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# Theoretical studies of Phenylmercury carboxylates

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Complexation Constants and Gas Phase Photo-  
Oxidation of Phenylmercurycarboxylates.

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# Executive Summary

Phenylmercury(II)-carboxylates used as catalysts in PU-systems will eventually be released into the environment. The phenylmercury(II) cation,  $C_6H_5Hg^+$ , forms various complexes with ligands present in natural and biological systems and knowledge about the stability of the carboxylates complexation constants are important in this respect. The phenylmercury(II)-carboxylates may also be emitted into the atmosphere where they will undergo photo-oxidation reactions.

The chemical bonding in a series of phenylmercury(II)-carboxylates, including estimates of the UV-absorption spectra and the carboxylate complexation constants have been obtained from quantum chemistry calculations. The results indicate that the phenylmercury(II)-carboxylates (acetate, propionate, 2-ethylhexanoate, octanoate and neodecanoate) have nearly the same dissociation constants and UV-spectra. The aqueous phase fate of these compounds and their rate of photolysis in the aqueous phase will therefore essentially be the same.

An evaluation of atmospheric radical reactions and direct photolysis of gaseous phenylmercury(II)-carboxylates suggests that direct photolysis by solar radiation is the dominant daytime sink, and that reactions with  $NO_3$  radicals are equally important during night-time. The atmospheric lifetime of phenylmercury(II)-carboxylates is estimated to be around 1 day.

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# Complexation Constants and Gas Phase Photo-Oxidation of Phenylmercurycarboxylates

## 1. Quantum chemistry studies on phenylmercurycarboxylates

Quantum chemical calculations of structure and bonding in phenylmercury carboxylates were carried out with the Gaussian 09 suite of programs [Frisch *et al.*, 2009]. Geometry optimizations and harmonic vibration frequencies were calculated employing the hybrid GGA functional MPW3LYP [Zhao and Truhlar, 2004] in conjunction with the 6-311++G(d,p) basis sets for hydrogen, carbon and oxygen [Krishnan *et al.*, 1980; Clark *et al.*, 1983], and the Stuttgart 1997 effective core potential basis set for mercury [Figgen *et al.*, 2005]; this combination of basis sets will be referred to as GST97. MPW3LYP/GST97 calculations have been proven to give reliable thermochemistry data for various organomercury compounds [Azenkeng *et al.*, 2008; Olson *et al.*, 2009].

The Natural Bond Orbital (NBO) method [Foster and Weinhold, 1980; Reed and Weinhold, 1983; 1985; Reed *et al.*, 1985; Carpenter and Weinhold, 1988; Reed *et al.*, 1988] was employed to further analyze the nature of bonding in the organo-mercury compounds. The electronic structure was also characterized by NMR shielding constants derived in the GIAO method (gauge independent atomic orbital method) [London, 1937; McWeeny, 1962; Ditchfield, 1974; Wolinski *et al.*, 1990; Cheeseman *et al.*, 1996].

Vertical excitation energies were derived in time-dependent DFT calculations (TDDFT) [Bauernschmitt and Ahlrichs, 1996; Casida *et al.*, 1998; Stratmann *et al.*, 1998; Van Caillie and Amos, 1999; 2000; Furche and Ahlrichs, 2002; Scalmani *et al.*, 2006].

Solvent effects have been considered in polarisable continuum model, PCM, calculations [Miertus *et al.*, 1981; Miertus and Tomasi, 1982; Pascual-Ahuir *et al.*, 1994; Cossi *et al.*, 1996; Barone *et al.*, 1997; Mennucci *et al.*, 1997; Mennucci and Tomasi, 1997; Barone and Cossi, 1998; Barone *et al.*, 1998; Cossi *et al.*, 1998; Cammi *et al.*, 1999; Cossi *et al.*, 1999; Tomasi *et al.*, 1999; Cammi *et al.*, 2000; Cossi and Barone, 2000; 2001; Cossi *et al.*, 2001; Cossi *et al.*, 2002; Cossi *et al.*, 2003]

## 2. Results from quantum chemistry

Depending on the issue in discussion, phenylmercury(II) carboxylates have been described as molecules, complexes or salts. An aqueous solution of phenylmercury acetate will in part dissociate in phenylmercury cations and carboxylate anions justifying the term “salt” [Parikh and Sweet, 1961]. On the other hand, phenylmercury acetate has a measurable vapour pressure at ambient temperatures which is normally associated with covalently bonded molecules [Lindström, 1958; Phillips *et al.*, 1959]. In the present report the phenylmercury(II) carboxylates will be referred to as complexes.

## 2.1 Structure of phenylmercury(II) carboxylates

Quantum chemistry calculations give *a priori* information about the electronic structure of a chemical system. Once the electronic structure is known, one can then derive all molecular properties and, in principle, predict how the molecule will behave under different conditions. In reality, today the electronic structure of a molecule can only be obtained approximately, and, consequently, quantum chemistry calculations will not give exact information. The strength quantum chemistry is, however, that the underlying reasons behind the non-exact prediction of the various methodologies are known and that calculated trends generally are correct.

Quantum chemistry was employed to elucidate the bonding and properties of phenylmercury(II) carboxylates. For the sake of brevity, the target phenylmercury compounds are referred to by their acronyms:  $\phi$ -Hg-OAc (phenylmercury acetate),  $\phi$ -Hg-OPr (phenylmercury propionate),  $\phi$ -Hg-OEtH (phenylmercury 2-ethylhexanoate),  $\phi$ -Hg-OOc (phenylmercury octanoate) and  $\phi$ -Hg-OnDc (phenylmercury 7,7-dimethylcnoate). The latter compound was taken as representative of the multitude of possible isomers covered by the CAS entry “Phenylmercury neodecanoate”.

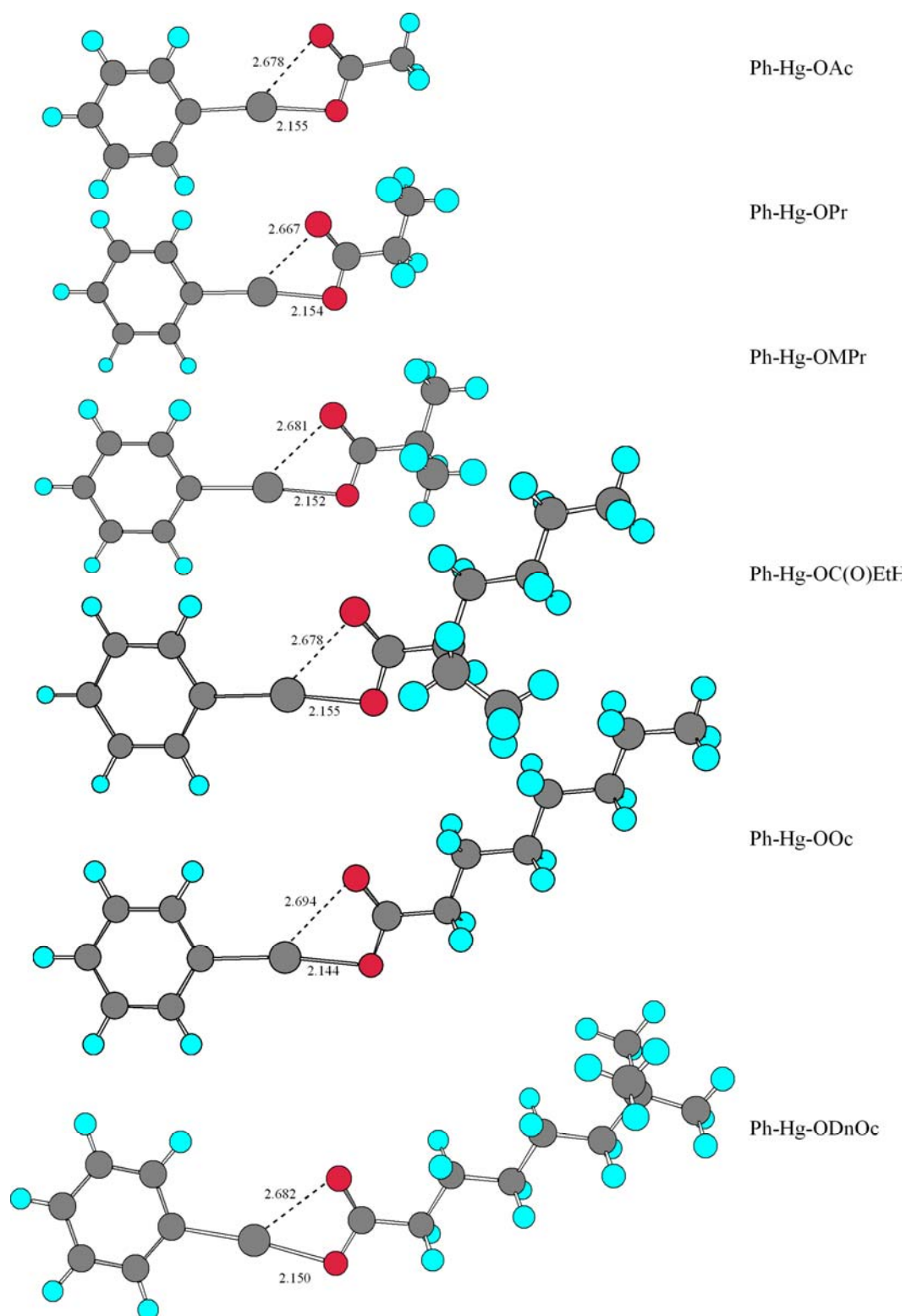
In addition to the target compounds the study was extended to include  $\phi$ -Hg-OMPr (phenylmercury 2-methylpropionate),  $\phi$ -Hg-OBu (phenylmercury butyrate),  $\phi$ -Hg-OMBu (phenylmercury 2-methylbutyrate),  $\phi$ -Hg-OEBu (phenylmercury 2-ethylbutyrate), and Me<sub>2</sub>Hg (dimethylmercury) - the only organomercury for which there are atmospheric chemistry literature data.

