

## Anthracene Oxidation in an Aqueous Sodium Hypochlorite Solution

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### Abstract

Anthracene was used as a model compound for condensed aromatics in coals and liquid fuels. Its oxidation in aqueous sodium hypochlorite solution at 30°C, 40°C and 50°C was investigated, respectively. The results from gas chromatography/mass spectrometry analysis show that anthracene can be converted to 22 products completely within 48 h. Non-chloro-substituted compounds are the main products and their total yield is much higher than that of chloro-substituted compounds, especially in the reaction for 96 h. Anthraquinone is the most abundant product and its yield reached maximum in the oxidation for 96 h at 40°C. The mechanisms for anthracene oxidation and chlorination are discussed.

**Keywords:** Anthracene; Aqueous sodium hypochlorite solution; Superoxide anion radical; Oxidation; chlorination

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### Introduction

Coals are much richer in condensed aromatic rings (CARs) than other fossil resources [1]. Many processes for converting coals to energy, such as gasification and combustion, involve oxidation. In addition, coal oxidation under mild conditions is considered to be a promising process to obtain valuable chemicals [2,3]. Therefore, understanding the mechanisms for the oxidation of CARs in coals is of great importance. On the other hand, condensed aromatics in liquid fuels are considered to be one of the major sources producing undesired exhaust emissions and causing hazardous and carcinogenic effects [4]. Converting the condensed aromatics to saturated components usually needs high hydrogen pressure and expensive catalysts. Alternative technology for removing condensed aromatics from liquid fuels should be taken into account. Sodium hypochlorite (NaOCl) is an effective oxidant for converting CARs in coals to benzenepolyoxylic acids along with small amounts of their chloro-substituted analogs and other species [5]. However, it is not clear how the CARs are oxidized in aqueous sodium hypochlorite solution. In this study, we used anthracene as a model compound for condensed aromatics in coals and liquid fuels and investigated its oxidation in aqueous sodium hypochlorite solution under mild conditions to understand how the condensed aromatics are oxidized and how to control the oxidation.

### Experimental

Anthracene, CH<sub>3</sub>CN, 37% hydrochloric acid, diazomethane, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O, aqueous sodium hypochlorite solution (6% available

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chlorine), and anhydrous Na<sub>2</sub>SO<sub>3</sub> are commercially purchased analytical reagents. Anthracene was purified by recrystallization in methanol followed by vacuum desiccation at 50°C for 2 h. Other organic reagents were distilled before use. Anthracene (0.5 mmol), aqueous sodium hypochlorite solution (20 mL), CH<sub>3</sub>CN (5 mL), and a magnetic stirrer were added into a glass tube reactor (inner volume 50 mL) in a J-KEM Synthesizer. The reactor was heated to a described temperature (30°C, 40°C or 50°C) and the mixture in the reactor was stirred at the temperature for a described period of time. After separating the unreacted anthracene from the reaction mixture, 1 g anhydrous Na<sub>2</sub>SO<sub>3</sub> was added into the reaction mixture to destroy excess NaOCl followed by acidification with a proper amount of 37% hydrochloric acid to pH 2-3. Then the treated reaction mixture was repeatedly extracted with (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O to afford extract solution. Concentrated extract solution was obtained by removing most of (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O from the above extract solution with a Büchi R-210 rotary evaporator, esterified with diazomethane in (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O and

analyzed with a Hewlett-Packard 6890/5973 gas chromatograph/mass spectrometer (GC/MS). The GC is equipped with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 30 m length, 0.25 mm inner diameter, 0.25  $\mu\text{m}$  film thickness). The MS is operated in electron impact (70 eV) mode and a quadrupole analyzer is used as a mass analyzer.

