Formation of Glyoxyloxyl Chloride, HC(O)C(O)Cl, in the Gas-phase Oxidation of Trichloroethene by NO_2

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Within the temperature range 303–416 K, the main products of the gas-phase oxidation of trichloroethene by NO_2 are nitrosyl chloride, ClNO, and glyoxyloxyl chloride, HC(O)C(O)Cl. Glyoxyloxyl chloride has been isolated by fractional condensation and identified by its infrared spectrum and molecular weight determination. It decomposed above 416 K into CO and HCl and was hydrolysed in the presence of water vapour to give glyoxylic acid, HC(O)C(O)OH. The values of the reaction rate constants for the consumption of NO_2 were $9.9 \pm 3 \times 10^{-4}$ and $2 \pm 1 \times 10^{-3}$ $dm^3\ mol^{-1}\ s^{-1}$ at 343.1 and 362.2 K, respectively. A reaction sequence is proposed to explain the formation of HC(O)C(O)Cl.

The reactions of NO_2 with halogenated alkenes have been the subject of several studies.[1–11] These works were generally undertaken for preparative purposes, providing evidence that NO_2 may act as a nitrating or oxidising agent.

$O_2NCF_2CCl_2NO_2$ and $O_2NCF_2CF_2NO_2$ were prepared, respectively, by reaction of NO_2 with CF_2CCl_2 and with CF_2CF_2.[4] The acyl fluoride, $O_2NCF_2C(O)F$, was reported to be a known product of the reaction of NO_2 with CF_2CF_2.[5] This acyl fluoride and FNO were detected as products in other studies of the latter reaction.[6,7] The production of $O_2NCFHC(O)Cl$, $O_2NC(CF_2Cl)ClC(O)Cl$ and $O_2NC(CF_3)ClC(O)Cl$ has been reported as a result of the respective nitrations of $CFHCCl_2$,[8] $C(CF_2Cl)ClCCl_2$ and $C(CF_3)ClCCl_2$.[9] The formation of $O_2NCF_2C(O)F$ and ClNO was observed in the reaction of NO_2 with CF_2CFCl.[10] $O_2NCF_2C(O)Cl$ and ClNO were found to be the main products of the reaction between NO_2 and CF_2CCl_2.[11]

Detailed kinetic and mechanistic studies were made only for the addition of NO_2 to CF_2CF_2[7] and CF_2CCl_2.[11] There are no data available on the addition of NO_2 to chlorinated ethenes. In this work the thermal reaction of NO_2 with trichloroethene, $CHClCCl_2$, is studied.

Results and Discussion

The reaction mixtures of 30 experiments performed at 303 and 323.1 K, varying the initial pressure of NO_2 between 12.3 and 192.6 mbar and that of trichloroethene between 13.3 and 81.2 mbar, were condensed together in a trap at liquid-air temperature and separated by fractional vacuum condensation. The volatile fraction at 173 K consisted of ClNO.[12] The non-consumed reactants, NO_2 and trichloroethene, were separated as volatile at 228 K. The residue remaining at 228 K consisted of an unidentified compound X. This was further purified by several freeze–thaw–evaporation cycles directly from the trap into the infrared cell. The cycles were repeated until the consecutive infrared spectra were identical. The spectrum thus obtained is illustrated in Fig. 1. In Table 1, comparison of the gaseous spectra of compound X, HC(O)C(O)H,[13] HC(O)Cl[14] and ClC(O)C(O)Cl[15] is presented together with tentative assignment of the bands.

