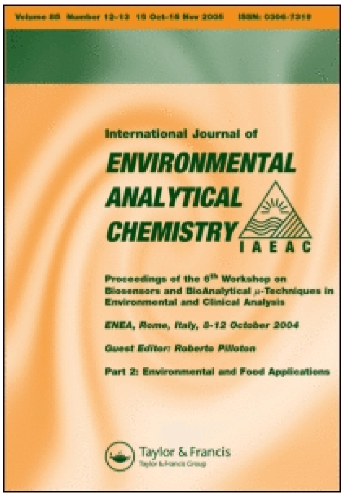

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$C_{24}H_{14}$ polycyclic aromatic hydrocarbons from the pyrolysis of catechol

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Polycyclic aromatic hydrocarbons (PAH) of the $C_{24}H_{14}$ isomer class, some of which are potent mutagens and carcinogens, are produced during the burning of solid fuels. For a clearer understanding of the formation of PAH, pyrolysis experiments have been performed in an isothermal laminar-flow reactor with the model fuel catechol (*ortho*-dihydroxybenzene) – a phenol-type compound representative of structural entities in complex solid fuels like coal, wood, and biomass. The catechol pyrolysis experiments are conducted at 1000°C and at a residence time of 0.3 s. The pyrolysis products are analysed by high-pressure liquid chromatography with ultraviolet-visible absorbance detection and mass spectrometric detection. Product analysis reveals that the $C_{24}H_{14}$ PAH products of catechol pyrolysis belong to three structural classes: perylene benzologues, fluoranthene benzologues and pyrene benzologues. The 12 $C_{24}H_{14}$ PAH identified in the present study are: benzo[*b*]perylene, naphtho[1,2-*b*]fluoranthene, naphtho[1,2-*k*]fluoranthene, dibenzo[*b*,*k*]fluoranthene, naphtho[2,3-*b*]fluoranthene, naphtho[2,3-*k*]fluoranthene, naphtho[1,2-*e*]pyrene, naphtho[2,3-*e*]pyrene, naphtho[1,2-*a*]pyrene, dibenzo[*a*,*e*]pyrene, dibenzo[*e*,*l*]pyrene, and dibenzo[*a*,*h*]pyrene. In addition to these, our earlier identifications of naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, and dibenzo[*a*,*i*]pyrene among the products of catechol pyrolysis bring the total number of $C_{24}H_{14}$ PAH identified as products of catechol pyrolysis to 15. Of these 15, 12 have been reported to be mutagens and 6 have been reported to be carcinogens. The UV spectra establishing the identities of the 15 $C_{24}H_{14}$ catechol pyrolysis products are presented.

Keywords: polycyclic aromatic hydrocarbons; catechol pyrolysis; $C_{24}H_{14}$ PAH; UV spectra; high-pressure liquid chromatography

1. Introduction

The combustion of solid fuels like coal, wood, and biomass is associated with high-temperature, oxygen-deficient zones where pyrolytic reactions dominate. In combustion systems, pyrolytic reactions are known to be the primary source of polycyclic aromatic hydrocarbons (PAH) and soot. The formation of PAH as well as their subsequent release into the environment are of concern for both environmental and health reasons, due to the inherent carcinogenicity [1–3] and mutagenicity [4,5] of some members of this compound class.

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Of particular importance are the $C_{24}H_{14}$ PAH. Many of these molecular weight 302 PAH are found throughout the environment: in petroleum products [6,7], coal and wood combustion emissions [8–15], coal tar [16–19], carbon black [20,21], diesel exhaust [22–24], urban aerosols [16,25,26], sediments [18,19,27], tyre fire products [28], vegetable oils [29], smoked meat and fish [30–32], asphalt [33], fly ash [34], and cigarette smoke [35–38].

The $C_{24}H_{14}$ PAH also exhibit high biological activity [1,2,4,5,18,19,39–51]. The $C_{24}H_{14}$ PAH benzo[*b*]perylene, dibenzo[*b,k*]fluoranthene, naphtho[1,2-*k*]fluoranthene, naphtho[2,3-*b*]fluoranthene, naphtho[1,2-*a*]pyrene, naphtho[2,3-*e*]pyrene, dibenzo[*a,e*]-pyrene, naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*a,h*]-pyrene, dibenzo[*a,e*]pyrene, and dibenzo[*e,l*]pyrene are reported to have mutagenic activity [4,5,9,39,43,51]. Naphtho[1,2-*b*]fluoranthene, naphtho[2,1-*a*]pyrene, dibenzo[*a,i*]pyrene, naphtho[2,3-*a*]pyrene, dibenzo[*a,e*]pyrene, and dibenzo[*a,h*]pyrene are reported to have carcinogenic activity [2,18,44–46,48–50,52]. The $C_{24}H_{14}$ PAH dibenzo [*a, l*]pyrene is one of the most carcinogenic and genotoxic PAH ever tested [5,41–43]. In addition, various studies [53–56] have shown that weak or non-carcinogenic PAH within a complex mixture can either increase the carcinogenicity of the mixture by acting as co-carcinogens or decrease the carcinogenicity by inhibiting the carcinogenic activity of strong carcinogens present in the mixture. Since not all PAH are carcinogenic or mutagenic [4,5], the distribution of PAH within a complex mixture determines the biological activity of the PAH mixture. Therefore, isomer-specific identification of PAH, $C_{24}H_{14}$ isomers in particular, among the products of solid fuels is of great importance.

For solid fuels like coal, wood, or biomass, which have very complex structures, the understanding of chemical pathways leading to PAH formation has been greatly facilitated by the use of model fuel compounds that are representative of structural moieties in these fuels [57–68]. For our experimental investigations into the formation of PAH during solid fuel pyrolysis and combustion, we have chosen catechol (*ortho*-dihydroxybenzene) as a model fuel for the following reasons: (1) catechol is a prominent structural entity in coal [69], tobacco [70], and lignin (a major component of wood [71]); (2) catechol is a major component in biomass tars [72] and tobacco smoke [36]; (3) catechol is a structural unit in flavonoids such as rutin and quercetin, as well as in chlorogenic acid, a common component of the leafy plant materials that make up some biomass fuels [70,73]; (4) catechol's relevancy is further strengthened by the demonstrated [74] similarity between PAH product distributions obtained from catechol pyrolysis and coal volatiles pyrolysis. Hence, catechol is a suitable model compound for investigating PAH formation from solid fuels.

