Photothermal Oxidative Destruction of Chloronaphthalene

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We have investigated the feasibility of using concentrated solar photons for the destruction of hazardous waste. Chloronaphthalene was chosen as the model compound for study, and light intensities were used that are close to those expected from a high-flux solar furnace. The results showed that the addition of ultraviolet photons to a reactor greatly accelerates the reaction rate for oxidation. The light intensity has an exponential effect on the degree of destruction, as predicted by earlier studies. Derived primary quantum yields in the gas phase are much higher than reported values in organic liquids: 0.2 for gas phase vs 0.002-0.005 for liquids. The products of incomplete oxidation were tentatively identified, and similar products were found in the presence or absence of ultraviolet light. At low temperatures, the ultraviolet light appeared to promote the formation of these products, while at higher temperatures, the light enhanced the destruction of the byproducts. It was found that, at a given destruction level, the product slate was similar with and without the light.

Introduction

Remediation of soil and groundwater sites that have been contaminated with hazardous waste is proving to be one of the greatest environmental challenges of this decade. Many current waste treatment technologies destroy the contaminant through high-temperature incineration. While incineration is effective at destroying the waste in a steady-state mode, it is prone to emissions of hazardous materials (products of incomplete combustion or PICs) upon upsets. The high temperatures involved also enhance the vapor-phase transport of volatile metal compounds. The National Renewable Energy Laboratory (NREL) has been investigating the use of high-flux solar photons to enhance the thermal, oxidative destruction of hazardous waste.

There are several potential advantages to the use of photochemistry to enhance the destruction process. The penetration of light through a fairly thick region of the reactor can have the effect of spreading out the zone of rapid reactions from a few millimeters for flames to many centimeters (depending on the optical depth of the reacting mixture) in a photothermal device. This thickened reaction front reduces the likelihood that a packet of waste will bypass the reaction zone due to turbulence. A second advantage is that the temperature of the reactor may be significantly lower than that used in conventional incineration for a given degree of destruction. Thus, volatile metal compounds, such as metal chlorides, would be less likely to be transported in the vapor phase and are more likely to be collected in the ash where they can be disposed of in an acceptable manner (or the metals can be recovered). A third benefit of solar-assisted waste destruction is that no outside fuel source is required to bring the reacting mixture up to temperature, since that energy comes from the sun. Removal of the requirement of a supplemental fuel has a major influence on downstream cleanup costs, since the reactor effluent would contain only the mineralized waste and not a large excess flow from the oxidation products of the fuel source. Finally, adding photons to the system may reduce the dangerous PICs which can be generated. The chlorine-carbon bonds of the hazardous PICs (e.g., chlorinated dioxins or furans) are preferentially photolyzed relative to carbon-hydrogen bonds. This leads to destruction of the PICs or a reduction in their toxicity.

The idea of using solar energy to destroy hazardous wastes was first investigated experimentally by Graham and Dellinger (1, 2), who used a xenon lamp solar simulator to decompose several chlorinated aromatic species at high temperatures. They found significant enhancements over thermal destruction efficiencies when the samples were irradiated. This group used a photon flux of 57 equivalent suns for much of their work, where one sun is defined as the solar radiation falling on a horizontal surface with and air mass of 1.5 (3). Using a simple model, Graham and Dellinger were able to extrapolate their results and project much larger effects for the high light levels, which are achievable in a typical solar furnace (up to 2000 suns); their projections have been born out in field experiments (4,5). These projections and field tests indicate that there is an exponential dependence of the destruction and removal efficiency (DRE) upon the ultraviolet light intensity for a given temperature.

This paper describes the results of experiments and analysis at NREL on the feasibility of the use of photons to accelerate the destruction of a model compound using a high-flux light source (up to 800 suns). We have chosen chloronaphthalene as our model compound for a number of reasons. Being an aromatic molecule, it represents a somewhat difficult compound to destroy due to the stability of the aromatic ring system. It is a chlorinated hydrocarbon, which is one of the large families of waste to be destroyed. It also has an absorption spectrum that overlaps with the solar spectrum. This is demonstrated in Figure 1, which displays the solar spectrum (3) together with the absorption spectra at 1-chloronaphthalene at several temperatures (6, 7). Also shown in Figure 1 are relative emission intensities of the argon-ion laser used as a light source in these studies.

