PATHWAYS OF FORMATION OF CHLORINATED PICs FROM THE THERMAL DEGRADATION OF SIMPLE CHLORINATED HYDROCARBONS*

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Summary

Emission of products of incomplete combustion (PICs) from hazardous waste incinerators continues to be a scientific, regulatory, and philosophical issue. Available data on PIC formation is subject to different interpretations, depending upon the particular bias of the observer. This manuscript presents a brief overview of the history and controversy surrounding PICs. Laboratory flow reactor data on PIC formation from simple mixtures and pure compounds is presented. Chemical kinetic and mechanistic arguments are used to identify pathways of formation of higher-molecular-weight chlorinated PICs. Implications concerning future research and PIC control strategies are briefly discussed.

Introduction

There has been much controversy and confusion over the possible emissions of toxic products of incomplete combustion (PICs) from facilities used for the thermal disposal of toxic organic wastes [1]. This topic is extremely important since it has had a dramatic impact on the regulation of hazardous waste incineration, siting of these facilities, and general acceptance of this technology by the public.

Unfortunately, the debate over the impact of PIC emission and what should be done to control these emissions has often turned into the proverbial "political football" by groups with their own special interests. The accusations of special interest have been broad and have included many organizations not

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typically considered in the special interest category. Academic and other research organizations have been suggested as promoting fear of toxic PICs to ensure continued funding of their pet research programs. It has also been suggested that government regulatory agencies have minimized the PIC issue so as to reduce an already overburdened regulatory work load. Industry is suspect in their usual contention that PICs are not problematical for seemingly obvious economic reasons, while environmental groups are accused of stirring up PIC hysteria just for the sake of a new cause. Environmental consultants may swing to one side of the issue or the other, depending upon who is paying the bill. Even the presumably impartial EPA Scientific Advisory Board (SAB) has been referred to in a favorite quote as "myopic, self-serving, academicians" by those who would disagree with their caution and concern over the potential for PIC emissions and the lack of reliable emissions data [2].

The sole purpose of this manuscript is to provide some basic scientific information on the formation of PICs during the thermal destruction of toxic organic wastes, with emphasis on destruction of chlorinated hydrocarbons (CHCs). We will attempt to address the scientific issues and leave the criticism to those who feel the need to serve their very special interests.

Background

The environmental controversy on emissions of PICs is often attributed to the laboratory observation of three products (hexachlorocyclopentadiene, hexachloroindenone, and hexachlorobenzene) from the thermal decomposition of the pesticide kepone [3]. The observation that the parent kepone was destroyed at less than $500\,°C$ for 2.0 s gas-phase residence time, while all the PICs required a higher temperature for destruction, caused considerable concern. Subsequent laboratory studies, which showed that very toxic polychlorinated dibenzo-p-dioxins (PCDDs) could be formed from condensed phase thermolysis of chlorobenzenes and chlorophenols [4,5] and polychlorinated dibenzo-furans (PCDFs) from the gas-phase thermal degradation of polychlorinated biphenyls (PCBs) [6,7], further served to heighten concern over PIC emissions. Numerous other laboratory studies of PIC formation have been performed in the past 10 years [8].

As full-scale incinerator testing began, emphasis was placed on determining destruction and removal efficiency (DRE) of selected principal organic hazardous constituents (POHCs) of the waste because only these compounds were the target of EPA regulation [9,10]. PICs were not regulated because of the difficulty in writing a scientifically defensible, enforceable regulation. However, as public and scientific concern grew, these same full-scale test data were re-examined for possible PIC formation. Of course, since the testing was not originally designed to observe PICs, the emissions data base was incomplete due to a variety of sampling and analytical problems and uncertainties well

known to the practitioner [10]. Because of the lack of reliable scientific data, discussion of PIC emissions has degenerated to bureaucratic interpretations of precisely what constitutes a PIC [11].

