

Experimental and theoretical studies on green and efficient deoxygenation using H₂O₂ catalyzed by Montmorillonite-K10 supported MnCl₂

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ABSTRACT

Oximes were oxidized to the corresponding carbonyl compounds in good to high yields by eco-friendly and green oxidant, H₂O₂ catalyzed by Montmorillonite K-10 supported Manganese(II) Chloride. The structures of these compounds were favorably compared with the results of ab initio calculations at three temperatures. Computational methods allow for the visualization of large amounts of structural data and the generation of related conformations for statistical and dynamic analyses. Clearly, further studies and trapping experiments are necessary to support this mechanism and to account for the formation of organic reagents.

Extensive measurements, as well as ab initio quantum computational reveal that the effect of temperature on formation of products as a function of the actual structures in a manner that is rather complicated. In this work, the formation of products is considered as the potentially more general reaction.

Keywords: Green Deoxygenation System; Hydrogen Peroxide; Montmorillonite K-10; Manganese (II) Chloride; Ab initio; Relative stability energies; Thermodynamic computation.

INTRODUCTION

Oximes are used not only for isolation, purification and characterization but also for protection of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds, deoxygenation such oximes provides an alternative method for the preparation of aldehydes and ketones[1]. Oxidation of organic substrates in aprotic solvents under mild and

neutral conditions is important in modern organic synthesis. Therefore, the search for new oxidizing reagents is of interest to synthetic organic chemists. For this purpose a large number of reagents have been developed in recent years with some success. In addition several solid supported oxidizing agents have also been reported in the literature.

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So far a good number of methods based on hydrolytic, reductive and oxidative reactions have been developed for deoxygenation. The methods based on oxidative reactions make use of several oxidizing agents. These include chromium reagents such as pyridinium chlorochromate [6], triethyl ammonium chlorochromate [3], unsupported chromium trioxide [6], polymer supported CrO_3 [7], alumina supported N-methyl piperidinium chlorochromate [8], ZrCl_4 on wet SiO_2 supported ammonium dichromate [9] and supported quinolinium fluorochromate [10]. Nonchromium oxidizing agents were included Rany nickel [11], dinitrogen tetroxide [12], dimethyl dioxirane [13], H_2O_2 over titanium silicalite-1 [14], zirconium sulfophenyl phosphate [15], N-haloamides [16], bismuth chloride [17], ammonium persulphate-silica gel [18], periodic acid [19], manganese triacetate [20], t-Butyl hydroperoxide [21], polymer supported anionic peroxomolybdenum complexes [22], activated MnO_2 [23], Dess-Martin periodinate [24], tetrabutylammonium peroxydisulphate [25], alumina supported potassium permanganate [26], wet SiO_2 supported $\text{Mg}(\text{HSO}_4)_2$ [27], N,N'-dibromo-N,N'-1,2-ethanediylbis(p-toluene sulfonamide) [28], polymer supported peroxotungstate complex [29], poly(4-vinyl-N,N-dichloro benzene sulfonamide) [30] and silica gel confined functional ionic liquids [31]. Montmorillonite clays have been extensively used as efficient supports for a variety of organic reagents [8, 32].

Then the proposed mechanisms for their formations are supported by *ab initio* calculations and are generalized. Finally, we report thermodynamic measurements and discuss the yields of product formation in the context of *ab initio* calculations.

EXPERIMENTAL AND COMPUTATIONAL SECTIONS

Some of the reagents reported for deoxygenation are often hazardous or very toxic, expensive or not readily available, they need to be freshly prepared or the reaction require drastic conditions, long reaction times and tedious workup. Thus a milder, green, selective,

nonhazardous and inexpensive reagent is still in demand. H_2O_2 is known to bring about certain desirable chemical transformations without creating unwanted byproducts, thereby eliminating many problems and costs associated with environmental cleanup. This paper describes the development of green, efficient H_2O_2 -based deoxygenation systems.

Clay supported reagents have been widely applied on organic synthesis mainly because of the ease of separation of the products, readily availability commercial clays, simple workup, selectivity and mild reaction conditions.

1-Preparation of Catalyst

The catalyst was prepared by the following procedure: Montmorillonite-K10 was added to a solution of manganese (II) chloride tetrahydrate in acetone (0.2 mmol.g⁻¹ montmorillonite).

