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.

Acknowledgment. We thank G. W. Ambrose-Ritchey, J. B. Davis, W. L. Henry, V. R. Hoover, and D. S. McFarland for technical assistance.

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.

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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Table I. Oxidation of Cyclododecanol by Metallic Nitrates[a]

reagent	solvent	yield and recovery, %		
		cyclododecanone	cyclododecanol	cyclododecene
$Cu(NO_3)_2$–SiO_2	CCl_4	98	1	1
$Cu(NO_3)_2$–SiO_2	*n*-hexane	91	3	0
$Cu(NO_3)_2$	CCl_4	6	82	2
$Zn(NO_3)_2$–SiO_2	CCl_4	96	1	0
$Zn(NO_3)_2$–SiO_2	*n*-hexane	94	5	1
$Zn(NO_3)_2$	CCl_4	5	92	3
$Hg(NO_3)_2$–SiO_2	CCl_4	93	2	4
$Hg(NO_3)_2$–SiO_2	*n*-hexane	43	50	1
$Hg(NO_3)_2$	CCl_4	26	58	2
$Cr(NO_3)_3$–SiO_2	CCl_4	48	52	0
$Cr(NO_3)_3$–SiO_2	*n*-hexane	88	2	0
$Cr(NO_3)_3$–SiO_2	$CHCl_3$	50	47	1
$Cr(NO_3)_3$	CCl_4	8	82	6
$Ce(NO_3)_3$–SiO_2	CCl_4	64	26	3
$Ce(NO_3)_3$–SiO_2	*n*-hexane	78	10	1
$Ce(NO_3)_3$–SiO_2	$CHCl_3$	9	83	4
$Ce(NO_3)_3$	CCl_4	10	85	2
$Fe(NO_3)_3$–SiO_2	CCl_4	64	1	0
$Fe(NO_3)_3$–SiO_2	*n*-hexane	78	0	0
$Fe(NO_3)_3$–SiO_2	$CHCl_3$	86	5	0
$Fe(NO_3)_3$	CCl_4	15	71	2
$Mn(NO_3)_2$–SiO_2	CCl_4	73	23	1
$Mn(NO_3)_2$–SiO_2	*n*-hexane	21	68	1
$Mn(NO_3)_2$	CCl_4	6	93	1
$AgNO_3$–SiO_2	C_2Cl_4	0	92	0
$AgNO_3$–SiO_2	CCl_4	57	1	1
$AgNO_3$–SiO_2	*n*-hexane	16	81	0
$AgNO_3$	CCl_4	2	98	0
$HgNO_3$–SiO_2	C_2Cl_4	47	5	1
$HgNO_3$–SiO_2	CCl_4	55	33	6
$HgNO_3$–SiO_2	*n*-hexane	37	54	1
$HgNO_3$	CCl_4	11	88	0
$Co(NO_3)_2$–SiO_2	C_2Cl_4	63	6	3
$Co(NO_3)_2$–SiO_2	CCl_4	46	48	3
$Co(NO_3)_2$	CCl_4	9	81	2
$Cd(NO_3)_2$–SiO_2	C_2Cl_4	77	1	0
$Cd(NO_3)_2$–SiO_2	CCl_4	31	66	1
$Al(NO_3)_3$–SiO_2	C_2Cl_4	65	3	3
$Al(NO_3)_3$–SiO_2	CCl_4	5	77	4
$Ni(NO_3)_2$–SiO_2	C_2Cl_4	52	8	2
$Ni(NO_3)_2$–SiO_2	CCl_4	6	81	3
$Mg(NO_3)_2$–SiO_2	C_2Cl_4	32	53	3
$Mg(NO_3)_2$–SiO_2	CCl_4	4	84	1
$Ce(NH_4)_2(NO_3)_6$–SiO_2	C_2Cl_4	6	35	11
$Ce(NH_4)_2(NO_3)_6$–SiO_2	CCl_4	12	73	2

[a] Cyclododecanol (1 mmol) and a nitrate (2 mmol) were heated in a solvent (10 mL) for 2 h. Nitrates/SiO_2 = 1 mmol/g.