## Results and Discussion

Anthracene were completely converted within 72 h, 48 h and 48 h when the reaction temperature was set to 30°C, 40°C and 50°C respectively. As **Figures 1-3** exhibit, 22 compounds were identified with GC/MS. The compounds can be classified into non-chloro-substituted compounds (NCSCs, i.e., peaks 4-6, 10-12, and 15) and chloro-substituted compounds (CSCs, i.e., peaks 1-3, 7-9, 13, 14, and 16-22), as shown in **Table 1** and **Figure 4**. The total yield of NCSCs is much higher than that of CSCs, especially in the reaction for 96 h. Anthraquinone is the most abundant product and its yield increased first and then decreased with prolonging the reaction time. In addition, the yield of anthraquinone from anthracene oxidation at 40°C is much higher than these at 30°C and 50°C, and reached the maximum (74.8%) in the oxidation for 96 h at 40°C. These facts indicate that selective formation of NCSCs (especially anthraquinone) can be achieved by controlling the reaction time and temperature. Interestingly, chlorine-substituted acetic acids only appear in the products from anthracene oxidation at 30°C and 50°C and chloroanthracenes were only detected in the products from anthracene oxidation at 40°C, although the reason needs investigating. The oxidation of coals [6-10] and their related model compounds [11-13] in aqueous sodium hypochlorite solution were extensively investigated. The oxidation of wheat straw [14] and rice husk [15] in aqueous sodium hypochlorite solution was also examined. Superoxide anion radical  $\text{O}_2^-$  is generally considered to be an active intermediate [16-19] for oxidizing unsaturated moieties, especially for CARs. However, to our knowledge, no reports clarified the mechanisms for the formation of  $\text{O}_2^-$  in aqueous sodium hypochlorite solution and the reaction of  $\text{O}_2^-$  with CARs. Ref. [20] proposed that  $\text{O}_2^-$  can directly abstract hydrogen on CARs to induce the oxidation of CARs. Such abstraction is extremely difficult, because the resulting aryl radicals are quite labile. Similarly, hydrogen abstraction from CARs by  $\text{O}_2^-$  is also impossible. As **Scheme 1** illustrates, there are ionization equilibria between  $\text{NaOCl}$  and its resulting  $\text{Na}^+$  and  $^-\text{OCl}$  and between  $^-\text{OCl}$  and its resulting  $\text{O}_2^-$  and  $\text{Cl}_2^-$ . Due to much larger superdelocalizability (1.314) at 9-position than that at other positions in anthracene [21],  $\text{O}_2^-$  tends to attack 9-position in anthracene. Thereby, the addition of  $\text{O}_2^-$  to 9-position in anthracene should be the initial and crucial step for anthracene oxidation. The subsequent step could be the elimination of  $-\text{OH}$  to get 9-oxy-10-anthryl radical (OAR) followed by  $\text{O}_2^-$  addition to