Recently, reviews of the status of incineration have included seemingly diverging viewpoints on the impact of PIC emissions [12,13]. These reviews, which contain varying degrees of bias, are actually emphasizing different aspects and parameters affecting PIC emissions. At the heart of the question is the scientific validity of the proposed arguments. The complexity of incineration is such that many issues are difficult to define, much less answer, and the debate continues. An extremely unfortunate development is that some practitioners and researchers have decided that personal and sarcastic attacks on results of EPA-sponsored research are the best means of slowing promulgation of regulations concerning PICs [14].

Laboratory flow reactor results

Laboratory studies of PIC formation were performed on two isothermal, high-temperature flow reactor systems, the Thermal Decomposition Analytical System (TDAS) and the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system. Both of these systems employ in-line analysis of the reactor effluent and have been well described in other publications [15,16]. These systems are designed to accept liquid, gaseous, or solid samples, pure compounds or mixtures, which are prevaporized in the sample insertion region. Elevated temperature diffusion and dispersion in the insertion region ensure complete mixing with the carrier gas, which has been verified in numerous experimental studies [16]. The narrow-bore quartz tubular reactor is designed to provide a square-wave thermal pulse and narrow gas-phase residence time distribution, both of which are difficult to achieve in more conventionally designed larger-bore quartz or stainless steel reactors. Because of the care taken to eliminate these temperature and residence time distribution inhomogeneities, which have been shown to seriously affect high-temperature flow reactor kinetic data, the small bore reactor results in some compromise in surface-to-volume ratio (40.5 cm^{-1}) [15]. Calculations suggest that wall-effects may be significant in the low-temperature initiation of reactant decomposition, but are insignificant at temperatures above 90% decomposition. This is largely due to the fact that wall reactions reduce the activation energies for reactions relative to gas-phase reactions. Thus, as temperatures become higher, the impact of wall reactions becomes less significant. This has been shown to be the case experimentally for several CHCs and hydrocarbons [16].

Figure 1 displays semi-quantitative PIC and POHC concentrations as a function of temperature for the thermal degradation of a simple mixture of toluene, ethyl cyanide, and 1,3,5 trichlorobenzene (gas-phase residence time ($\bar{t}_r$) of 2.0 s, fuel/O_2 equivalence ratio (ϕ) of 3.0) [17]. The PIC concentration
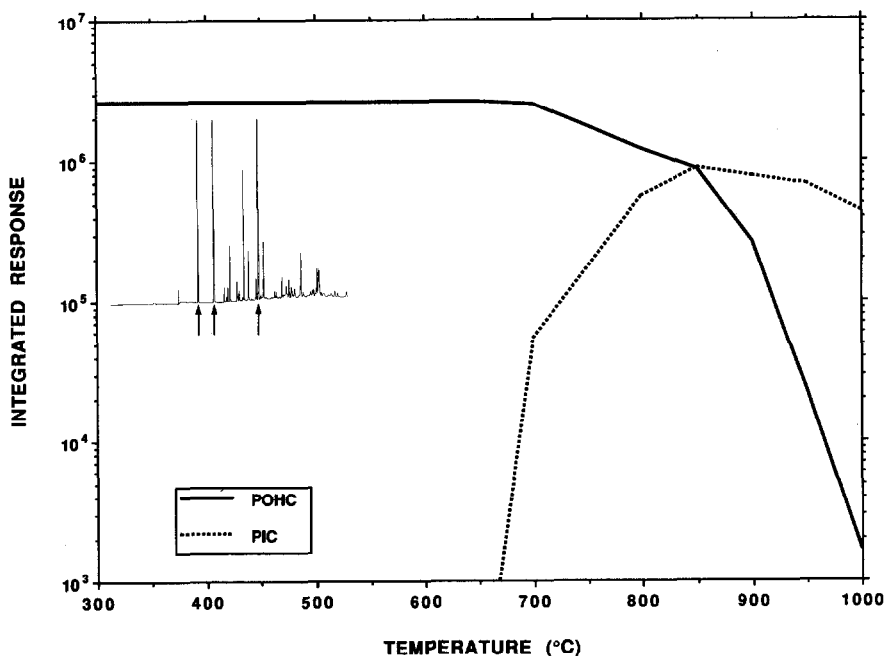
Fig. 1. PIC yield vs. POHC destruction as a function of temperature; calculated from total GC-FID area counts for a mixture of toluene, ethyl cyanide, and 1,3,5-trichlorobenzene. $\phi = 3.0$, $\bar{t}_r = 2.0$ s. Also shown is the GC-FID chromatogram at 850°C. The first arrow from the left is the FID response for benzene, the prominent PIC produced from this mixture. The second and third arrows are FID responses for toluene and 1,3,5-trichlorobenzene, respectively. The remaining POHC, ethyl cyanide, was destroyed below detection limits at this temperature.

