JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2005; **18:** 625–631
Published online 18 February 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.911

Theoretical study of the iodination of methoxybenzene by iodine monochloride

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Received 20 August 2004; revised 8 December 2004; accepted 20 December 2004

ABSTRACT: The pathway of the iodination of methoxybenzene by electrophilic iodine monochloride (ICl) was studied by using density functional theory (DFT) calculations at the B3LYP/6–311G* and MP2/6–311G*//B3LYP/6–311G* levels. The iodination occurs in the position *para* to the methoxy group, and proceeds in two steps. Initially, a π-complex forms between ICl and aromatic ring of methoxybenzene. With a barrier of 60.81 kcal mol^{-1} (1 kcal = 4.184 kJ), the π-complex can be activated to an intermediate σ-complex with energy 42.02 kcal mol^{-1} higher than that of the π-complex. The σ-complex then transforms easily (barrier 3.56 kcal mol^{-1}) into the final products, 1-iodo-4-methoxybenzene and HCl. The total iodination is slightly exothermic. Accompanying to the I—Cl bond breaking and C—I bond formation, a hydrogen atom migrates first to iodine and then to chlorine. According to NBO charge, Wiberg bond index and molecular orbital analysis, both charge separation and charge transfer occur during the iodination. Solvent effects were examined with the IEFPCM method and the B3LYP/6–311G* level. The results imply that polar solvents should play a key role in lowering the energy barrier, and favor the ion-pair route of the iodination reaction. Copyright © 2005 John Wiley & Sons, Ltd.
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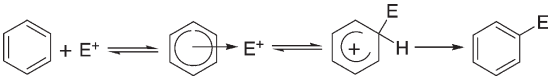
KEYWORDS: density functional theory; iodination; iodine monochloride; methoxybenzene; transition state; solvent effects

INTRODUCTION

Electrophilic aromatic substitutions are generally proposed as proceeding via a π- and a subsequent σ-complex (or Wheland intermediate) [Eqn (1)].[1–3] This proposal has been strongly evidenced by the experimental results that the π-complex and corresponding σ-complex were first formed along the reaction pathway.[4,5] However, the detailed mechanism, especially the transformation from π- to σ-complex, is still unclear. The understanding of the mechanism, desired for practical and theoretical purposes, has been the focus of recent investigations.[6]



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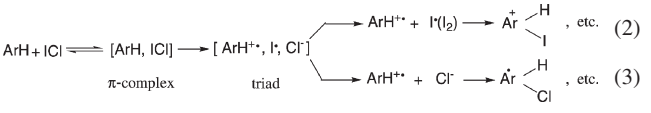
Iodine monochloride (ICl, CAS No. 7790-99-0) has been used as a neutral electrophile in aromatic substitutions and the mechanism has been also investigated experimentally.[7–19] It was reported that aromatic halogenation with ICl may proceed via a reactive triad. The triad may experience a radical-pair collapse to form iodination product [Eqn (2)], or an ion-pair collapse to form chlorination product [Eqn (3)].[15] In some cases, this mechanism agrees with the fact that the chlorination product and diiodine are usually produced as byproduct in the reactions using ICl as an attacking electrophile. However, this is not always so. For example, iodination of methoxybenzene with ICl was observed to undergo exclusive iodination without producing diiodine in dichloromethane,[15] which is difficult to explain by the triad intermediate mechanism. Zhong *et al.* carried out an in-depth study of on the bimolecular reaction of benzene and ICl with femtosecond time resolution.[18] They addressed another viewpoint that the iodination may occur via a covalent channel in which a covalent bond is formed between aromatic carbon and iodine in the transition-state region by reverse electron transfer (RET) from halogen back to the benzene donor [Eqn (4)].



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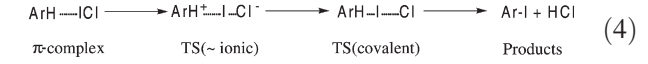

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Contract/grant sponsor: National Natural Science Foundation of China; *Contract/grant number:* 20171005.

So far, complete mapping of the whole course of electrophilic aromatic substitutions is still limited by the available techniques.[5] Therefore, theoretical calculations may play a key role in elucidating the mechanism. In fact, the structure and electronic nature of benzene-based π- and σ-complexes with various positive or neutral electrophiles have been studied theoretically in recent years.[20–26] For the benzene–ICl system, various conformations of the initial π-complex have also been calculated and compared.[20] However, there have still been no studies on the potential energy surface including both π- and σ-complexes, their transformation barrier and subsequent products.

