At low pH $K_{CT} \approx 0$ but K_q is significant. For the planar aromatics, ϕ_{ce} is observed for the cases in which K_q is less than 84 (i.e. the case of PMA-Py at pH 4). In an earlier publication by Delaire et al.⁴ $\phi_{ce} \approx 0.07$ was found for PMA-vDPA at high pH with SPV ($K_q \approx 90$ in Table III). We do not find charge separation for this case with use of an attenuated excitation beam (see Experimental Section), and given our methodology, we have difficulty measuring ϕ_{ce} values below 0.1 (ANI represents our lower limit). Thus it is possible for both PMA-Py/SPV at pH 4 and PMA-vDPA/SPV at pH 11 that ϕ_{∞} is merely below our detection limit. It is also possible that some photoionization occurred in the earlier work by Delaire et al.,²⁴ which can lead to an overestimate of ϕ_{ce} . We do obtain the same value of ϕ_{ce} as Delaire et al.⁴ for PMA-vDPA/SPV at low pH where photoionization is less facile. Thus we propose that the concept of a "tight" or "loose" quenching pair coined by Mataga et al.²⁵ can be quantified by treating static quenching data with a simple complexation model. Note that it is not the value of $a_s(Q)$ (which depends on [Q]) that is important, but rather the derived quantity, K_{q} . It remains to be seen if this idea can be applied to a wide range of systems.

Finally we return to the "hydrophobic protection" afforded by the protonated polyacid. Similar ideas have been advanced by Morishima et al.²⁶ and Schmehl et al.²⁷ The primary experimental evidence for this effect is the smaller fluorescence quenching rate at low pH for relatively nonpolar quenchers. (We note that the recombination rates of the radical ions, even for the cation-cation case, are rather similar to the fluorescence quenching rates, cf. Tables V and VIII.) Approximately half this diminution may be ascribed to the reduced diffusion constant of the polymer-bound chromophore. Thus it does not seem that the "hydrophobic protection" is all that effective. We conclude that the role of the collapsed polymer must be rather subtle: the chromophore must be sufficiently accessible that the quenching can occur while maintaining sufficient separation between the groups to prevent the immediate charge recombination reaction. Considering the simplicity of this scheme, it is perhaps surprising that the present systems provide 30-45% charge separation efficiency. We still do not understand the important structural features of the polymer that are required to enhance this process. Future work will examine other polymers by using similar chromophores.

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Registry No. 5, 1910-42-5; 6, 77951-49-6; (MA) (DPA) (copolymer), 92719-97-6; (MA) (A) (copolymer), 117897-81-1; (EA) (MA) (copolymer), 117897-83-3; (PA) (MA) (copolymer), 117897-85-5.

Kinetics of Reactions of Chlorinated Vinyl Radicals CH₂CCI and C₂Cl₃ with Molecular Oxygen

J. J. Russell,[†] J. A. Seetula,[‡] D. Gutman,^{*,‡} and S. M. Senkan^{*,†}

Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616, and Department of Chemistry, Catholic University of America, Washington, D.C. 20064 (Received: June 27, 1988; In Final Form: September 12, 1988)

The kinetics of the reactions of CH₂CCl and C₂Cl₃ radicals with O₂ have been studied in a tubular flow reactor coupled to a photoionization mass spectrometer in the temperature range 298-648 K. Radicals were produced by the homogeneous photolysis of a suitable precursor using an excimer laser. The observed or indicated reaction mechanisms as well as the rate constants, which were measured as a function of density and temperature, suggest that both of these reactions proceed via the formation of a short-lived bound RO_2 intermediate that can either decompose back to the original reactants or form new oxygen-containing products following internal rearrangement of the adduct. The Arrhenius expressions obtained from the measured rate constants are $5.0 (\pm 0.7) \times 10^{-12} \exp[330(\pm 200)/RT]$ for the CH₂CCl + O₂ reaction and 2.0 (±0.4) × $10^{-12} \exp[830(\pm 230)/RT]$ for the C₂Cl₃ + O₂ reaction in units of cm³ molecule⁻¹ s⁻¹ for rate constants and cal mol⁻¹ for the Arrhenius activation energies.