reagent (2 mmol) in a refluxing solvent (10 mL) under nitrogen. The molecular weight of nitrates on the support was calculated as anhydrous salts because it is difficult to estimate the amount of coordinated water of the nitrates. Brown gas appeared in the reaction vessel when the oxidation started and disappeared when the reaction was complete. Therefore, the reaction is easily monitored and followed by checking the presence or the absence of the gas. In the reactions of high conversion, almost pure oxidation products were isolated by removing the solid reagents by filtration and evaporating the solvents. The simple reaction operation increases the synthetic utility of this oxidation. Eluting the isolated solids with polar solvents such as acetone usually gave a little additional amounts of products and recovered alcohols. In this study the elution was always performed to improve material balance.

The activity of a lot of metallic nitrates that are presumed to be thermostable at reaction temperatures and inexpensive was investigated in the oxidation of cyclododecanol to cyclododecanone. Cyclododecene was also sometimes formed, but the yield of the olefin was less than 5%. The results are shown in Table I. The activity of the supported nitrates, which are represented by cationic parts only, decreased in the following order: Cu(II) = Zn(II) > Hg(II) = Cr(III) > Ce(III) = Fe(III) = Mn(II) > Ag(I) = Hg(I) > Co(II) > Cd(II) > Al(III) > Ni(II) > Mg(II), although the order depended somewhat on reaction temperatures. The yield of the ketone was less than 5% in the reaction of the nitrates of Ba(II), Ca(II), Pb(II), Li(I), Na(I), and NH_4(I) in refluxing CCl_4 and tetrachloroethylene. $Ce(NH_4)_2(NO_3)_6$–SiO_2 showed low activity. The nitrates of Fe(III), Cr(III), and Ce(III) are active at low temperatures, but they are unstable when heated in CCl_4. Ionic nitrates seems to be less reactive than covalent nitrates, which is in accordance with the tendency to oxidize a few organic compounds noted in the literature.[7]

Table II. Dependence of Activity of $Zn(NO_3)_2$ Supported on Various Solids[a]

solid	yield of cyclododecanone, %
silica gel BW-300 (Fuji-Davidson, 230–400 mesh)	86
silica gel 60 (Merck, 230–400 mesh)	83
silica gel 60H (Merck, for TLC)	75
silica gel 60 (Merck, 70–230 mesh)	47
active carbon (powder)	9
bentnite	7
alumina (ICN,N-Super I)	5
Celite 535	3
molecular sieves 3A (powder)	3
none	3

[a] Cyclododecanol (1 mmol) and $Zn(NO_3)_2$ (2 mmol) on a solid support (1 g) were heated in CCl_4 (10 mL) for 40 min.

Except for the reaction of $Fe(NO_3)_3$– and $AgNO_3$–SiO_2, side reactions seem not to have occurred very severely in the reactions in CCl_4, because the total of the yield of the ketone and the recovery of the alcohol was fairly high in any case.

Table I also shows the results of the reaction of the nitrates that were powdered, dried, and used without supporting. The activity of nitrates that were not supported was found to be very low. For example, the yield of the ketone was 98% in the presence of silica gel, while only 6% in the absence of the support in the reaction $Cu(NO_3)_2$ in CCl_4. These results indicate the necessity of silica gel for the satisfactory oxidation.

Various kinds of solid adsorbents were tested in the reaction of $Zn(NO_3)_2$ (Table II). Silica gel BW-300 (Fuji-Davidson, 230–400 mesh) and silica gel 60 (Merck, 230–400 mesh) were the most effective. Active carbon, bentnite, alumina, Celite, and molecular sieves were almost ineffective. These results suggest that the main role of silica gel is not to widen the surface of the nitrate salts. Unless otherwise noted, silica gel BW-300 was used throughout this study.

