

Highly Selective Photochemical and Thermal Chlorination of Benzene by Cl₂ in NaZSM-5

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Received: March 10, 1998; In Final Form: July 17, 1998

Loading of zeolite NaZSM-5 with benzene and chlorine from the gas phase at $-100\text{ }^{\circ}\text{C}$ resulted in spontaneous reaction to form chlorobenzene and 1,4-dichlorobenzene as the sole products. Thermal reaction at elevated temperature (up to $0\text{ }^{\circ}\text{C}$) accelerates the rates toward these products and yields, in addition, some 1,3-dichlorobenzene and a small ($<3\%$) amount of 1,2-dichlorobenzene. No higher chlorinated benzenes or chlorocyclohexanes are formed even upon 90% conversion of the loaded benzene. Reactions were monitored by in situ FT-infrared spectroscopy. Irradiation of 1,4-dichlorobenzene in the presence of Cl₂ in the zeolite with green or blue light produced 1,2,4-trichlorobenzene as the only product at high conversion. Such selectivities of benzene chlorination by elemental chlorine are much higher than obtained currently by traditional methods. The sharp increase of the reaction rate in NaZSM-5 compared to that in homogeneous liquid or gas phase and the effect of electronic excitation by visible light are attributed to an enhanced electrophilic character of the chlorine molecule.

I. Introduction

Partially chlorinated benzenes play a key role as industrial intermediates and fine chemicals.^{1–3} Chlorobenzene is an industrial solvent and intermediate in the manufacture of pigments, agricultural products, and pharmaceuticals.^{1,2} Higher chlorinated benzenes such as 1,4-dichlorobenzene are used for the production of thermoplastics.^{1–4} Trichlorobenzenes, especially the 1,2,4-isomer, play mainly a role as pesticides.⁴ Yet, existing synthetic methods of benzene chlorination by elemental chlorine are unselective. The traditional method is liquid-phase reaction of benzene with Cl₂ catalyzed by FeCl₃ or other Lewis acid catalysts.^{1,2} Since each chlorinated compound reacts further with Cl₂, the results are complex mixtures of chlorinated benzenes which require extensive separation processes for isolation of the desired product. To make such energy-intensive operations unnecessary and to avoid unwanted chlorinated products while minimizing the demand for the hazardous starting materials, substantial improvement of the selectivity of benzene chlorination is needed.

We have recently observed that large-pore alkali or alkaline-earth zeolites (type Y or L) can be used to achieve highly selective partial oxidation of small alkanes, olefins, or alkylbenzenes when the corresponding hydrocarbon–O₂ mixture is loaded into the pores from the gas phase and irradiated with visible light.⁵ The strong electrostatic properties of the solvent-free zeolite, coupled with the diffusional and steric constraints imposed by the micropores, might offer opportunities for controlled reaction of benzene with molecular chlorine under mild conditions. In fact, several groups have reported enhanced selectivity upon benzene chlorination by Cl₂ in zeolites. Most notably, Miyake⁶ found that when the reaction is conducted in a liquid slurry of NaZSM-5 at $100\text{ }^{\circ}\text{C}$, it stops at the dichlorobenzene stage with a para-to-ortho ratio of 4 (compared to 1.4 in the case of homogeneous liquid-phase chlorination catalyzed by FeCl₃).¹ On the other hand, van Bekkum reported that gas-phase chlorination at $175\text{ }^{\circ}\text{C}$ over HZSM-5 or NaHZSM-5 gave mainly hexachlorocyclohexanes, indicating

that Cl₂ addition, but very little substitution, took place.⁷ Chlorination in the large-pore zeolites NaY or X was found to yield a complex mixture of higher chlorobenzene isomers, including hexachlorobenzene.⁷ The only report on a highly selective chlorination by Cl₂ in a zeolite is that of van Dijk et al.⁸ When exposing a carbon tetrachloride solution of chlorine to a CCl₄ slurry of CaX loaded with chlorobenzene at room temperature, dichlorobenzene was formed at 95% selectivity with a para-to-ortho ratio of 24. However, no data were reported on the direct chlorination of benzene. High para selectivity (para/ortho = 32) has also been achieved by chlorination of chlorobenzene in partially decationated zeolite X, but with a reagent other than molecular chlorine (*tert*-butyl hypochlorite).⁹ On the other hand, high selectivity using Cl₂ has been observed by Turro and co-workers upon monochlorination of terminal methyl groups of *n*-alkanes occluded in pentasil zeolites by UV light.^{10,11}

We wish to report in this paper an in situ infrared spectroscopic study of thermal and visible light-induced reaction of benzene–Cl₂ gas mixtures loaded into zeolite NaZSM-5. Substantially improved product selectivities compared to existing methods were observed.