Electrophilic aromatic iodination of methoxybenzene (CAS No. 100-66-3) with ICl has been reported to undergo exclusive iodination with high regioselectivity of *para* substitution in dichloromethane.[15] In the present work, we selected this reaction as a model to study the mechanism of electrophilic aromatic substitution with ICl by theoretical calculation. The main aim of our work was to search for the possible mechanism for the reaction of methoxybenzene and ICl. Furthermore, based on the selected mode, we also tried to illuminate the unclear nature (such as the charge and bond character) in the transformation from π-complex to σ-complex.

COMPUTATIONAL METHODS

It is well known that DFT methods such as B3LYP[27–29] have been successfully used in the prediction of large conjugated molecules. Recently, this method was reported to yield excellent results for some more complicated species, e.g. partially bonded systems,[30] certain radical ions[31] and even some biradical structures that normally require a multireference treatment.[32–36] Therefore, in this study we chose the B3LYP method for geometry optimizations and frequency calculations and the MP2 method for single-point energy calculations.

The geometry was optimized at the B3LYP/6–311G* level.[37] Transition states were located using the synchronous transit-guided quasi-Newton (STQN) method.[38] Frequency calculations were performed following each optimization to obtain the zero point energy (ZPE) and to characterize all the stationary points located on the potential energy surface. Intrinsic reaction coordinate (IRC) calculations were performed to confirm the relationship of each transition state with its reactant and product. Furthermore, the energies were refined by single-point calculation at the MP2/6–311G*//B3LYP/6–311G* level. Charge distributions and Wiberg bond indices[39] were determined via natural bond orbital (NBO) analyses at the B3LYP/6–311G* level. Solvent effects were modeled using the integral equation formalism polarized continuum model[40] (IEFPCM), by means of geometry optimization and frequency calculation at the B3LYP/6–311G* level.

The Gaussian 98 program package[41,42] was employed for these calculations. All computations were carried out on PCs (CPU, 3000 MHz; memory, 1024 MB; operating system, Microsoft Windows XP) or a workstation (16 CPUs, 1024 MB memory, Linux system).

RESULTS AND DISCUSSION

Structure and energy

The calculated geometries of all stationary points along the reaction coordinate are shown in Fig. 1. Selected structural parameters are listed in Table 1. Total electronic energies are listed in Table 2. The potential energy surfaces given by DFT and MP2 calculations are practically identical, and the former has energy barriers even lower than those of the latter. Hence all the discussion below is based on results calculated at the B3LYP/6–311G* level.

The ICl–benzene π-complex has been reported to have an oblique structure with the iodine atom directed towards one of the six C—C bonds in terms of theoretical calculation.[20] Similarly, the present structure of the π-complex (π-R) between ICl and methoxybenzene is also oblique from the ring plane, but has the iodine atom facing the carbon atom *para* to the methoxy group (i.e. C-2) owing to the substitution effect. The carbon and oxygen atoms of the methoxy group in the stable structure are coplanar with the ring plane, indicating that the oxygen atom adopts an sp^2 hybridization, leaving a p-orbital and a pair of electrons to conjugate with the π-system of benzene ring. Furthermore, the angle θ in π-R is near 90° (79.6°), and $R_{\text{I—Cl}}$ (2.442 Å) is slightly longer than that of the isolated ICl molecule (2.389 Å), indicating a weak π interaction between ICl and methoxybenzene.

As the system is activated to transition state TS1, considerable structural change occurs. First, the I—Cl moiety migrates towards the ring plane with the iodine atom heading towards C-2 and θ changed from 79.6° to 6.3°, indicating that the interaction essentially transforms from π- to σ-character. Second, $R_{\text{C-2—I}}$ is shortened from 3.060 to 2.390 Å, whereas $R_{\text{I—Cl}}$ is lengthened from 2.442 to 2.677 Å, indicating that the partial C-2—I bond formation and I—Cl bond breaking happen in a concerted way. Third, $R_{\text{C-2—H-1}}$ is lengthened from 1.084 to 1.848 Å, whereas $R_{\text{I—H-1}}$ is shortened significantly from 3.140 to 1.701 Å, indicating the formation of a C···H···I hydrogen bond.