Equilibrium structures obtained at the MPW3LYP/GST97 level are collected in Figure 2.1. The important bond distances Hg–O and Hg–C, and the C–Hg–O angle in the various phenylmercury compounds are listed in Table 2.1 from which it can be seen that the C–Hg–O angles in all cases are approximate 174°. The Hg–O and Hg–C bond lengths also show little variation within the series. In the case of  $\phi$ -Hg-OAc, the C–Hg bond is 2.107 Å and Hg–O is about 2.15 Å. The Hg–O bond length becomes somewhat shorter in the longer chain carboxylates, which may be related to increased electron donation and thereby to stronger interaction between Hg and the carboxylate group.

**Table 2.1.** Selected bond lengths of phenylmercury carboxylates obtained in MPW3LYP/GST97 calculations.

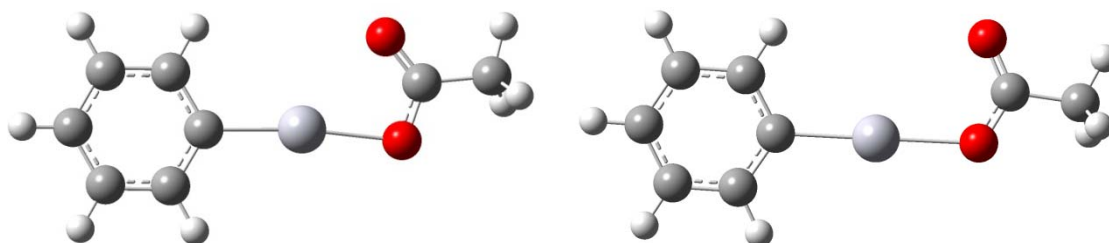
Molecule	Hg–O /Å	Hg···O /Å	Hg–C /Å	C–Hg–O /deg.
Me <sub>2</sub> Hg			2.151 (2.196)	179.9 (172.6)
$\phi$ -Hg-OAc	2.155 (2.206) <sup>a</sup>	2.678 (3.220)	2.107 (2.149)	173.6 (178.1)
$\phi$ -Hg-OPr	2.154 (2.208)	2.667 (3.097)	2.108 (2.145)	173.5 (174.4)
$\phi$ -Hg-OMPr	2.152 (2.217)	2.681 (3.165)	2.108 (2.151)	173.9 (172.6)
$\phi$ -Hg-OBu	2.151	2.685	2.108	174.6
$\phi$ -Hg-OMBu	2.151	2.683	2.108	174.1
$\phi$ -Hg-OEBu	2.143	2.689	2.108	174.7
$\phi$ -Hg-OEtH	2.155	2.678	2.108	173.9
$\phi$ -Hg-OOc	2.144	2.694	2.108	174.3
$\phi$ -Hg-OnDc	2.150	2.682	2.108	173.9

<sup>a</sup> Values in parentheses are obtained in PCM calculations mimicking the water solvent.



**Figure 2.1.** Structures of phenylmercury carboxylates obtained from quantum chemistry MPW3LYP/GST97 calculations.

Solvent effects have been considered in polarisable continuum model, PCM, calculations. For  $\phi$ -Hg-OAc the Hg–C and Hg–O bond lengths elongate in water, indicating that the Hg–C and Hg–O bonds become weaker in aqueous solution (see also section 2.2). Figure 2.2 compares the gas and the aqueous phase equilibrium structures of  $\phi$ -Hg-OAc from which it can be seen that the structure opens up (the Hg–O–C angle increases) in the aqueous phase due to the interaction with the medium.



**Figure 2.2.** Structure of phenylmercury acetate obtained from MPW3LYP/GST97 calculations. Left: gas phase structure. Right: aqueous phase structure obtained with the PCM model.

The Natural Bond Orbital (NBO) method was employed to further analyze the nature of bonding of Hg to C and O. Natural charges on the C, Hg, and O atoms in  $\text{Me}_2\text{Hg}$  and the phenylmercury carboxylates are collected in Table 2.2, while the complete charge distribution in  $\phi$ -Hg-OAc is shown in Figure 2.3. It can be seen that the Hg atom has a net positive charge of +1.1 in all the carboxylates. For the negatively charged C, O(–C) and O(=C) atoms, the values are in all cases close to -0.42 for C, -0.79 for O(–C), and -0.68 for the O(=C) atom, respectively.

Concerning the charge distribution in the phenyl ring only  $\text{C}_1$  is affected by the Hg-substituent. This suggests that the reactivity of the phenyl ring towards atmospheric radicals will not differ substantially from that of other substituted phenyls (phenols excepted).

**Table 2.2.** Partial charges on the C, Hg and O atoms in phenylmercury carboxylates based on NBO calculations at the MPW3LYP/GST97 level of theory.

