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Regioselective mononitration of chlorobenzene using caprolactam-based Brønsted acidic ionic liquids

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ABSTRACT

Three kinds of Brønsted acidic ionic liquids caprolactam benzenesulfonate ([CP]BSA), caprolactam hydrosulfate ([CP]HSO_4) and caprolactam *p*-toluenesulfonate ([CP]*p*TSA) were synthesized. The structures of the ILs were confirmed by ^{1}HNMR and FT-IR. Regioselective mononitration of chlorobenzene has been investigated in HNO_3–Ac_2Osystem with three ionic liquids. The sequence of the nitrification activity is [CP]HSO_4 > [CP]*p*TSA > [CP]BSA. With the caprolactam hydrosulfate as the catalyst the influences of reaction time, reaction temperature and the amount of the catalyst were studied in the nitration of chlorobenzene. The results showed that the optimum reaction conditions were as follows: when the mole ratio of chlorobenzene to ionic liquid was 10:1.5, the reaction temperature was 60 °C and the reaction time was 2.5 h, the yield of mononitro-chlorobenzene could reach 71.22%. And the mass ratio of para/ortho isomer was 7.74, which was much more than 2.0 of para/ortho isomer mass ratio obtained by nitric-sulfuric mixed acids as catalyst. Besides, the ionic liquid could be used repeatedly.

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1. Introduction

Nitrochlorobenzene mainly refers to *p*-nitrochlorobenzene and *o*-nitrochlorobenzene. As the important and basic organic raw material, they are widely used in the synthesis of diverse intermediates, including dyes, pigments, pharmaceuticals, pesticides, rubber chemicals, engineering plastics, and so on [1,2]. However, the usual industrial preparation of nitrochlorobenzene still uses the traditional process of nitration by nitric-sulfuric mixed acids [3], which exists two main problems. On the one hand, the selectivity for desired products is poor and the mass ratio of para/ortho isomer is only about 2.0. However, the market demand of *p*-nitrochlorobenzene is more than *o*-nitrochlorobenzene, which results in the relative surplus of *o*-nitrochlorobenzene and the waste of resources [4]. On the other hand, the reaction produces large amount of acid wastewater which is difficult to recycle, and not only corrodes the equipment, but also seriously pollutes the environment. Therefore, more and more domestic and foreign scholars have attached great importance to looking for high activity catalysts to improve the selectivity of the nitration of chlorobenzene and to explore green nitration approaches [5–12].

Ionic liquids (ILs) are defined as pure compounds consisting only of cations and anions (i.e., salts), most of which are liquid at room temperature. Ionic liquids have excellent thermodynamic stability and good solubility. Because of the negligible vapor pressure at room temperature and environmentally friendliness, they are known as green solvents and novel catalysts. ILs are now widely used in various types of chemical reactions. In addition, ionic liquids can meet the need of some particular reactions by changing the anions or cations, so they are often referred to as “designer solvents” [13–15].

Ionic liquids have also been got more and more applications in aromatics nitration. With 68% nitric acid as nitrating agent, Martin [16] investigated the nitration of aromatic compounds in the presence of the acidic imidazole-cation ionic liquids. In the hydrophobic ionic liquids, the nitration of benzene was carried out smoothly and got nearly quantitative yield of the mononitro-product. While the nitration of chlorobenzene was much slower than that of benzene, but the yield was higher and the ratio of para/ortho isomer was about 3. N.L Lancaster [17] studied several nitration systems on aromatic nitration using methylimidazolium-based ionic liquids as the catalysts, and they demonstrated that HNO_3/Ac_2O was the best nitration system. K. Smith [18] used ionic liquid as a recyclable catalyst to investigate aromatic nitration reactions with HNO_3/Ac_2O system and also achieved good results. But they all use expensive, higher toxicity alkyl-substituted imidazolium ionic liquids, such as 1-ethyl-3-methyl imidazolium ([emim]X), 1-butyl-3-methylimidazolium ([bmim]X)(X: BF_4^-, PF_6^-, $CF_3SO_3^-$), and so on.