The 65 theoretically possible $C_{24}H_{14}$ PAH isomers [11,75] include 10 benzologues of pyrene, 21 benzologues of fluoranthene, 2 benzologues of perylene, 19 benzologues of aceanthrylene, 12 benzologues of acephenanthrylene, and zethrene. As stated by Wise *et al.* [16,76], the large number of isomers, limited availability of reference standards, and poor resolution on conventional gas and liquid chromatographs [11,76] have made it extremely difficult, over the years, to identify and quantify the $C_{24}H_{14}$ PAH isomers. Despite these difficulties, 3 of the 10 $C_{24}H_{14}$ pyrene benzologues – dibenzo[*a,i*]pyrene, naphtho[2,1-*a*]pyrene and naphtho[2,3-*a*]pyrene – have been identified in previous catechol pyrolysis studies [74,77] from our research group. The detection of these three $C_{24}H_{14}$ PAH among catechol's pyrolysis products, the high biological activity of the $C_{24}H_{14}$ PAH in general, and recent improvements in chemical analysis methods have prompted us to perform new catechol pyrolysis experiments and a more detailed examination of the products for $C_{24}H_{14}$ PAH.

In the following, we describe the catechol pyrolysis experiments and present the analytical evidence supporting 12 new $C_{24}H_{14}$ PAH product identifications. The catechol pyrolysis experiments are carried out in an isothermal laminar-flow reactor at 1000°C and a residence time of 0.3 s. The PAH products are analysed by high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection and mass spectrometric detection. We present the UV spectral matches confirming the 12 new $C_{24}H_{14}$ PAH product identifications – along with those of the 3 previously identified, as those had not been previously shown. We also summarise literature findings on the identification of these 15 $C_{24}H_{14}$ PAH in other fuel mixtures and environmental samples, as well as findings on their carcinogenicity and mutagenicity.

2. Experimental

2.1 *Reactor system*

As detailed elsewhere [74,77–79], the catechol pyrolysis experiments are performed in a laminar-flow reactor system that consists of a fuel vaporiser, isothermal quartz flow reactor, and product collection system. Catechol pyrolysis experiments are performed by loading solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) as a fixed bed into a Pyrex tube placed vertically inside the fuel vaporiser, an isothermal oven maintained at 85°C for slight vaporisation of catechol. The vapor-phase catechol is entrained in a flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. The pyrolysis reactions take place at 1000°C and at atmospheric pressure inside the isothermal laminar-flow reactor, which consists of a 2-mm (inner diameter) quartz tube insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated furnace. The residence time for each experimental run is 0.3 s. The PAH products exiting the reactor are quenched to room temperature and collected with a condensed-phase product collection system (consisting of a Balston Teflon filter and dichloromethane solvent trap). The products dissolved in dichloromethane are concentrated with a Kuderna-Danish apparatus and exchanged into dimethylsulphoxide for subsequent analysis by HPLC.

2.2 *Product analysis*

To analyse the PAH products, two separate aliquots of the PAH/dimethylsulphoxide solution are injected into two separate high-pressure liquid chromatographs – one, a Hewlett-Packard Model 1050 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector (HPLC/UV); the other, an Agilent Model 1100 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector in series with a mass spectrometer (HPLC/UV/MS). Each HPLC uses a reversed-phase Restek Pinnacle II PAH octadecylsilica column (particle size, 5 μm; pore size, 110 Å; inner diameter, 4.6 mm; and length, 250 mm) and gradient elution to achieve component separation. The HPLC/UV employs a sample injection volume of 25 μL, a mobile-phase flowrate of 1.5 mL min^{-1}, and a time-programmed sequence of mobile phases that begins with 60 : 40 water : acetonitrile (ACN), ramps to pure ACN in 40 minutes, holds isocratic in ACN for 20 minutes, and then ramps to 100% dichloromethane (DCM) in 40 minutes. The HPLC/UV/MS employs an injection volume of 20 μL, a flowrate 1.0 mL min^{-1}, and a time-programmed sequence of mobile phases that begins with 50 : 50 water : methanol (MeOH), ramps to pure MeOH in 40 min, holds isocratic in MeOH for 60 min, ramps to 100% DCM in 40 minutes, and holds isocratic in DCM for 40 minutes. (Methanol is used in the solvent program of the HPLC/UV/MS since better mass spectra result. Acetonitrile generally gives better UV spectra, so it is used in the solvent program of the HPLC/UV. Of the 15 product component spectra presented in this paper, 13 are from the water/ACN/DCM program of the HPLC/UV. Two are from the water/MeOH/DCM program of the HPLC/UV/MS since these two components are better resolved with this solvent program).

After separation by either HPLC instrument, the catechol pyrolysis products in the eluent pass through a UV diode-array detector, which is set to simultaneously monitor five absorbance channels: 328–332 nm, 335–345 nm, 275–285 nm, 236–500 nm, and 190–520 nm. UV absorbance spectra, covering the range of 190–520 nm, are taken every 0.8 s at a resolution of 2 nm in the HPLC/UV and every 0.4 s at a resolution of 1 nm in the HPLC/UV/MS.

In the HPLC/UV/MS, products exiting the UV detector are introduced directly into a PhotoMate atmospheric-pressure photo-ionization (APPI) source, which is equipped with a krypton discharge lamp, emitting 10.0 eV and 10.6 eV photons perpendicularly to the vaporised effluent. The ions are detected by a high-energy dynode detector, which operates in the positive-ion, full-scan mode and monitors mass-to-charge ratios up to 700.

The mass spectrum obtained from the HPLC/UV/MS establishes the C_xH_y formula and molecular mass of each product component – $C_{24}H_{14}$ and 302, respectively, for the PAH identified in the present study. The UV spectrum establishes the exact aromatic structure of each product component, since UV spectra are isomer-specific. Thus, the $C_{24}H_{14}$ products of catechol pyrolysis are unequivocally identified by matching each $C_{24}H_{14}$ product component's UV absorbance spectrum with that of the appropriate $C_{24}H_{14}$ reference standard injected onto the HPLC/UV.