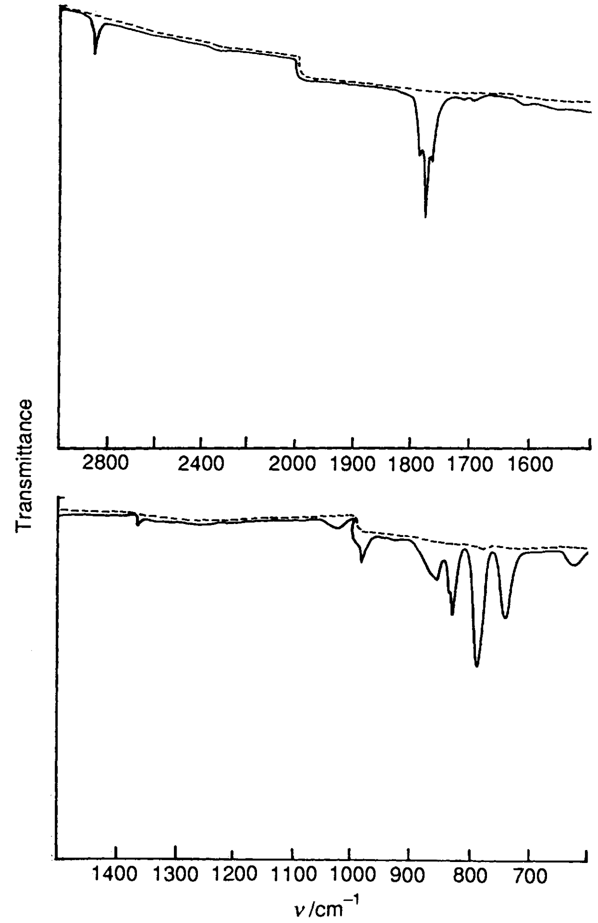


Fig. 1 Gaseous infrared spectrum of X, pressure 2.1 mbar

The reaction proceeded with no pressure change. Two series of experiments were performed at 343.1 and 362.2 K. Each experimental reaction mixture was analysed by means of IR spectroscopy after a given reaction time. To determine the amounts of the products and the reactants consumed, infrared calibration curves were constructed using pure compounds, thereby allowing the conversion of the absorption intensities at 735, 3097, 1806 and 2912 cm^{-1} to the pressure of X, $CClHCCl_2$, ClNO and NO_2, respectively. The analytical data of seven experiments are summarized in Table 2, where Δt is the reaction time, indices i and f signify initial and final, respectively, and N_2O_4 is the content of N_2O_4 calculated for each pressure of NO_2 using the corresponding equilibrium constant.[16]

The results indicated that the overall reaction is given by Scheme 1. The consumption of reactants is well represented by

Table 1 Comparison of the infrared spectra of gaseous X, HC(O)C(O)H, HC(O)Cl and ClC(O)C(O)Cl

X ν/cm^{-1}	HC(O)C(O)H ν/cm^{-1}	HC(O)Cl ν/cm^{-1}	ClC(O)C(O)Cl ν/cm^{-1}	Tentative assignment
2852	2836	2933.5		H–C
1783				
1777	1730	1783.5	1852 1770	C=O
1770				
1353	1312	1307		H–C
			1077	
1028	802		1060	C–C
984			988	
			980	
855				
828		932	795	Cl–C
781		739	777	
735				
625			724	Cl–C=O

Table 2 Analytical data of seven experiments

Run	T/K	Δt/min	$p(C_2Cl_3H_i)$/ mbar	$p(C_2Cl_3H_f)$/ mbar	$p(NO_{2i})$/ mbar	$p(N_2O_{4i})$/ mbar	$p(NO_{2f})$/ mbar	$p(N_2O_{4f})$/ mbar	p(X)/ mbar	p(ClNO)/ mbar
35	362.2	301.6	9.7	9.3	64.9	0.13	64.0	0.13	0.5	0.9
36	362.2	293.2	77.6	77.0	15.0	—	14.0	—	0.5	1.1
38	362.2	240.6	40.5	39.9	40.7	0.05	39.3	0.05	0.6	1.2
39	362.2	362.9	39.9	38.9	38.4	0.04	36.5	0.04	0.9	1.9
41	343.1	364.3	41.6	41.0	39.9	0.13	38.7	0.13	0.5	1.1
42	343.1	241.9	39.3	38.9	39.9	0.13	39.0	0.13	0.4	0.8
44	343.1	421.6	70.1	69.6	14.1	0.02	13.2	0.015	0.3	0.8

