CHEMICAL KINETICS AND CATALYSIS

The Interaction of Ozone with Chlorobenzene

T. A. Vysokikh, T. V. Yagodovskaya, S. V. Savilov, and V. V. Lunin

Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119992 Russia e-mail: sintestan@mail.ru

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Abstract—The reaction of ozone with chlorobenzene was studied over the temperature range 77–305 K. Ozone was found to oxidize chlorobenzene starting with 77 K to produce a complex mixture of ozonides and peroxides of various compositions. The products of the reaction between chlorobenzene and ozone formed over the temperature range 77–305 K were analyzed by IR Fourier transform spectroscopy.

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INTRODUCTION

Among the great number of problems that trouble the modern society, the protection of the environment is one of the most pressing. The diversity of harmful organic impurities in the biosphere is related to discharges of industrial wastes and utilization of domestic garbage by thermal treatment. This results in the release of chlorinated benzene derivatives formed in the thermal decomposition of polyethylene in the presence of a source of chlorine (e.g., sodium chloride) [1]. One of the methods for solving ecological problems such as the purification of waste water, air, drinking water, industrial wastes, and the products of garbage combustion is the use of ozone as an effective ecologically friendly oxidizer. For instance, chlorobenzene can long exist in the upper atmosphere, and this is one of the agents that destroy ozone in the stratosphere.

According to [2, 3], a decrease in the concentration of ozone in the ozone layer is related to the presence of active chlorine, whose source is HCl. A laboratory study of the interaction of ozone with HCl under the conditions close to stratospheric was performed. A model of atmospheric clouds (ice–HCl–ozone, T =77 K) [2, 3] was used to show that HCl interacted with ozone over the temperature range 77–273 K to produce chlorine oxides of various compositions. No similar data on chlorinated aromatic compounds were reported. This work is concerned with the possibility of the oxidation of chlorobenzene with ozone at temperatures close to the stratosphere temperature.

The oxidation of aromatic compounds with ozone has been studied poorly. As is suggested in many works [4– 10], the mechanism of the reaction between ozone and aromatic compounds is similar to the mechanism of ozone–olefin interactions. The properties of the ozonides produced, such as their impact or friction sensitivity, are somewhat different. According to [11], the charge-transfer complex formed initially under the action of ozone on a multiple bond can transform along three parallel directions, with the formation of moloozonide, σ -complex, and ion-radical pair at equilibrium with the complex. The σ -complex can transform into epoxy and oxy derivatives, and the ion-radical pair containing mobile hydrogen easily gives the R[•] and •OH radicals.

The ozonation of substituted benzenes was studied in [11-13]. The authors showed that the attack of ozone was electrophilic in character, that is, was directed at the atom with the lowest localization energy [11]. According to [11], the reactivity of aromatic compounds increases as the number of electron donor substituents in the ring grows. The presence of electron acceptor substituents in the aromatic ring decreases the rate of the reaction somewhat.

According to [14], the ozonation of chlorobenzene in chloroform at 228 K follows the scheme



EXPERIMENTAL

The reaction of ozone with chlorobenzene was performed following two procedures, by the oxidation of pure chlorobenzene with an ozone–oxygen mixture in a bubbling reactor over the temperature range 273–305 K and by the low-temperature ozonation of chloroben-



Fig. 1. IR spectra of the (1) ice–chlorobenzene system at 77 K, (2) ice–chlorobenzene–ozone system at 77 K, and (3) ice–chlorobenzene–ozone system at 273 K over the frequency ranges (a) 650-950 and (b) 1500-2300 cm⁻¹.

zene with the use of a flow vacuum electric discharge unit. The latter reaction was studied in situ by IR spectroscopy over the temperature range 77-292 K. The main part of the flow vacuum electric discharge unit was a discharge tube for the preparation of pure ozone from a glow discharge plasma in oxygen. The unit was connected to a low-temperature optical cell with a system of three golden mirrors, on which vapors of the substances studied condensed. Prior to measurements, the unit was evacuated to 10^{-4} torr. Water and chlorobenzene were sequentially deposited at 77 K onto the mirrors of the low-temperature optical cell from a vaporizer held at 292 K. The cell was mounted in the light beam path of an IR Fourier transform spectrometer. The reagents were introduced in a pulsed mode, by turning the capillary cock of the vaporizer. The ice-chlorobenzene system prepared this way was brought in contact at a 6×10^{-3} torr residual pressure (77 K) with ozone, whose initial pressure was 1.0 torr. Reaction products were analyzed by recording their IR spectra over the wave number range $600-2500 \text{ cm}^{-1}$.