3. Results and discussion

The HPLC chromatogram showing all the PAH and oxygen-containing aromatic products of catechol pyrolysis is presented elsewhere [74,80]. Figure 1 presents the portion of the HPLC chromatogram (from the HPLC/UV) in which the $C_{24}H_{14}$ PAH products of catechol pyrolysis (at 1000°C and 0.3 s) elute. Shown in red in Figure 1 are the chemical structures corresponding to the 15 catechol pyrolysis products whose mass spectra designate them as $C_{24}H_{14}$ PAH and whose UV spectra have permitted determination of their exact isomer-specific identities. In order of elution in Figure 1, the $C_{24}H_{14}$ PAH products of catechol pyrolysis at 1000°C and 0.3 s are: naphtho[1,2-*e*]pyrene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*e*]pyrene, naphtho[1,2-*a*]pyrene co-eluting with dibenzo[*a*,*e*]pyrene, naphtho[1,2-*k*]fluoranthene, benzo[*b*]perylene, dibenzo[*e*,*l*]pyrene, dibenzo[*b*,*k*]fluoranthene, naphtho[2,3-*b*]fluoranthene, naphtho[2,1-*a*]pyrene, dibenzo[*a*,*i*]pyrene, naphtho[2,3-*a*]pyrene, naphtho[2,3-*k*]fluoranthene, and dibenzo[*a*,*h*]pyrene. Except for the three noted in our earlier paper [74], none of the 15 $C_{24}H_{14}$ PAH have ever before been identified as products of catechol or any phenol-type fuel. In addition to the 15 $C_{24}H_{14}$ PAH products, Figure 1 shows in black the chemical structures of the 23 other PAH products of catechol pyrolysis that elute in the 40- to

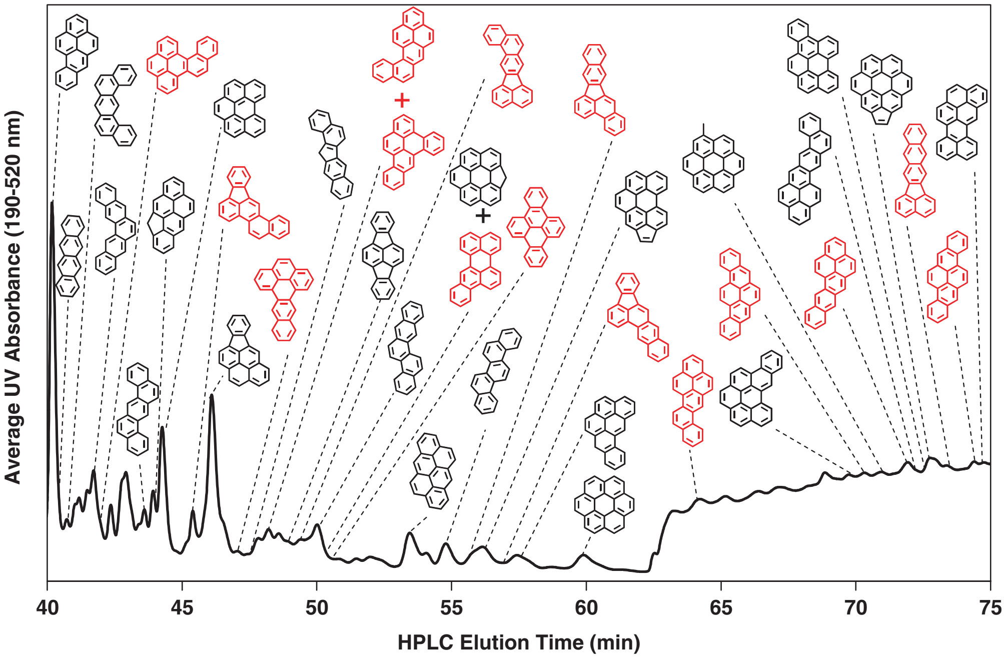

Figure 1. HPLC chromatogram of products of catechol pyrolysis (1000°C and 0.3 s) eluting from 40 to 75 min in the solvent program of the HPLC/UV.

Notes: The rise in the baseline at ~63 min corresponds to a change in HPLC mobile phase composition to UV-absorbing dichloromethane. Shown in red, the identified $C_{24}H_{14}$ PAH product components, in order of elution from left to right, are: naphtho[1,2-*e*]pyrene, naphtho[1,2-*b*]fluoranthene, naphtho[2,3-*e*]pyrene, naphtho[1,2-*a*]pyrene eluting with dibenzo-[*a,e*]pyrene, naphtho[1,2-*k*]fluoranthene, benzo[*b*]perylene, dibenzo[*e,l*]pyrene, dibenzo[*b,k*]fluoranthene, naphtho[2,3-*b*]fluoranthene, naphtho[2,1-*a*]pyrene, dibenzo[*a,i*]pyrene, naphtho-[2,3-*a*]pyrene, naphtho[2,3-*k*]fluoranthene, and dibenzo[*a,h*]pyrene. Three of these $C_{24}H_{14}$ PAH – naphtho[2,1-*a*]pyrene, dibenzo[*a,i*]pyrene, and naphtho[2,3-*a*]pyrene – have been identified in a previous catechol pyrolysis study in this series [74]. Shown in black, the PAH product components whose identifications are demonstrated elsewhere [74,81,82], in order of elution from left to right, are: benzo[*a*]pyrene [74], naphthacene [82], dibenz[*a,j*]anthracene [74], pentaphene [82], dibenz-[*a,h*]anthracene [74], 4*H*-benzo[*def*]cyclopenta[*mno*]chrysene [81], benzo[*ghi*]perylene [74], indeno[1,2,3-*cd*]pyrene [74], dibenzo[*a,h*]fluorene [82], indeno[1,2,3-*cd*]fluoranthene [74], benzo[*b*]chrysene, [74] 1*H*-benzo[*ghi*]cyclopenta[*pqr*]perylene [81] eluting with benzo[*b*]perylene, anthanthrene [74], picene, [74] benzo[*ghi*]cyclopenta[*cd*]perylene [74], 8*H*-dibenzo[*a, jk*]pyrene [82], coronene [74] dibenzo[*b,ghi*]perylene [82], 1-methylcoronene [82], phenanthro[2,3-*a*]pyrene [74], dibenzo[*e,ghi*]perylene [82], cyclopenta[*bc*]coronene [82], and naphtho[8,1,2-*bcd*]perylene [82].

75-min range of the HPLC chromatogram. The identifications of 12 of these 23 PAH have been reported in our previous catechol pyrolysis study [74]. The identifications of the 11 remaining PAH products will be reported in forthcoming papers [81,82].

