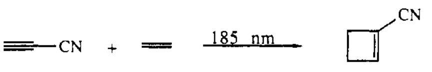
photochemical reactions of tricyanobenzenes with cyanoacetylene establishes that the tetracyanocyclooctatetraenes are not produced from excited tricyanobenzenes.

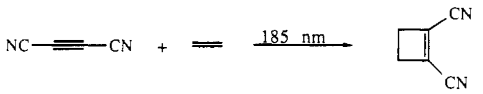
The photolysis of dicyanoacetylene in the presence of acetylene also yields tetracyanocyclooctatetraenes. It is proposed that the reaction of the excited state of dicyanoacetylene with the ground-state acetylene yields **8** which dimerizes to **2**, **3**, and possibly **5** (Scheme I, C). The other products of this photochemical reaction, the *E*,*Z* isomers of **6**, are formed by the ring opening of **8**. A similar opening of the oxetane formed by cycloaddition of benzaldehyde and 2-butyne has been reported.[43] It is not clear why **8**, when formed by reaction of an excited dicyanoacetylene with acetylene, rearranges to **6** while the same intermediate formed from excited cyanoacetylene does not. One explanation is the faster addition of cyanoacetylene than acetylene to **8**. The rearrangement of **8** to **6** has time to proceed because cycloaddition of **8** with acetylene is a slower reaction. This postulate is consistent with our failure to observe 1,2-dicyanobenzene as a product when dicyanoactylene is irradiated with acetylene with 254-nm light (Table IV) while 1,2,4-tricyanobenzene is a major product of the photolysis of cyanoacetylene with 254-nm light (Table I).

Excitation of cyanoacetylene–acetylene mixtures with 185- or 206-nm light is expected to produce either the singlet excited state of cyanoacetylene[31] or the metastable triplet excited state of acetylene.[44] Either excited state would be expected to undergo cycloadditions with ground-state molecules to yield the observed photoproducts (Tables II and III). The yield of each benzene derivative can be accounted for qualitatively by the extent of light absorbed by each monomer and the relative amounts of each monomer.

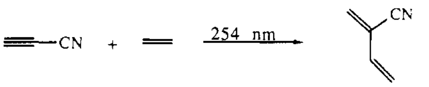
The photochemical formation of 1-cyanocyclobutene from ethylene and cyanoacetylene (eq 5) and the formation of 1,2-dicyanocyclobutene from ethylene and dicyanoacetylene (eq 6) with 185-nm light supports the reaction pathways proposed in Scheme I. The cycloadduct formed from ethylene generates a stable adduct while the highly reactive 1,2-dicyanocyclobutadiene excited state species undergoes a further cycloaddition with cyanoacetyene to give 1,3,5-tricyanobenzene. The cycloadducts were observed when 1-cyanocyclobutene was photolyzed in the gas phase by itself or in the presence of cyanoacetylene.[45]



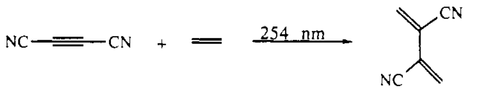
(5)



(6)



(7)



(8)

The formation of 2-cyano-1,3-butadiene by the 254-nm irradiation of mixtures of ethylene and cyanoacetylene (eq 7) and 2,3-dicyano-1,3-butadiene from dicyanoacetylene and ethylene (eq 8) is consistent with the formation of **6** from **8**. No products could be identified in the gas-phase photolysis of 2-cyano-1,3-butadiene. This is a surprising result in view of the facile photochemical cyclization of 2-cyano-1,3-butadiene to 1-cyanocyclobutene and 1-cyanobicyclobutane in acetonitrile.[46] We confirmed that the photolysis of 2,3-dicyano-1,3-butadiene in acetonitrile solution yields 1,2-dicyanocyclobutene.[47]

Acknowledgment. This research was supported by NASA Grant NGR 33-018-148. J.C.G. received a stipend from CNRS of France. We thank Professor Kevin T. Potts for the use of his PC MODEL program and for providing instruction and advice for its use. Professor Robert Strong provided valuable consultation on the spectroscopy of cyanoacetylene.

---

[43] Friedrich, L. E.; Bower, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6869–6870.

[44] Okabe, H. *J. Chem. Phys.* **1983**, *78*, 1311–1317.

[45] Cobb, R. L.; Mahon, J. E. *J. Org. Chem.* **1977**, *42*, 2597.

[46] Gale, D. M. *J. Org. Chem.* **1970**, *35*, 970.