To activate π-R to TS1, 60.81 kcal mol^{-1} are required. Over this barrier, the system goes to the σ-intermediate (σ-INT). The energy of σ-INT is 42.02 kcal mol^{-1} relative to π-R. The structure of σ-INT is similar to that of TS1, with $R_{\text{C-2—I}}$ further shortened and $R_{\text{I—Cl}}$ further lengthened slightly. The most remarkable change from TS1 to σ-INT is that the bridging H-1 has completely migrated to I, with $R_{\text{I—H-1}}$ (1.645 Å) close to the experimental H—I bond length (1.609 Å).[43]

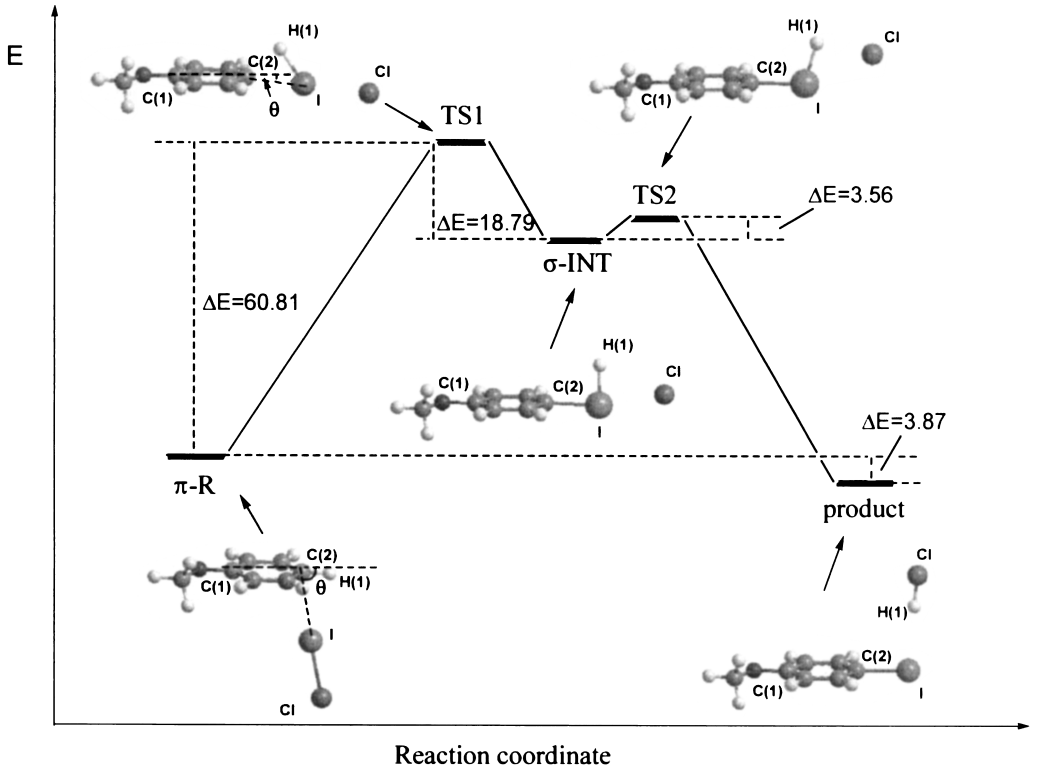


Figure 1. Energy diagram of methoxybenzene iodination with ICl along the reaction coordinate. The energies (kcal mol^{-1}) have been corrected for ZPE

Table 1. Selected structural parameters of the methoxybenzene–ICl stationary points[a]

Geometry	π-R	TS 1	σ-INT	TS 2	Product
C-2—H-1	1.084	1.848	2.713	3.049	3.693
C-2—I	3.062	2.390	2.197	2.169	2.133
I—Cl	2.442	2.677	2.708	2.904	4.115
I—H-1	3.140	1.701	1.645	1.676	2.812
Cl—H-1	5.472	3.970	2.873	2.247	1.302
θ	79.6	6.3	2.0	0.3	0.1

[a] Bond lengths are in Å and angles are in degrees. The numbers of the C and H atoms are shown in Fig. 1.

Starting from σ-INT, the system can be easily activated to the second transition state (TS2), which leads to the final product. The energy barrier of the second step is only 3.56 kcal mol^{-1}. It is obvious that from π-R across TS1 to σ-INT, the first step along the reaction path, is rate limiting.

