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Direct Mass Spectrometric Studies of the Destruction of Hazardous Wastes.

1. Catalytic Steam Re-Forming of Chlorinated Hydrocarbons

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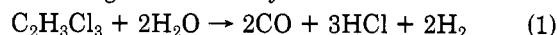
■ Catalytic steam re-forming behavior was studied for a number of chlorinated and nonchlorinated organic species using the direct sampling capabilities of the molecular beam mass spectrometer (MBMS). Steam re-forming is an often used chemical process that can convert hydrocarbons into largely CO and H₂. These screening studies investigated the possibility of using a catalytic steam re-forming environment to destroy hazardous waste by measuring destruction efficiencies and qualitatively comparing product slates with straight pyrolysis. For the steam re-forming, a rhodium catalyst on a reticulated alumina support was used and these observations were made. (1) Catalytic steam re-forming significantly enhanced the destruction of the compounds studied compared to destruction by pyrolysis. (2) Products of incomplete destruction are also significantly reduced, even for those species that are thermally stable. (3) Aromatics and acetonitrile are more difficult to steam re-form than aliphatic species. (4) A wide variety of species are susceptible to steam re-forming (including chlorine-containing species and acetonitrile) without any indication of catalyst deactivation over several 10-min periods. Two exceptions identified so far are the sulfur-containing species 3-methylthiophene and the phosphorus-containing species dimethyl methylphosphonate. Temperatures of the Rh catalyst must be maintained at 800 °C or above to keep the catalyst active, at 50% steam in helium, for many compounds.

I. Introduction

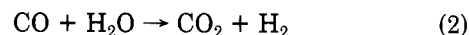
Combustion of hazardous wastes is a widely practiced technology which, by most accounts, is effective in achieving the currently mandated four-nines (99.99%) destruction of principal organic hazardous constituents (POHCs) (1-5). There remain, however, substantial concerns about incineration, particularly with regard to products of incomplete combustion (PIC). The nature of these PIC, and the circumstance of their formation, are the subject of active study in the laboratory and the field (6-10). Due to lack of continuous PIC and POHC emission monitors for field use, hazardous waste incineration is the cause of considerable environmental and public concern (as is the case with all waste incineration) (1). In addition, the rather severe combustion conditions imposed involve

high combustion temperatures, long combustion times, and often the use of substantial quantities of blended hydrocarbon fuels. These requirements can lead to NO_x formation and a substantial energy penalty. Finally, the very process of gas-phase combustion contains the reaction conditions for PIC formation under less than perfect mixing and combustor conditions.

As a result of these circumstances, there is a vigorous search for alternative destruction methods ranging from pyrolysis to catalytically enhanced combustion (11-18). Among these methods is a solar-assisted approach that involves catalytic steam re-forming of a range of chemical species, with the engineering configuration involving direct irradiation of the catalyst surface with highly focused solar energy (19, 20). This approach developed as an outgrowth of the CO₂ re-forming of CH₄ for solar energy storage and transport, where Rh showed superior resistance to coking (19). The re-forming is carried out by having relatively cold inlet gas make contact with dispersed rhodium (21) on a reticulated, open structure of alumina (22). The steam re-forming reaction has been studied using 1,1,1-trichloroethane as a model waste compound (23), where the steam re-forming stoichiometry was



In addition to the steam re-forming reaction, the water-gas shift reaction



also occurred to produce CO₂. It is envisaged that few thermal gas-phase reactions will occur before the material contacts the radiantly heated surface. Direct solar irradiation of the catalyst is postulated to be beneficial, whether or not any photoenhanced heterogeneous catalytic effects are present (19, 20). This is because the heat can be deposited directly on the site of the usually endothermic re-forming reactions, minimizing heat-transfer limitations. It is also possible that the absence of oxidative, gas-phase, radical-driven destruction reactions will minimize PIC formation [more generally, products of incomplete reaction (PIR)]. This system could be more forgiving of upsets, achieve high destruction efficiency (DE) at lower temperature, avoid NO_x formation, and require no auxiliary fuel or hydrocarbon source of hydrogen for highly chlorinated wastes, vis-à-vis incineration.

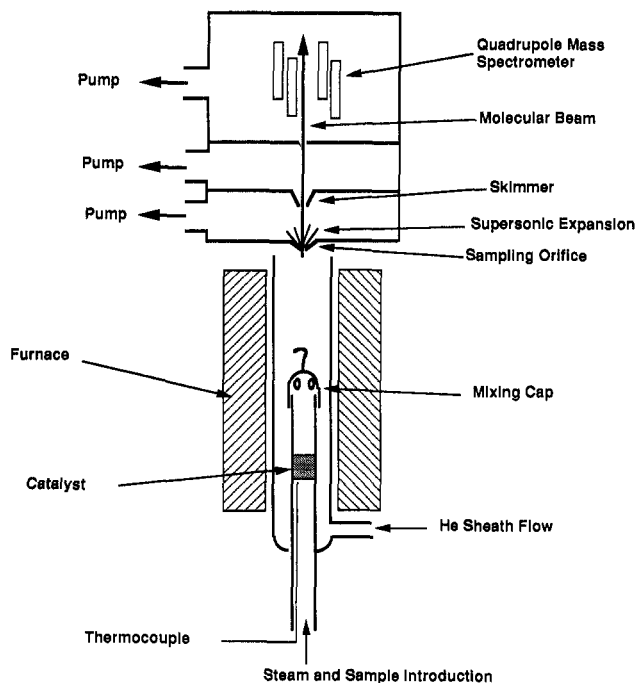


Figure 1. Schematic representation of SERI's molecular beam mass spectrometer (MBMS) showing the steam re-forming reactor. Samples flow through the inner quartz tube and over the catalyst. The products are mixed with the sheath flow before encountering the sampling orifice. In the MBMS, the products are formed into a molecular beam and analyzed by a quadrupole mass spectrometer.

