

UCRL-JC-121979 Rev 2
PREPRINT

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**This paper was prepared for submittal to the
Sixth International Conference
on Radioactive Waste Management and Environmental Remediation
October 12-16, 1997
Singapore, Republic of Singapore**

July 1997

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Destruction of Organic Wastes by Ammonium Peroxydisulfate with Electrolytic Regeneration of the Oxidant

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ABSTRACT

Research is reported concerning a new aqueous process for oxidative destruction of solid- and liquid organic wastes. This process uses acidified ammonium peroxydisulfate and operates at ambient pressure and at 80- to 100 °C. The oxidant may be efficiently regenerated by electrolysis of the sulfate by-product at Pt anodes, even in the presence of organic and inorganic contaminants expected to be entrained in the cycle. Integral rate constants were determined for the oxidation of 25 diverse organic compounds at low (50 ppm) concentrations through fixed-time experiments with excess oxidant and a Pt wire catalyst. For high initial concentrations, uncatalyzed mineralization rates were measured for waste surrogates including kerosene, triethylamine, ion exchange resin, oxalic acid, trinitrotoluene, and cellulose. A packed bed reactor was tested with ethylene glycol, with offgas analysis by mass-spectroscopy. Rate data extrapolate to throughputs of ~200 kg/m³-day. The process may benefit the destruction of highly toxic or specialized industrial wastes as well as the organic fraction of mixed wastes.

INTRODUCTION

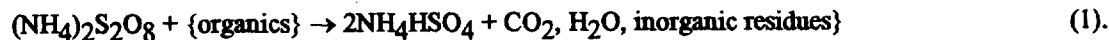
Aqueous-phase processes are being developed for destruction of highly toxic- or radioactivity-contaminated organic wastes for several reasons: [1] Water wets, dissolves or otherwise immobilizes toxic dust that might inadvertently escape from dry processes under upset conditions. The high heat capacity and heat of evaporation of the water buffer the system against thermal runaways that might result in venting. Non-gaseous products of oxidation remain within the liquid medium in a form amenable to further concentration or recovery by common separation processes, e.g. electro-deposition or ion-exchange. Existing aqueous-phase techniques include mediated electrochemical oxidation (MEO) and mediated chemical oxidation (MCO).

Mediated electrochemical oxidation uses a dissolved redox couple (e.g., Ag(I)/Ag(II), Co(II)/Co(III), or Fe(II)/Fe(III), etc.) as a charge transfer agent to link an electrode to oxidizable material dispersed in the electrolyte [1,2]. One application of MEO in nuclear waste treatment derives from the ability of Ag(II) to simultaneously destroy many organic substances while oxidizing PuO₂ residues to the soluble and recoverable plutonyl [Pu(O)₂²⁺] ion. Mediated chemical oxidation uses a terminal oxidant activated by a redox couple. For example, the oxidant maybe hydrogen peroxide catalyzed by Fe(II) [3], or pressurized oxygen catalyzed by FeCl₃ with Pt(IV) and Ru(III) co-catalysts[4]. Silver(II)-mediated peroxydisulfate oxidants have been developed for cleaning nuclear-industry equipment [5]. MEO an MCO processes generally have problems with catalyst retention, container stability and equipment cost.

To avoid dispersed catalysts and containment problems, we evaluated a process based on peroxydisulfate oxidation under conditions not requiring dispersed catalysts. This oxidant may be periodically regenerated from the sulfate byproduct by electrolysis. Such a process could be used to treat highly toxic or specialized wastes, for which conventional thermal treatments are unsuited because of problems of scale, equipment contamination or permitting. The process has been called "direct chemical oxidation," to distinguish it from mediated oxidation techniques [6].

TECHNICAL BASIS

Peroxydisulfate is among the strongest chemical oxidants. It has a standard electrode potential of 2.07 V, which is comparable to that of ozone [10]. The net oxidation reaction is:

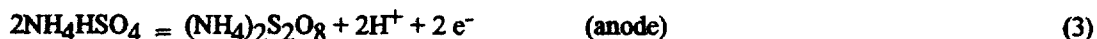


The initial reaction step is decomposition to form the sulfate radical anion (SRA) [7-9]:



This step is sluggish unless activated by heat, UV, noble metals or redox catalysts. The ammonium salt is favored because of high solubility and stability to oxidation by peroxydisulfate.

