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Short communication

Facile access to nitroalkanes: Nitration of alkanes by selective C—H nitration using metal nitrate, catalyzed by in-situ generated metal oxide

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ABSTRACT

Direct C − H functionalization of inactive alkanes is an important strategy to streamline the preparation of functional molecules. Herein, we describe an operationally simple and effective alkane C − H nitration reaction to access versatile nitroalkanes without cleavage of the C − C skeleton. Nontoxic and inexpensive metal nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) plays a dual role as catalyst precursors as well as nitro sources for the transformation. Experimental evidence and theoretical modeling have shown the formation of iron oxide as a key catalytic species for the alkane C − H and NO_2 activation, which favors a stepwise radical mechanism with initial alkyl radical formation.

1. Introduction

Nitro compounds are regarded as key building blocks [1,2] and ideal intermediates [3] for the generation of pharmaceuticals, dyes, explosives and materials in synthetic chemistry. In contrast to the easy nitration of aromatic C − H bonds, the preparation of nitroalkanes by the selective nitration of aliphatic C − H bonds is very challenging and much less investigated because of the difficulty of activation of alkane C—H bond. Currently, nitration of alkanes relies on harsh methodologies involving excess nitrogen dioxide or nitric acid under forced reaction conditions (250–450 °C) to generate thermally alkyl radicals by the alkane C—H bond scission [4,5]. Under such conditions, alkanes undergo the undesired C—C skeleton cleavage, exhibiting poor nitroalkane selectivity. Therefore, this vapor-phase approach present a number of critical drawbacks in terms of reactant structure, which is only limited to the nitration of methane, ethane and propane [4,6,7]. Thus, vapor-phase nitration of higher molecular weight hydrocarbons such as cycloalkane is in a less satisfactory state [8,9], since there are reactions which compete the thermal isomerization of the cycloalkane to alkenes with the further formation of the undesirable lower nitroalkanes. In the last few decades, although some strategies including ozone-promoted or laser-induced nitration with nitrogen dioxide and either nitration with unstable NO_2BF_4 have provided access to nitrocycloalkane, there has been a notable lack of recent progress in the selective nitration C—H bonds of cycloalkane (Scheme S1) [10–13].

In an industrial context, the development of mild and efficient methods for the selective nitration of C − H bonds is highly desirable, since nitrocyclohexane and nitrocyclohexene are easily by reduction to cyclohexanone oxime, which is a starting material for the manufacture of nylon-6 polymers [14–17]. Recently, Ishii and his co-workers [12,18,19] discovered that N-hydroxyphthalimide (NHPI) can serve a key catalyst for the nitration of low-carbon cycloalkanes under mild conditions, by the use of HNO_3 or NO_2 as a nitro reagent. However, most of NHPI was decomposed to phthalic acid and other products, and a large amount of NHPI catalyst (> 10 mol%) was required to achieve high conversion [13]. And later on, Yamaguchi et al. developed a $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ -catalyzed method for the nitration of various alkanes using nitric acid in acetic acid [20]. Nitration of cyclohexane is reported to give a 10% nitrocyclohexane yield with 90% selectivity, but the increase of conversion is still difficult issues. At present, all of the above-mentioned nitration reactions associated with the use of excess mineral HNO_3 or NO_2 as nitrating agents, which present a number of critical drawbacks with the difficulty of its handling and toxicity in terms of environmental impact [21]. Thus, a search for user-friendly and selective nitrating agents is a good research goal for the direct C − H activation in the C − N bond formation. Iron compounds have recently attracted great attention in organic transformation as nontoxic and inexpensive green elements [22]. Thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ is well known to in-situ generate nitrogen dioxide [23], which is a radical species, but no attention has been paid to direct alkane C − H functionalization of this method. Herein, we developed an efficient and facile radical nitration of various alkanes and

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Table 1
Effect of different metal nitrate as nitrating agent on nitration of cyclohexane.[a]