It is the objective of these studies to explore heterogeneous, catalytic destruction of a variety of hazardous compounds in a steam environment. In this paper we demonstrate the steam re-forming capability of Rh for a variety of chlorinated species typical of hazardous waste streams. The advantages of direct, free-jet, molecular beam, mass spectrometric (MBMS) sampling in real time for studying chlorinated compound reactions in flames have been shown by Chang et al. (24). We apply such sampling to laminar flow, tubular, reactors in this study. The qualitative application to the pyrolysis of chlorinated methanes is shown, followed by scouting studies of the catalytic steam re-forming of a range of chlorinated organics and other organic species on rhodium.

II. Experimental Section

The catalytic steam re-forming and pyrolysis experiments described in this paper were conducted using a high-temperature, atmospheric pressure, flow reactor and an MBMS sampling system. Figure 1 is a schematic diagram of the apparatus, showing the quartz flow-tube reactor at the bottom and the MBMS at the top. The particular reactor shown in the figure represents that used in steam re-forming experiments, but is similar to that used in the pyrolysis experiments. The use of this high pumping capacity MBMS as a probe of high-temperature chemistry has been extensively detailed elsewhere and the experimental system will be described only briefly (25–27).

In a typical experiment, reactions were carried out in the heated flow reactor maintained at atmospheric pressure and products were directly sampled and analyzed using the MBMS. In order to quantify results, gas flows were regulated by calibrated flow meters and liquid compounds were introduced using a calibrated syringe pump and vaporized through the valving, injection port, and heated chamber of a gas chromatograph. In some pyrolysis experiments, samples were introduced as a short pulse by injecting a known volume of liquid directly into the reactor.

With the steam re-forming reactor shown in Figure 1, samples were introduced at the bottom of the reactor into a flow of He and steam. This inner flow carried the species over the rhodium catalyst in the heated region of the reactor. At the top of the inner quartz tube, reaction products were mixed with a large flow (5 L/min) of helium before being sampled by the MBMS. This dilution by a large He flow minimizes the effect of varying reaction products and conditions on the free-jet expansion and the resultant relation between species concentration and observed mass spectral ion intensities, since the He dominates the free-jet expansion behavior. The pyrolysis reactor was a single-tube reactor, where samples were introduced into the bottom of the reactor and carried through the heated region of the reactor, in 5 L/min He, to the sampling orifice. As a preparation for both experiments, the temperature profiles of both reactors were measured using sheathed thermocouples. From these profiles and the gas flows, the residence times in the heated zones were determined. The furnaces heating the reactor are capable of temperatures up to 1200 °C, but during this study, temperatures were varied between 500 and 900 °C, as determined by sheathed thermocouples placed in the quartz reactor during experiments. In the steam re-forming reactor, the thermocouple was placed just downstream of the catalyst. The Reynolds numbers calculated for these experiments were low (usually much lower than 1000), ensuring laminar flow.

In the MBMS sampling system, reaction products are quenched in a supersonic expansion and mass-analyzed with a quadrupole mass spectrometer. The hot gases from tubular reactors are sampled through a small orifice (0.25 mm in diameter) at the end of a copper cone. The end of the reactor is centered around this cone so that a portion of the hot, flowing gas is sampled from the center of the reactor. The sampled gases pass through the orifice into a vacuum chamber held at 20 mTorr. This pressure differential causes an adiabatic expansion, cooling the gases and halting thermal reactions. In addition, after the sample is passed through the orifice, the system is configured so that the molecules undergo a minimum of collisions and bimolecular reactions are quenched. This expanded gas plume is then skimmed on its entrance to a 10^{-5} -Torr vacuum region. The beam passes through a final stage of differential pumping into the throat of a coaxial quadrupole mass spectrometer (Extrel) (28). Molecules are ionized by electron impact at the entrance to the quadrupole. Electron energies of ~22.5 eV are used. This low energy, plus the vibrationally and rotationally cooled molecules from the adiabatic expansion, minimizes, but does not eliminate, fragmentation. In all of these experiments, positive ions are detected using the conventional off-the-shelf capabilities of a quadrupole mass spectrometer and the ion signals are collected and processed with a Teknivent PC-based data collection system (29). During a typical experimental run, the mass range 5–300 amu is scanned each second and a digital signal (16 bit) corresponding to the intensity for each unit mass in this range is stored.