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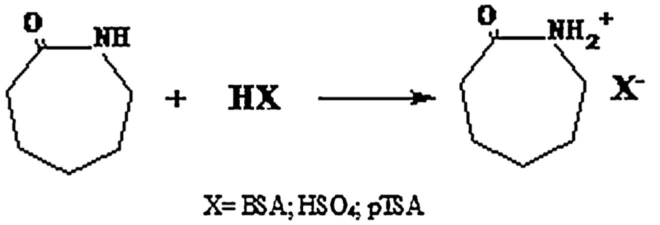

Fig. 1. Synthesis of caprolactam-based ionic liquids.

Caprolactam is a kind of amine derivatives, which can be formed the quaternary ammonium cation by acid–base neutralizing reaction. Thus, a new class of ionic liquids—caprolactam-based $[CP]^+$ ionic liquids [19] are synthesized. Caprolactam-based Brønsted acidic ILs are easy to be prepared and used, relatively cheaper, less toxic, and easily available. Therefore, compared to more expensive and highly toxic imidazole-based ionic liquids, they have a better environmental friendliness and economic feasibility. Lu Chunxu [20] used caprolactam-based ionic liquids as solvents and catalysts for the nitration of toluene. The influences of reaction temperature, reaction time and catalyst dosage on the yield and selectivity are investigated in the reaction. It was found that toluene was nitrated with higher para-selectivity in the presence of caprolactam-based ionic liquids. The yield of mononitro-compound could reach 37.1%. Qi Xiufang [21] researched caprolactam-based ionic liquids for the mononitration of toluene. The yield can be above 50–60% under suitable reaction conditions.

To date, the majority of research work in aromatic nitration using caprolactam-based ionic liquids is about the nitration of toluene, while it is still rarely reported about the nitration of chlorobenzene. Three caprolactam-based ionic liquids were synthesized, and respectively used in the regioselective mononitration of chlorobenzene with HNO_3/Ac_2O nitration system under the same conditions. The caprolactam-based ionic liquid which showed the best catalytic performances was chosen to optimize the reaction conditions on the nitration of chlorobenzene. The optimum conditions were determined, and the reusability of ionic liquid was investigated.

2. Experimental

2.1. Instruments and reagents

Reagents: chlorobenzene, caprolactam, benzene sulfonic acid, *p*-toluene sulfonic acid, sulfuric acid, nitric acid (65–68%), acetic anhydride, the above reagents are analytical grade.

Instruments: constant temperature magnetic stirrer (79–3), rotating evaporator (R206), UV–vis spectrophotometer (TU-1901), liquid chromatograph (Agilent1200, Agilent Technologies, America), FT-IR spectrometer (Tensor27, Bruker, Germany), ^1H NMR spectrometer (Avance600, Bruker, Germany).

2.2. Preparation of ionic liquids

The synthesis of ionic liquids includes one-step synthesis and two-step synthesis. Caprolactam-based ionic liquids were synthesized by one-step synthesis. Compared to the two-step synthesis, one-step synthesis reduces the introduction of the intermediate product, which improves the yield of ionic liquids. Furthermore, the product is easy to be purified without by products. Fig. 1 is the synthetic method of ionic liquids.

Specific steps: Benzene (30 mL) was added to a 100 mL flask containing 11.32 g of caprolactam (0.1 mol) full dissolved in water. Then under magnetic stirring, the certain amount of high concentration strong acid HX (benzenesulfonic acid, sulfuric acid, *p*-toluenesulfonic acid) (0.1 mol) was dripped slowly into the flask within 30 min in the ice bath. The reaction lasted for another 12 h at room temperature. Benzene was removed under reduced pressure, and the product was further dried at 70 °C under vacuum for 1 h. The stoichiometric caprolactam-based ionic liquids were almost obtained.

