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Kinetics and Mechanism of the Reaction of Cl Atoms with Nitrobenzene

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Smog chamber/FTIR techniques were used to study the kinetics and mechanism of the reaction of Cl atoms with nitrobenzene ($C_6H_5NO_2$) in 10−700 Torr of N_2, or air, at 296 K. The reaction proceeds with a rate constant $k(Cl + C_6H_5NO_2) = (9.3 \pm 1.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} to give C_6H_5Cl and NO_2 products in essentially 100% yield. The observed product yields suggest that the reaction proceeds via a displacement mechanism (probably addition followed by elimination). The UV−visible absorption spectrum of $C_6H_5NO_2$ was measured. Photolysis of $C_6H_5NO_2$ is estimated to occur at a rate of $(3 \pm 2) \times 10^{-5}$ s^{-1} for a solar zenith angle of 25° (representative of a typical summer day at 40°N) and is likely to be the dominant atmospheric loss mechanism for $C_6H_5NO_2$.

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 mechanism of organic compounds it is often convenient to use Cl atoms to initiate the sequence of photooxidation reactions. To facilitate the design and interpretation of such experiments, kinetic and mechanistic data concerning the reaction of Cl atoms with aromatic compounds are needed. We report here the results of a kinetic and mechanistic study of the reaction of Cl atoms with nitrobenzene in 10−700 Torr of N_2 or air diluent at 296 K. In addition, the UV spectrum and approximate photolysis quantum yield for nitrobenzene in the UV are reported, and these data are used to estimate the atmospheric photolysis rate of this species.

Experimental Section

FTIR Smog Chamber System at Ford. Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[2] The optical path length of the infrared beam was 27 m. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), 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 materials into the chamber. All experiments were performed at 296 K. All reactants were obtained from commercial sources at purities >99%. The samples of $C_6H_5NO_2$ 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 the UV irradiation of $C_6H_5NO_2/Cl_2$/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 are not a significant complication.

UV−Visible Absorption Spectrum Measurements at NCAR. The UV absorption spectrum of $C_6H_5NO_2$ was measured over the range 210−400 nm, using a diode array spectrometer system described in detail elsewhere.[3] The system consisted of a 90-cm long Pyrex absorption cell equipped with quartz windows. The output from a deuterium lamp was collimated through the absorption cell, focused onto the entrance slit of a 0.3 m Czerny−Turner spectrograph, and dispersed onto a 1024-element diode array detector. The spectrograph was equipped with a 300 grooves mm^{-1} grating, and provided spectra with a resolution of 0.6 nm. The wavelength scale of the spectrometer system was calibrated using emission lines from a low-pressure Hg Penray lamp. Spectra were obtained from the summation of 100 exposures of the diode array, each of 0.15 s duration. Spectra were measured both with the cell evacuated (I_o) and with the cell filled with a gaseous sample (I) and converted to absorbance (A), where $A = \ln(I_o/I)$.

$C_6H_5NO_2$ liquid was obtained from Aldrich Chemical Co. at a stated purity of >99%. Gas-phase $C_6H_5NO_2$ samples were obtained by expanding the vapor above a liquid sample into

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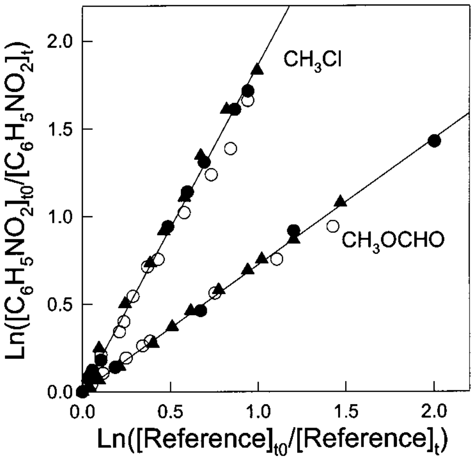


Figure 1. Decay of $C_6H_5NO_2$ versus the reference compounds (CH_3Cl or CH_3OCHO) in the presence of Cl atoms in 700 (circles) or 10 Torr (triangles) total pressure of either air (filled symbols) or N_2 (open symbols) diluent.

the absorption cell. Before use, the liquid $C_6H_5NO_2$ sample was purified by multiple freeze−pump−thaw cycles. Purified samples were transferred to the absorption cell, and absorbance spectra were recorded at room temperature (296 ± 2 K). The absorption cell was purged with a small flow of N_2 between measurements.

