

γ -Radiolysis of aqueous 2-chloroanisole

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Abstract

The radiation-induced degradation of 2-chloroanisole (2-ClAn) is investigated under various experimental conditions in neutral aqueous media as a function of absorbed radiation dose. The initial yields (G_i -values) of substrate degradation as well as those of the resulting major products were determined by HPLC analysis. Probable reaction mechanisms are suggested.

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1. Introduction

Halogenated methyl-phenyl ethers (methoxy-benzenes, anisoles) are ubiquitous in the environment (Jaffé, 1991) although they are not produced in industrial quantities. The isomer-specific separation and detection of 60 of the 134 possible congeners allowing an environmental fingerprinting have been reported (Pfeifer et al., 2001). Members of these substances have been detected in the marine atmosphere (Atlas et al., 1986; Pfeifer and Ballschmiter, 2002) in marine and freshwater fish (Jaffé et al., 1985; Jaffé and Hites, 1986; Paasivirta et al., 1987; Opperhuizen and Voors, 1987) in oysters (Miyazaki et al., 1981) in marine algae (Flodin and Whitfield, 2000) in effluents of municipal wastewater treatment plants (Shiraishi and Otsuki, 1985), in sediments (Watanabe et al., 1985), and in food (Seitz et al., 1999; Rij et al., 1996; Aung et al., 1996). The lower chlorinated congeners are responsible for the musty

odor of some waters (Benanou et al., 2003; Piriou et al., 2001) and the so-called corky taste of wines is ascribed to the presence of elevated levels of 2,4,6-trichloroanisole (Chatonnet et al., 2003; Michel, 2002; Capone et al., 1999; Pollnitz et al., 1996). Up to now no definite primary anthropogenic sources for the halogenated anisoles have been known. However, methyl-ethyl ethers are formed by many microorganisms by biomethylation of the respective phenols and halogenated phenols. Thus, for example, chlorophenols may be easily biotransformed into chlorinated anisoles (Kaufman, 1978; Neilson et al., 1983; Neilson, 1990; Palm et al., 1991). Chlorinated and other substituted benzenes, phenols and other aliphatic carbons represent the most important environmental pollutants (Blum and Speece, 1990, 1991a,b), thus contaminating waste water and ground water. Even under drinking water treatment procedure their formation may occur because granulated activated carbon (GAC) oxidized by chlorine becomes very active towards phenol (Voudrias et al., 1984, 1985a,b).

Ionizing radiation (γ -irradiation, high-energy electrons) is used for food treatment (Delincée, 1998) and,

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on the other hand, for the degradation of such biologically resistant pollutants both in drinking and in waste water (e.g. Gehringer et al., 1986, 1987, 1988a,b; Getoff, 1986, 1991, 1992a,b; Waite et al., 1992; Cooper et al., 1992, 1993). Therefore, the effect of radiation treatment on chloroanisoles is of interest. We already investigated the radiation-induced decomposition of 4-chloroanisole with regard to product analysis, elucidation of reaction mechanisms, and kinetics (Quint et al., 1996). Because of the influence of the substituent effects on the bond strengths (Suryan et al., 1989; Himu et al., 2000) it was of interest to compare these results with those obtained now using the ortho isomer.

2. Experimental

2.1. γ -Irradiation source

A ^{60}Co - γ -source ("Gammacell 220", Nordion International Inc., Canada) with an activity of about 20 kCi was used for irradiation under steady-state conditions. The dose rate was determined by means of Fricke-dosimeter using $G(\text{Fe}^{3+})^1 = 15.6$ as well as ferrous-cupric solutions with $G(\text{Fe}^{3+}) = 0.7$ (Getoff, 1967; Spinks and Woods, 1990).

2.2. Preparation of solution and analysis

2-Chloroanisole (2-ClAn) (Aldrich 99%) as well as the reference compounds: 2,4-hexadiendisäure (muconic acid, MAc) 98%, hydroquinone (HQ) 99%, resorcinol 99%, pyrocatechol (PyC) 99%, benzoquinone 98%, 2-methoxyphenol (2-MePh) 99%, 4-methoxyphenol (2-MePh) 99%, 3-methoxyphenol (3-MePh) 99%, 4-chlorophenol (4-ClPh) 98%, 3-chlorophenol (3-ClPh) 98%, 2-chlorophenol (2-ClPh) 98%, anisole (An) 99%, chlorobenzene 99% (all Merck), 4,4'-dihydroxybiphenyl 99% and 4,4'-dimethoxybiphenyl 99% (both Aldrich) were used as received.