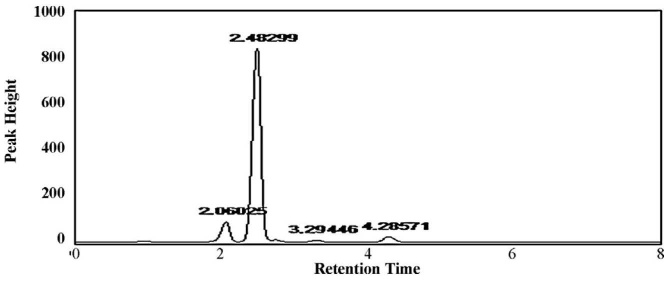

Fig. 2. The liquid chromatogram of the composition of the nitration products.

2.3. Nitration of chlorobenzene

In a three-necked flask equipped with a reflux condenser, some prepared ionic liquids were added and heated to the set reaction temperature under the water bath. Then, the chlorobenzene (50 mmol, 5.7 mL), the nitric acid (67%, 50 mmol, 3.5 mL), and over dosage acetic anhydride (75 mmol, 7.4 mL) were successively added under vigorously magnetic stirring. The reaction was conducted at a constant temperature for a certain time. The reaction mixture was cooled to room temperature and formed two layers after standing for some time. The bottom one was an aqueous phase containing the IL, and the upper one was an organic phase. The upper organic layer was removed by simple decantation and washed to neutral with a saturated solution of sodium bicarbonate and deionized water in turn, then dried under vacuum and analyzed by HPLC. The IL was recovered for reusing from aqueous solution by removing water with rotary evaporation and further drying at 70 °C under vacuum.

2.4. HPLC method

The composition of the nitration products were analyzed by HPLC. ZOBRAX Eclipse Plus-C18 3.5 μm 4.6 × 100 mm columns were used. A degassed and filtered mixture of methanol and water (70:30 v/v) were used as mobile phase. The flow rate was maintained at 1.0 mL/min. Detection was performed at 254 nm. The run time for each analysis was 8 min. All separations were carried out at ambient temperature. The liquid chromatogram was as follows.

The observed retention times of the reference compounds were found to be 2.06, 2.48, 3.29, and 4.28 min for *o*-nitrochlorobenzene, *p*-nitrochlorobenzene, *m*-nitrochlorobenzene and 2,4-dinitrochlorobenzene in Fig. 2. There is no trinitrochlorobenzene in the liquid chromatogram because it needs a higher temperature (90–100 °C) to generate. The yield in our paper is calculated to mononitrochlorobenzene. From the liquid chromatogram, we can obtain the ratio of mononitrochlorobenzene to all nitration products. The yield is the ratio of weight (wt. in formula) which is calculated by the formula below:

$$\text{Yield(wt.\%)} = \frac{\text{wt. of mononitrochlorobenzene}}{\text{wt. of all nitration products}} \times \frac{\text{obtained wt. of product}}{\text{theoretical wt. of product}} \times 100$$

Table 1
Effect of different ILs on nitration of chlorobenzene.

Ionic liquid	Isomer distribution (%)		Para/ortho	Yield (%)
	Ortho	Para		
[CP]HSO_4	12.35	74.49	6.04	50.45
[CP]*p*TSA	11.38	67.78	5.94	39.75
[CP]BSA	31.14	65.85	2.12	10.90

3. Results and discussion

3.1. Characterization and acidity determination of ionic liquids

The spectroscopic datas of ionic liquids synthesized above by ^{1}HNMR and FT-IR are as follows.

1. [CP]BSA: ^{1}H NMR(D_2O), δ(ppm) 1.47–1.63(m, 6H), 2.33(t, J = 5.3 Hz, 2H), 3.11(t, J = 4.5 Hz, 2H), 7.44(t, J = 7.7 Hz, 3H), 7.68(d, J = 7.6 Hz, 2H). FT-IR(KBr, ν/cm^{-1}), 3406(w), 2938(w), 2864(m), 1641(s), 1511(m), 1445(s), 1035(s), 761(s), 694(m), 497(w).

