

Kinetics and mechanism of the gas phase reaction of Cl atoms with iodobenzene

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Abstract

Smog chamber/FTIR techniques were used to study the kinetics and mechanism of the reaction of Cl atoms with iodobenzene (C₆H₅I) in 20–700 Torr of N₂, air, or O₂ diluent at 296 K. The reaction proceeds with a rate constant $k(\text{Cl} + \text{C}_6\text{H}_5\text{I}) = (3.3 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to give chlorobenzene (C₆H₅Cl) in a yield which is indistinguishable from 100%. The title reaction proceeds via a displacement mechanism (probably addition followed by elimination). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

A detailed understanding of the atmospheric chemistry of aromatic compounds is needed for an accurate assessment of their environmental impact following release into the atmosphere. Unfortunately, substantial uncertainties exist in our understanding of the atmospheric oxidation mechanisms of aromatic species [1]. In smog chamber studies of the atmospheric degradation mechanisms of organic compounds it is often convenient to use Cl atoms to initiate the sequence of photooxidation reactions. In flash photolysis

studies of the spectroscopy and kinetics of radical intermediates formed during the oxidation of aromatic compounds it is often convenient to produce the radicals via reaction of Cl atoms with suitable organic precursors. Kinetic and mechanistic data concerning the reaction of Cl atoms with aromatic compounds are needed to facilitate the design and interpretation of smog chamber and flash photolysis studies. We report here the results of the first kinetic and mechanistic study of the reaction of Cl atoms with iodobenzene.

2. Experimental

Experiments were performed in a 140 l Pyrex reactor interfaced to a Mattson Sirius 100 FTIR

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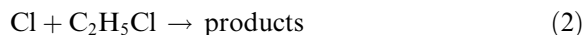
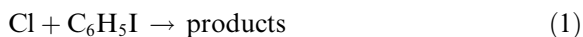
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spectrometer [2]. The optical path length of the infrared beam was 27 m. The reactor was surrounded by 22 fluorescent blacklamps (GE F40BLB), which were used to generate Cl atoms by photolysis of Cl_2 . Reactant and product concentrations were monitored by Fourier transform infrared spectroscopy using characteristic absorption features in the wavenumber range 700–1850 cm^{-1} . IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} . Reference spectra were acquired by expanding known volumes of reference material into the chamber. Experiments were performed at 296 K in 20–700 Torr of N_2 , air, or O_2 diluent. All reactants were obtained from commercial sources at purities >99%. Ultrahigh purity nitrogen and air diluent gases were used as received. The samples of $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{Cl}$ were subjected to repeated freeze-pump-thaw cycles before use. In smog chamber experiments unwanted loss of reactants and products via photolysis and heterogeneous reactions have to be considered. Control experiments were performed in which product mixtures obtained after UV irradiation of $\text{C}_6\text{H}_5\text{I}/\text{Cl}_2/\text{air}$ mixtures were allowed to stand in the dark in the chamber for 15 min. There was no observable (<2%) loss of reactants or products, showing that heterogeneous reactions or products are not a significant complication over the time scale of the present experiments. The IR features used for analysis were: $\text{C}_6\text{H}_5\text{I}$ (731 cm^{-1}), $\text{C}_6\text{H}_5\text{Cl}$ (741 cm^{-1}), C_2H_6 (822 cm^{-1}), C_2H_4 (949 cm^{-1}), $\text{C}_2\text{H}_5\text{Cl}$ (677, 1288 cm^{-1}). Analysis of the IR spectra was achieved through a process of spectral stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum.

3. Results and discussion

3.1. Relative rate study of the $\text{Cl} + \text{C}_6\text{H}_5\text{I}$ reaction in 20, 100 and 700 Torr of N_2 or air

The kinetics of reaction (1) were measured relative to reactions (2)–(4):



Initial reactant concentrations were 5–10 mTorr of $\text{C}_6\text{H}_5\text{I}$, 100 mTorr of Cl_2 , and 5–10 mTorr of one of the three references in 20, 100, or 700 Torr of either N_2 , or air, diluent. The observed loss of $\text{C}_6\text{H}_5\text{I}$ versus that of the reference compounds in the presence of Cl atoms is shown in Fig. 1. As seen from Fig. 1, there was no observable effect of total pressure (20–700 Torr) or nature of the diluent gas (N_2 or air) on the kinetics of reaction (1). Linear least-squares analysis of the data in Fig. 1 gives $k_1/k_2 = 3.77 \pm 0.25$, $k_1/k_3 = 0.56 \pm 0.05$, and $k_1/k_4 = 0.39 \pm 0.03$, quoted uncertainties are two standard deviations from the linear regressions. Using $k_2 = (8.04 \pm 0.57) \times 10^{-12}$ [3], $k_3 = (5.75 \pm 0.45) \times 10^{-11}$ [4], and $k_4 = (9.29 \pm 0.51) \times 10^{-11}$ [5] $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ we derive $k_1 = (3.03 \pm 0.29) \times 10^{-11}$, $(3.22 \pm 0.38) \times 10^{-11}$, and $(3.62 \pm 0.34) \times$