The 15 identified $C_{24}H_{14}$ PAH products of catechol pyrolysis belong to three structural classes: perylene benzologues, fluoranthene benzologues, and pyrene benzologues – each of which will be discussed separately. Figure 2 presents the UV spectral match unequivocally establishing the identity of the perylene benzologue; Figure 3, those of the five fluoranthene benzologues; Figures 4 and 5, those of the nine pyrene benzologues. Although we previously reported three of the $C_{24}H_{14}$ pyrene

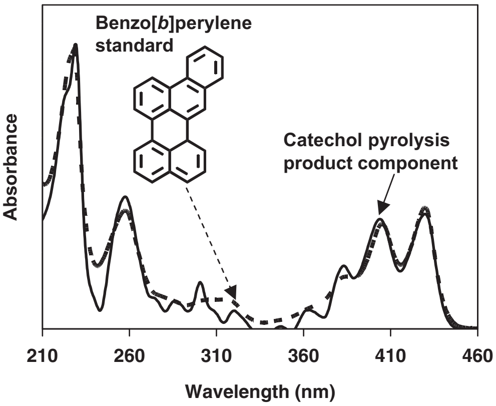

Figure 2. UV absorbance spectra of the reference standard of benzo[*b*]perylene (dashed line) and of a catechol pyrolysis product component (solid line) eluting at 50.8 min in Figure 1.
Note: Some spectral interference from co-eluting 1*H*-benzo[*ghi*]cyclopenta[*pqr*]perylene is evident at 288 and 300 nm in the spectrum of the catechol pyrolysis product component.

benzologue products (naphtho[2,1-*a*]pyrene, dibenzo[*a*,*i*]pyrene, and naphtho[2,3-*a*]pyrene) [74], the UV spectral matches confirming those identifications were not reported, due to the large number of compounds identified in that study [74]. They are included here for completeness. All of the catechol pyrolysis product component spectra in Figures 2–4 and 5a have been obtained with the water/ACN/DCM solvent program on the HPLC/UV; those in Figures 5b and 5c, for naphtho[1,2-*a*]pyrene and dibenzo[*a*,*e*]pyrene, have been obtained with the water/MeOH/DCM solvent program on the HPLC/UV/MS.

3.1 *Perylene benzologues*

Figure 2 presents the UV spectrum of the catechol pyrolysis product component eluting at 50.8 min in Figure 1, along with that of a benzo[*b*]perylene reference standard. Some very minor spectral interference from the co-eluting product 1*H*-benzo[*ghi*]cyclopenta-[*pqr*]perylene [81] is evident in the two small peaks at 288 and 300 nm in the spectrum of the catechol pyrolysis product component. The otherwise very close match between the two spectra in Figure 2, however, confirms this product component's identity as benzo[*b*]perylene.

As indicated in Table 1, benzo[*b*]perylene has been previously identified in a hard-coal flue-gas condensate [11] as well as in extracts of coal tar (SRM 1597) [19], urban air particulates (SRM 1648) [19], urban dust (SRM 1649a) [19], marine sediments (SRM 1941) [19], diesel particulates (SRM1650a) [23,24], wood soot [12], and carbon black [20]. Experimental carcinogenicity data are not available for benzo[*b*]perylene, but Durant *et al.* [5] have demonstrated benzo[*b*]perylene to be a human-cell mutagen, as indicated in Table 2.

3.2 *Fluoranthene benzologues*

Figure 3 presents the UV spectra of the five $C_{24}H_{14}$ fluoranthene benzologue products of catechol pyrolysis, along with the UV spectra of the respective PAH reference

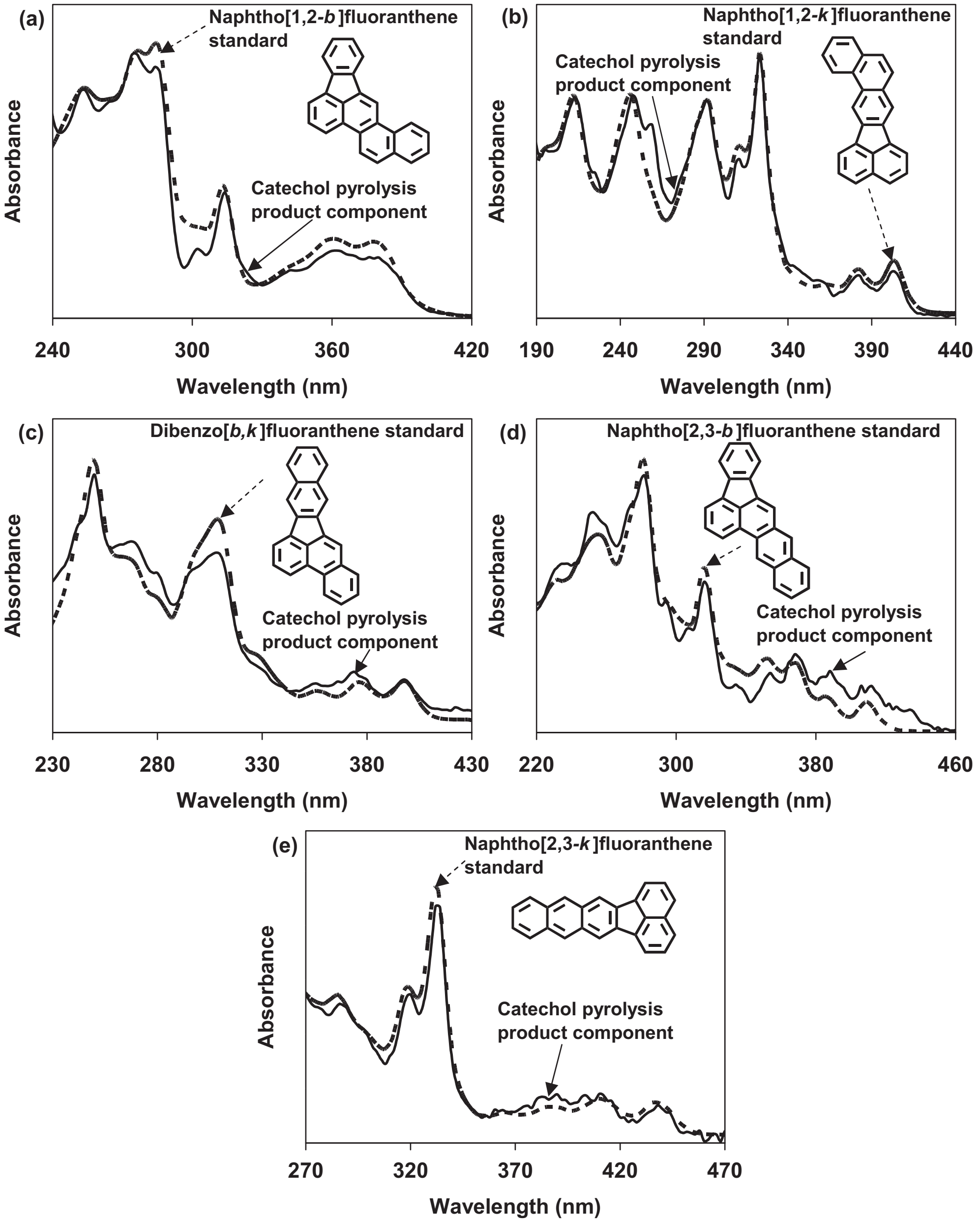

Figure 3. UV absorbance spectra of reference-standard (dashed line)/product-component (solid line) pairs of the $C_{24}H_{14}$ fluoranthene benzologues.