2. [CP]HSO_4: ^{1}H NMR(D_2O), δ(ppm)1.34–1.54(m, 6H), 2.23–2.29(t, J = 5.7 Hz, 2H), 3.01–3.07(t, J = 5.0 Hz, 2H). FT-IR(KBr, ν/cm^{-1}), 3101(w), 1919(m), 1603(s), 1422(s), 1056(s), 1012(s).

3. [CP]pTSA: ^{1}H NMR(D_2O), δ(ppm)1.61–1.77(m, 6H), 2.41(s, 3H), 2.49(t, J = 3.6 Hz, 2H), 3.26(t, J = 4.6 Hz, 2H), 7.38(d, J = 7.9 Hz, 2H), 7.71(d, J = 7.9 Hz, 2H). FT-IR(KBr, ν/cm^{-1}), 2948(w), 1678(m), 1505(m), 1179(s), 1026(w), 821(m), 681(s), 566(s), 484(w).

The Brønsted acidic strength of these caprolactam-based ILs was evaluated by UV–vis spectroscopy [22]. The dimethyl yellow (22.5 mg/L) acted as a Hammett indicator was respectively added to the same concentration solutions (0.32 mmol/L) of the above-mentioned ILs dissolved in methanol. UV–vis spectrophotometer was used to measure the absorption of Hammett indicator, and the results were shown in Fig. 3. The curve a in Fig. 3 is the absorption curve of the dimethyl yellow solution without ionic liquid, which showed that the absorption of the unprotonated form of dimethyl yellow only at a wavelength of 350–460 nm. After adding the ionic liquid, the ionized H^+ from ionic liquid is combined with dimethyl yellow to form protonated structure, then the absorption peak appears at 460–570 nm in the spectrum. For the same amount of the ionic liquid, the greater the Brønsted acidic strength and more the ionized H^+. If the protonated structure is formed more with dimethyl yellow, the absorption at 460–570 nm will become stronger while the absorption at 350–460 nm becomes weaker accordingly. The analysis results show that the Brønsted acidic strength of the three ionic liquids is in the order of [CP]HSO_4 > [CP]*p*TSA > [CP]BSA.

3.2. Effect of different ILs on nitration of chlorobenzene

Under the same conditions, three caprolactam-based ILs were respectively used for nitration of chlorobenzene, so that to investigate the influence of different anions on the reaction. The conditions were: the mole ratio of ionic liquid to chlorobenzene was 1:5, at 50 °C for 2 h. The results are listed in Table 1.

As shown in Table 1, the catalytic activities of the three ILs are in the order of [CP]HSO_4 > [CP]*p*TSA > [CP]BSA. According to the literature reported [23], for Brønsted acidic ionic liquid, the stronger the acidity is, the more hydrogen protons it can provide. In nitric acid and acetic anhydride nitration system, nitronium $NO_2{}^+$ dissociated from nitric acid attacked chlorobenzene, so as to facilitate the formation of nitrochlorobenzene. The determination of acidity demonstrates that the acidity of [CP]HSO_4 is the strongest among the three ILs. [CP]HSO_4 also can further provide one proton as Brønsted acid to promote nitric acid to form active agent nitronium ion favors to nitration reaction, so the yield is the highest. Also the catalytic activity of [CP]*p*TSA is obviously higher than that of [CP]BSA, which may be due to the structure of p-toluenesulfonate anion is more similar to chlorobenzene compared to benzenesulfonate anion. So the intermiscibility of [CP]*p*TSA is better and the ability to carry $NO_2{}^+$ into the organic phase is stronger, which make it show higher catalytic activity. Furthermore, it can be seen from Table 1, the magnitudes of the para/ortho selectivity are affected by the nature of the ILs. This suggests that a correlation exists between the degree of para-selectivity and the ability of electron-withdrawing substituent to induce an electrostatic attraction between substrate and ILs, causing greater hindrance at ortho-positions to such substituent [24,25]. For the same substrate and the same cation in the three ILs, the electron-withdrawing of anions generate great effect on the para-selectivity. For [CP]HSO_4 the effects were stronger, thus enhanced the electrostatic attraction between chlorobenzene and the IL, causing a greater hindrance at ortho-position. So it showed the best para-selectivity. As described above, the para-selectivity of [CP]*p*TSA is higher than that of [CP]BSA due to the higher polarity of [CP]*p*TSA, which give it good affinity to chlorobenzene. Therefore, [CP]HSO_4 was chosen as the catalyst for further study.