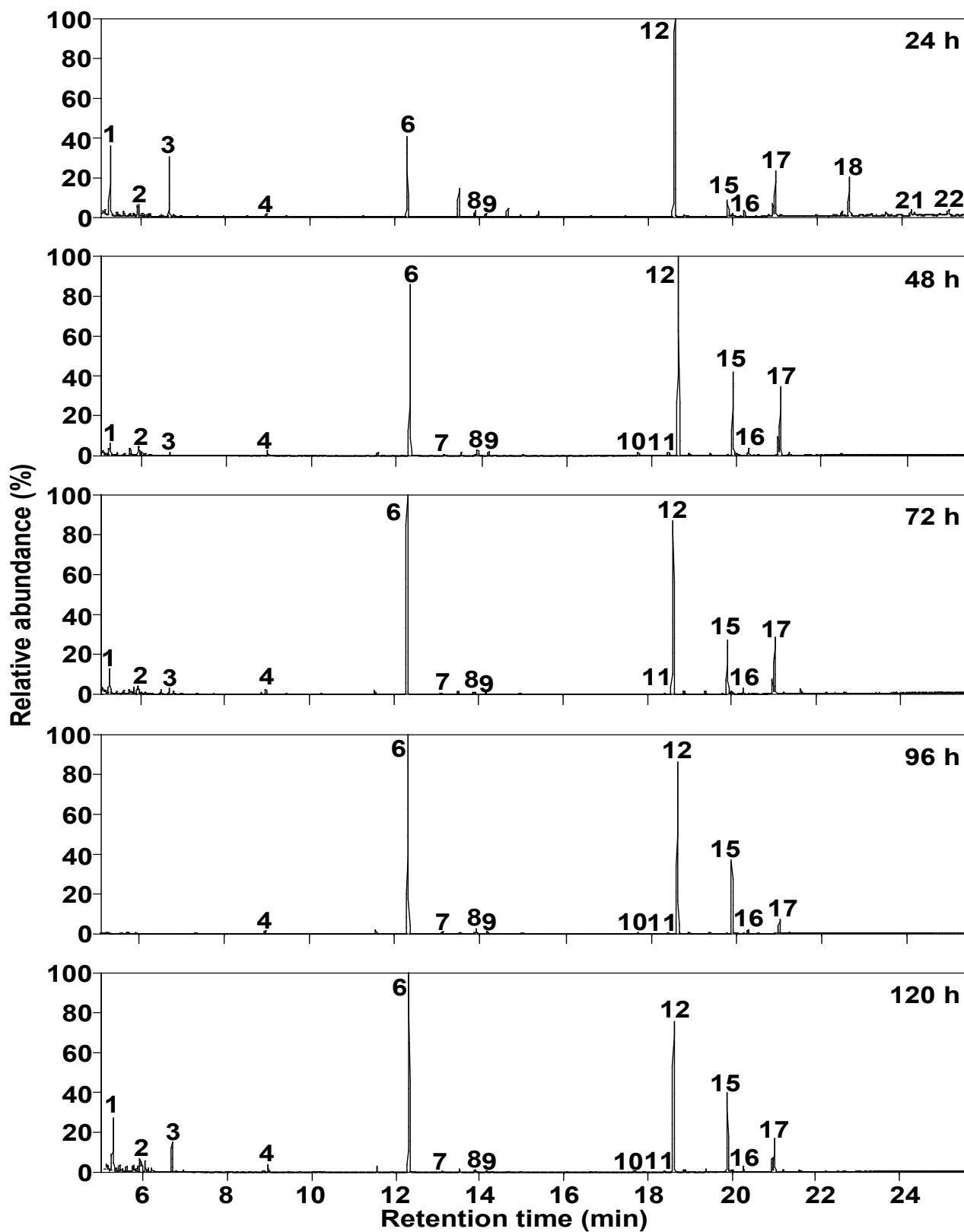
the 10-position in OAR and subsequent elimination of  $-\text{OH}$  to produce anthraquinone. The addition of  $\text{Cl}_2^-$  to the 9-position in anthracene can also be considered, but subsequent elimination of  $\text{HCl}$  is impossible. Instead,  $\text{Cl}_2^-$  tends to react with  $\text{Na}^+$  to get  $\text{NaCl}$  and  $\text{Cl}^-$ . The resulting  $\text{Cl}^-$  can attack the 9-position in anthracene, but the well known coupling reaction from 2  $\text{Cl}^-$  to produce stable  $\text{Cl}_2$  is much more competitive. Since the distance between 2 chlorine atoms in  $\text{Cl}_2$  is substantially smaller than that between 2 carbon atoms in the 9- and 10-positions in anthracene, the addition of  $\text{Cl}_2$  to the 9- and 10-positions seems to be difficult. As a result,  $\text{Cl}_2$  prefers to add to the 1- and 2-positions to induce anthracene chlorination (**Scheme 1**). The superdelocalizability of either the 1-position (1.073) or 2-position (0.922) is much smaller than that of the 9-position in anthracene, leading to much lower reactivity of anthracene toward chlorination than toward oxidation in aqueous sodium hypochlorite solution. Phthalic acid (PA) is the most abundant byproduct and its yield steadily increased by prolonging the reaction time. Detection of isobenzofuran-1,3-dione, 3- and 4- chlorophthalic acids (CPAs) indicates that both dehydration and chlorination of PA proceeded, as displayed in **Scheme 2**. The CPAs were not detected until the reaction for 120 h, suggesting that PA chlorination is difficult.

