

Photoreaction mechanisms of 2-chlorophenol and its multiple chloro-substituted derivatives studied by low-temperature matrix-isolation infrared spectroscopy and density-functional-theory calculations

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Abstract

Photoreaction mechanisms of 2-chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol and 2,4,5-trichlorophenol in low-temperature argon matrices are investigated by Fourier transform infrared spectroscopy. The observed infrared bands of photoproducts are assigned with an aid of density-functional-theory (DFT) calculations, where the 6-31++G** basis set is used to optimize geometrical structures. It is concluded that five-member-ring ketene, cyclopentadienyldenemethanone (CPYM), is produced through keto carbene, 2-oxocyclohexa-3,5-dienylidene, by dissociation of hydrogen chloride. The geometries of HCl–CPYM complexes in a matrix cage are derived from the vibrational shifts of the hydrogen chloride. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photoreaction of chloro-substituted phenols; Matrix isolation; DFT calculation; Cyclopentadienyldenemethanone; 2-Oxocyclohexa-3,5-dienylidene

1. Introduction

Chloro-substituted phenols are regarded as one of the precursors of dibenzodioxins and attract great interest in environmental problems [1,2]. A number of studies on thermal reactions in garbage furnace [3] and photoreactions in aqua systems have been reported [4]. For example, a photoreaction mechanism for production of dibenzodioxin from 2-chlorophenol in aqua systems was proposed in Scheme 1.

However, no experimental evidence for the production of dibenzodioxin has so far been obtained. Boule et al. [5–8] reported that a final photoproduct of 2-chlorophenol in aqua was cyclopentadienyl carboxy acid, which was produced by the addition of solvent water to cyclopentadienyldenemethanone (hereafter denoted as CPYM), as an intermediate (Scheme 2).

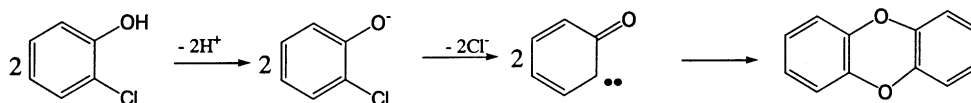
In their experiment, CPYM was not detected but only postulated, probably because of its high reactivity. On the other hand, Crosby and Wong [9] reported that octachlorodibenzodioxin was produced from pentachlorophenol by UV irradiation. No reports on the photoreaction of chlorophenols in gas phase seem to have been published.

In the present work, photoreaction mechanisms of 2-chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol and 2,4,5-trichlorophenol in low-temperature argon matrices have been studied with an aid of the density-functional-theory (DFT) method in order to examine the possibility of photoproduction of dibenzodioxin. Dependence of the photoreaction mechanisms on the number and position of chlorine atoms is also discussed.

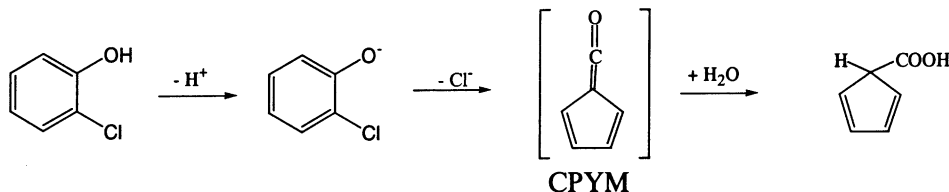
2. Experimental and calculation

All the samples were purchased from Tokyo Chemical Industry and used after vacuum distillation. The sample gases were diluted with argon gas (Nippon Sanso, 99.9999% purity) in glass cylinders, except for 2,4,5-trichlorophenol. The mixing ratio of sample/Ar was about 1/2000. The premixed gases were expanded through a stainless pipe (a diameter of 1/8 in.) and deposited in a vacuum chamber on a CsI plate, cooled by a closed cycle helium refrigeration (CTI Cryogenics, Model M-22) at about 15 K. Since the vapor pressure of 2,4,5-trichlorophenol was too low to transfer the vapor sufficiently into a glass cylinder, a small amount of the solid was placed in a glass pipe in the pathway of the deposition system. Argon gas was passed on the solid, where the flow rate

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Scheme 1.



Scheme 2.

was experimentally adjusted by a needle valve so as to obtain sufficient isolation. UV light from a superhigh-pressure mercury lamp was used to induce photoreaction, where a water filter was used to remove thermal reactions. Infrared spectra of the matrix samples were measured with an FT-IR spectrophotometer (JEOL, Model JIR-7000). The spectral resolution was 0.5 cm^{-1} , and the number of accumulation was 64. Other experimental details were reported elsewhere [10,11].

DFT calculations were performed by using the Gaussian98 program [12] with the 6-31++G** basis set, where the hybrid density functional [13], in combination with the Lee–Yang–Parr correlation functional (B3LYP) [14], was used to optimize the geometrical structures.

3. Results and discussion

3.1. 2-Chlorophenol

Fig. 1 shows an infrared spectrum of 2-chlorophenol in an argon matrix measured before UV irradiation. It is essentially consistent with that reported previously [15]. 2-Chlorophenol has two conformers, *syn* and *anti*, around the C–O axis (Scheme 3).

It seems that the *syn* conformer, which has intramolecular hydrogen bonding between the OH group and the chlorine atom, is more stable than the *anti* conformer. This is supported by our DFT calculation, where the relative energy of the *syn* conformer is calculated to be lower than that of the *anti* conformer by 13.1 kJ mol^{-1} . The calculated spectral pattern of the *syn* conformer is compared with the observed spectrum in Fig. 1. The wavenumbers of the observed bands are mostly consistent with the calculated values if a scaling factor of 0.98 is used, where the bands appearing around 750 , 1050 , 1200 and 1260 cm^{-1} show splitting probably because of Fermi resonance.