For irradiation experiments $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-ClAn was dissolved in triply distilled water which had been saturated with the respective gas before irradiation.

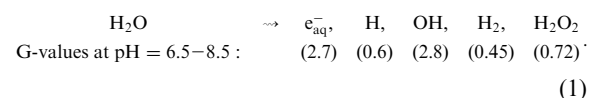
The Cl^- determination was performed spectrophotometrically by the mercury(II)-thiocyanate method described by Florence and Farrar (1971) using Perkin Elmer (Model 816; with computer and printer online).

The irradiated solutions under steady-state conditions were analyzed by HPLC (Hewlett Packard 1050, Spherisorb ODS2 125 mm column; eluent: $\text{H}_2\text{O}/$

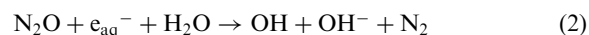
$\text{MeOH} = 50/50$ by volume). The HPLC was equipped with a multiple wavelength UV-detector with diode array and an HP-1049 electrochemical detector (ECD). The absorbance of the individual compounds was detected at 210, 225 and 280 nm. The ECD was run in oxidative mode at a potential of +0.9 V. The identity of the products was confirmed by comparison with the chromatograms and UV spectra of the standards.

3. Results and discussion

In airfree solution all primary products produced by water radiolysis (Eq. (1)) react with the substrate:



In solutions saturated with N_2O , the e_{aq}^- are converted into OH (Eq. (2)):



$k(\text{N}_2\text{O} + \text{e}_{\text{aq}}^-) = 0.91 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Janata and Schuler, 1982).

In the presence of oxygen both e_{aq}^- and H are transformed into peroxy radicals (Eqs. (3a) and (3b)):



$k(\text{H} + \text{O}_2) = 2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988).

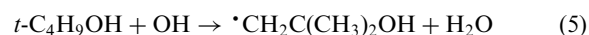


$k(\text{e}_{\text{aq}}^- + \text{O}_2) = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988):



$pK = 4.8$ (Getoff and Prucha, 1983).

In order to study the attack of H on the substrate, *t*-butanol (*t*-BuOH) was added to the solutions saturated with N_2O . Under these conditions the OH are scavenged by *t*-BuOH:



$k(t\text{-BuOH} + \text{OH}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Gohn and Getoff, 1977; Buxton et al., 1988).

The H-atoms react extremely slowly with *t*-BuOH; hence, their yield is not reduced under these conditions:



$k(\text{H} + t\text{-BuOH}) = 9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Neta et al., 1971).

Generally, it is assumed that the resulting *t*-BuOH radicals are rather unreactive.

¹G-value = number of formed or decomposed molecules per 100 eV (= $1.6 \times 10^{-17} \text{ J}$) absorbed energy. For conversion into SI-units multiply by 0.10364 to obtain $G(x)$ in $\mu\text{mol J}^{-1}$.

3.1. Reactions with OH (solutions saturated with N₂O)

The 5×10^{-4} mol dm⁻³ 2-ClAn solution was saturated with N₂O, irradiated with doses up to 0.6 kGy (dose rate of 266 Gy min⁻¹) and analyzed by HPLC immediately after irradiation. The products which could be detected as well as the degradation course of 2-ClAn in dependence of the absorbed dose are presented in Fig. 1. The compounds expected to be formed under the applied conditions were used as standards in the analytical procedure and are listed in Table 1.

In addition to Cl⁻ formation (see Table 2 and Fig. 6) three products could be identified: 2-chlorophenol (2-ClPh), 2-methoxyphenol (2-MePh) and a product with a retention time and a uv-spectrum like that of 4-chlorophenol (4-ClPh). Because 4-chloro-3-methoxyphenol and 2-chloro-3-methoxyphenol were not available as reference substances it could not be excluded that the detected compound could be one of them. This assumption is supported by the fact that the hydroxylated substances: 2-chloro-5-methoxyphenole, 5-chloro-2-methoxyphenole and 3-chloro-5-methoxyphenole show retention times in the neighborhood of 4-ClAn. The amounts of unidentified products were negligible. The total amount of identified products was about 28% of the decomposed 2-ClAn.