The mixture was stirred at room temperature for 2 hours. The solvent was then evaporated and the residue was dried at 115°C for 5 hours.

2-General Procedure for Deoxygenation

To a solution of 1mmol oxime in 10 ml DMF, 1g catalyst was added. The reaction mixture was stirred at 60°C and about 2.5ml H_2O_2 were added dropwise by the time indicated in table 1. The reaction progress was monitored by TLC (eluent: n-hexane: ethylacetate=7:3).

The reaction mixture was cooled to room temperature and then filtrated to recover the catalyst. The filtrate was extracted with toluene/ H_2O (15ml/15ml). The organic layer was dried over CaCl_2 and the solvent was then evaporated and the product purified by column chromatography over silica gel (eluent: n-hexane: ethylacetate=7:3).

3-AB Initio Calculations

QM calculations were carried out at the HF/6-31G level of theory using the Gaussian 98 package, and the resulting of optimized relative stability energies and thermodynamic functions have obtained. Appropriate symmetry constraints were used in geometry optimizations. Harmonic vibrational frequency analyses were performed for all stationary points. Zero-point vibrational energies (ZPE) and thermodynamic properties at 250C (room), 600C and 1530C (reflux

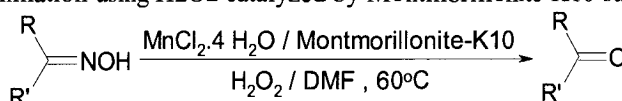
temperature) have calculated .10 reagents were optimized using the opt keyword, and then their connectivities to the appropriate minima were investigated with the IR calculations by freq keyword from checkpoint files.

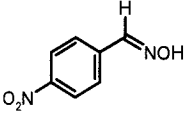
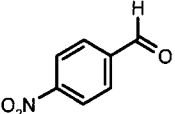
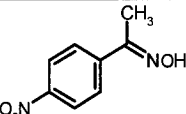
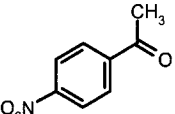
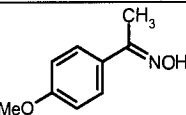
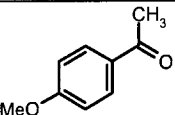
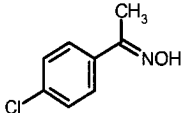
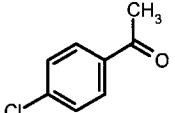
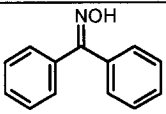
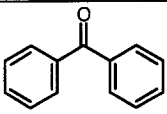
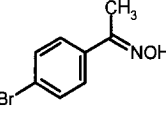
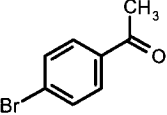
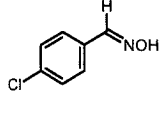
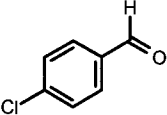
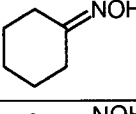
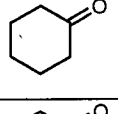
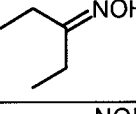
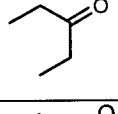
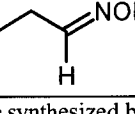
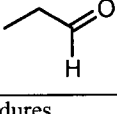
The application of these methods to systems of molecular interest has advanced tremendously in recent years to encompass models that describe local and global structural effects with great precision.

RESULTS AND DISCUSSION

We now report a convenient method for the deoxygenation of aromatic and aliphatic ketoximes and aldoximes to their corresponding carbonyl compounds using a clean, inexpensive, nontoxic, selective and mild reagent (H₂O₂) catalyzed by montmorillonite-K10 supported manganese(II) chloride (table 1). It is considerable that manganese(II) chloride is a non toxic salt.

Table 1. Deoxygenation using H₂O₂ catalyzed by Montmorillonite-K10 supported MnCl₂



Entry	Substrate ^a	Product ^b	Time(h)	Yield ^c (%)
1			4.5	90
2			4	97
3			4	85
4			5	90
5			3.5	95
6			5	78
7			3	70
8			6	95
9			5	90
10			5.5	95

a) All substrates were synthesized by known literature procedures.

b) All products were characterized by comparison of their m.p as well as their IR and ¹H NMR spectra with those of authentic samples.

c) Yields refer to isolated products.

