3156 *J. Phys. Chem.* **1995,** *99,* 3156–3161

Hydrogen-Atom-Induced Decomposition of Trichloroethylene at High Temperatures

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Received: June 30, 1994; In Final Form: September 29, 1994[⊗]

Mechanisms and rate constants for hydrogen atom attack on trichloroethylene have been determined in single-pulse shock tube experiments near 1050 K. Products from all the decomposition channels have been observed. The predominant process is the displacement of the chlorine at the least substituted site. The following rate expressions have been determined: $k(\mathrm{H^* + HClC{=}CCl_2 \rightarrow H_2C{=}CCl_2 + Cl^*}) = 6 \times 10^{13} \exp(-2439/T)$ cm^3 mol^{-1} s^{-1}; $k(\mathrm{H^* + HClC{=}CCl_2 \rightarrow HClC{=}CClH(cis + trans) + Cl^*}) = 3.7 \times 10^{13} \exp(-3946/T)$ cm^3 mol^{-1} s^{-1}; $k(\mathrm{H^* + HClC{=}CCl_2 \rightarrow {}^*HC{=}CCl_2 \text{ or } HClC{=}CCl^* + HCl}) = 3.8 \times 10^{14} \exp(-6686/T)$ cm^3 mol^{-1} s^{-1}. An upper limit for the rate constant of the abstraction process $\mathrm{H^* + HClC{=}CCl_2 \rightarrow {}^*ClC{=}CCl_2 + H_2}$ is 6.5×10^{10} cm^3 mol^{-1} s^{-1} at 1050 K. Rate constants for chlorine attack on H_2 at these temperatures are a factor of 13 smaller than those on mesitylene. The results are compared with those for hydrogen atom reactions with other unsaturated compounds. Some implications regarding the incineration of chlorinated organics will be discussed.

Introduction

Hydrogen atoms play a key role in the decomposition of organic molecules in high-temperature systems. This paper is a continuation of earlier work on their reactions with unsaturated compounds.[1] Most recently, the mechanisms and rate constants for hydrogen atom attack on perchloroethylene[2] have been investigated. It is expected that the accumulation of such information will provide a bsis for the estimation of rate constants of other reactions. The present interest in trichloroethylene is due to its importance as a component in hazardous waste mixtures and in the effluent during incineration. In several recent papers,[3,4] the use of elementary rate constant data for inferring details of the incineration process has been discussed.

Despite their importance, there is a lack of information on the mechanisms and rate constants for hydrogen atom attack on unsaturated species under high-temperature conditions. Indeed, much of the existing data on such processes have been obtained from the present series of measurements. For many unsaturated compounds, the experimental situation is made difficult by the possibility of multiple reaction channels. These can be classified as displacement (or more exactly in terms of single-step processes, addition at the double bond leading to the formation of a radical followed by ejection of a group or radical at the site of addition) and abstraction. The powerful modern techniques that monitor the temporal history of small reactive species such as hydrogen atoms can yield no information on the relative contributions of the various channels. Information on branching ratios is of key importance for the description of how compounds are destroyed in incineration processes. They also represent important basic information on thermal rate processes. A rate expression describing the sum of several processes is impossible to interpret in any fundamental fashion.

In the earlier work on the reactions of hydrogen atom with perchloroethylene,[2] it was demonstrated that contributions from the displacement and abstraction channels were both important. A summary of the results for these and related reactions can be found in Table 1. Ahmed and Jones[12] have determined rate constants for hydrogen atom attack on a number of chlorinated ethylenes at room temperature. These results can be found in Table 2. In the case of trichloroethylene, the pressure dependence cannot be due to fall-off effects, since the thermodynamics dictate the ejection of chlorine from the trichloroethyl radical upon addition of hydrogen. The reverse hydrogen-ejection reactino which would have resulted in an observed pressure dependence is much less favored. The observed pressure dependence is therefore indicative of experimental problems. Since the parameter that is measured is the hydrogen atom concentration, no information is obtained regarding the mechanism of the reaction. Ahmed and Jones also obtained an upper limit for the rate constant for H atom attack on perchloroethylene (also in Table 2). These results demonstrate that at room temperature, chlorine substitution lowers the reactivity of a molecule to hydrogen atom attack. In the course of this work, it will be possible to infer that the reactive channel observed by Ahmed and Jones is associated with addition at the least chlorine substituted site. Combination of the low- and high-temperature results permits the derivation of a rate expression that covers 300–1100 K. This yields information on the nature of the transition state and provides a basis for estimation and extrapolation for related systems.