Under these conditions 90% OH ($G_{OH} = 5.5$) and 10% H atoms ($G_H = 0.6$) are involved in the reaction mechanisms. The primary OH attack on the substrate leads to formation of OH-adducts (hydroxycyclohexadienyl radicals) on *ipso*-, *o*-, *m*- and *p*-position (see Eqs. (7)–(12)). The attack on *ipso*-position to OH or Cl leads to the formation of the corresponding phenoxyradicals (Eqs. (7) and (8)) resulting in the formation of 2-ClPh or 2-MePh, respectively (Eqs. (13) and (14)).

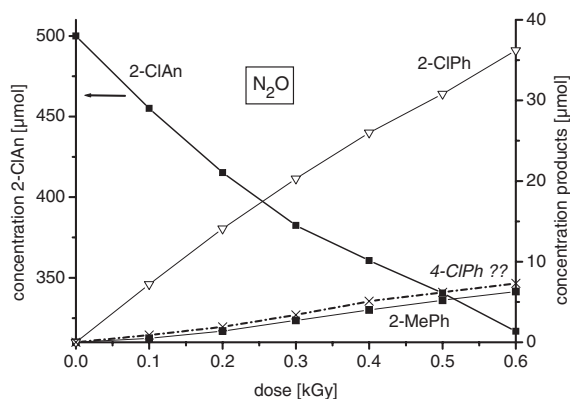
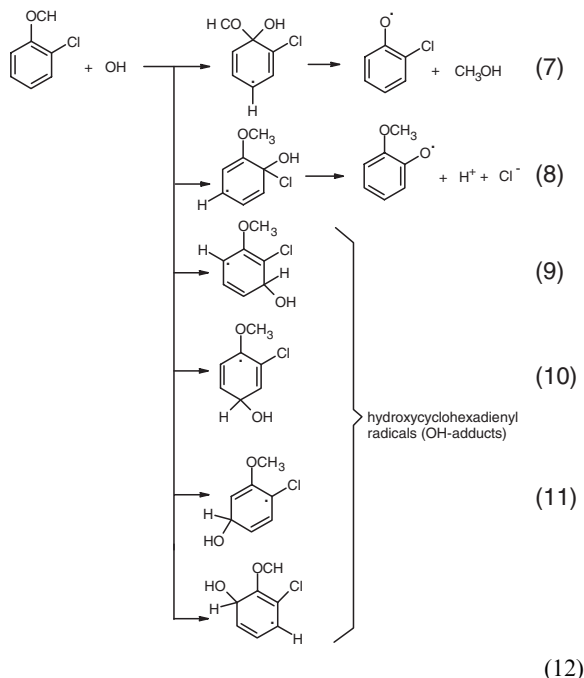


Fig. 1. Final products (right scale) and consumption of 2-ClAn (left scale) in dependence of absorbed dose observed by irradiation of aqueous 5×10^{-4} mol dm⁻³ 2-ClAn (pH 6.8) saturated with N₂O.

A third product (hydroxylated chloroanisole??) could not be exactly identified.



3.2. Reactions with H-atoms

As mentioned (Eq. (2)), in the solution saturated with N₂O, e_{aq}⁻ is converted into OH, but in the presence of *t*-BuOH all OH radicals are scavenged (Eq. (4)). However, since the reactivity of H atoms with *t*-BuOH is very low (see Eq. (6)) all H atoms ($G_H = 0.6$) are involved exclusively in the reaction with the substrate in addition to the *t*-BuOH radicals ($G_H = 5.5$).

In this case only one product, 2-chlorophenol (2-ClPh) could be detected (see Fig. 2).

The reaction of H-atoms with 2-ClAn leads to the formation of H-adducts (cyclohexadienyl radicals) on the aromatic ring (see Eqs. (13a) and (13b)). Eq. (13b) seems to be favored since the resulting intermediates, $\cdot\text{C}_6\text{H}_4\text{Cl}$ and $\cdot\text{C}_6\text{H}_4\text{OCH}_3$ (Eqs. (13a) and (13b)) may further react with *t*-BuOH forming 2-ClPh (Eq. (14)) and 2-MePh as final products.