The migration of H-1 from I to Cl is the dominant structural change in the second step, from σ-INT to TS2. $R_{\text{I—H-1}}$ is lengthened only slightly from 1.645 to 1.676 Å, whereas $R_{\text{Cl—H-1}}$ is shortened from 2.873 to 2.247 Å. The leaving Cl atom in TS2 is actually hydrogen bonded by H-1, because the I—Cl bond (2.904 Å) is remarkably weakened. As H-1 migrates to Cl ($R_{\text{Cl—H-1}}$ 1.302 Å), the iodination completes and the iodinated product, 1-iodo-4-methoxy-benzene (CAS No. 696-62-8), is loosely associated with HCl as the final product. Because the energy of the product is -3.87 kcal mol^{-1} relative to the initial π-R, the iodination is thermodynamically favored.

Table 2. Calculated electronic energies of the methoxybenzene–ICl system

	B3LYP/6–311G*			MP2/6–311G*//B3LYP/6–311G*	
Species	E_e[a] (a.u.)	ZPE[b] (a.u.)	E_r[c] (kcal mol^{-1})	E_e[a] (a.u.)	E_{r-s}[d] (kcal mol^{-1})
π-R	−7648.277423	0.134438	0	−7644.024358	0
TS 1	−7648.173951	0.127870	60.81	−7643.915214	68.49
σ-INT	−7648.206473	0.130452	42.02	−7643.946856	48.63
TS 2	−7648.198709	0.128354	45.57	−7643.936220	55.31
Product	−7648.279375	0.130231	−3.87	−7644.035629	−7.07

[a] Calculated electronic energies.
[b] Zero-point energy.
[c] Relative energies with ZPE corrections.
[d] Relative energies without ZPE corrections.

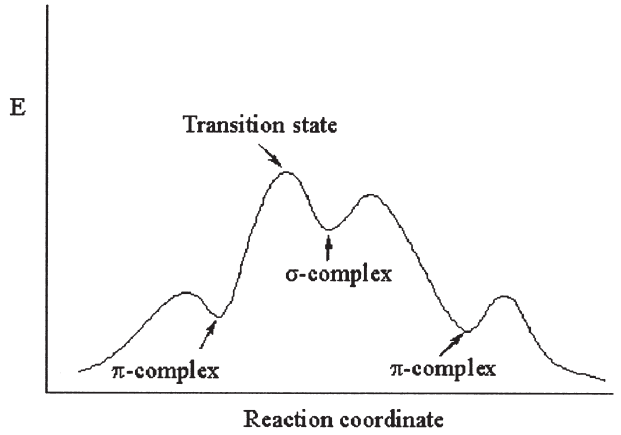


Figure 2. The compact energy profile of electrophilic aromatic substitutions

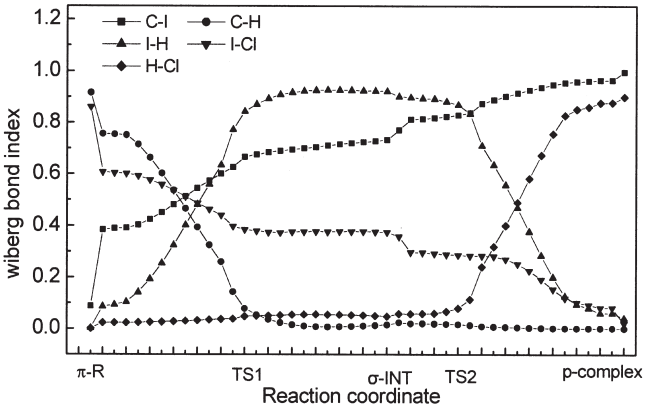


Figure 3. Selected Wiberg bond indices along the IRC

Apparently, the picture described above is different from the aforementioned radical-pair collapse mechanism [Eqn (2)]. A remarkable structure change during this process is the transfer of H-1 from C-2 first to iodine, and finally to chlorine, accompanying the formation of the C-2—I bond and the breaking of the I—Cl bond. By this route the reaction of ICl and methoxybenzene should produce only the product of 1-iodo-4-methoxybenzene and HCl, without the byproduct chlorinated methoxybenzene and diiodine. This deduction is in agreement with the experimental results.[15] In addition, the potential energy surface following the pathway is also identical with the compact energy profile of aromatic electrophilic substitutions deduced from the kinetic examinations (Fig. 2).[2] However, the high energy barrier of the rate-limiting step, which means a poor reactivity of this system, is inconsistent with the observation that the reaction of ICl and methoxybenzene occurs easily in dichloromethane.[15] In our opinion, solvent effects may play a key role on decreasing the energy barrier of iodination reaction (see the section Solvent effects, below).

