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Reactions of chloroethenes with atomic chlorine in air at atmospheric pressure

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Relative rate method at the temperature of 298 K and pressure of 1013 hPa and GC-MS detection were used for the study of kinetics of the reactions of Cl atoms with $H_2C=CCl_2$, *cis*-$ClHC=CHCl$, *trans*-$ClHC=CHCl$, $ClHC=CCl_2$, and $Cl_2C=CCl_2$. The reaction products were identified by FTIR spectroscopy. A mechanism for the atmospheric degradation of chloroethenes has been suggested.

Key words: atmospheric chemistry, chloroethenes, reaction rate constant, FTIR spectroscopy, reaction mechanism, chlorination, atomic chlorine.

Chloroethenes (CE) are widely used in industry in the synthesis of polyvinyl chloride and other polymers, as well as solvents for chemical purification and degreasing. They are formed as side products in the process of plastic waste burning in industry if the burning regime is not optimum. The worldwide production of dichloroethenes (DCE) reached 3.5 million metric tons in 1998 and during period 1996—2004 increased on average by 2.5% every year.[1] The combustion process of CE and chlorine-containing polymers leads to the emission of chlorine-containing gases to the environment, which can have negative consequences. Recirculation and burning of polymers is an important problem, too: in the processes indicated, significant emission of gases during pyrolysis and combustion is also possible, for which allowance should be made during optimization of production parameters. At present, technological studies in the field under consideration are mainly devoted to the aspects of the "end-of-life" of polyvinyl chloride. The main accent is made on the danger of smoke gases evolved on combustion of polyvinyl chloride and their purification during the combustion process. Almost nothing is known about possible natural sources of halogenated ethylenes. Biogenic emission of CE is rare. Halogenation of simple biogenic alkenes and terpenes with atomic chlorine and bromine was studied only in laboratory experiments.[2,3] Halogenated alkenes in the amount of halogen atoms formed in atmosphere have the same effect on the environment in industrial regions, as the reservoir forms of halogens in the Arctic at the time of polar sunrise.[4] To evaluate the influence of CE on the atmosphere, it is necessary to study their reaction channels and products during atmospheric degradation.

Though there is a number of publications on this question, elementary chemical processes of CE degradation in atmosphere are not entirely determined. Earlier,[5] we have studied kinetics of recombination of peroxy radicals ($CHCl_2CHClO_2$, $CHCl_2CCl_2O_2$, and $CCl_3CCl_2O_2$) formed in the chlorine-initiated oxidation processes of 1,2-dichloroethene, trichloroethene, and tetrachloroethene, respectively. However, the question about the reaction products remained open. The results published[6] on the study of the reaction products and channels during atmospheric degradation of CE are rather difficult to compare, since reactions of CE with atomic chlorine have been studied by different methods under different conditions. In the present work, we performed systematic study of the kinetics and mechanism of the reaction of CE with chlorine atoms at atmospheric conditions in a smog chamber using GC-MS and FTIR spectroscopy. The reaction rate constants of Cl atoms with CE (C_2Cl_4, C_2HCl_3, *cis*- and *trans*-isomers of $ClHC=CHCl$, and $H_2C=CCl_2$) are found and major gas-phase products of these reactions are determined.

Experimental

Relative rate method. The rate constants of the reaction of CE with Cl atoms were found by the relative rate (RR) method, in which the ratio of the reaction rate constants of molecules S and R (k_S and k_R) with Cl atoms is determined (by the slope coefficient of the line in the coordinates of Eq. (3), see further).

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The extent of the reagent transformations in the course of the reaction was measured.

$$S + Cl \xrightarrow{k_S} P, \qquad (1)$$

$$R + Cl \xrightarrow{k_R} P, \qquad (2)$$

where P are the products.

In this method the rate constant of the reaction of molecules R with the Cl atom must be known. Molecules S and R are consumed exclusively in the reactions with Cl atoms and are not involved into the secondary reactions with any other species. Therefore, the following expressions operate for the relative rate constant k_{rel}:

$$\ln\{[S]_0/[S]_t\} = k_{rel}\ln\{[R]_0/[R]_t\},\ k_{rel} = k_S/k_R, \qquad (3)$$

where $[S]_0$, $[R]_0$, $[S]_t$, and $[R]_t$ are the concentrations of molecules S and R at the initial and t moments of time, respectively. The k_{rel} value can be determined from the graph of the dependence of $\ln\{[S]_0/[S]_t\}$ *versus* $\ln\{[R]_0/[R]_t\}$. The data of independent experiments were analyzed using the least squares method, in which allowance was made for the uncertainties in the concentration of reagents.[7]