After measuring the spectrum of Fig. 1, the matrix sample was exposed to the UV light from a superhigh-pressure

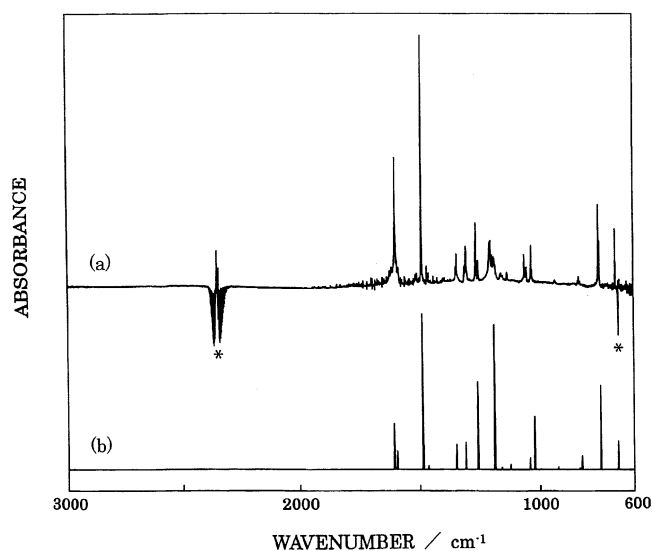
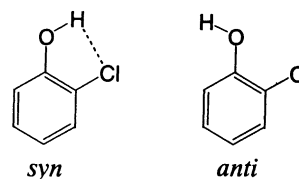


Fig. 1. Infrared spectrum of 2-chlorophenol. (a) Observed in an argon matrix; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

mercury lamp through a water filter. Gebicki and Krantz [16] carried out a similar experiment to observe photoisomerization from *syn* to *anti* and reported that the spectrum was unchanged. However, we observed increasing and decreasing bands, as shown in a different spectrum (Fig. 2) between those measured before and after 10 min UV irradiation. A strong peak appearing at 2130 cm^{-1} seems to be assignable to the C=C=O stretching mode of CPYM, which



Scheme 3.

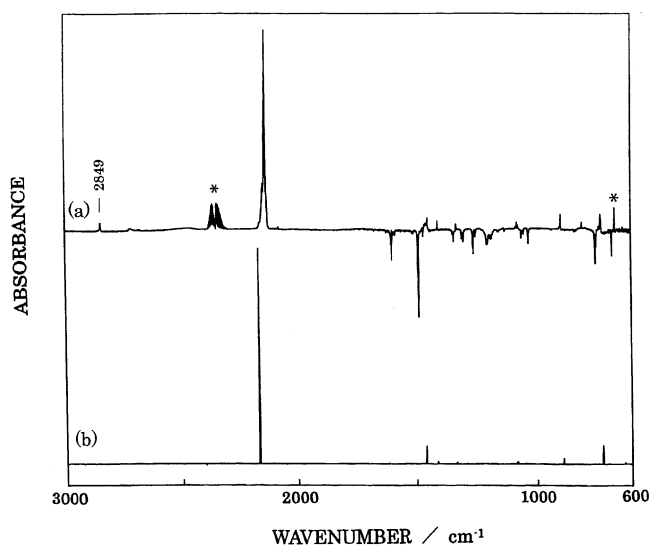


Fig. 2. Difference spectrum of 2-chlorophenol between those measured before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2849 cm^{-1} band is due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

is assumed as a reaction intermediate in the photoreaction of 2-chlorophenol in aqua [5]. Then, we performed a DFT calculation of CPYM and compared its spectral pattern with the observed spectrum in Fig. 2. The expanded spectrum in the region between 1700 and 600 cm^{-1} is given in Fig. 3. Although the relative intensities are slightly inconsistent, the observed vibrational wavenumbers of most bands are nearly consistent with the calculated values. The observed and calculated wavenumbers of CPYM are summarized in Table 1 with their relative intensities. Baird et al. [17,18] measured the infrared bands of CPYM produced by photolysis of dia-

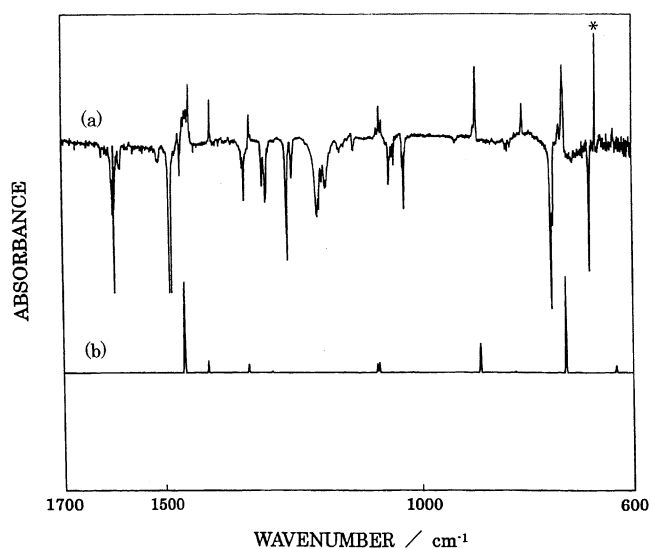


Fig. 3. Expanded spectrum of Fig. 2. (a) Observed in an argon matrix; a band marked with * represents CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

Table 1
Wavenumbers (cm^{-1}) and relative intensities of photoproduct for 2-chlorophenol (2-CP) and of cyclopentadienyldenemethanone (CPYM)

Photoproduct for 2-CP (observed)		CPYM			
ν	Intensity	Calculated ^a		Observed ^b	
		ν	Intensity	ν	Intensity
		3199	0.2		
3135	0.4	3195	0.3		
3102	0.2	3173	0.3		
3026	0.2	3160	0.3		
2140	23.0			2133	vs
2130	100	2161	100	2130	s
2078	0.6			2082 ^c	w
2075	1.2			2079 ^c	w
		1543	0.1		
1447	6.5	1459	8.3	1444	w
				1432 ^d	m
1404	4.8	1411	1.1	1396	w
				1385 ^d	w
				1380 ^d	w
1327	3.4	1331	0.8	1326	w
		1288	0.1		
1077	4.2	1084	0.8	1080	w
1073	2.7	1080	0.9		
		1016	0.1		
				927 ^d	w
896	8.0	890	2.7	901	m
807	2.8	823	0.1		
729	8.2	725	8.9	737	m
				699 ^d	w
635	1.8	631	0.6	640	w
		571	1.1	582	m
				527 ^d	w

^a Calculated at the level of DFT/B3LYP/6-31++G**. A scaling factor of 0.98 is used.