There are several attributes of the MBMS that make it useful for quick screening and qualitative high-temperature product analysis. The direct sampling allows detection of reactive and highly condensable species. In conventional trapping systems, these species are often difficult to measure, or they may undergo secondary reactions (30). "Direct sampling" in this case also includes the capability to monitor the products in real time as they are being produced. Finally, the MBMS allows the direct

sampling of the reactor at temperatures, pressures, and concentrations that would be realistic in a larger scale reactor.

One problem with the MBMS, as with mass spectrometry in general, is the difficulty in calibration for precise quantitative data. The molecular beam, the electron impact ionization, and the quadrupole filter itself all have mass discrimination effects that make it difficult to determine a sensitivity for a given molecular species *ab initio*. In addition, due to shutdown and startup procedures, there can be a small day-to-day drift in the instrumental sensitivity. To largely overcome this, known quantities of calibrants can be injected into the tube reactor, where a moderate temperature stream of helium carries the unreacted sample into the MBMS. The signal seen at the detector can be used to calculate an instrumental sensitivity for that compound. In addition, during all experiments, a tracer gas (argon) is introduced at a known concentration into the reactor. Ion signals can be normalized to this signal to account for small fluctuations in the instrumental sensitivity (such as might be caused by changing temperature). From these instrumental sensitivities, the concentrations of reactants and products can be determined to an accuracy of roughly 20%. The problem arises when products are detected for which there is no calibration. Under these circumstances, rough estimates are made based on the mass of the product. We have determined (based on the calibration of several components) that the sensitivity can be estimated in this way to within 1 order of magnitude. The product-by-product calibration procedure is time-consuming and detracts from the rapid screening capabilities of the instrument. For the purposes of this work, calibration was performed for all the starting materials to determine quantitative destruction efficiencies, while only a few of the products were calibrated. As the goal of this study is only a comparison of destruction efficiencies and qualitative product comparisons, no attempt was made to calibrate products for closure of carbon and chlorine balances. In addition, no effort was made to measure the kinetics for the steam-reforming process.

The rhodium catalyst used in the steam re-forming experiments was similar to that developed by Richardson (21). Rhodium nitrate was deposited on the reticulated alumina substrate (22) and reduced with hydrogen at 1000 °C. The particular support used in these experiments did not contain a wash coat. Such a wash coat is expected to increase the Rh dispersion and stability. Overall Rh weight percent on the alumina was 0.5, but the dispersion and overall surface area have not been measured for these first screening measurements.

III. Results

As a prelude to catalytic steam re-forming studies, pyrolysis experiments were conducted in the absence of the rhodium catalyst and CH_3Cl was used as a model compound to compare destruction efficiencies and product formation with and without the catalyst. To illustrate the screening abilities of the MBMS, Figure 2 shows raw mass spectra for pyrolysis of the chlorinated methanes. The products have not been unambiguously identified, but it is worth noting the dominance of species with higher masses than the parent compound (identified by the letter P) in these spectra.

The results from pyrolysis experiments with CH_3Cl in He, showing destruction levels versus temperature, are plotted in Figure 3 for three residence times (6.1, 3.7, and 2.7 s), where the initial concentration was ~1%. In this figure, the points represent experimentally measured

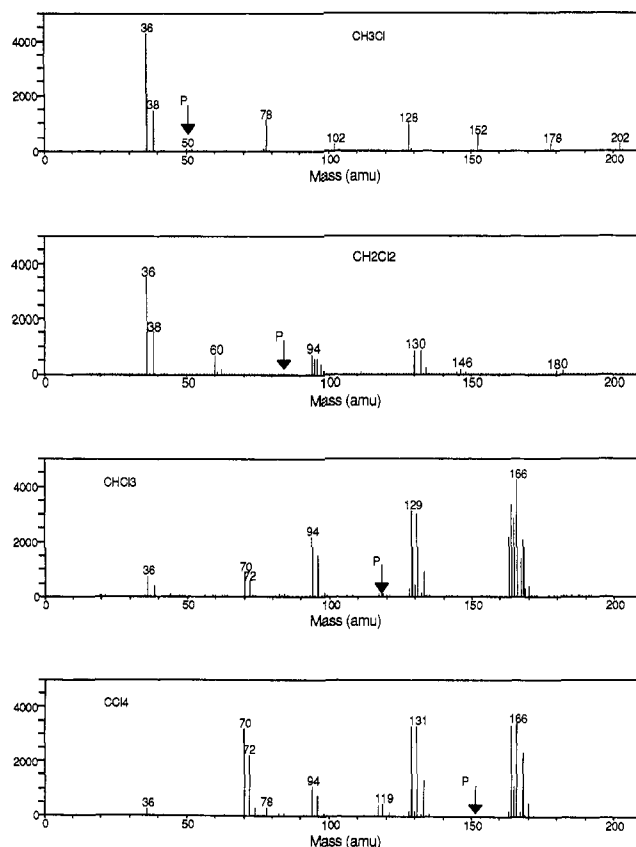


Figure 2. Plots of the mass spectra obtained from the pyrolysis of methyl chloride, dichloromethane, chloroform, and carbon tetrachloride. In each spectra, the P points to the parent ion for the species being pyrolyzed. As the spectra show, there are many species formed with masses greater than the parent. Residence time, 6.3 s; temperature, 800 °C.

values while the lines are empirically drawn. Catalytic steam re-forming destruction of CH_3Cl is also plotted in this figure where the carrier gas was 81% steam/18% He. The CH_3Cl concentration was ~1%, the weight hourly space velocity was ~106 g of CH_3Cl (g of Rh)⁻¹ h⁻¹, and the residence time in the heated zone of the reactor was less than 1.5 s. It should be noted that, at 500 °C, the activity of the catalyst toward the destruction of CH_3Cl degraded over time, which was presumably a result of coking, as was evident from a darkening of the catalyst. The activity of the "coked" catalyst was regenerated in steam at 700 °C, and at this temperature, the catalyst remained active throughout the runs with CH_3Cl .