Wiberg bond index

Chemical bond disruption and formation can be quantified by the Wiberg bond index, which reflects the superposition of electron density between two interacting atoms.[39] A large Wiberg bond index indicates a strong covalent bonding interaction between the two relevant atoms. Figure 3 shows the Wiberg bond indices of several bonds along the IRC.

From π-R to σ-INT, two bonds (C-2—I and I—H-1) are formed and two bonds (I—Cl and C-2—H-1) are broken. The most significant variations of the bond index happen on the path from π-R to TS1, rather than from TS1 to σ-INT. It may be inferred that bond disruption and formation are substantially involved in the activation of π-R to TS1 but not in the decay of TS1 to σ-INT. As far as the C-2—I bond is concerned, a remarkably covalent bonding character can be observed between the C-2 and iodine atom in both TS1 and σ-INT, which is in agreement with the covalent channel proposal of Zhong *et al.* [Eqn (4)].[18] Compared with C-2—I and I—Cl bonds, the C-2—H-1 and I—H-1 bonds change more significantly in bond index, which not only indicates the dominant effect of H-1 migration in the transformation, but also reflects more covalent bonding character of the two bonds involving the migrating hydrogen atom. Notably, the C-2—H-1 bond is already broken and the I—H-1 bond is almost completely formed in the transition state (TS1). This is different from the common notion of electrophilic aromatic substitution. For example, in the iodination of moderately activated substrates, the kinetic isotope effect (KIE) is determined to be close to unity, implying that the bond between the aromatic carbon and the hydrogen atom is not yet broken in the rate-limiting step.[44] There is still no information on KIE measurements on the iodination of methoxybenzene. In terms of the bond analysis above, it is predicted that the reaction of ICl and methoxybenzene may have a KIE different from unity.

From σ-INT to the product, the dramatic decrease in the bond index of I—H-1 and increase in that of Cl—H-1 happen concertedly during the conversion from TS2 to the product, indicating that H-1 migration from I to Cl is involved in this process. No other bond disruption or formation is involved during the activation of σ-INT to TS2. Furthermore, the bond indices of C-2—I and I—Cl are varied only slightly, indicating that the C-2—I formation and I—Cl disruption are essentially completed at the rate-limiting step. This may account for the large energy difference between TS1 and TS2.

Charge transfer and molecular orbital

The electric charges on some selected atoms obtained by natural population analysis (NPA) for all stationary points are summarized in Table 3. The net charge of the ICl unit is negative in π-R (-0.103 e). This has been attributed to the electron donation from occupied π-orbitals of the

Table 3. NPA charges on some selected atoms for the anisole-ICl system on the iodination pathway

Atom/unit	π-R	TS 1	σ-INT	TS 2	Product
I	0.183	0.573	0.777	0.696	0.148
Cl	−0.286	−0.583	−0.645	−0.699	−0.282
ICl	−0.103	−0.010	0.131	−0.002	—
$CH_3OC_6H_4$—I[a]	—	0.402	0.559	0.544	0.032

[a] The moiety includes iodine and methoxybenzene, but excludes H-1.

aromatic ring to an unoccupied σ*-orbital of ICl.[20] As the system overcomes the first energy barrier and transforms into σ-INT, the negative charge flows in the opposite direction. i.e. from ICl to methoxybenzene. As a result, the net charge of the ICl unit approaches neutral (-0.010 e) in TS1 and becomes positive (0.131 e) in σ-INT. Simultaneously, the positive charge on the iodine atom in ICl unit increases gradually from 0.183 e (π-R) to 0.573 e (TS1) to 0.777 e (σ-INT), whereas the chlorine atom becomes more negative along the same path. The charge separation effect of ICl occurring in the rate-limiting step makes both TS1 and σ-INT possess some character similar to the iodinated arenium cation. The positive charge of the methoxybenzene–iodine [with H-1 excepted] moiety is mainly localized on the iodine atom rather than on the aromatic ring (see Table 3), probably owing to the charge separation of the I—Cl bond and the charge transfer from iodine to H-1 (as discussed below). The positive charge of ICl in σ-INT becomes near neutral as the system is activated to TS2 (-0.002 e), partly owing to the negative charge flow from methoxybenzene to ICl. Simultaneously, the charge separation in the ICl unit remains large (0.696 e for I and -0.699 e for Cl).