is seen to steadily increase from 650°C (the temperature of initiation of the decomposition of the mixture) to 850°C (65% POHC decomposition), where the ratio of PIC to POHC yields approaches unity. This ratio increases at higher temperatures and reaches a maximum value of 80 at 1000°C. This behavior is qualitatively and quantitatively typical of the over 80 mixtures we have analyzed in this manner [17]. At least 50 PICs are detectable from the thermal degradation of this simple 3-component mixture.

This observed PIC formation behavior is of course a natural consequence of chemical reactions and kinetics. As a compound decomposes, it forms fragments which may themselves be stable or react with other species to form stable species of higher or lower molecular weight than the parent. The apparent stability of PICs (viz., their higher temperature required for destruction) is generally due to their reduced high temperature residence time, being formed downstream in the reactor. PICs may be either intrinsically *more or less* stable than their parent, based on *molecular reactivity*.

The observed PIC formation is clearly kinetically controlled and has been

successfully modeled using thermochemical reaction kinetic theory. Assuming the reactions are not grossly dissimilar in full-scale incinerators and laboratory reactors, the yield of PICs can be roughly estimated from POHC destruction efficiency and the type of data in Fig. 1. We have previously shown that relative trends observed for full-scale POHC DRE are predictable from laboratory flow reactor kinetic data of the type presented here [18]. This supports the premise that POHC emissions are also kinetically controlled as are PIC emissions, which can then be predicted from suitable laboratory flow reactor studies.

Some have incorrectly argued that POHC and PIC emissions are thermodynamically controlled or are approaching thermodynamic equilibrium [12]. Thermodynamic calculations have clearly shown that observed full-scale emissions are orders of magnitude greater than that predicted based on achievement of equilibrium [19]. Such calculations are useful to researchers, but are subject to abuse by practitioners who would use a computer calculation output which predicts low emissions to argue that emission levels of PICs are environmentally insignificant. This is clearly the type of practice that can only hurt the technology of incineration and undermine public trust in industry and government.

However, it must be realized that the data presented on PIC formation does not imply that these PICs are toxic. Mass spectral (MS) analysis is necessary to identify environmentally significant PICs and knowledge of their chemistry of formation is necessary to extrapolate laboratory data to field conditions. Of particular interest are simple chlorinated hydrocarbons (CHCs), i.e., methylene chloride, carbon tetrachloride, etc., and their propensity to form high-molecular-weight chlorinated PICs.

Condensed hydrocarbons and CHCs (viz., aromatics and polynuclear aromatic hydrocarbons (PAHs)) are expected to be especially prominent under oxygen-depleted conditions. It has been reported that PIC emissions actually decrease under pyrolytic conditions in full-scale incinerators [12,20]. This is contrary to accepted reaction kinetic theory, and seems inexplicable. Recently it has been demonstrated that PICs are absorbed on soot particles formed under pyrolytic or poor mixing conditions [21]. These particles are typically poorly characterized by chemical analysis of stack emissions. The Air Pollution Control Device (APCD) ash is subject to harboring many toxic PICs which are not analyzed in standard Toxic Characteristic Leaching Procedure (TCLP) test procedures [22]. Stack emissions may indeed be reduced under some conditions; however, total PIC emissions may increase in other effluents of the incinerator. Thus, formation of high molecular weight CHCs is of key importance.