Entry	Nitrating agent	Conv. (%)	Sel. (%)[b]				Yield (%)[c]
			A	B	C	D	
1	$LiNO_3$	3.6	38.5	–	21.5	7.7	1.4
2	KNO_3	3.6	64.5	–	15.3	8.8	2.3
3	$AgNO_3$	1.2	49.7	–	29.2	21.2	0.6
4	$Pb(NO_3)_2$	1.7	75.1	–	14.9	10.0	1.3
5	$Co(NO_3)_2{\cdot}6H_2O$	5.2	45.5	–	13.4	9.1	2.4
6	$Ni(NO_3)_2{\cdot}6H_2O$	3.3	54.3	–	16.2	9.0	1.8
7	$Mg(NO_3)_2{\cdot}6H_2O$	0.6	43.2	–	21.7	19.4	0.3
8	$La(NO_3)_3{\cdot}nH_2O$	1.3	53.3	–	20.5	26.2	0.7
9	$Al(NO_3)_3{\cdot}9H_2O$	37.0	78.8	5.4	4.6	5.7	29.2
10	$Bi(NO_3)_3{\cdot}5H_2O$	41.6	89.1	7.7	–	–	37.0
11	$Cr(NO_3)_3{\cdot}9H_2O$	48.0	92.4	4.2	–	–	44.3
12	$Fe(NO_3)_3{\cdot}9H_2O$	53.7	92.1	4.3	–	3.6	49.5
13	$Zr(NO_3)_4{\cdot}5H_2O$	29.9	88.1	8.5	–	–	26.3
14[d]	$Fe(NO_3)_3{\cdot}9H_2O$	60.9	83.1	4.3	1.9	1.5	50.6
15[e]	$Fe(NO_3)_3{\cdot}9H_2O$	53.1	93.1	3.0	–	2.5	49.5
16[f]	$Fe(NO_3)_3{\cdot}9H_2O$	17.3	74.4	9.5	–	8.7	12.9

[a] Reaction conditions: cyclohexane (1.78 mmol), $PhCF_3$ (5 mL), nitrate salts (5.35 mmol), 145 °C, 3 h.

[b] A = nitrocyclohexane, B = nitrocyclohexene, C = cyclohexanol, D = cyclohexanone.

[c] Yields are average values obtained from several runs and are based on cyclohexane used.

[d] Pure oxygen atmosphere.

[e] Nitrogen atmosphere.

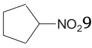
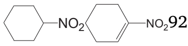
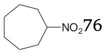
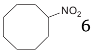
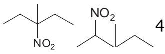
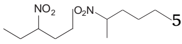
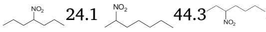
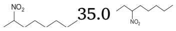
[f] A combination of HNO_3 and a small amount (0.04 mmol) of $Fe(NO_3)_3$.

alkylbenzenes using $Fe(NO_3)_3{\cdot}9H_2O$ to give nitro-compounds from the viewpoints of safety and economy. Moreover, it enables the nitrocycloalkanes formation that cannot be accessed effectively by other means so far, most notably nitrocyclohexane compounds (Scheme S1).

2. Results and discussion

We initiated our investigation by exploring the nitration of cyclohexane with simple, readily available $Fe(NO_3)_3{\cdot}9H_2O$ in $PhCF_3$ for the method development studies, where product selectivity (i.e., nitration versus oxidation or isomerization) may be problematic. Remarkably clean and smooth conversion (53.7%) to nitrocyclohexane was achieved $Fe(NO_3)_3{\cdot}9H_2O$ with under the conditions employed (Table 1, entry 12), affording nitrocyclohexane (92.1%) and nitrocyclohexene (4.3%) along with oxygenated products, cyclohexanone (3.6%). Other nitrated and oxidized products caused by the C − C skeleton cleavage of cyclohexane were not detected at our reaction conditions. In a set of nitro sources screened, it is noteworthy that both $Cr(NO_3)_3{\cdot}9H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ (entries 10 and 11) also show significant activity similar to that of $Fe(NO_3)_3{\cdot}9H_2O$, though slightly lower. Under similar conditions as for $Al(NO_3)_3{\cdot}9H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$ also demonstrated comparable efficiency but with a lower conversion and selectivity (entries 9 and 13), thus asserting the importance of the metal ion in nitration process. In contrast, other metal nitrate salts proved ineffective for this nitration reaction (entries 1–8), which could be attributed to the fact that in situ generation of NO_2 would be difficult for thermal decomposition of metal nitrate salts, as in the latter transformation. On the other hand, the nitration of cyclohexane with a combination of HNO_3 and a small amount of $Fe(NO_3)_3$ (as catalyst) led to nitrocyclohexane in poor yield (entry 16). The reaction under nitrogen atmosphere instead of oxygen performed well and produced nitrocyclohexane with a slightly higher selectivity (entries 12, 14–15). Among the solvents examined (Table S1), trifluorotoluene was found to be a good solvent. Meanwhile, $Fe(NO_3)_3{\cdot}9H_2O$ and self-decomposition iron oxide were almost insoluble in trifluorotoluene, which is easy to separate and reuse in a more practical nitration procedure. In other solvents such as CH_3COOH and CF_3COOH, the reaction was noticeably slower than in trifluorotoluene but provided exclusively the desired nitrocyclohexane and nitrocyclohexene products. Use of halogenated solvents noticeably decreased the conversion and selectivity of this reaction. In contrast, by employing the reactions in CH_3CN and DMF produced little nitro product. Screening of the parameter of temperature indicated that 145 °C was a more suitable temperature for the reaction (Table S2). A decrease in temperature to 125 °C resulted in a slower reaction that required more time (8 h) to reach similar results. By increasing the amount of nitrite, we were able to convert cyclohexane to the desired nitro product in virtually quantitative yield. The optimal amount of nitrite with 3.0 equiv. of cyclohexane in catalytic system is essential to the outcome of the reaction (Table S3), and the excess nitrate can be recycled by simple filtration. Under the optimized condition, a gram-scale (2 g) reaction resulted in 44% isolated yield of the desired nitro product.

