CoSALEN as a new catalyst for oxidation of fullerene C_{60}

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The effect of CoSALEN on anti-oxidative properties of fullerene C_{60} in the presence of O_2 in cumene was investigated. A comparison was made between the role of the CoSALEN as a catalyst in the C_{60} oxidation and oxidation in the presence of an initiator, i.e., AIBN. A mechanism is proposed for the catalytic role of CoSALEN in oxidation of C_{60}. Oxidation of octadecylaminofullerene C_{60} at the same conditions reveals that oxidation could be a result of hydroperoxidation of the unreacted sites of C_{60}. We conclude that C_{60} as well as its amino-derivatives enhance the efficiency of CoSALEN in the oxidation of cumene due to their radical scavenging property of their unreacted double-bond sites.

Keywords: Fullerene; CoSALEN; Catalyst; Oxidation

1. Introduction

The O_2-carrying property of synthetic cobalt Schiff bases have been studied extensively. The reversibility of dioxygen adduct formation was not demonstrated until 1938 when Tsumaki [1] showed that the color change observed upon exposing cobalt(II)di-(salicylal)-ethylenediimine (CoSALEN) to air was due to reversible oxygenation. Then, Bailes and Calvin [2] extensively studied O_2 carrier properties of Co(II) complexes with SALEN-type ligands. In the 1980s, Drago demonstrated the possibility of catalyzing oxidation of phenols by metal-dioxygen adducts. He showed that CoSALEN complexes catalyze the oxidation of different phenol derivatives due to their ability to produce hydroperoxide radicals and oxidation initiation [3].

Fullerene C_{60} is efficient in trapping radicals [4]. The high affinity of this nanoparticle as well as its derivatives towards reaction with radicals makes it a candidate as a radical scavenger [5]. The radical sponging property of C_{60} could be considered in terms of its reaction with peroxy radicals [6]. Basically, a radical addition mechanism was proposed to explain the formation of C_{60} peroxides [7].

The anti-oxidative property of C_{60} towards cumene oxidation was reported previously in the presence of 2,2-azo*bis*-iso-butyronitrile (AIBN) as initiator [8]. Thermal decomposition of AIBN is the key in the initiation of the oxidation reaction and C_{60} inhibits the oxidation via scavenging chain transfer radicals, cumylperoxyl

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radicals, as well as 1-cyano-1-propylperoxyl radicals formed at AIBN decomposition in the presence of O_2 [9].

In a previous report, fullerene C_{60} and its lipophilic amine derivative had strong efficiency in termination of cumene chain radical reaction due to their radical sponging property [8]. In this work, we investigate the effect of CoSALEN–O_2 on oxidation of C_{60} and its amine derivative.

2. Experimental

2.1. *Instrumentation and chemicals*

AIBN was purchased from Acros Organics (98%), C_{60} (98%) was purchased from BuckyUSA Company, octadecylamine was purchased from Aldrich (97%), and cumene (Fluka) was boiled under reflux over Na in a N_2 atmosphere for 2 h. Distillation under N_2 gave a fraction at b.p. of 152. The UV-Vis spectra were recorded on a Varian Cary 200 UV Bio Visual Spectrophotometer. The UV-Vis spectra of the reaction mixtures of samples in absence of AIBN were run during the reaction and the wavelengths of the observed bands are summarized in table 1.

2.2. *Oxidation rate measurement*

Both the apparatus and the measurement method have been described previously [10]. The final volume of sample solutions of cumene, toluene, diethylbenzene, *p*-xylene, and *sec*-butylbenzene both as reagent and as solvent were 5 mL and all measurements were done at 60°C. The concentrations of C_{60}, CoSALEN, and AIBN were also 5×10^{-4} M, 0.01 M, and 0.06 M, respectively, except where indicated. The amount of O_2 adsorption was measured both in the presence and absence of AIBN as initiator.

2.3. *Investigation of the effect of solvent*

The effect of solvent was observed in terms of their capability to act as H-donor reagent like cumene using organic solvents such as toluene, xylene, diethylbenzene, cumene, and *sec*-butylbenzene.

Table 1. The UV-Vis absorption bands on reaction mixtures for oxidation of cumene catalyzed by CoSALEN in presence of O_2.

Sample no.	Reaction mixture containing	λ_{max}	Absorbance
1	C_{60}	285.2	0.45
2	CoSALEN	284.8	2.15
3	CoSALEN + C_{60}	287.0, 382.7	2.97, 0.61

2.4. Preparation of octadecylaminofullerene C$_{60}$

The compound was prepared and characterized according to the previously reported procedure [11].