Notes: (a) naphtho[1,2-*b*]fluoranthene and catechol pyrolysis product component eluting at 45.5 min in Figure 1; (b) naphtho[1,2-*k*]fluoranthene and catechol pyrolysis product component eluting at 49.5 min in Figure 1 (Some spectral interference from an unidentified co-eluting compound is evident at 260 nm in the spectrum of the catechol pyrolysis product component); (c) dibenzo[*b*,*k*]-fluoranthene and catechol pyrolysis product component eluting at 55.8 min in Figure 1; (d) naphtho[2,3-*b*]fluoranthene and catechol pyrolysis product component eluting at 57.1 min in Figure 1; (e) naphtho[2,3-*k*]fluoranthene and catechol pyrolysis product component eluting at 73.5 min in Figure 1.

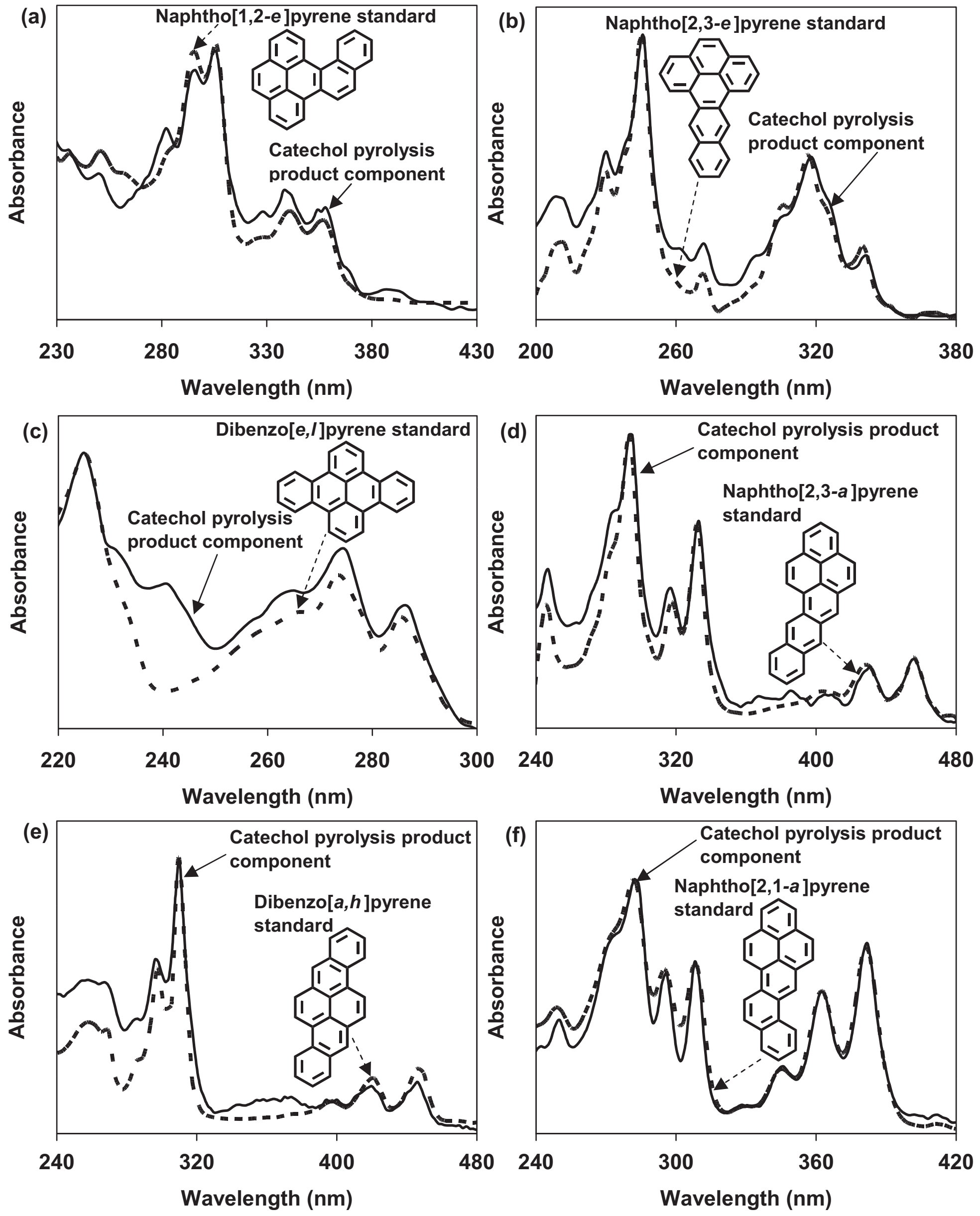

Figure 4. UV absorbance spectra of reference-standard (dashed line)/product-component (solid line) pairs of the $C_{24}H_{14}$ pyrene benzologues.

Notes: (a) naphtho[1,2-*e*]pyrene and catechol pyrolysis product component eluting at 42.1 min in Figure 1; (b) naphtho[2,3-*e*]pyrene and catechol pyrolysis product component eluting at 47.2 min in Figure 1; (c) dibenzo[*e,l*]pyrene and catechol pyrolysis product component eluting at 50.5 min in Figure 1; (d) naphtho[2,3-*a*]pyrene and catechol pyrolysis product component eluting at 72.1 min in Figure 1; (e) dibenzo[*a,h*]pyrene and catechol pyrolysis product component eluting at 74.5 min in Figure 1; (f) naphtho[2,1-*a*]pyrene and of a catechol pyrolysis product component eluting at 64.2 min in Figure 1. Some spectral interference from unidentified co-eluting compounds is evident in the spectrum of the catechol pyrolysis product component in (a) at 282 nm and (c) at 240 nm.