Table 2
Effect of reaction time on nitration of chlorobenzene.

Reaction time/h	Isomer distribution (%)		Para/ortho	Yield (%)
	Ortho	Para		
1.0	23.94	70.96	2.98	27.22
1.5	19.55	77.25	3.95	35.43
2.0	12.35	74.49	6.04	50.45
2.5	12.32	85.48	6.94	56.30
3.0	16.45	81.40	4.95	48.26

3.3. Effect of reaction time on nitration of chlorobenzene

When the process conditions of nitration of chlorobenzene were optimized, effect of reaction time on the yield and para-selectivity was first investigated. Taking caprolactam hydrosulfate ionic liquid as catalyst, other reaction conditions were the same as the previous. The results are showed in Table 2.

As known in Table 2, with the reaction time increases, the yield and regioselectivity increases rapidly within 2.5 h. When reaction time reaches to 2.5 h, the yield and the ratio of para/ortho achieve the maximum, which indicates that nitration reaction has almost been completed in 2.5 h. At the beginning, ortho-nitrochlorobenzene is formed quickly. But with the reaction proceeding, it is more beneficial to form para-nitrochlorobenzene. This may be because the increasing conversion of chlorobenzene leads to that the ratio of ionic liquid to chlorobenzene is gradually increasing, which provides ionization atmosphere for chlorobenzene and is helpful for its polarization. After the reaction time is extended to 3 h, however, the yield decreases slightly and para/ortho also significantly reduces. The result indicates that with the extension of reaction time, the dinitro-products are probably formed. So 2.5 h should be chosen as the appropriate reaction time.

3.4. Effect of reaction temperature on nitration of chlorobenzene

The reaction time was controlled in 2.5 h, and other reaction conditions were the same as before, to examine the impact of the reaction temperature on nitration of chlorobenzene. The results are shown in Table 3.

It can be seen from Table 3, nitration of chlorobenzene is more sensitive to temperature. The nitration is an endothermic reaction, and below 40 °C the nitrification is not easy to carry out so that the yield is low. With the reaction temperature increasing, the

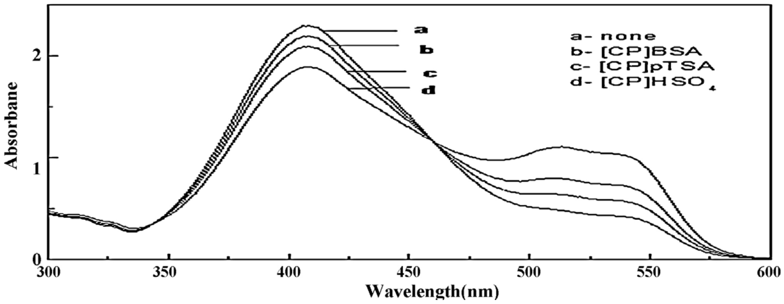

Fig. 3. Absorption spectra of dimethyl yellow for ILs in methanol.