Formation of chlorinated aromatics and olefins from chlorinated methanes

The thermal decomposition behavior of methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) was studied on the TDAS at $\bar{t}_r = 2.0$ s, $\phi = 3.0$, 1000 ppm, over a temperature

range of 300–1000°C [23]. The decomposition of these compounds could be readily modeled by using the kinetic data shown in Table 1 for the three principal reaction mechanisms. C–Cl bond rupture was the initial pathway of destruction for CCl_4, HCl elimination for $CHCl_3$, HCl elimination and C–Cl bond rupture for CH_2Cl_2, and C–Cl bond rupture for CH_3Cl. H-atom abstraction also made significant contributions to the destruction of CH_2Cl_2 and CH_3Cl.

The focus of this discussion is on PIC formation, specifically hexachlorobenzene (C_6Cl_6) and its apparent precursors from $CHCl_3$ and CCl_4 (cf. Figs. 2 and 3). No C_2 or higher PICs were observed from CH_3Cl and only 1,1-$C_2H_2Cl_2$, 1,2-$C_2CH_2Cl_2$, and C_2HCl_3 were observed from CH_2Cl_2. The formation of the

TABLE 1

Chloromethane destruction kinetics

Compound	C–Cl Bond rupture (s^{-1})	log k HCl elimination (s^{-1})	H abstraction (Cl) (cm^{3}mol^{-1}s^{-1})
CH_3Cl	$15.40 - 82.2/2.3RT$[a,32]	$14.00 - 87.0/2.3RT$ [33]	$13.50 - 3.1/2.3RT$ [33]
CH_2Cl_2	$16.42 - 79.4/2.3RT$[a]	$14.10 - 69.0/2.3RT$[a]	$13.35 - 2.3/2.3RT$[a]
$CHCl_3$	$16.19 - 77.5/2.3RT$[a]	$14.30 - 54.4/2.3RT$ [34]	$13.20 - 1.5/2.3RT$[a]
CCl_4	$16.30 - 72.0/2.3RT$[a]	–	–

[a]Estimated using thermochemical transition-state theory as outlined in Ref. 31.
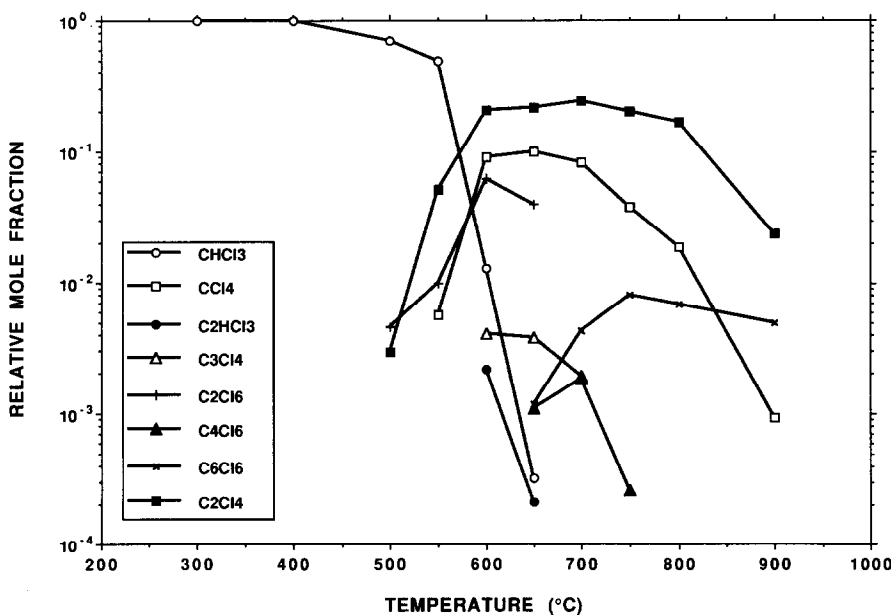