The sulfate product may be recycled to produce peroxydisulfate by electrolysis at 15-30 °C [10]. Typical electrolysis cells use a platinum or glassy-carbon anode, a graphite or lead cathode, and a porous ceramic separator. The predominant reactions are:



Oxygen, peroxymonosulfate and small amounts of ozone are also formed. The overall flow diagram of the process is shown in Figure 1. The electrolytic production of peroxydisulfate from sulfate ion constituted an intermediate step in the industrial production of hydrogen peroxide in the first half of this century. Water was oxidized by peroxydisulfate H_2O_2 in stainless steel reactors at $T > 60$ °C, and recovered by distillation. Materials used to contain peroxydisulfate include glass, porcelain, stainless steels tantalum, and PTFE [9].

OBJECTIVES

The purpose of this work is to determine the feasibility of bulk destruction of organic wastes using recycled peroxydisulfate, through three experimental efforts: (1) electrolysis of ammonium peroxydisulfate from contaminated recycled waste solutions was investigated, using inorganic and organic contaminants anticipated from general use; (2) a commercial total carbon analyzer (TCA) was modified and used to measure mineralization rates at very low concentrations for each of 25 diverse organic compounds; and (3) the time-dependent rates of oxidation to carbon dioxide were measured for higher concentrations of certain characteristic waste surrogates, i.e., triethylamine, kerosene, oxalic acid, ion exchange resins and ethylene glycol. Rate constants were then used to estimate the throughput of a batch reactor for materials having similar chemical structures.

EXPERIMENTAL APPARATUS AND PROCEDURES

Electrolysis Cell. A cylindrical electrolysis cell of typical industrial design was constructed of Pyrex and Teflon. A porous alumina separator divided the anode and cathode chambers (1.6 L each). The anodes were 1.3 mm Pt wires coiled around six water-cooled Pyrex tubes with an active anode area of 100 cm^2 . Six 1.27 cm graphite rods were cabled in parallel to form a cathode (720 cm^2). The cell was initially filled with 2.65 M H_2SO_4 + 1.59 M NH_4HSO_4 (Baker Analyzed Reagents). Constant-current electrolysis was carried out at currents of 20-100 A for up to 8 hours ($T = 16$ °C), with periodic polarization sweeps. Additives (0.4 g/L of NaNO_3 and 0.16 g/L of NaSCN) were used to improve anode polarization and retard Pt corrosion [10]. Samples were analyzed for total oxidizer by quenching with ferrous and titration against KMnO_4 .

Oxidation of diverse compounds. Integral rates of complete oxidation ("mineralization") of diverse compounds at 100 °C were determined using a modified laboratory total organic carbon analyzer (Model 700 TOC Total Organic Carbon; O.I. Analytical, Inc.; College Station TX). The quantity of CO_2 evolved in a fixed time was compared with that calculated for total oxidation of the carbon in the weighed sample (Table I). By choosing reaction times for which 90% of the CO_2 was evolved, a reaction rate could be bracketed that would be useful in estimating reaction times for chemically similar wastes at low concentrations (5- and 50 ppm-C).

The PTFE digestion vessel of the total carbon analyzer was injected with 0.5 ml of 0.84 N $\text{Na}_2\text{S}_2\text{O}_8$ and 0.2 ml of 0.523 M H_3PO_4 . After removal of background contamination (30 s), a 0.991 ml sample of the organic solution was injected over a 3 s interval. The evolved carbon dioxide was determined using an integrating IR absorption spectrometer. The initial concentrations were thus: organic reductant (0.002-0.02 N); oxidant (0.248 N); phosphoric acid (0.062 M). Sensitivity of CO_2 measurement was 0.1 ppm, with an expected accuracy of $\pm 1\%$.