II. Experimental Section

NaZSM-5 was prepared from NH₄ZSM-5 (Zeolyst product no. CBV15014, lot no. 15014-1525-63, SiO₂/Al₂O₃ = 150) by ion exchange using sodium acetate. The exchange was repeated until NH₄⁺ could not be detected by IR spectroscopy; hence, the Na/Al ratio was inferred to be 1. No Brønsted acid hydroxyl sites (OH stretch absorption at 3611 cm^{-1})¹² were observable by infrared. Self-supporting pellets of NaZSM-5 (approximately 8 mg, 12.5 mm diameter) were dehydrated overnight at $200\text{ }^{\circ}\text{C}$ in a miniature stainless steel vacuum cell contained within a liquid nitrogen cryostat (Oxford Instruments model DN1714). The infrared cell was evacuated with a Varian turbomolecular pump model V-60. Wafers were exposed to 500 mTorr of benzene at room temperature for 0.5 h, and then the sample

cell was evacuated to a gas pressure below 5 mTorr. The cell was cooled to temperature and allowed to stabilize over 1.5 h. Room-temperature chlorine was introduced into the cell in 500 mTorr increments, at 10 min intervals, for a final chlorine pressure of 2500 mTorr. The stepwise procedure was used to avoid a significant temperature rise upon Cl₂ loading, which might lead to uncontrolled reaction. Zeolite NaZSM-5 is transparent in the infrared at frequencies above 1300 cm⁻¹ and between 770 and 630 cm⁻¹. FT-IR spectra were collected in situ using an IBM Bruker model IR-44 spectrometer. One hundred scans at 1 cm⁻¹ resolution were coadded and ratioed against a background of the empty dehydrated pellet held at room temperature. The cryostat and cell were fitted with KCl windows to allow IR spectra collection and visible light irradiation without movement of the sample.

The samples were irradiated using an Ar⁺, a Kr⁺, or an Ar⁺ pumped dye laser (Coherent models Innova 90-5, Innova 300, and 599-01, respectively) for a fixed interval, and then the beam was blocked for IR spectra collection. Spectra were taken immediately upon ceasing irradiation and again after 5 min in the dark to monitor the effects of laser heating. Spectra for nonirradiated samples were collected at the same intervals to monitor the thermal reaction.

Fractional abundances were calculated by the following procedure. Resolved, characteristic peaks were selected for each species: 3040 cm⁻¹ for benzene, 1445 cm⁻¹ for chlorobenzene, 1437 cm⁻¹ for 1,2-dichlorobenzene, 1417 cm⁻¹ for 1,3-dichlorobenzene, 1392 cm⁻¹ for 1,4-dichlorobenzene, and 1375 cm⁻¹ for 1,2,4-trichlorobenzene. Each peak was chosen for minimal overlap with those of other species. This required selecting peaks other than the most or even the second most intense peak for each compound. For example, benzene, chlorobenzene, and 1,4-dichlorobenzene all have overlapping peaks around 1480 cm⁻¹. The peaks at 1437 and 1417 cm⁻¹ were selected for 1,2- and 1,3-dichlorobenzene, respectively, because it was impossible to reliably curve-resolve their overlapping peaks at 1460 and 1458 cm⁻¹. The relative extinction coefficients were calculated from those obtained from acetonitrile-*d*₃ solution infrared spectra. For this purpose, a minimum of eight solutions of each compound were prepared and measured. Relative integrated extinction coefficients, referenced against the 3040 cm⁻¹ absorption of benzene, were 0.69 ± 0.09 for chlorobenzene (1445 cm⁻¹), 0.9 ± 0.2 for 1,4-dichlorobenzene (1392 cm⁻¹), 1.2 ± 0.1 for 1,2,4-trichlorobenzene (1375 cm⁻¹), 1.0 ± 0.1 for 1,2-dichlorobenzene (1437 cm⁻¹), and 0.5 ± 0.1 for 1,3-dichlorobenzene (1417 cm⁻¹). Gas-phase spectra were also recorded, but the relative intensities of peaks for a given compound varied by as much as a factor of 4 compared with the case of authentic species in NaZSM-5. The most likely reason is the inhomogeneous local environment in the zeolite framework. This variance was much reduced in solution. Use of the solution extinction coefficients is justified by a comparison of ratios in solution and zeolite, where available. For example, infrared difference spectra of thermal chlorobenzene to 1,4-dichlorobenzene conversion in the zeolite give a ratio $I(1445\text{ cm}^{-1})/I(1392\text{ cm}^{-1})$ of 0.88 (Figure 5) compared to 0.79 in solution. Or, the ratio $I(3040\text{ cm}^{-1})/I(1445\text{ cm}^{-1})$ in the thermal benzene to chlorobenzene conversion is 0.54 in zeolite and 0.69 in solution. These values coincide within the experimental uncertainties.

