# Photochemistry of chrysene adsorbed
# on several types of particle

Zhong Jinxian, *    Mauldin R. F. ,    Dunstan, T. D. T,

Sanders, J. K. ,    Hipps, A. D. ,    Wehry, E. L. , Mamantov, G

Department of Chemistry, University of Tennessee, Knoxville, TN37996, USA

**Abstract**—The photochemistry of chrysene adsorbed on 6 types of particles was studied. Their half-lives determined on the different kinds of particles are different. The half-lives of chrysene adsorbed on fly ash are longer than on alumina or glass particles. This shows that fly ash can inhibit photodegradation of chrysene. The half-lives of chrysene adsorbed on ET and KA fly ash in which the Fe or C content is high are long. The photochemical products of chrysene adsorbed on glass particles were identified. These products are phenanthrenquinone, benzanthrone and dihydrobenz(a)anthracen -1(2H)- one. This is a reaction of photoxidation for chrysene toward ozone under conditions of this study.

Keywords: photochemistry; chrysene; half-lives; particles.

## 1   Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during the incomplete combustion of fuels or other organic matter. They are adsorbed on particulate matter and are subsequently dispersed into the atmosphere. The mutagenicity of PAHs brings to people's attention. However, it is note worthy that the observed carcinogenicity in animals or transformation in cell cultures is significantly greater than what can be accounted for by the concentrations of carcinogenic PAH determined in those samples (Kotin, 1954; Haeper, 1962; Epstein, 1966; Kigdon, 1971; Freeman, 1971; Mohr, 1976); both for ambient particulates and for automobile exhaust. Thus Gordon *et al.* (Gordon, 1973) reported that benzene extract of airborne particles collected in the Los Angeles area exhibited a cell transformation activity $10^2 - 10^3$ times stronger than attributable to its BaP content. This problem is often referred to as the "excess" carcinogenicity of particulate organic matter extracts.

These results support that those PAHs adsorbed on particulate matter undergo various changes in a complex atmospheric environment. Their photochemical reactions are important. Several reaction pathways are possible when PAHs are irradiated with ultraviolet light. These depend, of course, upon the size and structure of the PAH, and whether or not oxygen is present.

Daisey *et al.* (Daisey, 1983) investigated the rates and products of degradation of pyrene ad-

---

sorbed on well characterized particles in a modelsystem. Their results showed that even when the rates of degradation of pyrene adsorbed on different types of particles are similar, the relative proportions of products and the rates of products formation and degradation can be different. They found that the pyrenediols, pyrenediones and bipyrene were formed.

Scientists have detected Nitro - PAH, quinones, aldehyde and carboxylic acid as their reaction products in the atmosphere of PAHs (Siak, 1985; Hirayma, 1983; Talcoft, 1977; Pitts, 1977; Schuetzle, 1981; Xu, 1984; Sawicki, 1967; Pierce, 1976). Also, they have found many factors inhibit PAHs photochemical reactivity, such as carbon or iron content in fly ashes, particulate size and colour of coal stack ash (Robert, 1986; Korfmancher, 1980; 1981; Robert, 1985). So that PAH can exist in atmosphere for a long time.

In order to understand transformation of PAH, we have investigated the rates and products of degradation of chrysene adsorbed on fly ashes and other adsorbents. We used a vapor - deposition method for chrysene adsorption on adsorbents, and irradiated them with a ultraviolet lamp. Their products were detected by HPLC and GC /MS.

# 2   Experimental section

## 2.1   Materials

The fly ash samples used in this study were collected from the electrostatic precipitators of a steam plant burning Kaneb (KA) coal and East Tennessee Bituminous (ET) coal. Stack ash from texas (TX) lignite collected from an electrostatic precipitator of a coal - fired steam plant, was obtained from the Oak Ridge National Laboratory. UT fly ash was collected from the physical plant in the University of Tennessee burning washed Bituminous coal. Other adsorbents include alumina (neutral Brockman activity I), controlled porosity glass (100 Å average pore diameter obtained from Pierce Chemical Co. Rockford 111).

All adsorbents were sieved by USA standard sieves and the 75 — 125 μm fraction was used.

Chrysene was obtained from Aldrich Chemical Company and was purified, when necessary by vacuum sublimation.

## 2.2   Vapor deposition of chrysene

Chrysene was deposited on adsorbents from vapor phase using a diffusion cell - expanded adsorbed bed technique described previously (Miguel, 1979). Prior to deposition, each adsorbent was degassed for 24 hours by passing dry nitrogen over the adsorbent in the expanded bed at 250 ℃. The generator temperature of chrysene was kept at 210 ℃. The expanded bed was kept at 220 ℃. The nitrogen flow was 180 ml/min, and the deposition time was 24 hours.