Batch Oxidation of Triethylamine and Kerosene. Triethylamine was oxidized at an initial concentration 25 mM by reaction with 3.6 N sodium peroxydisulfate at 95 °C into a well-stirred 0.5 L vessel under reflux. The

reaction products were concentrated by precipitation of the excess sulfate by $\text{Ba}(\text{OH})_2$, and then analyzed for nitrate and nitrite by chromatography.

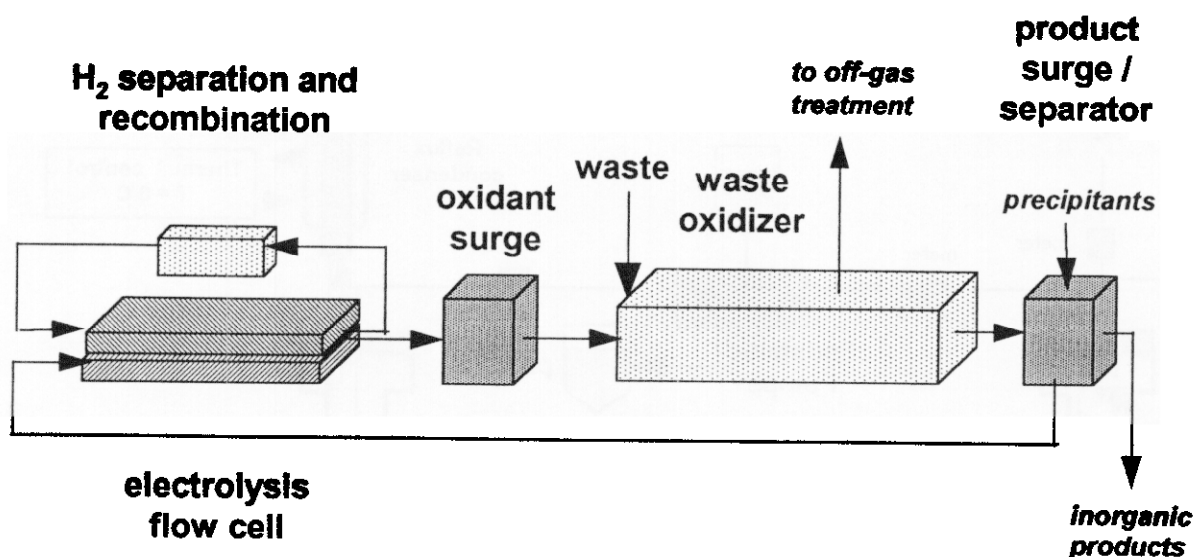


Fig. 1. Direct chemical oxidation uses electrolytic ammonium peroxydisulfate to oxidize organic liquids in a packed bed reactor operating at $T \sim 90^\circ\text{C}$.

Kerosene (predominate component, dodecane) was similarly oxidized at 100°C and without catalysis, by a solution of 4 N ammonium peroxydisulfate + 0.1 M H_2SO_4 . Five milliliters of kerosene were added to 50 ml of 0.1 M H_2SO_4 , and the 4N peroxydisulfate solution was added at a rate of 5 ml/min. Similar procedures were followed for trinitrotoluene, which dissolved from small pellets into the reaction medium.

Time-dependent oxidation of model organic compounds and water. Experiments on time-dependent oxidation of simple organic compounds and of pure water were performed in a controlled-temperature, 0.5 L Pyrex vessel. Solutions of sulfuric acid and ammonium peroxydisulfate (300 ml total) were preheated to the reaction temperature just before samples of an organic compound were injected to produce initial concentrations of 0.05-0.5 N. A solution of 1-1.5 N $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was generated by electrolysis and then pumped into the reaction vessel at a rate of 3-5 ml/min, until a quantity of oxidant equivalent to the reductant were added over a period of 3-30 minutes. Samples were taken at regular intervals and analyzed by a TCA; accuracy was pre-determined by tests with the same substances in calibrated samples.

Packed bed reactor with mass-spectroscopic analysis of off gas. Process scaleup parameters were determined using a modular packed bed reactor consisting of horizontal, heat-jacketed Pyrex tubes 25 mm in diameter and 0.3 L reaction volume (Figure 2). The tubes are filled with Rasching rings to impede mixing. Argon was allowed to flow over a free surface at the top of the reaction fluid to continuously remove gaseous reaction products, which were analyzed in a quadripole mass spectrometer (Hiden Analytical, Warrington, UK).