In the first step, we considered three thermal conditions, i.e.; room, 60°C and reflux temperatures. After several experiments, we found that 60°C is an appropriate temperature for this procedure. After that we carried out reactions without one of the three components, montmorillonite-K10, H₂O₂ and MnCl₂·4H₂O. The results suggested that in absent of one of these reagents no reaction occurred.

Then to demonstrate the recyclability of the catalyst, it was reused at least three cycles for further deoxygenation without a significant decrease in yield (table 2).

Table2. Reuse of the catalyst for deoxygenation of benzophenone

Run	Yield(%)
1	95
2	95
3	93

In the second step, we optimized the geometries of 10 substrates and products in table 1 at HF/6-31G level in 25°C, 60°C and 153°C, and relative stability energies have been showed in table 3, then obtained results have been compared with experimental yields (Fig.1). In this investigation, Optimized geometries of 10 samples (including substrates and products) indicate limit of differences between the calculated and experimental observed values.

Table3. Optimized parameters at HF/6-31G theory level of relative stability energies (ΔE) and thermal enthalpy (ΔH), thermal entropy (ΔS) and Gibbs free-energy (ΔG) profiles (25°C, 60°C and 153°C) for the oxidative reactions by organic reagents

Entry	ΔE (kcal.mol ⁻¹)	Temperature (°C)	ΔH (kcal.mol ⁻¹)	ΔS (cal.K ⁻¹ mol ⁻¹)	ΔG (kcal.mol ⁻¹)
1	-34479.6139	25	-34467.76077	6.582	-34469.72297
		60	-34457.57942	7.157	-34469.96267
		153	-34467.03413	8.596	-34470.69556
2	-34475.67896	25	-34464.33587	0.443	-34464.46827
		60	-34464.22606	0.789	-34464.48961
		153	-34463.87403	1.719	-34464.60632
3	-34473.0779	25	-34461.81645	1.318	-34429.96762
		60	-34461.70225	1.681	-34462.26135
		153	-34461.33767	2.642	-34462.4634
4	-34474.26689	25	-34462.956	0.971	-34463.2459
		60	-34462.8443	1.326	-34463.28606
		153	-34462.48474	2.273	-34463.4536
5	-62696.79397	25	-62684.89717	5.135	-62686.42827
		60	-62684.70515	5.743	-62686.61778
		153	-62684.13413	7.253	-62687.22332
6	-34474.24286	25	-34462.91897	0.996	-34463.21578
		60	-34462.80728	1.352	-34496.02595
		153	-34462.44834	2.297	-34463.42725
7	-34478.0998	25	-34466.27046	6.855	-34468.13423
		60	-34466.08597	7.441	-34468.56335
		153	-34465.53314	8.9	-34469.32451
8	-34476.41094	25	-34464.50467	5.305	-34466.08597
		60	-34464.32583	5.87	-34466.2805
		153	-34463.78994	7.286	-34466.89356
9	-34469.09829	25	-34457.65674	-6.178	-34455.81503
		60	-34457.55258	-5.847	-34455.60544
		153	-34457.21122	-4.95	-34455.10344
10	-34478.67032	25	-34466.70782	6.009	-34468.49934
		60	-34466.52899	6.575	-34468.71834
		153	-34465.99059	7.996	-34469.39667