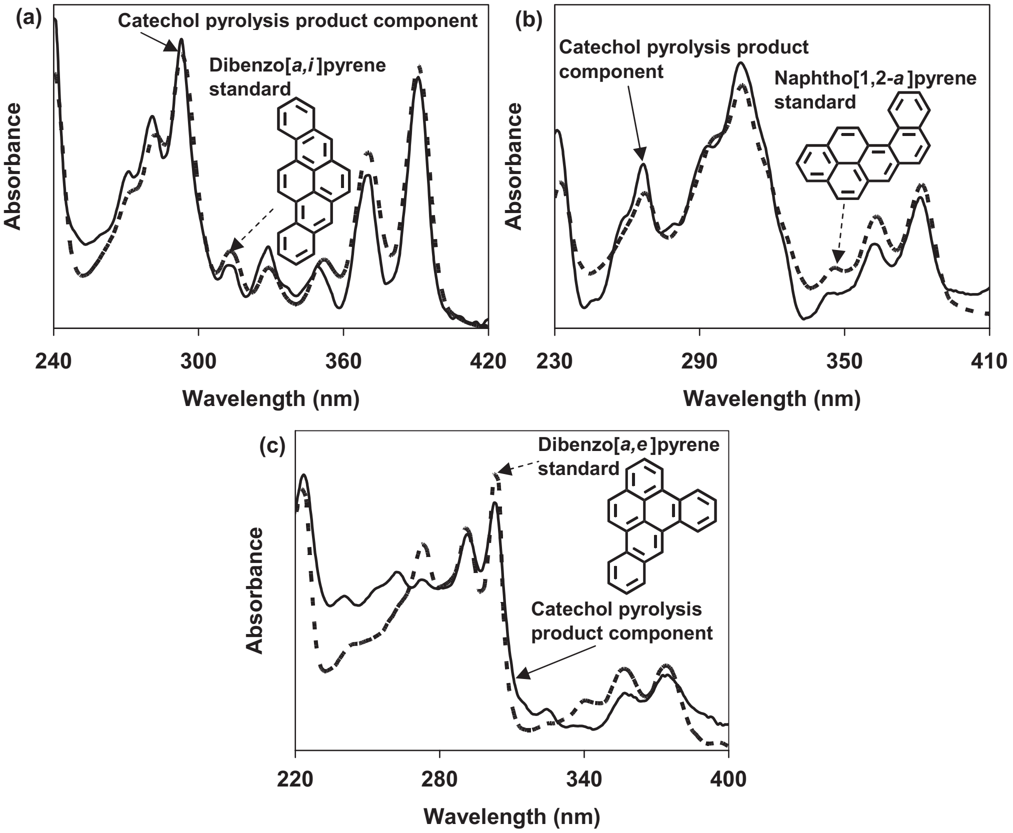

Figure 5. UV absorbance spectra of the reference-standard (dashed line)/product-component (solid line) pairs of the $C_{24}H_{14}$ pyrene benzologues.

Notes: (a) dibenzo[*a,i*]pyrene and catechol pyrolysis product component eluting at 70.5 min in Figure 1; (b) naphtho[1,2-*a*]pyrene and catechol pyrolysis product component eluting at 70.8 min in the solvent program of the HPLC/UV/MS and at 48.3 min in Figure 1, from the solvent program of the HPLC/UV; (c) dibenzo[*a,e*]pyrene and catechol pyrolysis product component eluting at 71.2 min in the solvent program of the HPLC/UV/MS and at 48.3 min in Figure 1, from the solvent program of the HPLC/UV. Some spectral interference from unidentified co-eluting compounds (molecular mass 276 and 288) is evident at 242, 262, and 325 nm in the spectrum of the catechol pyrolysis product component in (c).

standards: Figure 3a, naphtho[1,2-*b*]fluoranthene; Figure 3b, naphtho[1,2-*k*]fluoranthene; Figure 3c, dibenzo[*b,k*]fluoranthene; Figure 3d, naphtho[2,3-*b*]fluoranthene; and Figure 3e, naphtho[2,3-*k*]fluoranthene. The $C_{24}H_{14}$ fluoranthene benzologue products of catechol pyrolysis are produced in very small amounts (each <30 µg/g of fed catechol), so they exhibit very small peaks in Figure 1. In some cases, the $C_{24}H_{14}$ fluoranthene benzologues also elute close to other product components. There are thus some slight discrepancies, between the components' and standards' UV spectra of Figure 3, in a few of the peak heights (*e.g.*, at 308 nm in Figure 3c and at 255 nm in Figure 3d), and the component spectrum in Figure 3b even exhibits a peak at 260 nm that is due to an unidentified co-eluting compound. Nevertheless, the matching HPLC retention times of each of the component/standard pairs of Figure 3, the qualitative agreement in the UV spectral patterns, and the matching

Table 1. Previous identifications of catechol's $C_{24}H_{14}$ product PAH in environmental samples and the products of other fuels.

	Previously identified in																			
Compounds	Coal tar extract (SRM 1597)	Urban air particulates (SRM	Urban dust (SRM 1649a)	Marine sediment (SRM 1941)	Diesel particulates (SRM 1650a)	Cigarette smoke condensate	Urban aerosols	Coal -tar-contaminated	Coal fired residential furnaces	Hard-coal flue-gas condensate	Tire fire products	Carbon black	Coal soot extracts	Asphalt	Flyz ash	Coal-fired residential stoves	Motor vehicle exhaust condensate	Tar-cork	Wood soot extracts	Hard wood combustion
Benzo[*b*]perylene	X [19]	X [19]	X [19]	X [19]	X [23,24]					X [11]		X [20]							X [12]	
naphtho[1,2-*b*] fluoranthene	X [19]	X [19]	X [19]	X [19]			X [25]				X [28]		X [9]							
naphtho[1,2-*k*] fluoranthene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]			X [28]	X [21]								
dibenzo[*b*,*k*] fluoranthene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]		X [11]	X [28]		X [9]						X [12]	
naphtho[2,3-*b*] fluoranthene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]		X [11]										
naphtho[2,3-*k*] fluoranthene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]		X [11]	X [28]									
naphtho[1,2-*e*]pyrene	X [19]	X [19]	X [19]	X [19]		X [38]											X [38]	X [38]		
naphtho[2,3-*e*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]	X [15]		X [28]	X [21]								
dibenzo[*a*,*e*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]	X [37]	X [25]		X [13,15]		X [28]	X [20,21]	X [9]	X [33]	X [34]	X [10]				X [13]
naphtho[1,2-*a*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]	X [38]											X [38]	X [38]		
dibenzo[*e*,*l*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]		X [15]		X [28]		X [9]							
naphtho[2,1-*a*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]	X [15]			X [21]	X [9]							
dibenzo[*a*,*i*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]	X [37]	X [25]	X [18]	X [13,15]		X [28]	X [21]		X [33]	X [34]	X [10]				X [13]
naphtho[2,3-*a*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]		X [25]	X [18]			X [28]								X [14]	
dibenzo[*a*,*h*]pyrene	X [19]	X [19]	X [19]	X [19]	X [23,24]	X [37]		X [18]	X [13,15]		X [28]			X [33]	X [34]					X [13]