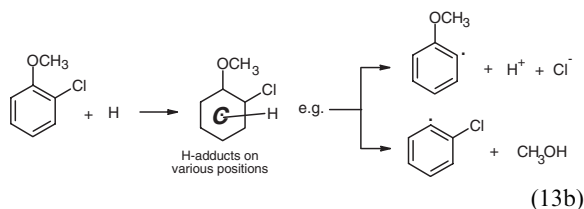


Table 1

List of compounds used as reference substances for HPLC

Retention time (min)	Name	Abbreviation	λ_{\max} (nm)	ϵ_{\max} (dm ³ mol ⁻¹ cm ⁻¹)
1.25	Muconic acid	Mac		
1.33	Hydroquinone	HQ	289	2740
1.44	Resorcinol			
1.61	Pyrocatechol	PyC	275	2390
1.75	Benzoquinone		244	
1.94	4-Methoxyphenol	4-MePh	287	2590
2.17	3-Methoxyphenol	3-MePh		
2.28	2-Methoxyphenol	2-MePh		
2.45	4,4'-Dihydroxybiphenyl			
2.73	2-Chloro-5-methoxyphenole	2-Cl-5-MePh	283 (230)	1570
3.18	2-Chlorophenol	2-ClPh		
3.87	4-Chlorophenol	4-ClPh	279	
4.31	5-Chloro-2-methoxyphenol	5-Cl-2-MePh	282 (228)	630 (1700)
4.80	3-Chloro-5-methoxyphenol	3-Cl-5-MePh		
5.37	Anisole	An		
7.51	4,4'-Dimethoxyphenyl			
8.01	2-Chloroanisole (substrate)	2-ClAn		
10.01	Chlorobenzene			
11.84	4-Chloroanisole	4-ClAn		
13.06	3-Chloroanisole	3-ClAn		

Table 2

Initial G_{r} -substrate degradation and product formation under various conditions

Substrate	Ar	Ar <i>t</i> -BuOH	N ₂ O	N ₂ O <i>t</i> -BuOH	Air
2-Chloroanisole (2-ClAn)	2.12	2.12	2.36	1.93	2.41
2-Chlorophenol (2-ClPh)	0.41	0.21	0.60	0.45	0.37
2-Methoxyphenol (2-MePh)	0.16	0.16	0.14	—	0.21
Anisole (An)	0.66	0.22	—	—	—
4-Chlorophenol (4-ClPh)??	—	—	0.18	—	—
Pyrocatechol (PyC)	—	—	—	—	0.23
Muconic acid (MAc)	—	—	—	—	0.31
Chloride (Cl ⁻)	1.16	1.1	1.81	0.57	1.44

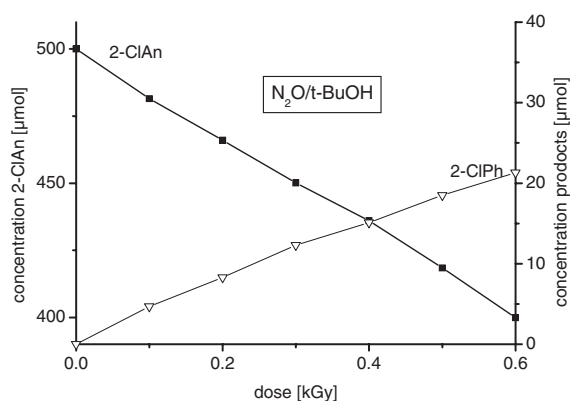
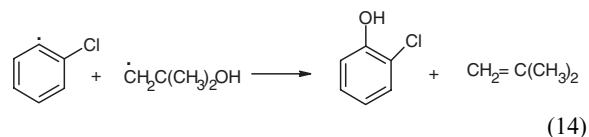


Fig. 2. Final products (right scale) and consumption of 2-ClAn (left scale) in dependence of absorbed dose observed by irradiation of aqueous 5×10^{-4} mol dm⁻³ 2-ClAn (pH 6.8) containing 5×10^{-2} mol dm⁻³ *t*-BuOH saturated with N₂O.