Molecule	Hg	C	O(–C)	O(=C)
$\text{Me}_2\text{Hg}$	0.944	-1.101		
$\phi$ -Hg-OAc	1.107	-0.415	-0.793	-0.679
$\phi$ -Hg-OPr	1.104	-0.415	-0.793	-0.682
$\phi$ -Hg-OMPr	1.103	-0.415	-0.795	-0.683
$\phi$ -Hg-OBu	1.104	-0.415	-0.792	-0.652
$\phi$ -Hg-OMBu	1.104	-0.416	-0.795	-0.684
$\phi$ -Hg-OEBu	1.106	-0.416	-0.788	-0.684
$\phi$ -Hg-OEtH	1.102	-0.416	-0.790	-0.691
$\phi$ -Hg-OOc	1.106	-0.416	-0.794	-0.681
$\phi$ -Hg-OnDc	1.105	-0.415	-0.792	-0.682

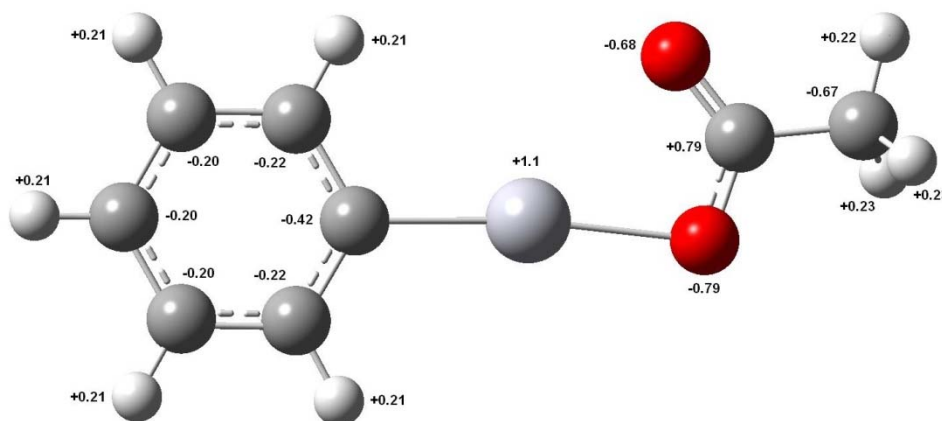
The charge distribution suggests that the phenylmercury carboxylates are ionic complexes and that there is little difference in the ionic character going from the acetate to the larger carboxylates; the net charges being -0.42 (phenyl), +1.1 (Hg) and -0.68 (carboxylate).

The chemical shifts in Nuclear magnetic resonance (NMR) are very sensitive to the electron distribution around the nuclei (shielding) and is therefore used as a diagnostic tool in the characterization of molecular bonding. The GIAO method is known as a reliable method to predict chemical shifts for different nuclei within larger molecules. The calculated isotropic and anisotropic NMR shielding constants are presented in Table 2.3. There is clearly, and obviously, a difference in the electron distribution around the Hg atom in covalently bonded Me<sub>2</sub>Hg and in the phenylmercury carboxylates, *c.f.* the net atomic charges. However, within the phenylmercury carboxylate series the isotropic and anisotropic shielding constant of Hg atom are quite constant indicating only minor differences in the electronic structure around the Hg atom in these compounds.

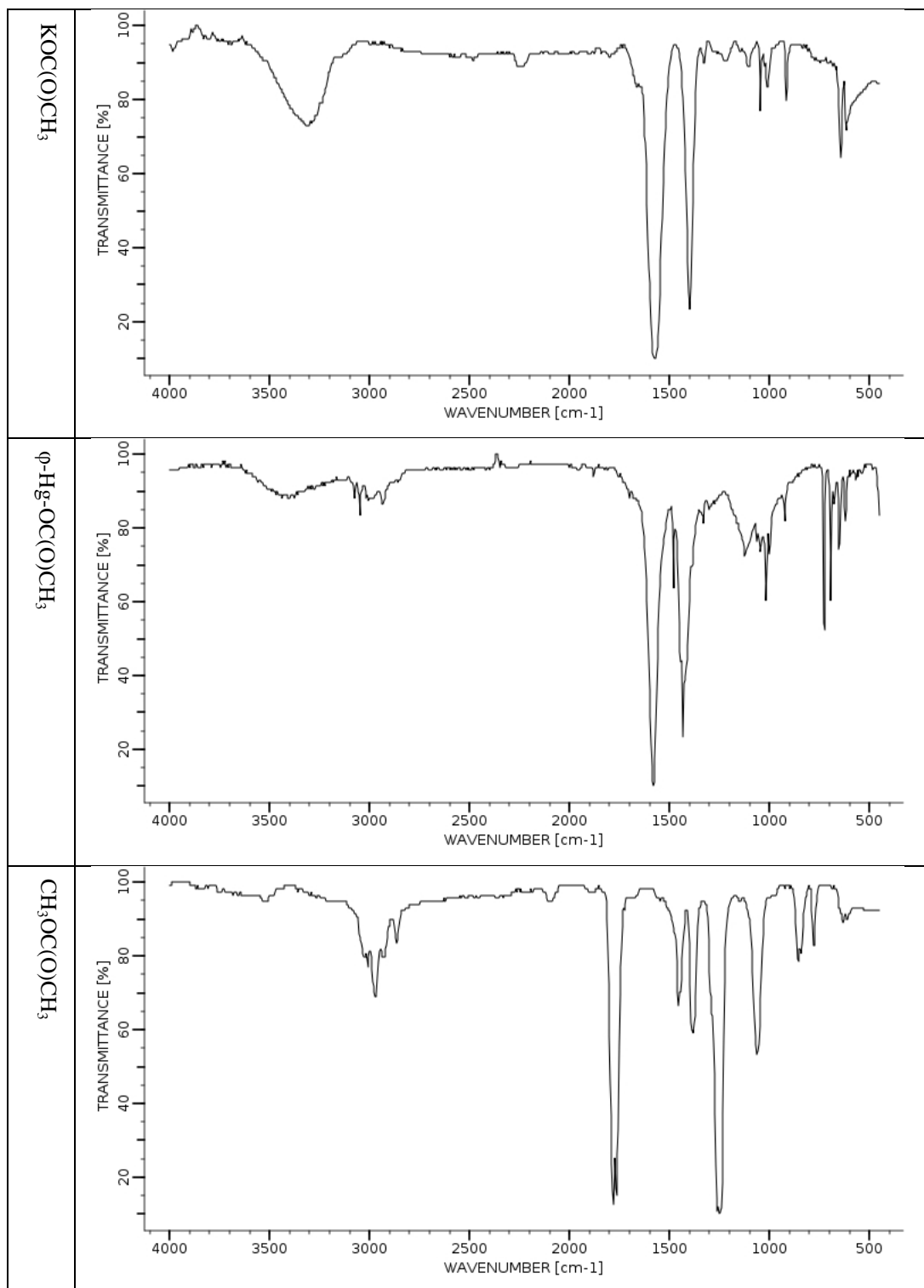
**Table 2.3.** Selected Isotropic (Iso) and Anisotropic (Aniso) shielding constants (/ppm) in phenylmercury carboxylates.

Molecule	Hg		C		O(-C)		O(=C)	
	Iso	Aniso	Iso	Aniso	Iso	Aniso	Iso	Aniso
Me <sub>2</sub> Hg	260.4	65.4	189.8	20.8				
φ-Hg-OAc	250.3	45.7	33.6	162.1	42.3	165.7	-76.6	282.2
φ-Hg-OPr	249.9	46.4	33.5	162.1	45.2	146.7	-65.6	269.9
φ-Hg-OMPr	250.8	47.1	33.4	163.5	47.6	162.1	-58.6	311.8
φ-Hg-OBu	251.8	46.4	33.6	163.7	49.2	174.4	-66.9	317.1
φ-Hg-OMBu	251.9	47.0	32.9	164.2	47.6	162.9	-58.1	310.2
φ-Hg-OEBu	252.3	46.7	33.1	165.1	49.0	157.3	-60.1	321.5
φ-Hg-OEtH	252.4	46.6	33.3	164.0	50.9	166.3	-60.0	316.8
φ-Hg-OOc	254.0	46.0	33.0	164.1	49.9	174.9	-67.5	321.3
φ-Hg-OnDc	254.6	45.5	33.3	164.2	48.4	174.5	-66.3	316.1

A comparison between the CO-stretching modes of the carboxylate group in the infrared spectra of phenylmercury acetate, potassium acetate (salt) and methyl acetate (covalent) clearly shows that phenylmercury acetate is an ionic complex:



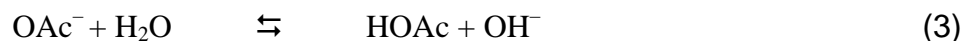
**Figure 2.3.** Charge distribution in phenylmercury acetate from NBO analysis.



