NO_x-catalyzed deep oxidation of toxic chloroorganics by dioxygen: possible application in environmental remediation

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Received 17 April 2000; accepted 26 June 2000

At 400–650 °C, NO_x catalyzes the deep oxidation by dioxygen of a wide range of toxic chloroorganics, including some of the most ubiquitous environmental contaminants, to carbon oxides, water, and inorganic chloride. The catalyst, NO_x, is not consumed in the reactions. Mechanistic studies suggest that the reactions are initiated by an atom abstraction from the substrate by NO_2.

Keywords: chloroorganics, nitrogen oxides, oxidations, oxygen

1. Introduction

Chlorinated organics are an important class of toxic pollutants that have become widely dispersed in the environment due to their use as solvents, degreasing agents, and in cleaning and fabrication applications [1]. For example, chloroorganics, such as tri- and tetrachloroethylene, are the principal constituents of DNAPL (denser than water nonaqueous phase liquids) that are present in 60% of the “superfund” sites [2]. Hence, the design of a suitable remediation procedure is of high societal importance and poses a significant scientific challenge. One obvious solution to the problem is bioremediation [3]. However, it is a very slow process and many of the chloroorganics are xenobiotic in character. In addition, when enzymes with low substrate specificity encounter such molecules, products that are xenobiotic often result (e.g., formation of the carcinogen vinyl chloride from polychlorinated ethylene). Among other remediation procedures, the most common is catalytic dechlorination to the parent hydrocarbon [4]; however, this is only a partial solution since the product, while less toxic, needs to be removed in a subsequent step. Catalytic oxidation procedures, such as TiO_2-catalyzed photooxidations [5] and the “Fenton” systems [6] involving H_2O_2 and a soluble transition metal catalyst are also not optimal in many situations. For example, photons are relatively expensive and the photooxidation systems cannot be employed where there is a dearth of sunlight. The Fenton system suffers from the requirement of separately producing and transporting H_2O_2, an unstable and potentially explosive chemical. In general all metal-catalyzed procedures face the problem of catalyst deactivation. Herein, we report a simple NO_x-catalyzed process for the deep oxidation of toxic chloroorganics by dioxygen. The system is capable of oxidizing a wide range of toxic chlorinated organics, including some of the most ubiquitous environmental contaminants.

2. Experimental

The procedure uses a flow reactor system. A mixture of NO, O_2, and N_2 (typical composition: 4.3, 8.7, and 87.0%, respectively) was bubbled through the desired substrate into a quartz tube (length 36.2 cm, diameter 1.9 cm; gas flow rate 500 ml/min) heated at temperatures ranging from 400 to 650 °C. The exiting mixture was passed through D_2O and/or $CDCl_3$ bubblers and finally analyzed by gas chromatography. The products trapped in the bubblers were analyzed by ^1H and ^{13}C NMR spectroscopy. Gravimetric silver nitrate analysis was performed to quantify the chloride ions liberated and collected in the D_2O bubblers.

3. Results and discussion

The oxidation procedure involves passing a mixture consisting of the substrate, NO, O_2, and N_2 through a heated flow reactor system. For all the substrates examined, oxidation did not occur at or below 400 °C. The results of one-pass oxidation of selected chlorinated organics at 575 °C are shown in table 1. The chlorinated substrates investigated were generally oxidized in moderate to good yields. As exemplified by 1,2-dichloropropane, more oxidation was observed with higher hydrocarbon character of the substrate. However, even with highly chlorinated species, such as tri- and tetrachloroethylene, a reasonable degree of oxidation was achieved. Note that in every case the substrate concentration (approximately 4 000–200 000 ppm) was many times that typically encountered in the environmental remediation situations (e.g., in “pump and treat” procedures) [1]. In order to ascertain whether the pro-

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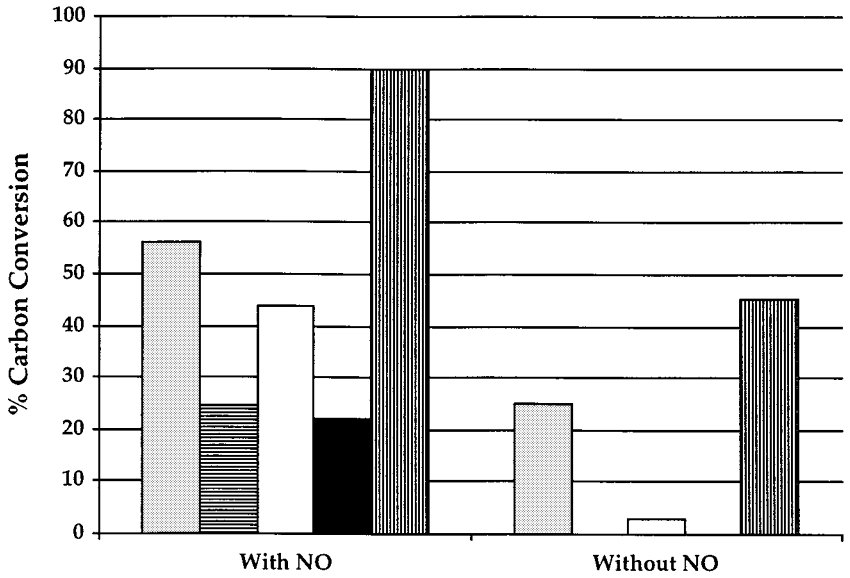