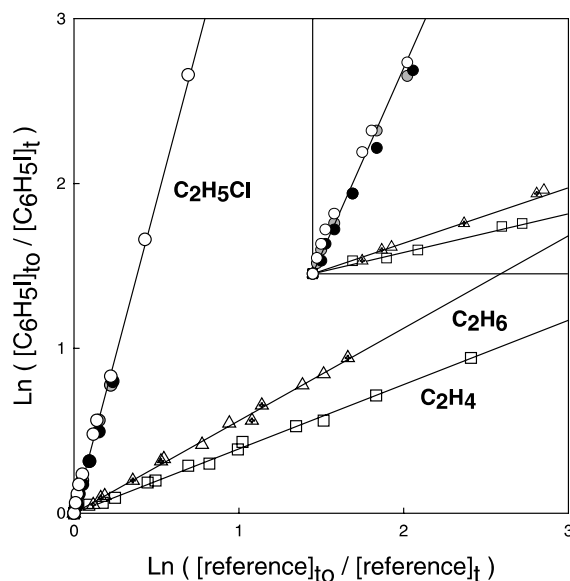


Fig. 1. Decay of $\text{C}_6\text{H}_5\text{I}$ versus the reference compounds $\text{C}_2\text{H}_5\text{Cl}$ (circles), C_2H_6 (diamonds) or C_2H_4 (triangles) in the presence of Cl atoms in 700 (open symbols), 100 (shaded symbols) or 20 (solid symbols) Torr of either air (cross-hair marked symbols) or N_2 (unmarked symbols) diluent. For clarification, the initial data range is included as an insert.

$10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We choose to cite a final value for k_1 which is the average of those determined using the three different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_1 = (3.3 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3.2. Product study $\text{Cl} + \text{C}_6\text{H}_5\text{I}$ in 700 Torr N_2 or O_2

To investigate the products of the reaction of Cl atoms with $\text{C}_6\text{H}_5\text{I}$, mixtures of 5.4–15.2 mTorr $\text{C}_6\text{H}_5\text{I}$ and 25–100 mTorr Cl_2 in 700 Torr of either N_2 , or O_2 , diluent were introduced into the reaction chamber and irradiated using the UV black-lamps. Consumptions of $\text{C}_6\text{H}_5\text{I}$ were in the range 3–90%. Fig. 2 shows spectra acquired before (A) and after (B) a 110 s irradiation of a mixture of 8.1 mTorr $\text{C}_6\text{H}_5\text{I}$ and 25 mTorr Cl_2 in 700 Torr of O_2 . The consumption of $\text{C}_6\text{H}_5\text{I}$ was 33%. Comparison of the IR features in panel B with the reference spectrum of $\text{C}_6\text{H}_5\text{Cl}$ given in panel C shows the

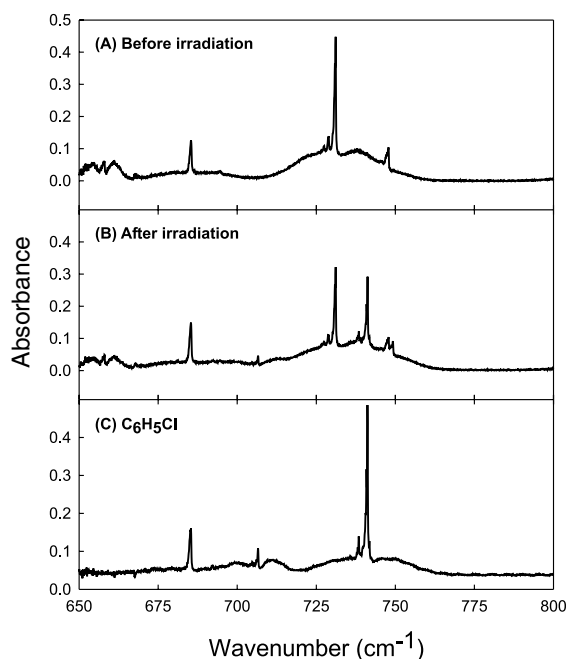


Fig. 2. IR spectra obtained before (A) and after (B) 110 s of irradiation of a mixture of 8.1 mTorr $\text{C}_6\text{H}_5\text{I}$ and 25 mTorr Cl_2 in 700 Torr of O_2 . Panel C is reference spectrum of $\text{C}_6\text{H}_5\text{Cl}$.

formation of this compound. The feature at 685 cm^{-1} is present in spectra for both $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{I}$. A small unidentified product feature was observed at 749 cm^{-1} . $\text{C}_6\text{H}_5\text{Cl}$ was the only carbon-containing product identified.