[47] **Note Added in Proof.** After this work was submitted for publication we discovered a report of the proposed thermal conversion of cyanoacetylene to 1,2-dicyanocyclobutadiene and the subsequent cycloaddition of the cyclobutadiene to [2,2]paracyclophane. Witulski, B.; Ernst, L.; Jones, P. G.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 1279.

Oxidative Cleavage of Ethers by Metallic Nitrates Supported on Silica Gel

Takeshi Nishiguchi* and Masahiro Bougauchi

Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan

Received April 10, 1990

Metallic nitrates supported on silica gel efficiently cleave and oxidize ethers to the corresponding aldehydes or ketones under mild conditions. Silica gel is essential for the efficient oxidation, and $Cu(NO_3)_2$ and $Zn(NO_3)_2$ are suitable for practical use. Overoxidation of the product aldehydes is not observed. In some cases alkyl nitrites are isolated in addition to the carbonyl compounds, and the decomposition of alkyl nitrites to the corresponding carbonyl compounds is promoted by the presence of metallic nitrates supported on silica gel. Mechanistic study suggests nitrogen dioxide is an active species.

Reactions utilizing reagents on insoluble inorganic supports often have the advantages of ease of operation, mild reaction conditions, and increased yields compared with their homogeneous counterparts.[1] In the course of stud-

Table I. Oxidation of Ethers by $M(NO_3)_n$–SiO_2[a]

ether	M	solvent	product, yield, %	recovery, %
cyclododecyl methyl ether	Zn	CCl_4	cyclododecanone, 87	18
hexyl ether[b]	Zn	isooctane	hexanal, 97	46
hexyl ether[b]	Zn	CCl_4	hexanal, 65; hexyl nitrite, 10	35
butyl ether[b]	Cu	CCl_4	butanal, 64; butyl nitrite, 25	27
2-hexenyl methyl ether	Zn	CCl_4	2-hexenal, 81	2
benzyl methyl ether	Zn	isooctane	benzaldehyde, 94	0
p-methylbenzyl methyl ether	Cu	isooctane	*p*-tolualdehyde, 83	0
p-chlorobenzyl methyl ether	Cu	isooctane	*p*-clorobenzaldehyde, 74	4
m-chlorobenzyl methyl ether	Cu	isooctane	*m*-clorobenzaldehyde, 81	14
p-fluorobenzyl methyl ether	Cu	isooctane	*p*-fluorobenzaldehyde, 81	0
p-nitrobenzyl methyl ether	Cu	isooctane	*p*-nitrobenzaldehyde, 65	5
benzyl ethyl ether	Zn	isooctane	benzaldehyde, 87	0
benzyl isopentyl ether	Zn	isooctane	benzaldehyde, 84; isopentyl nitrite, 23	0
benzyl hexyl ether	Cu	isooctane	benzaldehyde, 81; hexyl nitrite, 69; hexanal, 1	
benzyl ether[b]	Zn	CCl_4	benzaldehyde, 159	0
1,4-bis(methoxymethyl)benzene	Cu	CCl_4	4-(methoxymethyl)benzaldehyde, 70; 1,4-benzenedicarboxaldehyde, 9	24

[a] An ether (1 mmol) and $M(NO_3)_n$–SiO_2 (4 mmol) were heated under reflux in a solvent (20 mL) for 1 h. [b] One mole of the products from 1 mol of the ether was calculated as 100%.

ying oxidation of alcohols to aldehydes and ketones by metallic nitrates supported on silica gel ($M(NO_3)_n$–SiO_2),[2] we found ethers also are oxidized by these reagents. This oxidative cleavage of ethers to give aldehydes or ketones should be useful for organic synthesis because it occurs under neutral and mild conditions in simple experimental operations. To the best of our knowledge there is only one report of the controlled oxidation of an alkyl ether by a metallic nitrate; diethyl ether has been reported as reacting with $Cu(NO_3)_2$ to give a trace amount of acetaldehyde.[3,4] A part of our study has been reported preliminarily.[5]