Figure 1. The effect of the presence of NO_x on the % carbon conversion at 575 °C for several chloroorganics: (□) trichloroethylene, (▤) methylene chloride, (□) chlorobenzene, (■) tetrachloroethylene, and (▥) 1,2-dichloropropane.

Table 1
One-pass oxidation of selected chlorinated organics.

Substrate	Substrate[a]	CO	CO_2	Conversion (%)	
	(mmol)	(mmol)	(mmol)	Carbon[b]	Chlorine[c]
1,2-dichloropropane	4.1	9.0	2.1	90.0	87.0
Dichloromethane	71.8	17.7	0	24.7	19.7
Chloroform	27.5	5.22	11.3	60.1	36.9
1,1,1-trichloroethane	15.0	10.0	1.7	39.0	44.9
Trichloroethylene	8.9	5.7	4.3	56.0	34.1
Tetrachloroethylene	3.4	0.68	0.85	22.2	20.2
Chlorobenzene	0.98	1.61	0.961	43.7	41.0

[a] Amount of substrate passed through quartz tube heated to 575 °C.

[b] [CO(mmol) + CO_2(mmol)]/[mmol C atoms passed through furnace] × 100.

[c] [mmol chloride ions]/[mmol Cl atoms passed through furnace].

cedure was also effective for low substrate concentrations, the oxidation of trichloroethylene was repeated using 0.278 mmol of substrate and an average gas flow rate of 150 ml/min. 98.8% of the substrate was found to have been removed by deep oxidation and the concentration of the unreacted trichloroethylene in the effluent gas mixture was 40 ppm. Finally, since water is very often present along with the toxic organics in the environment, the oxidation of trichloroethylene (8.9 mmol) was attempted in the presence of water vapor (11.1 mmol). The extent of oxidation was essentially identical with that observed without the presence of water vapor (cf., table 1).

One of the objectives of this study was to demonstrate that NO_x is a *true* catalyst in the reaction. This involves demonstrating that (a) the oxidation is accelerated by the presence of NO_x and (b) the amount of NO_x remains unchanged, i.e., neither N_2 nor nitrogen-containing organic products are formed in the course of the oxidation. Figure 1 shows the extent of oxidation of several substrates by O_2 with or without the presence of NO_x. It is clear that oxidation is markedly enhanced in the presence of NO_x; indeed, in two instances (methylene chloride and tetrachloroethylene) there was *no* oxidation in the absence of NO_x. The extent of oxidation also exceeds the amount of NO_x employed, further confirming the catalytic role of NO_x. Finally, no N_2 derived from NO_x was detected by gas chromatography in experiments where N_2 was replaced by He in the inlet gas mixture. This result, together with the absence of nitrogen-containing organic reaction products, clearly indicates that there is *no* net consumption of NO_x and that NO_x is a true catalyst for the oxidation reaction. Therefore, in principle, NO_x can be recycled, the overall reaction being simply the deep oxidation of chloroorganics by dioxygen under relatively mild conditions.

The effect of temperature on the rate of oxidation was studied for trichloroethylene and 1,2-dichloropropane. In both cases, the extent of oxidation was found to increase with increasing temperature, leading to fairly linear Arrhenius plots (see figure 2 for trichloroethylene). From these plots, apparent activation energies (E_a) of 6.1 and 1.4 $\mathrm{kcal\,mol^{-1}}$ were obtained for trichloroethylene and 1,2-dichloropropane, respectively. These numbers should be treated with caution since the equilibrium constant for the reaction $2NO + O_2 \rightleftharpoons 2NO_2$, decreases with increasing temperature leading to a temperature dependence of the concentration of the C–H activating species. The difference in activation energies for the two substrates presumably reflects the difference in C–H bond energies (C_{sp^2}–H versus C_{sp^3}–H); as discussed below, the oxidations appear to be initiated by an atom-abstraction step.