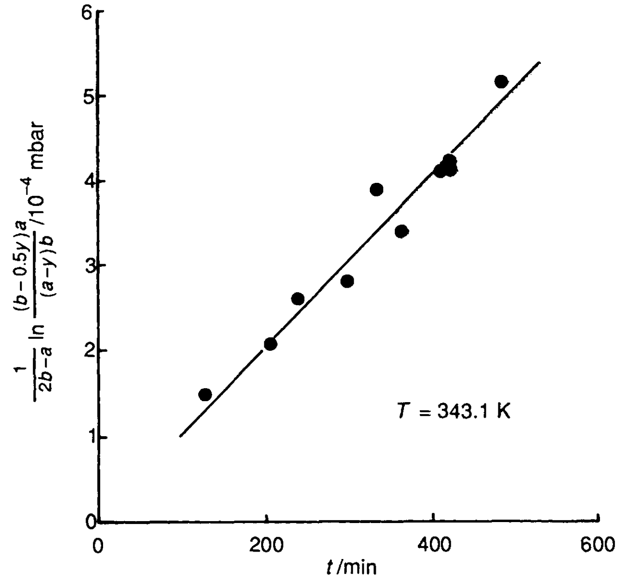


Fig. 2 Second-order plot for the reaction of NO_2 with $CHClCCl_2$ at 343.1 K

$$2NO + CClHCCl_2 \longrightarrow 2ClNO \times X$$

Scheme 1

eqn. (I). The values of the rate constants for the consumption of

$$-d(NO_2)/dt = -2d(CHClCCl_2)/dt = k(NO_2)(CHClCCl_2) \quad (I)$$

NO_2 equal to $9.9 \pm 3 \times 10^{-4}$ and $2 \pm 1 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} were derived, respectively, at 343.1 and 362.2 K using the expression $kt = 2(2b - a) \ln (b - 0.5y)a/(a - y)b$, which is the integrated form of the equation $dy/dt = k(a - y)(b - 0.5y)$, where a and b are the initial pressures of NO_2 and $CHClCCl_2$, respectively, t is the reaction time and y is the amount of ClNO (which equals the amount of NO_2) consumed. The error introduced by taking $NO_2 + N_2O_4 = NO_2$ falls within the experimental error limits. Fig. 2 shows the plot of $2(2b - a)^{-1} \ln (b - 0.5y)a/(a - y)b$ vs. t at 343.1 K. The straight line indicates that the reaction is second order.

Note from the value of k that the reaction is very slow. In order to increase the conversion of the reactants, to obtain greater amounts of the compound X, the reaction temperature was raised to 445 K. A rapid pressure increase was observed in the presence of an initial pressure of trichloroethene of 93.3 mbar and of NO_2 of 154.6 mbar. The main products were ClNO, ClH and CO. Small amounts of $COCl_2$, NO and N_2O were also observed, being identified by their infrared spectra.[17] Infrared bands corresponding to compound X were not observed. Two further experiments were performed under similar conditions, confirming the reproducibility of the results.

Subsequently, the reaction temperature was decreased to 416 K. At this temperature, the reaction proceeded with an almost constant pressure increase of 0.03 mbar min^{-1} from an initial pressure of C_2Cl_3H of 85.3 mbar and of NO_2 of 140 mbar. Two samples of the reaction mixture were withdrawn from the reaction vessel after 3 and 6 h. In the infrared spectrum of the first sample, bands corresponding to $CClHCCl_2$, ClNO, CO and X were observed, indicating the complete consumption of NO_2. In the infrared spectrum of the second sample the intensity of the bands of $CClHCCl_2$ and ClNO had remained constant, while those of X decreased, those of CO increased, and bands corresponding to ClH had appeared. The absence of the ClH bands in the spectrum of the first sample may be explained by the low intensity of the ClH infrared absorption. The spectra suggest that ClNO and X were formed primarily, X then decomposing into CO and ClH.