Results and Discussion

Reactions of Ethers. Unless otherwise noted, the oxidations in this study were carried out by heating an ether (1 mmol) and a $M(NO_3)_n$–SiO_2 (2 mmol; 3.5 mmol/g of SiO_2) in refluxing CCl_4 (20 mL) under nitrogen. A brown gas, which was identified as nitrogen dioxide (NO_2) by Saltsman's method[6] and is inferred to be the active oxidizing species in this oxidation, appears in the reaction vessel when the oxidation begins and disappears when completed. The oxidizing activity of supported metallic nitrates, which are represented by cationic parts only, decreases in the following order: Cu(II) > Zn(II) > Bi(II) > Ce(III) > Co(II) > Hg(II) ÷ Ni(II) > Fe(III) ÷ Ag(I) ÷ Mn(II) ÷ Cr(III) > Hg(I) > Cd(II) > Al(III) > Tl(I) ≫ Mg(II) ÷ Ca(II) ÷ Na(I) ÷ NH_4(I). A part of the detailed data of this results are noted in the communication.[5] This order of the reactivity is nearly the same as that observed in the oxidation of cyclododecanol[2] and suggests a similarity in the reaction mechanisms. The oxidizing ability of the reagents seems not to be related to the oxidation potential or the oxidation number of the metallic ions of the nitrates. For example, $Ce(NH_4)_2(NO_3)_6$, which is a well-known oxidizing reagent and contains Ce(IV), is less active than $Ce(NO_3)_3$.[5] This order of the activity seems to be related to the ability of the nitrates to give NO_2 because the higher the activity of the nitrates the larger the amount of the brown gas observed. The formation of NO_2 from covalent metallic nitrates has been reported.[4] The activity of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ that were powdered, dried, and used without being supported, is found to be almost negligible (Figure 1). Further, if these nitrates were not supported but only mixed with silica gel, they are as inactive as the ones used without supports. These results indicate that metallic nitrates are required to be in close contact with silica gel for the oxidation to occur efficiently. As solid supports chromatographic silica gels are the most effective, neutral alumina and bentnite clay are less effective, and active carbon, Celite 535, zeolite A-4, and molecular sieves 3A are ineffective.[7]

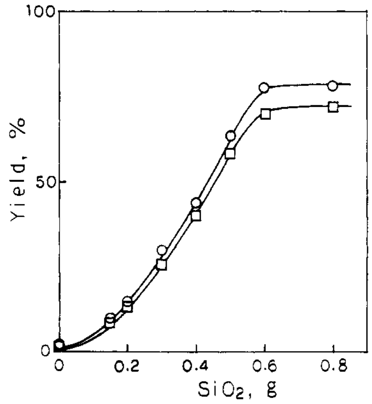


Figure 1. Yields of benzaldehyde vs the amount of silica gel. Benzyl cyclododecyl ether (0.5 mmol) and $Cu(NO_3)_2$– (○) or $Zu(NO_3)_2$–SiO_2 (□) (1 mmol) were heated in refluxing CCl_4 (10 mL) for 5 min.

Oxidation of several ethers was studied using $Cu(NO_3)_2$ and $Zn(NO_3)_2$, as representatives of the reagents. The results which do not overlap with the ones noted in the communication[5] are shown in Table I. Most of primary and secondary ethers gave the corresponding aldehydes and ketones in high yields. Relative initial rates in the oxidation of 2-hexenyl, benzyl, cyclododecyl, and nonyl methyl ethers by $Cu(NO_3)_2$–SiO_2 are found to be 184:89:32:1. This order shows the reactivity of O-substituents of ethers decreases in the order of allyl > benzyl

---

(1) For reviews, see: (a) *Preparative Chemistry Using Supported Reagents*; Laszlo, P., Ed.; Acadmeic Press: San Diego, 1987. (b) McKillop, A.; Young, D. W. *Synthesis* **1979**, 401 and 481. (c) Cornelis, A.; Laszlo, P.; Pennetreau, P. *Clay Minerals* **1983**, *18*, 437. (d) Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909. (e) Laszlo, P. *Acc. Chem. Res.* **1986**, *19*, 121. (f) Laszlo, P. *Science* **1987**, *235*, 1473.

(2) Nishiguchi, T.; Asano, F. *J. Org. Chem.* **1989**, *54*, 1531.

(3) Coard, L. C.; Powell, R. E. *J. Chem. Soc. A* **1967**, 296.

(4) Addison, C. C. *Coord. Chem. Rev.* **1966**, *1*, 58.

(5) Nishiguchi, T.; Bougauchi, M. *J. Org. Chem.* **1989**, *54*, 3001.

(6) Saltsman, B. E. *Anal. Chem.* **1960**, *32*, 135. Ho, T.-L. *Synthesis* **1973**, 347.