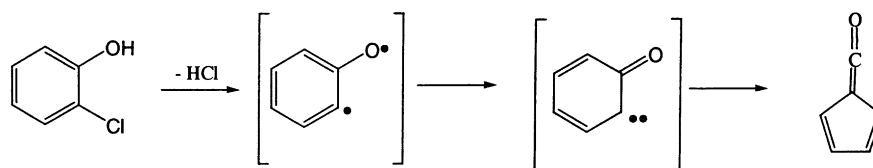
^b Experimental results in a CO matrix [17].

^c Assigned to ^{13}C species [17].

^d Assigned to other photoproduct(s) in this study.

zocyclopentadiene in a CO matrix. Their reported wavenumbers are consistent with those observed in the present work within 8 cm^{-1} except for the additional bands of the other photoproduct, 1432, 1385, 1380, 927, 699 and 527 cm^{-1} , as shown in Table 1. Then we conclude that CPYM is produced from 2-chlorophenol by electron rearrangements following the photodissociation of hydrogen chloride (Scheme 4).

We tried to observe the infrared bands of 2-oxocyclohexa-3,5-dienylidene, a precursor of CPYM, however, it failed, probably because the ketocarbene easily changes to CPYM by Wolff rearrangement even in low-temperature argon matrices. It is known that the reaction of the ketocarbene proceeds on either of the excited singlet or triplet surface. For example, Bonnichon et al. [19] reported that the triplet ketocarbene produced by photoreaction of 2-bromophenol in solutions has a long lifetime and yields *ortho*-benzoquinone *O*-oxide resulting from the addition of O_2 . On the other hand, the singlet ketocarbene, the lifetime of which is relatively short (subnanosecond), is speculated to change immediately



Scheme 4.

to CPYM by Wolff rearrangement. Since no infrared bands of the ketocarbene were observed even during UV irradiation in our matrix-isolation experiments, CPYM was possibly produced from the ketocarbene on the singlet surface.

A weak peak of hydrogen chloride is observed at 2849 cm^{-1} in Fig. 2, which shifts from the wavenumbers in gas phase by about 40 cm^{-1} [20]. This finding implies that hydrogen chloride interacts with CPYM through intermolecular hydrogen bonding. In order to investigate the interaction, a similar DFT calculation for the HCl–CPYM complex was also performed. The optimized structure is shown as complex I in Fig. 4, where HCl is not on the plane of CPYM. The hydrogen atom of HCl interacts with the oxygen atom of the C=C=O part of CPYM; the distance between the hydrogen and oxygen atoms is calculated to be 2.19 \AA . The vibrational wavenumber of hydrogen chloride in complex I, calculated to be 2842 cm^{-1} , is smaller than that of isolated species, 2882 cm^{-1} . The calculated difference, 40 cm^{-1} , is consistent with the observed value. On the other hand, the calculated wavenumbers of CPYM

in complex I are consistent with those of isolated CPYM within 5 cm^{-1} , except for the C=C=O stretching mode.

3.2. Dichlorophenols

Similar experiments were performed for dichlorophenols. The difference spectra for 2,3-, 2,4-, 2,5- and 2,6-dichlorophenols between those measured before and after 10 min UV irradiation are shown in Figs. 5–8, respectively. The figures are scaled so as to make the peak height of the strongest band around 2150 cm^{-1} nearly constant. By analogy with the spectral analysis for the photoreaction of 2-chlorophenol, these strong bands are assignable to the C=C=O stretching mode of chloro-substituted CPYM produced by dissociation of hydrogen chloride (Scheme 5).

A common product for 2,3- and 2,6-dichlorophenols is 2-chloro-CPYM, where the observed C=C=O stretching band, 2148 cm^{-1} , shifts 18 cm^{-1} from CPYM by substitution of chlorine atom. On the other hand, a common product for 2,4- and 2,5-dichlorophenols is 3-chloro-CPYM,

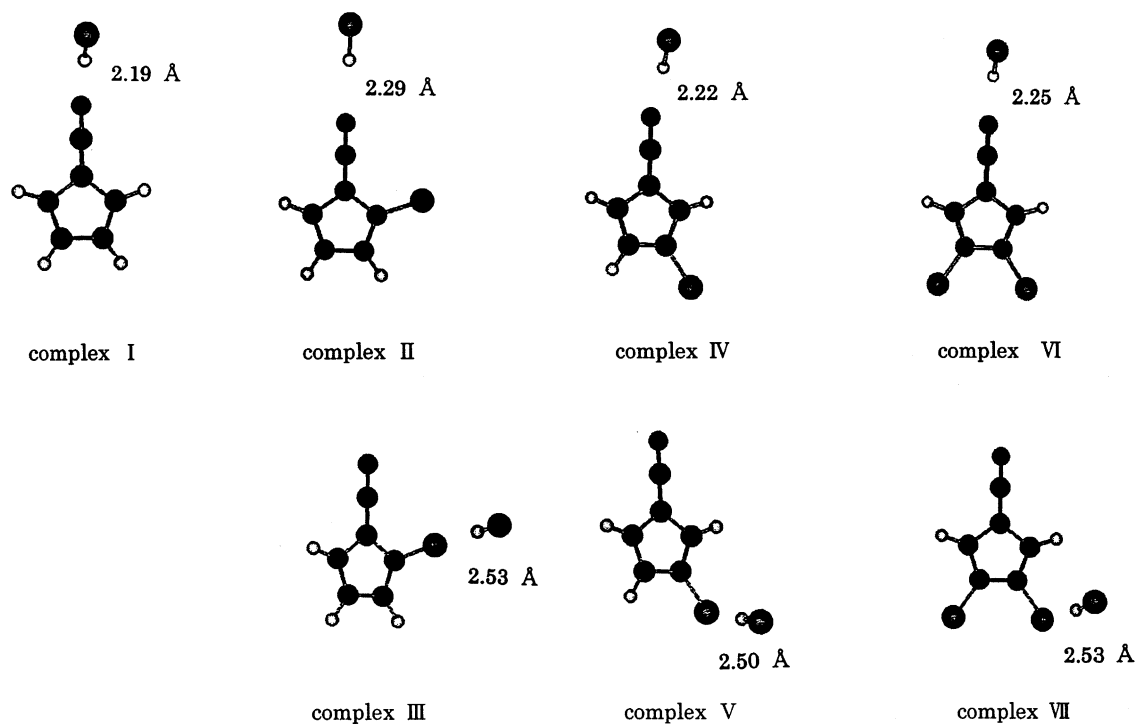


Fig. 4. Optimized geometry of complexes between HCl and CPYM or its chloro-substituted derivatives calculated at the B3LYP/6-31++G** level. Intermolecular distances are given in Å. Other bond distances and angles are available upon request.