A typical mass spectrum, which was obtained from the pyrolysis of CH_3Cl in pure helium, is shown in the top half of Figure 4. In this experiment, the flows were set so that the concentration of the CH_3Cl was ~6000 ppm and the residence time in the hot zone at the reactor was ~6.1 s. Under these conditions, ~99% of the CH_3Cl was destroyed and copious soot was formed. As a comparison, under similar destruction levels, the bottom half of Figure 4 shows a mass spectrum obtained when CH_3Cl was passed over the rhodium catalyst in steam and helium, at a temperature of 600 °C. Under these conditions, the residence time of the CH_3Cl in the heated zone of the reactor was short enough to minimize pyrolysis. To highlight any high molecular weight species, the portion from 50 to 300 amu is enhanced (the preamplifier gain was increased) by a factor of 90 in the inset. Note the essential absence of byproducts in the Rh case, compared to byproducts exceeding the remaining methyl chloride (masses 50 and 52) in the pyrolysis case. Additional experiments were con-

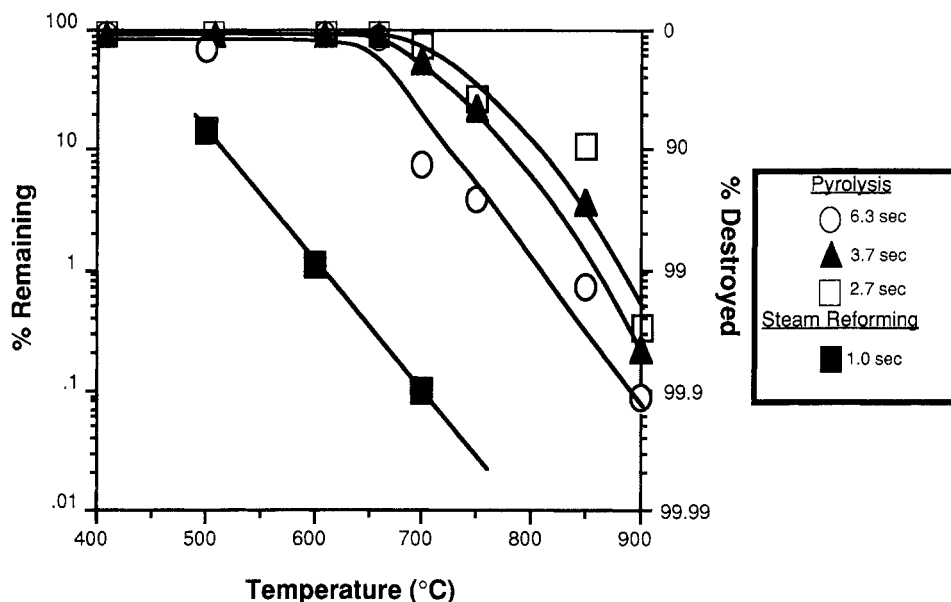


Figure 3. Plot of the destruction of methyl chloride as a function of temperature for pyrolysis and catalytic steam re-forming. The pyrolysis curves are empirical fits to the data points for three different residence times (6.3, 3.7, and 2.7 s). The steam re-forming curve is an exponential fit to the data points. In the steam re-forming experiments, the residence time in the heated portion of the reactor was 1 s.

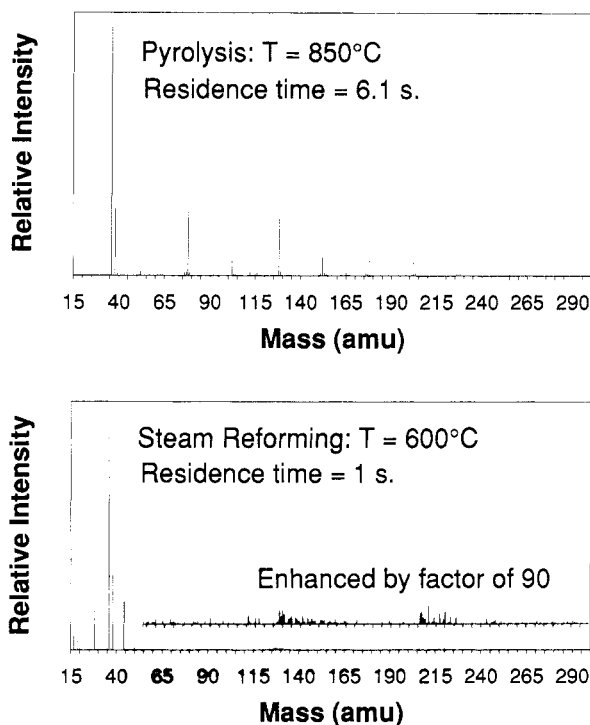


Figure 4. Comparison of the mass spectra for pyrolysis versus Rh catalytic steam re-forming of methyl chloride, for 99% destruction of the starting material. The top spectrum is for pyrolysis and the bottom two spectra are for steam re-forming. The inset is a plot of the mass range 52–300 amu enhanced by a factor of 90.