Benzene and all partially chlorinated benzenes were purchased from Aldrich (99% purity or higher) and used as received. Chlorine gas (Matheson, 99.99%) was purified by trap-to-trap distillation before use.

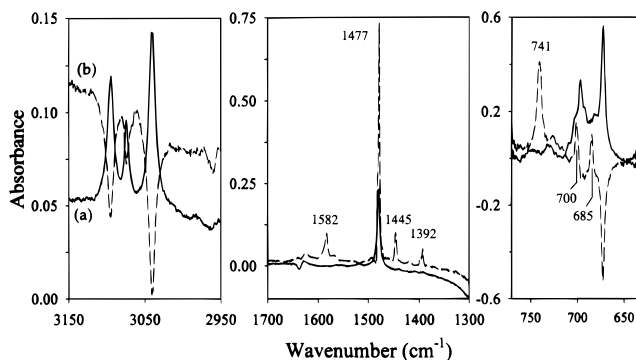


Figure 1. Thermal reaction of benzene with Cl₂ in NaZSM-5 at -100 °C: (a) infrared difference spectrum before and after adsorption of benzene (full trace); (b) difference spectrum after reaction of 90% of the loaded benzene (9.8 h reaction time, dashed line). The small spectral changes around 1630 cm⁻¹ are due to changes in the band profile of residual H₂O in the zeolite.

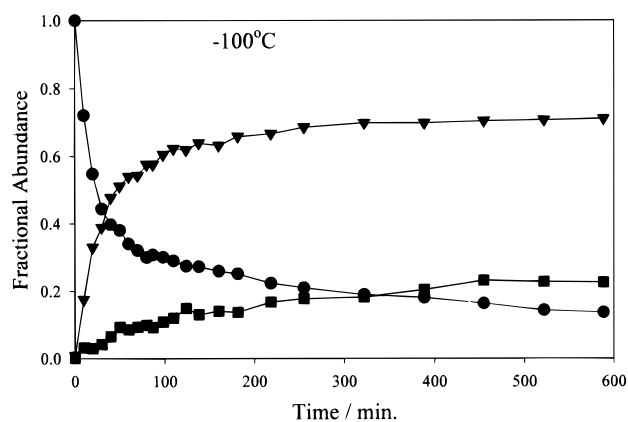


Figure 2. Kinetics of benzene + Cl₂ dark reaction in NaZSM-5 at -100 °C: ●, benzene; ▼, chlorobenzene; ■, 1,4-dichlorobenzene. For determination of fractional abundances, see Experimental Section.

III. Results

Upon admission of Cl₂ to benzene-loaded NaZSM-5, spontaneous thermal reaction was observed at temperatures as low as -100 °C. Subsequent irradiation with green or blue light resulted in additional reaction, furnishing products distinct from those of thermal chemistry. We will first present the thermal experiments, which will be followed by the results of the photochemical studies.

1. Thermal Chemistry. The infrared difference spectrum recorded upon loading of benzene into NaZSM-5 at -100 °C showed reactant absorptions at 673, 696, 1479, 1519, 1808, 1951, 3040, 3074, and 3094 cm⁻¹ (Figure 1, trace a). Exposure of the pellet to Cl₂ gas led to infrared product growth at 675, 685, 700, 741, 1392, 1397, 1445, 1477, 1568, and 1582 cm⁻¹ under concurrent loss of the benzene absorptions, as shown by trace b of Figure 1. The product bands (except for those at 1392 and 1397 cm⁻¹) have the same growth kinetics and agree with the spectrum of an authentic sample of chlorobenzene in NaZSM-5. The 1392 and 1397 cm⁻¹ absorptions, on the other hand, grew in much more slowly as can readily be seen from the kinetic plots of Figure 2. This doublet presumably reflects two distinct sites and coincides with a strong infrared absorption of an authentic sample of 1,4-dichlorobenzene in NaZSM-5. The latter also has an intense band at 1477 cm⁻¹ which overlaps with the strongest chlorobenzene absorption. No other chlorinated products were detected even upon conversion of over 80% of the loaded benzene. Interestingly, the infrared spectrum did