The reactivity of *t*-BuOH radicals is very low, however, under steady-state irradiation conditions it can play a significant role.

3.3. Reactions with H and e_{aq}^- (airfree solutions)

To study the degradation of 2-ClAn just by H and e_{aq}^- attack, the experiments were carried out in argon saturated solutions (5×10^{-4} mol dm⁻³ 2-ClAn, pH 8.6) containing *t*-BuOH (5×10^{-2} mol dm⁻³) as OH-scavenger. The degradation of 2-ClAn and the product formation as a function of dose is shown in Fig. 3.

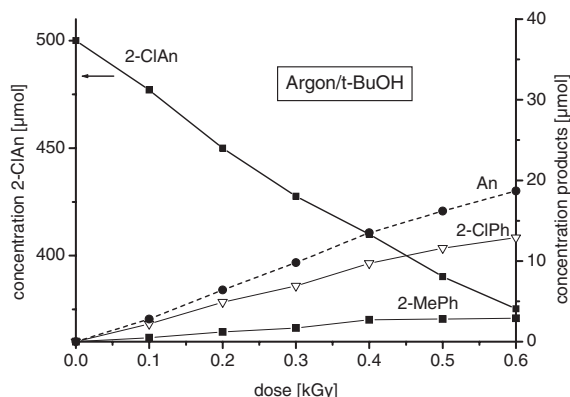
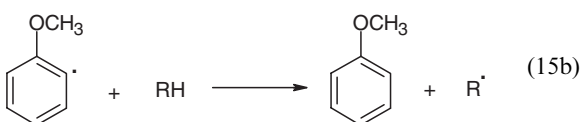
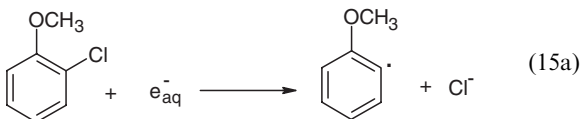


Fig. 3. Final products (right scale) and consumption of 2-ClAn (left scale) in dependence of absorbed dose observed by irradiation of aqueous airfree $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-ClAn (pH 6.8) containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ *t*-BuOH.

Under these conditions only e_{aq}^- ($G = 2.7$) and H atoms ($G = 0.6$) are involved in the degradation process, yielding $G(-2\text{-ClAn}) = 2.2$. The main product in this case was anisole (An) followed by 2-chlorophenol (2-ClPh) and small amounts of 2-methoxyphenol (2-MePh). The amount of 2-ClPh was half of that obtained in the case of H-attack only. Anisole is assumed to be formed due to Eqs. (15a) and (15b).



In airfree solutions without *t*-BuOH nearly equal amounts of e_{aq}^- ($G = 2.7$) and OH ($G = 2.8$) are formed in addition to H ($G = 0.6$) as a consequence of water radiolysis (Eq. (1)). The detectable final products obtained after reaction of these transients with 2-ClAn as well as the consumption of the substrate in dependence of dose is shown in Fig. 4.

In comparison to Fig. 3, the amount of 2-MePh remains nearly equal, the 2-ClPh production exceeds the formation of An. The build up of An is nearly the same as that under Ar/*t*-BuOH conditions. The product distribution corresponds to the radicals involved in the reaction and the reaction mechanisms suggested before (see Eqs. (7)–(13) and (15)).

3.4. Reactions with OH and $\text{O}_2^{\cdot-}$ (airated solutions)

Solutions of $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-ClAn solutions were irradiated in the presence of air, ($\text{O}_2 = 1.25 \times$

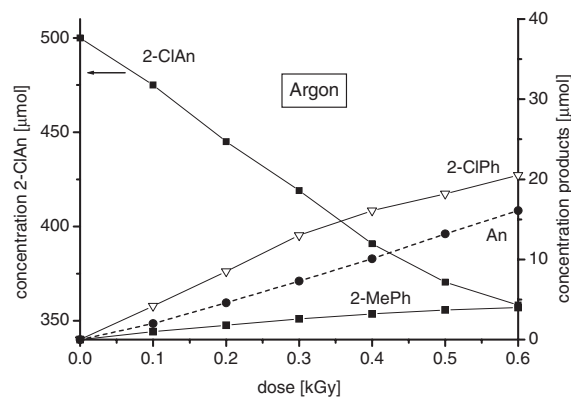


Fig. 4. Final products (right scale) and consumption of 2-ClAn (left scale) in dependence of absorbed dose observed by irradiation of aqueous airfree $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-ClAn (pH 6.8).