EXPERIMENTAL RESULTS AND DISCUSSION

Electrolysis of Ammonium Hydrogen Sulfate Solutions. Cell voltage and electrode potentials (ref. Pt/H_2) were found to be linear and without passivation or diffusion limitations over the current density range, $i = 1-30 \text{ kA/m}^2$; cell voltage was 5.5 V at $i = 10 \text{ kA/m}^2$. The coulombic efficiency, e , was determined to be 82% from an expression of Faraday's law:

$$d[\text{O}]/dt = e \{I/FV_a\}. \quad (5)$$

I is current; F is the Faraday constant; and V_a is the anolyte volume. Additions of sodium nitrate, -phosphate and -chloride (0.1 M) did not alter the coulomb efficiency or yield (Figure 3). The sulfate ion concentration is excess

(4.3M), and its oxidation predominates. A similar result was found for low levels of oxalic, formic and acetic acids. These results indicate that the recycle of sulfate is not substantially hindered by the presence of small amounts of waste residuals likely to be entrained into the cycle.

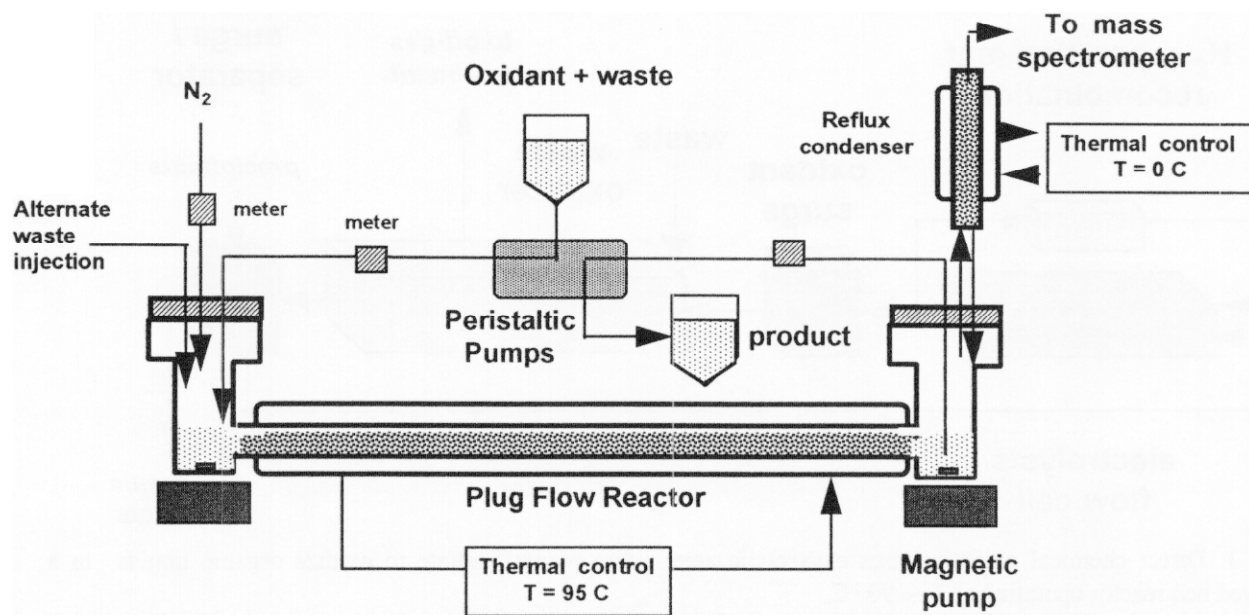


Figure 2. Experimental configuration of the horizontal packed-bed reactor.