**Figure 2.4.** Infrared spectra of potassium acetate, phenylmercury acetate and methyl acetate. Infrared spectral data from the Bio-Rad/Sadtler IR Data Collection was obtained from Bio-Rad Laboratories, Philadelphia, PA (US). Copyright © Bio-Rad Laboratories. All Rights Reserved.

## 2.2 Energies of complexation/dissociation

Phenylmercury carboxylates dissolved in water will partly undergo dissociation into a carboxylate anion and a phenylmercury cation, which both will enter into equilibrium with their corresponding acids and bases [Parikh and Sweet, 1961]. Taking  $\phi$ -Hg-OAc as example:



The energy changes in reaction (1) have been calculated for the gas phase and estimated for the aqueous phase employing the PCM model in which also the structures of the ions were optimized (see section 2.1) It is emphasized that the PCM model only simulates the dielectric properties of the medium and not any specific hydrogen bonding or proton transfer. The gas phase values have little relevance to the present study, but are included for completeness to illustrate trends. The results are summarized in Table 2.4 showing that the aqueous phase phenylmercury carboxylate dissociation equilibriums lie towards the undissociated carboxylate. The equilibriums (2) and (3), however, will drive equilibrium (1) towards the phenylmercury cation and acetate anion.

**Table 2.4.** Energy changes ( $\text{kJ mol}^{-1}$ ) in the reaction:  $\text{Ph-Hg-OCOR} \rightarrow \text{Ph-Hg}^+ + \text{OC(O)R}$  in the gas phase and in aqueous solution obtained from MPW3LYP/GST97 calculations.

Molecule	$\Delta E$		$\Delta H^a$		$\Delta G^a$	
	gas	aq.sol.	gas	aq.sol.	gas	aq.sol.
$\text{Me}_2\text{Hg}$	938.9	209.3	942.3	212.5	904.8	173.1
$\phi\text{-Hg-OAc}$	693.3	66.7	692.8	65.2	646.0	19.4
$\phi\text{-Hg-OPr}$	691.6	68.6	691.1	67.2	642.6	19.4
$\phi\text{-Hg-OMPr}$	687.3	68.5	686.3	67.2	638.9	19.1
$\phi\text{-Hg-OEtH}$	682.0		680.7		634.3	*
$\phi\text{-Hg-OOc}$	687.9	70.8	686.9	69.3	638.9	18.3
$\phi\text{-Hg-OnDc}$	687.8	70.8	686.5	69.7	641.0	15.2

<sup>a)</sup> Enthalpy and free energy changes at  $T = 298 \text{ K}$  and  $p = 1 \text{ atm}$ , respectively  $1 \text{ M}$  for the gas and aqueous phases. <sup>\*</sup>) Calculations running.

## 2.3 Vertical excitation energies

In order to compare the photolysis activity of these phenylmercury compounds, the vertical excitation energy ( $T_V$ ) was calculated with the TDDFT method for the first 3 excited singlet and triplet states at the same method with optimization. The result is listed in Table 2.5, which shows that the first singlet excited state will occur around 243 nm ( $f=0.0035$ ).

**Table 2.5.** The singlet (upper) and triplet (lower) excitation energies (/nm) and oscillator strengths (/atomic units) of phenylmercury carboxylates obtained in TD MPW3LYP/GST97 calculations.

Molecule	1st	2nd	3rd
Me <sub>2</sub> Hg	241.63 (0.0000)	241.58 (0.0000)	223.38 (0.2454)
	254.24 (0.0000)	247.95 (0.0000)	247.91 (0.0000)
φ-Hg-OAc	243.14 (0.0046)	242.13 (0.0011)	239.80 (0.0002)
	330.01 (0.0000)	274.40 (0.0000)	269.42 (0.0000)
φ-Hg-OPr	242.93 (0.0037)	241.51 (0.0020)	241.29 (0.0018)
	330.01 (0.0000)	274.31 (0.0000)	269.42 (0.0000)
φ-Hg-OMPr	243.90 (0.0054)	242.41 (0.0004)	241.77 (0.0209)
	330.03 (0.0000)	274.33 (0.0000)	269.45 (0.0000)
φ-Hg-OEtH	244.69 (0.0076)	242.52 (0.0067)	241.90 (0.0212)
	330.05 (0.0000)	274.33 (0.0000)	269.48 (0.0000)
φ-Hg-OOc	242.44 (0.0060)	241.49 (0.0005)	241.44 (0.0019)
	330.01 (0.0000)	274.19 (0.0000)	269.41 (0.0000)
φ-Hg-OnDc	242.57 (0.0053)	241.47 (0.0011)	241.45 (0.0020)
	330.01 (0.0000)	274.17 (0.0000)	269.41 (0.0000)

Chen and Osgood measured the UV absorption spectrum of Me<sub>2</sub>Hg and report a strong, structured continuum ( $X^1\Sigma_g \rightarrow B^1\Pi_u$ ) with the (0,0)-transition around 212.44 nm [*Chen and Osgood*, 1984]. A weaker and less structured continuum ( $X^1\Sigma_g \rightarrow A^1A_1$ ) stretches from around 217 to 253 nm. Both excitations result in dissociation. A simultaneous study by Irvine *et al.* report essentially the same observations [*Irvine et al.*, 1985]. The present TDDFT calculations place the strong  $X^1\Sigma_g \rightarrow B^1\Pi_u$  transition at 223 nm and the weak singlet/triplet structured/continuum bands around 242-254 nm in good agreement with experiment.

There are no UV spectra available for phenylmercury carboxylates.



## 2.4 Vertical ionization energies

The gas phase reaction of radicals, such as OH, Cl and NO<sub>3</sub>, with organomercury compounds proceeds in part via electrophilic attack on the mercury atom (see section 3.1). The energetics of such a process is related to the ionization potential of the substrate. Table 2.6 summarizes the calculated vertical ionization potentials for the compounds studied.

**Table 2.6.** The vertical ionization energy of CH<sub>3</sub>HgCH<sub>3</sub> and Ph-Hg-OC(O)CH<sub>3</sub> at the MPW3LYP/GST97 level.

Molecule	Me <sub>2</sub> Hg	φ-Hg-OAc	φ-Hg-OPr	φ-Hg-OMPr	φ-Hg-OBu	φ-Hg-OMBu	φ-Hg-OEtH	φ-Hg-OEtBu	φ-Hg-OOc	φ-Hg-OnDc
ΔE /eV	9.06	9.15	9.13	8.90	8.94	8.88	8.85	8.81	8.87	8.91

## 2.5 Summary of results from quantum chemistry calculations

The present quantum chemistry calculations indicate that the bonding around the Hg atom in the phenylmercury carboxylates studied is of ionic character and essentially independent of the nature of the carboxylate ion. Although the Hg–O bond length changes with 0.008 Å from acetate to octanoate, there is no similar systematic change in the net charge on the Hg and the interacting atoms. This is also reflected in the NMR shielding constants for the atoms in question.

Estimations of the energetics of the phenylmercury carboxylate dissociation in aqueous solution show little difference between the various phenylmercury carboxylates.

Calculation of the vertical excitation energies (UV-transitions) show that there are no real differences between UV absorption of the various phenylmercury carboxylates.

The first vertical ionization potential of the phenylmercury carboxylates show a systematic downward trend with carboxylate chain length and branching.

### 3. Atmospheric fate and lifetimes of phenylmercurycarboxylates

#### 3.1 Literature data

The literature is scarce on atmospheric gas phase reactions of organomercury compounds: the only relevant data available are concerned with the reactions of CH<sub>3</sub>HgCH<sub>3</sub> (Me<sub>2</sub>Hg, CAS: 593-74-8) with OH, Cl and NO<sub>3</sub>. There is no relevant information available for O<sub>3</sub> reactions.