This experimental investigation used the analytical capabilities of a molecular beam mass spectrometer (MBMS) to obtain quantitative destruction data and qualitative information concerning the formation of partially oxidized species. These data were used to allow a comparison between purely thermal oxidation and oxidation aided by the absorption of ultraviolet light.



Figure 1. Absorption spectrum of chloronaphthalene superimposed on the solar spectrum (AM1.5 reference 3). Also shown are the relative intensities of the laser emission lines (open circles).

Experimental Section

Most of the experimental equipment used in these studies has been described in detail elsewhere (8-12), and only a brief description will be provided here. In the experiments on the photodestruction of chloronaphthalene, we used a heated flow-tube reactor illuminated with an argon-ion laser and sampled with the MBMS.

Chloronaphthalene was introduced at a known rate to a 200 °C mixing cell using a calibrated syringe pump. Oxygen and helium were metered into this cell using rotameters. The mixture then passed through the photoreactor as shown in Figure 2. At the exit of the photoreactor, the product gases were mixed with a sweep flow of helium and convected to the MBMS for analysis. Reactor residence time was varied by changing the flow rates. Experiments were carried out at ambient pressure $(P_{\text{ambient}} = 0.82 \text{ atm at Golden, CO})$. The helium sweep flow (5 L/min) at the exit of the reactor served to keep the window clean and to provide the flow required by the inlet sampling orifice of the MBMS instrument. A smaller helium flow (14 mL/min) was introduced at the other end of the reactor to keep the downstream window clean. During oxidation reactions, the helium and oxygen flows were adjusted so that there is typically 20% oxygen in the reactor.

The triple-quadrupole mass spectrometer installed in the MBMS allows fragmentation mass spectra for a specific ion of interest to be obtained, which were of great use in determining chemical identities. In collisionally-induced dissociation (CID) experiments carried out here, the ion of a particular mass-to-charge ratio was selected by the first quadrupole (Q1) and then accelerated and allowed to collide with a bath gas (typically argon) in the second quadrupole (Q2). Collisional energies in Q2 are typically 15 eV. The ion fragments produced in Q2 were then measured with the third quadrupole (Q3). From the fragmentation spectra it was usually possible to determine the identity of the ion selected by the first quadrupole, especially when compared to the CID spectra of known standards. When CID spectra were not available, we can refer to electron-impact spectra which are often similar.

The light source used in these studies was a 20-W argonion laser (Coherent Inova 200-20-4), which was optimized for ultraviolet output. When operating on all lines from 300 to 340 nm, the output of the laser was over 2 W. Table 1 shows the power of each laser line as determined by the factory. We chose a laser rather than a solar simulator for the ability to conveniently direct, collimate, and measure the beam. While the laser with discrete lines does not truly represent the continuous solar spectrum, most of the species of interest have broad and fairly featureless absorption spectra, which reduces the effect of the noncontinuous light source (see Figure 1 for example). From 300 to 340 nm, the integrated spectral power of the laser represents a solar flux of nearly 800 suns over the same wavelength band, as determined by

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$$N_{\rm suns} = \frac{\sum_{300 \text{ nm}}^{340 \text{ nm}} P_{\rm laser}(\lambda)}{\int_{300 \text{ nm}}^{340 \text{ nm}} P_{\rm sun}(\lambda) \, d\lambda}$$
(1)

where $P_{\text{laser}}(\lambda)$ is the power level of the discrete laser lines, and $P_{\text{sun}}(\lambda)$ is the direct-normal power distribution of the solar spectrum under the AM1.5 conditions (3).