The activity of the oxidizing reagents was weakened by absorbing moisture in air. However, most of them, including $Cu(NO_3)_2$ and $Zn(NO_3)_2$, recovered the activity by

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Table III. Oxidation of Alcohols by $Cu(NO_3)_2$-SiO_2 and $Zn(NO_3)_2$-SiO_2[a]

			yield and recovery, %		
alcohol	metal	time, min	ketone/ aldehyde	alcohol	olefin
2-propanol	Cu	90	91[b]	0	0
cyclopentanol	Cu	45	91	0	0
cyclopentanol	Zn	60	97	3	0
cyclohexanol	Cu	60	96	0	0
cyclohexanol	Zn	30	92	4	0
2-methylcyclohexanol	Cu	30	97	0	0
2-methylcyclohexanol	Zn	30	100	0	0
4-*tert*-butylcyclohexanol	Cu	60	85	3	0
4-*tert*-butylcyclohexanol	Zn	90	86	5	0
cycloheptanol	Cu	30	97	0	0
cycloheptanol	Zn	30	82	0	0
cyclooctanol	Cu	30	98	2	0
cyclooctanol	Zn	45	92	0	0
2-octanol	Cu	30	98	0	0
1-phenylethanol	Cu	15	100	0	0
1-phenylethanol	Zn	15	94	6	0
1-phenyl-2-propanol	Cu	120	65	0	34
1-phenyl-2-propanol	Zn	120	58	1	43
diphenylmethanol	Cu	180	84	16	0
benzoin	Zn	360	84	15	
benzyl alcohol	Cu	30	90	10	
benzyl alcohol	Zn	60	92	8	
p-methylbenzyl alcohol	Cu	30	96	0	
p-methylbenzyl alcohol	Zn	40	99	0	
p-Anise alcohol	Cu	30	85	15	
p-anise alcohol	Zn	30	48	0	
m-chlorobenzyl alcohol	Cu	30	95	5	
m-chlorobenzyl alcohol	Zn	30	94	0	
p-chlorobenzyl alcohol	Cu	45	100	0	
p-chlorobenzyl alcohol	Zn	15	100	0	
2-hexen-1-ol	Cu	60	97	0	

[a] An alcohol (1 mmol) and a nitrate (2 mmol) on SiO_2 were heated in CCl_4 (10 mL). $Cu(NO_3)_2/SiO_2$ = 2.67 mmol/g. $Zn(NO_3)_2/SiO_2$ = 2 mmol/g. [b] 2-Propyl nitrite (11%) was detected.

being dried again and can be stored for long periods of time without loss of the activity under the conditions protected from moisture.

Oxidation of Various Alcohols. Oxidation of several alcohols were studied with $Cu(NO_3)_2$ and $Zn(NO_3)_2$, as representatives of the reagents, because they are active, stable in dry air, thermostable at reaction temperatures, inexpensive, mildly acidic, and of low toxicity for human body and environment. The results are summarized in Table III. Most of the simple secondary alcohols gave the corresponding ketones in high yields. Especially the oxidation of 1-phenylethanol was fast. However, the reaction of diphenylmethanol was slow perhaps because the adsorption of the alcohol onto silica gel was difficult due to steric hindrance. In the reaction of 1-phenyl-2-propanol considerable amount of 1-phenylpropene was formed. Benzyl alcohols and an allylic alcohol, 2-hexen-1-ol, yielded the corresponding aldehydes efficiently. Overoxidation of the formed aldehydes to the corresponding carboxylic acids was not observed in any case. Usual primary aliphatic alcohols such as 1-dodecanol, 2-phenylethanol, and cyclohexanemethanol were recovered unchanged. The resulting order of the reactivity of alcohols (benzylic > secondary ≫ primary) suggests that the key step of the process involves the formation of intermediates having a charge or an odd electron on the α-carbon of alcohols. It is noteworthy from a mechanistic view point that 2-propyl nitrite, whose structure was identified by an authentic sample,[8] was obtained in 11% yield in addition to 91% of acetone in the reaction between 2-propanol and $Cu(NO_3)_2$-SiO_2.

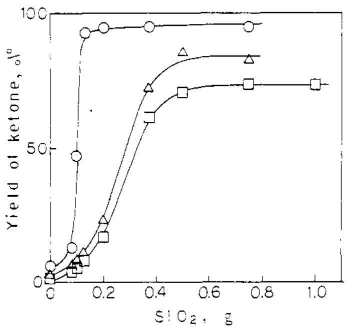

Figure 1. Yields of cyclododecene vs the amount of silica gel. Cyclododecanol (0.5 mmol) and $Cu(NO_3)_2$ (1 mmol) supported on silica gel were heated under reflux in CCl_4 (5 mL) for 2 h (○), 5 min (△), and 3 min (□).

