

**I. A BROAD SPECTRUM CATALYTIC SYSTEM FOR
REMOVAL OF TOXIC ORGANICS FROM
WATER BY DEEP OXIDATION**

**II. CHEMICAL RECYCLING OF PLASTICS TO USEFUL
ORGANICS BY OXIDATIVE DEGRADATION**

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**Metallic Palladium Catalyzed Deep
Oxidation of Nitro and Haloaromatics:
Effect of Added Dihydrogen versus
Carbon Monoxide**

Important Criteria for a Successful Deep Oxidation System for Water Purification

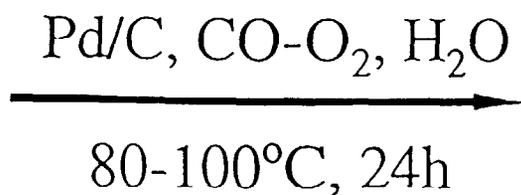
- Must be economical, i.e. inexpensive catalysts and reagents
- Must be applicable to a broad spectrum of toxic organics
- Must remove toxic organics from water without the introduction of further contaminants

Previously Studied Techniques for Removal of Toxic Organics from Water

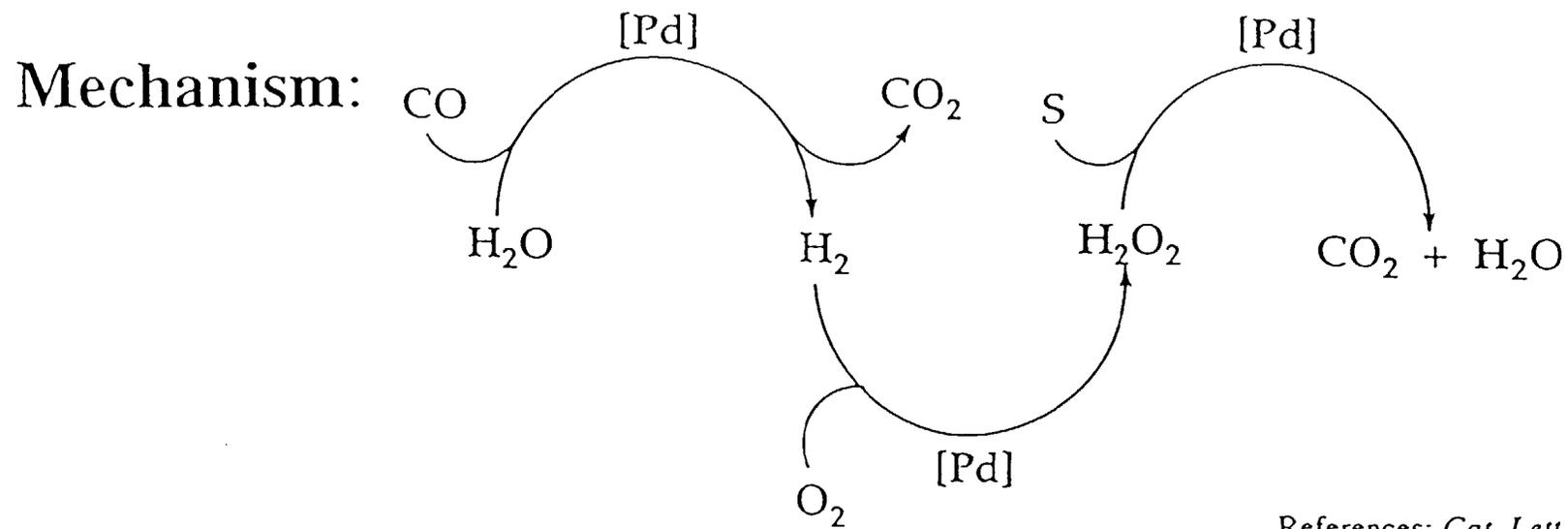
- Adsorption of organics on to activated carbon
- Photooxidation with TiO_2
- Fenton Oxidations with H_2O_2 and a soluble transition metal catalyst
- Supercritical water oxidations
- Oxidations employing metal complexes with macrocyclic ligands and persulfate ion as the oxidant

Original Oxidation System

Toxic Organics including
benzene, substituted
phenols, haloaromatics,
organophosphorus and
organosulfur compounds



**Deep oxidation
products:** CO,
CO₂, and H₂O



References: *Cat. Lett.*, 1996, 40, 95.
Cat. Lett., 1997, 49, 59.

(S = substrate)

Focus of Current Research

What would happen if CO was replaced with H₂?