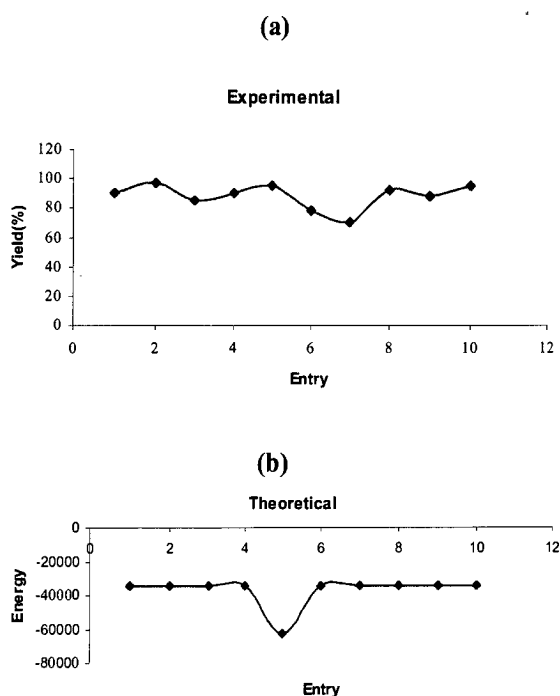


Fig.1. Investigation of **a)** experimental yields in table 1 and **b)** Calculated (HF/6-31G) Relative stability Energies (kcal/mol) for Species Found on Potential Energy Surfaces in table 3.

The standard enthalpies (ΔE) and thermal enthalpy (ΔH), thermal entropy (ΔS) and Gibbs free-energy (ΔG) for these compounds have obtained by theoretical methods in program package of Gaussian 98 at 25°C, 60°C and 153°C as thermodynamic computations (Table 3). The best results in different reagents have given in HF/6-31G level.

Ab initio calculations for aromatic and aliphatic ketoximes and aldoximes support the proposed mechanism.

The shape of the ΔH , ΔS and ΔG surfaces in figure 2(a, b, c) is a consequence of environment of the calculated reactions. Since both reaction pathways involve organic reagents, computational errors should be minimized, and a meaningful comparison of pairs of individual reactions can be made.

Then, changes of Gibbs free energy in the 10 organic agents in three temperatures by three have plotted in fig.2c. It turns out that the (HF) optimization is in good agreement with the experimental data. Also it is obvious that with

decreasing of temperature the stability increases in theoretical level (Fig.2).

Intermolecular reactions of these compounds provide one of the most versatile ways to construct relative substances.

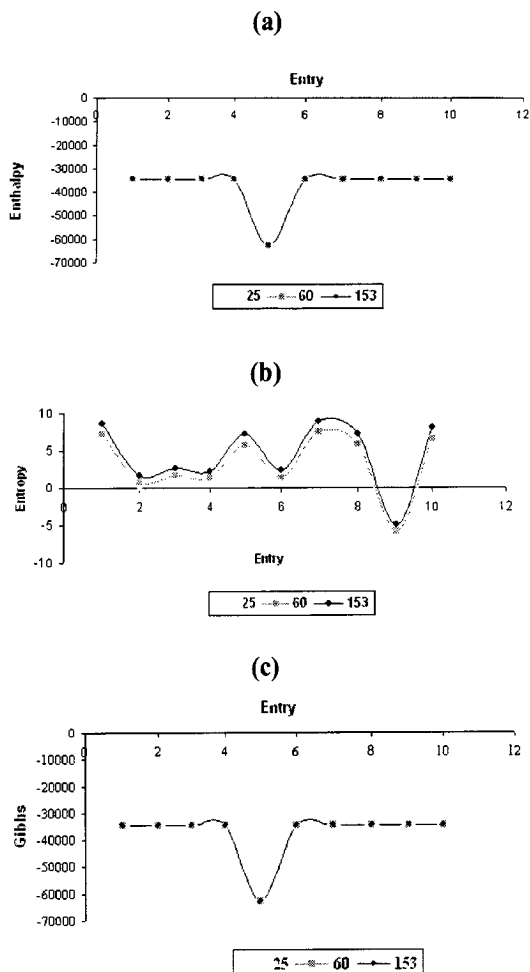


Fig. 2. HF/6-31G thermal enthalpy (ΔH), entropy (ΔS) and Gibbs free-energy (ΔG) profiles (25°C, 60°C and 153°C) for the oxidative reactions by organic reagents.

CONCLUSION

Remarkable structure which can be described as intramolecular reactants adduct for experimental yields. Also, this view is consistent with ab initio calculations.

The formation of the expected products has been attributed to the more favorable yields in the reactions and comparison to ab initio data shows good agreement with experimental results. Thermochemical computations presented here will allow their importance, or lack thereof, to be

demonstrated significant differences in the predicted equilibrium composition. This will

allow identification of the most important reactions, as well as the most important species, for indicated compounds.

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