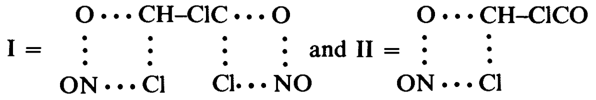
To increase the yield of X, another nine runs were carried out at 416 K with a reaction time of 3 h. The amount of volatile product at liquid-air temperature, corresponding to CO, was equal to the increase in reaction pressure. All residues that remained solid at 228 K were condensed together.

It was observed that if the infrared cell was not properly dried, X was hydrolysed in the cell to give ClH and a substance for which the infrared bands frequencies were similar to those of glyoxylic acid, HC(O)C(O)OH,[18] which, in turn, disappeared to be replaced by bands of a non-volatile compound at 666, 2313 and 2352 cm^{-1}. Comparison of these band frequencies with those of carbon suboxide, O=C=C=C=O[19] suggests the possibility of the enolization of HC(O)C(O)OH to O=C=C$(OH)_2$.

The molecular weight of X was determined with a Gow-Mac gas chromatograph, provided with a gas density balance detector, which gives the molecular weight, M, of an unknown compound using the equation:[20] $M = (KA/PV) + M_c$, where P and V are the pressure and the volume of the gas, K is the constant of the chromatograph, A is the peak area of the unknown compound and M_c the molecular weight of the carrier gas. A value of 90 ± 6 was obtained for M. The theoretical molecular weight of HC(O)C(O)Cl is 92.5. Above 410 K the compound X decomposed giving HCl and CO in a ratio of 1:2.

The infrared band frequencies of X, its molecular weight, and its decomposition and hydrolysis products suggest that X is the glyoxyloxyl chloride, HC(O)C(O)Cl. The only literature reference to this substance is that it was identified using dinitrophenylhydrazine as one of the products of the reaction between triethylamine and N,2,4,6-tetrachlorobenzanilide in CCl_4.[21]

To explain the results of this work within the temperature range 303–362.2 K, the following mechanism was considered.



$$\mathrm{I} = \begin{array}{cccc} \mathrm{O}\cdots & \mathrm{CH{-}ClC} & & \cdots\mathrm{O} \\ \vdots & \vdots & \vdots & \vdots \\ \mathrm{ON}\cdots & \mathrm{Cl} & \mathrm{Cl}\cdots & \mathrm{NO} \end{array} \quad \text{and II} = \begin{array}{cc} \mathrm{O}\cdots & \mathrm{CH{-}ClCO} \\ \vdots & \vdots \\ \mathrm{ON}\cdots & \mathrm{Cl} \end{array}$$

$$NO_2 + CHClCCl_2 \longrightarrow O_2N(CHClCCl_2) \quad (1)$$

$$O_2N(CHClCCl_2) + NO_2 \longrightarrow O_2N(CHClCCl_2)NO_2^* \quad (2)$$

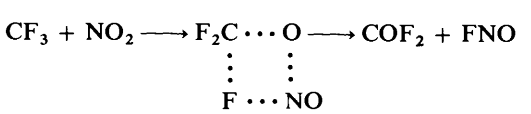
$$O_2N(CHClCCl_2)NO_2^* \longrightarrow \mathrm{I} \quad (3)$$

$$\mathrm{I} \longrightarrow \mathrm{II} + ClNO \quad (4)$$

$$\mathrm{II} \longrightarrow HC(O)C(O)Cl + ClNO \quad (5)$$

The reaction (1) was postulated on the basis of other studies of the reactions between NO_2 and alkenes[7,11,22–24] which demonstrated that the primary process is the additon of NO_2 to the double-bond-forming nitro radicals.

NO_2 is a very efficient radical scavenger. Its concentration in this work was many orders of magnitude higher than that of the nitro radicals. Consequently, they were rapidly scavenged by NO_2 to give an excited dinitro adduct *via* the reaction (2). The formation of an excited adduct was postulated in previous work to account for the formation of $O_2NCF_2C(O)Cl$ and ClNO in the reaction between NO_2 and CF_2CCl_2.[11] To explain the formation of COF_2 and FNO in the reaction of NO_2 with the radicals CF_3,[25] the following mechanism shown in reaction (6) is proposed. This process is similar to the reaction of NO_2 with $O_2NCF_2CF_2$ radicals,[7] which gives $O_2NCF_2C(O)F$ and FNO as the main products.