By eliminating the Water-Gas Shift step,
would the rate be accelerated?

For organic substrates in which a prereduction step can occur,
will H₂, a stronger reductant than CO,
facilitate the conversion to more reactive species,
and, thereby, increase the rate of deep oxidation?

Toxic Organics Examined

The reasons nitro and haloaromatics were chosen as model substrates.

- serious environmental hazards due to toxic effects on humans and wildlife
- present in aquatic environments in large quantities because of the uses as biocides, degreasing solvents, heat transfer fluids, and munitions
- precedence in the literature for their ability to undergo catalytic reduction

Deep Oxidation of Nitro and Haloaromatics

Substrate	Conversion with H ₂ -O ₂	Conversion with CO-O ₂	Side Products with H ₂ -O ₂ (mmol)	Side Products with CO-O ₂ (mmol)
nitromethane	94%	86%	ammonium (0.01) nitrate (>0.04) formic acid (0.06)	ammonium (0.01) nitrate (>0.04) formic acid (0.02)
p-nitrophenol	99+%	99+%	ammonium (0.10) nitrate (<0.04) formic acid (tr)	ammonium (0.06) nitrate (>0.08) formic acid (0.21)
m-nitrophenol	99+%	99+%	ammonium (0.06) nitrate (<0.04) formic acid (tr)	ammonium (0.06) nitrate (>0.08) formic acid (0.07)
nitrobenzene	99+%	98%	ammonium (0.07) nitrate (<0.04) formic acid (tr)	ammonium (0.04) nitrate (>0.08) formic acid (0.08)
nitrosobenzene	99+%	99+%	ammonium (0.02) nitrate (>0.08) formic acid (0.06)	ammonium (0.09) nitrate (<0.04) formic acid (tr) aminophenol (0.04) aniline (0.01) hydroquinone (tr)
azobenzene	96%	85%	ammonium (0.04) nitrate (<0.04) aniline (0.02)	ammonium (0.03) nitrate (<0.04) formic acid (0.01) aniline (0.02) hydroquinone (tr)

aniline	62%	87%	ammonium (0.05) nitrate (<0.04) formic acid (tr)	ammonium (0.07) nitrate (<0.04) formic acid (0.08)
1,2-dinitrobenzene	98%	99%	ammonium (0.10) nitrate (<0.04)	ammonium (0.05) nitrate (>0.04) formic acid (0.04)
1,4-dinitrobenzene	99%	88%	ammonium (0.14) nitrate (>0.08) formic acid (tr)	ammonium (tr) nitrate (<0.04) formic acid (tr)
1,3-dinitrobenzene	73%	77%	ammonium (0.10) nitrate (<0.04)	ammonium (0.01) nitrate (<0.04) formic acid (0.05)
1-chloro-3-nitrobenzene	99+%	86%	ammonium (0.08) nitrate (<0.04) formic acid (0.04) aniline (0.06)	ammonium (0.02) nitrate (>0.08) formic acid (0.03)
1-chloro-4-nitrobenzene	80%	85%	ammonium (0.03) nitrate (>0.08) formic acid (0.06)	ammonium (0.02) nitrate (>0.04) formic acid (0.03)
p-chlorophenol	96%	92%	formic acid (0.01)	formic acid (0.09) hydroquinone (0.06)
m-chlorophenol	99+%	89%	formic acid (0.02)	formic acid (0.09)
p-bromophenol	99+%	99%	formic acid (0.08)	formic acid (0.08) hydroquinone (0.03) p-hydroxybenzoic acid (0.04)
m-bromophenol	99+%	99+%	formic acid (0.09) hydroquinone (tr)	formic acid (0.04) m-hydroxybenzoic acid (0.08)

Reaction Conditions: 0.25 mmol substrate, 30 mg 5% Pd/C, 3 mL H₂O/HCl (pH=1), 100 psi H₂ or CO, 1000 psi N₂, 100 psi O₂, 130° C, 16 h.

Comparison of H₂-O₂ vs. CO-O₂ at Lower Conversion

Substrate	Conversion with H ₂ -O ₂	Conversion with CO-O ₂	Side Products with H ₂ -O ₂ (mmol)	Side Products with CO-O ₂ (mmol)
p-nitrophenol	79%	31%	ammonium (0.04) formic acid (0.06) hydroquinone (0.07)	ammonium (tr) formic acid (0.03) hydroquinone (0.04)
p-chlorophenol	89%	57%	formic acid (0.09) phenol (0.17)	formic acid (0.03) hydroquinone (0.10)
aniline	38%	16%	unidentified	unidentified
nitrobenzene	92%	67%	ammonium (0.11) aniline (0.28) hydroquinone (0.01)	ammonium (0.03) formic acid (0.13)

Reaction Conditions: 1 mmol substrate, 15 mg 5% Pd/C, 3 mL H₂O/HCl (pH=1),
100 psi H₂ or CO, 1000 psi N₂, 100 psi O₂, 90° C, 16 h.