Results

Relative Rate Study of the Cl + $C_6H_5NO_2$ Reaction in 10 and 700 Torr of N_2/Air. The kinetics of reaction 1 were measured relative to reactions 2 and 3:

$$\mathrm{Cl} + \mathrm{C_6H_5NO_2} \rightarrow \text{products} \qquad (1)$$

$$\mathrm{Cl} + \mathrm{CH_3Cl} \rightarrow \text{products} \qquad (2)$$

$$\mathrm{Cl} + \mathrm{CH_3OCHO} \rightarrow \text{products} \qquad (3)$$

Initial concentrations were 1.8−3.0 mTorr of $C_6H_5NO_2$, 100 mTorr of Cl_2, and 6−24 mTorr of the two references in 10 or 700 Torr of either N_2, or air, diluent. The observed loss of $C_6H_5NO_2$ versus those of the reference compounds in the presence of Cl atoms is shown in Figure 1. As seen from Figure 1 there was no observable effect of total pressure over the range 10−700 Torr, or nature of the diluent gas (air or N_2). Linear least-squares analysis of the data in Figure 1 gives $k_1/k_2 = 1.81 \pm 0.17$ and $k_1/k_3 = 0.71 \pm 0.06$ with the quoted uncertainties being ± two standard deviations. Using $k_2 = 4.8 \times 10^{-13}$ [4] and $k_3 = 1.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [5] we derive $k_1 = (8.67 \pm 0.81) \times 10^{-13}$ and $(9.95 \pm 0.84) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We estimate that the potential systematic errors associated with the uncertainties in the reference rate constants add 10% uncertainty range for k_1. Propagating this additional uncertainty gives $k_1 = (8.67 \pm 1.19) \times 10^{-13}$ and $(9.95 \pm 1.30) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_1 which is the average of those determined using two different reference compounds together with the error limits which encompass the extremes of the individual determinations. Hence, $k_1 = (9.3 \pm 1.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Product Study Cl + $C_6H_5NO_2$ in 10−700 Torr N_2 or Air. To investigate the products and mechanism of the reaction of Cl atoms with $C_6H_5NO_2$, mixtures of 4.7−10.0 mTorr $C_6H_5NO_2$ and 100 mTorr Cl_2 in either 10 or 700 Torr of either air or N_2 diluent were introduced into the reaction chamber and irradiated using the UV blacklamps. Typical consumptions of $C_6H_5NO_2$ were in the range 5−50%. Figure 2 shows spectra acquired before (A) and after (B) an 80 s irradiation of a mixture of 4.7 mTorr $C_6H_5NO_2$ and 100 mTorr Cl_2 in 700 Torr of air. Comparison of the IR features in panel B with reference spectra of C_6H_5Cl and NO_2 given in panels C and D shows the formation of these compounds. The product features in panel B at 795, 1265, 1315, 1685 (partly hidden at the left side of the broad feature at 1715 cm^{-1}), and 1715 cm^{-1} are due to formation of $ClNO_2$ and ClONO. C_6H_5Cl was the only carbon-containing product observed.

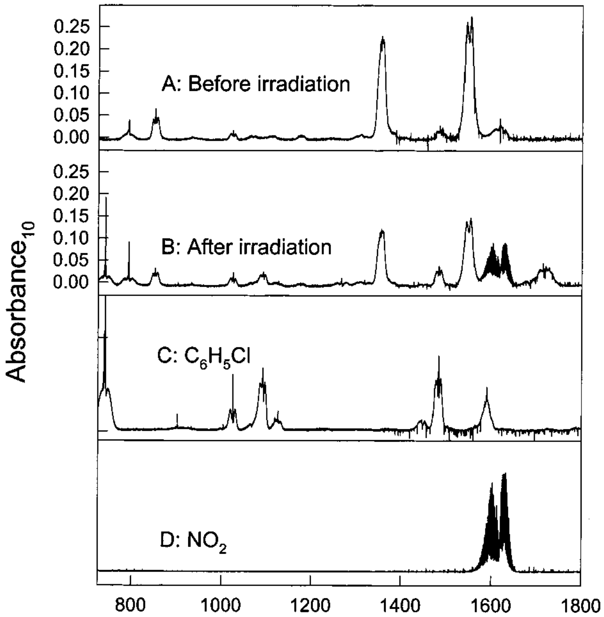


Figure 2. IR spectra obtained before (A) and after (B) 80 s of irradiation of a mixture of 4.7 mTorr $C_6H_5NO_2$ and 100 mTorr Cl_2 in 700 Torr of air. Panels C and D are reference spectra of C_6H_5Cl and NO_2, respectively.