Fig. 2. Thermal decomposition profile for trichloromethane. [$CHCl_3$] = 1000 ppm, $\bar{t_r}$ = 2.0 s, ϕ = 3.0.
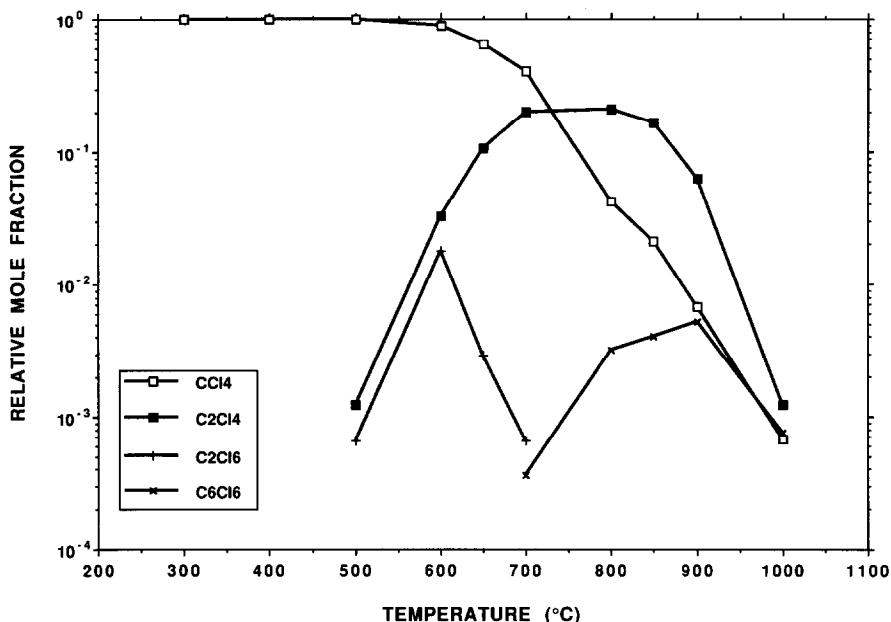
Fig. 3. Thermal decomposition profile for tetrachloromethane. $[CCl_4] = 1000\,\mathrm{ppm}$, $\bar{\xi} = 2.0\,\mathrm{s}$, $\phi = 3.0$.

simple olefins C_2HCl_3 and $C_2H_2Cl_2$ can be modeled by using straightforward bond rupture, elimination, abstraction, and recombination reactions [23,24]. However, the mechanisms of formation of hexachlorobutadiene (C_4Cl_6) and C_6Cl_6 in the observed yields are of special interest from an environmental and scientific viewpoint.

A plausible mechanism for the formation of C_4Cl_6 involves chlorine ($Cl^\bullet$) displacement from tetrachloroethylene (C_2Cl_4) by trichlorovinyl radical ($C_2Cl_3^\bullet$).

$$C_2Cl_3^\bullet + C_2Cl_4 \rightarrow C_4Cl_6 + Cl^\bullet \qquad\qquad \text{(Rxn 1)}$$
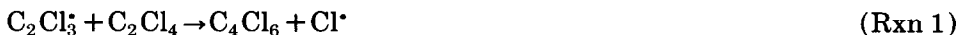
The trichlorovinyl radical is readily formed by H-abstraction from C_2HCl_3 by $Cl^\bullet$. Previous studies have shown that C_4Cl_6 rapidly decomposes via C–Cl bond rupture to form the resonance-stabilized pentachlorobutadienyl radical ($C_4Cl_5^\bullet$) [25].

$$C_4Cl_6 \rightleftharpoons C_4Cl_5^\bullet + Cl^\bullet \qquad\qquad \text{(Rxn 2)}$$

This radical can then react with the observed dichloracetylene (C_2Cl_2) via $Cl^\bullet$ displacement to produce C_6Cl_6.

$$C_4Cl_5^\bullet + C_2Cl_2 \rightarrow C_6Cl_6 + Cl^\bullet \qquad\qquad \text{(Rxn 3)}$$

We favor a concerted reaction involving cyclization and $Cl^\bullet$ displacement to form C_6Cl_6, although other researchers have proposed separate addition, cy-

clization, and H-elimination reactions for the formation of the hydrocarbon analog benzene from butadienyl radical and acetylene [26]. The relatively high yields of C_6Cl_6 (0.8%) for the low initial reactant concentration (1000 ppm) are striking and suggest that some novel reactions may be occurring.