Other Features

- ammonium decomposes slowly under standard conditions to give non-protonated nitrogen species
- nitrate is not an intermediate for the production of ammonium
- HCl can be replaced with H₂SO₄ or trifluoroacetic acid with little effect on the reactivity
- changes in pH dramatically alter the reactivity of the system
- for substrates which are unlikely to undergo a prereduction step, such as organophosphorus and organosulfur species, no acceleration of rate was observed for the H₂-O₂ system

Deep Oxidation of Organophosphorus and Organosulfur Compounds

Substrate	Conversion with H ₂ -O ₂	Conversion with CO-O ₂	Side Products with H ₂ -O ₂ (mmol)	Side Products with CO-O ₂ (mmol)
trimethylphosphine oxide	15%	40%	dimethylphosphinic acid (0.14) methylphosphonic acid (tr) formic acid (tr)	dimethylphosphinic acid (0.34) methylphosphonic acid (0.06) formic acid (tr)
dimethylphosphinic acid	16%	11%	methylphosphonic acid (0.15) formic acid (tr)	methylphosphonic acid (0.11) formic acid (0.27)
methylphosphonic acid	5%	10%	formic acid (tr)	formic acid (0.15)
dimethyl sulfide	66%	61%	dimethylsulfoxide (0.02) formic acid (tr)	dimethylsulfoxide (0.22) dimethylsulfone (0.04) formic acid (tr)
dimethylsulfone ^a	9%	6%	dimethylsulfoxide (0.03)	methylsulfoxide (0.05)

Reaction Conditions: 1 mmol substrate, 30 mg 5% Pd/C, 3 mL H₂O/HCl (pH=1)
100 psi H₂ or CO, 1000 psi N₂, 100 psi O₂, 90° C, 20 h.

^a0.5 mmol substrate.

Conclusion

Advantages of the current system:

- efficient metallic palladium-catalyzed deep oxidization of nitro and haloaromatics, as well as a broad range of other substrates
- dioxygen and the coreductants used are inexpensive and relatively safe for transport
- conditions used are mild compared to many alternate methods
- does not require the disposal of the parent aromatic in a subsequent step as other known procedures for the reductive removal of functionalities from aromatics do

**Chemical Degradation of Polymeric
Materials to Useful Organics Using
Nitric Oxides and Dioxygen**

Introduction to Chemical Recycling

Chemical recycling is defined as the breakdown of polymeric waste into materials that are reusable as fuel or chemicals, including monomers.

Specific types of chemical recycling include:

- **depolymerization** of condensation polymers to their monomeric units
- **pyrolysis**, or thermal degradation in oxygen starved environments, of addition polymers to generate oil or gas for fuel applications
- **refinery technologies** used to convert polymeric waste, usually addition polymers, into hydrocarbon feedstock

Recycling of Polymeric Materials

Major Types of Plastics by Recycling Code

Code	Type of Resin	Example Products	% of Plastic Produced
1	PET	soft drink bottles, medicine containers	0.5%
2	HDPE	milk bottles, detergent containers	21%
3	PVC	pipe, cooking oil bottles	6.5%
4	LDPE	wrapping films, grocery bags	27%
5	PP	diapers, syrup bottles	16%
6	PS	coffee cups, packing material	16%
7	Other		8.5%

Source: Table adapted from the MSW Factbook, Ver. 3.0, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.

Polymer Waste Recovered in Recycling Efforts

Code	Type of Resin	% of Plastic Recovered
1	PET	38%
2	HDPE	1.8%
3	PVC	0.1%
5	PP	0.9%
6	PS	0.4%

Source: Table adapted from Klemchuk, P.P.;Thompson, T. in *Emerging Technologies in Plastics Recycling*, Andrews, G.D.; Subramanian, P.M., eds. ACS, Washington, D.C., 1992, 79.

Why low recycling rates for addition polymers?

Economic factors such as low virgin material costs and high collection and sorting expenses

Machining problems associated with mixed plastic resins

One solution to these deterrents would be a recycling technique that would produce valuable organics from polymeric waste and be able to process mixed plastics, avoiding sorting costs.

