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AIR-NITRIC ACID DESTRUCTIVE OXIDATION OF ORGANIC WASTES

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Many organic materials have been completely oxidized to CO_2 , CO , and inorganic acids in a 0.1M HNO_3 /14.8M H_3PO_4 solution with air sparging. Addition of 0.001M Pd^{+2} reduces the CO to near 1% of the released carbon gases. To accomplish complete oxidation the solution temperature must be maintained above 130-150°C. Organic materials quantitatively destroyed include neoprene, cellulose, EDTA, TBP, tartaric acid, and nitromethane. The oxidation is usually complete in a few hours for soluble organic materials. The oxidation rate for non-aliphatic organic solids is moderately fast and surface area dependent. The rate for aliphatic organic compounds (polyethylene, PVC, and n-dodecane) is relatively very slow. This is due to the large energy required to abstract a hydrogen atom from these compounds, 99 kcal/mole. The combination of $\text{NO}_2\cdot$ and $\text{H}\cdot$ to produce HNO_2 releases only 88 kcal/mole. Under conditions of high $\text{NO}_2\cdot$ concentration it should be possible to oxidize these aliphatic compounds.

The development of a general process for the destructive oxidation of pure organic compounds could have many applications for environmental cleanup. A liquid phase oxidation process shouldn't produce any ash making the system more environmentally contained. A simple process that uses oxygen from air or another readily available cheap oxidant as the net oxidant would be relatively inexpensive per unit of waste consumed. This work represents studies into development of such a process. Nitric acid is used as a catalyst and oxidant since it can be regenerated by air in an acid recovery system and to some extent in the reaction solution.

Liquid phase oxidation of organic molecules should be easier than gas phase oxidation at a given temperature¹. This is due to the ability to produce high concentrations of the reactants and to the lessening of termination since radicals have a harder time diffusing to the walls. Direct oxidation of most organic compounds by HNO_3 , nitric acid, is energetically favorable but very slow due to its inability to break the carbon-hydrogen bond^{1,2}. The following heats of reaction, ΔH , values (in kcal/mole) are calculated, or approximated, using Table 1.

Table 1. Heats of Formation for Molecules and Radicals at 25°C.^{1,2}

Compound	ΔH_{form} (kcal/mole)	Compound	ΔH_{form} (kcal/mole)
CH ₃ CH ₃	-20	^a CH ₃ NO ₂ (aq)	-8
CH ₃ CH ₂ OH(aq)	-66	HCO ₂ H(aq)	-98
CH ₃ OH(aq)	-59	NO ₂ ·	8
CH ₃ CHO(aq)	-50	HNO ₂ (aq)	-28
CH ₃ CH ₂ ·	26	HNO ₃ (aq)	-49
^a CH ₃ (O)C·	-21	NO·	22
^a CH ₃ CH ₂ OOH	-35	H ₂ O	-68
^a CH ₃ CH ₂ OO·	23	CO ₂ (aq)	-98
CH ₃ ·	31	NH ₂ OH (aq)	-22

^a Approximated using other values^{1,2}.

R denotes an organic group unaffecteding the ΔH for the shown reaction. The oxidation of organic compounds is usually initiated by the production of organic radicals generated by dissolved NO₂· and NO· in solution. For many types of organic compounds the attack by NO₂· can be first order.

For aliphatic compounds high concentrations of NO₂· and NO· are needed.

A typical aliphatic carbon-hydrogen bond strength of 99 kcal/mole was used in the calculations². Adding oxygen to the solution, by air sparging, can set up a radical propagating oxidation mechanism. Organic radicals quickly react with molecular oxygen to form a peroxic radical.

The peroxic radical can easily abstract a hydrogen from even an aliphatic organic molecule since an oxygen-hydrogen bond is formed to break a carbon-hydrogen bond. This results in an organic hydroperoxide and another organic radical. Above 130-150°C the organic hydroperoxides decompose to release H₂O or CO₂¹.

The organic radicals can also be oxidized by nitric and nitrous acids or nitrated by $\text{NO}_2\cdot$.

Oxidation of the carbon-carbon bond is also possible but slow probably due to steric factors.

Methods and Materials

Weight measurements were taken using a Sartorius (Handy) balance. All chemicals used were of at least Reagent grade quality meeting ACS specifications except for the cellulose (Whatman 40 ashless filter paper) and neoprene (glovebox glove made by Siebe North, Inc., Charleston SC). Gas samples were analyzed on a Varian 3400 GC using Molecular Sieve-13X and Chromosorb 106 columns.