Experimental apparatus (Fig. 1). Kinetic measurements were performed at the pressure of 1013±15 hPa and temperature of 298±2 K in the synthetic air of a 250-L smog chamber (the chamber length was 220 cm, its diameter, 40 cm) made of stainless steel treated by electropolishing. For the photolysis of molecular chlorine, low-pressure mercury luminescent lamps with luminescent coating of the inside wall, emitting the long-wave UV radiation (Philips TLD-08, $\lambda_{max} \approx 370$ nm), were used. Chlorine atoms during photodissociation were formed in the ground electron state. The chamber temperature during experiments was kept constant. The reaction mixture was analyzed *in situ* using an Agilent 6890/5973 GC-MS instrument with chemical ionization (CI). The gas chromatograph worked in isothermic conditions at 46 °C. Excessive constant pressure of ~5 hPa was maintained in the reactor to guarantee a stationary current of ~20 $cm^3\ min^{-1}$. A sample of 0.5 cm^3 was taken during the inflow cycle into the gas chromatograph, which was diluted by 50 times before injection into the chromatographic column. Helium was used as a carrier gas. A 30-m DB-WAXetr chromatographic column with internal diameter of 0.25 mm and a 0.25-μm film of polyethylene glycol was used in all the experiments. The temperature of 100 °C was maintained in the region of the sample inlet and the loop. For the control of the inflow conditions of reagents, chemically inert gas (reference gas), perfluoro-1,2-dimethylcyclohexane, was feeded into the reactor. The change of concentrations in Eq. (3) can be neglected, since the dilution was insignificant.

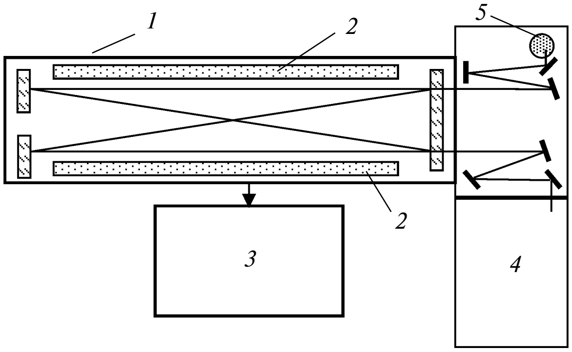

Fig. 1. The scheme of experimental apparatus: *1* is the smog chamber, *2* are the low pressure luminescent lamps, *3* is the GC-MS spectrometer, *4* is the FTIR spectrometer, *5* is the source of the IR irradiation.

The use for the "soft" CI of $[CH_5]^+$ ions allowed us to avoid fragmentation and overlap of mass spectra. A full mass spectrum of reagents and reaction products at the outlet of the gas chromatograph was analyzed at the beginning of an experiment to reveal characteristic mass peaks, which gave us a possibility to operate with selected individual ions. This allowed us to determine individual compounds quantitatively and decrease the background noise, as well as to remove the overlapping effect in the case of incomplete chromatographic separation. Relative concentrations of the reagents were found by the measurement of the ions $[MH]^+$ signal values.

The smog chamber was equipped with a system of mirrors providing multiple passage of the IR irradiation through it (White Cell), the optical distance was 120 m. The absorption IR spectrum in the smog chamber was recorded on a Bruker FTIR spectrometer (IFS-88).

The losses of CE due to the nonphotochemical reactions in the smog chamber was monitored before each experiment, they never exceeded 1—2% of total consumption of the compound during the experiment. To determine photostability, the UV irradiation of CE for 5 min was performed before beginning each experiment. The change in intensity of the mass spectra did not exceed 1—2%. Thus, the losses of compound due to the nonphotochemical reactions and direct photolysis were insignificant. For recording IR spectra of the reaction products of Cl atoms with CE, special experiments were carried out without addition of molecule R.

Reactants. Synthetic air ($[CO] + [NO_x] < 0.1$ ppm, $[C_nH_m] < 1$ ppm) was purchased from AGA. Commercial (Fluka) CE (C_2Cl_4, C_2HCl_3, *cis*-, *trans*-ClHC=CHCl, $H_2C=CCl_2$) of analytically pure grade were used in this work. Purity of CE was additionally controlled by GC-MS, in all the cases the content of CE in the sample was >98%. Partially fluorinated ether ($C_2F_5CH_2OMe$) from Fluorochem Ltd. (>98%) was used in experiments.