Of particular interest is the rate of Cl displacement in Rxn 1 versus the rate of H-displacement in the analogous hydrocarbon reaction due to the lower dissociation energy of the bond being broken, i.e.

$$C_2H_3^\cdot + C_2H_4 \rightarrow C_4H_6 + H^\cdot \qquad \text{(Rxn 4)}$$

If Rxn 1 is much more rapid than Rxn 4, then formation of chlorinated aromatic PICs could be much faster than aromatic hydrocarbons, and an environmentally important class of PICs may have been identified. To assess this possibility, we performed a straightforward but tedious Quantum RRK (QRRK) calculation of the specific rate constants over a temperature range of 23 to 2227°C [27].

The results for Rxn 1 are presented in Fig. 4. The data demonstrate that as temperatures approach combustion conditions (≥ 700°C) the Cl-displacement reaction (k_{disp}) dominates as compared to stabilization of the intermediate (k_{stab}). Comparison of the predicted rate constants for Rxn 1 and Rxn 4
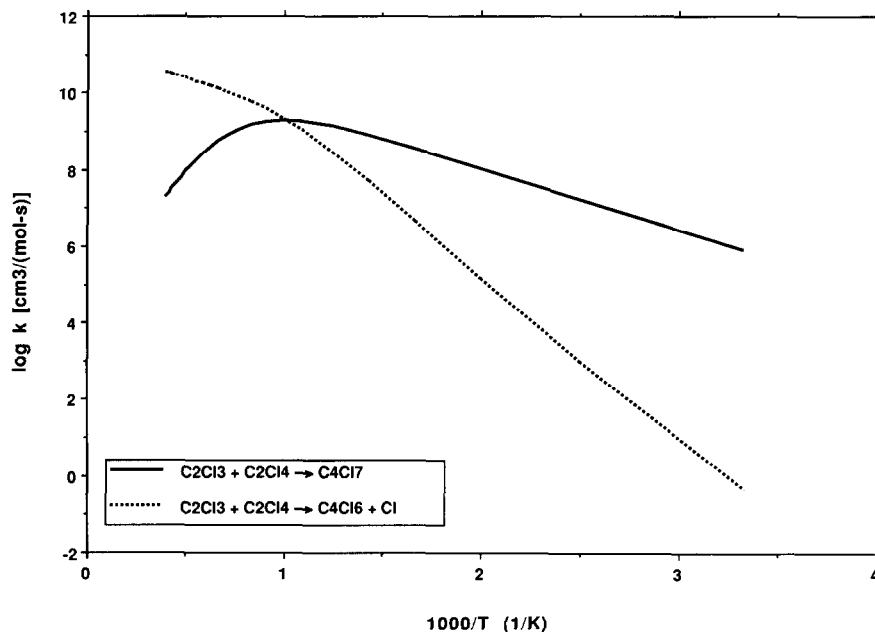

Fig. 4. Predicted effect of temperature upon $C_2^\cdot Cl_3 + C_2Cl_4$ addition at 1 atm. Solid line = predicted apparent rate constant for $C_2^\cdot Cl_3 + C_2Cl_4 \rightarrow C_4^\cdot Cl_7$. Dashed line = predicted apparent rate constant for $C_2Cl_3^\cdot + C_2Cl_4 \rightarrow C_4Cl_6 + Cl^\cdot$. Limited high-pressure rate constants estimated using techniques outlined in Ref. 31.

are depicted in Fig. 5. The results indicate that the chlorocarbon reaction is faster than its hydrocarbon analog for all temperatures investigated. The ratio of the rate constants of Rxn 1 to Rxn 4 is greater than a factor of 30 at 700°C, a factor of ~14 at 1000°C, and at factor of ~6.5 at 1400°C.