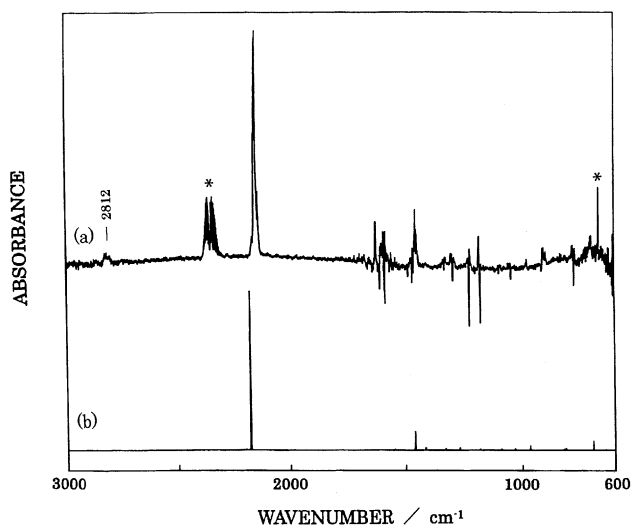


Fig. 5. Difference spectrum of 2,3-dichlorophenol measured between those before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2812 cm^{-1} band is due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

the C=C=O stretching band of which is observed at 2134 cm^{-1} . The expanded difference spectra for 2,3- and 2,6-dichlorophenols are compared with the spectral pattern of 2-chloro-CPYM obtained by the DFT calculation in Fig. 9. The bands marked with \circ , appearing commonly in the both spectra, are consistent with the calculated spectral pattern of 2-chloro-CPYM. A few additional bands marked with \times appeared in the both spectra. Increasing bands appearing around the decreasing bands of 2,3-dichlorophenol, Fig. 9(a), may be assigned to the change of bandwidths. Since the signal-to-noise ratio in

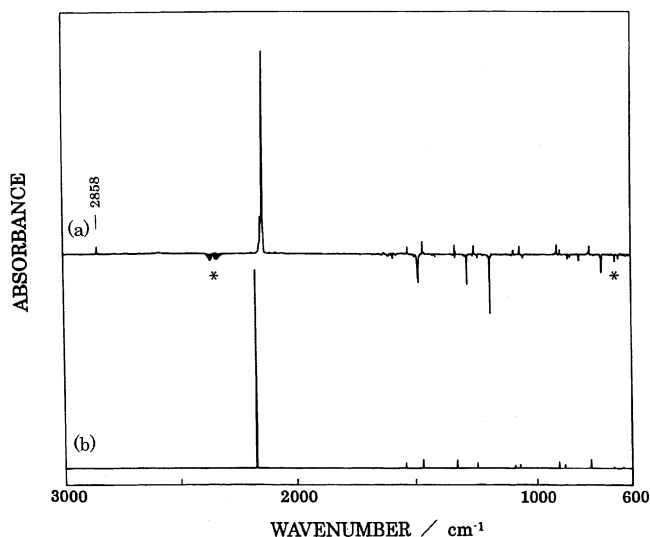


Fig. 6. Difference spectrum of 2,4-dichlorophenol between those measured before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2858 cm^{-1} band is due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

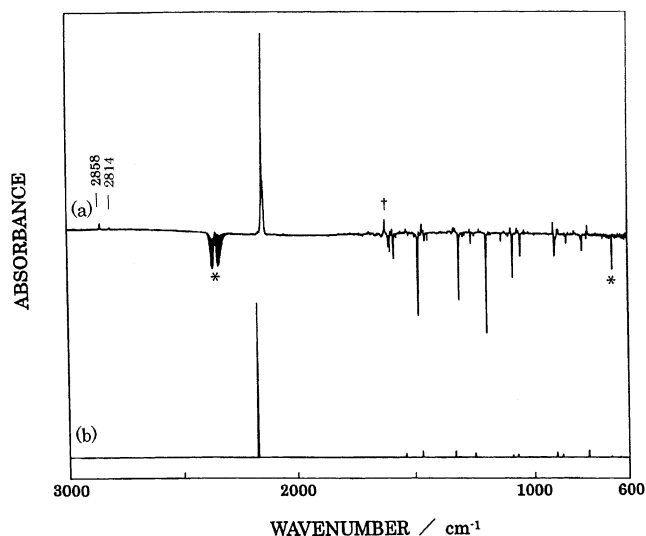


Fig. 7. Difference spectrum of 2,5-dichlorophenol between those measured before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2858 and 2814 cm^{-1} bands are due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

Fig. 9(a) is worse than that in Fig. 9(b), it seems that the photoreactivity of 2,3-dichlorophenol is lower than that of 2,6-dichlorophenol.