Results and Discussion

Determination of the reaction rate constants by the relative rate method. Partially fluorinated ether $C_2F_5CH_2OMe$ (**1**) in concentration comparable with the concentration of CE was used in all the experiments as the compound competing with CE in the reactions with chlorine atoms. The concentration of CE in the mixture at the beginning of experiment usually was 2—6 ppm, whereas the content of Cl_2 in the chamber was 10—20 ppm. The choice of compound **1** is due to the fact that the rate constant of the reaction of this ether with atomic Cl has been recently studied. For the reaction Cl + **1** → P (P are the products), the rate constant is found[8] to be $4.0(0.8) \cdot 10^{-11}$ $cm^3\ molecule^{-1}\ s^{-1}$ (here and further, the error of statistical analysis is given in parentheses 3σ). In addition, relative concentrations of compound **1** are found using the signal in the mass spectrum on the line at $m/z = 165$, which is conveniently placed with regard to the lines of CE under study.

Figure 2 shows the data on three independent experiments, in which the signal of C_2Cl_4 was measured on the line at m/z = 167 [M + H] ($C_2Cl^{37}Cl^{35}{}_3H^+$). Analysis of the data gives the following value for the ratio of the reaction rate constants: $k_{\mathrm{Cl}\,+\,\mathrm{C_2C_{14}}}/k_{\mathrm{Cl}\,+\,\mathbf{1}} = 1.12(0.12)$. From this it follows that the absolute rate constant of the reaction of Cl atoms with C_2Cl_4 is equal to $4.5(1.0)\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. The known[9] value for this rate constant, $4.0\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} (Table 1), is very close to that obtained in our experiments.

The data from other experiments with CE are given in Fig. 3 and the results in Table 1 are compared with the values obtained by the direct measurements at room temperature.

Study of the products. For determination of the reaction products of Cl atoms with CE, the mixture contained reagents in the same concentrations that in kinetic experiments. The difference was that reagent R has not been placed into the smog chamber.

Figure 4 shows the IR spectra of a mixture of reagents $Cl_2C=CCl_2$, Cl_2, and air before and after photolysis, when all the tetrachloroethene was consumed in the reaction with chlorine atoms. The spectrum of the products is rather simple and mainly is formed by trichloroacetyl chloride (CCl_3COCl), as well as by small amount of phosgene (CCl_2O), which was inferred from the absorption bands for the C=O and C—Cl functional group with the maxima at 1827 and 850 cm^{-1}, respectively. Figure 5 shows the IR spectra recorded for the reaction of $ClHC=CCl_2$ with Cl atoms. In the spectrum of the products, acetyl chlorides CCl_3COCl (with wave numbers 740, 802, 850, 988, 1790 cm^{-1}) and $CHCl_2COCl$ (with wave numbers 587, 740, 802, 988, 1076, 1790, 1824 cm^{-1}), as well as phosgene and formyl chloride are identified. The IR spectra recorded for the reaction of *trans*-ClHC=CHCl with Cl atoms are shown in Fig. 6. The spectrum of the products is almost identical to the spectrum recorded for the reaction of *cis*-ClHC=CHCl with Cl atoms and is a superposition of the absorption spectra of dichloroacetyl chloride ($CHCl_2COCl$), phosgene, and formyl chloride (CHClO). The latter compound can be identified by the C—H group

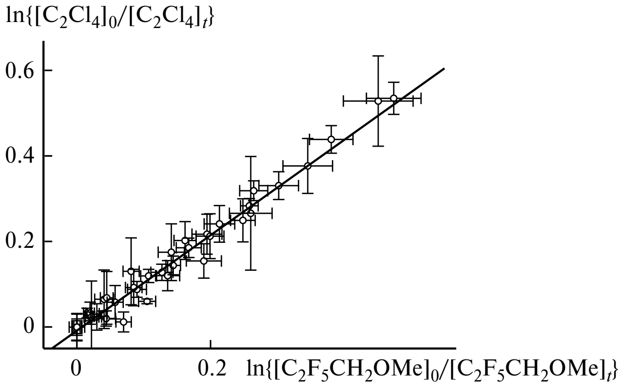

Fig. 2. The dependence of $\ln\{[C_2Cl_4]_0/[C_2Cl_4]_t\}$ on $\ln\{[C_2F_5CH_2OMe]_0/[C_2F_5CH_2OMe]_t\}$ for 39 measurements in three independent experiments; the result of linear regression (errors 3σ): $y = (-0.008\pm0.013) + (1.12\pm0.12)x$.

