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

ARTICLE *in* CHEMICAL PHYSICS LETTERS · DECEMBER 2001

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(01)01318-5

5 AUTHORS, INCLUDING:

M. P. Sulbaek Andersen
California State University, Northridge

Ole John Nielsen
University of Copenhagen

28 December 2001

Chemical Physics Letters 350 (2001) 423–426

ELSEVIER

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

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

M.P. Sulbaek Andersen [a], D.A. Ponomarev [b], O.J. Nielsen [c], M.D. Hurley [d,*], T.J. Wallington [d]

[a] *Department of Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark*
[b] *St. Petersburg Forest Technical Academy, 194021 St. Petersburg, Russia*
[c] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark*
[d] *Ford Research Laboratory, SRL-3083, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121-2053, USA*

Received 20 August 2001; in final form 11 October 2001

Abstract

Smog chamber/FTIR techniques were used to study the kinetics and mechanism of the reaction of Cl atoms with iodobenzene (C_6H_5I) in 20–700 Torr of N_2, air, or O_2 diluent at 296 K. The reaction proceeds with a rate constant $k(Cl + C_6H_5I) = (3.3 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} to give chlorobenzene (C_6H_5Cl) in a yield which is indistinguishable from 100%. The title reaction proceeds via a displacement mechanism (probably addition followed by elimination).

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 Sirus 100 FTIR

* Corresponding author. Fax: +1-313-594-2923.
E-mail address: mhurley3@ford.com (M.D. Hurley).

0009-2614/01/$ - see front matter
PII: S0009-2614(01)01318-5

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 C_6H_5I and C_6H_5Cl 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 C_6H_5I/Cl_2/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: C_6H_5I (731 cm^{-1}), C_6H_5Cl (741 cm^{-1}), C_2H_6 (822 cm^{-1}), C_2H_4 (949 cm^{-1}), C_2H_5Cl (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 $Cl + C_6H_5I$ reaction in 20, 100 and 700 Torr of N_2 or air

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

$$Cl + C_6H_5I \rightarrow \text{products} \tag{1}$$

$$Cl + C_2H_5Cl \rightarrow \text{products} \tag{2}$$

$$Cl + C_2H_6 \rightarrow \text{products} \tag{3}$$

$$Cl + C_2H_4 \rightarrow \text{products} \tag{4}$$

Initial reactant concentrations were 5–10 mTorr of C_6H_5I, 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 C_6H_5I 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] cm^3 molecule^{-1} s^{-1} we derive $k_1 = (3.03 \pm 0.29) \times 10^{-11}$, $(3.22 \pm 0.38) \times 10^{-11}$, and $(3.62 \pm 0.34) \times$

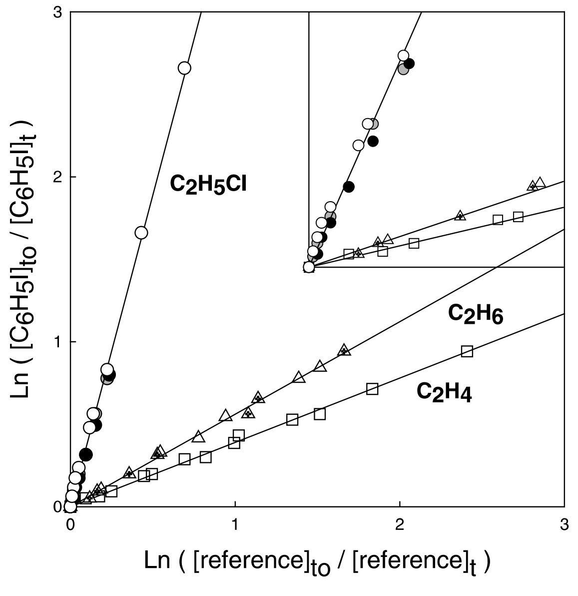


Fig. 1. Decay of C_6H_5I versus the reference compounds C_2H_5Cl (circles), C_2H_6 (diamonds) or C_2H_4 (triangles) in the presence of Cl atoms in 700 (open symbols), 100 (shaded symbols) or 20 (solid symbols) Torr of either air (cross-hair marked symbols) or N_2 (unmarked symbols) diluent. For clarification, the initial data range is included as an insert.

10^{-11} cm^3 molecule^{-1} 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, $k_1 = (3.3 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

3.2. Product study $Cl + C_6H_5I$ in 700 Torr N_2 or O_2

To investigate the products of the reaction of Cl atoms with C_6H_5I, mixtures of 5.4–15.2 mTorr C_6H_5I 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 blacklamps. Consumptions of C_6H_5I 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 C_6H_5I and 25 mTorr Cl_2 in 700 Torr of O_2. The consumption of C_6H_5I was 33%. Comparison of the IR features in panel B with the reference spectrum of C_6H_5Cl given in panel C shows the formation of this compound. The feature at 685 cm^{-1} is present in spectra for both C_6H_5Cl and C_6H_5I. A small unidentified product feature was observed at 749 cm^{-1}. C_6H_5Cl was the only carbon-containing product identified.