The laser beam was expanded to fill the entire volume of the reaction vessel. The radial beam profile was measured with a calibrated power meter and had a roughly Gaussian profile. The absorption levels were determined by measuring the beam power at the reactor vessel exit with a broad-area photodiode. We have determined the average photon flux from measurements of the laser beam profile where the reactor is positioned and the values are also collected in Table 1. It was assumed that the relative intensities of the laser lines were the same as measured at the factory. Typical absorption levels $(1 - I/I_0)$ during experiments were between 5 and 25%. Thus, we were close to the optically thin limit under all conditions.

During a typical experiment, the gas flows were started through the heated reactor, and chloronaphthalene was injected at a steady rate into the flow until the chloronaphthalene ion signal (m/z = 162) came to a steady state, as determined by the MBMS, typically within a few seconds. After a few more seconds, the laser light was turned on, and the ion signals were allowed to come to a steady state. This allowed a direct, real-time comparison between thermal and photothermal reactions. During a single experiment, this procedure was repeated for several flow rates (keeping the concentration of oxygen and chloronaphthalene constant). These experiments usually lasted about 10 min, and mass spectra were stored roughly every second. Noise levels were reduced by averaging over many scans. Background spectra were obtained at the beginning of every experiment when there was no chloronaphthalene present.

Calibrations for chloronaphthalene consisted of injecting the liquid at fixed rates into flowing helium held at 200 °C with the flows set so the residence time in the heated zone of the reactor was less than 1 s. These conditions ensured no thermal destruction of the substrate but were at sufficiently high temperatures to make the calibrations accurate. The ion signal for the chloronaphthalene (m/z)= 162) was measured for injection rates covering roughly an order of magnitude. A linear fit to the data provided an instrumental sensitivity for chloronaphthalene. To correct for changes in sensitivity due to temperature and other experimental parameters, argon was added as an internal standard. Signal corrections are made by normalizing the chloronaphthalene signal to the argon signal (m/z = 40). In addition to chloronaphthalene, the instrument was calibrated directly for CO, CO_2 , and C_2H_2 . Instrument sensitivities of other components were estimated.



Figure 2. Photothermal flow-tube reactor. Tube inside diameter = 2.2 cm; reaction zone length = 2 cm.

Table 1.	Fluxes	of Argon-Ion	Laser as a	a Function of	
Waveleng	th				

wavelength (nm)	photon energy (kcal/mol)	power at λ ^a (mW)	photon flux (photon cm ⁻² s ⁻¹)
300.3	95.2	160	3.89×10^{16}
302.5	94.5	255	$6.20 imes 10^{16}$
305.5	93.6	175	$4.25 imes 10^{16}$
333.6	85.7	550	1.34×10^{17}
334.4	85.5	550	$1.34 imes 10^{17}$
335.8	85.2	285	$6.93 imes 10^{16}$
total		1975	$4.80 imes 10^{17}$
^a Determin	ed by the laser ma	anufacturer.	

1-Chloronaphthalene (90%), with the balance being 2-chloronaphthalene) was obtained from Aldrich and was used without further purification. A limited number of experiments were performed with 99% pure 1-chloronaphthalene (Kodak) to assess the effect of the impurity. We found no significant change in the results when the 2-isomer was eliminated. Helium and oxygen used were technical grade (99.95% for helium and 99.6% for oxygen).

Results

The chloronaphthalene destruction levels from the experiments are summarized in Figure 3 and Table 2. Figure 3 shows plots of the thermal and photothermal destruction of 1-chloronaphthalene as a function of residence time in the hot zone of the reactor at several temperatures. The experimental points were fit to an exponential function in order to obtain apparent firstorder rate constants. These empirical rate constants are listed in Table 2. Although our instrumental sensitivity was not great enough to measure the destruction rates at very high DREs (i.e., six-nines), we can make extrapolations using the first-order rate constants. Figure 4 shows a plot of the photothermal destruction of chloronaphthalene as a function of UV light intensity. These experiments were conducted at 650 °C with a residence time of approximately 17 s. The intensity of the laser light was monitored using a photodiode in the laser head. The average photon flux in the reactor (expressed as number of equivalent suns) was estimated by integrating over the measured radial light intensity distribution in the reactor. The bottom part of Figure 4 shows the apparent first-order rate constant as a function of light intensity. As can be seen in the top part of Figure 4 (semilog plot), the destruction