The ozonation of liquid chlorobenzene was studied in the bubbling reactor. The unit contained ozonizer, trap, ozonometer, reactor, and connecting pipes. An ozone–oxygen mixture was introduced into the reactor filled with chlorobenzene through an exhaust pipe with a glass splitter for the gas mixture jet. The splitter welded at the end of the pipe had the shape of a hollow ball. The reaction was performed at the initial ozone concentration 90–92 g/ml; the volume flow rate of the O_3/O_2 gas mixture was 0.2 l/min. The products were analyzed IR spectroscopically (FSM 1201), by gas chromatography (Agilent Technologies 6890N with a flame-ionization detector), and chromato-mass spectrometrically (Finnigan MAT 112S with a Varian 3300 gas chromatograph).

RESULTS AND DISCUSSION

When gaseous ozone was introduced into the lowtemperature cell with a layer of water and chlorobenzene deposited on the surface of mirrors at 77 K, the instantaneous interaction of ozone with the system was observed, which manifested itself by the appearance of new characteristic bands in the IR spectrum (Fig. 1).

The wave numbers of the products of chlorobenzene interaction with ozone at 77 K are listed in Table 1. The spectra of the reaction products were different from that of the initial ice–chlorobenzene system (Fig. 1, spectra *1* and 2), they contained new absorption bands that might be assigned to stretching vibrations of phenols and the corresponding ozonides.

The absorption bands of ozone (656 and 678 cm⁻¹) and chlorobenzene (740 cm⁻¹) disappeared as the temperature of the sample increased to 273 K, and the intensities of the characteristic lines at 1727, 1688, and 886 cm⁻¹ decreased (Fig. 1, spectra 2 and 3). These lines can be assigned to ozonides of aromatic compounds. Simultaneously, new absorption bands at 854, 1752, and 1850 cm⁻¹ corresponding to vibrations of aromatic peroxide compounds (830–890 and 1755–1785 cm⁻¹ [18–20]) appeared. This was evidence that the reaction between chlorobenzene and ozone continued.

Groups of absorption bands of the corresponding ozonides and peroxo compounds (886 cm⁻¹), ozone (1267 and 1285 cm⁻¹), and chlorobenzene (1446, 1477, and 1700 cm⁻¹) [18–20] disappeared sequentially as the temperature of the sample increased to 292 K and the

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Ι	II	Assignment
656, 678, 1105	612, 705, 1110 [2, 15]	Ozone O–O bond stretching vibrations
1267, 1285	1260, 1280 [16, 17]	
1688	1660–1620 [18]	Stretching vibrations of the C=C bond conjugated with the O atom
886, 1727	882, 1720 [18]	Ozonide O–O stretching vibrations
3595	3654 [19]	Phenol absorption bands
2980, 3061	3030–3060 [19, 20]	Chlorobenzene C-H stretching vibrations
1700	1625–1575 [19, 20]	Chlorobenzene aromatic ring in-plane C=C stretching
1477	1475–1525 [19, 20]	vibrations
1446	1465–1440 [19, 20]	
685, 704	680–720 [19]	Monosubstituted benzene out-of-plane C-H bending
908	900 [19]	vibrations
746	742 [20]	C–Cl stretching vibrations

Table 1. IR absorption spectra of the ice–chlorobenzene-ozone system at 77 cm⁻¹; wave numbers ν (cm⁻¹) according to (I) our and (II) literature data

Table 2. IR spectrum of the solid phase; wave numbers v (cm⁻¹) according to (I) our and (II) literature data

Ι	II	Assignment
3650-3100	3400, 3220 [21]	H ₂ O stretching vibrations
3069	3030–3060 [19, 20]	C–H stretching vibrations
1585	1590–1575 [19, 20]	Aromatic ring C=C stretching vibrations
1477	1475–1525 [19, 20]	
1446	1440–1465 [19, 20]	
1154	1175–1125 [19, 20]	Aromatic compound in-plane C-H bending vibrations
1081	1110–1070 [19, 20]	
1023	1070–1000 [19, 20]	
1004	1000 [18]	Peroxo compound O–O vibrations
904, 1770, 1792	882, 1772, 1792 [18]	Ozonide O–O vibrations
740	742 [20]	C–Cl stretching vibrations
684, 702	720–680 [19]	Out-of-plane C–H bending vibrations
		1

compounds specified were removed from the surface of the low-temperature cell mirrors.

When pure chlorobenzene was ozonized in the bubbling reactor, a virtually instantaneous change in liquid phase coloration was observed. The intensity of the color of chlorobenzene increased as the temperature of the reactor grew, and the solution took on various tinges of yellow. At 273 K, it was pale yellow with a tinge of green, at 293 K, it was yellow, and, at 305 K, it was bright yellow. According to [14], the observed coloration could be caused by the formation of a colored π -complex between chlorobenzene and ozone. Subsequent bubbling of the ozone–oxygen mixture through chlorobenzene first caused turbidity and then the precipitation of a white powder.