## 2.3   Irradiation experiments

The irradiation source used in this work was an ultraviolet enhanced output lamp (cermaz Xenox illuminator, ILC Technology, Sannvale California, model lx 300UV) powered by a cermax ps 300 — 1 power supply. The output of the irradiation source was filtered by a cell (20cm path length) containing water for attenuation thermal changes. The ends of the cell were made of quartz so that the ultraviolet radiation or actinic region of the spectrum could pass. The irradiation cell used in this study was made of quartz. A solid quartz rod was connected to one side so

that the substrate was mixed during rotation of the cell. The cell was attached via a ground glass joint to the end of a rotatory evaporator motor and a slight vacuum ( via a ground water aspirator ) was applied. The cell was rotated at about 60 cycles per minute and was typically about 43 cm from the source. Chemical actinometry indicated the radiant intensity to which samples were exposed was approximately 0.7W/cm².

### 2.4  **Extraction and concentration of photochemical products**

The photochemical products were extracted by sonication using acetone for one half hour. The extracts were concentrated in a rotatory concentrator until the volume was about 1ml. The samples were kept in a refrigerator.

### 2.5  **Analytical procedures**

The photochemical products were analyzed by HPLC. The chromatography conditions are as follows:

Column adsorbosphere($C_{18}$), particulate size = 13$\mu$m, i. d. = 4. 6mm, length = 15cm; mobile phase composition methanol:water = 85:15; flow rate:1ml/min;detector:UV－254nm;

The photochemical products were identified by GC - MS. The GC - MS conditions are as follows: Column:HP -5 or Ultra 2 composition 5% diphenyl, 95% dimethyl polysiloxane, length = 25m, i. d. = 0. 33mm. Carrier gas:helium; Column flow:0. 5ml/min; Initial temperature:120℃ (6 minutes); Rate:5℃/min; Final temperature:280℃; Injection port temperature:200℃; Detector: Electron - impact ms.

## 3  **Results and discussion**

Degradation of chrysene adsorbed on six types particles under light conditions, in most of the experiment where decomposition of the PAH was observed, the decomposition rate ($-dc/dt$) showed a linear dependency on the first order of the concentration of PAH, $-dc/dt = KC$ or in other words:

$$\ln c = -Kt + \ln C_0, \tag{1}$$

where $t$ is the time, $C_0$ is initial concentration of PAH and $K$ is the decay constant. When $C = C_0/2$, $t$ is half - life, $t_{1/2}$. We obtained from Equation (1).

$$t_{1/2} = \ln 2/K. \tag{2}$$

The value of $K$ was obtained by estimating the slope by a least squares procedure.

The half - lives for the degradation of chrysene adsorbed on six types of particles under light conditions are summarized in Table 1.

Table 1  **Half - lives of chrysene adsorbed on different particles under light**

| Particle | UT | KA | ET | TX | Alumina | Glass |
|---|---|---|---|---|---|---|
| Half - Lives,hrs | 100. 9±16. 4 | 92. 06±1. 9 | 58. 38±3. 8 | 34. 49±3. 2 | 11. 38±0. 14 | 8. 256±0. 011 |

The concentrations of C, Fe and Al in particles used in this study are shown in Table 2. It is clear from Table 1 and 2 that chrysene underwent efficient photodegradation when adsorbed on TX, ET, KA, UT, $Al_2O_3$ and glass adsorbents, the half - lives for the degradation of chrysene

adsorbed on different particles are different. The half-lives on fly ashes were longer by 3. 5—12 times than that on glass, longer 3—9 times than that on $Al_2O_3$. The half-lives on UT and KA fly ashes were the longest, where as half-lives on $Al_2O_3$ and glass particles were the shortest. Obviously, the photochemical degradation of chrysene adsorbed on particles relates to the concentration of C and Fe, the highest concentration of C is UT fly ash, next is KA fly ash. The highest concentration of Fe is KA fly ash, next is KA fly ash. Their half-lives are the longest. On $Al_2O_3$ and glass particles without C and Fe. The photochemical degradation of chrysene adsorbed on these particles is the fastest. The photosensitivity of adsorbed PAH is strongly dependent on the nature of the surface on which the compound is adsorbed. This suppression of the photochemistry of PAH adsorbed onto coal fly ash may be related to a stabilization of their ground electronic states.