Table 2
Nitration of different substrates with ferric nitrate.[a]

Entry	Substrate	Conv. (%)	Sel.(%)
			Product
1	Cyclopentane	42.1	 97.0
2	Cyclohexane	53.7	 92.1 4.3
3[b]	Cycloheptane	37.6	 76.9
4[b]	Cyclooctane	29.6	 66.1
5	3-Methylpentane	27.5	 42.8 16.7
6	N-hexane	29.9	 50.9 49.1
7	N-heptane	23.0	 24.1 44.3 31.6
8[b]	N-octane	36.2	 35.0 30.8

[a] Reaction conditions: alkane (1.78 mmol), $PhCF_3$ (5 mL), ferric nitrate (5.35 mmol), 145 °C, 3 h.

[b] Reaction time 24 h at 110 °C.

With the optimal conditions in hand, the scope of the protocol was explored for the reactions of a series of alkanes with $Fe(NO_3)_3{\cdot}9H_2O$ to nitro compounds, and representative results are summarized in Table 2 and Table S4. First, nitration reactions of cyclic alkanes were examined. In Table 2, the conversion is 42.1% and selectivity is 97.0%, which is higher than that for cyclohexane in terms of selectivity though lower in terms of conversion. On the other hand, seven-membered cycloheptane or eight-membered cyclooctane was difficult to nitrate selectively, and gave slightly lower yield (37.6% conversion with 76.9% selectivity for cycloheptane; 29.6% conversion with 66.1% selectivity for cyclooctane) because of the formation of ketone byproducts. Next, several aliphatic hydrocarbons were subjected to the nitration under these reaction conditions. The nitration of 3-methylpentane occurred at the tertiary position in preference to the methylene group, giving 3-methyl-3-nitropentane and 3-methyl-2-nitropentane, in 42.8% and 16.7% selectivity, respectively. Treatment of n-hexane with $Fe(NO_3)_3{\cdot}9H_2O$ at 145 °C led to an approximate 1:1 regioisomeric mixture of 2-nitrohexane and 3-nitrohexane at 29.9% conversion. The same preference was observed as well in the case of n-heptane with 100% nitroalkane product, whereas n-octane having a longer carbon chain was less selective giving 65.8% selectivity, respectively. Finally, the protocol was extended for the reaction of various alkylbenzenes with $Fe(NO_3)_3{\cdot}9H_2O$ (Table S5). Toluene was difficult to nitrate selectively on the methyl group, giving the (nitromethyl)benzene product in less than 6.5% selectivity, along with benzene ring substituted products such as p-nitrotoluene (60.9%) and o-nitrotoluene (21.6%). Actually, nitration of aromatic ring was also observed for benzene under these reaction conditions. It is noted that the nitration of ethylbenzene only occurred

Table 3
Effect of different isolated metal oxides as catalysts on nitration of cyclohexane.[a]