2.5. Preparation of CoSALEN

The compound was prepared and characterized according to the procedure reported [12].

3. Results and discussion

We investigate the effect of CoSALEN, C$_{60}$, and both (figures 1a, c, and d, respectively) on oxidation of cumene by O$_2$ in the presence of AIBN. Their O$_2$ uptake is compared with the blank sample (without CoSALEN and C$_{60}$) shown in figure 1(b). As expected, there was no O$_2$ uptake during the reaction of cumene with AIBN in the presence of C$_{60}$ (figure 1a) in comparison with the blank sample (figure 1b) up to ~1 h. Addition of CoSALEN demonstrates a significant increase in the O$_2$ consumption (figure 1c). In spite of our previous observation for oxidation inhibition of cumene in the presence of C$_{60}$ and ZDDP complex [8], upon replacing of ZDDP by CoSALEN the oxidation process was facilitated. To ensure the role of C$_{60}$, the reaction was conducted in the absence of fullerene. The results shown in figure 1(d) confirm the synergistic effect of C$_{60}$ on O$_2$ consumption rate.

The effect of AIBN was investigated, and the results (figure 2) show that the presence of AIBN has no significant effect on the amount of O$_2$ consumption and the content of C$_{60}$ effectively determines the rate of O$_2$ uptake. Practically, it reveals that the complex has more catalytic role in O$_2$ adsorption than AIBN.
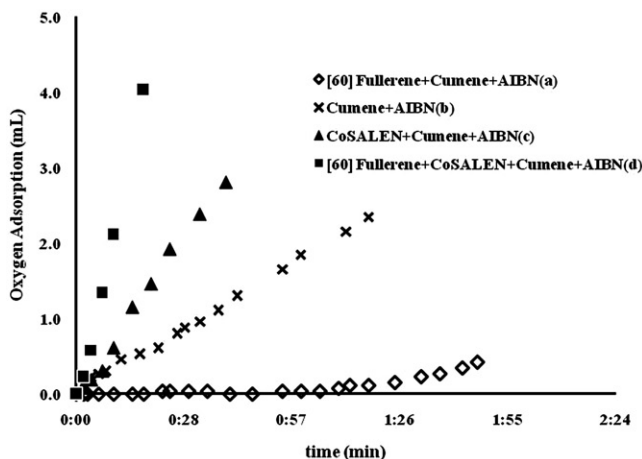

Figure 1. The effect of: (a) C$_{60}$, (b) blank sample, (c) CoSALEN, and (d) CoSALEN + C$_{60}$ on cumene oxidation measured by O$_2$ uptake in the presence of AIBN.
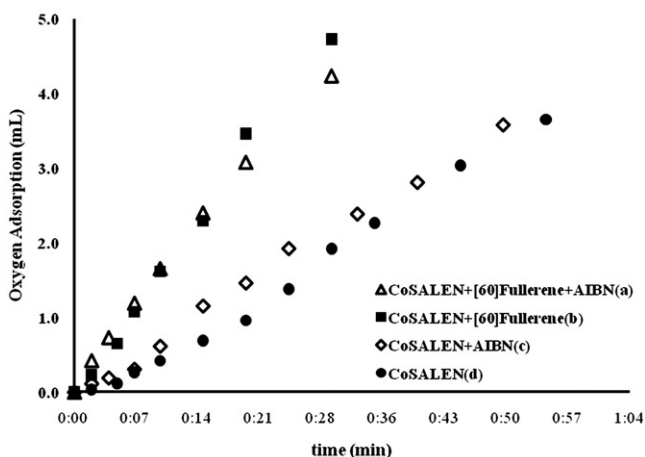
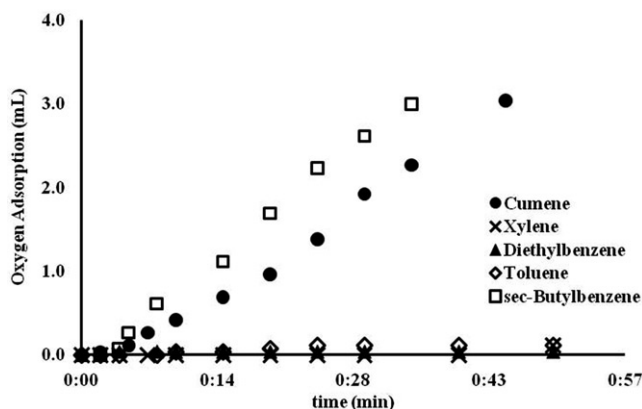Figure 2.   The effect of AIBN on O_2 consumption in solutions of CoSALEN and/or C_{60} in cumene.

