while the use of nitropropanes results in much higher yield of PA.

Organic oxidations with cerium(IV) in aqueous methanesulfonic acid can be performed with the ceric ion fully dissolved or with suspensions of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ in $CH_3SO_3H(aq)$. In either case, similar yields were obtained with *p*-methylanisole, 2-methylnaphthalene, and 2-*tert*-butylnapthalene (lines 14, 18, and 20, Table II). Very different results are obtained in the oxidation of *m*-phenoxytoluene. Homogeneous solutions of Ce(IV) in 9 M aqueous methanesulfonic acid gave none of the desired *m*-phenoxybenzaldehyde, while a suspension of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ in 9 M $CH_3SO_3H(aq)$ resulted in a 28% yield (39% selectivity based on *m*-phenoxytoluene) of *m*-phenoxybenzaldehyde. These results are very similar to those obtained with a suspension of ceric trifluoroacetate ($Ce(CF_3CO_2)_2(OH)_2$) in aqueous trifluoroacetic acid.[19] In general, it is difficult to cleanly oxidize *m*-phenoxytoluene to *m*-phenoxybenzaldehyde because two rings are available for oxidation and the *m*-phenoxy substituent promotes reactions on the ring rather than the side chain.[19,33] The enhanced selectivity demonstrated here may be the result of a direct reaction between *m*-phenoxytoluene and the solid $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ or a slow release of soluble Ce(IV), thus moderating the oxidation.

**Organic Oxidations with Mixtures of Chromium and Ceric Methanesulfonate.** In general, chromium(VI) is a nonselective oxidant for the reactions listed in Table II. One exception is in the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone (menadione). Chromium(VI) is used commercially in the production of menadione, giving a yield of up to 58% based on 2-methylnaphthalene.[34,35] A considerable excess of sodium dichromate must be used in this reaction, and the yield based on Cr(VI) is only 28%. With ceric methanesulfonate, yields of 55% and 49%, based on organic substrate and Ce(IV), respectively, were obtained. Even better results were obtained by adding a small of $CrO_3$ (on an equivalents basis, 5% of the amount of ceric methanesulfonate). Addition of more Cr(VI) resulted in poorer results. This, coupled with the inferior results obtained with chromium alone[34,35] suggest that the ceric methanesulfonate is not simply reoxidizing the Cr(VI), but that cerium(IV) and chromium(VI) act together as an organic oxidant. The chromium ions are maintained in the +6 oxidation state by reoxidation of Cr(III) to Cr(VI) by Ce(IV).

Small amounts of ceric ion have been used to modify what are primarily Cr(VI) oxidations,[36,37] but we are not aware of examples of chromic ions enhancing Ce(IV) oxidations, as shown here. We postulate that a cerium–chromium compound is involved at some stage of the oxidation to give the higher selectivity than with cerium alone. In support of this, crystalline, orange solids that analyze for $Ce_3Cr_5O_{39}H_{18}$ were isolated from mixtures of Ce(IV) and Cr(VI) at low concentration of methanesulfonic acid. The structure of this material is unknown, but an interaction between cerium and chromium seems likely (probably via oxide and/or hydroxide bridges) since it is insoluble in water and dilute $CH_3SO_3H(aq)$. In contrast, $CrO_3$, $Na_2Cr_2O_7$, and $NaCrO_4$ are very soluble in water and dilute $CH_3SO_3H(aq)$. Mixed complexes between Cr(VI) and ceric nitrate have recently been prepared and formulated as $[Ce(NO_3)_2]CrO_4{\cdot}2H_2O$ and $[Ce(NO_3)_3]_2CrO_4$.[38,39] These mixed complexes cleanly oxide benzyl alcohols to benzaldehydes in benzene under conditions where the parent compounds, ceric ammonium nirate and potassium dichromate, are ineffective.[38,39]

## Conclusions

Aqueous methanesulfonic acid provides an ideal medium for ceric oxidations of alkyl aromatic and polycyclic aromatic substrates to yield aldehydes, ketones, and quinones. The benefits of methanesulfonic acid include low cost, safety, low nucleophilicity, stability to anodic and Ce(IV)

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oxidations, and high solubility of Ce(III) and Ce(IV). The above features also lead to electrochemical regeneration with high current efficiencies at high current densities and fast organic oxidations. High selectivity has been shown with a wide range of organic reactants. The availability of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ as a solid permits facile generation of acidic ceric solutions of differing concentrations. It also gives rise to some unusual reactivity when used as an oxidant in the solid state. We have also uncovered a novel ceric–chromic interaction in the solid state and in solution, which can lead to enhanced selectivity in the production of menadione.