The data collected was generated from two similar but different oxidation systems. The first used a peristaltic pump to circulate air through a closed system starting with (and continuing in order) a three liter reaction vessel containing a liter of reactant solution, an ice trap, a 26.6 liter polypropylene bottle, a 30 ml gas sample vessel, and then re-entering the peristaltic pump. The system was connected to an inverted burette, in acidic solution, used to measure changes in the gas volume of the system. The total gas volume of the system was 29.0 ± 0.2 liters. The air entered the reaction solution through a three inch diameter medium glass frit plate generating very small bubbles in the solution. The air circulation rate for this system was maintained at 500 ml/minute. The all-glass three liter reaction vessel set in a heating mantle and had four ground glass openings which provided access for a thermometer, an air cooled condenser (air outlet), air sparge inlet, and sample introduction-holder port. Gas samples were taken at the beginning, end, and during the oxidation reaction. Carbon balance results gave a combined error of $\pm 3\%$.

The second system was of a flow-through design. A peristaltic pump was used to push air through the reaction system. The incoming air was stripped of CO_2 using Ascarite-II (Thomas Scientific). The air was delivered to the reaction vessel at 100 ml/minute. The reaction vessel was the same as described above except that a smaller glass frit sparger was used. The gas stream leaving the reaction vessel was scrubbed of $\text{NO}_2\cdot$ by a 0.5M sulfamic acid solution. The products of the $\text{NO}_2\cdot$ reaction with the sulfamic acid was nitric acid (stays in solution) and N_2 gas. The gas stream then entered approximately 100 grams of Ascarite-II in a polypropylene bottle. Weighing the bottle before and after the reaction determined the weight of CO_2 produced from the oxidation. The gas stream then entered a column of Pd metal on a Kieselguhr support maintained above 140°C . The Pd/Kieselguhr catalyzes the air oxidation of any CO in the gas stream to CO_2 . The generated CO_2 is then absorbed and weighed on a second bottle of Ascarite-II. Calibration of this system for the absorption of CO and CO_2 was accomplished by adding a weighed amount of dried sodium oxalate to concentrated sulfuric or phosphoric acid. In the

absence of oxidizing compounds an equal molar amount of CO and CO₂ is formed. Carbon balances from the calibration determined a combined accuracy of $\pm 2\%$.

Results and Discussion

The onset of oxidation for the soluble organic compounds was about 120°C. Gram quantities of organic material was oxidized per run. At 140°C the oxidation was complete in less than 15 minutes (NO₂· stopped being released from the solution). The results of the carbon balance studies are tabulated in Table 2. Complete oxidation, within experimental error, was obtained for the compounds listed (with the exception of tartaric acid) for at least one of the runs. Tartaric acid should also be completely oxidizable. The purpose for the oxidation of tartaric acid was to determine the fraction of CO released. The results show that a more highly oxidized compound, such as tartaric acid, releases a smaller fraction of CO. The production of CO was very pronounced for TBP (tributylphosphate) and nitromethane. The result for nitromethane is not surprising since it should be quickly hydrolysed to formic acid in a strong mineral acid at these temperatures³.

Dehydration of formic acid to CO and water is slightly endothermic (4 kcal/mole)² but probably quick in 14.8M H₃PO₄ which is a strong dehydrating agent. The strong dehydrating ability of the reaction solution is probably aiding in the decomposition of the organic oxidation products. Cellulose is rapidly carbonized at around 140°C to form carbon and water.

The carbon formed is easily attacked by the nitric acid. It is possible that the relative production of CO and CO₂ is determined by competing mechanisms; the CO by a dehydration mechanism and the CO₂ produced by oxidation with HNO₃ and NO₂·.

The slightly endothermic ΔH for this last reaction shows how dehydration to produce CO can compete with oxidation to produce CO₂.

Carbon-nitrogen bonds are relatively weak (~ 75 kcal/mole)¹ so complete oxidation of EDTA (ethylene-diamine-tetraacetic acid) was not surprising. Oxidation of TBP was performed to test the ability to destroy nearly aliphatic compounds. Butanol, a hydrolysis product of TBP, resembles an aliphatic compound except for the alcohol group. The weakening of the adjacent carbon-hydrogen bonds by this lone oxygen seems to be sufficient to start the chain oxidation

Table 2. Carbon Balance for Oxidation of Various Organic Compounds
in a 0.05-0.1M HNO₃/14.8M H₃PO₄ Solution, 120-160°C.

Compound	Co-catalyst Metal (conc.)	Percentage Carbon Released as CO ₂ and CO	Percentage CO of CO ₂ and CO
cellulose	none	98±2 ^a	20±1
"	Pd (0.0012M)	99±2	0.9±1
"	Rh (0.003M)	97±3 ^a	6.3±1.5
EDTA	none	99±2	25±1
"	Pd (0.0012M)	>91±2	0.9±1
"	Rh (0.003M)	>84±3 ^a	19±1.5
TBP	none	103±3 ^a	43±1 ^b
"	Pd (0.0012M)	-	1.3±1
nitromethane	none	101±2	60±1
"	Pd (0.0012M)	-	2.3±1
tartaric acid	none	>96±2	15±1
neoprene	Pd (0.001)	101±10	<17

^a GC analysis observed no H₂, methane, or ethane.