ducted to compare pyrolysis of CH_3Cl in pure helium to pyrolysis in steam and to compare pyrolysis with and without the alumina support. These included product measurements in 80% steam with and without the catalyst support in place. The results of these tests showed destruction levels and a slate of products similar to that in pure helium without the support.

The most noticeable difference between pyrolysis in pure helium and pyrolysis in helium and steam is that in pure helium copious soot was formed, whereas in steam, no visible soot was formed (though soot precursors were abundant).

In addition to monitoring the parent, the MBMS allows simultaneous monitoring of the pyrolysis products. Figure 5 shows a plot of the estimated concentration of these products as a function of temperature. Concentrations were determined by introducing known quantities of calibrants into the reactor at lower temperatures. For those chemicals that were not readily available (i.e., phenylacetylene), the instrumental sensitivity was extrapolated from measured sensitivities for several other compounds. These estimates of absolute concentration are probably only good to within 1 order of magnitude, but the relative concentrations are much more accurate. The species estimated by extrapolation are marked with an asterisk. In the legend of this plot, the products are tentatively identified and the detection limits for these species are given. The lower detection limits were determined as the noise level at that mass times the sensitivity. This figure is meant to provide a comparison to products seen from catalytic steam re-forming of CH_3Cl . In the catalytic steam re-forming experiments, the products listed in this figure were all below detection limits.

The steam re-forming catalyst was also tested with the chlorinated and nonchlorinated organic compounds listed in Table I. The results are shown graphically in Figure 6 for 800 °C conditions. Some of the more heavily chlorinated compounds (such as C_2HCl_3) deactivated the catalyst at 700 °C, by an apparent buildup of coke. At 800 °C, none of the compounds listed in Table I deactivated the catalyst over a typical exposure of 10 min. Table I lists the experimental conditions and the level of destruction for these species over the steam re-forming catalyst and in a pyrolytic environment. A general observation was made that in all of the steam re-forming experiments listed in Table I, no products other than CH_4 , CO , CO_2 , HCl , and N_2 were detected, with the exception of dichloroethylene from trichloroethane under partial conversion at temperatures below 700 °C.

Runs were also conducted with the sulfur-containing species 3-methylthiophene to determine if sulfur poisoned the catalyst. Figure 7 shows a time-resolved experiment where 3-methylthiophene was injected into the reactor during a steam re-forming experiment with CH_4 (at 800 °C). This figure contains a plot of the CH_4^+ ($m/z = 16^+$),

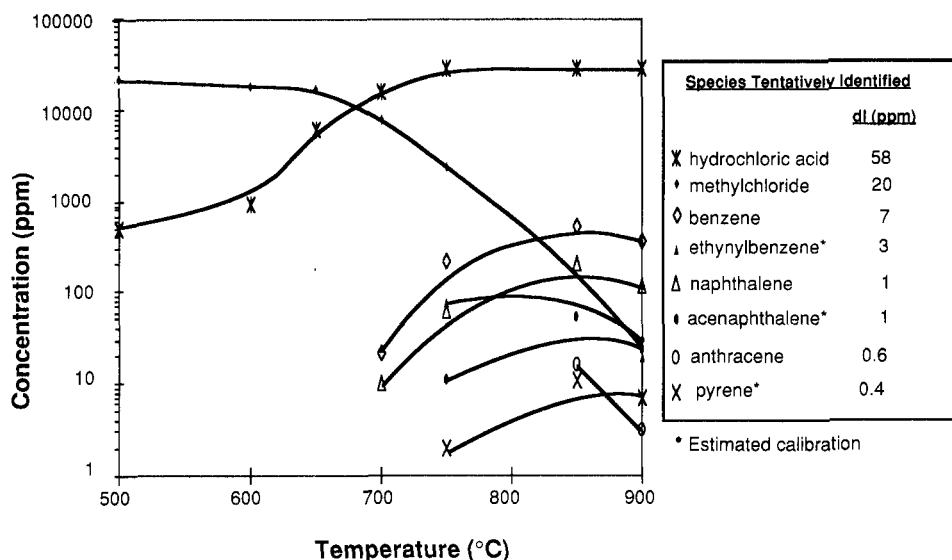


Figure 5. Plot of the concentration of pyrolysis products from methyl chloride (initial concentration, 20 000 ppm) as a function of temperature. (See Table II for an identification of the species.) The concentrations of species marked with an asterisk have been determined using estimated calibrations. (See text.) The residence time was 6.3 s in these experiments. In the legend are the tentatively identified product names, as well as the detection limits (dl) in ppm. During steam re-forming, all of these species (with the exception of HCl) were below the detection limit.