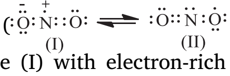
Entry	Cata.	Nitrating agent	Conv.(%)	Sel. (%)[b]				Yield (%)
				A	B	C	D	
3	Fe_2O_3	$Al(NO_3)_3·9H_2O$	58.3	86.0	5.7	1.5	2.6	50.1
4[c]	Fe_2O_3	$Al(NO_3)_3·9H_2O$	47.5	84.9	4.4	2.1	2.9	40.3
5	Cr_2O_3	$Al(NO_3)_3·9H_2O$	53.9	83.0	9.7	1.1	1.6	44.8
6	Bi_2O_3	$Al(NO_3)_3·9H_2O$	48.9	81.9	8.1	1.2	3.9	40.0
7	Fe_2O_3	$Al(NO_3)_3·9H_2O$	52.0	89.8	5.2	0.3	2.4	46.7
8	Fe_2O_3	$AgNO_3$	0.5	55.1	–	31.7	13.2	0.3
9	Fe_2O_3	$Co(NO_3)_2·6H_2O$	1.3	42.2	–	18.0	16.8	0.5
10	Fe_2O_3	$Zr(NO_3)_4·5H_2O$	49.5	88.2	6.6	0.5	1.2	43.6

[a] Reaction conditions: 0.02 mmol isolated metal oxide, cyclohexane (1.78 mmol), $PhCF_3$ (5 mL), nitrate salts (5.35 mmol), 145 °C, 3 h.

[b] A = nitrocyclohexane, B = nitrocyclohexene, C = cyclohexanol, D = cyclohexanone.

[c] Using 0.02 mmol Fe_2O_3 (prepared) as catalyst. Yields are average values obtained from several runs and are based on cyclohexane used.

on the ethyl side-chain group to give 96.8% nitro-compound selectivity, with the benzene ring remaining intact. This can be attributed to a lower C—H bond energy of ethyl group in ethylbenzene. Furthermore, tetrahydronaphthalene was also nitrated to only give the alkyl mono-nitrated product, and no nitration of benzene ring was detected.

To probe the possibility of the ferric oxide species acting as a catalyst, the ferric oxide from the $Fe(NO_3)_3·9H_2O$ decomposition was isolated by filtrating and washing with ethanol after the reaction, and the α-Fe_2O_3 structure was confirmed by the XRD analysis (Fig. S1) [24]. Employing the isolated ferric oxide (1.1 mol%) as an additive, the nitration of cyclohexane with $Al(NO_3)_3·9H_2O$ or $Zr(NO_3)_4·5H_2O$ as the nitrating agent showed higher activity than that of $Al(NO_3)_3·9H_2O$ or $Zr(NO_3)_4·5H_2O$ alone (Table 3, entry 3), and the conversion of cyclohexane was improved from 37.0% to 58.3%. When other metal oxides such as Bi_2O_3 and Cr_2O_3 were used as a additive, the nitration of cyclohexane with $Al(NO_3)_3·9H_2O$ was efficiently promoted and the activity was similar to that of Fe_2O_3. These results implied that the self-decomposition metal oxide might be the active catalyst in the current catalytic nitration reaction. To gain further insight, density functional theory (DFT) is employed to understand the influence of ferric oxide on the reaction in the catalysis (Fig.S2 and Fig. 1). First, adsorption of cyclohexane molecules takes place on Fe—O sites, understanding the exact nature of these species for the C—H bond activation under reaction conditions is critically important. In Fig. S2B, cyclohexane dissociately adsorbs on the surface of Fe_2O_3 (001) with an adsorption energy of −0.83 eV. The H atom of cyclohexane binds with the O atom of Fe—O sites with the distance of 3.565 Å (which is further supported by charge density difference, as shown in Fig. S3B), and the C − H bond of cyclohexane elongates from 1.107 Å (free cyclohexane) to 1.112 Å. Additionally, the H 1 s and O 2p bands are smearing upon a wide range of energy levels through the valence band between −7.5 to −2.5 eV from state-by-state atom-projected density of states (PDOS) (Fig. 1), without strong anti-bonding above the Fermi level. Thus, the lowest unoccupied molecular orbitals (LUMO) in a low-spin, Fe—O sites are expected to be the two orthogonal p* orbitals, which would direct the approach of the C—H bond to a bent p*-approach trajectory [25]. This markedly reduces the energy barrier for the first C—H band homolytic pathway. In Fig. S2C, NO_2 adsorbs on Fe atom of Fe_2O_3 with the Fe—O distance of 1.870 Å and the N=O bond length obviously changes from 1.234 Å (free NO_2) to 1.384 Å. The O–N–O angle (decreased by 20°) is in this case 112° and the adsorption energy −2.04 eV. Meanwhile, as the LUMO level of NO_2 becomes occupied (Fig. 1), the adsorbate constitutes a system with an even number of electrons, which leads to the broadening of 2p* band with an edge near the Fermi level and the significant charge-transfer (about 0.23 electron) from the surface Fe atom to the adsorbed NO_2 molecule (the charging of NO_2 is more efficient in the presence of a backing metal, as shown in Fig. S3). Thus, the NO_2 radical molecule as a resonance hybrid ( $\underset{(I)}{:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:\overset{+}{\dot{N}}::\ddot{O}:} \rightleftharpoons \underset{(II)}{:\ddot{O}::\ddot{N}:\underset{\cdot\cdot}{\dot{O}}:}$) is partially bent via its polarization to more (I) with electron-rich oxygen by the effect of Fe_2O_3 species, C—H attraction reaction can ensue. Consequently, partial metal nitrate can act as an active nitrating agent for unreactive alkanes.