Figure 3.   The effect of different solvents on O_2 consumption of CoSALEN.

UV-Vis spectroscopy was applied to understand chemical changes during the reaction. Both increasing intensity of the band at *ca* 285 nm as well as formation of a new band at 383 nm indicate some chemical changes (table 1).

The effect of solvent on oxidation reaction was also investigated. According to the data in figure 3, solvents such as toluene, xylene, and diethylbenzene showed no O_2 adsorption while the amount of the adsorption by cumene and *sec*-butylbenzene were considerable. The O_2 adsorption of CoSALEN in cumene and *sec*-butylbenzene are due to the ability of these solvents to release radical hydrogen at the initiation step of the reaction. This is consistent to the results (summarized in table 2) from autoxidation of aromatic hydrocarbons with only one reactive hydrogen available for abstraction towards O_2 [13].

The catalytic character of CoSALEN in oxidation of hindered phenols is well known [3]. According to the proposed mechanism shown in scheme 1, hydrogen radical released from phenol (HOX) binds to coordinated O_2 and initiates the oxidation reaction.

Table 2.   Relative reactivity of some aromatic hydrocarbon solvents towards O_2.

Hydrocarbon	Relative reactivity	Hydrocarbon	Relative reactivity
$PhCH(CH_3)_2$	1.0	$PhCH_2CH_3$	0.18
$PhCH_2CH=CH_2$	0.8	$PhCH_3$	0.015
$(Ph)_2CH_2$	0.35		
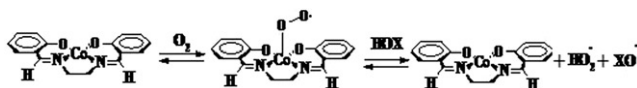
Scheme 1.   The mechanism for the oxidation of hindered phenols (HOX) by CoSALEN.
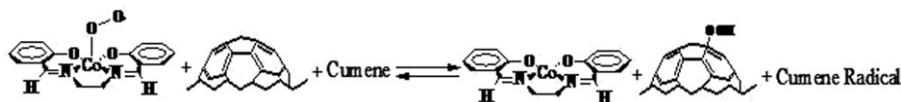
Scheme 2.   The proposed mechanism of C_{60} oxidation by CoSALEN.

Our experiments support the catalytic reaction of O_2 with cumene in the presence of CoSALEN, following the same mechanism with oxidation of phenols due to release of hydrogen and formation of cumene radical [13]. The increase in the amount of O_2 consumption during cumene oxidation (figure 2c) could be attributed to the high tendency of C_{60} in sponging hydroperoxide radicals that are produced by CoSALEN–O_2. Scavenging of free hydroperoxide radicals by C_{60} could shift the equilibrium shown in scheme 2 to the left. This suggests the mechanism in terms of the role of C_{60} shown in scheme 2.

We also investigated the effect of CoSALEN on anti-oxidative properties of the lipophilic aminofullerene C_{60}, i.e., octadecylaminofullerene C_{60}, which has been shown to be an efficient anti-oxidant [8] for cumene oxidation in the presence of AIBN. Since the amination of the C_{60} was supposed to leave less unreacted double bonds on C_{60}, the derivative should show less tendency to O_2 uptake in the cumene oxidation by CoSALEN than C_{60}. As evident from figure 4, similar to C_{60}, the octadecylamino-fullerene increases the rate of O_2 consumption by CoSALEN.

Oxygen adsorption of CoSALEN was measured at higher concentrations of C_{60} as well as its derivative (figure 5). Upon doubling the concentration of C_{60}, there were more differences between C_{60} and its derivative in terms of their maximum limit of O_2 adsorption, confirming that the more the availablility active sites on the C_{60} moiety in each case, the higher is the O_2 uptake.