Charge transfer along the reaction coordinate can also be elucidated through molecular orbital interactions (Fig. 4). As π-R converts into σ-INT, negative charge flows from the $\pi_{C\text{-}2—C\text{-}3}$ orbital (localized) of methoxybenzene to the σ*-orbital of ICl [Fig. 4(a) and (b)], strengthening the π-I bond but weakening the I—Cl bond. As the reaction proceeds forwards, a non-bonding orbital of the iodine atom with a lone electron pair (LP) overlaps with the σ*-orbital of C-2—H-1 [Fig. 4(c)], resulting in charge transfer from iodine to H-1 and the migration of hydrogen in this step. From TS2 to the product, a lone pair, residing in a non-bonding orbital of the chlorine atom, overlaps with the σ*-orbital of I—H-1 [Fig. 4(d)], resulting in negative charge flow from Cl to I—H-1, migration of H-1 from iodine to chlorine and a decrease in positive charge in the methoxybenzene–iodine moiety (H-1 excepted, see Table 3).

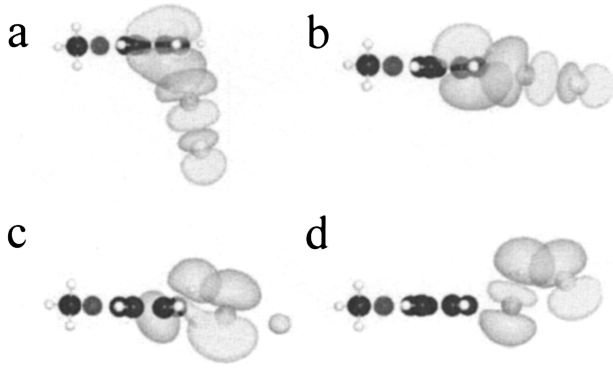
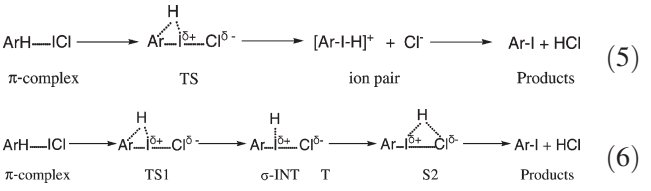


Figure 4. Selected orbital interaction on the isocontour of the natural localized molecular orbital (NLMO). (a) π-R: $\pi_{C\text{-}2—C\text{-}3}$; $\sigma^*_{I—Cl}$. (b) A point on the IRC pathway from π-R to TS1: $\pi_{C\text{-}2—C\text{-}3}$; $\sigma^*_{I—Cl}$. (c) The same structure as (b): $\sigma^*_{C\text{-}2—H\text{-}1}$; LP_I. (d) TS2: $\sigma^*_{I—H\text{-}1}$; LP_{Cl} (LP = lone pair)

The charge separation effect of the ICl unit in TS1, σ-INT and TS2 implies that the iodination may proceed via an ion-pair route [Eqn (5)]. On the other hand, the charge transfer during iodination suggests the involvement of covalent bonds in the whole transformation, namely a covalent route [Eqn (6)], which requires sufficient overlap between the electron-donating orbital and electron-accepting orbital. Therefore, both mechanisms may coexist and the real pathway of iodination may depend on the nature of the substrate and the polarity of the solvent.



Solvent effects

Solvent effects on stationary points were determined by the IEFPCM method with CCl_4 (non-polar), CH_2Cl_2 (poorly polar), CH_3COCH_3 and CH_3CN (polar) as solvents. The relative energies for all stationary points calculated in the gas phase and in the presence of the solvent reaction field are compared pictorially in Fig. 5, and the selected structure parameters of TS1, σ-INT and TS2 are given in Table 4.

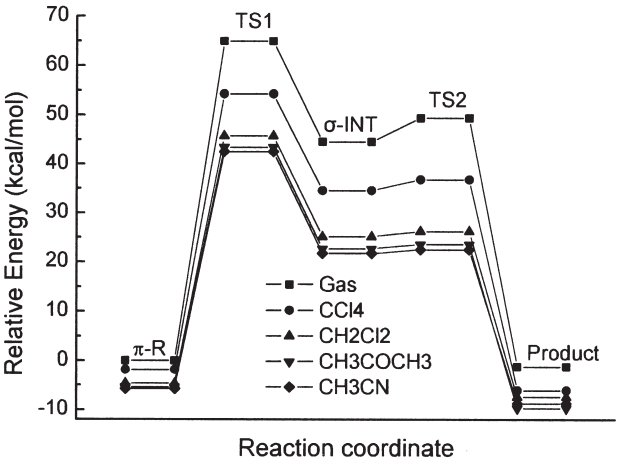


Figure 5. Relative energies (no ZPE correction) for the iodination reaction of methoxybenzene with ICl in gas and different media