Figure 3. Chloronaphthalene destruction as a function of residence time in the hot zone at 538 and 633 °C (top) and at 722 and 772 °C (bottom). Initial chloronaphthalene concentrations shown in the figure, $[O_2]_o = 20\%$. Solid squares show the ion intensities for chloronaphthalene (m/z = 162) in the absence of ultraviolet radiation; open squares show the ion intensities in the presence of ultraviolet light. Lines are least-squares fit an exponential decay with time.

level is exponentially dependent upon light intensity in agreement with the results of Graham and Dellinger (1, 2).

A typical mass spectrum of the products from the thermal decomposition of 1-chloronaphthalene is shown in Figure 5. This spectrum was collected from an experiment with a residence time of 1.4 s and the temperature of 772 °C, which gave a DRE of 68%. The spectrum on the top of the figure shows the mass region 20-200 amu while the bottom spectrum is an expanded section from 60 to 200 amu. The large peaks centered around 162 and 127 amu are the parent and fragment ions



Δ

60

Figure 4. Effect of light intensity on the destruction level of chloronaphthalene (top). The bottom curve shows the apparent first-order rate constant for this decay as a function of light intensity. The temperature during this experiment was 650 °C, the concentration was 2730 ppm, and the residence time in the hot zone was about 17 s.

for chloronaphthalene. Notice that the peak at mass 162 is roughly three times the intensity of the peak at mass 164, representing the natural abundance of 37 Cl. In addition, there are small peaks at 163 and 165 that arise from the natural abundance of 13 C in chloronaphthalene.

The smaller peaks in this spectrum are enhanced in the plot at the bottom of Figure 5. As can be seen from this enhancement, there are numerous byproducts produced from the partial oxidation of chloronaphthalene. It was found that, in the presence of ultraviolet light, the mass spectrum was qualitatively similar. This may suggest that although the ultraviolet light can dramatically alter the reaction rate, the reaction pathways are similar with and without photons. However, there is also the possibility that these byproducts are formed by reaction channels that only play a minor role in the oxidation of chloronaphthalene. It should be noted that the sum of the intensities of these peaks is roughly an order of magnitude smaller than that of the chloronaphthalenes. This suggests that even in the incomplete conversion of chloronaphthalene (68% remaining), these species do not build up to an appreciable extent. Table 3 lists the major reaction intermediates observed.

Figure 5. Typical mass spectrum for chloronaphthalene thermal oxidation; T = 772 °C, t = 1.4 s.

Mass (amu)

120

140

160

180

200

100

80

In order to help in the identification of these products, CID mass spectra were obtained using a simple flow-tube reactor. In these experiments, a mixture of 80% helium and 20% oxygen was passed through the tube reactor, which was heated to 700 °C by a tube furnace. Chloronaphthalene was then introduced batchwise into the flowing gas. All CID spectra were collected with argon as a collision gas, and the pressure in Q2 was held constant (the pressure in the Q2 region could not be monitored directly but was measured with an ion gauge on Q1). The ions in Q2 were accelerated to a kinetic energy (laboratory frame) of roughly 15 eV. The CID spectra of phenylacetylene, benzaldehyde, and benzoic acid were obtained as standards by introducing these compounds into a flow of pure helium held at 500 °C. As an example, Figure 6 shows the CID mass spectra obtained from benzaldehyde (bottom) and the product of thermal oxidation of chloronaphthalene with a mass of 106 (top). Based upon these CID spectra, some plausible identities for these peaks are shown in Table 3.