The experiments are carried out in a single-pulse shock tube.[13] In earlier studies, it has been demonstrated that by taking advantage of the unique conditions achievable in such a device, it is possible to isolate individual hydrogen atom reactions for study. When this is coupled with a complete analysis of all the stable final products, branching ratios can be determined to high accuracy.

Hydrogen atom can react with trichloroethylene through reactions 1–4 in Table 3. The first two processes are displacement reactions and as noted earlier involve the initial formation of the hydrogen atom adduct, followed by ejection of the chlorine atom from the newly formed chlorinated ethyl radical. In the present experiments, and for many high-temperature systems, adduct formation is the rate-determining step. The rate of decomposition of the adduct is sufficiently rapid so that its reactions with other compounds in the system need not be considered. Quantitative conversion to the olefin is affected.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

TABLE 1: Past Work on Hydrogen Atom Attack on Organics at Higher Temperatures

compd and total rate const at 1025 K	rate expression and rate const[b] at 1025 K	
	displacement [group]	abstraction [group]
1,3,5-trimethylbenzene[6]	$6.7 \times 10^{13} \exp(-3255/T)$[$CH_3$]	$3.7 \times 10^{14} \exp(-4342/T)$[H]
8.2×10^{12}	2.8×10^{12}	5.4×10^{12}
trichloroethylene[a]	$6 \times 10^{13} \exp(-2439/T)$[Cl]	$3.8 \times 10^{14} \exp(-6686/T)$[Cl]
6.9×10^{12}	5.5×10^{12}	0.6×10^{12}
	$3.7 \times 10^{13} \exp(-3946/T)$[Cl]	
	0.8×10^{12}	
isobutene[5]	$1.7 \times 10^{13} \exp(-1808/T)$[$CH_3$]	$1.7 \times 10^{14} \exp(-4024/T)$[H]
6.3×10^{12}	2.9×10^{12}	3.4×10^{12}
toluene[6]	$1.2 \times 10^{13} \exp(-2578/T)$[$CH_3$]	$1.2 \times 10^{14} \exp(-4138/T)$[H]
3.1×10^{12}	1.0×10^{12}	2.1×10^{12}
perchloroethylene[2]	$2 \times 10^{14} \exp(-4650/T)$[Cl]	$1.2 \times 10^{15} \exp(-7484/T)$[Cl]
2.9×10^{12}	2.1×10^{12}	0.8×10^{12}
p-chlorotoluene[9]	$3.5 \times 10^{13} \exp(-3710/T)$[$CH_3$]	$9.6 \times 10^{13} \exp(-4265/T)$[H]
2.9×10^{12}	0.9×10^{12}	1.5×10^{12}
	$4.8 \times 10^{13} \exp(-4795/T)$[Cl]	
	0.5×10^{12}	
1,2,3-trichlorobenzene[8]	$1.9 \times 10^{13} \exp(-2954/T)$[Cl]	
1.7×10^{12}	1.1×10^{12}	
o-dichlorobenzene[7]	$1.2 \times 10^{14} \exp(-5196/T)$[Cl]	
0.75×10^{12}	0.75×10^{12}	
phenol[10]	$2.2 \times 10^{13} \exp(-3990/T)$[OH]	$1.1 \times 10^{14} \exp(-6240/T)$[H]
0.70×10^{12}	0.45×10^{12}	0.25×10^{12}
chlorobenzene[7]	$2.2 \times 10^{10} \exp(-4531/T)$[Cl]	
0.26×10^{12}	0.26×10^{12}	
methane[11]		$2.4 \times 10^{14} \exp(-7000/T)$[H]
0.26×10^{12}		0.26×10^{12}

[a] This work. [b] In $cm^3/(mol\ s)$.

TABLE 2: Rate Constants for Hydrogen Addition to Some Chlorinated Ethylenes from the Results of Ahmed and Jones

pressure, mol/cm^3	rate const[a] for compds			
	C_2Cl_4	C_2Cl_3H	1,1-$C_2Cl_2H_2$	C_2ClH_3
3.8×10^{-8}		5.5×10^{10}	2.8×10^{11}	1.3×10^{11}
5.5×10^{-8}		6.3×10^{10}	3.6×10^{11}	1.6×10^{11}
7.1×10^{-8}	$<7.8 \times 10^{9}$	7.2×10^{10}	3.8×10^{11}	1.8×10^{11}

[a] In $cm^3/(mol\ s)$.