The same qualitative result is expected for Rxn 2 and Rxn 3. Thus for equal concentrations of precursors, the formation of chlorinated aromatic hydrocarbons is expected to be faster than aromatic hydrocarbons. The formation of PAHs, chlorinated PAHs, and possibly soot and chlorinated soot may proceed by similar displacement pathways [28,29]. Thus, one might expect the efficient formation of highly condensed chlorocarbons for highly chlorinated waste streams with appropriate precursors.

Recapitulation and conclusions

The parameters affecting PIC formation are numerous and complex. The chemistry is far more complex than the chemistry of POHC destruction, which is moderately well characterized. Clearly, there are many unresolved issues, and much research is needed on the subject.

From a scientific standpoint we can make several seemingly obvious (yet debated) observations concerning PICs:
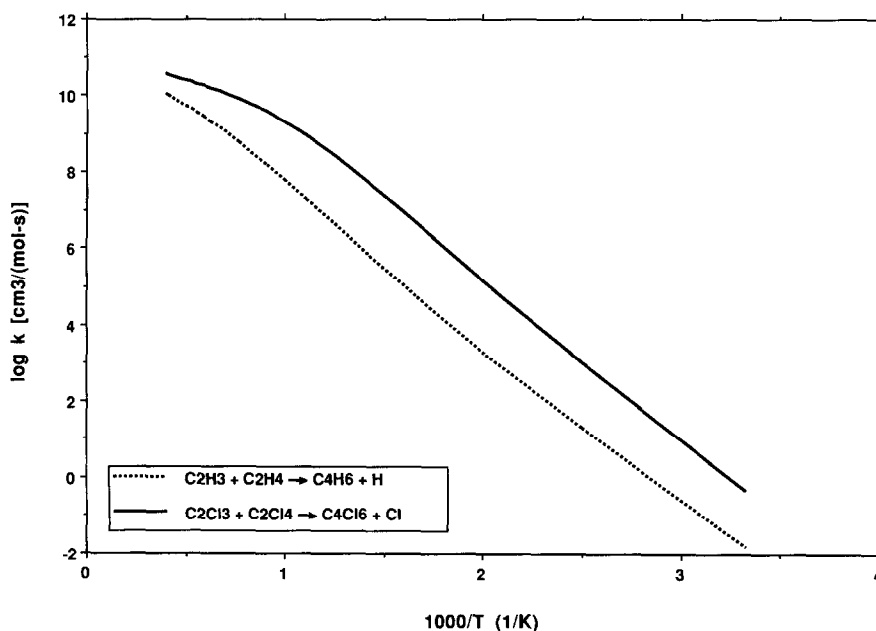

Fig. 5. Predicted effect of temperature upon Rxn 1 and Rxn 4 at 1 atm. Limiting high-pressure rate constants for $C_2H_3^* + C_2H_4$ addition obtained from Ref. 35.

1. PIC formation is a natural and expected consequence of POHC destruction.
2. Their formation and destruction are chemical reaction kinetically controlled.
3. Their destruction is kinetically feasible; however, they usually require higher destruction temperature than the parent POHCs.
4. Highly chlorinated compounds may efficiently form higher-molecular-weight chlorinated PICs.

It has previously been argued that increased chlorination of hydrocarbon molecules by $Cl^{\cdot}$ attack is inefficient due to the high rate of the reverse $Cl^{\cdot}$ displacement by $H^{\cdot}$ [30]. Thus, the reactions of chlorinated olefinic species discussed in this paper seem to offer the only homogeneous pathway to formation of high-molecular-weight chlorinated compounds. Further study of the intermediates in the proposed reaction sequences is indicated. Mitigation strategies for chlorinated PIC emissions may be developed by a fuller understanding of the mechanism of their formation.

Although every effort has been made to comply with the scientific process in this manuscript, experience has shown that statements are often quoted or interpreted out of their context from these research reports. Furthermore, obvious scientific observations are circumvented by the user by generating a smokescreen of pseudo-scientific theory and arguments. Only when the issue of PIC formation moves from the arena of politics to that of science will real progress in protecting the environment be realized, and special interest groups will no longer delay implementation of environmentally secure toxic waste disposal options.

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