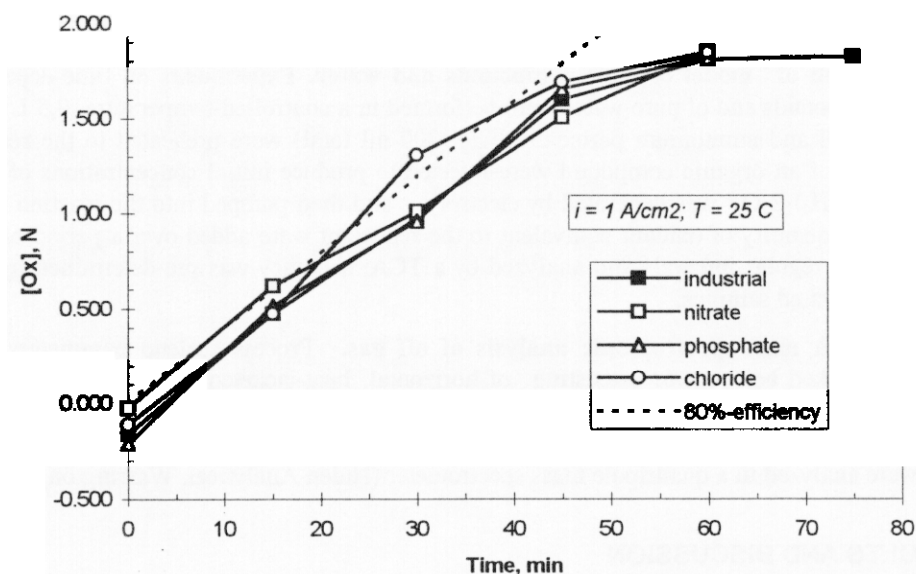


Fig. 3. Electrolysis of $(\text{NH}_4)_2\text{SO}_4$ at 1 A/cm^2 (80 A/L) alone and with Cl^- , PO_4^{3-} , NO_3^- additions.

Survey of diverse compounds. Integral destruction rates for 25 compounds bearing diverse functional groups are summarized in Tables I-III. Table I gives the number of equivalents (n) required for complete oxidation of one mole to carbon dioxide and (as appropriate) sulfate, chlorate, or nitrate products. Also given are the carbon fraction of the reductant (f_c); the initial oxidant/reductant equivalents ratio; the theoretical $[c(0)]$ and apparent $[c(t)]$ carbon concentrations (ppm-carbon); and the extent of the reaction (E) after the time interval Δt .

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In most cases, a reaction time of $\Delta t = 2.5$ min allowed ~90% conversion of organic carbon to carbon dioxide, from which an integral rate constant, k_a , was estimated using a formal first order reaction equation:

$$- \{[R(t)] - [R(0)]\} / \Delta t = k_a [O] \quad (6a)$$

$$\{[R(t)] - [R(0)]\} = c(t) \rho n (0.586) / f_c 1000 M_w \quad (6b)$$

Here $[R(0)]$ and $[R(t)]$ are the initial and final concentrations of the organic; $[O]$ is the initial oxidant concentration; ρ is density. The factor 0.586 corrects for sample dilution. Oxidant concentration decreased little over the 3-min. reaction times, as determined separately.

For all but two compounds, the measured integral rates fell into the narrow range of $k_a = 0.006$ - 0.02 min^{-1} . Urea, which is hydrolyzed without charge transfer, was slowest to react. Oxalic acid and formic acid possess carbon in the highest oxidation states tested: C(III) and C(II) respectively. The slowness of oxidation of these compounds and the small number of charge transfer steps required to produce CO_2 suggest that the last step of oxidation to CO_2 is the slowest. The slowness of the oxidation of the triethylamine (0.0076 min^{-1}) is consistent with the discovery of trialkylamines in the residues following Fe(III)-catalyzed peroxide destruction of ion exchange resins containing amino groups [3]. Four of the tested compounds are surrogates for products of the hydrolytic or oxidative decontamination of chemical warfare agents[11]. Methyl phosphonic acid; 2,2'-thiodiethanol; and di-isopropyl-methyl-phosphonate (DIMP), have similar bonds to those of GB, Mustard, and VX. The test on triethylamine was intended to simulate the branch of the VX molecule bearing an amino group [14]. These compounds were fully oxidized in about 3 min.