The presence of ultraviolet photons has a major impact on the profiles of the intermediates of reaction. The top half of Figure 7 shows a plot of the profile of the sum of

Table 3. Reaction Intermediates Observed in Photothermal and Thermal Destruction of Chloronaphthalene^s

mass	identification	formula
78	benzene	C_6H_6
94	phenol	C ₆ H₅OH
102	ethynylbenzene	C ₈ H ₆
104	styrene	C_8H_8
105, 106	benzaldehyde	C_7H_6O
112	chlorobenzene	C ₆ H ₅ Cl
116	indene	C_9H_8
118	ethynylphenol	C ₈ H ₅ OH
128	naphthalene	$C_{10}H_8$
130	indenone	C ₉ H ₆ O
136	chloroethynylbenzene	C ₈ H ₇ Cl
139, 140	chlorobenzaldehyde	C7H5OCl
144	naphthol	C ₁₀ H ₇ OH
146	indenedione	$C_9H_2O_2$
152	chloroethynylphenol	C ₈ H ₄ CIOH
158	naphthaquinone	$C_{10}H_6O_2$
152	chloroindenone	C ₉ H ₅ ClO

^a Product identifications are based upon CID results.



Figure 6. Comparison of the CID spectrum with that of benzaldehyde (MW = 106 Da) (bottom) introduced as a standard with that of the product of chloronaphthalene oxidation at m/z = 106 (top).

the intermediates in Table 3 at 722 °C. The concentrations of the intermediates were determined using techniques discussed in the experimental section. As the plots show, the overall levels of products are small compared to the starting level of the chloronaphthalene (≈ 2000 ppm). The plots also show that, at longer residence times, fewer intermediates are produced in the presence to ultraviolet light. The largest effect of the photons is to accelerate the chemistry; that is, shift the rise and decay curves to shorter residence times. The bottom half of this figure shows the sum of these products as a function of the amount of chloronaphthalene removed. As can be seen from this plot, at 722 °C, the curves with and without ultraviolet light nearly overlap. That the product profiles as a function of destruction level are similar with and without light again suggests that the reaction channels are similar



Figure 7. Profiles of the sum of the reaction intermediates as a function of residence time at 722 °C (top) and as a function of degree of destruction (bottom). [Chloronaphthalene]_o = 2500 ppm; $[O_2]_o = 20\%$.

in the presence of ultraviolet light and that the light increases the reaction severity.

Discussion

The thermal and photothermal destruction of chloronaphthalene is obviously a very complex series of reactions, and it is difficult to obtain intrinsic rate constants from the data in Figure 3. Nevertheless, a comparison of empirical rate constants to assess the effect of photoreactions can be illustrative. Thus, we have fit the data in Table 2 and Figure 3 to a first-order decay to extract *apparent* global rate constants for the photothermal $(k_{\rm ph/th})$ and thermal $(k_{\rm th})$ destruction of chloronaphthalene. The good exponential fit of the data in Figure 3 indicates that first-order kinetics does a good job of globally describing the substrate destruction.

The thermal destruction is that which occurs with the laser off, while the photothermal destruction is that which occurs with the laser on. From these two rate constants, we can *define* a photolytic rate constant, k_{ph} , by setting the total rate of destruction to be a linear sum of the photolytic and thermal processes as

$$\frac{\mathrm{d}[\mathrm{CN}]}{\mathrm{d}t}\Big|_{\mathrm{ph/th}} = (k_{\mathrm{ph}} + k_{\mathrm{th}})[\mathrm{CN}]$$
(2)

where $k_{\rm ph} = k_{\rm ph/th} - k_{\rm th}$, and [CN] is the chloronaphthalene concentration. The definition of $k_{\rm ph}$ is not meant to imply that the thermal and photo processes are independent and can be decoupled. Rather, we are defining a quantity that is indicative of the rate of acceleration of the reaction due to the addition of photons. Curves of the three rate constants ($k_{\rm th}$, $k_{\rm ph/th}$, and $k_{\rm ph}$) are shown as a function of temperature in Figure 8. Figure 8 also shows the photolytic rate constant for reactions done in a pure helium atmosphere. These rate constants, $k_{\rm He}$, were obtained by subtracting the thermal rate constant in helium from the photothermal rate constant in helium and are included to show the effect of removal of oxygen from the reaction system.



Figure 8. First-order rate constants for chloronaphthalene destruction as a function of temperature. Rate constants are as defined in the text. The inset shows a comparison between the measured chloronaphthalene rate constant under pyrolytic conditions (hellum atmosphere, crosses) and the calculated primary rate constant (triangles).