Table 1. The rate constants for the reaction of Cl atoms with chlorinated ethenes at 298 K

Compound	k_{rel}(298 K)[a]	k(298 K)$\cdot10^{11}$ /cm^3 molecule^{-1} s^{-1}	Method[b]	Reference
$Cl_2C=CCl_2$	1.12(0.12)	4.5 (1.0)	RR-GC/MS	The present work
		3.9(0.3)	FP-RF	10
		4.13(0.25)	RR-GC	11
		4.0	Estimation	9
$HClC=CCl_2$	2.17(0.14)	8.7(1.8)	RR-GC/MS	The present work
		8.1(0.08)	RR-GC	11
trans-HClC=CHCl	2.45(0.21)	9.8(2.1)	RR-GC/MS	The present work
		9.6(0.2)	RR-GC	11
cis-HClC=CHCl	3.06(0.17)	12.2(2.5)	RR-GC/MS	The present work
		9.6(0.1)	RR-GC	11
$H_2C=CCl_2$	3.30(0.2)	13.2(2.8)	RR-GC/MS	The present work
		14.0(0.14)	RR-FTIR	11
$H_2C=CHCl$		12.7(0.25)	RR-GC	11

[a] Measurements were performed using the reaction of Cl atoms with $CF_3CF_2CH_2OMe$ (**1**), for which $k_{\mathrm{Cl}\,+\,\mathbf{1}} = 4.0(0.8)\cdot10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, as a comparison reaction.

[b] RR-GC/MS stands for the relative rate method in combination with GC-MS, FP-RF stands for the method of resonance fluorescence in combination with a flow-tube reactor, RR-GC stands for the relative rate method in combination with GC, RR-FTIR stands for FTIR spectroscopy in combination with a flow-tube reactor.