Notes: Numbers in brackets indicate the numbers of the references reporting that product's identification.

Table 2. Literature findings on the carcinogenicity and mutagenicity of catechol's $C_{24}H_{14}$ product PAH.

Compound	Mutagenic*	Carcinogenic
Benzo[*b*]perylene	Yes [5]	Not available
Naphtho[1,2-*b*]fluoranthene	No [5]	Yes [52]
Naphtho[1,2-*k*]fluoranthene	Yes [4]	Not available
Dibenzo[*b*,*k*]fluoranthene	Yes [4]	No [47,48]
Naphtho[2,3-*b*]fluoranthene	Yes [4]	Not available
Naphtho[2,3-*k*]fluoranthene	No [4]	Not available
Naphtho[1,2-*e*]pyrene	No [39]	Not available
Naphtho[2,3-*e*]pyrene	Yes [5]	No [1,2,18,45,48]
Dibenzo[*a*,*e*]pyrene	Yes [4,5]	Yes [2,18,44–46,48–50]
Naphtho[1,2-*a*]pyrene	Yes [39,51]	Not available
Dibenzo[*e*,*l*]pyrene	Yes [5]	No [1,2,18,45,48]
Naphtho[2,1-*a*]pyrene	Yes [4,5]	Yes [2,18,44–46,48–50]
Dibenzo[*a*,*i*]pyrene	Yes [5]	Yes [2,18,44–46,48–50]
Naphtho[2,3-*a*]pyrene	Yes [5]	Yes [2,18,44–46,48–50]
Dibenzo[*a*,*h*]pyrene	Yes [5]	Yes [2,18,44–46,48–50]

Notes: *References [4] and [5] use a mutagenicity assay based on human h1A1v2 cells, and references [34] and [46] use a mutagenicity assay based on *S. typhimurium* TA 100.

wavelengths of UV absorption for each pair – all substantiate the identifications of the catechol pyrolysis product components of Figures 3a, 3b, 3c, 3d and 3e, as naphtho[1,2-*b*]fluoranthene, naphtho[1,2-*k*]fluoranthene, dibenzo[*b*,*k*]fluoranthene, naphtho[2,3-*b*]fluoranthene, and naphtho[2,3-*k*]fluoranthene, respectively.

As demonstrated in Table 1, all five fluoranthene benzologues identified here as catechol pyrolysis products have been previously identified in the extracts of coal tar (SRM 1597) [19], urban air particulates (SRM 1648) [19], urban dust (SRM 1649a) [19], marine sediments (SRM 1941) [19], and urban aerosols [25]. Four of the five, in different combinations, have also been found in diesel particulates (SRM1650a) [23,24], tyre fire products [28] and coal-tar-contaminated sediments [18]. Naphtho[1,2-*k*]fluoranthene and dibenzo[*b*,*k*]fluoranthene have been identified in carbon black [20] and wood soot extracts [12], respectively. Table 1 further indicates that two of the $C_{24}H_{14}$ fluoranthene benzologue products have been identified in coal soot extracts [9], and three have been identified in a hard-coal flue-gas condensate [11]. The fact that the $C_{24}H_{14}$ fluoranthene benzologue products of catechol pyrolysis are also present in the products of practical fuels and in environmental samples helps to corroborate catechol's relevancy as a model fuel for the study of PAH formation.

As evident in Table 2, Durant *et al.* [4,5] have tested the human cell (h1A1v2 cells) mutagenicity of the five $C_{24}H_{14}$ fluoranthene benzologue products identified in the present study. They found the mutagenicity of dibenzo[*b*,*k*]fluoranthene comparable to that of benzo[*a*]pyrene. Naphtho[1,2-*k*]fluoranthene and naphtho[2,3-*b*]fluoranthene were moderately mutagenic but less mutagenic than benzo[*a*]pyrene. Naphtho[1,2-*b*]fluoranthene and naphtho[2,3-*k*]fluoranthene were inactive in these bio-assays [4,5]. Naphtho[1,2-*b*]fluoranthene, however, has been reported to be moderately carcinogenic by Weyand *et al.* [52] In the studies of Lee *et al.* [48] and Lacassagne *et al.* [47], dibenzo[*b*,*k*]fluoranthene did not exhibit carcinogenicity, but experimental carcinogenicity data for the other three $C_{24}H_{14}$ fluoranthene benzologue products of catechol pyrolysis are not available.

3.3 *Pyrene benzologues*

Figures 4 and 5 present the UV spectra of the nine $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis, along with the UV spectra of the respective PAH reference standards: Figure 4a, naphtho[1,2-*e*]pyrene; Figure 4b, naphtho[2,3-*e*]pyrene; Figure 4c, dibenzo[*e*,*l*]pyrene; Figure 4d, naphtho[2,3-*a*]pyrene; Figure 4e, dibenzo[*a*,*h*]pyrene; Figure 4f, naphtho[2,1-*a*]pyrene; Figure 5a, dibenzo[*a*,*i*]pyrene; Figure 5b, naphtho-[1,2-*a*]pyrene; Figure 5c, dibenzo[*a*,*e*]pyrene. As with the $C_{24}H_{14}$ fluoranthene benzologues, the $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis are produced in small amounts (each <20 μg/g of fed catechol). Figure 1 also reveals that – even though two of the nine $C_{24}H_{14}$ pyrene benzologue products, naphtho[2,1-*a*]pyrene and dibenzo[*a*,*i*]-pyrene, elute cleanly as pure components – five of the nine elute very close to other product components, and two (naphtho[1,2-*a*]pyrene and dibenzo[*a*,*e*]pyrene) even co-elute in the water/ACN/DCM solvent program of Figure 1. Hence, for the five $C_{24}H_{14}$ pyrene benzologue products eluting close to other components, spectral interference from the near-eluting components causes some minor discrepancies between the product components' and standards' UV spectra in Figure 4: at 210 nm and 272 nm in Figure 4b, at 260 nm and 360 nm in Figures 4e, and, more markedly, at 282 nm in Figure 4a and at 240 nm in Figure 4c. Despite the interference from the near-eluting compounds, however, the closely matching UV spectra in Figures 4a–4e and the matching HPLC retention times of each of the component/standard pairs confirm the identifications of the catechol pyrolysis product components of Figures 4a, 4b, 4c, 4d and 4e as naphtho[1,2-*e*]pyrene, naphtho[2,3-*e*]pyrene, dibenzo[*e*,*l*]pyrene, naphtho[2,3-*a*]pyrene, and dibenzo[*a*,*h*]pyrene, respectively.