TABLE 3: Processes of Pertinence to Present Study

$H^* + C_2HCl_3 \rightarrow$ 1,1-$CH_2CCl_2 + Cl^*$ (1)
$H^* + C_2HCl_3 \rightarrow$ 1,2-$C_2H_2Cl_2$ (cis−trans) $+ Cl^*$ (2)
$H^* + C_2HCl_3 \rightarrow HCl + {}^*HC{=}CCl_2 \rightarrow C_2HCl + Cl^*$ (3)
$H^* + C_2HCl_3 \rightarrow HCl + {}^*HClC{=}CCl^* \rightarrow C_2HCl + Cl^*$
$H^* + C_2HCl_3 \rightarrow H_2 + {}^*C_2Cl_3 \rightarrow C_2Cl_2 + Cl^*$ (4)
$Cl + C_2HCl_3 \rightarrow HCl + C_2Cl_3 \rightarrow C_2Cl_2 + Cl$ (5)
hexamethylethane → 2-*tert*-butyl → 2-isobutene + 2H[6] (6)
H + mesitylene $\rightarrow H_2 + (CH_3)_2C_6H_3CH_2$ (7)
H + mesitylene $\rightarrow CH_3 + m\text{-}(CH_3)_2C_6H_4$ (8)

This is due to the weakness of the β C−Cl bond in the radical. A typical rate expression is that for the unimolecular decomposition of the 1,1,2,2,tetrachloroethyl radical or $5 \times 10^{13} \exp(-10\,300/T)\ s^{-1}$.[14] Note the 83 kJ/mol activation energy characteristic for cleavage of β C−Cl bonds in chlorinated alkyl radicals.[14] The consequence is lifetimes much smaller than a microsecond under the present conditions that can be compared with the experimental test time in these shock tube experiments of 500 μs, leading to a total of 10^6−10^7 collisions. In the displacement reaction, a hot molecule is initially formed; thus, the lifetime may be even shorter than that postulated. On the other hand, the decomposition of the stabilized radical is in the fall-off region so that actual lifetimes may be longer. Rough estimates of all these effects have been made, and it is clear that the newly formed radical must have extremely short lifetimes. With the low concentrations and short experimental test time, decomposition through β C−Cl is overwhelmingly the preferred pathway for the adduct's destruction. The competing β C−H bond cleavage has typical activation energies in the 160 kJ/mol range and will lead to lifetimes 4 orders of magnitude larger. The results of hydrogen abstraction from the mesitylene inhibitor were not detectable in accordance with the short lifetime of the adduct. These considerations justify the use of olefin concentrations as a quantitative measure of the extent of reaction. All of these arguments are validated through experiments carried out with wide variations in reactant concentrations (see below).

Reactions 3 and 4 involve Cl and hydrogen atom abstraction, followed by the rapid decomposition through chlorine ejection of the chlorinated vinyl-type radical. Here again, the correctness of the quantitative results, which is based on stable product analysis, is dictated by the instability of the radicals that are formed after the initial hydrogen atom attack. For reaction 3, it is not possible to distinguish between the contributions from the abstraction of the two different types of chlorine atoms that are present. The products from reaction 4 can also arise from the sequence of the reaction as summarized in reaction 5. As will be seen subsequently, the results suggest that this is an important source for the dichloroacetylene that is found in these experiments. Under the present conditions, Cl cannot abstract a Cl from trichloroethylene due to the high reaction endothermicity and any abstraction reaction can only be through attack on the hydrogen in the molecule. Chlorine addition to the double bond at the high temperatures encountered here will be rapidly reversed. Note that what is termed "abstraction" in the present discussion can also occur as a consequence of addition followed by elimination of HCl leading to the conversion of an alkyl to a vinyl-type radical. We are, however, unaware of any direct evidence of hydrogen chloride elimination from chlorinated alkyl radicals. In stable compounds, activation energies for such processes are in the 170−240 kJ/mol range.[14]

Experimental Section

Experiments are carried out in a heated single-pulse shock tube.[6] The details of the apparatus have been described in previous papers.[6−9] The procedure involves generating known quantities of hydrogen atoms from the decomposition of trace quantities of a thermally labile hydrocarbon, hexamethylethane, which decomposes through reaction 6 in Table 3, in the presence of much larger quantities of two molecules, the target, trichloroethylene, and the standard, 1,3,5-trimethylbenzene (mesitylene), and making a careful quantitative analysis of all the resulting reaction products. Since the mechanism for hydrogen atom attack on mesitylene involves reactions 7 and 8 in Table 3, then the presence of hydrogen atoms is uniquely established through the detection of *m*-xylene. The rate expressions for these processes have been determined previously (see Table 1). A comparison of the measured yields of *m*-xylene and any other product traceable to the hydrogen-atom-induced decomposition of the target molecule leads to the rate constant for the latter process. From earlier studies, the rate expression for hexamethylethane decomposition is[13]