(7) Benzyl cyclohexyl ether (1 mmol) and $Zn(NO_3)_2$ (2 mmol) supported on a solid (1 g) were heated in refluxing CCl_4 (20 mL) for 1 h. Yields of benzaldehyde and cyclohexanone are shown in the parentheses; silica gel BW-300 (Fuji-Davison, 230–400 mesh) (71%, 29%), silica gel 60 (Merck, 230–400 mesh) (70%, 28%), silica gel 60 (Merck, 70–230 mesh) (69%, 29%), silica gel 60 H (Merck, for TLC) (65%, 26%), alumina (ICN, N-super I) (45%, 18%), bentnite clay (37%, 11%), active carbon (powder) (7%, 2%), molecular sieves 3A (powder) (6%, 2%), Celite 535 (5%, 2%), zeolite A-4 (synthetic, 200 mesh) (2%, 1%).

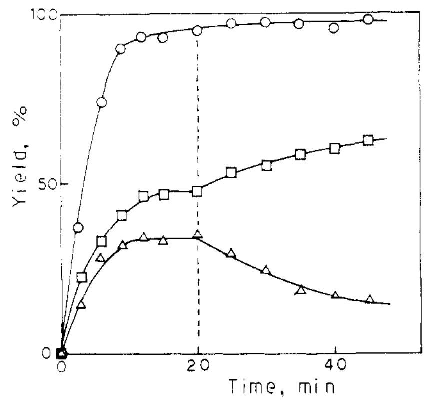


Figure 2. Oxidation of benzyl cyclohexyl ether: benzaldehyde (○); cyclohexanone (□); cyclohexyl nitrite (△). The ether (1 mmol) and $Cu(NO_3)_2$–SiO_2 (2.4 mmol) were heated in refluxing CCl_4 (12 mL). After 20 min of heating, more $Cu(NO_3)_2$–SiO_2 (1.2 mmol) was added.

> secondary alkyl ≫ primary alkyl. Considerable amounts of alkyl nitrites were detected in some reactions of ethers containing alkyl groups. Overoxidation of the formed aldehydes to the corresponding carboxylic acids was not observed in any case. In the reaction between benzyl cyclohexyl ether and $Cu(NO_3)_2$-SiO_2, the yields of benzaldehyde, cyclohexanone, and cyclohexyl nitrite were 95, 47, and 35%, respectively at a reaction time of 20 min and did not change thereafter (Figure 2). At this stage, more $Cu(NO_3)_2$–SiO_2 was added. An increase of the yield of the ketone and the decrease of that of the nitrite were observed. This result shows that the supported reagent promotes the decomposition of the nitrite to the ketone and that the nitrate added first is consumed within 20 min.

Figure 1 shows the dependence of the yield of benzaldehyde on the amount of silica gel (grams) in the reaction between benzyl cyclohexyl ether (0.5 mmol) and $Cu(NO_3)_2$– and $Zn(NO_3)_2$–SiO_2 (1 mmol). The increase of the yields shows the increase of the reaction rate because the reactions is not completed. This result suggests that the activity per 1 mmol of the nitrates becomes constant when the amount of silica gel reaches 0.6 g and the nitrates cover most of the surface of silica gel as a monolayer.[8]

When the amount of benzyl cyclohexyl ether is changed and that of $Zn(NO_3)_2$–SiO_2 is constant (1 mmol), the initial reaction rate is in proportional to the concentration of the ether at an ether/$Zn(NO_3)_2$ ratio of less than 0.2 but independent at a ratio of greater than 0.4. This result suggests that only the ether adsorbed onto the surface of the support is oxidized and that the silica gel surface is almost completely saturated with the ether when the concentration of the ether is high.

The ratio of the initial rate of the oxidation of benzyl methyl ether to that of α,α-dideuteriobenzyl methyl ether (k_H/k_D) was 2.7 in the reaction of $Cu(NO_3)_2$–SiO_2 and 3.1 in the one of $Zn(NO_3)_2$–SiO_2.[9] The fairly large k_H/k_D values suggest that the cleavage of the bond between the hydrogens and α-carbon of the benzyl group is the rate-determining step.