The majority of the substrates were cleanly oxidized to carbon monoxide and dioxide with only a trace of organic by-products formed. The oxidation of chloroform, however, resulted in the formation of distinguishable

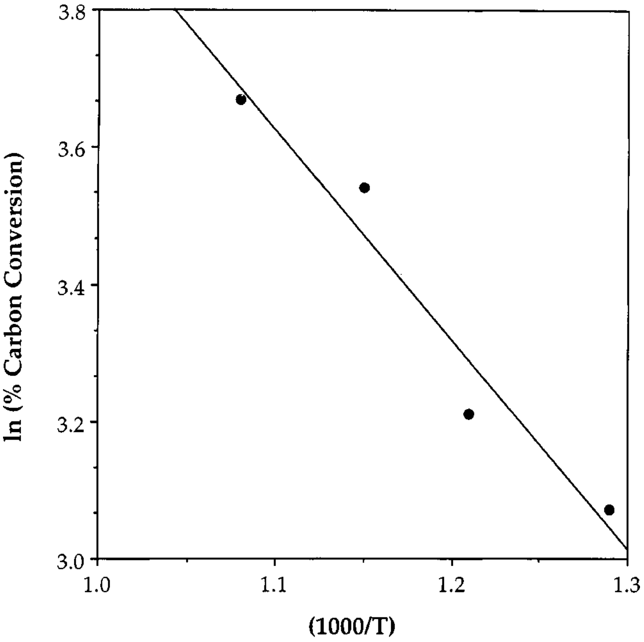
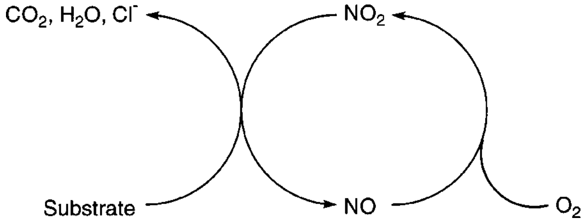


Figure 2. Arrhenius plot for the oxidation of trichloroethylene.

by-products, including trichlorethylene, dichloromethane, and 1,1,2,2-tetrachloroethane. Furthermore, a white solid formed at the entrance of the first bubbler corresponded to the species $(CCl_3CCl_2)_2$, as confirmed by mass spectroscopy. These by-products clearly indicate the intermediacy of free-radicals and carbenes, such as CCl_3, CCl_2, and CHCl. This suggests that the oxidations are initiated through an atom abstraction step. The mechanistic scenario was further confirmed by an experiment where NO_x was replaced with $K_2S_2O_8$, a well-known radical oxidant [7]. Chloroform was oxidized using a procedure similar to that described above, except that NO_x was eliminated and the gas mixture was passed through a hot tube containing a 2 cm plug of $K_2S_2O_8$ (2.7 g). The formation of the same by-products was observed. It is important to note that the by-products are themselves capable of being oxidized by the NO_x/O_2 system, thereby posing no hindrance to the total oxidation of the substrate.

A key mechanistic question involves the identity of the radical initiator in the NO_x system. Both NO and NO_2 are odd-electron species and are, in principle, capable of atom abstraction. Little or no oxidation of chloroform was observed when the reaction was run with NO but no O_2 (gas mixture: NO 5%, N_2 95%). On the other hand, a substantial amount of chloroform was oxidized (23% of 27.5 mmol) when the gas mixture consisted of NO_2 and N_2, but *not* excess O_2 (gas mixture: NO_2 5%, N_2 95%). Additionally, approximately 6% of the chloroform was converted to $(CCl_3CCl_2)_2$. These experiments clearly suggest that the NO_x-mediated oxidations are intiated by attack of the substrate by NO_2. Scheme 1 outlines the mechanism of the NO_x-mediated oxidation of chloroorganics by dioxygen. Note that NO reacts quite rapidly with O_2 to form NO_2.



Scheme 1.

4. Conclusion

In conclusion, we have discovered a system capable of oxidizing a wide range of toxic chlorinated organics by dioxygen, resulting in the formation of carbon monoxide, carbon dioxide, and inorganic chloride. NO_x acts as the catalyst and is not consumed in the reaction. Unlike metal-catalyzed transformations, catalyst deactivation is not an issue. Additionally, the avoidance of a solid catalyst makes the system simple to implement. The procedure constitutes a potentially low-cost alternative for the removal of bulk quantities of toxic chlorinated organics. The remaining traces can then be removed using a more expensive procedure.

Acknowledgement

This research was supported by a grant from the National Science Foundation.

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