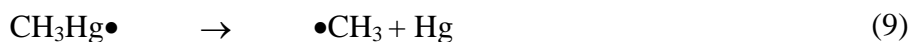
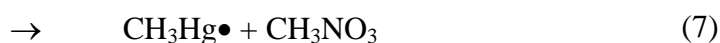
Niki *et al.* [Niki *et al.*, 1983a] investigated the Me<sub>2</sub>Hg reaction with Cl atoms and determined the reaction rate of Cl with Me<sub>2</sub>Hg relative to that of n-C<sub>4</sub>H<sub>10</sub>; they reported  $k_{\text{DMHg+OH}}/k_{\text{n-C}_4\text{H}_{10}+\text{OH}} = 1.25 \pm 0.06$ . Taking today's recommended rate coefficient  $k_{\text{n-C}_4\text{H}_{10}+\text{OH}} = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [IUPAC, 2010] places  $k_{\text{Me}_2\text{Hg+Cl}} = (2.6 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . CH<sub>3</sub>HgCl was identified as the major product, and the HCl yield in the reaction was less than 5% indicating that H-abstraction from the methyl group is only a minor route. Both the kinetic and the product studies were therefore interpreted in terms of a predominant displacement reaction:



In a parallel study Niki *et al.* [Niki *et al.*, 1983b] investigated the Me<sub>2</sub>Hg reaction with OH radicals and determined the reaction rate of OH with Me<sub>2</sub>Hg relative to those of CH<sub>2</sub>=CH<sub>2</sub> and CH<sub>3</sub>CH=CH<sub>2</sub>. They found  $k_{\text{CH}_2=\text{CH}_2+\text{OH}}/k_{\text{DMHg+OH}} = 0.428 \pm 0.033$  and  $k_{\text{CH}_3\text{CH}=\text{CH}_2+\text{OH}}/k_{\text{DMHg+OH}} = 1.413 \pm 0.114$  at 700 torr. Taking today's recommended high-pressure rate coefficients  $k_{\text{CH}_2=\text{CH}_2+\text{OH}} = 7.9 \times 10^{-12}$  and  $k_{\text{CH}_3\text{CH}=\text{CH}_2+\text{OH}} = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1 bar [Atkinson *et al.*, 2006] places  $k_{\text{Me}_2\text{Hg+OH}} = (1.9 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Again, both the kinetic and the product studies were interpreted in terms of a predominant displacement reaction:



Sommar *et al.* [Sommar *et al.*, 1996] measured the rate coefficient for the reaction of NO<sub>3</sub> radicals with Me<sub>2</sub>Hg in the temperature region 258 to 358 K, and reported an Arrhenius expression for the rate,  $3.2 \times 10^{-11} \exp[-(1760 \pm 400)/T]$ , and  $k_{\text{NO}_3+\text{DMHg}} = 8.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. They observed the formation of elementary mercury in an amount of around 3 % of NO<sub>3</sub> reacted and suggested the displacement reaction to dominate:



With assumed average OH (day), Cl (day) and NO<sub>3</sub> (night) radical concentrations of  $1 \times 10^6$ ,  $2 \times 10^3$  and  $1 \times 10^9 \text{ cm}^{-3}$ , the atmospheric lifetime of Me<sub>2</sub>Hg with respect to these radicals are  $\tau_{\text{OH}} \approx 15 \text{ h}$ ,  $\tau_{\text{Cl}} \approx 22 \text{ d}$  and  $\tau_{\text{NO}_3} \approx 3 \text{ h}$  at 298 K. In conclusion, the atmospheric night-time chemistry constitutes the major chemical gas phase sink for Me<sub>2</sub>Hg.

Me<sub>2</sub>Hg does not absorb at wavelengths longer than 290 nm and will therefore not undergo photolysis in the troposphere. The phenylmercury carboxylates all absorb in the actinic region. However, no UV spectra have been published. Baughman *et al.* reported UV spectra of phenylmercury hydroxide, the phenylmercury ion and diphenylmercury [Baughman *et al.*, 1973], and present an empirical photolysis half-life of phenylmercury acetate of  $t_{1/2} = 16 \pm 2$  hours (corresponding to a photolysis lifetime  $\tau_{\text{photol}} = 23$  hours).

### 3.2 Estimation of the atmospheric lifetimes of phenylmercury carboxylates

The Atmospheric Oxidation Program for Microsoft Windows (AOPWIN) estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals [Meylan and Howard, 1993]. It also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds. The rate constants estimated by the program are then used to calculate atmospheric half-lives for organic compounds based upon average atmospheric concentrations of hydroxyl radicals and ozone. The program manual states: “The estimation methods used by AOPWIN are based upon the structure-activity relationship (SAR) methods developed by Atkinson and co-workers [Atkinson and Carter, 1984; Atkinson, 1986; 1987; 1991; Kwok et al., 1992; Kwok and Atkinson, 1995; Kwok et al., 1996]. AOPWIN incorporates updated fragment and reaction values as cited in Kwok and Atkinson [Kwok and Atkinson, 1995]. In addition, Syracuse Research Corporation has derived some additional fragment and reaction values from new experimental data.”

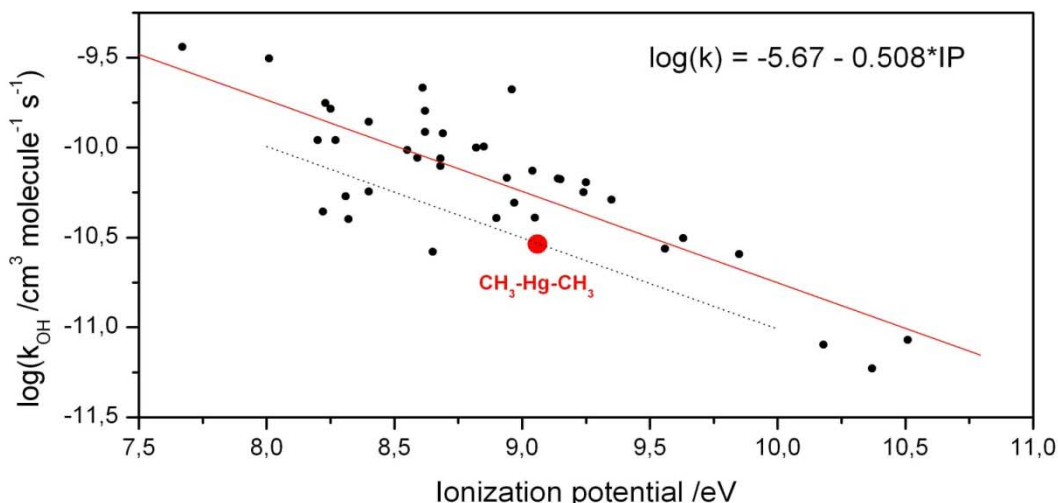
**It is stressed that organomercurials are not within the applicability domain of the AOPWIN model and the use of the model is solely to get an estimate of the reactivity associated with the phenyl- and carboxylate fragments.**

Table 3.1 summarises the predictions of the AOPWIN program for the OH rate constants for reaction with dimethylmercury and a series of phenylmercury carboxylates. The output from this program is collected in Annex A (page 25) from which it can be seen that the program describes the reactions as a combination of H-abstraction from the aliphatic part of the molecule and an addition to the aromatic ring. The experimental evidence for a predominant displacement reaction is not included/considered in the AOPWIN program, and this should be kept in mind when using the results of AOPWIN.