To gain insights on the reaction pathway, additional experiments were performed (Scheme S2). First, an intermolecular competition experiment between cyclohexane and benzene showed 56.7% nitrocyclohexane and 2.5% nitrobenzene, which is also supported by the fact that no benzene ring substituted process occurred in an intramolecular competition experiment using cyclohexylbenzene substrate. Furthermore, no nitrocyclohexane product was observed when the reaction with $Fe(NO_3)_3·9H_2O$ was performed in the presence of radical scavengers, such as TEMPO and BHT. These results indicate that alkane nitration might involved a radical process. Second, deuterium kinetic isotope effect (KIE) was evaluated by the reaction of a 1:1

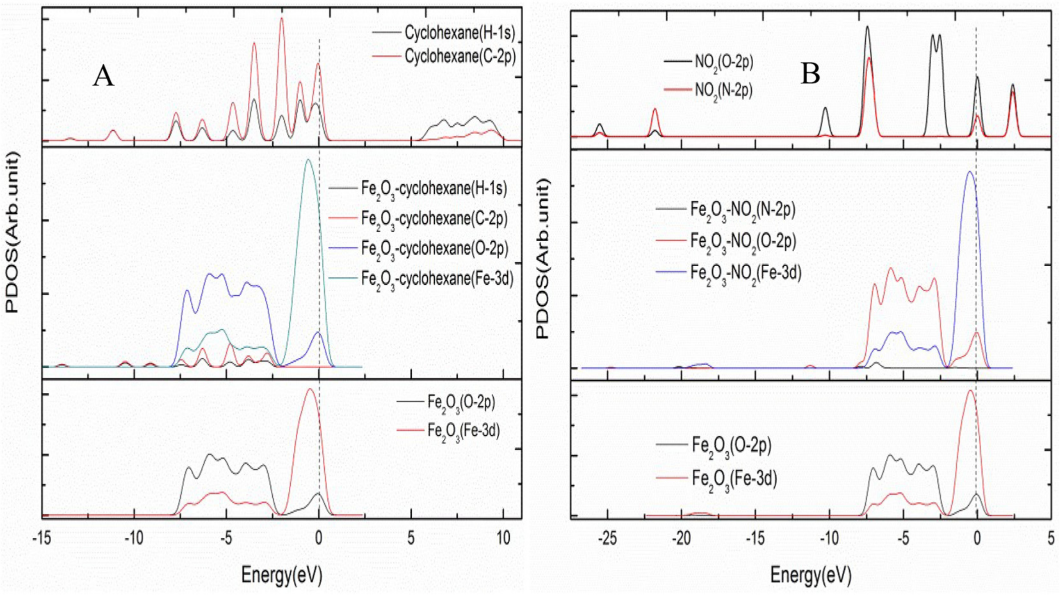


Fig. 1. Electronic density of states of cyclohexane (A) and NO_2 (B) adsorption on α-Fe_2O_3 (001).