Present Work

Although several techniques exist for the chemical recycling of polymeric waste, no current methods attempt to convert addition polymers to valuable organics such as monomeric compounds.

The oxidative degradation of a wide variety of addition and condensation polymers to useful organics has been achieved under mild conditions by a mixture of nitrogen oxides and dioxygen.

The polymeric substrates included:

Polystyrene

High Density Polyethylene

Low Density Polyethylene

Polypropylene

Polymethylmethacrylate

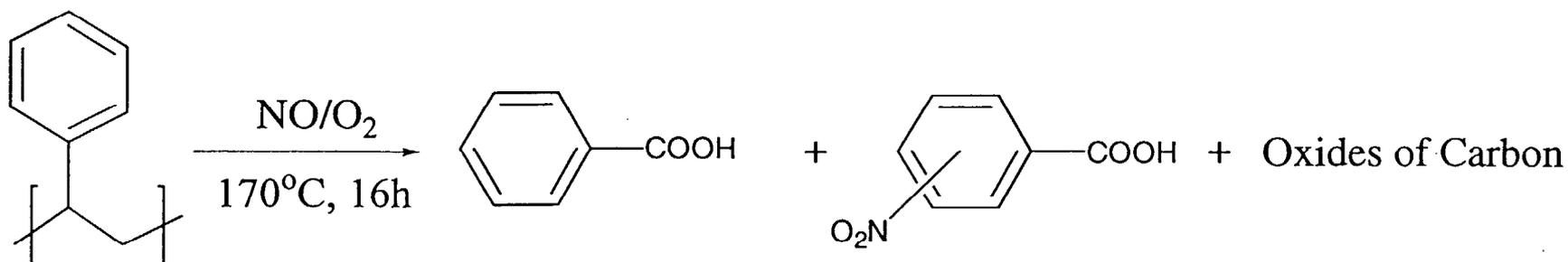
Polyacrylic acid

Nylon 6,6

Standard Reaction Conditions:

Reactions were carried out in 125mL Parr pressure reactors using glass liners. The polymeric material was reacted in an atmosphere of 40psi NO, 500psi N₂, and 100psi O₂ for 16h at 170°C.

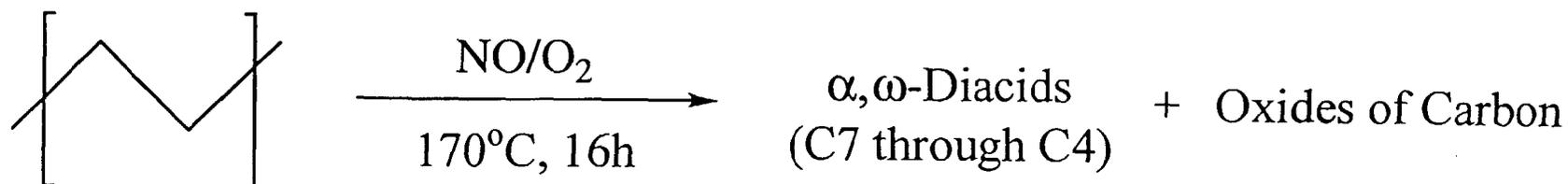
Polystyrene Oxidation to Benzoic Acid and Its Derivatives



Polystyrene Mw 280,000 Under Standard Conditions

Starting Material	Non-Volatile Products	Products	mmol
0.26 g	0.19 g	benzoic acid	0.66
		4-nitrobenzoic acid	0.12
		3-nitrobenzoic acid	0.12
		3,5-dinitrobenzoic acid	tr