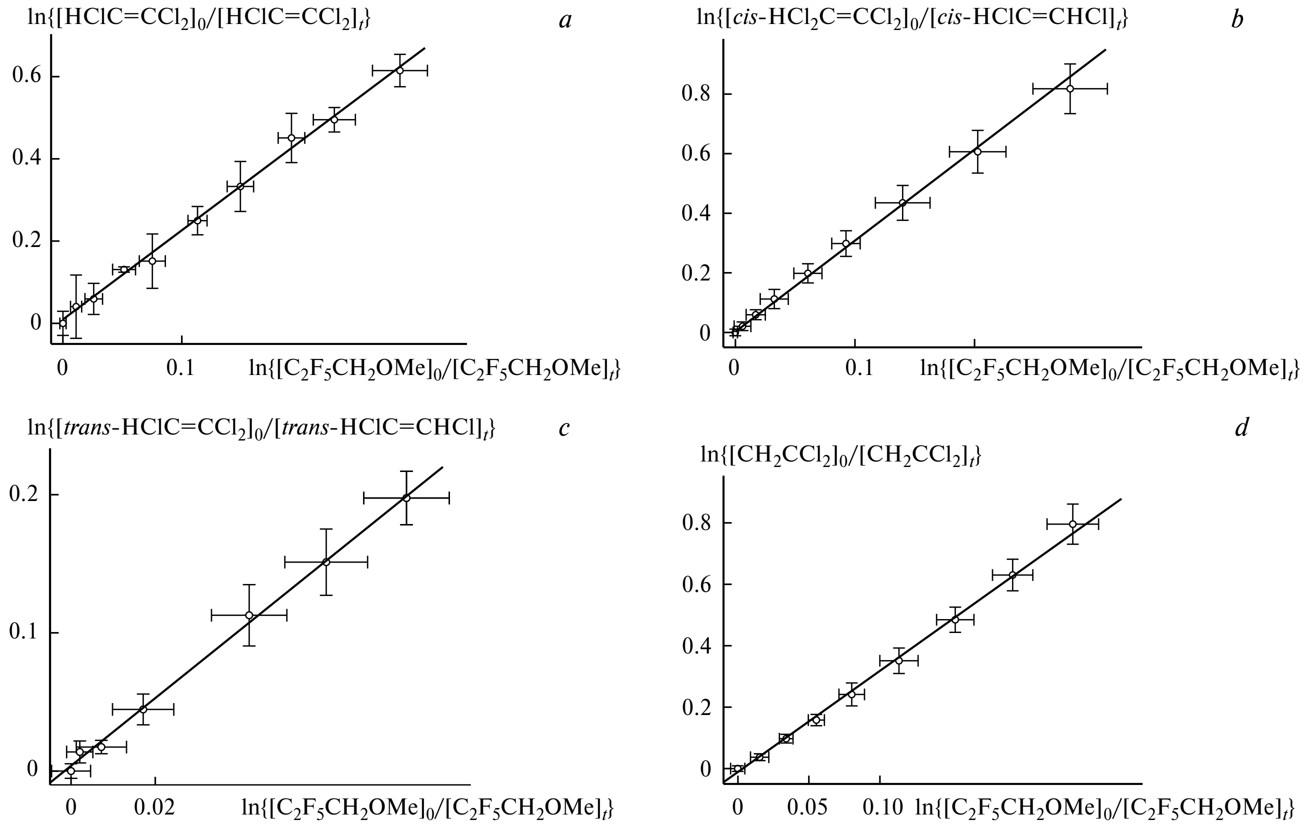

Fig. 3. The dependence of ln{[S]$_0$/[S]$_t$} on ln{[C$_2$F$_5$CH$_2$OMe]$_0$/[C$_2$F$_5$CH$_2$OMe]$_t$} during the reaction with Cl atoms; S = ClHC=CCl$_2$ (*a*), *cis*-ClHC=CHCl (*b*), *trans*-ClHC=CHCl (*c*), H$_2$C=CCl$_2$ (*d*); the result of linear regression (errors 3σ): $y = (0.009\pm0.015) + (2.17\pm0.14)x$ (*a*), $y = (0.002\pm0.011) + (3.06\pm0.17)x$ (*b*), $y = (0.004\pm0.006) + (2.45\pm0.21)x$ (*c*), $y = (-0.011\pm0.014) + (3.30\pm0.20)x$ (*d*).

stretching band at 2933 cm^{-1},[12] which overlaps with the rotation-vibrational structure of HCl. Finally, Fig. 7 shows the IR spectra recorded for the reaction of 1,1-dichloroethene with Cl atoms. On the analysis of the spectra, chloroacetyl chloride (ClCH$_2$COCl) and phosgene were identified as the products. Figure 8 illustrates a partial change of the IR spectrum for this reaction. During the reaction, a part of the spectrum characteristic of the C=C bond disappears and absorption bands for the C=O bonds appear, which are characteristic of the CE transformation products.

The FTIR spectroscopy data were complemented by the GC-MS analysis. In this procedure, the photolysis products were pumped off through a trap cooled by liquid nitrogen, then the trap was defrosted and the mixture was analyzed. The products were analyzed by mass spectrometry using CI to record [MH]$^+$ ions. When products of the reaction Cl + Cl$_2$C=CCl$_2$ were analyzed, only ions with *m/z* 99 were reliably identified, that corresponds to phosgene. The ions with *m/z* 163, 147, 99, and 65 were found in the system Cl + ClHC=CCl$_2$. Comparison with the IR spectroscopic data allows us to state that the ions with *m/z* 99, 65, and 147 can be assign to, respectively, phosgene, CHClO, and one of the isomers Cl$_3$C—COH or Cl$_2$HC—COCl. The ions with *m/z* 113 and 115 (Cl$_2$HC—COH), 99 (CCl$_2$O) were recorded in the system Cl + *trans*-ClHC=CHCl. The peaks of low intensities for the ions with *m/z* 113 and 115 (Cl$_2$HC—COH), 77 (ClHC=C=O), and 65 (CHClO) were found in the system Cl + *cis*-ClHC=CHCl and the ions with *m/z* 113 (ClH$_2$C—COCl), 99 (CCl$_2$O), in the system Cl + + H$_2$C=CCl$_2$.

The data on the products identified by the analysis are given in Table 2.

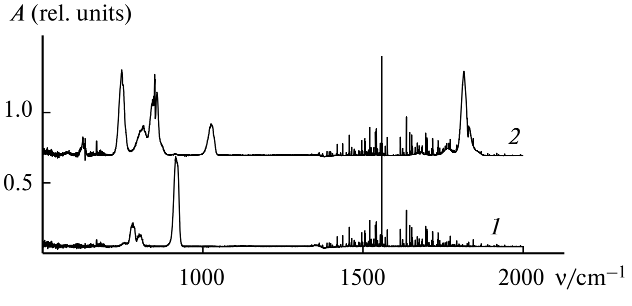

Fig. 4. The IR spectra of Cl$_2$C=CCl$_2$ (*1*) and products of its reaction with Cl atoms in air (*2*). Here and in Figs 5—7, the spectra of the products are displaced along the ordinate axis.