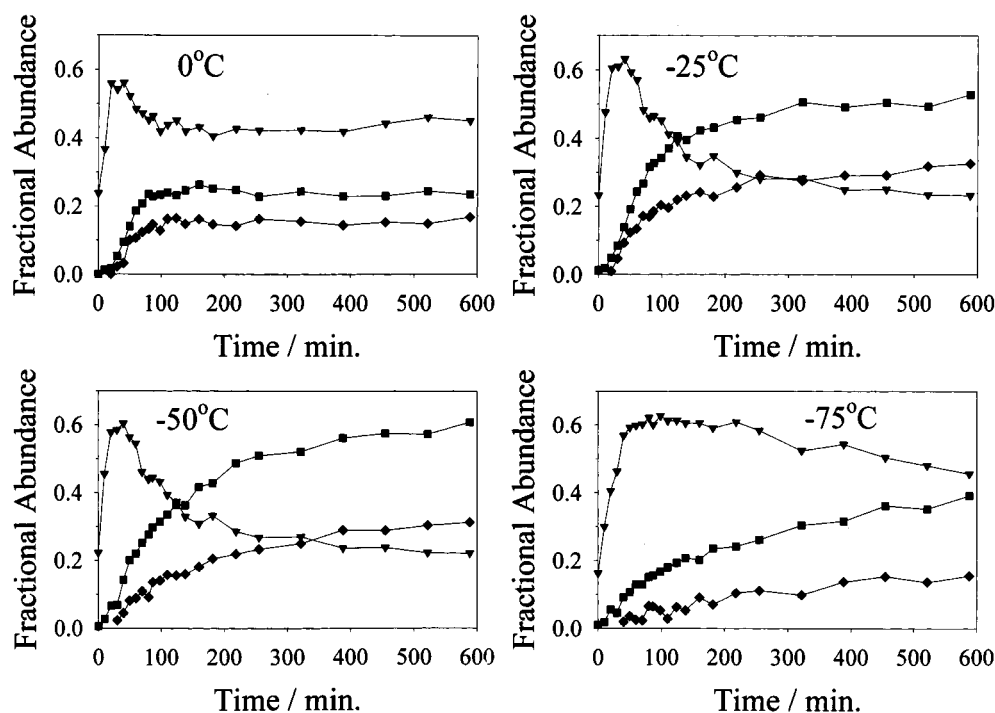


Figure 3. Kinetics of benzene + Cl₂ dark reaction in NaZSM-5 in the temperature range -75 to 0 °C: ▼, chlorobenzene; ■, 1,4-dichlorobenzene; ◆, 1,3-dichlorobenzene.

not exhibit an absorption of the HCl coproduct in the 2500 – 3000 cm^{-1} region. Instead, a very broad band grew in with a maximum around 3300 cm^{-1} and fwhm of 300 cm^{-1} . We attribute this band to surface OH groups formed upon spontaneous dissociation of HCl to H^+ and Cl^- in the presence of the high electrostatic fields around the Na^+ ions. The red shift relative to free $\nu(\text{OH})$ and the large width are due to H-bonding interaction with benzene and chlorobenzenes. Similar observations about the behavior of HCl in cation-exchanged zeolites have been reported recently by Ozin¹³ and earlier by Angell and Schaffer.¹⁴

When raising the zeolite temperature above -100 °C, a substantial increase of the reaction rate was observed. Figure 3 shows the growth behavior of the chlorinated benzenes at -75 , -50 , -25 , and 0 °C. Aside from the two products observed at -100 °C, chlorobenzene and 1,4-dichlorobenzene, there is growth of 1,3-dichlorobenzene at -75 °C and higher temperatures as indicated by bands at 1417 and 1460 cm^{-1} . Identification is again based on comparison with the spectrum of an authentic sample in NaZSM-5. Traces of 1,2-dichlorobenzene were detected at -50 °C and above by the characteristic absorption at 1437 cm^{-1} , but the growth never exceeded 3% even at $>90\%$ conversion of the benzene. Aside from these chlorinated benzenes, no other product absorption was detected. This is in stark contrast to the previous observation of mainly (saturated) chlorocyclohexanes in experiments conducted over ZSM-5 at high temperature.⁷ While not apparent below -50 °C because of too small a signal, the absorbance growth of the dichlorobenzene products at $T > -50$ °C exhibits a clear induction period. This confirms that they are formed by chlorination of chlorobenzene. Comparison of Figure 2, Figure 3a, and Figure 3b shows that there is increased chlorobenzene-to-dichlorobenzene conversion as the temperature is raised from -100 to -50 °C. However, the product growth behavior changes little from -50 to -25 °C, and the conversion of chlorobenzene to dichloro products decreases upon further rise to 0 °C (Figure 3c,d). This is due to a steep decrease in Cl₂

