

FTIR-ATR Spectroscopic Characterization of Monochlorophenols and Effects of Symmetry on Vibrational Frequencies

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Abstract

In this study, characterization of monochlorophenols (*o*-, *m*-, *p*-chlorophenol) has been observed by using FTIR spectroscopy as well as the effects of molecule symmetry on vibrational frequencies of molecule. Vibrational modes of monochlorophenols investigated by means of ATR which is the best choice for liquid phase. The observed infrared bands of monochlorophenols are assigned with their geometrical structures. Isomers with their same chemical formula and molecular weights would be a critical choice to express ideas about symmetry effects on characteristic wavenumbers of molecules. It is concluded that symmetry of molecules affects the wavenumber of functional group in the molecule.

Keywords: FTIR, monochlorophenols, characterization, ATR

Özet

Bu çalışmada, (*o*-, *m*-, *p*-klorofenol) monoklorfenollerin karakterizasyonu FTIR spektroskopisi kullanılarak elde edilmiş, buna ek olarak molekül simetrisinin moleküle ait titreşim frekansları üzerine etkisi gözlenmiştir. Monoklorfenollerin titreşim modları incelenirken sıvılar için en iyi seçim olan ATR seçilmiştir. monoklorfenollerden elde edilen kırmızı-altı bandlar, monoklorfenollerin geometrik yapıları göz önüne alınarak atfları yapılmıştır. Molekülün simetrisinin özgün dalga sayılarının üzerine etkisini açıklayabilmek adına seçim yapılırken tamamıyla molekül formülleri ve molekül ağırlıkları aynı olan izomerler seçilmiştir. Molekülün simetrisinin, fonksiyonel grupların özgün dalga sayılarına etki ettiği sonucuna varılmıştır.

Anahtar kelimeler: FTIR, monoklorfenoller, karakterizasyon, ATR

1. Introduction

Monochlorophenols (MCPs) are organic chemicals formed from phenol by substitution in the phenol ring with one atom of chlorine. Monochlorophenols are solid at room temperature, except for 2-MCP, which is a liquid. Studies on the carcinoge-

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nicity exhibited that MCPs appeared to be promoters and MCPs are listed as priority pollutants by the U.S. Environmental Protection Agency (EPA). Euro Chlor Group carried out risk assessment of monochlorophenols related to the chlorine industry, specifically for the marine environment and according to the methodology laid down in the EU Risk Assessment Regulation (1488/94) and the Guidance Documents of the EU Existing Substances Regulation (793/93) (Euro Chlor, 2002, 2-42). Chloro-substituted phenols attract great interest in Environmental problems. Due to hazardous and dangerous effects of MCPs, it became an urgent problem to identify the monochlorophenols. From this point of view, researchers focused on the work about the development of sensitive and selective methods for determination of these substances. For identification of MCPs in any kind of sample, FTIR spectroscopic investigation is one of the best choices with its quick, cheap and unique results. Until now studies of researches to investigate MCPs had been based some halogenated phenols (Chetty et al, 2003, 984-985) and gas form of p-chlorophenol and theoretical measurements (Zierkiewicz et al, 2000, 11685-11692). dispersed fluorescence spectra of 4-chlorophenol (para-chlorophenol) had been investigated by other scientists (Imhof et al, 2002, 264–270). In this study, infrared spectral investigation of MCPs carried out in ambient conditions. ATR (Attenuated Total Reflection) accessory is preferable to other techniques of FTIR spectroscopy due to perfect contact between sample and the ATR crystal.

2. Experimental

Monochlorophenols (MCPs); 2-chlorophenol (98 %, Merck), 3-chlorophenol (95%, Fluka) and from 4-chlorophenol (99 %, Fluka) were used without any purification. The IR measurements were performed on a Perkin Elmer BX FTIR spectrometer at a resolution of 4 cm^{-1} . The ATR cell equipped ZnSe crystal (45° angle of incidence) as the internal reflection element. Each ATR spectrum was recorded with the blank ATR cell as the background.

3. Results and Discussion

MCPs are position isomers; they have similar chemical properties as they differ only in the location of the functional group. All MCPs share the same chemical formula and molecular weight, but have different arrangements of atoms in the molecules as they are exhibited in Fig. 1.

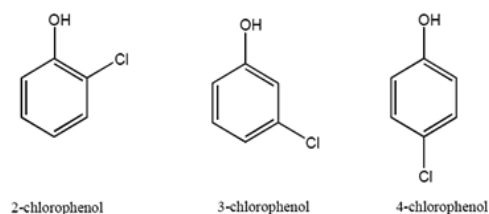


Figure 1. Structure of the monochlorophenols.