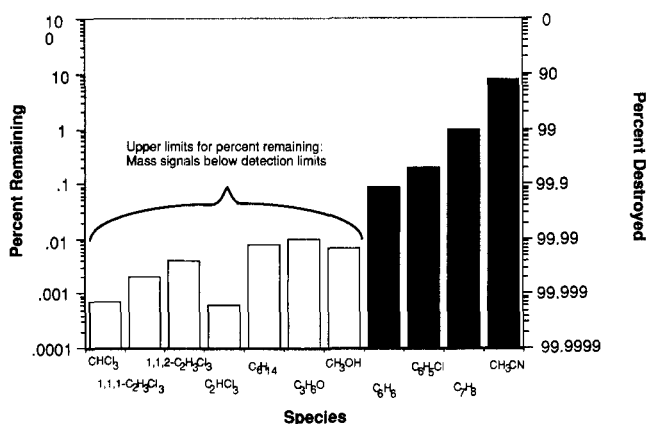


Figure 6. Graphical comparison of catalytic steam re-forming efficiencies for a variety of compounds passed over Rh at 800 °C in 50% steam. For the seven species on the left side of this plot, the destruction was high enough so that the amount remaining was below detection limit, and therefore, the plotted percents remaining for these species are only upper limits. For the four species on the right, the plotted destruction efficiencies were the actual measured values.

the CO_2^+ ($m/z = 44^+$), and the methylthiophene signal ($m/z = 98^+$) as functions of time. At 100 s, CH_4 was introduced and was re-formed, producing CO_2 . Thus, the signal for 44^+ is high and that for 16^+ is low. At roughly 270 s, the 3-methylthiophene was injected. Notice how shortly thereafter the 16^+ signal increased and the 44^+ decreased and stayed low even after the 3-methylthiophene was turned off (450 s). This indicates that steam re-forming of CH_4 ceased, presumably due to poisoning of the catalyst by the sulfur. However, it was found that addition of a small amount of O_2 ($\sim 1\%$) in steam regenerated the catalyst at 800 °C. A single experiment with a small quantity of dimethyl methylphosphonate also showed rapid catalyst deactivation, with phosphoric and phosphorous acid as major products with or without the catalyst at 800 °C.

IV. Discussion

The results plotted in Figures 3 and 4 demonstrate the enhanced destruction capability for catalytic steam re-forming of CH_3Cl compared to strictly thermal destruction. As these plots show, the temperature required for com-

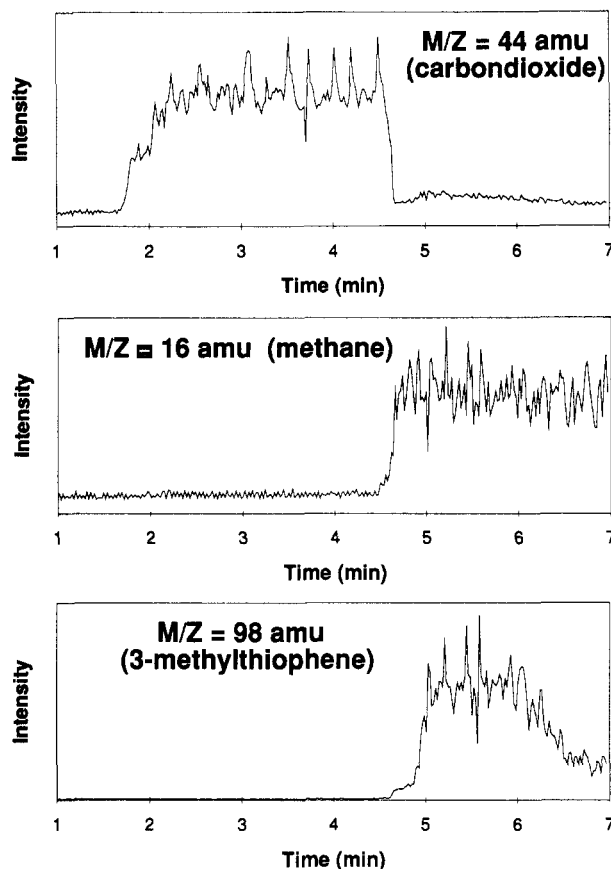


Figure 7. Rapid deactivation of the rhodium catalyst by 3-methylthiophene at 800 °C. The three plots show the ion intensities for CO_2 , CH_4 , and 3-methylthiophene as a function of time. At 100 s, the methane was introduced into the reactor and the rhodium converted it into CO_2 and CO . At ~ 270 s, the 3-methylthiophene was introduced and the catalyst was almost instantly deactivated, as is shown by the decrease in the CO_2 signal and the increase in the CH_4 signal.

parable levels of destruction by steam re-forming and pyrolysis is more than 200 °C lower for catalytic steam re-forming at the weight hourly space velocity [WHSV = $106 \text{ g of CH}_3\text{Cl h}^{-1} (\text{g of Rh})^{-1}$] used. In another interpretation, for a given temperature, the level of destruction is more than 2 orders of magnitude greater with catalytic