## Experimental Section

All chemicals were reagent grade (Aldrich) and used as received unless otherwise noted. Water was dionized. Methanesulfonic acid (99.5%) was obtained from Pennwalt and hydrated cerous carbonate (99%) was obtained from Molycorp. *p-tert*-Butylbenzaldehyde (95%) was obtained from Lancaster Synthesis Ltd. Literature procedures were used for the synthesis of 2-*tert*-butylnaphthalene[40] and 6-*tert*-butyl-1,4-naphthoquinone.[41]

Reaction yields were determined by gas chromatography on a Shimadzu GC-8A with a 60 m. × 0.245 mm fused silica capillary column (liquid phase = DB-5, J+W no. 28711). Depending on the reactant and products being followed, the chromatograms were obtained at an isothermal oven temperature of 140–260 °C; injector and FID detector temperatures were 40 °C higher than oven temperatures. Elemental analyses were performed by Huffman and Galbraith Laboratories.

Electrochemical studies were performed with a custom-made plate-and-frame type electrolytic cell[42] of approximate dimensions: 25 × 5 × 2 cm (length × width × thickness). The following components (in order) were bolted together: titanium backing plate/viton gasket/anode/viton gasket (with hole for anolyte chamber)/Nafion 390 membrane/viton gasket (with hole for catholyte chamber)/316 stainless steel cathode and backing plate. The anolyte and catholyte chambers were oval and had dimensions of 170 × 30 × 1.5 mm (length × width × thickness). Anolyte and catholyte solutions were pumped through the chambers at a rate of 500 mL/min from 500-mL round-bottom flasks via 0.25-in. Teflon lines, which were attached to holes in the backing plates leading into the anolyte and catholyte chambers. The pumps were March Model TE-MDX-MT-3 explosion-proof pumps. Electrolyses were conducted at constant current with a Hewlett-Packard Model 6428B DC power supply. Voltages ranged from 2 to 5 V, depending on the current. Cerium(IV) concentrations were determined by titration with 0.05 N ferrous ammonium sulfate with use of ferroin indicator. Platinum-clad niobium screens were obtained from Texas Instruments; reticulated titanium coated with $IrO_x$ was obtained from Eltech, and Nafion 390 membrane was obtained from Du Pont.

**Preparation of Ce(IV) in Aqueous Methanesulfonic Acid. Typical Procedure.** Methanesulfonic acid (240 g) was added slowly to a stirred suspension of 53 g of cerium(III) carbonate (obtained as pentahydrate) in 160 mL of water. Upon completion of $CO_2$ evolution, the resultant solution contained 0.6 M cerous methanesulfonate [$Ce(CH_3SO_3)_3$] and 6 M of free methanesulfonic acid.

The above solution (320 mL) was introduced into a 500-mL round-bottom flask and pumped through the anolyte compartment of a plate-and-frame type electrolytic cell. The anode was a platinum-clad niobium expanded mesh having both surfaces coated with 63.5 μm of platinum (total surface area of ca. 150 cm$^2$). The anolyte compartment was separated from the catholyte compartment by a commercial perfluorinated ion exchange membrane (Nafion 390). The anolyte compartment was maintained at a temperature of 50 °C while a constant current of 10 amps was passed for 25.5 min, resulting in an orange anolyte solution having a Ce(IV) concentration of 0.48 M (current efficiency of 97%). The catholyte compartment contained a stainless steel cathode and caused a clean reduction of protons to hydrogen gas.

**$Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$, Ceric Methanesulfonate.** Methanesulfonic acid (276 g) was added slowly to a stirred suspension of 219 g of cerium carbonate (obtained as the pentahydrate) in 150 mL of water. Upon completion of $CO_2$ evolution, water was added to make the volume 450 mL, containing 1.8 M cerous methanesulfonate ($Ce(CH_3SO_3)_3$) and 1 M of free methanesulfonic acid.

The above solution was introduced into the anolyte compartment of a plate-and-frame type electrolytic cell. The anode was a platinum-clad niobium sheet having the surface coated with 63.5 μm of platinum (total surface area ca. 50 cm$^2$). The anolyte was separated from the catholyte compartment by a commercial perfluorinated ion exchange membrane (Nafion 390). The anolyte temperature was ca. 40 °C. A constant current of 5 amps was passed for 54 min, followed by 3 amps for 211 min. The resulting mixture had a total cerium(IV) content of 0.531 mol (94.6% current efficiency). The catholyte compartment contained a stainless steel cathode and caused a clean proton reduction to hydrogen gas.

The above anolyte mixture was stirred overnight at ambient temperature, and the solid was then collected by filtration. The solid was then washed with 150 mL of acetonitrile and dried under vacuum at 60 °C overnight, yielding 97.3 g of yellow solid. This yellow solid had the following elemental analysis, in agreement with $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$. Calcd Ce, 36.65; C, 6.28; S, 16.75; H, 2.62. Found: Ce, 36.2; C, 6.59; S, 16.97; H, 2.57.