Introduction

The development of a better understanding of the chemical kinetics of pyrolysis and oxidation of chlorinated hydrocarbons (CHCs) is of considerable importance because of their involvement in many practical processes. For example, chlorinated compounds are responsible for inhibiting flame propagation^{1,2} and for pro-moting soot formation in flames.^{3,4} These reactions are also important in the combustion of hazardous chemical wastes which frequently contain CHCs.⁵⁻⁷ Finally, the production of valuable chemicals by the controlled oxidation of chlorinated hydrocarbons has promising new commercial applications. For example, a chlorine-catalyzed oxidative pyrolysis (CCOP) process has recently

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[‡]Catholic University of America

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been developed to convert methane into ethylene and acetylene.8 The presence of O_2 in the CCOP process has eliminated the problem of coke formation, which limited the practical utility of other chlorine-catalyzed pyrolysis processes.9

In our laboratories, studies are in progress to develop a detailed kinetic model for the CCOP process to gain a better understanding of the pathways to the desired C₂ products and of the role of O₂ in soot suppression. The model will also be used to identify the process conditions that produce the maximum yield of C₂ hydrocarbons while suppressing the formation of significant concentrations of larger hydrocarbons, particularly those that lead on to the formation of high molecular weight polymeric products.

The formation of aromatics, soot, and coke in hydrocarbon pyrolysis is believed to begin via the addition of vinyl radicals to unsaturated C_2 species:^{10,11}

$$C_2H_3 + C_2H_2 \rightarrow C_4H_5 \tag{1}$$

$$C_2H_3 + C_2H_4 \rightarrow C_4H_7 \tag{2}$$

In the presence of molecular oxygen, these molecular weight growth processes can be suppressed due to a competing fast, highly exothermic reaction of the vinyl radicals with oxygen that appears to efficiently scavenge the C_2H_3 radicals:¹²

$$C_2H_3 + O_2 \rightarrow CH_2O + HCO \tag{3}$$

(The products CH_2O and HCO ultimately are oxidized to $CO^{13,14}$) A mechanism similar to reaction 3 has also been established for the reactions of C_3H_3 with O_2 .¹⁵

Analogous reaction pathways have not yet been observed for the reactions of chlorinated vinyl radicals with O₂ but have been postulated to describe experimental observations in the combustion of chlorinated hydrocarbons.⁷ For example, detailed chemical kinetic modeling of C2HCl3 flames indicates that the reaction of C_2Cl_3 with O_2 is likely to be an important elementary step in determining the extent of growth of high molecular weight products.¹⁶ In this model, the following mechanism was used:⁷

$$C_2Cl_3 + O_2 \rightarrow COCl_2 + COCl \tag{4}$$

It is possible that the mechanism of oxidation of the CH₂CCl radical is similar:

$$CH_2CCI + O_2 \rightarrow CH_2O + COCI$$
(5)

We have now studied the kinetics of the reactions of $C_2H_{3-x}Cl_x$ radicals with O_2 to establish the mechanisms of these important elementary reactions as well as to determine their rate constants over a wide temperature range. In this paper we report the results obtained for two of these radicals, CH2CCl and C2Cl3. Because not all of the chlorinated vinyl radicals could be prepared in sufficient yield by UV photolysis, the scope of the current investigation was restricted to the title reactions.

Experimental Section

The details of the experimental apparatus used and the procedures employed both to identify mechanisms and to measure rate constants have been described previously.^{12,15,17} Therefore only a summary is presented here. Pulsed (5 Hz) unfocused 193or 248-nm radiation from a Lambda Physik EMG 101E excimer laser was directed along the axis of a heatable tubular reactor with a 1.05-cm i.d. Gas flow velocities in the tube were near 5 m s⁻¹, a flow rate adequate to completely replace gases in the reactor between laser pulses. Both Pyrex and quartz reactors usually coated with Teflon were used in these experiments to suppress heterogeneous loss of the free-radical reactants (although some experiments were conducted using uncoated walls). The flowing gas contained the radical precursors in low concentrations (<0.004%) as well as an excess of $[O_2]$ (over the initial free-radical concentration), whose concentration was varied (keeping $[O_2]/$ [CHC] > 50-100). The carrier gas (He) was always in large excess (>99%). The gas from the reactor was sampled through a 0.40-mm hole in the side of the reactor and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the mass spectrometer. As the gas beam transversed the ion source, a portion was photoionized and then mass selected. Temporal ion signals were recorded from a short time before each laser pulse to 26-28 ms after the pulse by using a multichannel scaler. Data from 5000-30000 repetitions of the experiment were accumulated before the data were analyzed.