Figure 3 shows plots of the observed formation of C_6H_5Cl and NO_2 versus the loss of $C_6H_5NO_2$ following UV irradiation of C_6H_5Cl/Cl_2 mixtures in N_2 or air diluent. The straight lines in Figure 3 are linear least-squares fits to the data. The curved line through the NO_2 data in panel A is a second-order fit to the data to aid in visual inspection of the data trend. We ascribe the curved nature of the product plot for NO_2 at 700 Torr (Figure 3A) to loss of NO_2 via reaction with Cl atoms to give the two isomers $ClNO_2$ and ClONO:[6]

$$\mathrm{Cl} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{ClNO_2/ClONO} + \mathrm{M} \qquad (4)$$

Reaction 4 is an association reaction and has a rate which increases with total pressure from $k_4 = 4 \times 10^{-13}$ at 10 Torr to $k_4 = 2 \times 10^{-11}$ cm^{-3} molecule^{-1} s^{-1} at 700 Torr.[4] Chlorine atoms react with $ClNO_2$ with a rate constant of 5.5×10^{-12} cm^{-3} molecule^{-1} s^{-1} (independent of total pressure) to regenerate NO_2.[7] Reaction 4 represents a substantial loss of NO_2 for experiments conducted at high pressure but is much less significant at lower pressures. Simulations using the Acuchem chemical kinetic program[8] confirmed that the curvature of the NO_2 yield in Figure 3A is consistent with expectations based upon the discussion above. The reaction of Cl atoms with C_6H_5Cl proceeds extremely slowly and is not important in this work.[9] Linear least-squares analysis of the data in Figure 3 gives molar yields of chlorobenzene at 700 and 10 Torr of 113 ± 6% and 107 ± 8%, respectively, and a 100 ± 9% yield of NO_2 at 10 Torr total pressure. Quoted errors are two standard deviations from the regression analysis. Possible systematic errors associ-

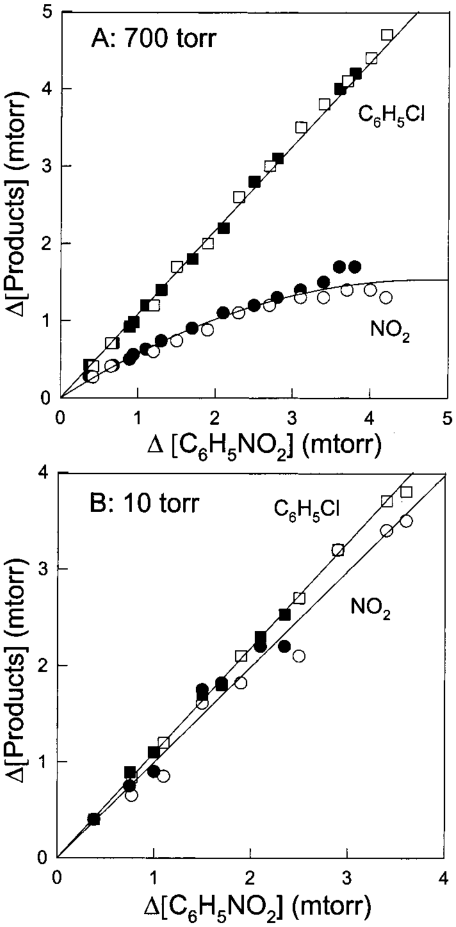
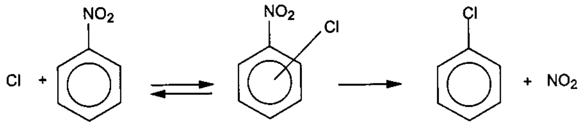


Figure 3. Yield of C_6H_5Cl (squares) and NO_2 (circles) versus loss of $C_6H_5NO_2$ in 700 (A) or 10 (B) Torr of either N_2 (open symbols) or air (filled symbols).