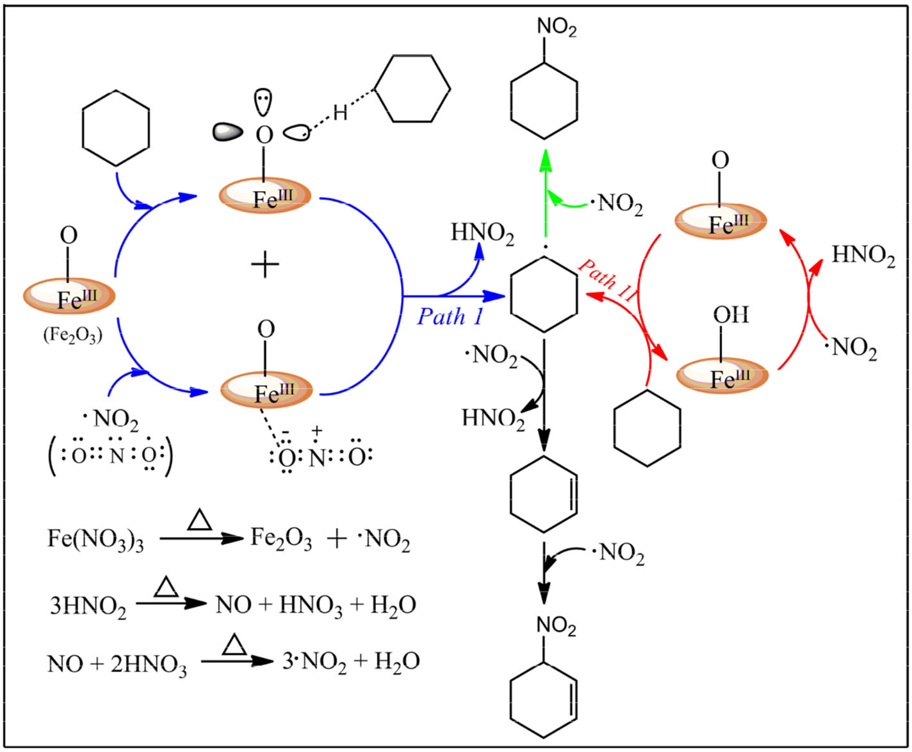


Fig. 2. Proposed mechanism for self-decomposition metal oxide-catalyzed C—H nitration reactions.

mixture of deuterated cyclohexane and cyclohexane, producing an intermolecular competitive KIE of 2.3. This large value suggests that cyclohexane C—H bond cleavage is the rate-determining step of the nitration. Finally, we conducted the dynamics of spectral changes during the nitration of cyclohexane with time (Fig. S4). The UV–Vis spectra of reaction mixture containing 0.02 M cyclohexane, recorded shortly (5–10 min) after reaction, exhibits a strong absorbance at 290 nm, which indicated the evolution of nitrogen dioxide. After the reaction for 40 min, a significant blue shift (280 nm) is observed in the reaction mixture spectrum, which was indicative of the formation of the nitrocyclohexane product. Particularly, this spectral intensity at 280 nm became much stronger upon prolonging the reaction time from 40 min to 60 min, which confirmed that there should be an obvious induction period for cyclohexane nitration. This is further explained by reaction profiles of the nitration of cyclohexane in Fig.S5.

On the basis of the experiments above and literature precedents [13,18,26], a plausible mechanism for Fe_2O_3-catalyzed sp^3 C − H nitration of cyclohexane is proposed (Fig. 2). The NO_2 radical and ferric oxide as catalytic species are first formed from thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ under reaction conditions. The active ferric oxide species plays a dual role, as the polarization of NO_2 to bent NO_2 molecule with electron-rich oxygen and the activation of cyclohexane. Subsequently, H-atom abstraction reaction of activated cyclohexane by bent NO_2 molecule gives a cyclohexyl radical and HNO_2. Thus, the radical traps another NO_2 to give nitrocyclohexane. It is reported that HNO_2 can be converted into NO_2 and H_2O under heating conditions [13,27], and the generated NO_2 is reused in the present nitration, which is the reason why this reaction can be performed without addition of O_2. In addition, the possibility that the direct formation of cyclohexyl radical on Fe_2O_3 species by H-atom abstraction (or single electron transfer), followed by the reaction with NO_2 to nitrocyclohexane as another path cannot be ruled out, because the nitration of cyclohexane proceeded with an shorter induction period (20 min) in the presence of Fe_2O_3 species. A small amount of nitrocyclohexene product provides support for the generation of cyclohexyl radical intermediate, which is obtained by elimination of hydrogen atom with NO_2 to give cyclohexene with further nitration.

3. Conclusion

In summary, we reported the first a new set of nitrating reagents for highly selective nitration reaction of alkanes. Various alkanes and alkyl side-chain of aromatic compounds were nitrated in excellent yields, by the use of cheap and easy-to-handle metal nitrate compared with NO_2 and nitric acid. Under the present conditions, carbon-carbon bond cleavage reactions for cyclohexane nitration hardly proceed, affording nitrocyclohexane (92.1%) and nitrocyclohexene (4.3%) along with oxygenated products, cyclohexanone (3.6%).

Declaration of Competing Interest

The authors declare that they have no known competing financialinterestsor personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106035.

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