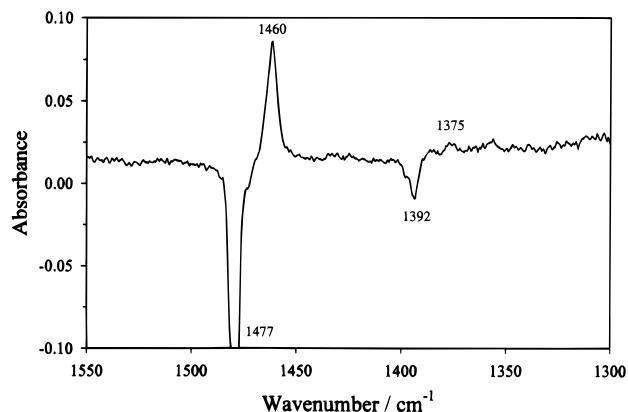


Figure 4. Green light-induced reaction of 1,4-dichlorobenzene with Cl₂ in NaZSM-5 at -100 °C. Shown is the infrared difference spectrum upon 90 min 514 nm irradiation at 700 mW cm^{-2} .

gas adsorption in the zeolite above -50 °C, leading to quantitative consumption of chlorine within 5 h (-25 °C) or 3 h (0 °C) after start of reaction.

2. Photochemical Reaction. Since 1,4-dichlorobenzene is the exclusive final product of thermal benzene chlorination at -100 °C, it would be interesting to accomplish further chlorination to a commercially important trichlorobenzene product. We have explored this possibility by using visible light for inducing reaction of 1,4-dichlorobenzene with Cl₂ in NaZSM-5 at -100 °C. Upon loading of the zeolite with 1,4-C₆H₄Cl₂ and Cl₂ (2.5 Torr) at -100 °C, no dark reaction was noted. When irradiating with 514 nm CW laser light at 700 mW cm^{-2} for 90 min, we observed 70% depletion of the reactant under concurrent growth of a strong band at 1460 cm^{-1} and a very weak feature at 1375 cm^{-1} (Figure 4). These two product bands are assigned to 1,2,4-trichlorobenzene according to authentic spectra of the molecule in zeolite. No other chlorinated product could be detected. Note that a laser heating effect is ruled out by the fact that 1,2,4-trichlorobenzene is not formed thermally even at 0 °C.

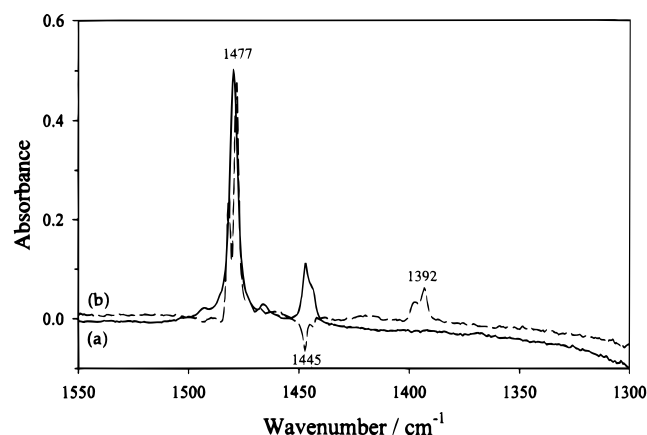


Figure 5. Thermal reaction of chlorobenzene with Cl_2 in NaZSM-5 at -100°C : (a) infrared difference spectrum before and after adsorption of chlorobenzene (full trace); (b) difference spectrum after exposure to Cl_2 for 80 min (dashed trace).

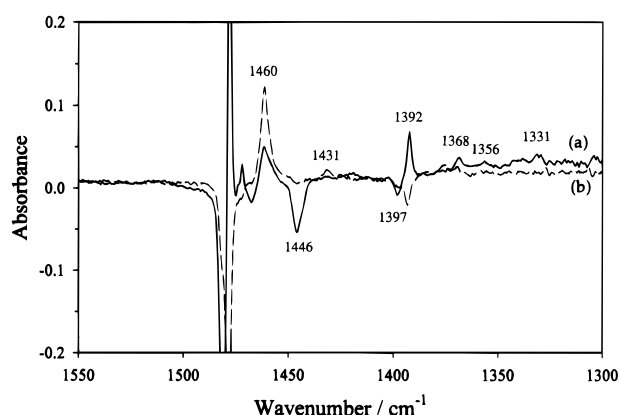


Figure 6. Green light-induced reaction of chlorobenzene and Cl_2 -loaded NaZSM-5 at -100°C : (a) infrared difference spectrum upon 60 min irradiation at 514 nm (solid trace); (b) difference spectrum taken after continued photolysis for 360 min (dashed line).