ated with uncertainties in the calibration of the reference spectra for $C_6H_5NO_2$, C_6H_5Cl, and NO_2 combine to give an additional approximately 10% uncertainty in the molar yields for C_6H_5Cl and NO_2. Within the experimental uncertainties the observed formation of C_6H_5Cl and NO_2 accounts for 100% of the loss of $C_6H_5NO_2$. The simplest interpretation of the observed product yields is that the reaction of Cl atoms with $C_6H_5NO_2$ occurs via a displacement mechanism in which the incoming Cl atom displaces the NO_2 group. In light of the known propensity of Cl atoms to form short-lived adducts with aromatic compounds[9-13] it seems reasonable to speculate that the reaction mechanism probably proceeds via the formation of the C_6H_5-NO_2-Cl adduct which then decomposes to give $C_6H_5Cl + NO_2$:



Wahner and Zetzsch[14] 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.

UV−Visible Absorption Spectrum of $C_6H_5NO_2$. The spectrum of $C_6H_5NO_2$ was recorded at NCAR over the wavelength range 225−400 nm. As seen in Figure 4, the spectrum of $C_6H_5NO_2$ in the region of relevance for tropospheric chemistry (>295 nm) consists of a broad featureless shoulder with an absorption cross section of approximately 3.5×10^{-19} cm^2 molecule^{-1} (base e) at 300−340 nm. The spectrum measured here is very similar to that reported by Galloway et al.,[15] though our cross sections appear to be 15−20% lower. The gas-phase UV spectrum of $C_6H_5NO_2$ is very similar in shape to that reported in liquid hexane,[1] solvent effects result in an approximate 20 nm red shift of the $C_6H_5NO_2$ spectrum in hexane.

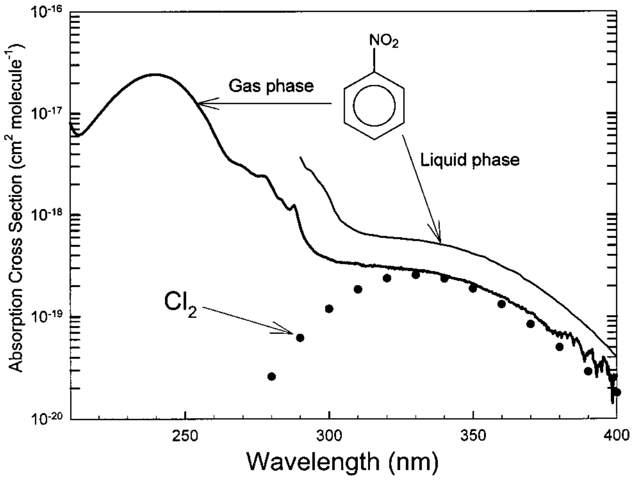


Figure 4. UV−visible spectrum (base e) of $C_6H_5NO_2$ in the gas phase (thick line, this work) and in liquid hexane (thin line).[1] The circles show the absorption spectrum of Cl_2.[4]

To determine a first-order photolysis rate (j) for $C_6H_5NO_2$ in the atmosphere, wavelength-dependent cross section, $\sigma(\lambda)$, quantum yield, $\phi(\lambda)$, and actinic flux, $I(\lambda)$, data are required:

$$j = \int_\lambda \sigma(\lambda)\phi(\lambda)I(\lambda)\mathrm{d}\lambda$$

To the best of our knowledge, no gas-phase photolysis quantum yield data are available for $C_6H_5NO_2$. To provide information concerning $\phi(\lambda)$, experiments were performed using the atmospheric reaction chamber at NCAR[16] in which mixtures of C_6H_5-NO_2 in either 700 Torr N_2 or 250 Torr N_2 and 450 Torr O_2 were irradiated using the output of a Xe arc lamp with a 7−54 filter allowing transmission of 250−420 nm light. The gas mixtures were left to stand in the chamber for 2.5 h during which time the Xe lamp was switched on for 96 min. A small but discernible loss of $C_6H_5NO_2$ was observed, corresponding to a pseudo first-order rate of approximately 1.5×10^{-5} s^{-1} in the dark and 3×10^{-5} s^{-1} with UV irradiation. There was no observable difference in behavior in experiments in N_2 or N_2/O_2 diluent. NO_2 was observed as a photolysis product with yields of about 50% relative to the amount of $C_6H_5NO_2$ *that was photolyzed*. No NO_2 was observed in the absence of UV irradiation. Molecular beam studies[12] have shown that three pathways are operative in the near-UV photolysis of $C_6H_5NO_2$, producing either NO_2, NO, or O atoms. The large but nonunity NO_2 yield observed here is consistent with the molecular beam findings.