$$CF_3 + NO_2 \longrightarrow \begin{array}{cc} \mathrm{F_2C}\cdots & \mathrm{O} \\ \vdots & \vdots \\ \mathrm{F}\cdots & \mathrm{NO} \end{array} \longrightarrow COF_2 + FNO \quad (6)$$

The rearrangement and the resulting configuration of the dinitrite adduct, **I**, and its subsequent decomposition may be rationalized in terms of the competition for the carbon atom electrons between the electron-deficient oxygen atom of NO_2 and the electrophilic chlorine atom.

It is well known that the formation of a C–O bond in the oxy radicals CCl_3O, CCl_2FO, $CClF_2O$ and CF_2ClCCl_2O, weakens the C–Cl bond, leading to the rapid detachment of the chlorine atoms and to the corresponding carbonyl halides: $COCl_2$,[25] COFCl,[26], COF_2[27] and $CF_2ClC(O)Cl$.[28] The elimination of ClNO can thus be explained in terms of the concomitant weakening of the C–Cl bond when the C–O bond is forming and the lower bond-dissociation energy of the C–N bond compared with the C–O bond.[29]

It has been reported by other authors that nitrosyl halides, XNO, where X = F or Cl, are formed, in addition to $O_2NCF_2C(O)F$, as the main products of the reactions of NO_2 with CF_2CF_2[6,7] and CF_2CFCl,[10] respectively. Two vicinal chlorine atoms attached to the same carbon atom enhance the weakening of the C–Cl bond. It is therefore more likely that the dinitrite adduct decomposition will occur principally *via* reaction (4), followed by the extrusion of the second ClNO *via* reaction (5).

Applying the steady-state approximation method to the mechanism, eqn. (II) is obtained for the consumption of NO_2.

$$-d(NO_2)/dt = 2k_1(NO_2)(CHClCCl_2) \quad (II)$$

Comparing eqn. (I) with eqn. (II), it is found that $k = 2k_1$.

The decomposition of HC(O)C(O)Cl may be compared with that of glyoxal[30] and that of formyl chloride.[14]

$$HC(O)C(O)Cl \xrightarrow{>416\,K} 2CO + HCl$$

$$HC(O)C(O)H \xrightarrow{>1100\,K} 2CO + H_2$$

$$HC(O)Cl \xrightarrow{298\,K} CO + HCl$$

The vapour hydrolysis of HC(O)C(O)Cl, giving glyoxalic acid and HCl, resembles that of the oxalyl chloride which gives oxalic acid and HCl.[31]

Experimental

The reactants were commercial-grade products. Trichloroethene was purchased from Mallinckrodt Chemical, freshly opened and purified by several trap-to-trap distillations on a vacuum line, the fraction that distilled between 266 and 271 K being retained each time. NO_2 was obtained from Matheson Gas Products. NO was eliminated from NO_2 by a series of freeze–thaw cycles in the presence of O_2 until the disappearance of the blue colour due to N_2O_3. Finally, the degassed NO_2 was purified by fractional distillation, using the fraction that distilled between 193 and 233 K.

The experiments were performed in a conventional static system for studying gaseous reactions, consisting of a vacuum line and a spherical quartz bulb of 180 cm^3 as a reactor vessel, connected to a quartz spiral gauge used as a zero instrument with respect to a mercury manometer. The reactants were kept in traps at liquid-air temperature. A Lauda thermostat maintained the temperature to within ±0.1 K. The infrared spectra were recorded on a Perkin-Elmer 325 spectrometer, using a 10 cm cell with sodium chloride windows. The chromatograms for determining the molecular weight were performed on a Gow-Mac chromatograph, provided with a density balance detector, using a 5% SE-30 on CG column. N_2 used as a carrier gas was dried by being passed slowly through a Pyrex coil maintained at liquid-air temperature, to prevent the hydrolysis of HC(O)C(O)Cl. The chromatograph constant, *K*, was determined using pure CF_3OF.

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