## Conclusions

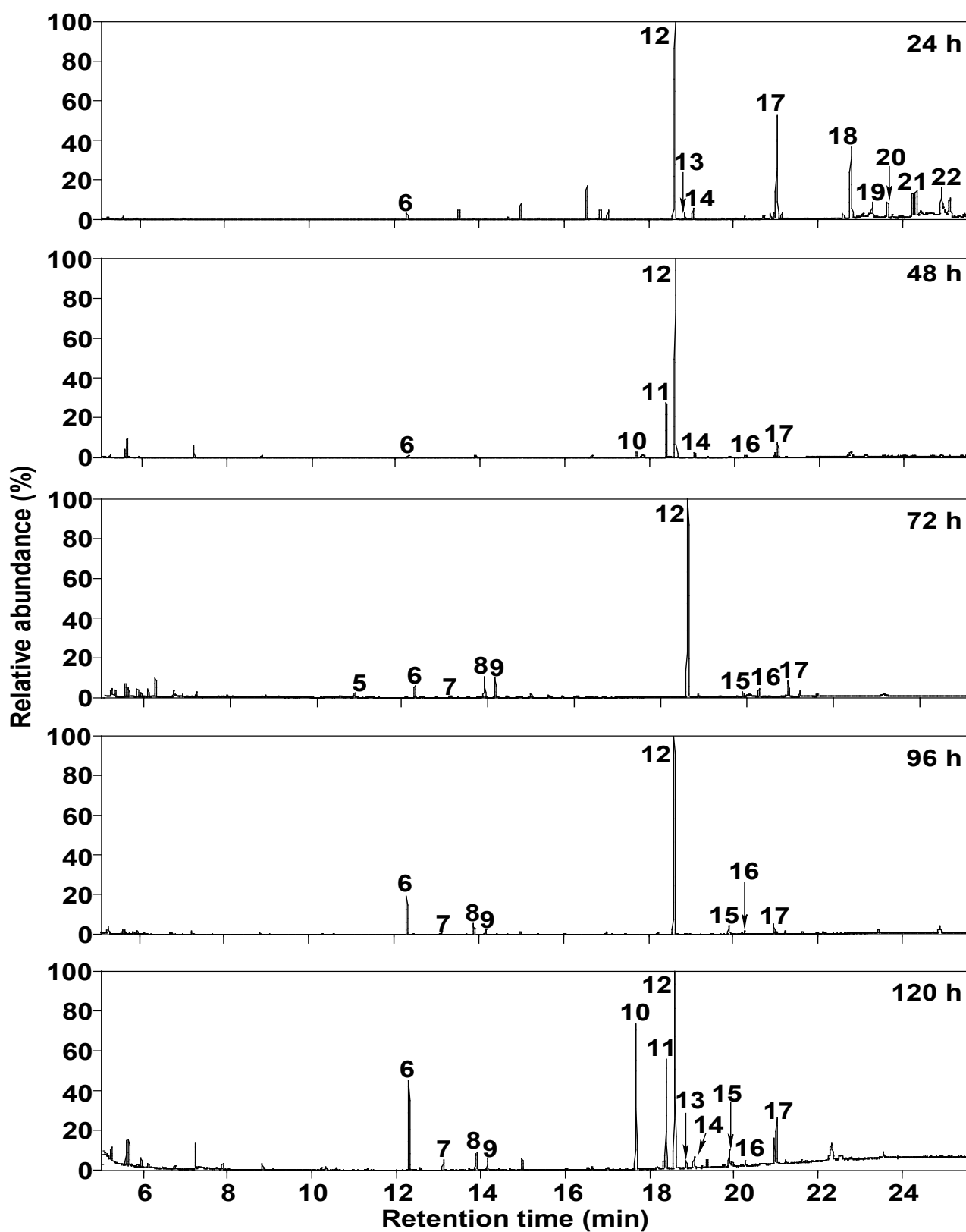
The mechanisms for anthracene oxidation and chlorination were reasonably proposed by this investigation. The addition of  $\text{O}_2^-$  to the 9-position in anthracene plays a crucial role in the formation of anthraquinone. According to the result, some coal conversion processes, especially mild coal oxidation, may involve in  $\text{O}_2^-$  addition to active sites of CARs in coals. Selective coal oxidation to afford specific oxygen-containing aromatics, like anthraquinone, could be achieved by controlling the reaction conditions. Such a process not only provides a probe for understanding the structures of CARs in coals, but also facilitates obtaining valuable chemicals, especially oxygen-containing aromatics, from coals. In addition, converting CARs in liquid fuels to water-soluble oxygen-containing aromatics could be a promising approach for effectively removing CARs from liquid fuels.