yield increases significantly. This is mainly because the increase of temperature improves the solubility of chlorobenzene in acid phase and decreases the viscosity and the surface tension between two phases. Therefore, the diffusion effect will increase and be conductive to mass transfer process. Elevating reaction temperature is also beneficial to the generation of para-nitrochlorobenzene. As the nitration of chlorobenzene belongs to electrophilic substitution reaction and the activation energy of para-nitrification is minimum, while the ortho-product is controlled by kinetics and the para-product is controlled by thermodynamics, so increasing the temperature is helpful for the formation of product controlled by thermodynamics [26]. When the temperature elevated and the electron movement accelerated, with the frequency of collision between the H^+ and the reactant molecules increasing, the reaction probably increases. But when the temperature rises to 70 °C, nitric acid is easily decomposed to generate more NO_2, dinitro-byproducts increases, so that the yield declines and para/ortho reduces. Therefore, 60 °C is chosen as the optimum reaction temperature.

3.5. *Effect of amount of ionic liquid on nitration of chlorobenzene*

The reaction temperature was 60 °C, reaction time was 2.5 h, other reaction conditions remained the same as above, to investigate the effect of the amount of ionic liquid on nitration of chlorobenzene. The results are shown in Table 4.

The data in Table 4 shows that the yield of nitrochlorobenzene increases with the increase of the amount of ionic liquid, and the para-selectivity is significantly improved. When the mole ratio of [CP]HSO_4 ionic liquid to chlorobenzene substrate is 1.5:10, the yield and para-selectivity are the best. The [CP]HSO_4 catalyst shows the good catalytic activity and para-selectivity, that is, para/ortho isomer mass ratio is greatly increasing in comparison to 2.0 of para/ortho ratio obtained by nitric-sulfuric mixed acids as catalyst. The increasing yield with the amount of catalyst can be attributed to more proton acid provided by more Brønsted acidic ionic liquids, while para-selectivity of the nitration reaction was improved with the increasing amount of catalyst, which may be ascribed to a greater electron spin density on 4-C of benzene ring under the ionic environment offered by the catalyst [24]. Thereby it is in favor of the polarization of chlorobenzene substrate and improving the electronegativity and nucleophilic ability of the para-position. When the mole ratio of [CP]HSO_4 catalyst to substrate increases to 2:10, the yield and para-selectivity of nitrification are beginning to lower and significantly decrease with further increasing the catalyst amount. This may be because the concentration of nitric acid is diluted by a large number of ionic liquid, so that the activity and the yield of nitration reduce. Excessive ionic liquid increases the solvation effects, affects the polarization of the chlorobenzene substrate, and weakens the nucleophilic ability of para-position, results in the decline of para/ortho ratio. Therefore, the optimum mole ratio of ionic liquid to chlorobenzene is 1.5:10.

Table 3
Effect of reaction temperature on nitration of chlorobenzene.

Temperature (°C)	Isomer distribution (%)		Para/ortho	Yield (%)
	Ortho	Para		
30	21.05	75.48	3.59	32.30
40	14.54	83.03	5.71	46.28
50	12.32	85.48	6.94	56.30
60	12.19	86.91	7.13	65.36
70	20.2	79.80	3.95	45.28

3.6. *Effect of ionic liquid reused on nitration of chlorobenzene*

After the reaction is finished, the ionic liquid was recovered by vacuum distillation to remove the water and most of acetic acid, dried at 70 °C under vacuum for 2 h. Then it continued to be used for chlorobenzene nitration as the catalyst under the same conditions to investigate the effect of ionic liquid reused on the nitration of chlorobenzene. The results are shown in Fig. 4. As can be seen from Fig. 4, the yield and para/ortho ratio of nitrochlorobenzene decrease a little, and [CP]HSO_4 still exhibits good catalytic activity and regioselectivity after it is reused for five cycles. It not only indicates the excellent recycling performance of the ionic liquid [CP]HSO_4, but also indicates that the structure of the ionic liquid [CP]HSO_4 is stable after regeneration process. The yield of nitration slightly decreases with increasing of the recycling times, which may be ascribed to the accumulation of byproducts in the recovery process for ionic liquids.