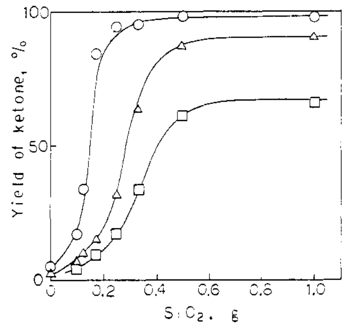

Figure 2. Yields of cyclododecene vs the amount of silica gel. Cyclododecanol (0.5 mmol) and $Zn(NO_3)_2$ (1 mmol) supported on silica gel were heated under reflux in CCl_4 (5 mL) for 2 h (○), 30 min (△), and 8 min (□).

Dependence of Yield of Ketone on Amount of Silica Gel. Figures 1 and 2 show the dependence of the yield of cyclododecanone on the amount of silica gel (grams) in the reaction between cyclododecanol (0.5 mmol) and $Cu(NO_3)_2$- or $Zn(NO_3)_2$-SiO_2 (1 mmol) in CCl_4 (5 mL). In the 2-h reactions the oxidation almost completed when the amounts of silica gel were more than 0.15–0.2 g, although it hardly proceeded in the absence of the adsorbent. In the reactions of shorter periods in which the oxidation did not complete, the yields increased with the increment of the amount of silica gel until the amount reached about 0.5 g. The yield became constant when over 0.5 g of silica gel was used. This fact shows that the oxidation activity of the nitrates rises along with the increase of the amount of silica gel at first and then it becomes constant when the amount is larger than 0.5 g. This critical loading value, 2 mmol of nitrate per gram of SiO_2, appears to be the saturation amount of the nitrates on silica gel surface. At this critical value, the surface area, which is effectively covered with a nitrate moiety, is assumed to be 0.4 nm^2, because the surface area of silica gel WB-300 is known to be about 500 m^2 g^{-1}.[9] The same order of values have been reported for monolayer coverage of $KMnO_4$[10] and 1-dodecanol[11] on silica gel surface. These results suggests that the activity of the oxidation reagents becomes constant when the nitrate molecules covered the surface of silica gel as monolayer. As described before, it seems the main role of silica gel is not to widen the surface of the nitrates because the other examined solid supports are almost in-

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Table IV. Dependence of Yield of Ketone on Metallic Nitrate/Alcohol Ratio[a]

			yield and recovery, %		
metal	time, min	nitrate cyclooctanol	cyclooctanone	cyclooctanol	cyclooctene
Cu	30	2.0	98	2	0
Cu	30	1.5	98	0	0
Cu	45	1.0	93	3	1
Cu	180	0.5	60	29	11
Cu	180	0.5[b]	18	44	32
Cu	180	0.25	18	66	22
Zn	45	2.0	91	5	0
Zn	45	1.5	86	7	8
Zn	90	1.5[b]	30	3	47
Zn	90	1.0	86	4	6
Zn	180	0.5	45	20	23
Zn	180	0.5[b]	6	64	19

[a] Cyclooctanol (1 mmol) and a nitrate supported on SiO_2 were heated in CCl_4 (10 mL). $Cu(NO_3)_2/SiO_2$ = 2.67 mmol/g. $Zn(NO_3)_2/SiO_2$ = 2 mmol/g. [b] This reaction was carried out under oxygen atmosphere.

effective. It is speculated that silica gel forms a special reaction field where alcohols and nitrates are accumulated by adsorption and the nitrates are activated by hydroxyl groups of silica gel surface. This speculation is supported by the result that the oxidizing reagent has the most suitable dryness as stated before and by the report that water content of silica gel governs number and nature of hydroxyl groups of the surface of the solid.[6c,12]

Table IV shows the results obtained by changing the molar ratio of cyclooctanol to $Cu(NO_3)_2$– or $Zn(NO_3)_2$–SiO_2. When the amount of the nitrates was more than that of the alcohol, the yield of cyclooctanone was quantitative. However, the yield of the ketone was 45–60% when the nitrate/alcohol ratio was 0.5. These results suggest that the only one of the two nitrato groups of the nitrates is used for the oxidation. It is inferred that metallic compounds that have been formed in the process of the oxidation promote the dehydration of alcohols, for the increased olefin formation was observed when the nitrate/alcohol ratio decreased. By changing nitrogen atmosphere to oxygen atmosphere, the oxidation was suppressed and the olefin formation was promoted.