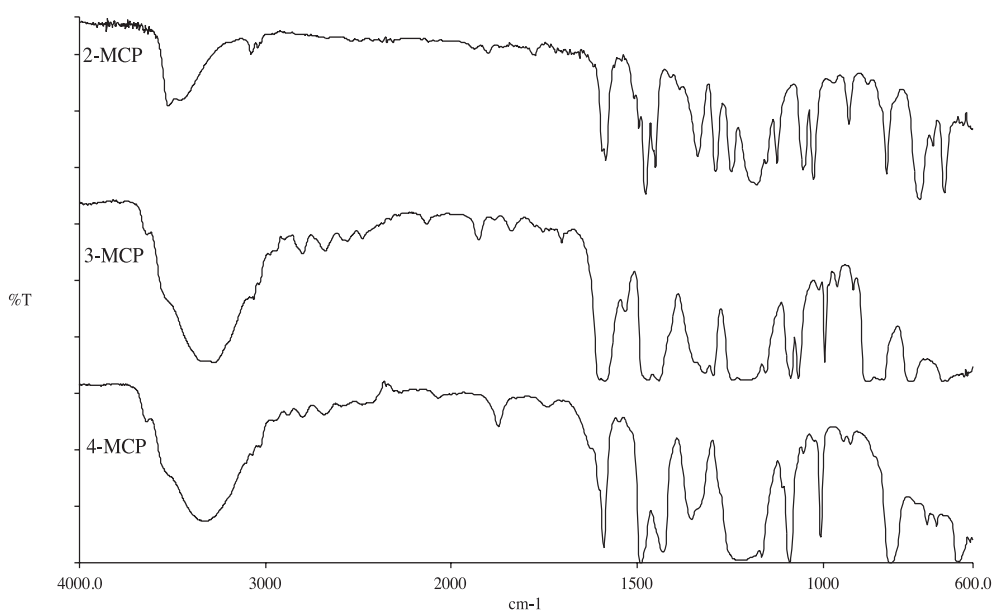


Figure 2. IR spectra of bulk monochlorophenols; 2-MCP (2-chlorophenol), 3-MCP (3-chlorophenol), 4-MCP (4-chlorophenol).

Characteristic wavenumbers of bulk MCPs obtained from Fig. 2 are as follows : IR (ATR, cm⁻¹) **For 2-MCP:** 3521s, 3453 m, 3076 m, 3039 w, 2537 w, 2449 w, 2311 w, 2121 w, 1936 w, 1900 m, 1774 m, 1718 w, 1685 w, 1654 w, 1636 w, 1617 w, 1593 m, 1584 s, 1495 s, 1478 s, 1450 s, 1411 w, 1387 w, 1337 s, 1290 s, 1249 m, 1179 m, 1154 w, 1125 s, 1055 s, 1027 m, 972 w, 932 m, 882 w, 831 s, 743 s, 707 m, 676 s, 625 w, 601 w. **For 3-MCP:** 3271 b, 3060 w, 3033 w, 2800 m, 2677 m, 2559 m, 2475 m, 2125 m, 1924 m, 1881 w, 1834 m, 1753 w, 1702 m, 1584 s, 1531 m, 1472 s, 1442 m, 1318 s, 1296 s, 1242 w, 1202 b, 1154 m, 1088 s, 1068 s, 1013 m, 997 s, 963 m, 921 m, 885 b, 841 m, 767 b, 683 w, 624 w, 615 w. **For 4-MCP:** 3331 b, 3068 w, 3025 w, 2878 w, 2796 m, 2682 m, 2588 w, 2068 w, 1872 m, 1743 m, 1589 s, 1584 w, 1491 s, 1431 m, 1354 m, 1223 b, 1165 m, 1090 s, 1008 s, 947

m, 928 m, 821 s, 723 w, 698 w, 636 m. * b: broad, m: medium, s: strong, w: weak intensity of transmittance.

2-MCP: The strong band at 3521 cm^{-1} is assigned to free OH bond (Silverstein et al, 1991, 110). Bands between 1585 and 1450 cm^{-1} are attributed to the aromatic ring C=C stretching vibrations (Bandara et al, 2001, 312-313; Kung et al, 1991, 704). The bands at 1249 , 1154 , 1125 and 1027 cm^{-1} correspond to ring C-H in-plane bending vibrations (Bandara et al, 2001, 312; Kung et al, 1991, 703). The band at 1055 cm^{-1} is assigned to a Cl- sensitive vibration. Bands at 1337 and 1179 cm^{-1} are attributed to O-H deformation and bending vibrations (Bandara et al, 2001, 313; Kung et al, 1991, 704; Shchukin et al, 2004, 426; Colthup et al, 1964, 275).

3-MCP: As Silverstein and coworkers (Silverstein et al, 1991, 110) indicated before the band between 3550 - 3200 cm^{-1} belong phenol compounds is attributed to hydroxyl band. Bands at 1584 and 1472 cm^{-1} ring stretching vibrations (Kung et al, 1991, 705). The band at 1088 cm^{-1} is assigned to C-Cl bond (Silverstein et al, 1991, 130).