Fig. 3 shows the observed formation of $\text{C}_6\text{H}_5\text{Cl}$ versus the loss of $\text{C}_6\text{H}_5\text{I}$ following UV irradiation of $\text{C}_6\text{H}_5\text{I}/\text{Cl}_2$ mixtures in 700 Torr of either O_2 or N_2 diluent. As seen from Fig. 3, there was no discernable difference between the results obtained in O_2 and N_2 diluent. The straight line in Fig. 3 is a linear least-squares fit which gives a $(101 \pm 7)\%$ molar yield of chlorobenzene in 700 Torr of either N_2 and O_2 . Quoted errors are two standard deviations from the regression analysis. We estimate that possible systematic errors associated with uncertainties in the calibration of the reference spectra for $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{Cl}$ combine to give an additional 10% uncertainty in the $\text{C}_6\text{H}_5\text{Cl}$ product yield. Within the experimental uncertainties, the observed formation of $\text{C}_6\text{H}_5\text{Cl}$ accounts for 100% of the loss of $\text{C}_6\text{H}_5\text{I}$.

The reaction of Cl atoms with iodobenzene can proceed either via abstraction or displacement. Abstraction would give a phenyl radical and ICl as initial products. Displacement would give

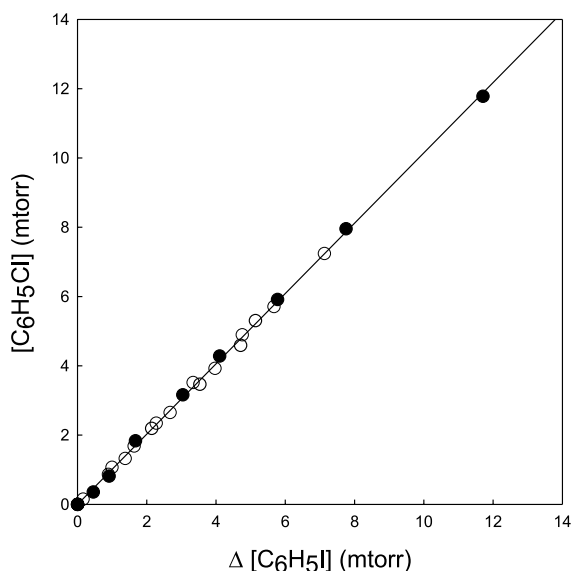
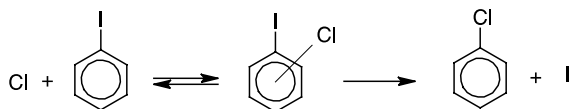


Fig. 3. Yield of $\text{C}_6\text{H}_5\text{Cl}$ versus loss of $\text{C}_6\text{H}_5\text{I}$ in 700 Torr of either N_2 (filled symbols) or O_2 (open symbols).

chlorobenzene and an I atom. In 700 Torr of N₂ diluent the fate of the phenyl radical will be the reaction with molecular chlorine to give chlorobenzene and a chlorine atom. In 700 Torr of O₂ diluent the phenyl radical will add O₂ rapidly to give a phenyl peroxy radical [6] which, in turn, will react to give 4-phenoxyphenol via formation of a phenoxy radical [7]. From the fact that chlorobenzene is observed as a product in essentially 100% yield in the absence *and presence* of O₂ we conclude that the reaction of Cl atoms with C₆H₅I occurs via a displacement mechanism in which the incoming Cl atom displaces the I atom. In light of the known propensity of Cl atoms to form short-lived adducts with aromatic compounds [8,9] it seems reasonable to speculate that the reaction mechanism probably proceeds via the formation of the C₆H₅I–Cl adduct which then decomposes to give C₆H₅Cl + I.



A similar process has been proposed for the reaction of Cl atoms with nitrobenzene [10]. Wahner and Zetzsch [11] have speculated that a similar mechanism may play a role in the reaction of OH radicals with chlorinated aromatics with decomposition of the adduct proceeding in part via loss of a Cl atom. Reaction (1) is not a convenient source of phenyl radicals for laboratory study.

3.3. Conclusions

It is shown here that the reaction of Cl atoms with C₆H₅I occurs with a rate constant of

$(3.3 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K in 20–700 Torr of air or N₂ diluent. The mechanism of the reaction is rather unusual for a gas-phase reaction involving Cl atoms. The reaction proceeds via a displacement mechanism to give C₆H₅Cl as the sole carbon-containing compound.

Acknowledgements

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