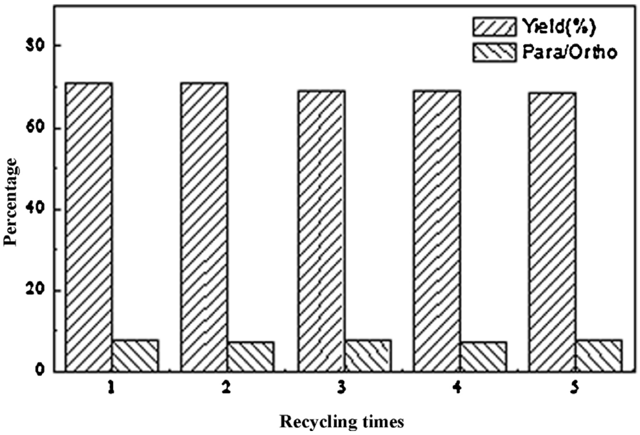

Fig. 4. Effect of ionic liquid reused on nitration of chlorobenzene.

Table 4
Effect of amount of ionic liquid on nitration of chlorobenzene.

Chlorobenzene:[CP]HSO_4(mol:mol)	Isomer distribution (%)		Para/ortho	Yield (%)
	Ortho	Para		
10:1	14.90	81.50	5.46	57.84
10:1.5	11.27	87.20	7.74	71.22
10:2	12.19	86.91	7.13	65.36
10:2.5	14.54	83.03	5.71	56.30

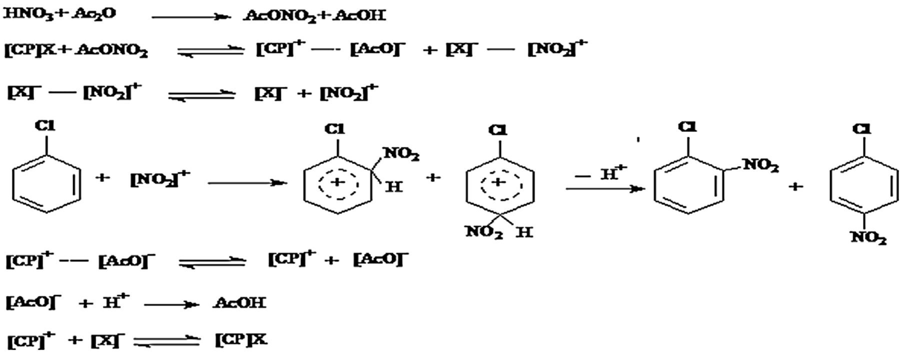

Fig. 5. The pathway and mechanism for the nitration of chlorobenzene.

3.7. *The pathway and mechanism for the nitration of chlorobenzene with caprolactam-based ionic liquids*

Taking caprolactam-based ionic liquid as the catalyst and nitric acid/acetic anhydride as the nitrification system, the pathway and mechanism for the nitration of chlorobenzene are speculated by reference to the literature [27]. As shown in Fig. 5.

4. Conclusion

(1) Three kinds of low toxicity caprolactam-based Brønsted acidic ionic liquids were synthesized. These ionic liquids have many advantages such as the cheaper and more easily available raw materials, the simple preparation process and the mild reaction conditions. So they are the novel, safe, and environmentally friendly ionic liquids.

(2) Used in the nitration of chlorobenzene as catalyst, this kind of ionic liquids showed good catalytic activity and para-selectivity, and the catalytic activity of [CP]HSO_4 was the best. The yield of mononitro-chlorobenzene could reach 71.22%, and the ratio of para/ortho was 7.74 under the optimum reaction conditions: the reaction temperature is 60 °C, the reaction time is 2.5 h, and the mole ratio of chlorobenzene to ionic liquid is 10: 1.5.

(3) [CP]HSO_4 showed the excellent reusability, and the regenerated ionic liquid could be recycled for at least five times without noticeably lowering of the catalytic activity and the para/ortho ratio. Therefore, the nitrification process of chlorobenzene using [CP]HSO_4 as catalyst has a good prospect in industrial application.

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