$$k_6 = 3 \times 10^{16} \exp(-34\,500/T)\ \mathrm{s}^{-1}$$

Then from the product yield of isobutene (from the rapid decomposition of the *tert*-butyl radical), one can deduce a reaction temperature through the equation

$$1/T = 38 - \log(k_6)/34\,500$$

This circumvents a major error source in single-pulse shock tube experiments, uncertainty in reaction temperature, and as will be seen below leads to highly precise results. Note that the concentration of isobutene gives a direct measure of the number of hydrogens released into the system. Comparison with the product yields provides a means of checking for all possible important processes.

Analysis of the reaction mixture is by gas chromatography with flame ionization detection. Two types of columns are used for the gas analysis. First, a 6-ft Poropak N[15] column is used for the analysis of the lighter compounds including chloro- and dichloroacetylene. A wide-bore 30-m dimethylsiloxane capillary column is used for analysis of the compounds ranging from isobutene to mesitylene and included 1,1-dichloroethylene, *trans*-1,2-dichloroethylene, and *cis*-1,2-dichloroethylene. It is assumed that the FID acted as a carbon atom counter.

The two mixtures used in these studies are (a) 200 ppm hexamethylethane, 2% trichloroethylene, and 1% mesitylene in argon and (b) 100 ppm hexamethylethane, 2% trichloroethylene, 0.5% mesitylene, and 20% H_2 in argon. The variations in reactant concentrations serve the function of testing the postulated reaction mechanism. In addition to the requirement that the target molecules be present in overwhelming amounts in comparison to the source species, the relative concentrations are set so as to optimize the accuracy of the concentration measurements. The large amount of hydrogen added to the second mixture represent another test of the mechanism. The $Cl + H_2 \rightarrow HCl + H$ reaction converts many of the chlorine atoms that are released into the system into hydrogen atoms. If the postulated mechanisms are correct, the presence of H_2 can serve to increase the number of hydrogens available for attack and amplifies the product yields. As will be seen subsequently, these tests are satisfactory for the three major products. This is one of the key facets of this type of experiment; the capability of testing proposed mechanisms for the decomposition of complex compounds with many reaction channels through wide variations in the reactive environment. Comparison of the product yields in the presence and absence of H_2 leads to a determination of the chain length for induced decomposition in the system with H_2. From this information, it proved to be possible to obtain relative rate constant data on chlorine atom attack on mesitylene and the hydrogen molecule. A key prerequisite for these experiments is the necessity for a high degree of thermal stability of the target molecules in comparison to the hydrogen atom source since it is assumed that the H atom source produces H atoms on a fast time scale compared to the thermal decomposition of the targets. Thus, the target molecules are assumed to be unchanged in concentration by the heating. For this study, it is estimated that differences in unimolecular decomposition rate constants are of the order of 4−5 orders of magnitude. The organic reagents used in these studies are from Aldrich Chemicals.[15] Except for vigorous degassing, no attempt was made at further purification. Gas chromatography indicated the presence of small traces of 1,1-dichloroethylene in the trichloroethylene. This was subtracted from the product yields in the course of the data analysis. High-purity-grade argon was purchased from Matheson.

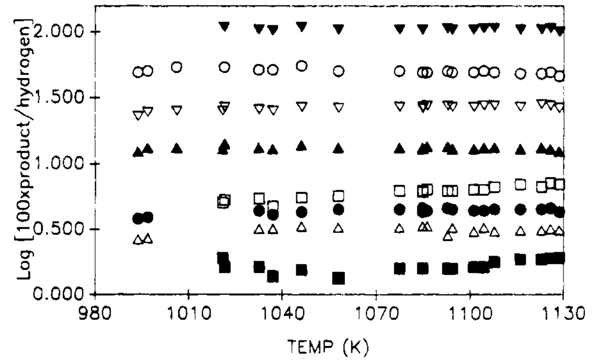

Figure 1. Product distributions normalized to hydrogen released into the system from the hydrogen-atom-induced decomposition of trichloroethylene as a function of temperature. Reaction mixture contains 200 ppm hexamethylethane, 2% trichloroethylene, and 1% mesitylene in argon. (▼) Sum of products, (○) 1,1-dichloroethylene, (▽) 2,4-dimethylbenzyl [calculated], (▲) *m*-xylene, (□) chloroacetylene, (●) *trans*-1,2-dichloroethylene, (△) *cis*-1,2-dichloroethylene, and (■) dichloroacetylene. Pressures are from 2 to 6 atm.