The two $C_{24}H_{14}$ pyrene benzologue products eluting at 64.2 and 70.5 min in Figure 1 are not affected by other components, so the UV spectral matches for these two products, in Figures 4f and 5a, respectively, are very clear – establishing the identities of these components as naphtho[2,1-*a*]pyrene and dibenzo[*a*,*i*]pyrene, respectively.

The two remaining $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis, co-eluting at 48.3 min in the water/ACN/DCM solvent program of Figure 1, are better resolved by the water/MeOH/DCM solvent program on the HPLC/UV/MS. Therefore, Figures 5b and 5c present the UV spectra of these two $C_{24}H_{14}$ pyrene benzologue products (eluting at 70.8 min and 71.2 min, respectively, in the water/MeOH/DCM solvent program), along with the UV spectra of the respective PAH reference standards. As with the other $C_{24}H_{14}$ products, the effects of low product concentrations and co-elution are evident in the spectra of the catechol pyrolysis product components in Figures 5b and 5c. Figure 5b shows slight discrepancies in the peak heights (at 232 nm, 267 nm, and 308 nm) between the UV spectrum of the naphtho[1,2-*a*]pyrene standard and that of the catechol pyrolysis product component. The UV spectrum of the catechol pyrolysis product component in Figure 5c exhibits peaks at 242, 262, and 325 nm that are due to un-identified co-eluting components. Despite these spectral interferences, the UV spectra of the catechol pyrolysis product components in Figures 5b and 5c are in agreement with both the spectral patterns and the wavelengths of peak absorbance in the UV spectra of the respective reference standards. This agreement, along with the matching HPLC retention times of the component/standard pairs, confirms the identities of the $C_{24}H_{14}$ product components of Figures 5b and 5c as naphtho[1,2-*a*]pyrene and dibenzo[*a*,*e*]pyrene, respectively.

As evident in Table 1, the nine $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis have also been identified in the same four environmental reference materials shown to contain the one $C_{24}H_{14}$ perylene benzologue and the five $C_{24}H_{14}$ fluoranthene benzologue products of catechol pyrolysis: coal tar extract (SRM 1597) [19]; urban air particulates (SRM 1648) [19]; urban dust (SRM 1649a) [19]; and marine sediment (SRM 1941) [19]. As also shown in Table 1, however, the $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis have been reported in a higher number and broader range of fuel product mixtures than either of the other two classes of $C_{24}H_{14}$ PAH.

As evident in Table 2, the literature reports several studies on the biological activity of the $C_{24}H_{14}$ pyrene benzologues. Table 2 shows that except for naphtho[1,2-*e*]pyrene [39], all of the $C_{24}H_{14}$ pyrene benzologue products of catechol pyrolysis have been found to be mutagenic [4,5,39,51]. Also, dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*i*]pyrene, dibenzo[*a*,*h*]pyrene, naphtho[2,1-*a*]pyrene, and naphtho[2,3-*a*]pyrene have been reported to be carcinogenic [2,18,44–46,48–50]. However, various studies [1,2,18,45,48,83] have found that naphtho[2,3-*e*]pyrene and dibenzo[*e*,*l*]pyrene are not carcinogens, and experimental carcinogenicity data for naphtho[1,2-*e*]pyrene and naphtho[1,2-*a*]pyrene are not available.

4. Summary and conclusions

In order to understand better the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis of the model fuel catechol in a laminar-flow reactor at 1000°C and 0.3 s. The products collected have been analysed by HPLC with UV and mass spectrometric detection. Product analysis reveals that catechol pyrolysis produces 15 $C_{24}H_{14}$ PAH products – a PAH isomer class that is known to contribute significantly towards the carcinogenicity and mutagenicity of PAH mixtures [1,4,5,19,39–43]. The 15 identified $C_{24}H_{14}$ PAH products of catechol pyrolysis include a perylene benzologue, five fluoranthene benzologues, and nine pyrene benzologues. Of the 15 identified $C_{24}H_{14}$ PAH products, naphtho[2,1-*a*]pyrene, naphtho[2,3-*a*]pyrene, and dibenzo[*a*,*i*]pyrene were identified in our previous catechol pyrolysis study [74]. The 12 newly identified $C_{24}H_{14}$ PAH products of catechol pyrolysis are: benzo[*b*]perylene, naphtho[1,2-*b*]fluoranthene, naphtho[1,2-*k*]fluoranthene, dibenzo[*b*,*k*]fluoranthene, naphtho [2,3-*b*]fluoranthene, naphtho[2,3-*k*]fluoranthene, naphtho[1,2-*e*]pyrene, naphtho [2,3-*e*]pyrene, naphtho[1,2-*a*]pyrene, dibenzo[*a*,*e*]pyrene, dibenzo[*e*,*l*]pyrene and dibenzo-[*a*,*h*]pyrene. Of the 15 $C_{24}H_{14}$ PAH products of catechol pyrolysis, 12 have been reported to be mutagens [4,5,51] and 6 have been reported to be carcinogens [49,50,52].

The $C_{24}H_{14}$ PAH identified in the present study have been identified previously in various environmental samples and product mixtures from other fuels – including cigarette smoke [38], coal tar extracts [19,76], diesel particulates [23,24], and urban aerosols [25]. Therefore the insights gained into the mechanisms of $C_{24}H_{14}$ PAH formation from the model fuel catechol [74,77–80,84] should also be of relevance to the formation of this important class of PAH from practical fuels and processes.

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