Dependence of Initial Rates on Various Factors. Initial reaction rates were able to be measured easily because no induction period was observed in any case examined. The rate, which was measured under the conditions that the amount of cyclododecanol was changed and that of $Zn(NO_3)_2$–SiO_2 (2 mmol per gram of SiO_2) was constant (1 mmol), shows that it increased sharply and then became nearly constant as the amount of the alcohol increased (Figure 3). This result suggests that only the alcohol molecules that had been adsorbed onto the surface of the catalyst were oxidized and the surface was almost completely covered with the alcohol when the alcohol/$Zn(NO_3)_2$ ratio reached around 0.1, that is, the amount of the alcohol became about 0.1 mmol.

The oxidation rate of cyclododecanol (1 mmol) by $Cu(NO_3)_2$–SiO_2 (2 mmol) hardly changed when the amount of CCl_4 increased two or four times without changing the other conditions. This result also suggests that the surface of the solid reagent was saturated with the alcohol and only the adsorbed alcohol reacted.

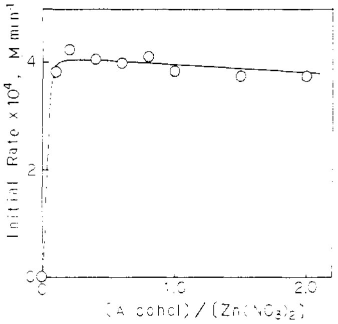

Figure 3. Initial rates vs the amount of cyclododecanol. The alcohol and $Zn(NO_3)_2$–SiO_2 (1 mmol; 2 mmol g^{-1} of SiO_2) were heated in refluxing CCl_4 (10 mL).

Reaction Mechanism. Although Laszlo et al. have presumed a mechanism involving nitrosonium cation NO^+ for the oxidation of secondary alcohols by clay-supported $Fe(NO_3)_3$,[1d,2] we would like to propose a radical mechanism for the oxidation by $Cu(NO_3)_2$– and $Zn(NO_3)_2$–SiO_2 on the following grounds. (1) By changing the atmosphere from nitrogen to oxygen, the formation of cyclooctanone was considerably retarded and that of cyclooctene was promoted, as described before. As radical reactions are generally influenced by the presence of oxygen, which is a biradical, these results may be explained by the presumption that the oxidation involves radicals and was inhibited by oxygen while the dehydration, which seems to proceed in ionic mechanism, was not influenced by oxygen and became the main reaction. (2) The brown gas was observed while the oxidation was in progress and disappeared when the reaction was complete. This result suggests nitrogen dioxide, which is a radical, was formed during the oxidation. (3) Secondary ethers were oxidized by the nitrate reagents under nearly the same conditions as secondary alcohols are oxidized.[13] For example, acetone (57% yield) and 2-propyl nitrite (20% yield) were formed in the reaction between 2-propyl ether (1 mmol) and $Cu(NO_3)_2$ (2 mmol, 2.7 mmol per gram of SiO_2) in refluxing CCl_4 (10 mL) for 30 min. This result suggests that radical species abstracted the α-hydrogen of the ether. It is assumed that the same kind of reactions occurred in the oxidation of alcohols. The decomposition of 2-propyl nitrite to acetone in the presence of $Cu(NO_3)_2$–SiO_2 seemed slower than the oxidation of 2-propanol. Therefore, we consider the nitrous esters are not main intermediates in the oxidation of alcohols, although Laszlo et al. have assumed they are in the oxidation of secondary alcohols by clay-supported $Fe(NO_3)_3$.[2b] (4) The yield of cyclododecanone was reduced to half by the addition of 10 mol % of 2,6-di-*tert*-butylhydroquinone and 2,4,6-tri-*tert*-butylphenol, which are sterically hindered radical scavengers in the 30-min reaction of $Cu(NO_3)_2$–SiO_2. (5) Rates of the oxidation of meta or parasubstituted benzyl alcohols was divided into two groups, and in each group the ρ-value of the Hammett equation was nearly zero as seen in Figure

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[12] Turro, N. J. *Tetrahedron* **1987**, *43*, 1589.