The gases were obtained from Linde (He, >99.995%) and Matheson (O_2 , >99.99%) and were used as provided. The liquids were obtained from Aldrich (1,1-C₂H₂Cl₂, >99%) and Kodak $(C_2Cl_4, >99\%)$. The C_2Cl_4 was degassed by using freezepump-thaw cycles, and the 1,1-C₂H₂Cl₂ was purified by fractional distillation.

Three photoionization energies were used in this investigation. A chlorine resonance lamp (8.9-9.1 eV) was used to detect CH₂CCl radicals, a hydrogen lamp (10.2 eV) was used to detect C₂Cl₃, C₂Cl₄, and 1,1-C₂H₂Cl₂, and an argon resonance lamp (11.6-11.8 eV) was used to detect CH₂O formed in the experiments

Initial conditions in these experiments were chosen to essentially isolate the reaction of interest for kinetic study. The elementary processes consuming the chlorovinyl radicals were the reaction with O_2 (reaction 4 or 5) and a heterogeneous first-order wall loss process. By use of extremely low initial free-radical concentrations (typically $(2-5) \times 10^{10}$ molecules cm⁻³, based on measured extent of photolysis of the radical precursor), radical-radical and radical-atom reactions were suppressed, i.e., they had negligible rates compared to the reaction under study. This condition was achieved and verified by reducing the concentration of the radicals (either by attenuation of the photolysis laser intensity or by lowering the free-radical precursor concentration) until the measured radical decay constant (in the absence of O_2) no longer depended on these variables.

Under the pseudo-first-order conditions used in these experiments (O_2 in excess), the chlorovinyl radicals decayed exponentially in both the absence and presence of O_2 . A rate constant for a particular temperature and gas density was determined from the slope of the line fitted through the measured radical exponential decay constants vs $[O_2]$. A representative ion signal decay profile and decay constant plot from one set of experiments to determine k_5 is given in Figure 1.

The effect of total gas pressure on both k_4 and k_5 was investigated. Over the range of conditions covered (a 2.5-fold change in pressure) no measurable effect of pressure on either rate constant was observed. The conditions of experiments and results obtained from all experiments are presented in Table I.

Study of the CH₂CCl + O₂ Reaction

Rate Constant Determinations. Reaction 5 was studied between 295 and 520 K by using only the Teflon-coated Pyrex reactor to reduce heterogeneous wall loss of the CH₂CCl radical. The Teflon coating determined the upper temperature limit for these experiments.

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Figure 1. Plot of CH₂CCl decay constants vs [O₂] for experiments conducted at 377 K. Inserts are reactant and product ion-signal profiles recorded during experiments conducted at $[O_2] = 2.7 \times 10^{13}$ molecules cm⁻³ (closed circle on figure). Lines through the ion-signal data are exponential functions from nonlinear least-squares fits. These fits yielded a CH₂CCl decay constant of 330 s⁻¹ and a CH₂O growth constant of 333 s⁻¹.

Photolytic Source of CH₂CCl. The CH₂CCl radicals were generated by the 193-nm laser photolysis of $1,1-C_2H_2Cl_2$. Nearly 25% of the precursor photodecomposed by using the unfocused radiation from the photolysis laser.

Experiments were conducted to identify the photolysis pathways. The products C_2HCl , C_2H_2 , and CH_2CCl appeared instantly following the laser pulse, indicating the presence of three photolysis routes:

1,1

$$C_2HCI + HCI$$
 (6a)

$$-C_2H_2CI_2 - C_2H_2 + 2CI (or + CI_2)$$
 (6b)

$$L \rightarrow CH_2CCI + CI$$
 (6c)

No attempt was made to establish the relative importance of each route because this information was not required for the determination of rate constants. In addition, calibration of mass spectrometer signals would have been difficult since no standard sources of the CH2CCl radical (from another well-characterized reaction) or of C₂HCl (from commercial sources) are available. However, on the basis of the magnitudes of the product ion signals, all of the above photolysis paths appear to be of comparable significance.