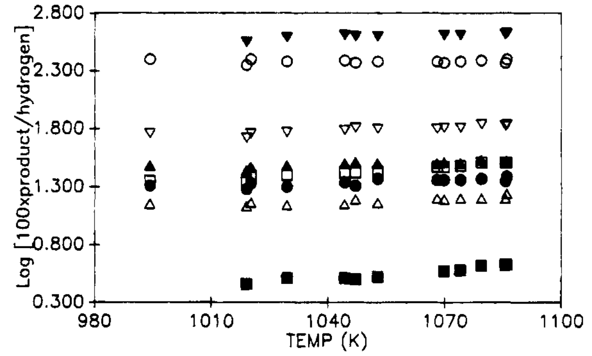

Figure 2. Product distributions from the hydrogen-atom-induced decomposition of trichloroethylene as a function of temperature. Reaction mixture contains 100 ppm hexamethylethane, 20% hydrogen, 2% trichloroethylene, and 1% mesitylene in argon. (▼) Sum of products, (○) 1,1-dichloroethylene, (▽) 2,4-dimethylbenzyl [calculated], (▲) *m*-xylene, (□) chloroacetylene, (●) *trans*-1,2-dichloroethylene, (△) *cis*-1,2-dichloroethylene, and (■) dichloroacetylene. Pressures are from 2 to 6 atm.

Results

Figures 1 and 2 contain data on the product yields from the shock tube experiments in terms of the hydrogen atoms (as inferred from the isobutene yields) released into the system. 1,1-Dichloroethylene is the main reaction product. Its concentration is close to a factor of 6 higher than that of the other products. All the other compounds that can be expected to result

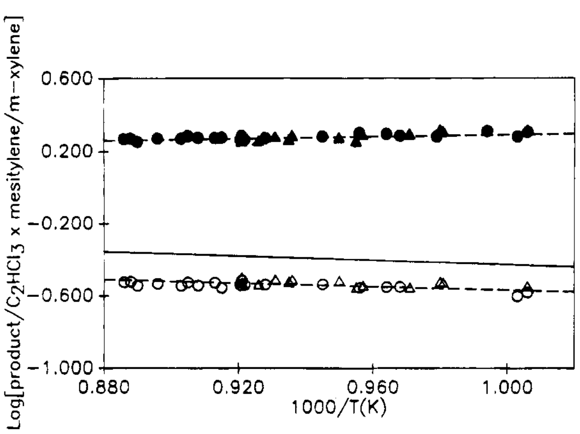

Figure 3. Ratio of normalized yields of 1,1-dichloroethylene and *m*-xylene (filled symbols) and 1,2-dichloroethylene (cis and trans) and *m*-xylene (unfilled symbols) from the hydrogen-atom-induced decomposition of trichloroethylene. Circles are for reaction mixture containing 200 ppm hexamethylethane, 2% trichloroethylene, and 1% mesitylene in argon. Triangles are for reaction mixtures containing 100 ppm hexamethylethane, 2% trichloroethylene, 0.5% mesitylene, and 20% H_2. Dashed lines represent best fit through points. Solid line is analogous similar data from H + tetrachloroethylene, multiplied by 0.5 to take into consideration the two sites in this compound.

from the hydrogen-atom-induced decomposition of trichloroethylene are found. These compounds are 1,2-dichloroethylene (cis and trans), chloroacetylene, and dichloroacetylene. In addition, the methyl displacement product from mesitylene, *m*-xylene, is also present. Isobutene from hexamethylethane decomposition is another product and as noted earlier served as the marker for hydrogen atoms released into the system and a measure of the average reaction temperature. The concentration of 2,4-dimethylbenzyl radical is also given in Figures 1 and 2. The concentration of this radical is based on earlier studies that determined the branching ratio for hydrogen atom attack on mesitylene to be

$$k_8/k_7 = 5.5 \exp(1087/T)$$

A certain amount of methane and C_2 hydrocarbons is also present. Their concentrations are not needed in the data analysis. The amounts present are, however, not inconsistent with the present analysis. From the products that are detected, it is possible to carry out a mass balance on the basis of the hydrogen released into the system. It can be seen that in Figure 1, where H_2 was not added, the results indicate that every hydrogen atom leads to the formation of a product. Thus, all the hydrogen released into the system has been accounted for. This represents another check of the reaction mechanism. In contrast, where large quantities of H_2 are added so that the ratio of hydrogen to mesitylene is 40 to 1, it appears there are 4 mol of products for each mole of hydrogen atom released into the system.