Table 2　Elemental composition of fly ashes　　　　　(Unit: %)

| Element | UT | KA | ET | TX |
|---|---|---|---|---|
| C | 13. 8[c] | 5. 5[c] | 0. 5[b] | 0. 5[b] |
| Fe | 5. 46[a] | 5. 945[a] | 1. 7[b] | 3. 4[b] |
| Al | 4. 1[a] | 14. 29[a] | 15. 5[b] | 7. 5[b] |

Note: a: by atomic adsorption spectrometry; b: from reference 25;

c: by Galbraith Laborotories Inc, Knoxville, TN, USA

C and Fe in fly ashes can be resistant to photodegradation of chrysene adsorbed on them. The surface of carbon particles is more active for adsorption of PAH than the surface of other elements. In addition, carbon particles have higher specific surface areas. It can appear that specific chemical interactions occur between carbon particle surface and adsorbed PAH. Griest *et al.* (Griest, 1981; 1984) have noted that the sorptivity of ash particles size fractions and subfractions increases with increasing carbon content, in part because the carbonaceous ash particles tend to exhibit larger specific surface areas than $Al_2O_3$, glass or other particle of low carbon content.

Dunstan (Dunstan, 1989) determined the adsorption isotherms and heats of adsorption of pyrene on three principal subfraction of KA carbonaceous, mineral and magnetic. The results showed that the carbonaceous subfraction is the strongest adsorbent and has the greatest ability to stabilize adsorbed pyrene towards photodegradation. Yokeley *et al.* (Yokeley, 1985) discussed a relationship between the color of the adsorbent and the photodegradation of adsorbed pyrene, due to the high C and/or Fe and the dark colour ash there are high ability to suppress photolysis of adsorbed pyrene.

Fig. 1 is the liquid chromatogram of photochemical products of chrysene adsorbed on glass particles after irradiation for 0, 4 and 48 hours respectively. The chrysene eluted with a retention time of 14 minutes. The peak with retention 3 minutes is solvent. Other peaks are products. From comparison of the chromatogram in Fig. 1, it can be seen that the photochemical products were present under irradiation for 0 hour. But with time of irradiation increasing, the content of the chrysene was decreasing and the content of photochemical products was increasing. Fig. 2 shows a typical chromatogram of the products of chrysene adsorbed TX after irradiation for 24

hours. From Fig. 2, it can be seen that products with a retention time of 6 minutes and 21 minutes were not present, but a product with retention time of 37 minutes was not detected. Fig. 3 is a typical chromatogram of the products of chrysene adsorbed on the ET fly ash after irradiation for 48 hours. From Fig. 3, however, degradation of chrysene is slower, there were four photochemical products presented.
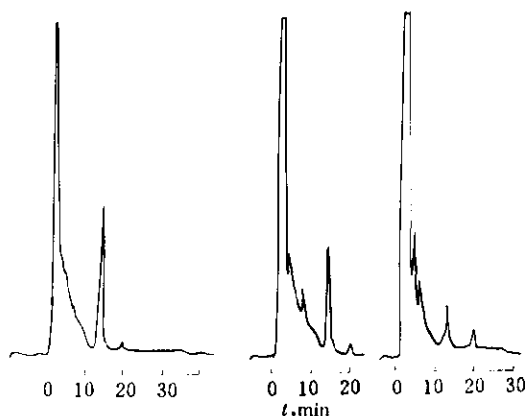


Fig. 1    Liquid chromatogram of chrysene adsorbed on glass particle
after irradation for 0, 4 and 48 hours



Fig. 2    Liquid chromatogram of chrysene adsorbed on
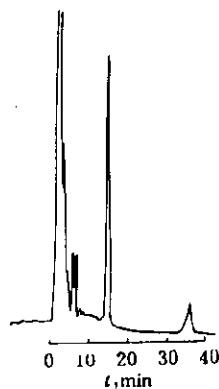TX under irradiation 24 hours

Fig. 3    Liquid chromatogram of chrysene adsorbed on
ET under irradiation 48 hours

Photochemistry of chrysene adsorbed on glass particles. Fig. 4 is total ion chromatogram of photochemical products of chrysene adsorbed on glass particles after irradiation for 48 hours. The peaks of interest have the mass spectra, these peaks correspond to phenathrequinone, benzanthrone and dihydrobenz(a)anthracen -1(2H)- one with Fig. 4, respectively. Benzanthrone was

identified as two isomers. These compounds are expected photooxidation products. Other peaks were identified in Fig. 4. Such as the 4th peak is pyrene, the internal standard compound; 7th peak is chrysene; 1st and 8th peaks are phthalate; 2nd, 9th and 10th peaks are ditertamylquinone, methyl - dioctylmethacrylate and benenic acid, respectively. They may be derived from the solvent.
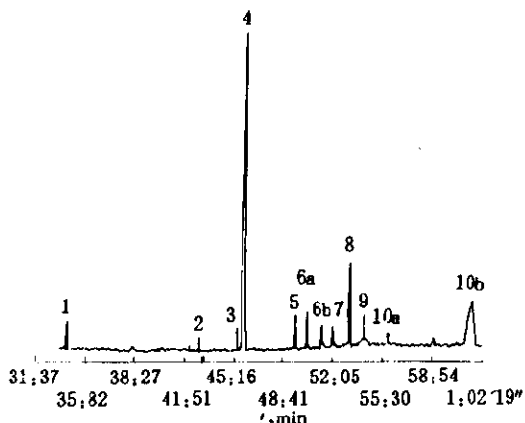