Table 4. Selected structure parameters of the methoxybenzene–ICl stationary points in different solvents[a]

	Geometry	Gas	CCl_4	CH_2Cl_2	CH_3COCH_3	CH_3CN
TS1	C-2—I	2.390	2.355	2.314	2.304	2.300
	I—Cl	2.677	2.776	2.943	3.002	3.027
σ-INT	C-2—I	2.197	2.175	2.152	2.147	2.146
	I—Cl	2.708	2.822	3.027	3.066	3.092
TS2	C-2—I	2.169	2.149	2.135	2.133	2.132
	I—Cl	2.904	3.059	3.297	3.367	3.396

[a] Bond lengths are in Å. The serial numbers of C and H atoms are shown in Fig. 1.

Since TS1, σ-INT and TS2 possess large dipole moments ($\mu = 10.14$, 9.89 and 11.72, respectively) and strong charge separation effects (Table 3), they are strongly influenced by the polar solvent. Remarkably, TS2 gains much more stabilization energy than TS1 and σ-INT by increasing the solvent polarity. Finally, the potential energy is almost leveled in the case of σ-INTs in CH_3COCH_3 and CH_3CN. On the other hand, in these three structures $R_{C\text{-}2—I}$ is slightly shortened, whereas $R_{I—Cl}$ is considerably lengthened when the solvent polarity is gradually increased. This indicates that the iodination reaction may proceed mainly via the ion-pair route [Eqn (5)] with only a single transition state (e.g. TS1) in the highly polar medium, whereas it would proceed via the covalent route in the gas phase or the poorly polar medium.

Unlike the transition states and intermediate, π-R and product exhibit small dipole moments ($\mu = 5.27$ and 4.25, respectively) and weak charge-transfer effects, hence they are slightly influenced by the solvent. As a result, the activation energy of the rate-limiting step (from π-R to σ-INT) is reduced by increasing the dielectric constant. This means that solvents, especially polar solvents, should play a key role in lowering the energy barrier for the iodination of methoxybenzene with ICl.

CONCLUSION

The iodination of methoxybenzene by ICl is a typical electrophilic aromatic substitution. The present reaction pathway can be divided into two steps. First, the pre-reactive π-complex is activated to an intermediate σ-complex 42.02 kcal mol^{-1} higher in energy, the barrier of the rate-limiting step being 60.81 kcal mol^{-1}. Second, the σ-complex transforms into the final product 1-iodo-4-methoxybenzene and HCl with a barrier of 3.87 kcal mol^{-1}. Accompanying the C-2—I bond formation and I—Cl bond disruption, a hydrogen atom migrates from carbon to iodine in the first step and from iodine to chlorine in the second step. During the iodination, both charge transfer between the reactants and charge separation within the ICl unit are significant, indicating the complicated nature of the bonding, which suggests that the reaction may undergo an ion-pair route or a covalent route depending on the nature of the substrate and the experimental conditions. Furthermore, solvent effects indicate that solvents, especially polar solvents, may effectively lower the reaction energy barrier and favor the ion-pair route. Similar mechanisms may be expected for aromatic substitutions with other halogen species.

Acknowledgments

This work was sponsored by the National Natural Science Foundation of China (20171005). We thank Professor Yun-Dong Wu for his invaluable suggestions and discussions on solvent effect calculations.