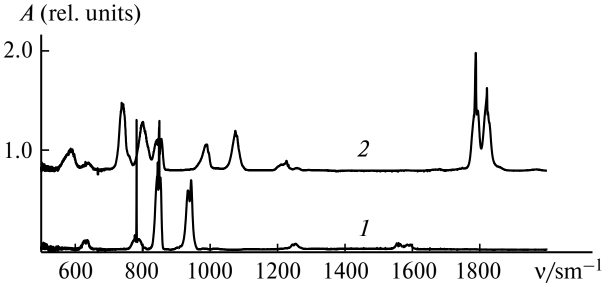

Fig. 5. The IR spectra of $ClHC=CCl_2$ (*1*) and products of its reaction with Cl atoms in air (*2*).

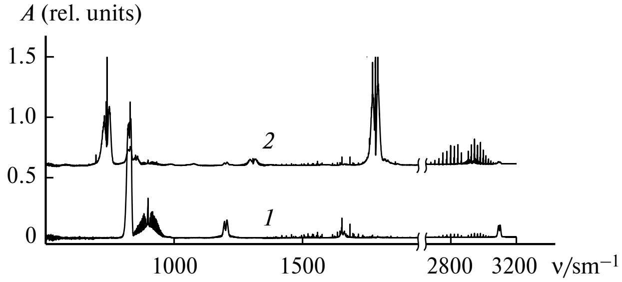

Fig. 6. The IR spectra of *trans*-$ClHC=CHCl$ (*1*) and products of its reaction with Cl atoms in air (*2*).

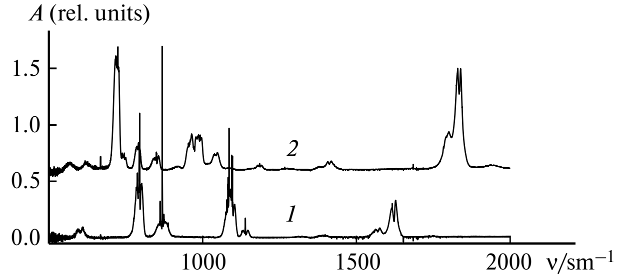

Fig. 7. The IR spectra of $H_2C=CCl_2$ (*1*) and products of its reaction with Cl atoms in air (*2*).

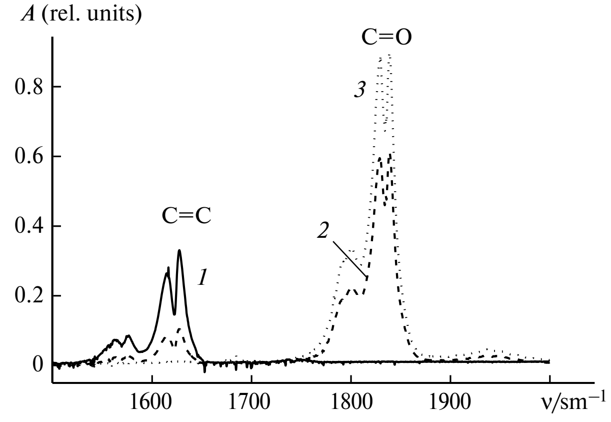

Fig. 8. The change in the IR spectrum in the region 1500—2000 cm^{-1} of the reaction mixture Cl + O_2 + $H_2C=CCl_2$ depending on the photolysis time: 0 (*1*), 120 (*2*), and 300 s (*3*).

Table 2. The products identified in the reactions of Cl atoms with chlorinated ethenes in air (1 atm, 298 K)

Chlorinated ethylene	Major products	Minor products
$Cl_2C=CCl_2$	$Cl_3C—COCl$	CCl_2O
$ClHC=CCl_2$	$Cl_3C—COCl$, $Cl_2HC—COCl$	CCl_2O, CHClO; HCl; CO
trans, *cis*-$ClHC=CHCl$	$Cl_2HC—COCl$	CCl_2O, CHClO; HCl; CO
$H_2C=CCl_2$	$ClH_2C—COCl$	CCl_2O, CHClO; HCl; CO

Reaction rate. It is known that the reactions of CE with Cl atoms have third order, but at the pressure of 1 atm predominantly proceed in the high pressure regime. Since many studies[6] were performed at low pressures, their results cannot be directly compared with the present work data. The results obtained for the reaction of Cl with CE are summarized in Table 1. Tetrachloroethene is the only CE, for which the reaction rate constant value is recommended.[9] The data obtained in the present work agree with the results of systematic studies[10,11] of the CE reactions kinetics. Note that in contrast to the values published earlier,[11] the rate constant for the reaction of *cis*-$ClHC=CHCl$ with atomic chlorine determined by us is by ~30% higher than the rate constant for the reaction of *trans*-$ClHC=CHCl$. However, the rate constants agree within the indicated measurement errors. To sum up, our data indicate a somewhat higher reaction rate of *cis*-isomer CE with Cl atoms as compared to *trans*-isomer. Similar behavior was also found for the reactions with radicals $^{\cdot}OH$ (see Refs 13 and 14) and $^{\cdot}NO_3$.[15,16] This was also confirmed by recent calculations using molecular orbital theory.[17]