4-MCP: The strong band at 1589 cm^{-1} in the spectrum of bulk 4-MCP can be attributed to C=C stretching (Pandit et al, 2001, 267; Zierkiewicz et al, 2000, 11688). This band was observed as 1590 cm^{-1} by other scientists who had studied the interaction between activated carbon surfaces and adsorbed phenol derivatives (Paku_a et al, 2005, 154). The band at 1355 cm^{-1} and bands between the range of 1250 - 1150 cm^{-1} are attributed to the in-plane bending of C-H bonds (Pandit et al, 2001, 267). Bands between 900 and 675 cm^{-1} assigned to the out of plane bending of the ring C-H bonds (Pandit et al, 2001, 267; Silverstein et al, 1991, 109). As it is shown in Fig.2., the band at 821 cm^{-1} was attributed to mostly out- of-plane bending of the ring C-H vibration in an another study (Zierkiewicz et al, 2000, 11691).

For 2-MCP, the bands at 1584 , 1478 and 743 cm^{-1} show a ring vibration. C-H stretches between 3140 - 3000 cm^{-1} indicate the presence of 1,2- substituted aromatic ring. Bands between 1100 and 1000 cm^{-1} demonstrate hydroxyl group of aromatic ring. For 3-MCP, the bands between 3100 - 3000 cm^{-1} together with the range of 1625 - 1575 shows characteristic bands of aromatic compounds. In fingerprint region of 4-MCP spectrum, bands at 821 , 723 , 698 , 636 cm^{-1} show unique wavenumbers of this isomer. The wavenumbers of phenol are taken from Silverstein (Silverstein et al, 1991, 110) and other IR spectral data of MCPs are summarized in Table 1. MCPs are represented by a Cl atom and an OH group, bound to the aromatic ring. Functional group position of the molecule affects vibrational frequencies. It was ob-

tained that the closer the Cl atom to OH group of the ring, the higher the wave number of OH group for MCPs in Fig.2. As the Cl atom distances from the OH group, the vibration frequencies of the hydroxyl group shifts towards lower frequencies.

Table 1. The IR frequencies (cm^{-1}) of MCPs and assignments.

Phenol	2-MCP	3-MCP	4-MCP	Assignment (type of vibration)I
3373	3521	3344	3331	OH stretching
	3453			OH stretching
	3076	3060	3068	Aromatic C-H stretching
3045	3039	3033	3025	Aromatic C-H stretching
2000-1667				Overtone or combination bands
1595	1584	1584	1589	C=C ring stretching
1499	1495	1472	1491	C=C ring stretching
1470	1478	1442	1431	C=C ring stretching
1360	1337	1318	1355	In plane O-H bending
1224		1242	1223	C-O stretching
	1249			in-plane C-H bending
	1179			O-H deformation bending
	1154		1166	in-plane C-H bending
	1125			in-plane C-H bending
	1055	1088	1090	C-Cl
	1027			in-plane C-H bending
810			821	Out of plane C-H bending
752			723	Out of plane C-H bending
690			698	Out of plane ring C=C bending
650			636	Out of plane OH bending
	743			C=C ring stretching

MCPs (chloro-substitued phenols) are planar, belong to same point group as phenol. It is point group C_s . Phenol exhibited a broad band at 3373 cm^{-1} , after a chlorine atom attachment to phenol OH (Hydroxyl group) OH stretching vibrational frequency shifts to higher frequency in 2-MCP, then OH stretching frequency shifts to lower level in 3-MCP, lower than that for 4-MCP. The same results obtained in

plane OH bending at $\sim 1300\text{ cm}^{-1}$, except 4-MCP, symmetry of 4-MCP give rise to increase of hydroxyl group frequency in this region. For 4-MCP, Cl atom and OH group are in the same line, that makes vibration of OH group faster than the other position of isomers. C-Cl vibration frequencies of isomers show a gradual increase from 2-MCP towards 4-MCP. Generally after a substitution of phenol C=C ring vibrational frequency decreasing at $1478\text{-}1431\text{ cm}^{-1}$.

Conclusion

The three isomers of monochlorophenol show different wavenumbers in their unique spectra. The FTIR spectroscopic results indicate that the para position with respect to the -OH group in monochlorophenols shows different behavior in plane OH bending vibrations and C=C ring stretching at $1584\text{-}1470\text{ cm}^{-1}$ compare to 2-MCP and 3-MCP. Results for vibrational frequencies of 4-MCP could be presumably connected to geometry of 4-MCP. All data about monochlorophenols by FTIR-ATR would be helpful to detect which is the one of MCPs. Due to the same retention time of isomers of MCPs in gas chromatography (Crespin et al, 1999, 168), it could not be observed which isomer is available in the sample. The use of Infrared spectroscopy is a solution of the problem to detect the isomer of MCPs.

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