**Table 3.1.** AOPWIN predicted rate constants for the reaction of OH radicals with various mercury compounds.

Molecule	$k_{OH}/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
	Experimental	AOPWIN
Me <sub>2</sub> Hg	19 ± 2	16.3
φ-Hg-OAc		2.0
φ-Hg-OPr		2.4
φ-Hg-OMPr		2.9
φ-Hg-OEtH		8.3
φ-Hg-OOc		9.3
φ-Hg-OnDc		8.5

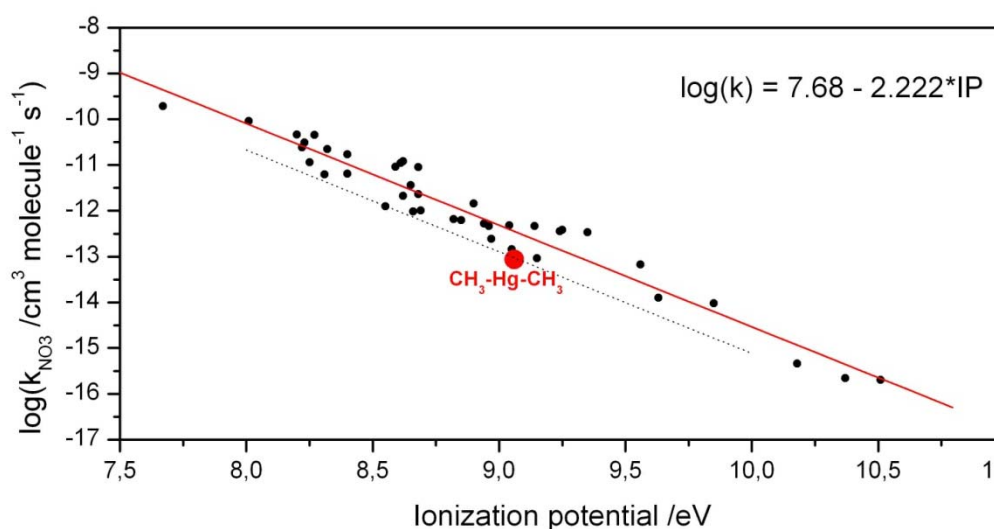
The quantum chemistry calculations (see section 2.1) indicate that the mercury atom in dimethylmercury has a net positive charge of +0.94 and that this net charge increases to +1.10 in the various phenylmercury carboxylates. The mere size of the mercury atom implies that steric hindrance to attack directly on the mercury atom does not vary much either, and to a first approximation one may therefore assume that the gas phase displacement reaction (electrophilic attack) will dominate also in the OH and NO<sub>3</sub> radical reaction with the phenylmercury carboxylates. The OH addition reaction to the aromatic ring is around 10 times slower than the displacement reaction, while the aliphatic H-abstraction reactions increase in importance with the chain length.



**Figure 3.1.** Correlation between the logarithms of the rate constant for the addition reactions OH as a function of the first vertical ionization potential of the substrate. Data from Wayne *et al.* [Wayne *et al.*, 1991].

In the transition state of the radical addition to the mercury atom a certain degree of correlation between the kinetic data and the ionization potentials can be expected. Figure 3.1 shows this correlation for OH radical addition reactions with various organics, while Figure 3.2 shows the similar plot for the NO<sub>3</sub> radical. The two figures also include the experimental data for dimethylmercury combined with the ionization potential calculated in the present work; the data fit the correlations well. Taking the calculated vertical ionization potentials for the phenylmercury carboxylates and including the Me<sub>2</sub>Hg offset in the correlation, places the displacement rate constants  $k_{\text{OH,displ.}}$  and  $k_{\text{NO}_3,\text{displ.}}$  for phenylmercury acetate at  $1.7 \times 10^{-11}$  and  $5.9 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively.

Table 3.2 summarises estimates of the gas phase reactivity of the phenylmercury carboxylates towards reaction with NO<sub>3</sub> radicals and OH radicals derived as the sum of rate constants for



**Figure 3.2.** Correlation between the logarithms of the rate constant for the addition reactions NO<sub>3</sub> as a function of the first vertical ionization potential of the substrate. Data from Wayne *et al.* [Wayne *et al.*, 1991].

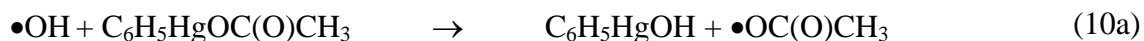
displacement, addition to the aromatic ring, and aliphatic H-abstraction. It is stressed that the numbers presented should be used with caution. The results from quantum chemistry, however, support the experimental evidence that the displacement reaction is the dominant route in the OH reaction with phenylmercury carboxylates.

The NO<sub>3</sub> radical reacts quite fast with Me<sub>2</sub>Hg in a displacement reaction [Sommar *et al.*, 1996], and similar fast reactions are expected for the phenylmercury carboxylates, Table 3.2. The aliphatic H-abstraction reactions by NO<sub>3</sub> radicals are slow [Wayne *et al.*, 1991] and they can be neglected in the present case. Similarly, the NO<sub>3</sub> radical reacts slowly with aromatic rings and may also be neglected for the phenylmercury carboxylates [Wayne *et al.*, 1991].

**Table 3.2.** Estimated NO<sub>3</sub> rate constants (/10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and OH rate constants (/10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for their reactions with various mercury compounds.

Molecule	$k_{\text{OH,displ.}}$	$k_{\text{OH,add. to phenyl ring}}$	$k_{\text{OH}\cdot\text{H-abstr. from carboxylate}}$	$k_{\text{OH,tot}}$	$k_{\text{NO}_3}$
Me <sub>2</sub> Hg	19.0			19.0	87
φ-Hg-OAc	17.1	1.9	0.04	19.0	55
φ-Hg-OPr	17.5	1.9	0.5	19.9	61
φ-Hg-OMPr	22.9	1.9	0.9	25.7	197
φ-Hg-OEtH	25.4	1.9	6.3	33.6	313
φ-Hg-OOc	23.7	1.9	7.3	32.9	230
φ-Hg-OnDc	n.c.	1.9	6.5		n.c.

Taking phenylmercury acetate as example, the displacement reaction may in principle take two routes:



The enthalpies of reaction have been estimated in MPW3LYP/GST97 calculations giving  $\Delta_r H_{(10a)} = -4.4$  and  $\Delta_r H_{(10b)} = -5.4$  at 298 K in concord with the net charges of the phenyl- and acetyl-groups (-0.42 and -0.68, respectively). With nearly identical enthalpies of reaction the barriers to dissociation cannot be much different, and it is concluded that both processes will occur, but that reaction (10b) will dominate.

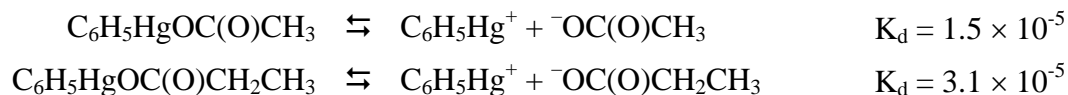
As mentioned, there are no UV spectra available for phenylmercury carboxylates. Baughman *et al.* reported UV spectra of phenylmercury hydroxide, the phenylmercury ion and diphenylmercury [Baughman *et al.*, 1973], which all absorb in the actinic region above 290 nm. The quantum chemistry results show that the absorption is due to a spin-forbidden S<sub>0</sub> → T transition of the phenyl group, which become active through the heavy atom Hg spin-orbit coupling. The calculations also show that position and the strength of the UV absorption is essentially equal for all the phenylmercury carboxylates. Consequently, all phenylmercury carboxylates will have will all have the same photolysis lifetime in the aqueous phase. As water has no or only very little influence on the UV absorption of the phenylmercury carboxylates, the compounds will essentially absorb at the same wavelengths in the gas phase as in the aqueous phase. The aqueous phase quenching by interaction with water, however, is expected to be larger than the gas phase quenching by O<sub>2</sub>/N<sub>2</sub>. Consequently, the photolysis lifetime of phenylmercury carboxylates in the gas phase will be very similar to or shorter than that of the aqueous phase.

In a conservative estimate of atmospheric lifetime of gaseous phenylmercury carboxylates one may assume a generic rate constant for reaction with OH radicals of  $10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  – a factor of 2 lower than estimated from correlation diagrams. Similarly, for the reaction of phenylmercury carboxylates with  $\text{NO}_3$  radicals one may assume a generic rate constant of  $20 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  – a factor of 2-10 lower than estimated from correlation diagrams. A 24-hour average OH concentration of  $5 \times 10^5 \text{ cm}^{-3}$  and a 12 hour night time  $\text{NO}_3$  concentration at  $1 \times 10^9 \text{ cm}^{-3}$  places the estimated lifetimes  $\tau_{\text{OH}} \approx 55$  hours and  $\tau_{\text{NO}_3} \approx 14$  hours, which should be compared to the estimated photolysis lifetime of  $\tau_{\text{photol}} \approx 23$  hours. In conclusion, the average atmospheric lifetime of gaseous phenylmercury carboxylates is around 1 day.