Reaction mechanism. Trichloroacetyl chloride is the major product found in the oxidation process of tetrachloroethene with Cl atoms (see Table 2). This agrees with the recent study,[18] in which formation of 68% and 87% of trichloroacetyl chloride in the atmosphere containing or containing no NO_x, respectively, was reported. The mechanism of the reaction in the NO_x-free atmosphere is as follows:

$$Cl + Cl_2C=CCl_2 \longrightarrow Cl_3C—CCl_2^{\cdot}, \quad (4)$$

$$Cl_3C—CCl_2^{\cdot} + O_2 \longrightarrow Cl_3C—CCl_2O_2^{\cdot}, \quad (5)$$

$$Cl_3C—CCl_2O_2^{\cdot} + RO_2^{\cdot} \longrightarrow$$
$$\longrightarrow Cl_3C—CCl_2O^{\cdot} + RO^{\cdot} + O_2, \quad (6)$$

$$Cl_3C—CCl_2O^{\cdot} \longrightarrow Cl_3C—COCl + Cl, \quad (7a)$$

$$Cl_3C—CCl_2O^{\cdot} \longrightarrow CCl_2O + {}^{\cdot}CCl_3. \quad (7b)$$

Channel (7a) predominates over channel (7b). Here and further in Schemes on mechanism of reactions, $RO_2^{\bullet}$ means peroxy radicals formed by oxidation of the main compound. The sequence of the reactions similar to (5)—(7a) will result in the transformation of radicals $^{\bullet}CCl_3$ to the final product CCl_2O.

In the reaction of trichloroethene, the major products are acetyl chlorides $Cl_3C{-}COCl$ and $Cl_2HC{-}COCl$, and minor products are CCl_2O and CHClO. In the work,[19] oxidation of trichloroethene at 357 °C activated by the photodissociation of chlorine has been studied and a conclusion has been drawn that addition of Cl to the least chlorinated carbon atom in trichloroethene is at least by 8 times more probable than addition to the most chlorinated carbon atom. Our results indicate somewhat less difference in the reactivity. A mechanism for the oxidation of $ClHC{=}CCl_2$ has been suggested, the first steps of which are as follows:

$$\mathrm{Cl + ClHC{=}CCl_2 \longrightarrow Cl_2HC{-}CCl_2^{\bullet}}, \tag{8a}$$

$$\mathrm{Cl + ClHC{=}CCl_2 \longrightarrow {}^{\bullet}ClHC{-}CCl_3}, \tag{8b}$$

$$\mathrm{Cl_2HC{-}CCl_2^{\bullet} + O_2 \longrightarrow Cl_2HC{-}CCl_2O_2^{\bullet}}, \tag{9}$$

$$\mathrm{HCl_2C{-}CCl_2O_2^{\bullet} + RO_2^{\bullet} \longrightarrow} \\ \mathrm{\longrightarrow HCl_2C{-}CCl_2O^{\bullet} + RO^{\bullet} + O_2}, \tag{10}$$

$$\mathrm{Cl_2HC{-}CCl_2O^{\bullet} \longrightarrow Cl_2HC{-}COCl + Cl}, \tag{11a}$$

$$\mathrm{Cl_2HC{-}CCl_2O^{\bullet} \longrightarrow {}^{\bullet}CHCl_2 + CCl_2O}, \tag{11b}$$

$$\mathrm{{}^{\bullet}ClHC{-}CCl_3 + O_2 \longrightarrow {}^{\bullet}O_2CHCl{-}CCl_3}, \tag{12}$$

$$\mathrm{{}^{\bullet}O_2CHCl{-}CCl_3 + RO_2^{\bullet} \longrightarrow} \\ \mathrm{\longrightarrow {}^{\bullet}OCHCl{-}CCl_3 + RO^{\bullet} + O_2}, \tag{13}$$

$$\mathrm{{}^{\bullet}OCHCl{-}CCl_3 + O_2 \longrightarrow OClC{-}CCl_3 + HO_2^{\bullet}}, \tag{14}$$

$$\mathrm{{}^{\bullet}OCHCl{-}CCl_3 \longrightarrow CHClO + {}^{\bullet}CCl_3}. \tag{15}$$

The radicals $^{\bullet}CHCl_2$ and $^{\bullet}CCl_3$ formed will produce the final products, phosgene and CCl_2O, in further reactions. Since the major registered oxidation products are $CCCl_3COCl$ and $CHCl_2COCl$ (see Table 2), it is obvious that the reactions (11a) and (14) are the main channels for the formation of the products from the intermediate alkoxy radicals (RO).