A study of the liquid phase by gas chromatography showed that the major solution component was chlorobenzene (98 vol %). The composition of the complex mixture of ozonation products (2 vol %) was analyzed by chromato-mass spectrometry; it was found to contain phenol and chlorophenols.

The solid phase formed in the reaction was insoluble in either water or organic solvents (*n*-pentane, *n*-hexane, ethanol, benzene, and toluene). It exploded in the dry state in air under the slightest mechanical actions.



Fig. 2. IR spectrum of the solid phase at 292 K over the frequency range 500-3500 cm⁻¹.

Wetting the precipitate with solvents decreased the probability of explosion.

To model the composition of the solid phase formed, a sample deposited on a KBr pellet was analyzed IR spectroscopically. The results are shown in Fig. 2 and listed in Table 2. A comparison of the vibrational frequencies observed with the literature data allowed us to approximately assign them to stretching vibrations of the chlorobenzene ozonide molecule likely stabilized by the presence of chlorine in the benzene ring. According to [11, 14, 22], the following interaction mechanism can be suggested:



The major product at early stages is moloozonide.

To summarize, a comparison of the experimental and literature data showed that ozone reacted with chlorobenzene over a wide temperature range (77–305 K) with the formation of a complex mixture of compounds and moloozonide as an intermediate product.

REFERENCES

- Lehrbuch der ökologischen Chemie: Grundlagen und Konzepte für die ökologische Beurteilung von Chemikalien, Ed. by F. Korte (G. Thieme, Stuttgart, 1992; Mir, Moscow, 1997).
- T. V. Yagodovskaya, R. A. Gromov, A. V. Zosimov, and V. V. Lunin, Zh. Fiz. Khim. **73** (5), 857 (1999) [Russ. J. Phys. Chem. **73** (5), 751 (1999)].
- T. V. Yagodovskaya, S. V. Savilov, A. V. Zosimov, and V. V. Lunin, Zh. Fiz. Khim. 74 (6), 1149 (2000) [Russ. J. Phys. Chem. 74 (6), 1028 (2000)].
- V. D. Komissarov and I. N. Komisarova, Izv. Akad. Nauk SSSR, Ser. Khim., 677 (1973).
- 5. S. D. Razumovskii and G. E. Zaikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2657 (1971).

- P. S. Baley, S. Bath, F. Dobinson, et al., J. Org. Chem. 29, 697 (1964).
- M. G. Sturrock, B. J. Cravy, and V. A. Wing, Can. J. Chem. 49, 3047 (1971).
- P. S. Baley and J. E. Batterbee, J. Org. Chem. 29, 1400 (1964).
- P. S. Baley, J. E. Batterbee, and A. G. Lane, J. Am. Chem. Soc. 90 (4), 1027 (1968).
- C. R. Noller and G. K. Kaneko, J. Am. Chem. Soc. 57, 2442 (1935).
- 11. V. A. Yakobi, Tr. Mosk. Khim.-Tekhnol. Inst. im. Mendeleeva, No. 103, 66 (1979).
- 12. V. A. Yakobi, Zh. Fiz. Khim. 66 (4), 867 (1992).
- A. V. Mamchur, G. A. Galstyan, and E. V. Potapenko, Neftekhimiya 42 (4), 287 (2002) [Pet. Chem. 42 (4), 257 (2002)].
- J. P. Wibaut and F. L. J. Sixma, Recl. Trav. Chim. Pays-Bas 71, 761 (1952).
- M. K. Wilson and R. D. Ogg, J. Chem. Phys. 18 (5), 766 (1950).
- T. V. Yagodovskaya, L. I. Nekrasov, and N. P. Klimushina, Zh. Fiz. Khim., No. 4, 902 (1967).

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- 17. T. V. Yagodovskaya, M. R. Khadzhi-Ogly, and L. I. Nekrasov, Zh. Fiz. Khim. **60** (4), 922 (1986).
- Technique of Organic Chemistry, Ed. by A. Weissberger, Vol. 9: Chemical Applications of Spectroscopy, Ed. by W. West (Interscience, New York, 1956; Inostrannaya Literatura, Moscow, 1959).
- 19. L. A. Kazitsyna and N. B. Kupletskaya, Application of UV, IR, NMR, and Mass Spectroscopy in Organic

Chemistry (Mosk. Gos. Univ., Moscow, 1979) [in Russian].

- 20. A. D. Cross, *An Introduction to Practical Infra-Red Spectroscopy* (Butterworths, London, 1960; Inostrannaya Literatura, Moscow, 1961).
- 21. G. V. Yukhnevich, *Infrared Spectroscopy of Water* (Nauka, Moscow, 1973) [in Russian].
- 22. R. Criegee, Chimia 22, 392 (1968).