## 4. Dissociation of phenylmercury carboxylates in the aqueous phase

### 4.1 Literature data

There is only one experimental study of phenylmercury carboxylate dissociation in aqueous solution. Parikh and Sweet [Parikh and Sweet, 1961] reported the dissociation constants for phenylmercury acetate and propionate:



In deriving these dissociation constants Parikh and Sweet assumed  $K_b = 1.31 \times 10^{-10}$  for phenylmercuric hydroxide,  $K_a = 1.754 \times 10^{-5}$  ( $\text{p}K_a = 4.756$ ) for acetic acid and  $K_a = 1.336 \times 10^{-5}$  ( $\text{p}K_a = 4.874$ ) for propionic acid.

Table 4.1 lists ionization (dissociation) constants for selected organic acids. [Serjeant and Dempsey, 1979] With the exception of 2,2-dimethyl propionic acid, which apparently is a slightly weaker acid, all the relevant carboxylic acid have about the same strength in aqueous solution.

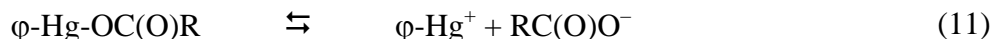
**Table 4.1.** Ionization constants of selected organic acids in aqueous solution.<sup>a</sup>

Acid	T /°C	pK <sub>a</sub>
CH <sub>3</sub> COOH	25	4.756
CH <sub>3</sub> CH <sub>2</sub> COOH	25	4.87
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	25	4.83
(CH <sub>3</sub> ) <sub>2</sub> CHCOOH	25	4.84
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	20	4.83
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>3</sub> )CHCOOH	20	4.83
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> COOH	20	4.80
(CH <sub>3</sub> ) <sub>3</sub> CCOOH	20	5.03
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	20	4.85
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> COOH	18	4.84
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	25	4.89
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	25	4.89
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> )CHCOOH	?	4.6

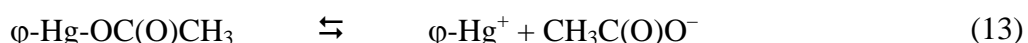
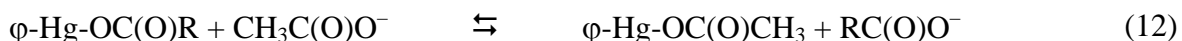
<sup>a</sup> Data from Serjeant and Dempsey (1979).

## 4.2 Estimation of the dissociation constant for phenylmercury carboxylates

The quantum chemistry calculations of the dissociation reaction of interest will invariably be biased by model errors:



Instead of calculating Gibbs Free energy for reaction (11) directly, we consider the thermodynamic cycle (11) = (12) + (13):



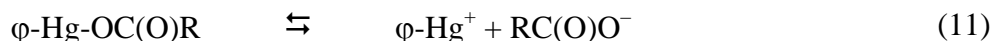
The quantum chemistry solvation model errors are expected to largely cancel in the isodesmic reaction (12). Given  $K_d = 1.5 \times 10^{-5}$  for the dissociation of phenylmercury acetate (reaction (13)), the quantum chemistry calculations of the Gibbs Free energy of solvation can be used to calculate  $K_d$  for the other phenylmercury carboxylates,  $\Delta_{\text{diss}}G^\circ = \Delta G^\circ(11) = \Delta G^\circ(12) + \Delta G^\circ(13)$ . Table 4.2 summarises the derived dissociation constants for various phenylmercury carboxylates.

**Table 4.2.** Dissociation constants and Gibbs Free Energy changes ( $\text{kJ mol}^{-1}$ ) at 298 K in the reaction:  $\text{Ph-Hg-OCOR} \rightarrow \text{Ph-Hg}^+ + \text{OC(O)R}$  in aqueous solution obtained from MPW3LYP/GST97 calculations.

Acronym	Formula	$\Delta G^a$	$K_d$
$\varphi\text{-Hg-OAc}$	$\varphi\text{-Hg-OC(O)CH}_3$	27.5	$1.5 \times 10^{-5}$
$\varphi\text{-Hg-OPr}$	$\varphi\text{-Hg-OC(O)CH}_2\text{CH}_3$	27.5	$1.5 \times 10^{-5}$
$\varphi\text{-Hg-OMPr}$	$\varphi\text{-Hg-OMPPr}$	27.2	$1.7 \times 10^{-5}$
$\varphi\text{-Hg-OEtH}$	$\varphi\text{-Hg-OEtH}$	*	
$\varphi\text{-Hg-OOc}$	$\varphi\text{-Hg-OC(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	26.4	$2.4 \times 10^{-5}$
$\varphi\text{-Hg-OnDc}$	$\varphi\text{-Hg-OC(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C(CH}_3)_3$	23.3	$8.2 \times 10^{-5}$

<sup>a</sup>) Calculation running.

We notice that the calculations place  $K_d$  for phenylmercury propionate to be the same as that of the acetate contrasting the experimental result ( $3.1 \times 10^{-5}$  vs.  $1.5 \times 10^{-5}$ ) [Parikh and Sweet, 1961]. The calculations, however, suggest that the dissociation constants of the phenylmercury carboxylates considered increase slightly with the size of the carboxylate. As the ionization constants for the organic acids (Table 4.1) are nearly identical, it is concluded that the various phenylmercury carboxylates will all dissolve in water undergoing the same pH-dependent reactions as phenylmercury acetate:







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## 5. Annex A. Output from AOPWIN



SMILES : C[Hg]C

CHEM : Dimethylmercury

MOL FOR: C2 H6 Hg1

MOL WT : 230.66

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 16.3200 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Aromatic Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 16.3200 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 0.655 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 7.865 Hrs

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database Structure Match:

Chem Name : Dimethyl mercury

CAS Number: 000593-74-8

Exper OH rate constant : 19 E-12 cm<sup>3</sup>/molecule-sec

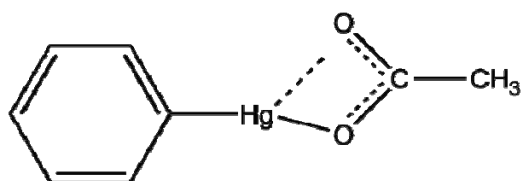
Exper OH Reference: ATKINSON,R (1989)

Exper Ozone rate constant: --- cm<sup>3</sup>/molecule-sec

Exper NO<sub>3</sub> rate constant : 8.7 E-14 cm<sup>3</sup>/molecule-sec

-----

Phenylmercury acetate, CAS: 62-38-4



SMILES : CC(=O)O[Hg]c1ccccc1

CHEM : Phenylmercury acetate

MOL FOR: C8 H8 O2 Hg1

MOL WT : 336.74

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 0.0422 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 1.9920 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 5.369 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 64.434 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

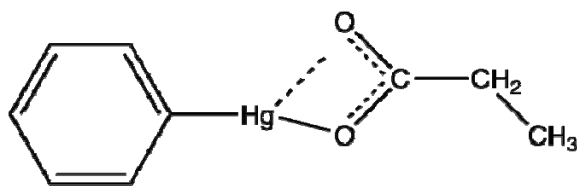
(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

-----



Phenylmercury propioate, CAS: 103-27-5



SMILES : CCC(=O)O[Hg]c1ccccc1

CHEM : Phenylmercury propioate

MOL FOR: C9 H10 O2 Hg1

MOL WT : 350.77

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 0.4568 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 2.4067 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 4.444 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 53.332 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