**Oxidation of Organic Substrates with Ce(IV) in Aqueous Methanesulfonic Acid. Typical Procedure.** A solution containing 0.5 M "$Ce(CH_3SO_3)_4$" in 3 M $CH_3SO_3H$(aq) was prepared as described above. This solution (130 mL) was heated at 60 °C and purged with nitrogen for 15 min. A solution of 1.28 g of naphthalene in 30 mL of 1,2-dichloroethane was added. After being stirred vigorously for 45 min, the resulting mixture was cooled and extracted with 300 mL of methylene chloride. Quantitative analysis by gas chromatography showed a 92% conversion of naphthalene and a 98% selectivity to 1,4-naphthoquinone (based on naphthalene consumed).

**Oxidations with Ceric Methanesulfonate. Typical Procedure.** A solution of 2.3 g of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ in 14 mL of water was stirred and heated at 60 °C for 5 min. Methanesulfonic acid (6.5 mL) was added dropwise over approximately 45 s. The solution was purged with nitrogen, and then 125 μL of *p*-xylene was added. After being stirred vigorously for 30 min, the resulting mixture was cooled and extracted with 30 mL of methylene chloride. Quantitative analysis by gas chromatography showed a 98% conversion of *p*-xylene with a 80% selectivity to *p*-tolualdehyde (based on the *p*-xylene consumed).

**Oxidation of Organic Substrates with Ce(IV) in Aqueous Methanesulfonic Acid and Acetonitrile. Typical Procedure.** A slurry of 0.6 M "$Ce(CH_3SO_3)_4$" in 0.8 M $CH_3SO_3H$(aq) was prepared electrolytically as described above. This mixture (100 mL) was heated at 60 °C and purged with nitrogen for 15 min. A solution of 1.28 g of naphthalene in 30 mL of 1,2-dichloroethane was added, followed immediately by 30 mL of acetonitrile. The mixture was stirred vigorously for 10 min, cooled, and then extracted with 300 mL of methylene chloride. Quantitative analysis by gas chromatography showed 0.08 g of naphthalene and 1.44 g of 1,4-naphthoquinone (91.4% yield, 97.2% selectivity).

**Oxidation of 2-Methylnaphthalene with Ce(IV)–Cr(VI) in Aqueous Methanesulfonic Acid and Acetonitrile.** To 83 mL of 0.73 M "$Ce(CH_3SO_3)_4$" and 2.8 M $CH_3SO_3H$ in water was added 0.10 g of $CrO_3$ in 6.0 mL of water. This solution was heated to 75 °C and purged with nitrogen, and then 1.42 g of 2-methylnaphthalene in 30 mL of 1,2-dichloroethane was added. Acetonitrile (30 mL) was immediately added, and the mixture was stirred vigorously for 30 min. The mixture was cooled and then extracted with 300 mL of methylene chloride. Quantitative analysis by gas chromatography showed 0.11 g of 2-methylnaphthalene, 0.98 g of 2-methyl-1,4-naphthoquinone (65% yield based on substrate, 54% yield based on oxidant), and 0.26 g of 6-methyl-1,4-naphthoquinone (17% yield based on substrate, 14% yield based on oxidant).

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The above procedure without $CrO_3$ gave a 55% yield of 2-methyl-1,4-naphthoquinone based on substrate (48% based on oxidant) and an 18% yield of 6-methyl-1,4-naphthoquinone based on substrate (16% based on oxidant).

**$Ce_3Cr_5O_{30}H_{18}$, Ceric Chromic Oxide/Hydroxide.** A solution of 0.38 g of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ in 1.0 mL of water was mixed with a solution of 0.35 g of $CH_3SO_3H$ and 0.29 g of $Na_2CrO_4$ in 1.0 mL of water. Mixing for several minutes resulted in dissolution of the the initially formed yellow solid. The solution was filtered and allowed to stand overnight, resulting in orange crystals. These crystals were collected by filtration, washed with water, and dried overnight under vacuum at 60 °C. Anal. Calcd: Ce, 35.65; Cr, 22.07; H, 1.52; C, 0.00; S, 0.00. Found: Ce, 34.71; Cr, 22.06; H, 1.09; C, 0.39; S, 0.04.

**Oxidation of *m*-Phenoxytoluene with Solid Ceric Methanesulfonate.** A mixture of 8.72 g of $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ and 100 mL of 9.3 M $CH_3SO_3H(aq)$ was stirred at 110 °C and purged with nitrogen for 15 min. Addition of 1.0 mL of *m*-phenoxytoluene was followed by stirring at 110 °C for 70 min. The resulting red-brown mixture was cooled and extracted with 300 mL of methylene chloride. Quantitative analysis by gas chromatography showed 73% conversion of the *m*-phenoxytoluene and 39% selectivity to *m*-phenoxybenzaldehyde.