Products of the $CH_2CCl + O_2$ Reaction. A search was conducted at both 377 and 540 K for possible products of reaction 5. The only product detected was CH_2O (formaldehyde). Other potential detectable products that were searched for but not detected include COCl, C₂HCl, C₂H₂, HCO, and C₂H₂ClO₂. Since both C_2H_2 and C_2HCl were produced in the photolysis process, a further increase in the ion signals of these potential products was searched for when O_2 was added. No such increases were detected. These results indicate that some of the possible reactive routes including $C_2HCl + HO_2$, $C_2H_2 + ClO_2$, and CHClO + HCO are not of major importance under the conditions of these experiments.

Other potential products are undetectable by using our photoionization mass spectrometer, i.e., HO₂, Cl, and CH₂CClO₂. Detection of either HO₂ or Cl is not possible because their ionization potentials are above the highest photoionization energy

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ADLE I:	Conditions and	Results of Rate	Constan	t Experiments"
	10 ⁻¹⁶ [He],	$10^{-13}[O_2],$	k _w ,	$k \times 10^{12}, \mathrm{cm}^3$
<i>T</i> , K	atom cm ⁻³	molecule cm ⁻³	s ⁻¹	molecule ⁻¹ s ⁻¹
$C_2Cl_3 + O_2$ Reaction k_4				
297 Tf ^ø	4.81	1.01-5.74	101	8.39
312 Tf	4.91	1.34-4.76	66	6.86
342 Tf	4.87	0.92-5.09	79	7.13
377 Tf	4.86	1.52-6.84	56	6.05
417 Tf	4.86	1.01-5.84	53	5.34
417	12.0	1.32-7.03	57	6.09
468 Tf	4.83	1.29-7.66	50	5.39
468	4.79	1.17-8.49	52	4.79
520 Tf	4.78	2.27-8.94	53	4.86
520	4.81	1.26-8.94	51	4.36
585	4.77	1.37-9.23	68	3.86
648	4.75	1.87-8.80	167	3.74
$k_{4} = 2.0 \ (\pm 0.4) \times 10^{-12} \ \exp\{830 \ (\pm 230) \ cal \ mol^{-1}/RT\}$				
cm ³ molecule ⁻¹ s ⁻¹				
$CH_2CCl + O_2 \rightarrow Products$ k_5				
295 Tf	4.79	0.91-4.39	123	8.90
298 Tf	9.66	1.36-5.58	103	8.39
312 Tf	4.76	1.06-4.32	113	8.31
342 Tf	4.76	0.74-4.86	101	8.25
377 Tf	4.86	1.09-5.28	102	7.78
377 Tf	17.2	1.07-4.87	100	7.36
417 Tf	4.84	0.77-5.50	89	7.29

520 Tf 4.78 1.08-5.67 98 6.83

$$k_5 = 5.0 \ (\pm 0.7) \times 10^{-12} \ \exp\{330 \ (\pm 200) \ \text{cal mol}^{-1}/RT\}$$

 $\text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}$

0.83-4.71

85

09

7.10

468 Tf

4.71

1 78

^aRange of radical-precursor concentrations used: $(1-2) \times 10^{12}$ molecules cm⁻³ for both C_2Cl_4 and $1,1-C_2H_2Cl_2$. ^bTf, Teflon-coated reactor.

available for these studies (11.8 eV). The formation and subsequent partial stabilization of CH2CClO2, the initial adduct formed by any addition process, cannot be ruled out just because it was not detected, since RO_2 radicals are known to be generally difficult or impossible to detect by mass spectrometry.^{15,17}

The CH₂O ion signal rises exponentially, mirroring the observed exponential decay of CH₂CCl (see the lower insert in Figure 1). The fact that the measured exponential growth constant of CH₂O is the same as the decay constant of the CH_2CCl radical is presented as proof that CH₂O is an initial product of reaction 5. At long reaction times, the CH₂O signal declines slightly due to secondary reactions involving other free radicals and chlorine atoms.