As can be seen in Figure 8, $k_{\rm ph}$ is a very strong function of temperature. This effect is probably due to the free radicals generated by the primary photolytic event participating in chain-propagating reactions. The radical chain length in this case would be expected to be a strong function of temperature as the chain length is determined by the relative rates of chain-propagating reactions have larger activation energies than chain-terminating reactions (the activation energy for chain-terminating reactions is close to zero). The temperature dependency of $k_{\rm ph}$ could be due to the quantum yield, ϕ , being a strong function of temperature, but this does not seem likely.

Consider the rate constant values at the lower temperature end of Figure 8. At 538 °C, the photolytic rate constants for reactions in helium and in 20% oxygen converge $(k_{\rm ph} = k_{\rm He})$. In helium at low temperatures, we would expect the $k_{\rm He}$ to represent the rate of a primary photoevent, that is the reaction

$$C_{10}H_7CI \xrightarrow{n\nu} C_{10}H_7 + CI^{\bullet}$$
(3)

is the main substrate destruction channel (13). If the photodestruction of chloronaphthalene is due entirely to a primary photoevent (that is, the radical chain length is unity), then the first-order primary photolytic rate constant, $k_{1^{\circ}ph}$, is given by

$$k_{1^{\circ}\rm ph} = \phi \sigma J \tag{4}$$

as suggested by Graham and Dellinger (1, 2), where ϕ is the primary quantum yield, σ is the absorption cross section, and J is the photon flux. When oxygen is present, however, chain-propagation reactions can occur, such as Scheme 1

shown in Scheme 1. As temperatures are lowered, the rate of chain-propagating steps slows while the chain-terminating steps have approximately the same rate. Thus, the radical chain length shortens and in the limit approaches unity. At this limit, the photolytic rate constant, $k_{\rm ph}$, is identically equal to the primary photolysis rate constant given in eq 4. The convergence of $k_{\rm ph}$ and $k_{\rm He}$ at 538 °C leads us to believe that we have reached this limit and that the chloronaphthalene destruction is due only to primary quantum events. If so, we can determine the quantum yield, ϕ , defined in eq 4 at 538 °C from $k_{\rm ph}$ if we know the absorption cross section, σ , at that temperature.

Mackey et al. (6, 7) have measured the absorption cross section for chloronaphthalene in the gas phase as a function of wavelength at various temperatures. Their data were interpolated using an exponential function in temperature in order to find σ_{λ} (538 °C). The quantum yield for this process is then determined by

$$\phi(538 \text{ °C}) = \frac{k_{\rm ph}(538 \text{ °C})}{\sum_{\lambda} \sigma_{\lambda}(538 \text{ °C})J_{\lambda}}$$
(5)

where the summation is over the four ultraviolet laser wavelengths, and J_{λ} is the photon flux from the laser as given in Table 1. From this equation, we derive a value for the quantum yield ϕ at 538 °C of 0.2. This gas-phase quantum yield is significantly higher than the value of ϕ = 0.002-0.005 reported for liquids (14). One might expect the gas-phase value to be higher than that obtained on liquid because of solvent cage effects and a reduced intersystem crossing rate for the excited electronic state (14, 15). It is also possible that the quantum yield reported here represents an upper limit to the true quantum yield for reaction 3 since chain reactions may not have been eliminated.

If we assume for the moment that the quantum yield is not a function of temperature, then we can use the data on absorption cross section as a function of temperature from ref 6 to compute the $k_{1^{\circ}ph}$ at any temperature:

$$k_{1^{\circ}\mathrm{ph}}(T) = \sum_{\lambda} \sigma_{\lambda}(T) J_{\lambda} \phi \tag{6}$$

The inset of Figure 8 shows the comparison of the calculated rate constant for primary photolytic events, from eq 6, with the experimentally measured k_{He} . The close agreement of the two curves supports the concept that only primary photolytic events are occurring in the pure helium system at all temperatures. This also indicates that secondary chain reactions are not important in the oxygen system at 538 °C. Furthermore, it suggests that the primary quantum yield is at most a weak function of temperature. The gentle temperature dependence of the absorption cross section from ref 6 cannot account for the strong temperature dependence of k_{ph} as shown in Figure 8. Thus, we conclude that the enhanced rate of destruction is due to secondary chain reactions with oxygen-containing species acting as important chain carriers.