Table I. Integral first order rate constant k_a calculated from the extent of oxidation, as measured by CO_2 evolution using a total carbon analyzer. ^a

No	Compound	M_w g/mol	n eq/mol	(R(0)) mM	Ratio [O]/[R]	C(0) ppm	C(t) ppm	Δt min	E %	$10^2 k_a$ 1/min
1	Urea	60.06	0	1.16	N/A	43.19	41.03	2.5	95	0.36
2	oxalic acid dihydrate	126.00	2	1.17	116.86	43.47	44.00	2.5	101	0.38
3	nitromethane	61.04	8	2.51	13.59	46.76	41.61	11.5	89	0.63
4	Salicylate-Na salt	160.10	28	0.36	27.14	46.81	46.17	5.5	99	0.73
5	formic acid	46.03	2	2.47	55.14	46.09	42.25	2.5	92	0.73
6	Triethylamine	101.19	36	0.14	53.62	15.80	14.70	2.5	93	0.76
7	DMSO	78.13	18	1.30	11.67	48.40	46.46	11.5	96	0.79
8	DIMP	180.18	44	0.18	34.57	23.39	23.20	2.5	99	1.26
9	Na-EDTA	372.24	39	0.22	31.25	41.71	39.67	2.5	95	1.34
10	4-chloropyridine HCL	150.01	21	0.46	28.04	43.15	39.26	2.5	91	1.43
11	4-amino-pyridine	94.12	20	0.47	28.82	44.09	42.33	2.5	96	1.47
12	acetic acid	60.05	8	1.19	28.64	44.36	44.54	2.5	100	1.54
13	sucrose	342.29	48	0.20	28.01	45.35	44.79	2.5	99	1.55
14	Methylphosphonic acid	96.02	8	1.21	28.20	22.53	22.50	2.5	100	1.56
15	2,2'-thiodiethanol	122.18	28	0.38	25.47	28.51	28.30	2.5	99	1.71
16	1,4-dioxane	88.11	20	0.63	21.73	46.79	44.84	2.5	96	1.94
17	ethylene glycol	62.07	10	1.28	21.27	47.80	44.96	2.5	94	1.95
18	formamide	45.04	5	2.52	21.68	46.90	46.47	2.5	99	2.01
19	Na-lauryl sulfate	288.38	72	0.21	17.99	47.08	44.71	2.5	95	2.32

^aConditions: T= 100°C ; $[\text{H}_3\text{PO}_4] = 0.0574 \text{ M}$; $[\text{S}_2\text{O}_8^{-2}] = 0.245 \text{ N}$; 0.3 cm^2 Pt wire catalysis.

Amino groups in wastes such as triethylamine tend to resist aqueous oxidation, and the distribution of nitrogen oxidation states in the product is not known. The organic fraction was substantially mineralized (> 98.8%, as C) in 13 minutes; and to < 0.5 ppm (>99.97%) in 21 minutes. (Table III) Most amino nitrogen remains as

ammonium ion. The presence of low concentrations of nitrite indicate possible reduction of nitrite by organic free radical intermediates.

Oxidation of Organics at Initially High Concentration. Kerosene is a mixture of duodecane and various aromatic compounds. The water-insoluble phase had disappeared after 70 min. of vigorous stirring. Solution analysis indicated 1.30 ppm carbon remaining. After an additional 70 min. of oxidation, the concentration was 0.27 ppm. It is suggested that the rapid solution of the insoluble kerosene is due to the ready attack of the SRA on the aromatic double bond, followed by solution as complex alcohols.

Table II. Oxidation of triethylamine by peroxydisulfate in a batch reactor.