[13] The study about this reaction is now progressing.

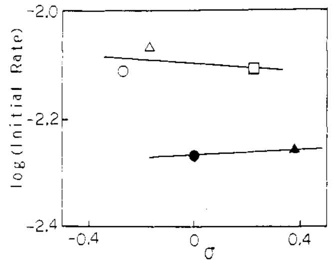
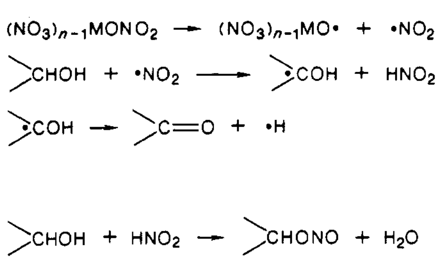


Figure 4. Plots of logarithm of initial rates vs Hammett substituent constants. A meta- or para-substituted benzyl alcohol (1 mmol) and $Cu(NO_3)_2$–SiO_2 (2 mmol; 2.7 mmol g^{-1} of SiO_2) in CCl_4 (10 mL) were heated at 60 °C. Substituent; *p*-methoxy (○), *p*-methyl (△), *p*-chloro (□), H (●), and *m*-chloro (▲).

4. The result that the electronic effect of the substituents are not effective suggests, though not clearly, that not ions but radicals are formed as intermediates. The fact that the para-substituted benzyl alcohols reacted faster than the meta- and the nonsubstituted alcohols may be explained by the inference that the intermediates formed from the former alcohols can resonate with the substituents but the ones from the latter ones cannot.

The observations described above are compatible with a radical pathway. Therefore, we would like to propose the following scheme for the oxidation of alcohols.



The formation of NO_2 radical from covalent nitrates has been described in the literature.[7] The speculation that the formation of NO_2 is promoted by the adsorption of the nitrates on silica gel is mentioned previously. Further, it is noteworthy that N_2O_4, which is usually equilibrated with NO_2, has been reported to oxidize organic compounds,[14] including benzyl alcohols.[15]

Experimental Section

General. Reagents and solid supports were purchased and used without purification. Solvents were distilled and stored with molecular sieves (3A). 2-Propyl nitrite was prepared by the method in the literature.[7] GLC analyses were carried out with a 25 m × 0.25 mm i.d. fused silica capillary column OV-1 or OV-1701. ^1H NMR spectra were recorded on a Hitachi R-600 (60 MHz) instrument. IR spectra were taken with Hitachi 285 spectrometer. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel $60F_{254}$ (E. Merck) glass-supported plates.

An Example of the Preparation of Oxidizing Reagents. To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (4.83 g, 20 mmol) in acetone (20 mL) or water (20 mL) was added chromatographic silica gel WB-300 (10 g) at once with shaking. Then the solvent was removed in a rotary evaporator. The blue powder formed was dried further at 130 °C under reduced pressure (7 × 10^2 Pa) with stirring until no more water condensed into a trap cooled with dry ice. One gram of this reagent contains about 1.45 mmol of $Cu(NO_3)_2$.

The other nitrates and their drying temperatures (°C) are as follows: $Zn(NO_3)_2 \cdot 6H_2O$ (130), $Hg(NO_3)_2 \cdot 0.5H_2O$ (70), $Cr(NO_3)_3 \cdot 9H_2O$ (90), $Ce(NO_3)_3 \cdot 6H_2O$ (60), $Fe(NO_3)_3 \cdot 9H_2O$ (55), $Mn(NO_3)_2 \cdot 6H_2O$ (130), $AgNO_3$ (170), $Hg_2(NO_3)_2 \cdot 2H_2O$ (60), $Co(NO_3)_2 \cdot 6H_2O$ (80), $Cd(NO_3)_2 \cdot 4H_2O$ (50), $Al(NO_3)_3 \cdot 9H_2O$ (150), $Ni(NO_3)_2 \cdot 6H_2O$ (50), $Mg(NO_3)_2 \cdot 6H_2O$ (200), $Pb(NO_3)_2$ (200), $Ca(NO_3)_2$ (200), $LiNO_3$ (150), $NaNO_3$ (200), NH_4NO_3 (150), and $Ce(NH_4)_2(NO_3)_6$ (150). These reagents were stored in a vessel sealed with parafilm or over P_2O_5 in a desiccator.