The observed wavenumbers for 2-chloro-CPYM are summarized and compared with the calculated values in Table 2. The observed wavenumbers of the product for 2,3-dichlorophenol are found to be slightly different from those of the product for 2,6-dichlorophenol. This difference may be caused by the interaction with a co-product, hydrogen chloride. In fact, the bands of the co-product, HCl, are observed at 2812 and 2858 cm^{-1} for 2,3-dichlorophenol

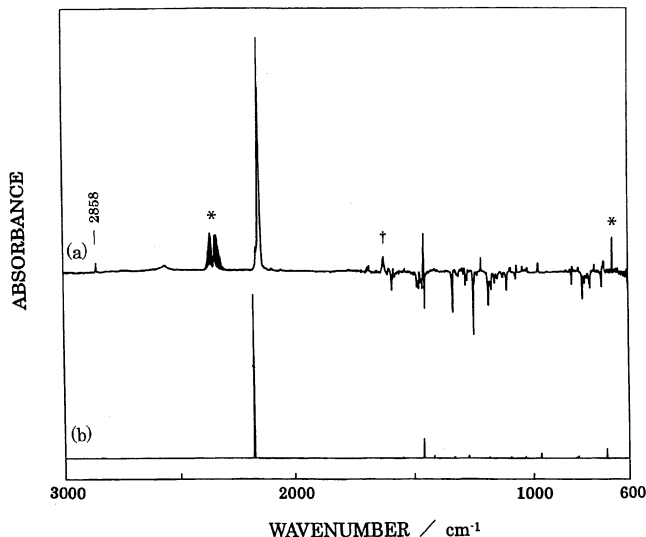
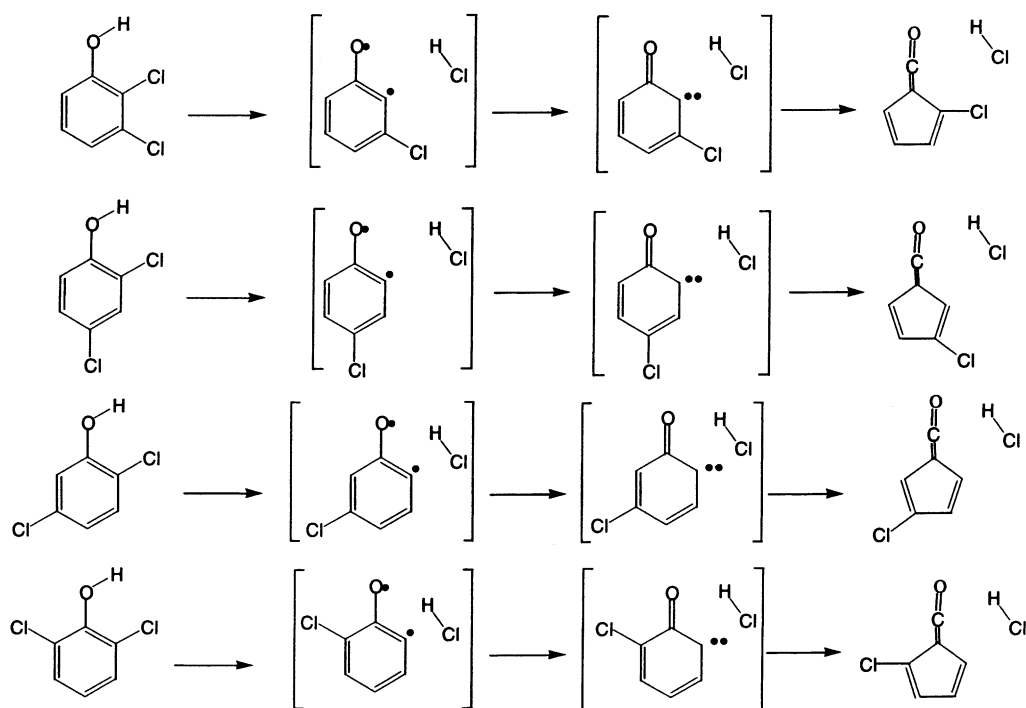


Fig. 8. Difference spectrum of 2,6-dichlorophenol between those measured before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2858 cm^{-1} band is due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.



Scheme 5.

and 2,6-dichlorophenol, respectively. Since HCl produced from 2,3-dichlorophenol exists near the chlorine atom of 2-chloro-CPYM, it may interact with 2-chloro-CPYM in complex III at the chlorine atom, as shown in Fig. 4. On the other hand, HCl produced from 2,6-dichlorophenol is far from the chlorine atom of CPYM. Therefore, it interacts

Table 2

Wavenumbers (cm^{-1}) and relative intensities of photoproducts for dichlorophenols (DCPs) and of 2-chloro-cyclopentadienyliidenemethanone (2-chloro-CPYM)

Photoproduct for 2,3-DCP (observed)		Photoproduct for 2,6-DCP (observed)		2-Chloro-CPYM (calculated) ^a	
ν	Intensity	ν	Intensity	ν	Intensity
				3201	0.1
				3191	0.1
				3169	0.3
2160	7.0	2158	9.4		
2146	99.2	2148	100	2172	100
2143	100	2146	77.9		
2134	27.1				
		2094 ^b	0.8		
		2051 ^b	0.6		
1453	21.6	1455	16.6	1460	11.9
1407	1.3	1407	0.9	1415	1.6
1322	2.0	1320	1.9	1328	0.9
				1268	1.5
				1180	0.7
1090	4.0	1087	2.0	1091	0.7
1056	4.0	1062	3.0	1032	1.0
976	4.0	975	4.0	967	2.8
				894	0.0
				824	0.5
813	3.1	812	2.0	816	1.3
705	7.1	709	4.6	697	5.8
701	7.9	704	4.3	697	5.8
				642	0.5

^a Calculated at the level of DFT/B3LYP/6-31++G**. A scaling factor of 0.98 is used.

^b May be assigned to ¹³C species.