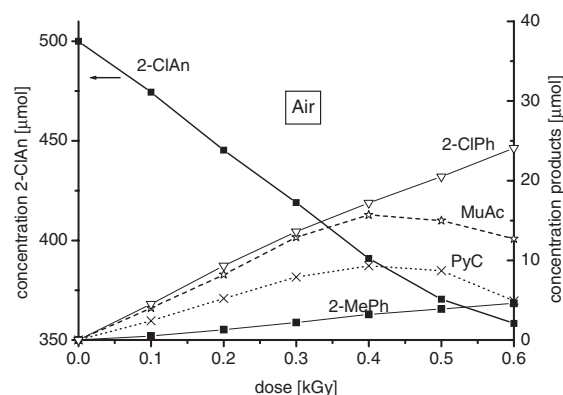
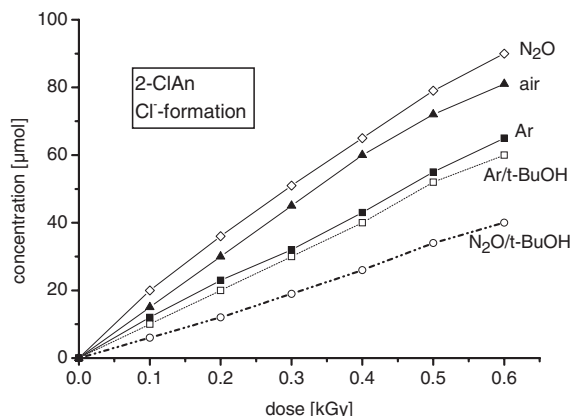


Fig. 5. Final products (right scale) and consumption of 2-ClAn (left scale) in dependence of absorbed dose observed by irradiation of aqueous $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-ClAn (pH 6.8) saturated with air ($\text{O}_2 = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$).

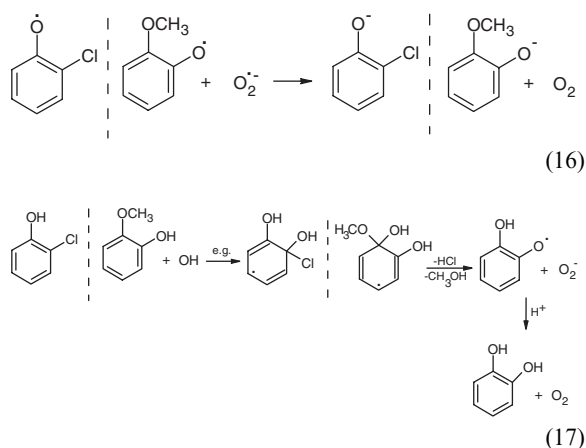
$10^{-3} \text{ mol dm}^{-3}$) with doses up to 0.6 kGy (dose rate of 266 Gy min^{-1}) and analyzed by HPLC immediately after irradiation. The products, which could be detected as well as the consumption of 2-ClAn are presented in Fig. 5.

The number of products obtained under these experimental conditions is higher. Besides 2-ClPh, 4-ClPh and 2-MePh also muconic acid (MuAc) and pyrocatechol (PyC) are formed (see also Table 2). In addition a rather high $G(\text{Cl}^-) = 1.54$ was detected (see Fig. 6 and Table 2).

Under airated conditions e_{aq}^- and H atoms are converted into peroxy radicals ($G = 3.3$), see reactions (3a) and (3b). At the applied pH (6.8) only $\text{O}_2^{\cdot-}$ are existing (see Eq. (4)). Therefore, in neutral aerated media 46% OH and 54% $\text{O}_2^{\cdot-}$ species are operative. It has been shown (Cudina and Josimovic, 1987) that $\text{O}_2^{\cdot-}$