An Example of the Oxidation Reaction. Cyclododecanol (92.3 mg, 0.5 mmol), $Cu(NO_3)_2$–SiO_2 (0.69 g, 1 mmol; 2 mmol per gram of SiO_2), and *n*-pentadecane (25 μL), which is an internal standard in GLC analysis, were heated under nitrogen atmosphere in refluxing CCl_4 (5 mL) while being stirred. The brown gas came out. The reaction was monitored by TLC (1:3 ethyl acetate/*n*-hexane). Five minutes later, the brown gas and the alcohol disappeared. The reaction mixture was transferred to a small glass column with a cotton plug. The solid was separated by filtration and eluted with acetone (10 mL). The filtrate and the eluent were combined and submitted to GLC analysis. Cyclododecanone (0.49 mmol, 98%), cyclododecene (0.005 mmol, 1%), and cyclododecanol (0.004 mmol, 1%) were detected.

Other oxidation reactions were also carried out in a similar way.

Initial Rate Measurement. To a reaction vessel in which an oxidizing reagent (1 mmol), an internal standard, and a solvent (4 mL) had been heated in a bath was added an alcohol (0.5 mmol) in the solvent (1 mL). Four or five reactions in which the amounts of reagents and solvents and reaction temperatures were the same were carried out for various reaction periods for which the conversions of the starting materials fell in the range of 5–40%. From the linear parts of the conversion vs time curves, the initial rates were calculated.

Registry No. $Cu(NO_3)_2$, 3251-23-8; $Zn(NO_3)_2$, 7779-88-6; $Hg(NO_3)_2$, 10045-94-0; $Cr(NO_3)_3$, 13548-38-4; $Ce(NO_3)_3$, 10108-73-3; $Fe(NO_3)_3$, 10421-48-4; $Mn(NO_3)_2$, 22405-70-5; $AgNO_3$, 7761-88-8; $HgNO_3$, 10415-75-5; $Co(NO_3)_2$, 10141-05-6; $Cd(NO_3)_2$, 10325-94-7; $Al(NO_3)_3$, 13473-90-0; $Nc(NO_3)_2$, 13138-45-9; $Mg(NO_3)_2$, 10377-60-3; $Ce(NH_4)_2(NO_3)_6$, 10139-51-2; 2-propanol, 67-63-0; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; 2-methylcyclohexanol, 583-59-5; 4-*tert*-butylcyclohexanol, 98-52-2; cycloheptanol, 502-41-0; cyclooctanol, 696-71-9; 2-octanol, 123-96-6; 1-phenylethanol, 98-85-1; 1-phenyl-2-propanol, 698-87-3; diphenylmethanol, 91-01-0; benzoin, 119-53-9; benzyl alcohol, 100-51-6; *p*-methylbenzyl alcohol, 589-18-4; *p*-anise alcohol, 105-13-5; *m*-chlorobenzyl alcohol, 873-63-2; *p*-chlorobenzyl alcohol, 873-76-7; 2-hexen-1-ol, 2305-21-7; acetone, 67-64-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; 2-octanone, 111-13-7; acetophenone, 98-86-2; 1-phenyl-2-propanone, 103-79-7; benzophenone, 119-61-9; benzil, 134-81-6; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; *p*-anisaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; cinnamaldehyde, 104-55-2; cyclododecanol, 1724-39-6; cyclododecanone, 830-13-7; cyclododecene, 1501-82-2; isopropyl nitrite, 541-42-4; phenylpropene, 637-50-3.

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(14) Addison, C. C. *Chem. Rev.* **1980**, *80*, 21.
(15) Field, B. O.; Grundy, J. *J. Chem. Soc.* **1955**, 1110.