## Acknowledgements

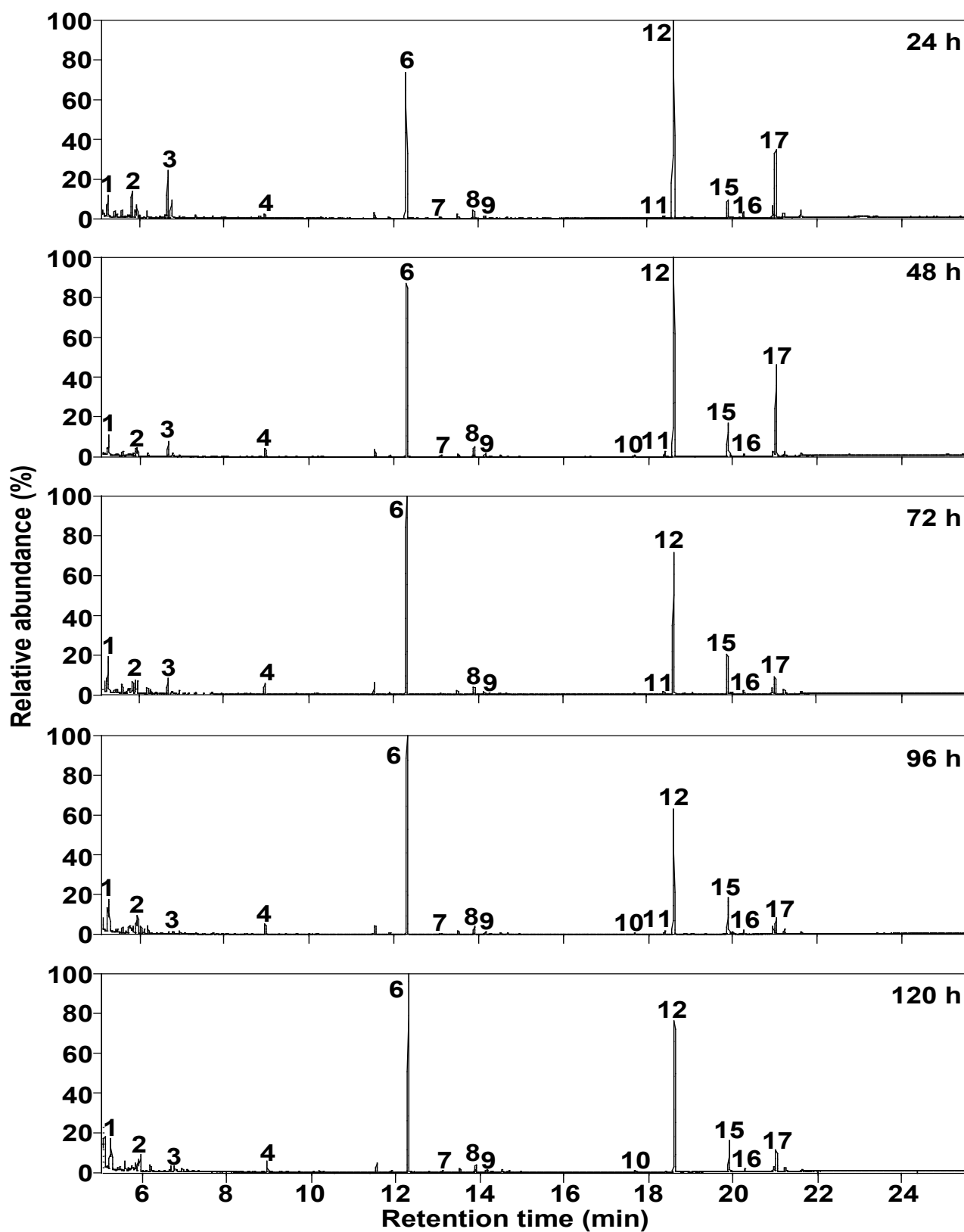
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**Figure 1** Total ion chromatograms of the methyl esterified products from anthracene oxidation in ASHCS at 30°C.