Oxidative Degradation of High and Low Density Polyethylene

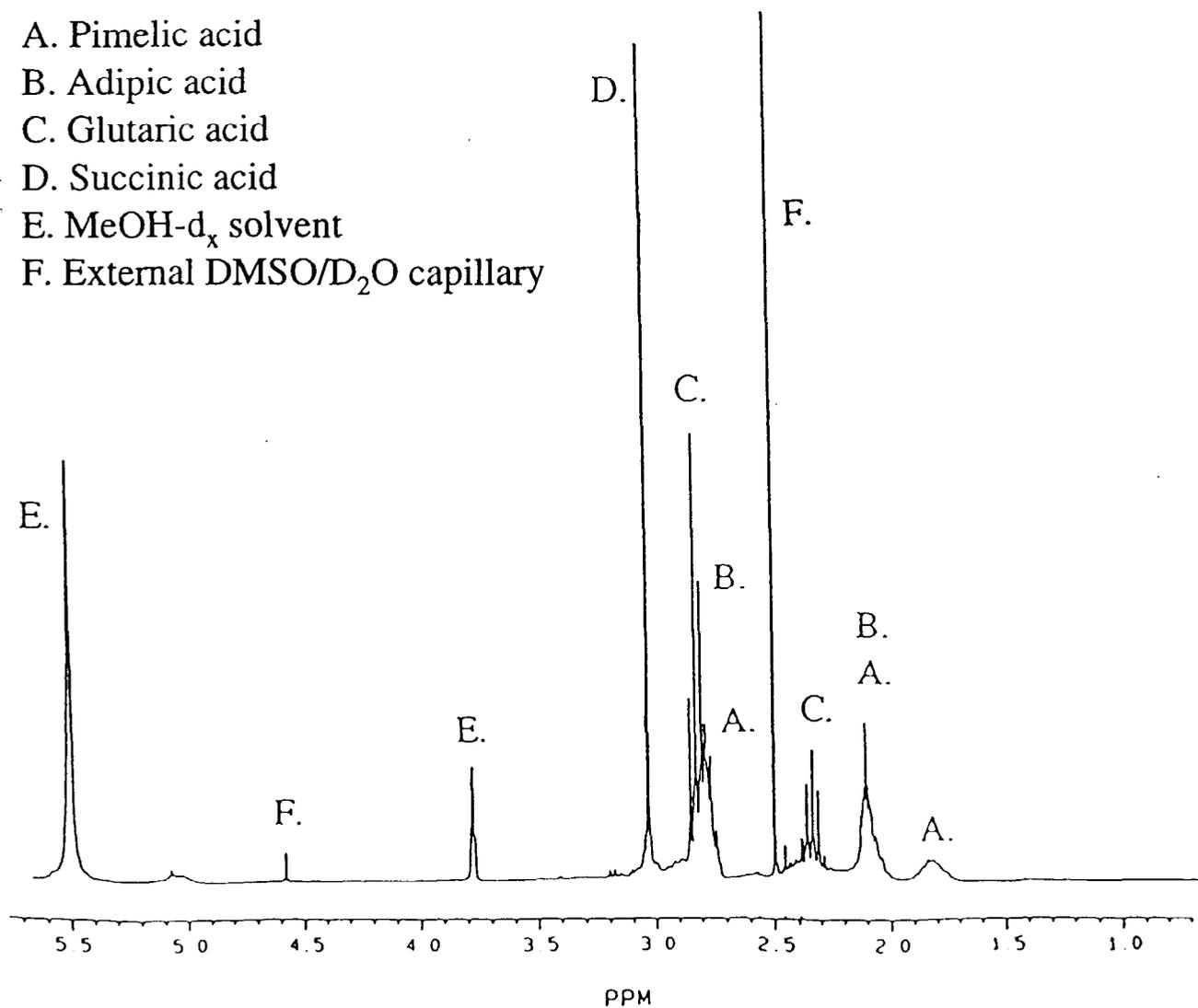


Starting Material	Non-Volatile Products	Products	(g)
HDPE (0.27 g)	0.21 g	succinic acid	0.08
		glutaric acid	0.07
		adipic acid	0.02
		pimelic acid	0.03
		unidentified organics	tr
		LDPE (0.26 g)	0.22 g
		glutaric acid	0.06
		adipic acid	0.02
		pimelic acid	0.01
		unidentified organics	tr

Note: Reactions carried out under 150psi O₂

$^1\text{H-NMR}$ of HDPE after reaction under standard conditions

- A. Pimelic acid
- B. Adipic acid
- C. Glutaric acid
- D. Succinic acid
- E. MeOH- d_x solvent
- F. External DMSO/ D_2O capillary



Oxidation of Other Polymeric Materials

Polymer Substrate	Starting Material (g)	Non-Volatile Products (g)	Products (g)
Polypropylene ^a M _w 250,000	0.26	0.15	acetic acid unknown ketones and carboxylic acid species
Nylon 6,6 ^b	0.26	0.16	succinic acid 0.01 glutaric acid 0.01 adipic acid 0.06 acetic acid tr
Polymethylmethacrylate M _w 96,200	0.26	0.15	oligomers, M _w 985
Polyacrylic acid M _w 450,000	0.25	0.16	oligomers

^a 70 psi NO

^b reaction at 135°C

Conclusions

Advantages of the NO/O₂ Chemical Recycling System:

- can be applied to a broad range of polymeric materials
- uses relatively mild conditions and avoids further environmental problems such as air pollution
- generates materials more valuable than hydrocarbon feedstock from addition polymers
- makes processing of mixed plastics more feasible with proper organic separation techniques