Figures 3 and 4 contain the results of plotting the ratio of the normalized concentration of each of the chlorinated product with that of *m*-xylene. Should the postulated mechanism be correct, this is also the ratio of the rate constants for the various reactions of interest, or more specifically,

$$k_i/k_8 = (\text{product}_i/\text{trichloroethylene})(\text{mesitylene}/m\text{-xylene})$$

where the subscript *i* refers to a particular reaction channel. An essential condition for the correctness of the mechanism is that this ratio be invariant despite variations in the reactant concentrations at a particular temperature. As noted earlier, the presence of hydrogen serves as another test for the mechanism. From the data in Figures 3 and 4, it can be seen that this is the case for the postulated products from the displacement of the chlorine from the two positions and the abstraction of chlorine. However, this criterion is not met in the case of abstraction of hydrogen from trichloroethylene (leading to dichloroacetylene). This can be seen in Figure 4 where the results for this product do not collapose to a single line.

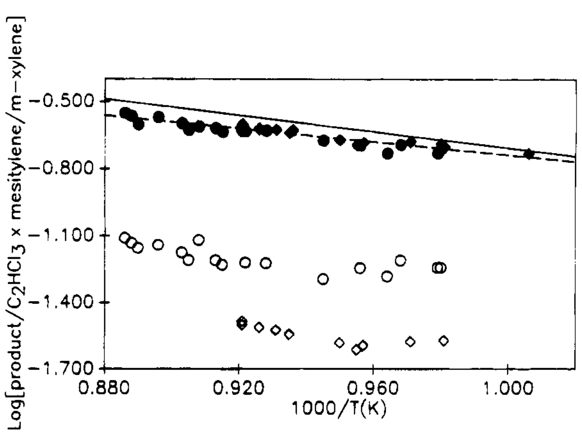

Figure 4. Ratio of normalized yields of chloroacetylene and *m*-xylene, (filled symbols) and dichloroacetylene and *m*-xylene (unfilled symbols) from the hydrogen-atom-induced decomposition of trichloroethylene. Circles are for reaction mixture containing 200 ppm hexamethylethane, 2% trichloroethylene, and 1% mesitylene in argon. Diamonds are for reaction mixtures containing 100 ppm hexamethylethane, 2% trichloroethylene, 0.5% mesitylene, and 20% H_2. Dashed lines represent best fit through points. Solid line is the result from an analogous process in H + tetrachloroethylene multiplied by 0.75.

On the basis of the results in Figures 3 and 4, the following ratios as a function of temperature have been obtained:

$$k_1/k_8 = 0.89 \pm 0.2 \exp(816 \pm 122/T)$$

$$k_2/k_8 = 0.55 \pm 0.1 \exp(-691 \pm 220/T)$$

$$k_3/k_8 = 5.6 \pm 1 \exp(-3431 \pm 225/T)$$

The uncertainties given above are a reflection of the scatter of the data. More meaningful values, based on past experience with such studies, are an uncertainty in the *A* factor of a factor of 1.5 and 4 kJ/mol in the activation energy. It should be noted that k_2 is based on the sum of the trans and cis isomers that are formed. From the results in Figures 1 and 2, it can be seen that the ratio of the two compounds is near 1.3 or at the equilibrium value. Substituting into the rate expression for methyl displacement from mesitylene by hydrogen leads to the following rate expressions:

$$k_1 = 6 \times 10^{13} \exp(-2439/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$k_2 = 3.7 \times 10^{13} \exp(-3946/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$k_3 = 3.8 \times 10^{14} \exp(-6686/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Factoring in the uncertainty in the rate expressions for the standard reaction leads to an uncertainty of 8 kJ/mol in the activation energy and a factor of 2.5 in the *A* factor. In terms of the rate constants, the estimated uncertainties are a factor of 1.25.

From a chain length of 4 in the case where hydrogen is added in 40-to-1 excess in comparison to the mesitylene, one can deduce that for every chlorine released into the system, 3 react with the hydrogen to 1 reacting with mesitylene. A possible conclusion is that the rate constant for chlorine reaction with mesitylene is a factor of 13 larger than that with H_2.