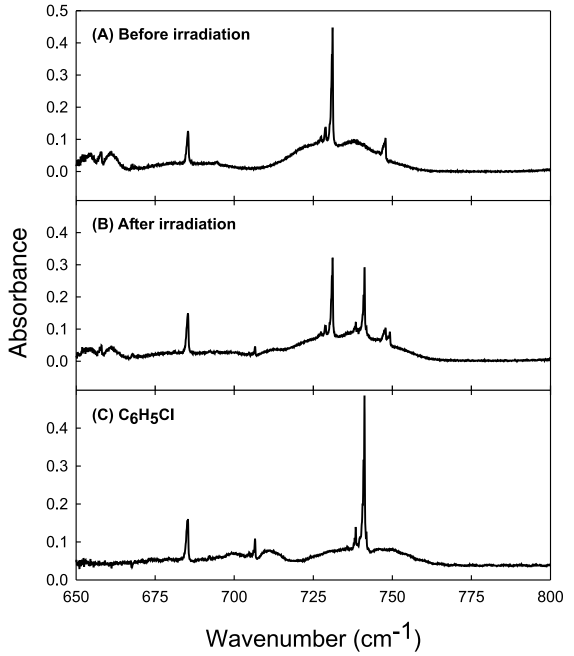


Fig. 2. IR spectra obtained before (A) and after (B) 110 s of irradiation of a mixture of 8.1 mTorr C_6H_5I and 25 mTorr Cl_2 in 700 Torr of O_2. Panel C is reference spectrum of C_6H_5Cl.

Fig. 3 shows the observed formation of C_6H_5Cl versus the loss of C_6H_5I following UV irradiation of C_6H_5I/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 ± 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 C_6H_5I and C_6H_5Cl combine to give an additional 10% uncertainty in the C_6H_5Cl product yield. Within the experimental uncertainties, the observed formation of C_6H_5Cl accounts for 100% of the loss of C_6H_5I.

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

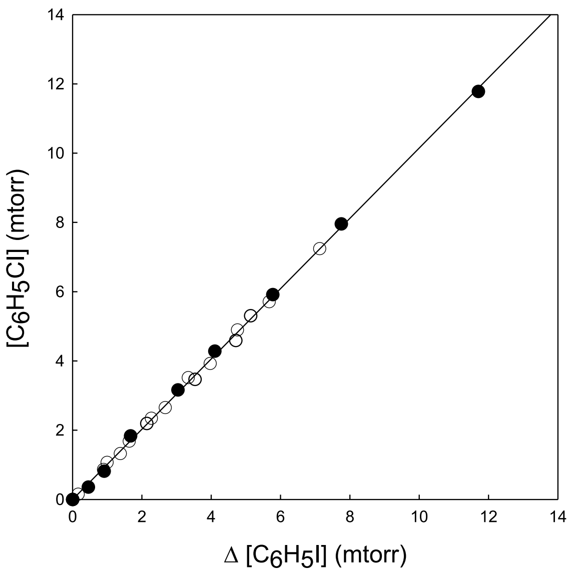
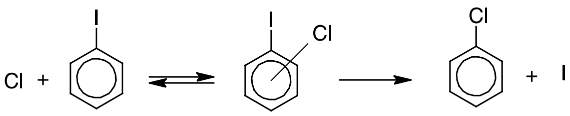


Fig. 3. Yield of C_6H_5Cl versus loss of C_6H_5I in 700 Torr of either N_2 (filled symbols) or O_2 (open symbols).

chlorobenzene and an I atom. In 700 Torr of N_2 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 O_2 diluent the phenyl radical will add O_2 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 O_2 we conclude that the reaction of Cl atoms with C_6H_5I 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 C_6H_5I–Cl adduct which then decomposes to give $C_6H_5Cl + I$.



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 C_6H_5I occurs with a rate constant of $(3.3 \pm 0.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K in 20–700 Torr of air or N_2 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 C_6H_5Cl as the sole carbon-containing compound.

Acknowledgements

We thank Christian Lohse (University of Southern Denmark) for helpful discussions.

References

[1] J.G. Calvert, R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.J. Wallington, G. Yarwood, Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, Oxford, 2001.
[2] T.J. Wallington, S.M. Japar, J. Atmos. Chem. 9 (1989) 399.
[3] P.H. Wine, D.H. Semmes, J. Phys. Chem. 87 (1983) 3572.
[4] G.S. Tyndall, J.J. Orlando, T.J. Wallington, M. Dill, E.W. Kaiser, Int. J. Chem. Kinet. 29 (1997) 43.
[5] T.J. Wallington, J.M. Andino, I.M. Lorkovic, E.W. Kaiser, G. Marston, J. Phys. Chem. 94 (1990) 3644.
[6] T. Yu, M.C. Lin, J. Am. Chem. Soc. 115 (1993) 4371.
[7] J. Platz, O.J. Nielsen, T.J. Wallington, J.C. Ball, M.D. Hurley, A.M. Straccia, W.F. Schneider, J. Sehested, J. Phys. Chem. A 102 (1998) 7964.
[8] O. Sokolov, M.D. Hurley, T.J. Wallington, E.W. Kaiser, J. Platz, O.J. Nielsen, F. Berho, M.T. Rayez, R. Lesclaux, J. Phys. Chem. A 102 (1998) 10671.
[9] G.A. Russell, J. Am. Chem. Soc. 80 (1958) 4987.
[10] L. Frøsig, O.J. Nielsen, M. Bilde, T.J. Wallington, J.J. Orlando, G.S. Tyndall, J. Phys. Chem. A 104 (2000) 11328.
[11] A. Wahner, C. Zetzsch, J. Phys. Chem. 87 (1983) 4945.