Table I. Listing of Observed Destruction Efficiencies for Compounds Passed over the Rhodium-on-Alumina Catalyst^a

species	DE, %	SR vs PY ^b	conditions		concn, vol %	feed mode ^c	steam, ^d vol %	WHSV ^e
			temp °C	res time, s				
CH ₃ Cl (methyl chloride)	0	PY	500	2.7	1.7	C	0	
	85	SR	500	1.3	1.9	C	80	106
	0	PY	600	2.7	1.3	C	0	
	99	SR	600	1.2	1.9	C	80	106
	27	PY	700	2.7	1.2	C	0	
CHCl ₃ (chloroform)	99.9	SR	700	1.1	1.9	C	80	106
	>99.9993	SR	800	1.0	1.5	C	50	193
C ₂ H ₃ Cl ₃ (1,1,1-trichloroethane)	34	PY	500	2.2	0.07	B	80	
	98.2	PY	700	1.7	0.06	B	80	
	99.6	SR	500	2.2	0.4	B	80	58
C ₂ H ₃ Cl ₃ (1,1,2-trichloroethane)	99.996	SR	700	1.7	0.8	B	80	115
	>99.998	SR	800	1.0	1.2	C	50	285
C ₂ HCl ₃ (trichloroethylene)	>99.996	SR	800	1.0	1.3	C	50	310
	64	PY	700	1.7	0.08	B	80	
	>99.9994	SR	800	1.0	1.3	C	50	305
C ₆ H ₁₄ (hexane)	>99.992	SR	800	1.0	0.33	C	50	30.4
C ₃ H ₆ O (acetone)	>99.99	SR	800	1.0	1.6	C	50	167
CH ₃ OH (methanol)	>99.993	SR	800	1.0	2.9	C	50	167
C ₆ H ₆ (benzene)	99.91	SR	800	1.0	1.3	C	50	183
C ₆ H ₅ Cl (chlorobenzene)	99.8	SR	800	1.0	1.1	C	50	222
C ₇ H ₈ (toluene)	99	SR	800	1.0	1.1	C	50	182
CH ₃ CN (acetonitrile)	92	SR	800	1.0	3.0	C	50	222

^a 3-Methylthiophene and dimethyl methylphosphonate rapidly deactivate the catalyst at 800 °C. ^b SR, steam re-forming; PY, pyrolysis. ^c C, continuous; B, batch. ^d Balance is He. ^e Gram of waste per gram of Rh per hour.

steam re-forming. Similar enhancements in destruction were seen for other species (see Table I). Some catalysts were exposed to chlorinated compounds for up to 10 min, without apparent loss of activity. The crucial question, yet to be answered, is that of the long-term activity of such an expensive catalyst as rhodium.

Tentative identification of the species represented in the mass spectra shown in Figure 4 demonstrates the difference in product formation for equal levels of destruction with and without the rhodium steam re-forming catalyst. The two intense peaks on the left of the upper spectrum (from pyrolysis) correspond to masses of 36 and 38 and are identified as resulting from HCl. The peak at mass 50 results from unreacted CH₃Cl, while the peaks at higher masses result from molecular growth products (leading to polynuclear aromatics and soot), which are tentatively identified in Table II. Formation of polynuclear aromatics had been noted in earlier work concerning the pyrolysis of CH₃Cl (31–34). In the lower spectrum (from catalytic steam re-forming), there are peaks at (*m/z*) 16⁺ from CH₄, 18⁺ from H₂O, 28⁺ from CO, 36⁺ and 38⁺ from HCl, 40⁺ from the Ar tracer, 44⁺ from CO₂, and 50⁺ and 52⁺ from CH₃Cl. The other apparent peaks in the spectrum arise from noise, indicating that destruction of the CH₃Cl produces negligible byproducts of mass higher than the starting material. By contrast, the pyrolysis spectra of Figure 2 show many molecular byproducts, some chlorinated, heavier than the starting material. By comparing the peak intensities in Figure 4, one can see that many of the products present in the pyrolysis spectrum are greatly lowered in the catalytic steam re-forming spectrum. For some of these species (benzene for example), this amounts to a decrease in their formation by 2 orders of magnitude. Similar differences in product slates are seen for the other species listed in Table I. For chlorinated species, the only products seen at 800 °C over Rh were CH₄, CO, CO₂, and HCl, while for acetonitrile, N₂ was formed and for the phosphonate, inorganic, phosphorus-containing acids were obtained.

It is possible that the Rh catalyst could synthesize low levels of polychlorinated dioxins and furans, as has been

Table II. Products Tentatively Identified in Pyrolysis of CH₃Cl in Helium at 800 °C^a

mass	formula	species
26	C ₂ H ₂	acetylene
36	HCl	hydrochloric acid
52	C ₄ H ₄	vinylacetylene
78	C ₆ H ₆	benzene
102	C ₈ H ₈	ethynylbenzene
128	C ₁₀ H ₁₀	naphthalene
152	C ₁₂ H ₁₂	acenaphthalene
152	C ₁₂ H ₁₂	ethynynaphthalene
178	C ₁₄ H ₁₄	anthracene
178	C ₁₄ H ₁₄	phenanthrene
202	C ₁₆ H ₁₆	ethynylanthracene
202	C ₁₆ H ₁₆	pyrene
202	C ₁₆ H ₁₆	fluoranthene

^a Residence time, 6.3 s.

postulated by several researchers (35, 36). However, most experimental evidence indicates that such reactions occur in the temperature range of 200–500 °C (37), far below the anticipated temperature for Rh. In addition, the steam environment, versus an oxidizing environment, should mitigate against these oxygenated compounds (we see no Cl_2 over the catalyst).