The ratio of the normalized yields of dichloroacetylene and *m*-xylene is not invariant with the addition of H_2 (see Figure 4) and changes in relative concentrations of the target gases. The analysis given above cannot be applicable to this situation. The most likely possibility is that chlorine abstraction of hydrogen from trichloroethylene is also making a contribution. Unfortunately, this is a very minor reaction channel, and the precision of the data is poor. Therefore, no attempt has been made to derive rate expressions. The data do permit the setting of an upper limit for hydrogen atom abstraction of hydrogen from trichloroethylene. From the results on Figure 5, one finds at 1050 K this value to be 6.5×10^{10} cm^3 mol^{-1} s^{-1}.

Discussion

Also included in Figures 3 and 4 are the comparable results from hydrogen atom reaction with perchloroethylene. The rate constants for the displacement reaction for perchloroethylene have been reduced by a factor of 2 in order to place everything on the same basis. It can be seen that hydrogen for chlorine substitution has a definite enhancing effect on the rate constant for displacement or, more properly, for addition. The overall effect at these temperatures is a factor of 6. Interestingly, there is a small retarding effect for addition to the position containing the two chlorine atoms. The magnitude of this difference is about a factor of 1.4 and is significant since all the present measurements are based on the ratio of rate constants and the overall error should not exceed 5−10%.

The results for abstraction, where the earlier data for perchloroethylene have been multiplied by a factor of 0.75, taking into account the presence of only three chlorines in trichloroethylene, are essentially the same as that in the present determinations. It appears that hydrogen for chlorine substitution has minimal effects on the rate constants for chlorine abstraction. At the low temperatures of these experiments, the measured concentrations of *cis*- and *trans*-dichloroethylene obtained from these studies are not due to the thermal isomerization process but are equal to the equilibrium constant. The present results suggest that an equilibrium mixture is directly attained from the decomposition of the 1,1,2-trichloroethyl adduct.

The factor of 13 difference in rate constants for Cl reaction with mesitylene and H_2 can be compared with values as close as a factor of 60 derived from Baulch et al.[16] of $k(\mathrm{Cl} + \mathrm{H_2}) = 1.3 \times 10^{13} \exp(-2200/T)$ cm^3 mol^{-1} s^{-1}, assuming that the room-temperature results of Wallington et al.[17] of 7.2×10^{13} cm^3 mol^{-1} s^{-1} for Cl reaction with *m*-xylene have no temperature dependence, refer to the abstraction process, and can be carried over to mesitylene after correction for the nine vs six hydrogens. The factor of 5 discrepancy may be due to the following factors. The recommendations of Baulch et al. cover only the data up to 600 K. There have been other recommendations[16] that suggest values of factors of 3−4 higher at the reaction temperature near 1050 K. Wallington et al. have given cogent reasons for relating their rate constant to an abstraction process. Nevertheless, it is possible that there are contributions from addition processes in the room-temperature determinations. On the other hand, the present results may be effected by contributions from hydrogen atom combination processes with the benzyl-type radicals that are created in the studies where large excesses of H_2 are added. Note that in the system where H_2 is not added, all the hydrogens have been accounted for. Thus, it is not likely that a factor of 13 can be greatly increased in this manner.

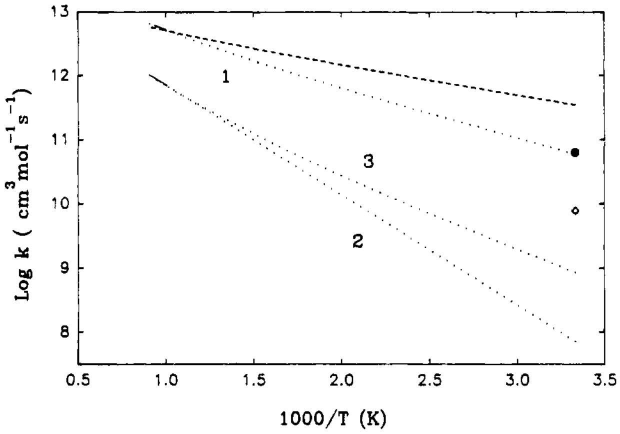

Figure 5. Arrhenius plots of data on hydrogen addition to ethylene, trichloroethylene, and tetrachloroethylene. Experimental results from present study: (— -) Addition at least chlorinated site; (—) addition at most chlorinated site; (- - -) recommended data for 0.5H + ethylene, (●) results or Ahmed and Jones for H + trichloroethylene, (◇) upper limit of Ahmed and Jones for 0.5H + tetrachloroethylene, (• • •) best modified Arrhenius fit of low- and high-temperature data on H + trichloroethylene at least substituted position (1) and extrapolated H + trichloroethylene at least substituted position (2), linear dependence; (3) T^2 dependence in preexponential factor.