A series of experiments were performed to find out whether such high selectivity for the 1,2,4-trichloro isomer can also be obtained by direct chlorination of benzene or chlorobenzene. Since C_6H_6 and $\text{C}_6\text{H}_5\text{Cl}$ react thermally with Cl_2 at temperatures as low as -100°C , photochemical and thermal reaction will proceed concurrently in these systems. Figures 5 and 6 show the result for chlorobenzene as starting material. Trace a of Figure 5 is the infrared spectrum of $\text{C}_6\text{H}_5\text{Cl}$ in NaZSM-5 before loading of chlorine. Admission of Cl_2 over a period of 80 min leads to spontaneous reaction to form 1,4-dichlorobenzene, as can be seen in the difference spectrum b of Figure 5. Subsequent irradiation at 514 nm (700 mW cm^{-2}) results in reaction of $>90\%$ of the remaining chlorobenzene within 60 min as shown by trace a of Figure 6. The positive band at 1392 cm^{-1} signals continued production of 1,4-dichlorobenzene, while the new absorption at 1460 cm^{-1} indicates photogeneration of 1,2,4-trichlorobenzene. The depletion at 1397 cm^{-1} suggests that the higher frequency site of 1,4-dichlorobenzene reacts preferentially with Cl_2 to form the 1,2,4-trichloro product. Apart from the trichlorobenzene bands, very weak growth is detected at 1368, 1356, 1338, and 1331 cm^{-1} . These features do not increase upon continued photolysis and are in a spectral region characteristic for CH bending modes of alkanes.¹⁵ Therefore, we assign them tentatively to hexachlorinated cyclohexane. As expected, prolonged irradiation leads mostly to conversion of 1,4-dichlorobenzene to 1,2,4-trichlorobenzene. If one records the spectrum after 420 min photolysis and subtracts

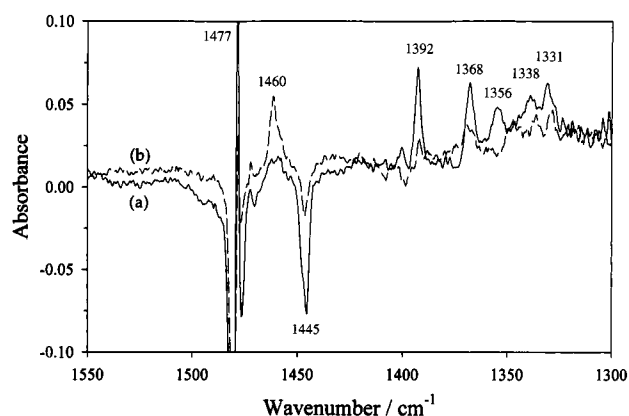


Figure 7. Green light-induced reaction of benzene and Cl_2 -loaded NaZSM-5 at -100°C : (a) difference spectrum upon 60 min irradiation at 514 nm (solid trace); (b) difference spectrum after continued photolysis for 360 min (dashed trace).

the spectrum after 60 min irradiation, one notices a net loss at $1397/1392\text{ cm}^{-1}$ (1,4-dichlorobenzene) under concurrent growth at 1460 cm^{-1} (1,2,4-trichlorobenzene); see trace b of Figure 6. A very weak product band at 1431 cm^{-1} , not apparent after just 60 min photolysis, is assigned to 1,2,3,4-tetrachlorobenzene based on comparison with authentic spectra and on the pronounced induction period.

In the benzene photochlorination experiment, a NaZSM-5 pellet loaded with C_6H_6 was first exposed to chlorine in the dark at -100°C . The spectrum observed upon thermal reaction was the same as shown in Figure 1, featuring growth of chlorobenzene and 1,4-dichlorobenzene. After the bulk of the loaded benzene had reacted thermally with Cl_2 , irradiation with 514 nm laser light at 700 mW cm^{-2} led to rapid chlorobenzene-to-1,4-dichlorobenzene conversion, as can be seen in the infrared difference spectrum taken after 60 min photolysis (Figure 7, trace a). This is signaled by the depletion at 1445 cm^{-1} and concurrent growth at 1392 and 1477 cm^{-1} . The latter overlaps with the decreasing benzene absorption due to reaction of the remaining C_6H_6 . As in the case of photochlorination of chlorobenzene, we observe growth at 1368, 1356, 1338, and 1331 cm^{-1} which indicates formation of chlorocyclohexanes. The difference spectrum taken after 60 and 420 min irradiation (Figure 7, trace b) is dominated by continued chlorobenzene-to-1,4-dichlorobenzene conversion as well as growth at 1460 cm^{-1} . The latter is due to 1,2,4-trichlorobenzene produced by photochlorination of the 1,4-dichloro isomer. Fractional abundances in this particular experiment could not be determined reliably because of a factor of 2 discrepancy between the relative extinction coefficients of 1,4-dichloro- and 1,2,4-trichlorobenzene in solution and zeolite.