It is also evident from figure 5 that there is a termination for both cases (but at different levels of O_2 consumption), which could be attributed to deactivation of the CoSALEN catalyst. To prove this, we added the same amount of catalyst after termination of the reaction. In this case, the rate of O_2 absorption increased abruptly confirming catalyst deactivation; this experiment is shown in figure 5(a).
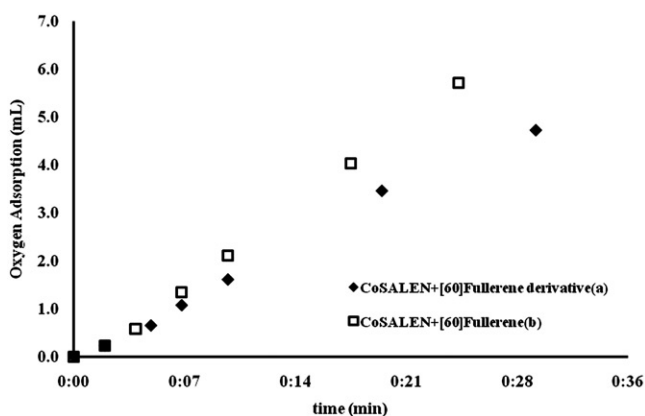
Figure 4. O$_2$ uptake by CoSALEN in cumene in the presence of: (a) C$_{60}$, (b) octadecylaminofullerene (5×10^{-4} M in terms of C$_{60}$ contents).
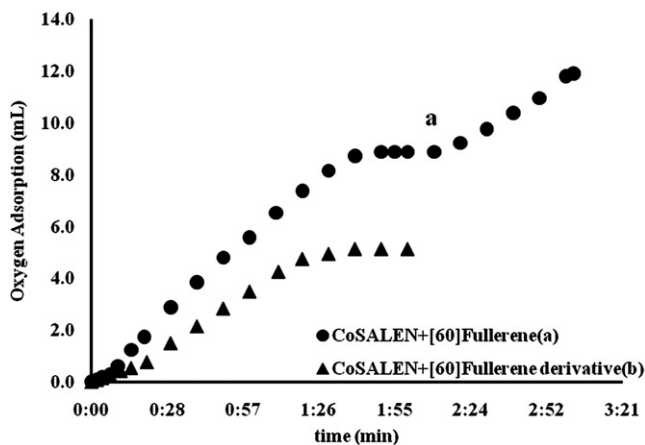

Figure 5. The effect of C$_{60}$ concentration on O$_2$ adsorption limit in cumene: (a) CoSALEN + C$_{60}$ (10^{-3} M) and the effect of a new portion of CoSALEN added to the reaction mixture. The catalyst was added at point (a) at the same concentration of the catalyst, and (b) CoSALEN + octadecylaminofullerene (10^{-3} M in terms of C$_{60}$ content).

C$_{60}$ has more active sites (carbon double bonds) than its amine derivative, adsorbs more hydroperoxyl radicals and rapidly deactivates the catalyst.

Acknowledgment

References

[1] T. Tsumaki. *Bull. Chem. Soc. Jpn*, **13**, 252 (1938).
[2] R.H. Bailes, M. Calvin. *J. Am. Chem. Soc.*, **69**, 1886 (1947).
[3] A. Zombeck, R.S. Drago, B.B. Corden, J.H. Gaul. *J. Am. Chem. Soc.*, **103**, 7580 (1981).

[4] L. Gan, S. Huang, X. Zhang, A. Zhang, B. Cheng, H. Cheng, X. Li, G. Shang. *J. Am. Chem. Soc.*, **124**, 13384 (2002).
[5] H.S. Nalwa (Ed.). *Encyclopedia of Nanoscience and Nanotechnology*, Vol. 3, p. 572, American Scientific Publishers, New York (2004).
[6] G. Liangbing. *C.R. Chimie*, **9**, 1001 (2006).
[7] S. Huang, Z. Xiao, F. Wang, L. Gan, X. Zhang, X. Hu, S. Zhang, M. Lu, Q. Pan, L. Xu. *J. Org. Chem.*, **69**, 2442 (2004).
[8] B. Ghanbari, A.A. Khailli, Z. Taheri, B. Mohajerani, M. Soleymani Jamarani. *Fuller. Nanotub. Car. N.*, **15**, 439 (2007).
[9] W. Ford, T. Nishioka, F. Qiu. *J. Org. Chem.*, **65**, 5780 (2000).
[10] L. Bateman, J.I. Cunneen. *J. Chem. Soc.*, 1596 (1955).
[11] B. Ghanbari, Z. Taheri, M. Shekarriz, S. Taghipoor, B. Mohajerani, M. Soleymani Jamarani. *Fuller. Nanotub. Car. N.*, **14**, 315 (2006).
[12] M. Calvin, R.H. Bailes, W.K. Wilmarth. *J. Am. Chem. Soc.*, **68**, 2254 (1946).
[13] G.A. Russel. *J. Am. Chem. Soc.*, **78**, 1047 (1956).