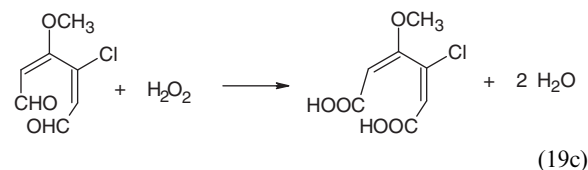
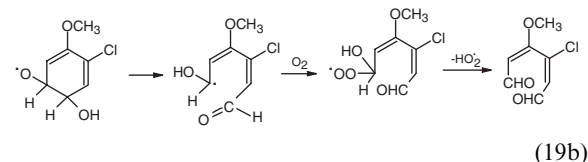
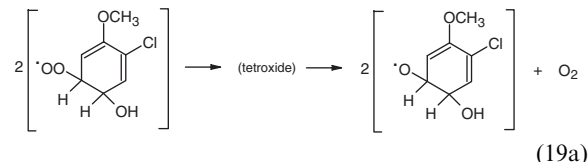
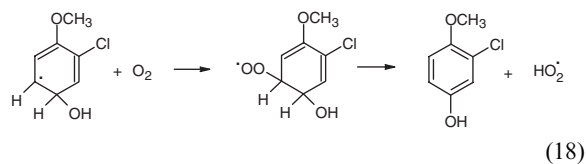
Fig. 6. Formation of Cl^- under different conditions.

reduce phenoxyl radicals efficiently to the hydroxyl compounds ($2k = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). 2-ClPh and 2-MePh are formed under these conditions (Eq. (16)), which in turn are radiolyzed and give rise to hydroquinone as final product of Eq. (17).



Similar reaction mechanisms concerning the decomposition of phenol (Getoff, 1986, 1993), chlorophenols (Getoff and Solar, 1986, 1988), chlorobenzenes (Getoff, 1990) and 4-chloroanisole (Quint et al., 1996) were previously discussed.

The chloromethoxyhydroxycyclohexadienyl radicals (see Eqs. (7)–(12)) can also react with oxygen either by HO_2^\bullet -elimination from the formed peroxy radicals or by ring fragmentation leading to muconic acids (Eqs. (18) and (19a)–(19c)).



At higher doses in air saturated solution the formation of PyC and MuAc shows deviation from linearity (see Fig. 5) due to oxygen consumption during radiation.

3.5. Dechlorination process

Like in the case of 4-ClAn (Quint et al., 1996) the Cl^- -yield exhibit a linear dependence on dose up to 0.6 kGy for all applied reaction conditions which is shown in Fig. 6. The corresponding initial G -values (G_i) are compiled in Table 2, together with those of formation of identified product and substrate degradation.

In contrast to the results obtained for 4-ClAn (Quint et al., 1996) the highest $G_i(\text{Cl}^-)$ value ($= 1.8$) was obtained for N_2O saturated solutions. It matches approximately the $G_i(2\text{-ClAn})$ diminished by $G_i(2\text{-ClPh})$. In the presence of $t\text{-BuOH}$ the $G_i(\text{Cl}^-)$ is drastically reduced to nearly a third of the value obtained without $t\text{-BuOH}$ ($= 0.57$). On the other hand, there is no difference between the $G_i(\text{Cl}^-)$ values obtained in Ar saturated solutions with and without $t\text{-BuOH}$ added ($= 1.1$).

In airated solutions the Cl^- yield is lower than that for the 4-ClAn isomer (Quint et al., 1996), $G_i(\text{Cl}^-) = 1.44$ and 1.9, respectively.

4. Conclusion

The radiolysis of 2-chloroanisole (2-ClAn) is studied as a function of the absorbed dose under various experimental conditions in neutral aqueous solutions. The formation of final products is followed by HPLC-analysis up to a dose of 0.6 kGy. The results obtained

are compared with those observed at the radiolysis of the 4-Cl isomer (Quint et al., 1996).

The highest degradation yield as well as the highest product yield are observed in solutions saturated with N₂O and/or air, followed by those ones obtained in airfree media and N₂O saturated solutions in the presence of t-BuOH. The formation of Cl[−] ions is observed under all implemented conditions. This indicates that not only e_{aq}[−] can split off a Cl-atom, but also in the frame of all other reaction steps Cl[−] ions can be liberated, e.g. as a consequence when H- or OH-radicals are forming adducts on adjacent position. For illustration of the possible degradation mechanisms some more basic reaction steps are suggested.

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