The second product formed by reaction 5, COCl, was not detected. This could have been caused by the instability of COCI (it may decompose instantly into CO + Cl as it is produced by the highly exothermic $CH_2CCl + O_2$ reaction) or by other factors. For example, COCl would not be detectable if its ionization potential is higher than the highest available photoionization energy (11.6 eV). Finally, if the radical undergoes an unusually rapid heterogeneous loss process, its concentration may not have risen to detectable levels.

Study of the $C_2Cl_3 + O_2$ Reaction

Rate Constant Determinations. Reaction 4 was studied between 297 and 648 K by using a Teflon-coated as well as an uncoated quartz reactor. In this study, the upper temperature limit was determined by the observed onset of the thermal decomposition of C₂Cl₃.

At the C₂Cl₃ radical mass number (m/e = 129), there was a small (typically $0.1[C_2Cl_3]_0$), apparently constant second contribution from an unknown photoproduct that was not influenced by the presence of O_2 in the system. This additional signal, which was treated as a shifted base line, could be measured and was subtracted from the C_2Cl_3 ion signal profiles as the first step in the data analysis procedure leading to the determination of rate constants. The use of this corrective procedure did not alter the precision of the rate constant measurements, but it did increase

the estimated probable uncertainty (from $\pm 15\%$ for k_5 to $\pm 20\%$ for k_4). These limits take into account the accuracies of measurements (gas flow rates and total pressure) and data analysis procedures (including the accuracy of the radical decay constant determinations).

Photolytic Source of C_2Cl_3 . The C_2Cl_3 radicals were produced by the photolysis of C_2Cl_4 by using 248-nm laser pulses. In spite of the use of lower energy radiation, photodecomposition of C_2Cl_4 still proceeded by more than one route:

$$\Gamma^{--}$$
 C₂Cl₂ + 2Cl (or + Cl₂) (7a)

$$C_2Cl_4 \longrightarrow C_2Cl_3 + Cl$$
 (7b)

Again, on the basis of the ion signals of the observed photoproducts $(C_2Cl_2 \text{ and } C_2Cl_3)$ both routes 7a and 7b appear to be of major importance.

Products of the $C_2Cl_3 + O_2$ Reaction. For identification of the mechanism of the $C_2Cl_3 + O_2$ reaction, a product search was conducted at 417 K using the two highest mass spectrometer photoionization energies, 10.2 and 11.6 eV. The possible products searched for but not detected include ClO_2 , ClO, $COCl_2$, $C_2Cl_3O_2$, C_2ClO_2 , and C_2Cl_2 . Since C_2Cl_2 was also produced in the photolysis process, the search again involved looking for an increase in the $C_2Cl_2^+$ ion signal upon addition of O_2 . No product was directly observed, but some evidence for the formation of $COCl_2$ (phosgene) was seen. The only route that can clearly be excluded from being important is the formation of $C_2Cl_2 + ClO_2$.

The products of reaction 4 are not directly detectable. The possible reasons for the undetectability of COCl were discussed above. COCl_2 has an ionization potential (11.84 eV¹⁸) that is too high to permit detection of this likely product. The appearance potential of COCl⁺ from COCl₂ is lower, in fact low enough (11.2 eV^{18}) to be a detectable ionization product of $COCl_2$ in these studies. A measurable COCl⁺ ion signal was observed to appear following initiation of the reaction. However the signal was extremely low, preventing determination of its temporal behavior (e.g., its rise time). The signal appeared to originate from a stable product since it did not decrease during the typical observation time of 25 ms. In these experiments, free-radical products typically display a sharp rise followed by a sharp fall in concentration due to reactions with O_2 that both form and consume them. Although there is some indication that the products shown in reaction 4 are the correct ones, these experiments have not been able to provide conclusive proof.