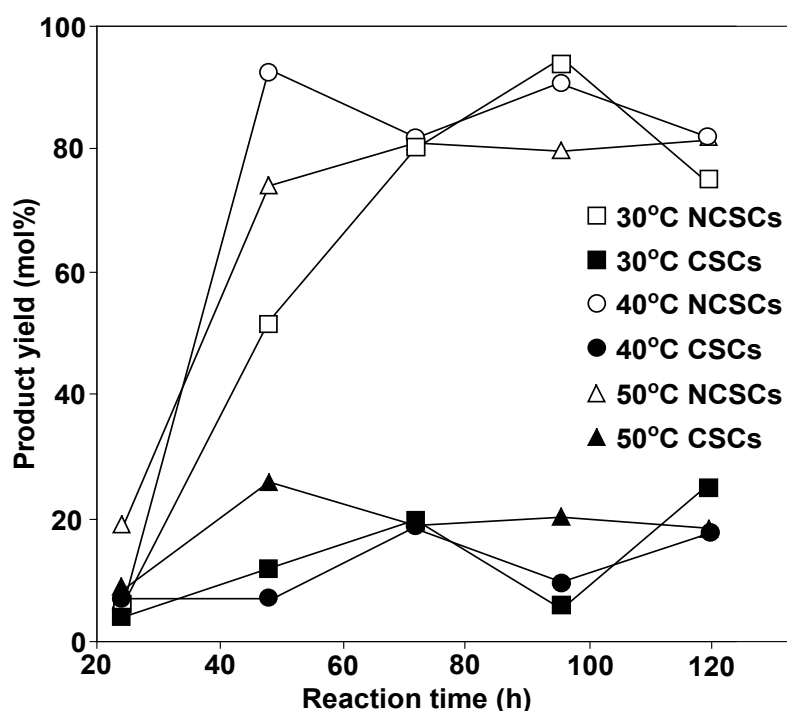
**Figure 2** Total ion chromatograms of the methyl esterified products from anthracene oxidation in ASHCS at 40°C.