Photolysis at shorter, blue wavelengths led to the same products, but at faster rates. The results are summarized in the form of kinetic plots in Figure 8. There is a substantial acceleration of chlorobenzene consumption and growth of 1,4- $\text{C}_6\text{H}_4\text{Cl}_2$ and 1,2,4- $\text{C}_3\text{H}_3\text{Cl}_3$ as the photon energy is raised from 514 to 488, to 458 nm. No reaction was observed when irradiating with the CW dye laser at longer wavelengths, 580 or 647 nm, using comparable laser power and irradiation times. At the shortest wavelength, 458 nm, chlorination of 1,2,4-trichloro- to 1,2,3,4-tetrachlorobenzene was detected by growth at 1431 cm^{-1} .

IV. Discussion

The well-established mechanism of thermal reaction of molecular chlorine with benzene consists of electrophilic attack

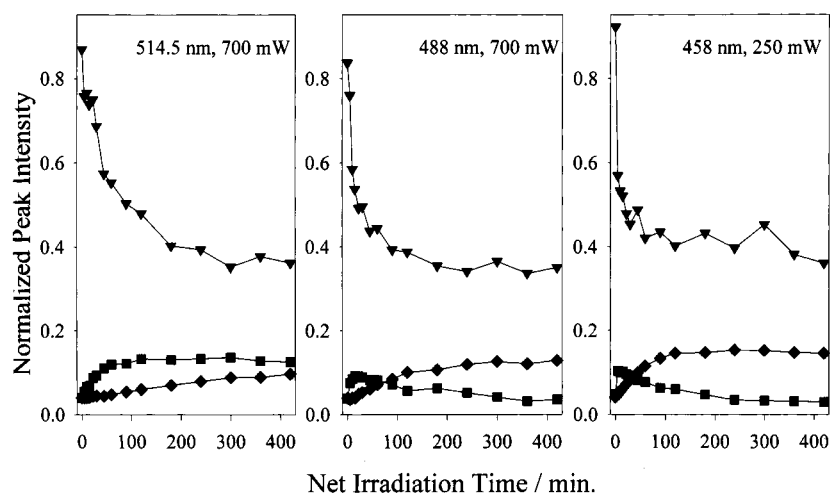


Figure 8. Photolysis wavelength dependence of benzene + Cl_2 product absorbance growth kinetics. Photolysis was preceded by 80 min dark reaction at -100°C , leading to nearly quantitative conversion of C_6H_6 : (\blacktriangledown) chlorobenzene, 741 cm^{-1} ; (\blacksquare) 1,4-dichlorobenzene, 1392 cm^{-1} ; (\blacklozenge) 1,2,4-trichlorobenzene, 1460 cm^{-1} .

of Cl_2 on the aromatic ring to form a transient arenium ion (Wheland intermediate), followed by proton elimination to yield chlorobenzene. Existing benzene chlorination methods use Lewis acids such as AlCl_3 or FeCl_3 as catalysts.^{16,17} Zeolite ZSM-5 consists of intersecting channels with a diameter of 5.5 \AA .¹⁸ Each Al introduces a negative charge into the aluminosilicate framework, which is mainly located on the oxygens. The negative charge is compensated by extraframework Na^+ ions. The shielding of these cations is very poor. Therefore, the Na^+ ions can act as strong Lewis acids, especially when no solvent is present that would attenuate the effect of the positive charges. By polarizing the Cl_2 , the Na^+ ions activate the molecule toward electrophilic attack on the benzene. The fast chlorination of benzene, even at -100°C , is attributed to the Lewis acidity of the Na^+ . It is further aided by the high concentration of benzene $\cdot\text{Cl}_2$ complexes in the zeolite pores. Benzene does not react with chlorine in gas or solution phase even at room temperature.¹⁹

We attribute the selectivity of the second reaction step, chlorination of chlorobenzene to 1,4-dichlorobenzene at -100°C , to a steric effect of the zeolite pores on the transition state (transition-state shape selectivity).²⁰ Benzene has a kinetic diameter of 5.8 \AA .²¹ The transition state leading to 1,4-dichlorobenzene is not expected to be hindered sterically by the zeolite walls if the chlorobenzene molecule is oriented with the molecular axis parallel to the channel axis. By contrast, the transition state leading to 1,2- or 1,3-dichlorobenzene is sterically hindered by the channel for any orientation of the chlorobenzene. Apparently, the activation barriers to 1,2- or 1,3-dichlorobenzene block these paths at -100°C , but they become accessible as minor reaction channels at $T \geq -75^\circ\text{C}$. Complete selectivity toward 1,4-dichlorobenzene upon direct chlorination of benzene with elemental chlorine is unprecedented.