The mechanism for catalytic steam re-forming is not well-understood, but for hydrocarbons it has been suggested that the reactions proceed through surface-bound carbon (38). The results presented here seem to be consistent with a mechanism where complete re-forming occurs on the catalyst surface. Furthermore, the fact that under conditions of partial destruction no intermediates were seen (except for trichloroethane), suggests that the rate-limiting step is the initial decomposition of the starting material. For steam re-forming of hydrocarbons, an initial step is thought to be the breaking of C–C bonds (38). This may account for the different destruction levels seen in Table I (higher levels of destruction seen for aliphatic compounds compared to aromatic compounds).

Regarding the other compounds tested (Table I), several observations can be made. (1) High levels of destruction were obtained by steam re-forming over the rhodium catalyst for a wide variety of compounds. As Table I and Figure 6 show, destruction efficiencies greater than 99% were obtained for most compounds at 800 °C. This is consistent with studies conducted by Richardson using 1,1,1-trichloroethane (23), where extremely fast kinetics were measured under partial conversion conditions. (2) Steam re-forming over Rh seems to be less effective in destroying aromatic species. Similar results were obtained in other studies in this laboratory with tars from wood pyrolysis (39), and this behavior is well-documented in the literature (38). Acetonitrile is also difficult to destroy. It should be pointed out, though, that even when lower levels of destruction were obtained, no products other than those predicted by eqs 1 and 2 were seen (except for trichloroethane). This suggests that the Rh catalyst may be forgiving of upsets as far as undesirable byproducts are concerned. (3) As with CH_3Cl , the products seem to be limited to a few easily treated species. For chlorinated species, the products are H_2 , HCl , CO , CO_2 , and CH_4 . For the nitrogen-containing compound, the products are H_2 , N_2 , CO , CO_2 , and CH_4 . (4) The first, brief test with methylthiophene at 800 °C showed such rapid deactivation that final products and intermediates could not be determined reliably. With the phosphorus surrogate of nerve gases or pesticides (dimethyl methylphosphonate), catalyst deactivation was too rapid to demonstrate any catalytic benefit. The production of inorganic acids may indicate that noncatalytic steam re-forming will be a useful process for destruction.

In a large-scale steam re-forming system, pyrolysis of gases before they can encounter the steam re-forming catalysts may produce species that are resistant to steam re-forming, which may demonstrate an advantage of the radiant heating capability of a solar process. For instance, when a larger catalyst bed is heated, the gases may be preheated and aromatic species similar to those shown in Figure 2 may be produced. As Table I shows, these chemicals are more difficult to destroy. (These pyrolysis species are not a problem in this study because of the short residence time in the reactor before the catalyst is encountered (<1 s)).

V. Conclusion

The ability of rhodium to act as a steam re-forming catalyst and to destroy a large variety of organic species

was demonstrated using the detection capabilities of the MBMS. Furthermore, the temperature required for destruction by catalytic steam re-forming was greatly reduced relative to pyrolysis. In addition, the production of hazardous products is reduced by orders of magnitude, vis-à-vis pyrolysis. The thermal reaction channels are drastically altered by the steam re-forming catalyst.

Possible problems with a rhodium steam re-forming catalyst include rhodium cost, coking, migration of the Rh, and sulfur or phosphorus poisoning. Longer term studies, with catalyst characterization, need to be carried out. Studies also need to be conducted with less expensive steam re-forming catalysts to identify possible alternatives to Rh. In addition, rapid coking can occur for highly chlorinated species at lower temperatures. Finally, sulfur and phosphorus seem to poison the catalyst, but activity may be recoverable with the addition of O_2 .

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Registry No. Rh, 7440-16-6; CH_3Cl , 74-87-3; CHCl_3 , 67-66-3; $\text{C}_2\text{H}_5\text{Cl}$, 71-55-6; $\text{C}_2\text{H}_3\text{Cl}_3$, 79-00-5; C_2HCl_3 , 79-01-6; C_6H_{14} , 110-54-3; $\text{C}_3\text{H}_6\text{O}$, 67-64-1; CH_3OH , 67-56-1; C_6H_6 , 71-43-2; $\text{C}_6\text{H}_5\text{Cl}$, 108-90-7; C_7H_8 , 108-88-3; CH_3CN , 75-05-8; C_2H_2 , 74-86-2; HCl , 7647-01-0; C_4H_4 , 689-97-4; C_8H_8 , 536-74-3; $\text{C}_{10}\text{H}_{10}$, 91-20-3; 3-methylthiophene, 616-44-4; dimethyl methylphosphonate, 756-79-6; acenaphthalene, 208-96-8; ethynynaphthalene, 2949-26-0; anthracene, 120-12-7; phenanthrene, 85-01-8; ethynylantracene, 78053-56-2; pyrene, 129-00-0; fluoranthene, 206-44-0.

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