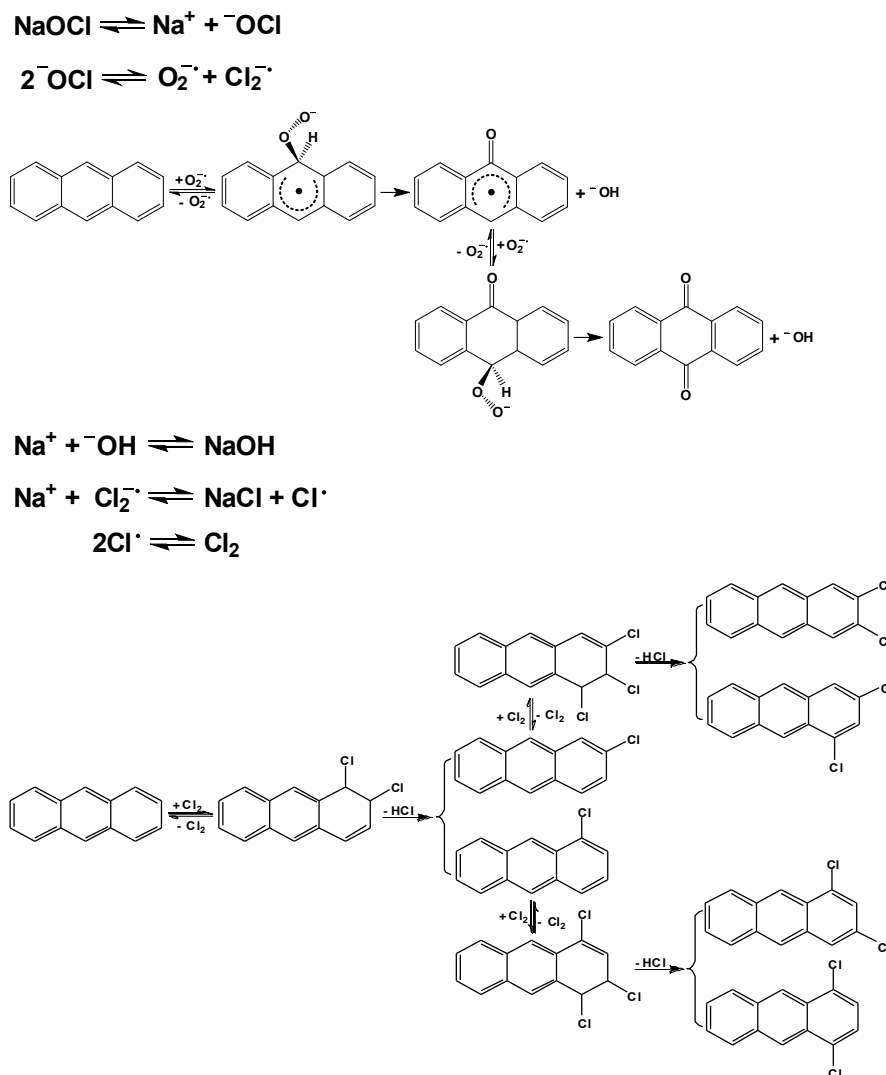


**Figure 3** Total ion chromatograms of the methyl esterified products from anthracene oxidation in ASHCS at 50°C.

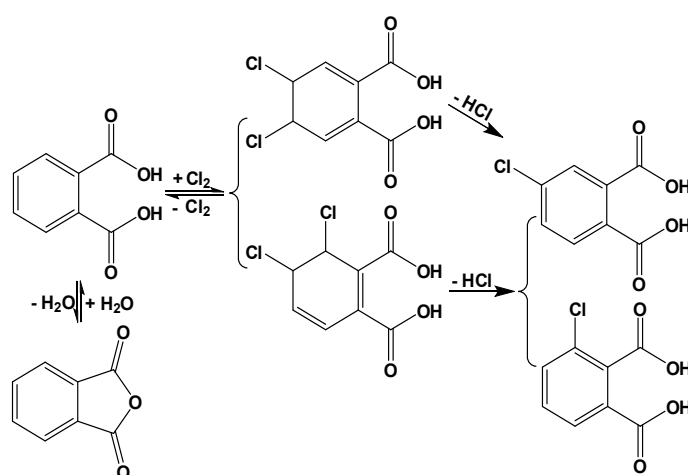
**Table 1** Yields (mol %) of the products from anthracene oxidation in ASHCS at different temperatures.

Peak	Parent product	30°C					40°C					50°C				
		24 h	48 h	72 h	96 h	120 h	24 h	48 h	72 h	96 h	120 h	24 h	48 h	72 h	96 h	120 h
1	2-Chloroacetic acid	1.2	1.5	4.8		9.5						1.3	4.0	8.3	10.8	8.2
2	2,2-Dichloroacetic acid	0.4	1.4	2.2		3.4						1.2	1.1	2.1	2.9	2.1
3	2,2,2-Trichloroacetic acid	0.9	0.3	0.9		3.8						1.9	1.9	2.5	0.3	0.8
4	Malonic acid	Trace	0.4	0.7		1.0						0.2	1.3	2.0	1.9	2.0
5	Isobenzofuran-1,3-dione								1.7							
6	Phthalic acid	1.3	17.9	34.9	39.7	33.5	0.1	0.8	3.6	12.1	12.1	6.1	29	40.1	41.6	39.0
7	2-(Ethoxycarbonyl) benzoic acid		0.1	0.3	0.5	0.2			0.4	0.9	1.4	0.1	0.3		0.2	0.3
8	3-Chlorophthalic acid	0.1	0.7	0.3	1.3	0.5			6.3	5.6	5.0	0.4	1.8	1.6	1.8	1.8
9	4-Chlorophthalic acid	Trace	0.3	0.3	0.6	0.3			5.6	1.9	1.6	0.1	0.5	0.5	0.5	0.5
10	Biphenyl-2,2'-dicarboxylic acid		0.3		0.3	0.3		1.8			19.7		0.2		0.3	0.3
11	Anthrone		0.3	0.2	0.2	0.2		20.6			17.1	0.1	0.9	0.5	0.7	
12	Anthraquinone	4.1	24.9	34.8	40.7	28.5	5.2	69.7	74.0	74.8	29.1	11.2	37.0	31.1	28.5	34.0
13	Chloroanthracene						0.1				1.3					
14	Chloroanthracene						0.3	1.7			1.9					
15	Pyromellitic acid	0.3	8.2	9.3	13.1	12.3			1.3	3.1	2.7	0.8	5.5	7.3	6.7	6.1
16	Chloroanthraquinone	0.1	0.7	1.1	0.8	1.0		0.7	2.4	1.2	0.9	0.3	0.4	0.7	0.6	0.6
17	Dichloroanthracene	0.8	6.8	10.2	2.8	5.5	2.3	4.7	4.7	0.4	7.2	3.1	16.1	3.3	3.2	4.3
18	Trichloroanthracene	0.1					1.9									
19	Trichloroanthracene						0.5									
20	Trichloroanthracene						0.4									
21	Trichloroanthracene	0.1					0.6									
22	Tetrachloroanthracene	0.2					0.8									

**Figure 4** Time profiles of the yields of NCSCs and CSCs from anthracene oxidation in ASHCS at different temperatures.



**Scheme 1** Possible mechanisms for anthracene oxidation and chlorination in ASHCS.



**Scheme 2** Possible mechanisms for PA dehydration and chlorination in ASHCS.

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