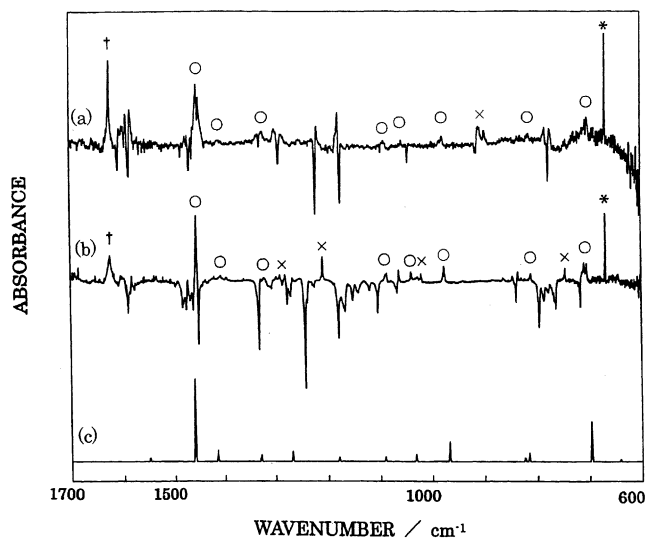


Fig. 9. Expanded spectra of Figs. 5 and 8. (a) Photolysis of 2,3-dichlorophenol in an argon matrix. (b) Photolysis of 2,6-dichlorophenol in an argon matrix. (c) Spectral pattern of 2-chloro-CPYM calculated by DFT/B3LYP/6-31++G**. Common bands marked with ○ are assigned to 2-chloro-CPYM. Bands marked with ×, *, and † represent other products, CO₂ in atmosphere, and H₂O in matrices, respectively.

with 2-chloro-CPYM in complex II at the C=C=O part, as shown in Fig. 4. This interaction is similar to that of the complex produced from 2-chlorophenol. The DFT calculations for HCl–2-chloro-CPYM complexes predict that complex III is more stable than complex II by 2.4 kJ mol⁻¹. The calculated wavenumbers of HCl in complex III and complex II are 2790 and 2869 cm⁻¹, respectively. These are roughly consistent with the corresponding bands observed at 2812 and 2858 cm⁻¹ for 2,3-dichlorophenol and 2,6-dichlorophenol, respectively. Then, we assign the observed bands, 2812 and 2858 cm⁻¹, to complex III and II, respectively. Our assignment is also supported by a comparison of the observed wavenumbers of complex II, 2858 cm⁻¹ and complex I, 2849 cm⁻¹: the difference between HCl–CPYM and HCl–2-chloro-CPYM, 9 cm⁻¹, is roughly consistent with the calculated value, 14 cm⁻¹.

In the case of 2,4-dichlorophenol and 2,5-dichlorophenol, a common product is 3-chloro-CPYM. The calculated spectral patterns are compared with the observed spectra in Figs. 7 and 8. Their expanded spectra are shown in Fig. 10. All the increasing bands of 2,4-dichlorophenol, marked with ○, are assignable to 3-chloro-CPYM, while additional small bands of the other product marked with × appear in the spectrum of 2,5-dichlorophenol. The observed wavenumbers of 3-chloro-CPYM are summarized in Table 3 and compared with the calculated values. The hydrogen chloride band, observed at 2858 cm⁻¹ in Figs. 6 and 7, is equal to that of 2,6-dichlorophenol. Then, it is concluded that hydrogen chloride produced from both 2,4-dichlorophenol and 2,5-dichlorophenol interacts at the C=C=O part of

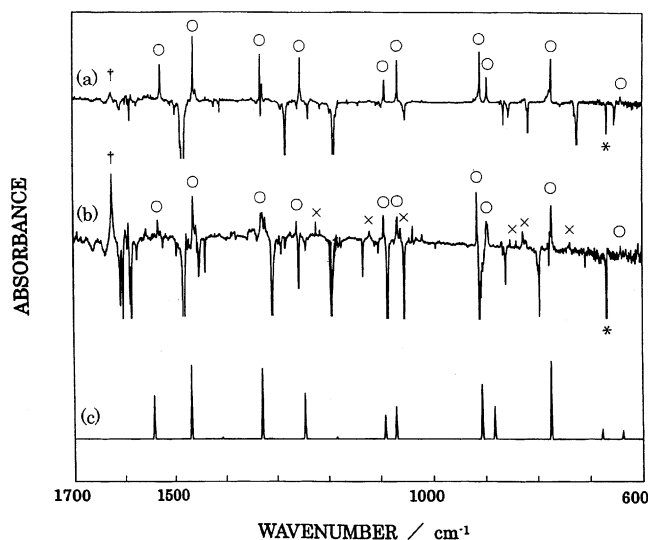


Fig. 10. Expanded spectra of Figs. 6 and 7. (a) Photolysis of 2,4-dichlorophenol in an argon matrix. (b) Photolysis of 2,5-dichlorophenol in an argon matrix. (c) Spectral pattern of 3-chloro-CPYM calculated by DFT/B3LYP/6-31++G**. Common bands marked with ○ are assigned to 3-chloro-CPYM. Bands marked with ×, *, and † represent other products, CO₂ in atmosphere, and H₂O in matrices, respectively.

Table 3
Wavenumbers (cm⁻¹) and relative intensities of photoproducts for dichlorophenols (DCPs) and of 3-chloro-cyclopentadienyliidene-methanone (3-chloro-CPYM)

Photoproduct for 2,4-DCP (observed)		Photoproduct for 2,5-DCP (observed)		3-Chloro-CPYM (calculated) ^a	
ν	Intensity	ν	Intensity	ν	Intensity
3223	0.5			3212	0.1
3122	0.5			3203	0.1
3043	0.5			3184	0.0
2142	17.7	2140	100	2166	100
2134	100	2135	25.9		
2104	10.0				
2080 ^b	1.2				
2054 ^b	0.9				
1527	3.6	1532	1.7	1542	2.5
1462	6.1	1462	4.2	1468	4.2
				1407	0.1
1330	4.4	1329	2.6	1328	4.0
1325	1.7	1325	2.4	1328	4.0
1253	4.2	1260	1.7	1246	2.6
				1184	0.1
1091	2.1	1091	2.5	1091	1.4
1066	3.9	1066	2.4	1070	1.9
910	5.0	916	5.2	907	3.1
897	2.3	897	1.9	883	1.9
				880	0.0
773	4.1	773	3.5	774	4.5
				677	0.6
641	0.1	641	0.3	638	0.5

^a Calculated at the level of DFT/B3LYP/6-31++G**. A scaling factor of 0.98 is used.