The fact that chain reactions play a significant role in the photothermal oxidative destruction of chloronaphthalene suggests that the solar benefit will be greater than that predicted by photolysis alone (eq 4). Thus, compounds that absorb only a small amount of solar radiation may show a significant photoeffect upon their thermal destruction. This is especially true at higher temperatures where chain reactions become more important. Furthermore, the extent of chain reactions should be highly dependent upon the waste concentrations, being favored at higher concentrations.

Brezinsky and co-workers (16-18) have examined the thermal oxidative reactions of aromatic compounds from the standpoint of elementary reaction mechanisms. The products shown in Table 3 are, for the most part, consistent with these aromatic oxidation mechanisms. Some of the carbonyls have not been identified before but are predicted by the models.

Based on the above results, several comments can be made about the applicability of homogeneous photothermal chemistry to hazardous waste destruction. It is apparent from Table 2 and Figure 4 that a high flux of ultraviolet photons greatly increases the rate of waste oxidation for a given temperature. However, similar rates can be obtained in a thermal reactor by increasing the temperature. A more compelling argument for photothermal waste incineration can be made based on the data from Figure 7. The level of PICs produced for a given residence time is greatly reduced. The ability of the C-Cl bond to be photolyzed means that the most hazardous PICs, the chlorinated hydrocarbons, are selectively destroyed.

To properly assess the value of a photothermal incinerator, we must consider the fluid mechanics of a conventional thermal incinerator in addition to the chemistry. Conventional incinerators operate in a turbulent regime. Most of the oxidation occurs in a narrow flame-front, a zone a few millimeters thick in which oxidizing free radicals are far in excess of their equilibrium values. The turbulent nature of the system can lead to local extinguishment of the flame due to flame stretch. Thus, there is a finite probability that a packet of waste will pass through a breach in the front and not be destroyed. Oxidizing radical concentrations are much lower in the thermal afterburner zone, so destruction rates are much slower. Compare this system to a photothermal reactor. In this configuration, the zone in which free radicals are generated is equal to the optical depth of the reactor. As opposed to a few millimeters in a thermal system, this zone of rapid oxidation can be tens of centimeters or more. With a wide flame-front, there is less chance that a molecule of waste will pass through the reaction zone unoxidized.

Conclusions

We have investigated the feasibility of using concentrated solar photons to effect a more efficient and reliable destruction of hazardous waste. Chloronaphthalene was chosen as the model compound for study. The results showed that the addition of ultraviolet photons to a reactor greatly accelerates the reaction rate for nonflaming oxidation. The light intensity has an exponential effect on the degree of destruction. Derived primary quantum yields in the gas phase are much higher than reported values in organic liquids: 0.2 vs 0.002-0.005.

Photothermal destruction of hazardous waste appears promising in applications where very high degrees of destruction are required (such as chlorinated dioxins), because the illuminated zone is, in effect, a very broad flame-front. Other advantages of photothermal destruction are the reduced volatilization of hazardous metal compounds and the elimination of the need to dilute the waste with excess fuel and air. The need for the substrate to absorb in the solar spectrum may limit the applicability of solar photothermal waste destruction.

Symbols

$k_{ m ph}$	photolytic rate constant
$k_{ m th}$	thermal rate constant
$k_{ m ph/th}$	photothermal rate constant
k_{He}	photolytic rate constant in helium
$k_{1^{\circ}\mathrm{ph}}$	primary photolytic rate constant
φ	quantum yield
σ	absorption cross section
J	photon flux
ν	frequency of light
λ	wavelength of light
h	Plank's constants
Р	laser power
t	time
Т	Temperature

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