Time min.	Oxidant, equiv.	Total mass g	C ppm	NO ₃ ⁻ ppm	NO ₂ ⁻ ppm	Mole-fraction N as nitrate	Mol- fraction N as nitrite	Mol-fraction N as NH ₄ ⁺	Mol- fraction to CO ₂
0	0	100.3	1850	0	0	0	0	1.00	0
13	0.094	137	22	14	7	0.012	0.008	0.98	>0.988
21	0.151	160	0	34	10	0.035	0.014	0.95	>0.9997

Table III. Uncatalyzed, batch oxidation of kerosene (predominately dodecane)

Time min.	Mass of reaction medium, g	Total oxidant added, Equiv.	Carbon, ppm-wt as C	Carbon unoxidized, g C	Extent of destruction
0	54	0	59060	3.17	0.0
70	564	1.4	1.30	0.00073	0.99977
140	1073	2.8	0.27	0.00029	0.99991

Table IV. Summary of the oxidation experiments with model chemicals

Compound	[R(0)], N	[R(t _f)], N	t _f min	Int k ₂ min ⁻¹	T, °C	Rate, ml/min	Oxidant ^a
Ethylene glycol	0.23	<0.002	30	0.035	94	5	1.14 N + 2 M H ₂ SO ₄
Ethylene glycol	0.39	<0.002	30	0.054	90	4.9	1.45 N + 0.1 M H ₂ SO ₄
Oxalic acid	0.048	<2x10 ⁻⁴	15	0.030	88	2.8	1.14 N + 2 M H ₂ SO ₄
Triethylamine	0.032	<5x10 ⁻⁴	12	0.037	95	3.3	1.14 N + 2 M H ₂ SO ₄
Dowex I-x4	0.10	<2x10 ⁻⁴	3	—	95	3.3	1.26 N + 2 M H ₂ SO ₄

^aOxidant (except for 1.45 N) produced by electrolysis cell and determined by titration.

High concentrations of model organic materials (Table IV) were oxidized in 0.3 L batches in a 0.5 L reaction vessel, with the oxidant produced in the electrolysis cell being pumped into the vessel at the indicated rate. In all cases, little or no induction period was observed between the injection of oxidant and the beginning of carbon dioxide evolution. This indicates that the final oxidation step leading to the evolution of carbon dioxide is slowest. Of these compounds, only the oxidation of the ion exchange resin Dowex I-x4 (containing amino and sulfate groups on a polystyrene base) was too fast to reveal the shape of the oxidation-time profile. Resin oxidation proceeds in two steps: the resin is first converted to soluble organic ion products, which are then oxidized at a slower rate [6]. From the formal rate constants, it appears that the oxidation of initially high concentrations of organics are several times higher than those for the same compounds at <50 ppm found in Table I.

Reactions in the Packed Bed Reactor. The oxidation of ethylene glycol in the horizontal packed bed reactor was monitored using the mass spectrometer to detect carbon dioxide in the rapid overflow argon stream. The reaction medium (organic and oxidant) were mixed cold, and then rapidly heated upon injection into the column. Carbon dioxide was evolved within a few minutes, indicating that initial oxidation steps were rapid compared with the oxidation of the intermediate carboxylate groups resulting in CO₂ evolution. (Figure 4). Oxygen evolution was slow— following after most of the organic had been consumed. The small second wave of CO₂ is of unknown origin. A trace amount of formaldehyde (0.001 x CO₂ concentration) was detected in the overflow, which indicates the importance of off gas retention and treatment in any practical application of this process.

Interpretation of Results. Mechanistic and kinetic models of peroxydisulfate oxidation reactions have been reviewed by House [7] and recently by Minisci [8] and Peyton [9]; acid catalyzed reactions with water have been studied by Koltoff and Miller [12] with extensions to higher concentrations in presence of organics by Goulden [13]. Mild thermal or redox stimuli of peroxydisulfate promotes formation of the sulfate free radical, SRA, which is an effective charge transfer oxidant for organic reducing agents:



SRA reactions are generally fast and result in products determined by competition kinetics. Beylerian [14] measured the rate of the monomolecular homolysis reaction (8) at 35-45 °C, finding the rate of formation first order in peroxydisulfate, with a rate constant of $1.52 (10^{-5}) \text{ min}^{-1}$ at 40 °C, with an activation energy of $29 \pm 1 \text{ kcal/mol}$. Extrapolation to 90-100 °C yields $k_a = 0.009-0.027 \text{ min}^{-1}$, consistent with the rate of destruction of organics we have tested.