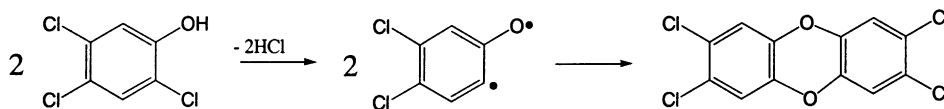
^b May be assigned to ¹³C isotope species.

3-chloro-CPYM in complex IV, as well as that dissociated from 2-chlorophenol and 2,6-dichlorophenol. A small infrared band of HCl caused by dissociation from 2,5-dichlorophenol is also observed at 2814 cm⁻¹, which is nearly equal to that from 2,3-dichlorophenol, 2812 cm⁻¹. Then, this band seems to be assignable to HCl in complex V interacting at the chlorine atom of 3-chloro-CPYM. Since the relative energy of complex V is calculated to be lower than that of complex IV by 4 kJ mol⁻¹, isomerization from complex IV to complex V may be caused by using excess energy in UV-induced photodissociation. The details of the HCl-transfer process are not understandable at the present stage.

3.3. 2,4,5-Trichlorophenol

If dimerization of 2,4,5-trichlorophenol occurs with dissociation of hydrogen chloride, the most toxic dibenzodioxin, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, seems to be produced (Scheme 6).

A difference spectrum of 2,4,5-trichlorophenol in an argon matrix between those measured before and after 10 min UV irradiation is shown in Fig. 11. We searched for the bands of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin reported by Gurka



Scheme 6.

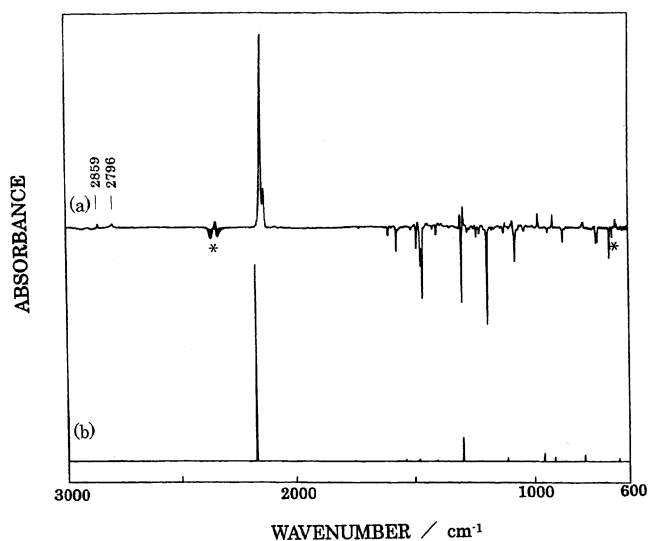


Fig. 11. Difference spectrum of 2,4,5-trichlorophenol between those measured before and after 10 min UV irradiation. (a) Observed in an argon matrix; the 2859 and 2796 cm^{-1} bands are due to HCl; bands marked with * represent CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

et al. [21,22], but could not find them clearly. Then, we performed the DFT calculation of 3,4-dichloro-CPYM, which is analogous to the products obtained by photolysis of other 2-chlorophenols. The calculated spectral pattern in the region between 1700 and 600 cm^{-1} is compared with the

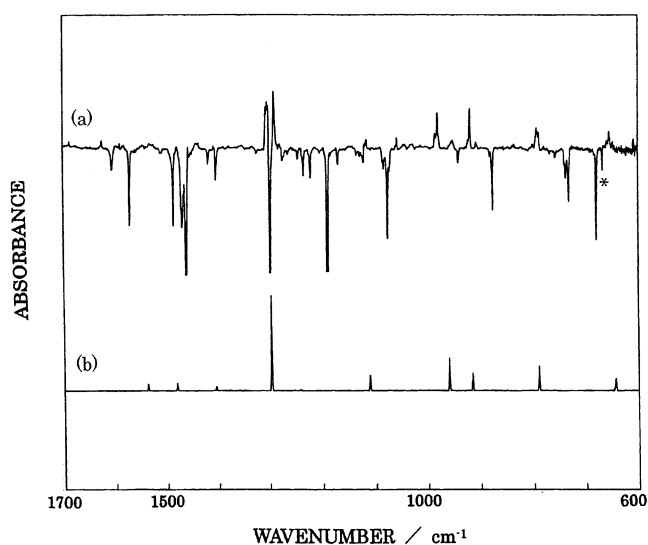


Fig. 12. Expanded spectrum of Fig. 11. (a) Observed in an argon matrix; bands marked with * represents CO_2 in atmosphere. (b) Calculated by DFT/B3LYP/6-31++G**.

observed spectrum in Fig. 12. The observed wavenumbers are consistent with the calculated wavenumbers, as summarized in Table 4. However, the consistency is slightly worse than those of CPYM, 2-chloro-CPYM and 3-chloro-CPYM, probably because DFT calculations for molecules containing multiple halogen atoms do not work so well as other simple molecules [23].

The hydrogen chloride caused from 2,4,5-trichlorophenol by photodissociation is observed at 2859 cm^{-1} , which is nearly equal to those in the case of 2,4-dichlorophenol, 2,5-dichlorophenol, and 2,6-dichlorophenol. Then, this band is assignable to HCl interacting at the C=C=O part of 3,4-dichloro-CPYM in complex VI in Fig. 4, whose calculated value is 2861 cm^{-1} . In addition to this band, an

Table 4

Wavenumbers (cm^{-1}) and relative intensities of photoproduct for 2,4,5-trichlorophenol (2,4,5-TCP) and of 3,4-dichloro-cyclopentadienyli-denemethanone (3,4-dichloro-CPYM)

2,4,5-TCP (observed)		3,4-Dichloro-CPYM (calculated) ^a	
ν	Intensity	ν	Intensity
3145	0.5	3212	0.1
		3210	0.1
2159	8.8		
2153	21.4		
2150	36.4		
2145	90.3		
2142	95.9		
2140	100	2168	100
2087 ^b	0.9		
		1538	0.9
		1481	1.0
		1405	0.5
1305	9.5	1296	12.2
1303	10.5	1296	12.2
1300	9.6	1296	12.2
1289	12.1	1296	12.2
		1242	0.1
		1171	0
1116	2.6	1111	2.0
984	3.3	959	4.2
980	8.0	959	4.2
918	9.4	915	2.3
793	4.7	790	3.2
788	3.9	790	3.2
		718	0
		646	0.4
655	4.3	644	1.5

^a Calculated at the level of DFT/B3LYP/6-31++G**. A scaling factor of 0.98 is used.