Although the slow photolysis rate observed in the presence of a comparable wall loss rate makes quantitative analysis difficult, we conclude that the $C_6H_5NO_2$ photolysis rate in the chamber is approximately $(1.5 \pm 1.0) \times 10^{-5}$ s^{-1}. The circles in Figure 4 show the literature data for absorption cross sections of Cl_2.[4] By chance, there is a reasonable match between the absorption cross sections of Cl_2 and $C_6H_5NO_2$ in the range 320−400 nm, while below 320 nm the $C_6H_5NO_2$ absorption is substantially greater than that of Cl_2. Calculations were performed to quantify the relative overlap of the lamp emission spectrum with the absorption spectra of Cl_2 and $C_6H_5NO_2$. The ratio of the overlap integrals is 0.5 (i.e., if the photolysis quantum yield was unity for both species, $C_6H_5NO_2$ would photolyze twice as fast as Cl_2 in the chamber). The measured photolysis rate of Cl_2 in the chamber is 5×10^{-4} s^{-1}. From three pieces of information, (i) the ratio of the observed $C_6H_5NO_2$ and Cl_2 photolysis rates in the chamber (approximately 0.03), (ii) the calculated ratio of overlap integrals (0.5), and (iii) the unity photolysis quantum yield of Cl_2,[4] we estimate that the photolysis quantum yield for $C_6H_5NO_2$ in the wavelength range 250−420 nm is approximately 0.015.

Adopting $\phi(\lambda) \approx 0.015$ for all wavelengths and using actinic flux data from Finlayson-Pitts and Pitts,[17] a photolysis rate of 3×10^{-5} s^{-1} is obtained for $C_6H_5NO_2$ for a solar zenith angle of 25° (representative of a typical summer day at 40°N), corresponding to a photolysis lifetime of about 10 h, with an uncertainty of about a factor of two to three. $C_6H_5NO_2$ reacts slowly with OH radicals and ozone ($k_{OH} = 1.40 \times 10^{-13}$, $k_{O3} < 7 \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-11}), for typical atmospheric concentrations of $[OH] = 1 \times 10^6$ and $[O_3] = 1.2 \times 10^{12}$ cm^{-3} (50 ppb) the lifetime of $C_6H_5NO_2$ with respect to reaction with OH and O_3 is 80 days and >4 years, respectively. It seems likely that photolysis is the dominant atmospheric loss of $C_6H_5NO_2$. At this point it should be noted that the photolysis experiments described here employed a range of UV wavelengths (250−420 nm) which extend beyond the tropospheric cutoff of 290 nm. In fact, approximately 1/4 of the absorption by $C_6H_5NO_2$ in the chamber occurs below 290 nm, which may lead to an overestimate of the quantum yield in the actinic region of the spectrum and thus an overestimate of the atmospheric photolysis rate. However, we believe it unlikely that the magnitude of such an overestimation would be sufficient to change the conclusion that photolysis dominates the atmospheric chemistry of $C_6H_5NO_2$.

Arey et al.[18] measured a photolysis quantum yield of $\phi(\lambda) = 3.5 \times 10^{-3}$ for 2-methyl-1-nitronaphthalene under atmospheric conditions. Even this lower quantum yield (an order of magnitude lower than our estimate for nitrobenzene) would be sufficient to allow photolysis to dominate the loss of nitrobenzene. As with the other nitroaromatic compounds studied to date (1- and 2-nitronaphthalene,[19,20] and 2-methyl-1-nitronaphthalene),[18] photolysis dominates the atmospheric chemistry of $C_6H_5NO_2$.

Conclusions

It is shown here that the reaction of Cl atoms with $C_6H_5NO_2$ occurs with a rate constant of $(9.3 \pm 1.9) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K in 10−700 Torr of air or N_2 diluent. The mechanism of the reaction is unusual for a gas-phase reaction involving Cl atoms. The reaction proceeds essentially 100% via a displacement mechanism to give C_6H_5Cl and NO_2 products. The UV−visible spectrum of $C_6H_5NO_2$ has been measured. The dominant atmospheric fate of $C_6H_5NO_2$ is photolysis which is estimated to occur at a rate of $(3 \pm 2) \times 10^{-5}$ s^{-1} for a solar zenith angle of 25° representative of a typical summer day at 40°N).

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