REFERENCES

1. Lowery TH, Richardson KS. *Mechanism and Theory in Organic Chemistry* (3rd edn). Harper and Row: New York, 1987; 623.
2. Taylor R. *Electrophilic Aromatic Substitution*. Wiley: New York, 1990; 31.
3. March J. *Advanced Organic Chemistry*. Wiley: New York, 1992; 501.
4. Hubig SM, Kochi JK. *J. Am. Chem. Soc.* 2000; **122**: 8279–8288.
5. Vasilyev AV, Lindeman SV, Kochi JK. *New J. Chem.* 2002; **26**: 582–592.
6. Lenoir D. *Angew. Chem. Int. Ed.* 2003; **42**: 854–857.
7. Lambourne LJ, Robertson PW. *J. Chem. Soc.* 1947; **69**: 1167–1168.
8. Keefer RM, Andrews LJ. *J. Am. Chem. Soc.* 1950; **72**: 5170.
9. Bennett FW, Sharpe AG. *J. Chem. Soc.* 1950; **72**: 1383–1384.
10. Papa D, Ginsberg HF, Lederman I, DeCamp V. *J. Am. Chem. Soc.* 1953; **75**: 1107–1110.
11. Jones B, Richardson EN. *J. Chem. Soc.* 1953; **75**: 713–715.
12. Andrews LJ, Keefer RM. *J. Am. Chem. Soc.* 1957; **79**: 1412–1416.
13. Berliner E. *J. Am. Chem. Soc.* 1956; **78**: 3632–3637.
14. Olah G, Pavlath A, Varsanyi G. *J. Chem. Soc.* 1957: **79**: 1823–1829.
15. Hubig SM, Jung W, Kochi JK. *J. Org. Chem.* 1994; **59**: 6233–6244.
16. Turner DE, O'Malley RF, Sardella DJ, Barinelli LS, Kaul P. *J. Org. Chem.* 1994; **59**: 7335–7340.
17. Eberson L, Hartshorn MP, Radner F, Persson O. *J. Chem. Soc., Perkin Trans. 2* 1998; 59–70.
18. Zhong DP, Bernhardt TM, Zewail AH. *J. Phys. Chem. A* 1999; **103**: 10093–10117.
19. Fabbrini M, Galli C, Gentili P, Macchitella D, Petride H. *J. Chem. Soc., Perkin Trans. 2* 2001; 1516–1521.
20. Ammal SSC, Ananthavel SP, Venuvanalingam P, Hedge MS. *J. Phys. Chem. A* 1998; **102**: 532–536.
21. Su JT, Zewail AH. *J. Phys. Chem. A* 1998; **102**: 4082–4099.
22. Grozema FC, Zijlstra RWJ, Swart M, Van Duijnen PT. *Int. J. Quantum Chem.* 1999; **75**: 709–723.
23. Smith WB. *J. Phys. Org. Chem.* 2002; **15**: 347–352.
24. Smith WB. *J. Phys. Org. Chem.* 2003; **16**: 34–39.
25. Heidrich D. *Angew. Chem. Int. Ed.* 2002; **41**: 3208–3210.

26. Litao Ch, Heming X, Jijun X, Xuedong G. *J. Phys. Chem. A* 2003; **107**: 11440–11444.
27. Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785–789.
28. Miehlich B, Savin A, Stoll H, Preuss H. *Chem. Phys. Lett.* 1989; **157**: 200–206.
29. Sosa C, Lee C. *J. Chem. Phys.* 1993; **98**: 8004–8011.
30. Ruiz E, Salahub D, Vela A. *J. Am. Chem. Soc.* 1995; **117**: 1141–1142.
31. Bally T, Sastry GN. *J. Phys. Chem. A* 1997; **101**: 7923–7925.
32. Engels B, Hanrath M. *J. Am. Chem. Soc.* 1998; **120**: 6356–6361.
33. De Proft F, Schleyer PVR, Van Lenthe JH, Stahl F, Geerlings P. *Chem. Eur. J.* 2002; **8**: 3402–3410.
34. Breton GW, Shugart JH. *J. Org. Chem.* 2003; **68**: 8643–8649.
35. Kwon O, Almond Å, McKee ML. *J. Phys. Chem. A* 2002; **106**: 6864–6870.
36. Özkan I, Kinal A, Balci M. *J. Phys. Chem. A* 2004; **108**: 507–514.
37. Pross A, Glukhovtsev MN, McGrath MP, Radom L. *J. Chem. Phys.* 1995; **103**: 1878–1885.
38. Peng CY, Ayala PY, Schlegel HB, Frisch MJ. *J. Comput. Chem.* 1996; **17**: 49–56.
39. Wiberg KB. *Tetrahedron* 1968; **24**: 1083–1096.
40. Tomasi J, Mennucci B, Cancès E, *J. Mol. Struct. (Theochem)* 1999; **464**: 211–266.
41. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill ÅW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.7*. Gaussian: Pittsburgh, PA, 1998.
42. Glendening ED, Reed AE, Carpenter JE, Weinhold F. *NBO Version 3.1*. Theoretical Chemistry Institute, University of Wisconsin, Madison.
43. Huber KP, Herzberg G. *Molecular Spectra and Molecular Structure*. *Constants of Diatomic Molecules*, vol. IV. Van Nostrand: New York, 1979.
44. Galli C. *J. Org. Chem.* 1991; **56**: 3238–3245.