Fig. 4　Total ion chromatogram of photochemical products of chrysene
adsorbed on glass particles after irradiation 48 hours

Peaks: 1st=phthalate, 2nd=ditertamyquinone; 3rd=phenanthrenequinone; 4th=pyrene;
5th=methyl - dioctylme - thacrylate; 6th(a)=benzanthrone; 6th(b)=benzphenanthrenone;
7th=chrysene; 8th=phthalate; 9th=dihydrobenz(a)anthracen -1(2H)- one;
10tha=benenic acid; 10thb=10a isomer

From these products, it can be shown that it is reaction of photooxidation for chrysene toward ozone under our conditions. Because the ultraviolet radiation intensity is many times than that of the sun, under these conditions, the molecules of oxygen occur as follows:

$$O_2 \longrightarrow O+O, \qquad O+O_2 \longrightarrow O_3.$$

It is generally accepted that ozone can degradation unsubstituted PAH according to two different mechanisms:

(1) A one - step nearly simultaneous electrophilic - nucleophilic attack on olefinic bonds with electron density will originally yield a primary ozonide.
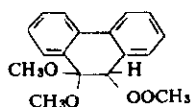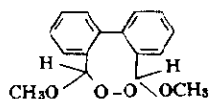


(1)

This intermediate is unstable at room temperature and will further decompose to result in ring opening with formation of aldehyde and/or carboxylic acid functional groups (Criegee, 1957).

(2) A two‑step electrophilic attack on the carbon atoms with the lowest paralocalization energy; originally, a complex is formed here and this is followed by a second nucleophilic 1, 4 addition by the same or by a second molecule of ozone to yield and finally a quinone. Other intermediates may also be involved here (e. g. epoxides phenols).
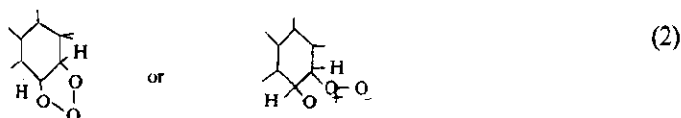


$$(2)$$

# References

Criegee R. Rec Chem Prog, 1957;18;11

Dunstan DT, Mauldin RF, Zhong JX. ES&T, 1989;23;3

Epstein SS, Joshi Aj. Nature, 1966;212;1305

Falkh L . Aromatic Hydrocarbons IV Arch Ind Health, 1956;13;13

Fox MA. Science, 1979;205;582

Freeman AE, Price PT, Bryao RT. Proc Natl Acad Sci. USA, 1971;68;445

Gordon RJ, Bryan RT, Rhim JS. Int J Cancer, 1973;12;223

Griest WH, Caton JE. Polynuclear aromatic hydrocarbons chemical analysis and biological face columbus OH, 1981;791

Griest WH, Tomking BA. Sci Total Environ, 1984; 36;209

Griest WH, Tomkin BA. Oak Ridge National Laboratory, Oak Ridge TN Personal Communication Nov. 1984

Hirayma T, Nohara MT, Ando M. Mutat Res, 1983;122;273

Hueper WC, Neal J. Arch Pathol, 1962;74;89

Kingdon RH. Tex Rep Bol Med, 1971;29;110

Korfmacher WA, Wehry EL, Mamanto G. Science; 1980; 207;763

Korfmacher WA, Webry EL, Mamanto G. ES&T, 1980;14;1094

Korfmacher WA, Mamanto G, Webry EL. ES&T, 1981;15;137

Kotin P, Falk HL, Mader P. Arch Ind Hyg, 1954;9;153

Miguel AH. ES&T, 1979;13;1229

Mohr U, Rezhik‑Schuller. Bakteriol Hyg 1, Abt Orig B, 1976;163;425

Pierce RC, Katz M. ES&T, 1976;10;45

Pitts JN. Toxical Lett, 1977;1;65

Robert A, Mamantov G, Wehry EL. ES&T, 1986; 20(1);86

Sawicki E. Environ Health, 1976;14;46

Schuetzle D. Int J Environ Analytical Chemistry, 1981;9;93

Siak J, Chan TL, Gibson TL. Atmos Environ, 1985;19;369

Talcott R, Wei ET. J Natl Cancer Inst, 1977;19;369

Taskar PK, Solomon JJ, Daisey JM. Proceedings of the 8th Inter symp on PAHs, 1983;1285

Thomas JF. ES&T, 1968;2;33

Tebbens BD. Am Ind Hyg Assoc J. 1966; 27;415

Xu XB, Zhong JX. Acta Scientiae Circumstantiae, 1984;4(3);296