While benzene and Cl_2 form a weak (π -donor, σ -acceptor) charge-transfer complex which has been well characterized in solution,²² it is unlikely that the excited charge-transfer state is involved in the photoinduced reaction. The benzene–chlorine charge-transfer band in solution absorbs in the UV region.²² It is to be expected that the charge-transfer state of $\text{C}_6\text{H}_6\cdot\text{Cl}_2$ complexes with favorable orientation with respect to the strong electrostatic field in the vicinity of Na^+ ions²³ will be stabilized, resulting in a red shift of the absorption into the visible range. We have encountered such an effect in the case of hydrocarbon

O_2 collisional complexes in alkali and alkaline-earth zeolites.^{5,24} However, benzene is known to reside near the extraframework cations²⁵ while halogen molecules tend to prefer sites at the negatively charged cage wall.²⁶ This implies that most charge-transfer dipoles ($\text{C}_6\text{H}_6^+\cdot\text{Cl}_2^-$) are oriented antiparallel to the electrostatic field around the Na^+ ion. Nevertheless, due to the mobility of benzene and chlorine molecules in the zeolite, a small fraction may be oriented parallel to the field and absorb visible light. However, even if complexes are excited to the charge-transfer state by visible light, the electron distribution of this state would be altered in a way that makes the chlorine species less, not more, reactive toward electrophilic attack on the benzene ring. Therefore, it is unlikely that reaction would be triggered from that state.

By contrast, photoexcitation of Cl_2 with green or blue light generates an electronic state with much stronger electrophilic character than the ground-state molecule. Two excited states are contributing to absorption of Cl_2 in the visible, namely, the weakly bound $^3\pi_{\text{g}}+\pi_{\text{u}}$ state with the 0–0 transition at $18\,147\text{ cm}^{-1}$ (551 nm)²⁷ and the repulsive $^1\pi_{\text{u}}$ state. The latter gives rise to a broad, structureless absorption in the near-UV with a tail extending to about 450 nm .²⁸ Both excited states originate from the electron configuration $\text{KKLL}(\sigma_{\text{g}}3\text{s})^2(\sigma_{\text{u}}3\text{s})^2(\sigma_{\text{g}}3\text{p})^2(\pi_{\text{u}}3\text{p})^3(\sigma_{\text{u}}3\text{p})$ in which a $\pi_{\text{g}}3\text{p}$ electron is promoted to the $\sigma_{\text{u}}3\text{p}$ orbital. The vacancy created in the $\pi_{\text{g}}3\text{p}$ orbital renders the excited chlorine molecule a substantially better electrophile than ground-state $\text{Cl}_2(^1\Sigma_{\text{g}}^+)$, resulting in enhanced reactivity toward benzene or chlorobenzene compared to the case of the dark thermal system. In the case of 1,4-dichlorobenzene, only the electronically excited Cl_2 molecule is sufficiently electrophilic to cause reaction. This interpretation is strongly supported by the finding that excitation of $\text{Cl}_2\cdot\text{benzene}$, chlorobenzene, or 1,4-dichlorobenzene complexes leads to reaction even with 514 nm light despite the fact that these quanta lie 560 cm^{-1} (1.6 kcal mol^{-1}) below the chlorine dissociation threshold (500 nm).²⁸ While generation of free Cl atoms is possible at wavelengths shorter than 500 nm , the predominant formation of benzene substitution rather than free-radical addition products indicates that the excited Cl_2 molecule undergoes electrophilic attack even at photon energies above the dissociation limit.

V. Conclusions

This infrared spectroscopic study of benzene chlorination by Cl_2 shows that 1,4-dichlorobenzene is formed as the sole

dichloro product when loading the reactant gas mixture into zeolite NaZSM-5 at -100 °C. Such selectivity is unprecedented. Even at elevated temperatures (≤ 0 °C) or high conversion, no products other than chlorinated benzenes are observed. Irradiation with green or blue light affords selective conversion of 1,4-dichlorobenzene to 1,2,4-trichlorobenzene as a unique photochemical product. At the same time, the rate of benzene and chlorobenzene reaction with Cl₂ is enhanced by the photons. In the latter case, chlorocyclohexanes were formed as byproducts.

The photochemical results suggest that the excited Cl₂ reacts in the $^3\pi_{0+u}$ state in which the molecule is substantially more electrophilic than in the ground state. This may open up opportunities for new synthesis based on electrophilic reactions that cannot be accomplished by thermal means. Electronic excitation by visible light renders the electrophile more reactive, and the zeolite pores afford the high concentration of reactant complexes required for efficient bimolecular photoreaction.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098.

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