Table II. Decomposition of Nitrites[a]

nitrite	additive	yield and recovery, % aldehyde or ketone	 nitrite
hexyl nitrite	none	0	96
	SiO_2	2	90
	$Cu(NO_3)_2$	0	98
	$Cu(NO_3)_2$–SiO_2	40	53
cyclohexyl nitrite	none	0	100
	SiO_2	9	92
	$Cu(NO_3)_2$	0	99
	$Cu(NO_3)_2$, SiO_2[b]	16	65
	$Cu(NO_3)_2$–SiO_2	85	9
	$Zn(NO_3)_2$	0	100
	$Zn(NO_3)_2$, SiO_2[b]	11	66
	$Zn(NO_3)_2$–SiO_2	83	6
benzyl nitrite[c]	none	0	100
	SiO_2	9	85
	$Cu(NO_3)_2$	11	81
	$Cu(NO_3)_2$–SiO_2	80	11

[a] A nitrite (1 mmol) and an additive (2 mmol for a nitrate and a supported nitrate, or 0.5 g for SiO_2) were heated in refluxing CCl_4 (20 mL) for 15 min. [b] The nitrate was not supported but only mixed with silica gel. [c] Reaction time was 30 min.

The yields of the oxidation products were reduced to about a half by changing the reaction atmosphere from nitrogen to oxygen.[5] The yields of benzaldehyde and cyclohexanone were reduced to about half by the addition of 15 mol % (to $Cu(NO_3)_2$) of 2,4,6-tri-*tert*-butylphenol, which is a sterically hindered radical scavenger, in the 15-min reaction between benzyl cyclohexyl ether and $Cu(NO_3)_2$–SiO_2 in CCl_4.[10] These results suggest participation of radical species in this oxidation because radical reactions are generally influenced by the presence of oxygen and radical scavengers. Further, the logarithm of initial rates in the oxidation of *p*-methyl-, *p*-fluoro-, *p*-chloro-, and *p*-nitrobenzyl methyl ethers by $Cu(NO_3)_2$–SiO_2 in CCl_4 linearly depended on the on Hammett substituent constants to give −0.34 as the value of ρ. The fact that the electronic character of the substituents has little influence over the reaction also suggests that radical rather than ionic intermediates are formed.[11]

Reactions of Nitrites. From the reaction of ethers with supported metallic nitrates, stable alkyl nitrites are isolated. This result suggests that formation of carbonyl compounds occurs via alkyl nitrites. To examine this possibility, reactions of alkyl nitrites were carried out under the various conditions shown in Table II. We find that $Cu(NO_3)_2$– and $Zn(NO_3)_2$–SiO_2 greatly promote the decomposition of the nitrites to the carbonyl compounds, while if the nitrates are only mixed with silica gel little decomposition occurs. A similar promoting effect of $Cu(NO_3)_2$–SiO_2 is also shown in Figure 2. Therefore, the carbonyl compounds are thought to be formed at least partly via nitrites.

Reaction Mechanism. In the oxidative cleavage of ethers by $M(NO_3)_2$–SiO_2, we propose a radical process in which NO_2 is the active species. Participation of radical species is inferred from an inhibiting effect of oxygen and the radical scavenger and the small influence of electronic character of the substituents, as described above. The

---

(8) This critical loading value, 1.7 mmol of nitrate per gram of SiO_2, appears to be the amount of saturation leaving the space for the adsorption of other reactants on silica gel surface. At this critical value, the surface area most of which is effectively covered with a nitrate moiety is assumed to be 0.5 nm^2, because the surface area of silica gel WB-300 is known to be about 500 m^2/g. The same order of values have been reported for monolayer coverage of other reagents on silica gel surface. See: ref 2 and Jazzaa, A. A.; Clark, J. H.; Robertson, M. *Chem. Lett.* **1982**, 405. Ogawa, H.; Hagiwara, T.; Chihara, T.; Teratani, S.; Taya, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 627. Nishiguchi, T.; Kamio, C. *J. Chem. Soc., Perkin Trans. 1* **1989**, 707.

(9) The reason why k_H/k_D values are different in the reaction of $Cu(NO_3)_2$– and $Zn(NO_3)_2$–SiO_2 is not clear yet.

(10) The weakness of the inhibiting effect of the phenol may be explained by the speculation that the phenol and radical species are fixed tightly on the surface of silica gel by adsorption.