Another weak signal at m/e = 110, corresponding to $C_2Cl_2O^+$, was also observed in these experiments. Although the weakness of this signal also prevented the determination of its temporal behavior, it had the general characteristics of a stable product. This observation suggests that there may be a significant additional route of the for the $C_2Cl_3 + O_2$ reaction:

$$C_2Cl_3 + O_2 \rightarrow C_2Cl_2O + ClO \tag{8}$$

Discussion

Mechanisms of Reactions 4 and 5. The search for reaction products and the trend in reaction rate constants (see below) establish that the mechanism shown for reaction 4 is clearly an important one. While it is not certain that it is the only important route, as there was some evidence that C_2Cl_2O formation also occurs, some of the possible alternate routes can be classified as insignificant (particularly those leading to the formation of alkynes, i.e., C_2Cl_2).

Although there are indications that reaction 5 proceeds to the products as written, the evidence is not conclusive. However a route leading to the formation of the possible chlorinated alkyne in reaction 5, i.e., C_2HCl , was also shown to be unimportant.

The mechanisms that could be confirmed (or indicated) and the mechanisms that could be excluded for reactions 4 and 5 show

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Figure 2. Arrhenius plots of measured $C_2H_{3-x}Cl_x$ (x = 0, 1, and 3) and O_2 reactions. Points for $C_2H_3 + O_2$ reaction are from ref 12. Solid lines through data are the Arrhenius rate constant functions given in Table I.

that the reactions of chlorinated vinyl radicals with O_2 proceed, in part, by the same mechanism as the $C_2H_3 + O_2$ reaction,^{12,19} i.e.

$$c_{2}Cl_{3} + O_{2} \rightleftharpoons \begin{bmatrix} 0 \cdots 0 \\ c_{1} & c_{2} \\ c_{1} & c_{2} \end{bmatrix} \longrightarrow COCl_{2} + COCl \quad (9)$$

The reactions begin as addition processes forming RO_2 radicals. The final products result from ring closure to form an excited radical structure that rapidly decomposes to the observed or indicated products. There is evidence that at atmospheric pressure and at ambient temperature, a $C_2H_3O_2$ intermediate formed in reaction 3 can be partially stabilized by collisions, and not all of the reaction proceeds onward via decomposition to form new products.²⁰ It is far less likely that this stabilization will occur at highly elevated temperatures, particularly those characteristic of combustion processes.

The previously used presumption in the kinetic modeling of oxidation processes involving chlorinated hydrocarbons^{7,16} that the reactions of all chlorinated vinyl radicals with O_2 proceed by mechanisms analogous to that of the $C_2H_3 + O_2$ reaction is at least partially verified by the observations made in this investigation. However, for some of these reactions there are also indications for the presence of a competing mechanism involving the formation of ketenes, and this should be considered in future modeling studies.

Rate Constants of Reactions 4 and 5. The measured rate constants for reactions 4 and 5 are plotted on an Arrhenius plot in Figure 2. Also shown for reference purposes is the Arrhenius expression for the $C_2H_3 + O_2$ reaction rate constant reported by Slagle et al.¹² These rate constants are independent of gas density (over the range covered, $(5-17) \times 10^{16}$ molecules cm⁻³), indicating that collisions are not involved in the rate-determining processes.

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What is apparent in Figure 2 is that the rate constants for three $C_2H_{3-x}Cl_x + O_2$ reactions (x = 0, 1, and 3) are quite similar, particularly at ambient temperature. However, there is a noticeable trend toward an increasingly negative activation energy as the degree of chlorine substitution increases, from -0.25 to -0.83 kcal mol⁻¹ as x changes from 0 to 3.

The temperature dependence of these rate constants can be accounted for by the nature of the overall reaction mechanism;12,19 initial association followed by either dissociation back to the original reactants or rearrangement and finally decomposition into the final observed products. (One explanation that accounts for the independence of the overall rate constants on pressure is that the lifetime of the $C_2H_{3-x}Cl_x-O_2$ adduct is short compared to the time between collisions.) The measured rate constant of a $C_2H_{3-x}Cl_x + O_2$ reaction is that of the association step multiplied by the fraction of the adducts formed that proceed on to the final products.²¹ If the fraction is 1, then the measured rate constant is equivalent to the high-pressure limit rate constant for a more standard reversible addition reaction. It is likely that this fraction is near 1 for all three $C_2H_{3-x}Cl_x + O_2$ reactions at ambient temperature since the measured rate constants are close to (actually somewhat higher) than the high-pressure limit rate constant of the $C_2H_5 + O_2$ reaction^{22,23} (the closest reversible R + O₂ reaction that can be used for comparison purposes).