The above procedure was repeated with the same materials, but with the cerium(IV) dissolved in solution. This can be accomplished by dissolving $Ce(CH_3SO_3)_2(OH)_2{\cdot}H_2O$ in water and then adding acid (vide supra) or by electrochemical oxidation of an appropriate Ce(III) solution. With the ceric material fully dissolved, only 27% of the *m*-phenoxytoluene was consumed and no *m*-phenoxybenzaldehyde was produced.

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**Registry No.** $Ce_3Cr_5O_{30}H_{18}$, 118977-38-1; $Ce(CH_3SO_3)_2(OH)_2$, 118920-74-4; toluene, 108-88-3; *p*-chlorotoluene, 106-43-4; *o*-chlorotoluene, 95-49-8; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; 1,2,3,5-tetramethylbenzene, 527-53-7; *p*-*tert*-butyltoluene, 98-51-1; *p*-ethyltoluene, 622-96-8; *p*-isopropyltoluene, 99-87-6; ethylbenzene, 100-41-4; 1,2,3,4-tetrahydronaphthalene, 119-64-2; *p*-methylanisole, 104-93-8; styrene, 100-42-5; anthracene, 120-12-7; naphthalene, 91-20-3; 2-methylnaphthalene, 91-57-6; 1-nitronaphthalene, 86-57-7; 2-*tert*-butylnaphthalene, 2876-35-9; ceric methanesulfonate, 107355-42-0; benzaldehyde, 100-52-7; *p*-chlorobenzaldehyde, 104-88-1; *o*-chlorobenzaldehyde, 89-98-5; *p*-tolualdehyde, 104-87-0; *o*-tolualdehyde, 529-20-4; *m*-tolualdehyde, 620-23-5; 2,4,6-trimethylbenzaldehyde, 487-68-3; *p*-*tert*-butylbenzaldehyde, 939-97-9; *p*-methylacetophenone, 122-00-9; *p*-ethylbenzaldehyde, 104-87-0; *p*-isopropylbenzaldehyde, 122-03-2; acetophenone, 98-86-2; 1-tetralone, 529-34-0; *p*-anisaldehyde, 123-11-5; 9,10-anthraquinone, 84-65-1; 1,4-naphthoquinone, 130-15-4; 2-methyl-1,4-naphthoquinone, 58-27-5; 6-methyl-1,4-naphthoquinone, 605-93-6; 5-nitro-1,4-naphthoquinone, 17788-47-5; 6-*tert*-butyl-1,4-naphthoquinone, 63382-81-0; 2-*tert*-butyl-1,4-naphthoquinone, 51595-06-3; *m*-phenoxytoluene, 3586-14-9; *m*-phenoxybenzaldehyde, 39515-51-0.

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# Oxidation of Alcohols by Metallic Nitrates Supported on Silica Gel

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Several metallic nitrates supported on silica gel efficiently oxidized secondary alcohols and primary benzyl and allyl alcohols to the corresponding ketones and aldehydes under mild conditions. Especially, $Cu(NO_3)_2$ and $Zn(NO_3)_2$ are suitable for practical use. Silica gel was essential for the efficient oxidation in any case. Overoxidation of the formed aldehydes was not observed. Some mechanistic studies suggest that the key step of the process involves the formation of radical species.

The supported reagent technique has received increasing attention in recent years.[1] As for the oxidation of alcohols to ketones and aldehydes with metallic nitrate complexes, Laszlo et al. reported the oxidation with $Fe(NO_3)_3$ impregnated on K 10 bentnite clay.[1b,d,2] This reagent has been reported to be unstable in air.[1d] In the course of studying dehydration of alcohols catalyzed by metallic salts supported on silica gel,[3] we found several metallic nitrates impregnated on silica gel oxidize alcohols efficiently. Most of these reagents are stable in dry air, and this oxidation is quite easy to perform. A part of this study has been reported preliminarily.[4]

## Results and Discussion

**Activity of Reagents.** The oxidizing reagents supported on silica gel (abbreviation, $M(NO_3)_n$–$SiO_2$) were prepared by the following procedure: chromatographic silica gel was added to a metallic nitrate dissolved in water or acetone. The mixture was evaporated and dried under reduced pressure at an appropriate temperature (usually 50–130 °C), at which the nitrate is inferred not to decompose[5] (see the Experimental Section). Insufficient or excessive drying caused the decline of the oxidizing activity. The importance of the amount of water in supported reagents has been mentioned in several reports.[6] Unless otherwise noted, the oxidation reaction in this study was carried out by heating an alcohol (1 mmol) and a nitrate

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