(11) Bryant, D. K.; Challis, B. C.; Iley, J. *J. Chem. Soc., Chem. Commun.* **1989**, 1027.

$$(NO_3)_{n-1}MONO_2 \rightarrow (NO_3)_{n-1}MO^{\bullet} + {}^{\bullet}NO_2$$

$$R^1R^2\,CHOCHR^3R^4 + {}^{\bullet}NO_2 \rightarrow R^1R^2\,{}^{\bullet}COCHR^3R^4 + HNO_2$$

$$R^1R^2\,{}^{\bullet}COCHR^3R^4 + {}^{\bullet}NO_2 \rightarrow R^1R^2\,C(ONO)OCHR^3R^4$$

$$R^1R^2\,C(ONO)OCHR^3R^4 \rightarrow R^1R^2\,C{=}O + R^3R^4CHONO$$

fairly large k_H/k_D value described before suggests the second reaction is the rate-determining step. We infer a similar scheme for the decomposition of nitrites to carbonyl compounds which is promoted by $M(NO_3)_n$–SiO_2. These

$$R^3R^4CHONO + {}^{\bullet}NO_2 \rightarrow R^3R^4\dot{C}ONO + HNO_2$$

$$R^3R^4\dot{C}ONO \rightarrow R^3R^4C{=}O + {}^{\bullet}NO$$

two schemes seem to be compatible with the results described so far.

As described earlier, NO_2 disappears when the oxidation is completed even if an excess amount of metallic nitrates are used; the brown gas is not observed while $M(NO_3)_n$–SiO_2 are heated in CCl_4 or isooctane in the absence of ethers, the nitrates which have not been supported or have been only mixed with silica gel are hardly effective, and $Cu(NO_3)_2$–SiO_2 is prepared by drying at 130 °C. These facts suggest that NO_2 is not formed by simple thermal decomposition of nitrates but is formed only when the nitrates are in close contact with reductive substances such as ethers and alcohols and that the contact is mediated by the adsorbent. Another function of silica gel seems to be holding the NO_2 formed on its surface. Apparently the surface of silica gel forms a reaction field where ethers and NO_2 are accumulated by adsorption in high concentration.

In conclusion metallic nitrates supported on silica gel are considered as "solid nitrogen dioxide", which can be used in a simple experimental procedure to provide a useful oxidation.

Experimental Section

General. Para-substituted benzyl methyl ethers, benzyl hexyl ether, 2-hexenyl methyl ether, cyclododecyl methyl ether, and 1,4-bis(methoxymethyl)benzene were prepared by the method reported in the literature.[12] α,α-Dideuteriobenzyl methyl ether was also prepared from α,α-dideuteriobenzyl alcohol[13] and methyl iodide in a similar way. Nitrites were synthesized by the procedure described in the literature.[14] GLC analyses were carried out with a 25 m × 0.25 mm i.d. fused silica capillary column OV-1 or OV-1701.

An Example of the Preparation of Oxidizing Reagents. To a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.69 g, 7 mmol) in water (10 mL) was added 230–400-mesh chromatographic silica gel WB-300 (2 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 (5–15 Torr) with stirring until most of the moisture is removed. The reagent has the highest activity just when the color of the powder begins to change from blue to green and loses the activity when it changes to green completely. If the brown gas is evolved during the drying, the reagent has not the activity. Usual dying time is about 30 min. One gram of this reagent (3.5 mmol/g of SiO_2) contains about 2.11 mmol of $Cu(NO_3)_2$.

The other supported nitrates were dried at the temperatures reported in the previous paper.[2] The dried reagents were stored in a vessel sealed with parafilm or over P_2O_5 in a desiccator.

An Example of the Oxidation by a Supported Nitrate. Benzyl cyclohexyl ether (188 mg, 1 mmol) and $Cu(NO_3)_2$–SiO_2 (1.14 g, 2.4 mmol; 3.5 mmol/g of SiO_2) were heated under nitrogen atmosphere in refluxing CCl_4 (12 mL) while being stirred. The brown gas came out. The reaction was monitored by TLC (1:4 ethyl acetate/*n*-hexane). Ten minutes later, the brown gas disappeared. After 15 min of heating, *n*-pentadecane (0.1 mL), which is an internal standard in GLC analysis, was added and the reaction mixture was transferred to a small glass column with a cotton plug. The solid was separated by filtration and eluted with acetone (3 mL). The filtrate and the eluate were combined and submitted to GLC analysis. Benzaldehyde (0.92 mmol, 92%), cyclohexanone (0.47 mmol, 47%), and cyclohexyl nitrite (0.35 mmol, 35%) were detected. Other oxidation reactions were also carried out in a similar way.

Initial Rate Measurement. Into 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 ether (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, because no induction period was observed in any case, as shown in Figure 2.

---

[12] Brown, C. A.; Barton, D. *Synthesis* **1974**, 434.

[13] Bunnett, J. F.; Davis, G. T.; Tanida, H. *J. Am. Chem. Soc.* **1962**, *84*, 1606.

[14] Noyes, W. A. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 108.