While there is generally little temperature dependence in association rate constants, there can be a significant temperature dependence in the fraction of adducts that proceed to form new products.²¹ Thus a significant negative activation energy for the measured rate constants implies that reformation of reactants becomes increasingly the more favored decomposition pathway for the $C_2H_{3-x}Cl_x-O_2$ adduct as temperature increases. For this to be the case, the potential energy barrier for the rearrangement of the $C_2H_{3-x}Cl_x-O_2$ adduct (leading to the formation of new products) must generally be lower than that for dissociation back to the original reactants (although the density of states for the two competing decomposition paths also determines this temperature dependence).

The trend in negative activation energies of the $C_2H_{3-x}Cl_x + O_2$ reactions with increasing chlorine substitution suggests that while the rearrangement barrier in all three cases is below that of the dissociation path, it becomes increasingly less so as more chlorine atoms are incorporated into the vinyl radical. This trend results in the $C_2Cl_3 + O_2$ association becoming more reversible with increasing temperature than is the case for the $C_2H_3 + O_2$ reaction. These changes in the *relative* heights of the two relevant potential energy barriers with chlorine substitution cannot be large since the rate constants and activation energies of the $C_2H_{3-x}Cl_x + O_2$ do not vary significantly.

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Pulse Radiolysis of 2,4,5-Trichlorophenol: Formation, Kinetics, and Properties of Hydroxytrichlorocyclohexadienyl, Trichlorophenoxyl, and Dihydroxytrichlorocyclohexadienyl Radicals

R. Barton Draper, Marye Anne Fox,*

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Ezio Pelizzetti,

Dipartimento di Chimica Analitica, Universita di Torino, via Giuria 5, Torino 10126, Italy

and Nick Serpone

Department of Chemistry, Concordia University, 1455 deMaisonneuve Blvd. West, Montreal, Quebec H3G 1M8, Canada (Received: June 30, 1988)

Pulse radiolysis has been used to optically and kinetically characterize the transient free radicals formed by the reaction of H[•], N₃[•], or OH[•] with 2,4,5-trichlorophenol (TCP-OH). The hydroxy-2,4,5-trichlorocyclohexadienyl radical (H-TCP-OH) formed by H[•] addition to TCP-OH [$k = (1.1 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$] has an absorption maximum at 360 nm with $\epsilon_{360} = (4700 \pm 1000) \text{ M}^{-1} \text{ cm}^{-1}$. The 2,4,5-trichlorophenoxyl radical (TCP-O[•]) formed by the reaction of N₃[•] with TCP-O⁻ [$k = (4.3 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$] has an absorption maximum at 360 nm with $\epsilon_{360} = (4.3 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$] has an absorption maximum at 430 nm with $\epsilon_{430} = (3600 \pm 600) \text{ M}^{-1} \text{ cm}^{-1}$. The di-hydroxy-2,4,5-trichlorocyclohexadienyl radical (HO-TCP-OH) formed by OH[•] radical addition to TCP-OH [$k = (1.2 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$] has an absorption maximum at 320 nm with $\epsilon_{320} = (5300 \pm 250) \text{ M}^{-1} \text{ cm}^{-1}$. The principal isomer formed by the reaction of OH[•] with TCP-OH is the 1,6-dihydroxy-2,4,5-trichlorocyclohexadienyl radical, which has a pK_a of 4.8 ± 1.0 . The solution absorption from each radical decays via second-order kinetics on the millisecond time scale.

Introduction

Chlorinated phenols represent an important class of pollutants that have been introduced into the environment as herbicides and fungicides. These compounds are generally resistant to chemical, photochemical, and biological degradation in the environment, making disposal, particularly of contaminated water, difficult. Lemaire and co-workers have found, however, that direct photolysis, using 290-nm light, initiates degradation of these toxic materials, leading to dechlorination via either ionic or radical intermediates, depending on the position of chlorine substitution. Dechlorination is generally considered a detoxification reaction; however, the intermediacy of free radicals in some of these pro-

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