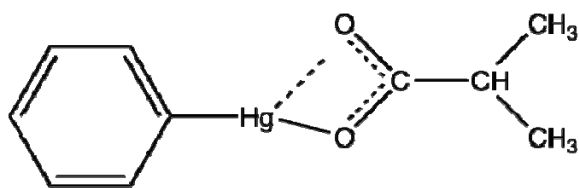
\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

-----

Phenylmercury isobutyrate, CAS: 13864-39-6



SMILES : CC(C)C(=O)O[Hg]c1ccccc1

CHEM : Phenylmercury isobutyrate

MOL FOR: C10 H12 O2 Hg1

MOL WT : 364.80

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 0.9360 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 2.8858 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 3.706 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 44.477 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

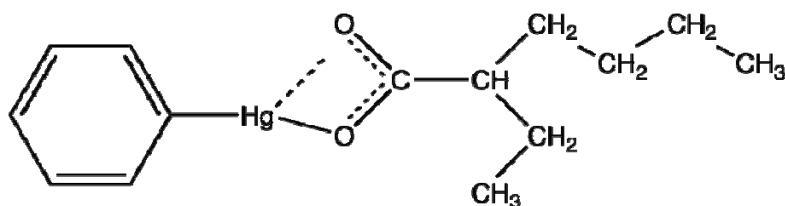
----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

Phenylmercury 2-ethylhexanoate, CAS: 13302-00-6.



SMILES : [Hg](OC(=O)C(CC)CCCC)c(ccc1)cc1

CHEM : Phenylmercury 2-ethylhexanoate

MOL FOR: C14 H20 O2 Hg1

MOL WT : 420.90

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 6.3682 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 8.3180 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 1.286 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 15.431 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

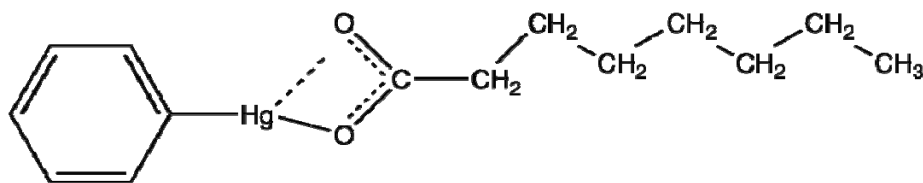
\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

-----

Phenylmercury octanoate, CAS: 13864-38-5



SMILES : c1([Hg]OC(=O)CCCCC)ccccc1

CHEM : Phenylmercury octanoate

MOL FOR: C14 H20 O2 Hg1

MOL WT : 420.90

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 7.3244 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 9.2743 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 1.153 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 13.840 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

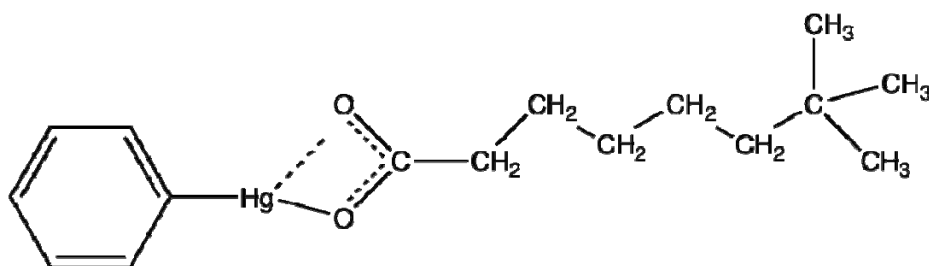
----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

Phenylmercury 7,7-dimethyloctanoate. <sup>a)</sup>



SMILES : c1([Hg]OC(=O)CCCCC(C)(C)C)ccccc1

CHEM : Phenylmercury neodecanoate

MOL FOR: C16 H24 O2 Hg1

MOL WT : 448.96

----- SUMMARY (AOP v1.92): HYDROXYL RADICALS (25 deg C) -----

Hydrogen Abstraction = 6.5102 E-12 cm<sup>3</sup>/molecule-sec

Reaction with N, S and -OH = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Triple Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

Addition to Olefinic Bonds = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

\*\*Addition to Aromatic Rings = 1.9498 E-12 cm<sup>3</sup>/molecule-sec

Addition to Fused Rings = 0.0000 E-12 cm<sup>3</sup>/molecule-sec

OVERALL OH Rate Constant = 8.4600 E-12 cm<sup>3</sup>/molecule-sec

HALF-LIFE = 1.264 Days (12-hr day; 1.5E6 OH/cm<sup>3</sup>)

HALF-LIFE = 15.172 Hrs

..... \*\* Designates Estimation(s) Using ASSUMED Value(s)

----- SUMMARY (AOP v1.91): OZONE REACTION (25 deg C) -----

\*\*\*\*\* NO OZONE REACTION ESTIMATION \*\*\*\*\*

(ONLY Olefins and Acetylenes are Estimated)

Experimental Database: NO Structure Matches

<sup>a)</sup> The CAS CAS no. 26545-49-3, Phenylmercury OC(O)[C<sub>9</sub>H<sub>19</sub>-neo], covers a multitude of structural isomers.



Utførende institusjon University of Oslo, Department of Chemistry, CTCC	ISBN-nummer
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Oppdragstakers prosjektansvarlig Claus Jørgen Nielsen	Kontaktperson i Klima- og forurensningsdirektoratet Marit Kopangen	TA-nummer 2750/2010
		SPFO-nummer

	År 2010	Sidetall 33	Klima- og forurensningsdirektoratets kontraktnummer 3010094
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Utgiver Klima- og forurensningsdirektoratet	Prosjektet er finansiert av Klima- og forurensningsdirektoratet
--	--

Forfatter(e) Yizhen Tang, Claus Jørgen Nielsen
Tittel - norsk og engelsk Theoretical studies of Phenylmercury carboxylates - Complexation Constants and Gas Phase Photo-Oxidation of Phenylmercurycarboxylates
Sammendrag – summary Phenylmercury(II)-carboxylates used as catalysts in PU-systems will eventually be released into the environment. The phenylmercury(II) cation, C <sub>6</sub> H <sub>5</sub> Hg <sup>+</sup> , forms various complexes with ligands present in natural and biological systems and knowledge about the stability of the carboxylates complexation constants are important in this respect. The phenylmercury(II)-carboxylates may also be emitted into the atmosphere where they will undergo photo-oxidation reactions. The chemical bonding in a series of phenylmercury(II)-carboxylates, including estimates of the UV-absorption spectra and the carboxylate complexation constants have been obtained from quantum chemistry calculations. The results indicate that the phenylmercury(II)-carboxylates (acetate, propionate, 2-ethylhexanoate, octanoate and neodecanoate) have nearly the same dissociation constants and UV-spectra. The aqueous phase fate of these compounds and their rate of photolysis in the aqueous phase will therefore essentially be the same. An evaluation of atmospheric radical reactions and direct photolysis of gaseous phenylmercury(II)-carboxylates suggests that direct photolysis by solar radiation is the dominant daytime sink, and that reactions with NO <sub>3</sub> radicals are equally important during night-time. The atmospheric lifetime of phenylmercury(II)-carboxylates is estimated to be around 1 day.

4 emneord Fenylkvikksølvforbindelser, dissosiasjon, nedbrytning i atmosfæren, QSAR	4 subject words Phenylmercury compounds, dissociation, atmospheric degradation, QSAR
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## **Climate and Pollution Agency**

The Climate and Pollution Agency reports to the Ministry of the Environment and has 325 employees, based mainly in Oslo. We implement government policy on pollution. We act as advisers guardians and stewards for the environment. Our most important fields of work include climate change, chemicals, marine and freshwater environment, waste management, air quality and noise. Our vision is a future without pollution.

We are working to

- reduce greenhouse gas emissions
- reduce the spread of hazardous substances harmful to health and the environment
- achieve integrated and ecosystem-based management of the marine and freshwater environment
- increase waste recovery and reduce emissions from waste
- reduce the harmful effects of air pollution and noise

TA-2750 /2010