^b May be assigned to ^{13}C species.

Table 5
Observed and calculated wavenumbers (cm^{-1}) and relative intensities of hydrogen chloride interacting with CPYM or its chloro-substituted derivatives

Reactant	Observed		Calculated ^a	
	ν	Intensity	ν	Assignment ^b
2-Chlorophenol	2849	3.7	2842	Complex I
2,3-Dichlorophenol	2812	4.9	2790	Complex III
2,4-Dichlorophenol	2858	3.8	2856	Complex IV
2,5-Dichlorophenol	2858	2.7	2856	Complex IV
	2814	0.9	2780	Complex V
2,6-Dichlorophenol	2858	3.8	2869	Complex II
2,4,5-Trichlorophenol	2859	4.4	2861	Complex VI
	2796	3.1	2794	Complex VII

^a Calculated at the level of DFT/B3LYP/6-31++G**. A scaling factor of 0.98 is used.

^b See Fig. 4.

infrared band is observed at 2796 cm^{-1} . This band is nearly equal to that in the case of 2,3-dichlorophenol. Then this band is assignable to HCl interacting at the chlorine atom of 3,4-dichloro-CPYM in complex VII in Fig. 4, whose wavenumber is calculated to be 2794 cm^{-1} . Since the relative energy of complex VII is 3.4 kJ mol^{-1} lower than that of complex VI, isomerization similar to 2,5-dichlorophenol may occur. The observed and calculated wavenumbers of HCl interacting with CPYM or its chloro-substituted derivatives are summarized in Table 5.

4. Conclusions

We observed infrared spectra of photoproducts of 2-chlorophenol, 2,3-, 2,4-, 2,5-, 2,6-dichlorophenols, and 2,4,5-trichlorophenol in low-temperature argon matrices. The observed infrared bands are assigned to the corresponding CPYM by a comparison with the results obtained by DFT calculations, where 6-31++G** basis set is used to optimize geometry. By a detailed analysis of wavenumbers of a co-product, HCl, it is found that hydrogen chloride dissociated from 2,3- and 2,6-dichlorophenols interact with 2-chloro-CPYM at the chlorine atom and the C=C=O part, respectively. On the other hand, hydrogen chloride dissociated from 2,4- and 2,5-dichlorophenols interact with 3-chloro-CPYM at the C=C=O part. In the cases of photodissociation of 2,5-dichlorophenol and 2,4,5-trichlorophenol, migration of hydrogen chloride from the C=C=O part to the chlorine atom occurs. Although chloro-substituted phenols are regarded as one of the precursors of toxic dibenzodioxins, no infrared bands of dibenzodioxins were detected in UV photolysis of 2-chlorophenol and its

multiple chloro-substituted derivatives in low-temperature argon matrices, where the reaction between two ketocarbenes seems to occur hardly.

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References

- [1] Y.I. Skurlatov, L.S. Ernestova, E.V. Vichutinskaya, D.P. Samsonov, I.V. Semenova, I.Y. Rod'ko, V.O. Shvidky, R.I. Pervunina, T.J. Kemp, J. Photochem. Photobiol. A 107 (1997) 207.
- [2] Y. Okamoto, M. Tomonari, J. Phys. Chem. A 103 (1999) 7686.
- [3] W. Roland, H. Hanspaul, Chemosphere 38 (1999) 529.
- [4] K. Ballschmiter, R. Bacher, Dioxine Chemie, Analytik, Vorkommen, Umweltverhalten und Toxikologie der Halogenierten Dibenzo-*p*-dioxine und Dibenzofurane, VCH, Weinheim, 1996.
- [5] P. Boule, C. Guyon, J. Lemaire, Chemosphere 11 (1982) 1179.
- [6] C. Guyon, P. Boule, J. Lemaire, Tetrahedron Lett. 23 (1982) 1581.
- [7] P. Boule, C. Guyon, J. Lemaire, Chemosphere 13 (1984) 603.
- [8] P. Boule, C. Guyon, J. Lemaire, Toxicol. Env. Chem. 7 (1984) 97.
- [9] D.G. Crosby, A.S. Wong, Chemosphere 5 (1976) 327.
- [10] M. Nakata, S. Kudoh, M. Takayanagi, T. Ishibashi, C. Kato, J. Phys. Chem. 104 (2000) 11304.
- [11] S. Kudoh, M. Takayanagi, M. Nakata, J. Photochem. Photobiol. A 123 (1999) 25.
- [12] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Peterson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wang, J.L. Andres M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian98 (Revision A.1), Gaussian, Inc., Pittsburgh, PA, 1998.
- [13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [14] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [15] G.T. Reedy, S. Bourne, P.T. Cunningham, Anal. Chem. 51 (1979) 1535.
- [16] J. Gebicki, A. Krantz, J. Am. Chem. Soc. 106 (1984) 8097.
- [17] M.S. Baird, I.R. Dunkin, M. Poliakoff, J. Chem. Soc., Chem. Comm. (1974) 904.
- [18] M.S. Baird, I.R. Dunkin, N. Hacker, M. Poliakoff, J.J. Turner, J. Am. Chem. Soc. 103 (1981) 5190.
- [19] F. Bonnichon, C. Richard, G. Grabner, Chem. Commun. (2001) 73.
- [20] G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra, van Nostrand Reinhold, New York, 1945, p. 535.
- [21] D.F. Gurka, S. Billets, J.W. Brasch, C.J. Riggle, Anal. Chem. 57 (1985) 1975.
- [22] D.F. Gurka, J.W. Brasch, R.H. Barnes, C.J. Riggle, S. Bourne, Appl. Spectrosc. 40 (1986) 978.
- [23] H. Yoshida, A. Ehara, H. Matsuura, Chem. Phys. Lett. 325 (2000) 477.