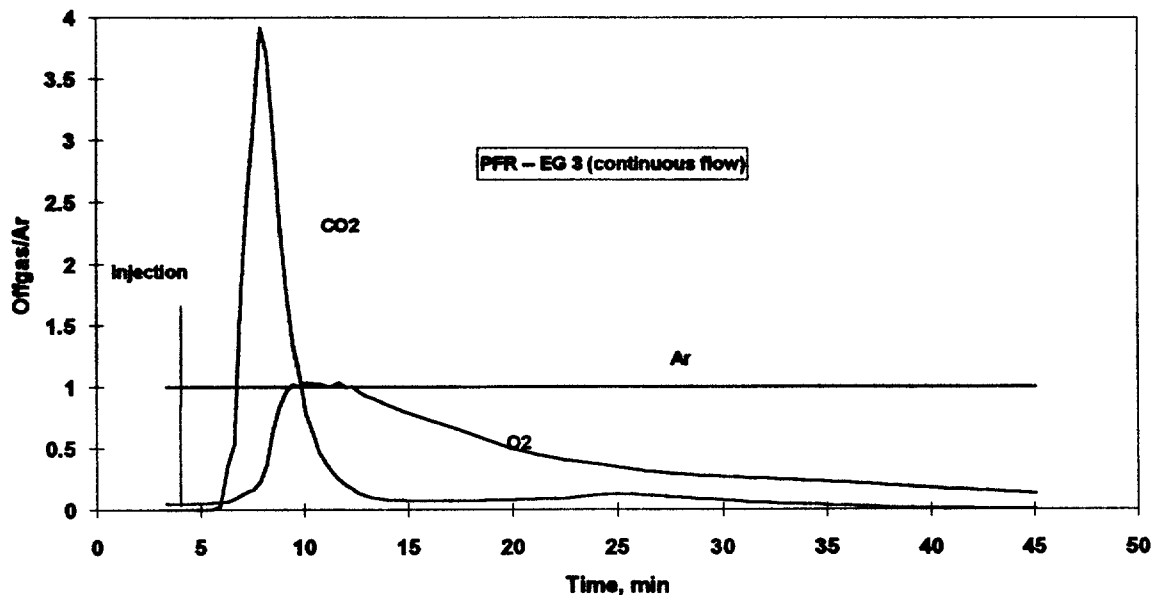


Fig. 4. Rate of carbon dioxide and oxygen evolution for continuous cycling of the oxidant and reductant through the PFR, with argon gas overflow for diagnostics.

The rate of reduction of $S_2O_8^{-2}$ found with pure water at moderate temperatures (30-60 °C) is accelerated by the addition of organic reducing agents. The rate increase depends on the identity of the reducing agent but is not proportional to its concentration. The enhanced rate has been explained by the formation of organic free-radical intermediates, which accelerate the decomposition of the peroxydisulfate by (7). The formation of a free radical intermediate R^{\cdot} , from the action of $SO_4^{\cdot -}$ on R, leads to a steady state equation of the form

$$-d[R]/dt = k_3 [S_2O_8^{-2}] + k_4 [R^{\cdot}][S_2O_8^{-2}] = k_a [S_2O_8^{-2}] \quad (8)$$

The near constant rate of mineralization of organics in our study (expressed in units of normality) indicates that SRA formation is generally rate-determining, while the greater rate of oxidation of high concentrations may result from the accelerated formation of the SRA by organic radical intermediates.

From a practical standpoint, an integral rate constant of 0.02 min^{-1} suggests that a digester supplied with peroxydisulfate to maintain an average concentration of 3 N should sustain organic destruction rates of about 0.05 equivalents per liter per minute, at 80% coulomb efficiency. For organic compounds having a typical equivalent

weight of 3 g-carbon/equiv, a 1 m³ batch reactor should process 200 kg (as carbon) in one day. The parasitic oxidation of water can be minimized by operating at low acid concentrations (0.01-0.1 M). This work at 0.1 M acid showed efficiencies of about 80% for ethylene glycol, but as low as 30% for triethylamine.

ACKNOWLEDGMENTS

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. We gratefully acknowledge support by the Laboratory Directed Research and Development; and continued support of the Mixed Waste Focus Area of the U.S. Department of Energy.

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