^b Determined from butanol (a hydrolysis product of TBP)

process. Oxidation of compounds of this type have been said to act like a candle that has been lit on one end¹. The carbon atoms are oxidized in order down the chain.

The surface oxidation of neoprene (poly [2-chloro-1,3-butadiene]) was found to be even, allowing measurement of the surface area and weight loss during its destruction. The oxidation rate at varying temperatures has been measured for this compound, Figure 1. The activation energy, E_a, was determined to be 22.9 kcal/mole with a frequency factor, A, of 7.68E11 s⁻¹. The release of chloride during the oxidation had no observable effect at the low concentration, up to 0.1M, formed by the destruction of the neoprene. Oxidation of neoprene is relatively rapid due to carbon-carbon double bond weakening of carbon-hydrogen bonds in α positions relative to the double bond¹.

The oxidation of aliphatic compounds such as polyethylene, PVC (polyvinylchloride), and n-dodecane was found to be unmeasureably slow in this reaction solution below 180°C. In an air sparged system the concentration of NO· and NO₂· should be too low for reactions (1) and (2) to have any appreciable effect. In near 0.1M HNO₃ solution reactions (3), (4), and (5) would be hampered by destruction of the organic radicals by reactions (6), (7), and (8). It should be possible though under the right reaction conditions to oxidize aliphatic compounds by reactions (3), (4), and (5) or (6), (7), and (8) in this temperature range¹.

Two platinum group metals were studied as co-catalysts, palladium and rhodium. Palladium performed better in reducing the percentage of organic carbon released from solution

as CO. The palladium metal formed during the oxidation of CO is reoxidized back to Pd^{+2} by nitric acid.

Unlike palladium, rhodium formed a significant amount of N_2O when used as a co-catalyst. Rhodium catalyzes the $\text{NO}\cdot$ oxidation of CO to produce CO_2 and N_2O^4 . Even though the extent to which palladium is aiding in oxidation of the organic materials in solution is unknown, palladium is known to be an effective catalyst for oxidation of many types of organic compounds⁵.

During some runs when an air sparge rate of 500 ml/minute was used, the solution temperature had to be raised to near 150°C to complete the oxidation. This is probably due to the formation of hydroperoxide compounds which decompose in the $130\text{-}150^\circ\text{C}$ range¹. The extent to which the oxygen is interacting with the organic radicals is unknown. Oxygen could also enter as an oxidant by oxidizing dissolved $\text{NO}\cdot$ to $\text{NO}_2\cdot$. Even though the self-decomposition of organic hydroperoxides have a high activation energy¹, the concentration of these compounds are self limiting

Conclusions

Complete oxidation of many types of organic compounds is possible in a 0.1M HNO_3 /14.8M H_3PO_4 solution with air sparging. Oxidation of aliphatic compounds will require different and maybe more extreme conditions (i.e, pressurization and high nitric acid concentrations). Trace amounts of palladium should be capable of minimizing the production of CO to near 1% of the released carbon gases. Use of palladium should also minimize the production of N_2O which can not easily be reoxidized to HNO_3 .

The released HNO_3 , NO, and NO_2 can be reoxidized in a standard air driven acid recovery system providing a cheap source of oxidant. There should be no ash produced from the process making this process more environmentally contained. There are existing resins that can be used to absorb hazardous metals such as mercury, silver, lead, and cadmium that work well in phosphate solutions⁶. The reaction conditions were relatively mild, ambient pressure and $< 180^\circ\text{C}$, making the process potentially easy and cheap to implement. Phosphoric acid, H_3PO_4 , and its solutions only mildly attack common stainless-steels (such as 304-L), especially at room temperature⁷. This would make handling and containing process solutions in plumbing and tanks safe and inexpensive.

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Notation

ΔH - standard heat (enthalpy) of reaction, ΔH°_{298}
R - an organic group unaffected by the ΔH for the shown reaction.
neoprene - poly(2-chloro-1,3-butadiene)
EDTA - ethylenediaminetetraacetic acid
TBP - tributylphosphate
tartaric acid - 2,3-dihydroxybutanedioic acid
Acsarite-II - solid NaOH on a solid support (for CO₂ absorption).
Kieselguhr - diatomaceous earth (silica from the skeletons of diatoms).

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Figures

Figure 1. Oxidation Rate, R , for Neoprene in 0.1M HNO_3 /14.8M H_3PO_4 Solution at Varying Temperature.

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