The upper limit of 6.5×10^{10} cm^3 mol^{-1} s^{-1} at 1050 K for hydrogen abstraction by hydrogen atoms from trichloroethylene is comparable to that of the analogous reaction (on a per hydrogen basis) with methane or 7.6×10^{10} cm^3 mol^{-1} s^{-1}. It is a factor of 3 smaller than that for the abstraction of a chlorine from either perchloroethylene or trichloroethylene. Unfortunately, the bond energies for trichloroethylene are uncertain. The significance of these comparisons is thus unclear.

These results suggest most strongly that the lower temperature data of Ahmed and Jones are concerned completely with addition to the least substituted site. Extrapolating the present results to room temperature leads to a rate constant that is a factor of 3 larger than that reported by Ahmed and Jones. If one assumes a temperature-dependent preexponential factor, the following rate expression fits all the results:

$$k_1 = 2.63 \times 10^{10} T^{0.97} \exp(-1412/T)\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

This can be seen in Figure 5. A linear Arrhenius dependence, ignoring the temperature dependence deduced here, will require an activation energy of about 4 kJ/mol smaller. These results are suggestive of a small or negligible increase in the heat capacity of the transition state with temperature and that is in the range of values that can be obtained from comparable reactions involving hydrogen + olefinic hydrocarbons. This is in contrast to the simple bond-breaking reaction where there is a "tightening" of the transition state with temperature. One can therefore expect an *A* factor for the reverse radical decomposition reaction to be in the "normal" category. Also in Figure 5 are the results of the most recent evaluation of rate constant data for H + ethylene.[18] There is clearly a large contribution from the activation energies to the differences in rate constants at low temperatures for reactions of molecules with or without chlorine. This is partly compensated for by a smaller difference in *A* factors. At the temperature of these studies, the Arrhenius plots in fact cross each other. Unfortunately, the possible errors in the rate expressions make uncertain the significance of the observed difference in *A* factors. Also included in Figure 5 are the results from the rate expression for hydrogen addition to the most chlorinated site. As mentioned earlier, this is very close to 0.5, the rate constant for addition of the hydrogen atom to perchloroethylene. A linear extrapolation of these results to room temperature leads to rate constants that are orders of magnitude lower than the maximum number reported by Ahmed and Jones. Assuming a T^2 dependence of the preexponential factor leads to values that are still a factor of 15 too low. The actual value of the rate constant of hydrogen addition to perchloroethylene at room temperature may be considerably lower than the upper limit set by Ahmed and Jones.

The room-temperature rate constant for H atom addition to ethylene (3.6×10^{11} cm^3 mol^{-1} s^{-1}) is nearly the same as that determined by Ahmed and Jones for 1,1-dichloroethylene and a factor of 2 larger than their value for addition to vinyl chloride. As noted before, the present study establishes that for the low-temperature studies, the addition must be to the site that does not contain chlorine. Addition to the site that does not contain chlorine means these reactions are reversible, and one must consider the possibility that at the low pressures where Ahmed and Jones carried out their experiments, fall-off effects may make a contribution. However, the rough equality for reactions with ethylene and 1,1-dichloroethylene suggests that data for the latter are near the high-pressure limit. It is possible that the smaller rate constant for vinyl chloride may arise from its being further into the fall-off region.

It is interesting to compare the rate expressions for hydrogen reactions with perchloroethylene with those for comparable processes with trichloroethylene. For the latter, the rate parameters are all lower. This is, however, not much larger than the expected experimental uncertainty. The general trends, revealing an order of magnitude difference in the *A* factor between abstraction and displacement is maintained. Since it is generally assumed that the direction for addition is controlled by the relative stability of the radicals, the large difference in rate constants and activation energies for addition at the two sites in trichloroethylene is suggestive of a considerably stronger C—H bond in the least chlorine substituted position in 1,2,2-trichloroethane. Unfortunately, there are no bond dissociation energy data to check this prediction.

The present results demonstrate the greater stability of the more chlorinated species with respect to hydrogen atom attack. A particularly interesting aspect of the result is that the order of reactivity is quite similar to that for OH attack.[19] Thus, in an incineration system, if one begins with a mixture of chlorinated olefins, the reactions will lead to an ultimate mixture that will favor the more highly chlorinated species. This is usually observed. In contrast, for the chlorinated aromatics, the most chlorinated compounds appear to be the most reactive. Thus, the result of hydrogen atom reaction with a mixture of chlorinated aromatics will lead to distributions that will be increasingly skewed to the least chlorinated compound.

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JP9416580