For *cis*- and *trans*-$ClHC{=}CHCl$ in the reactions with Cl, formation of dichloroacetyl chloride was mainly observed together with insignificant yields of products CCl_2O and CHClO. This contradicts the data in Ref. 20, according to which the main reaction gives product CHClO, with the formation of CCl_2O and isomerization of $ClHC{=}CHCl$ through the secondary channels.

The results obtained in the present work allows one to suggest for isomers $ClHC{=}CHCl$ the following mechanism of degradation initiated by the reaction with Cl atoms:

$$\mathrm{Cl + ClHC{=}CHCl \longrightarrow Cl_2HC{-}CHCl^{\bullet}}, \tag{16}$$

$$\mathrm{Cl_2HC{-}CHCl^{\bullet} + O_2 \longrightarrow Cl_2HC{-}CHClO_2^{\bullet}}, \tag{17}$$

$$\mathrm{Cl_2HC{-}CHClO_2^{\bullet} + RO_2^{\bullet} \longrightarrow} \\ \mathrm{\longrightarrow Cl_2HC{-}CHClO^{\bullet} + RO^{\bullet} + O_2}, \tag{18}$$

$$\mathrm{Cl_2HC{-}CHClO^{\bullet} + O_2 \longrightarrow Cl_2HC{-}COCl + HO_2^{\bullet}}, \tag{19}$$

$$\mathrm{Cl_2HC{-}CHClO^{\bullet} \longrightarrow {}^{\bullet}CHCl_2 + CHClO}. \tag{20}$$

Analysis of the products shows that the reaction channel (19) predominates over channel (20). Radicals $^{\bullet}CHCl_2$ through the sequence of reactions similar to (17)—(19) will further lead to the formation of additional amount of CCl_2O. Dichloroacetyl chloride formed in the reaction (19) can further react with excess of Cl atoms forming oxalyl chloride $C_2O_2Cl_2$, which readily photodissociates to Cl atoms and CO. Formyl chloride is thermally unstable and easily decomposes to CO and HCl. Formation of these products was inferred from analysis of the spectrum (see Fig. 6).

Chloroacetyl chloride is the major product of 1,1-dichloroethene oxidation with atomic chlorine, CCl_2O and CHClO are formed as well (no formation of CHClO was found in Ref. 21). The fact that the IR spectrum of the products does not exhibit trichloroacetaldehyde indicates that addition of the Cl atom takes place predominantly to the CH_2 group. The following mechanism can be suggested for the oxidation:

$$\mathrm{Cl + H_2C{=}CCl_2 \longrightarrow ClH_2C{-}CCl_2^{\bullet}}, \tag{21}$$

$$\mathrm{ClH_2C{-}CCl_2^{\bullet} + O_2 \longrightarrow ClH_2C{-}CCl_2O_2^{\bullet}}, \tag{22}$$

$$\mathrm{ClH_2C{-}CCl_2O_2^{\bullet} + RO_2^{\bullet} \longrightarrow} \\ \mathrm{\longrightarrow ClH_2C{-}CCl_2O^{\bullet} + RO^{\bullet} + O_2}, \tag{23}$$

$$\mathrm{ClH_2C{-}CCl_2O^{\bullet} \longrightarrow ClH_2C{-}CClO + Cl}, \tag{24a}$$

$$\mathrm{ClH_2C{-}CCl_2O^{\bullet} \longrightarrow {}^{\bullet}CH_2Cl + CCl_2O}. \tag{24b}$$

The only direct channel for the formation of CHClO can involve radicals $^{\bullet}CH_2Cl$, formed in the channel (24b). Therefore, the reaction channel (24a) predominates over channel (24b).

Atmospheric implications. Degradation of CE in the oxidation with Cl atoms leads to the formation of chloroacetyl chlorides, phosgene, and formyl chloride. Hydrolysis of phosgene gives CO_2 and HCl, whereas formyl chloride is thermally unstable and decomposes to CO and HCl or, alternatively, can hydrolyze in atmospheric drops to yield formic and hydrochloric acids. Chloroacetyl chlorides will hydrolyze in drops forming partially chlorinated acetic acids, the influence of which on the environment is not yet completely established at present.

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