Environmental Health Perspectives
Vol. 73, pp. 215-221, 1987

Organic Emissions from Coal Pyrolysis: Mutagenic Effects

by Andrew G. Braun,* Mary J. Wornat,† Amitava Mitra,† and Adel F. Sarofim†‡

Four different types of coal have been pyrolyzed in a laminar flow, drop tube furnace in order to establish a relationship between polycyclic aromatic compound (PAC) evolution and mutagenicity. Temperatures of 900K to 1700K and particle residence times up to 0.3 sec were chosen to best simulate conditions of rapid rate pyrolysis in pulverized (44–53 μm) coal combustion. The specific mutagenic activity (i.e., the activity per unit sample weight) of extracts from particulates and volatiles captured on XAD-2 resin varied with coal type according to the order: subbituminous > high volatile bituminous > lignite > anthracite. Total mutagenic activity (the activity per gram of coal pyrolyzed), however, varied with coal type according to the order: high volatile bituminous >> subbituminous = lignite >> anthracite, due primarily to high organic yield during high volatile bituminous coal pyrolysis. Specific mutagenic activity peaked in a temperature range of 1300K to 1500K and generally appeared at higher temperatures and longer residence times than peak PAC production.

Introduction

In the United States, coal combustion is responsible for a substantial but difficult to quantify fraction of the polycyclic aromatic compounds (PAC) emitted into the atmosphere (*1,2*). In areas where coal is widely used for space heating, the chemical composition of ambient air particulates is similar to that in coal soot (*3*). Clearly, incomplete coal combustion plays a significant role in atmospheric pollution. As particulates originating from coal combustion are animal (*4*) and human (*5*) carcinogens, the effects of atmospheric coal combustion PAC on human health may be substantial.

Air pollution standards are concerned with the control of particulate, NO_x, and SO_x emissions rather than the level of potentially carcinogenic PAC. Unfortunately, there is a possibility that many furnaces operating in compliance with these standards are emitting substantial quantities of toxic materials. For example, the total amount of bacterial mutagens emitted by a residential oil burner was similar when operated under low and high sooting conditions (*6*). Although less organic material was emitted at low sooting, its specific mutagenic activity was sufficiently high that it counterbalanced the reduced mass of emitted material. Paradoxically, toxic organic emissions are often increased by processes, such as staged combustion, designed to reduce NO_x emissions (*7*). Hence there is a need to quantify the emission of PAC from coal-fired systems.

Coal combustion is thought to occur in two stages. In the first stage coal is pyrolyzed, releasing volatiles that burn in diffusion or partially premixed flames. The second stage is the combustion of char, the solid carbonaceous residue. Under ideal circumstances all PAC generated during pyrolysis are consumed during combustion, leaving only CO_2, water, and inorganic materials in the effluent. However, inadequate time, temperature, or oxidant concentrations can leave some of the pyrolysis products unburned.

A systematic investigation of the factors which influence the level of mutagen emissions from coal furnaces must begin with a study of coal pyrolysis. We have therefore collected gas and particulate samples during nonoxidative coal pyrolysis under controlled conditions using a laminar flow drop tube furnace. Experimental variables were coal type, pyrolysis temperature, and residence time. Samples were collected, weighed and tested for mutagenic activity in bacteria. We wished to document the appearance and disappearance of bacterial mutagens with time and temperature and to relate mutagen production to coal type.

Materials and Methods

Coals

The coals chosen for this study were a Montana lignite, a Montana Rosebud subbituminous, a Pittsburgh high volatile bituminous, and a Primrose anthracite.

*Department of Applied Biological Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139.
†Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.
‡Author to whom correspondence should be sent.

Coal samples were obtained from the Pennsylvania State Coal Sample Bank, University Park, PA. Elemental composition and other properties are presented in Table 1.

Furnace

The organic extracts examined in this study were derived from coals pyrolyzed in a laminar flow drop-tube furnace, whose design was a modification of one originally developed at the British Coal Utilization Research Association (*8*) and subsequently used by other workers (*9–12*). This type of furnace simulates the rapid pyrolysis of coal—a process common to pulverized coal combustion and entrained flow gasification. These processes normally involve finely ground coals, heated at very high rates to high temperatures. The experimental conditions of this study were selected to simulate industrial processes.

The apparatus has been described in detail elsewhere (*9*). Briefly, a fluidized stream of 44- to 53-μm coal particles were injected in argon into a 50.8 mm diameter laminar flow drop tube chamber electrically heated to temperatures in the range of 900K to 1700K. In a typical run, between 0.3 and 04. g of coal were injected into the furnace. Pyrolysis products were collected at several points with a water-cooled copper probe by changing the injector to collector distance. On entering the probe, gases and particles were quenched by a stream of cooled argon that entered the probe through openings in its tip and through sintered inner surfaces. The continual argon flow through the wall of the collection tube prevented particles from diffusing to its inner surface. The sampling stream passed through a centripeter and a four-stage Andersen cascade impactor to collect and separate soot and char particles. Gases passing through a final teflon filter were routed through a bed of XAD-2 resin to collect volatile organics.

By taking samples at successively longer distances from the injector, the products of increasingly long pyrolysis times can be collected. Thus, distance between injector and collector can be directly related to particle residence time in the furnace. Unfortunately there is a complex, nonlinear relationship between the distance traversed by the coal particle and the time the particle is at nominal furnace temperature. Even under carefully controlled conditions, particle velocity, and therefore, residence time, are related to gas temperature and position in the furnace. A theoretical model relating these parameters has been constructed by Nenniger (*10*) and can be used to estimate particle residence time as a function of distance between injector and collector. In the current study, samples were taken at four injector-collector distances: 3.8 cm, 7.6 cm, 11.4 cm, and 15.2 cm. The approximate residence times at these distances are estimated by Nenniger's model to be roughly <50 msec, 100 msec, 200 msec, and 300 msec, with the numbers varying predictably with temperature.

Sample Processing

Char, soot, and XAD-2 resin were separately extracted for 18 hr with methylene chloride in a Soxhlet extractor. Each extract was concentrated from 500 mL to roughly 5 mL in a rotary evaporator. To determine extract concentration, an aliquot was taken to dryness and its weight measured on a microbalance. The remaining extract was dried under nitrogen and stored at 4°C. Care was taken to avoid exposure to near ultraviolet light.

Bacterial Mutagen Measurements

Extract dissolved in dimethyl sulfoxide was tested for its ability to induce 8-azaguanine resistant mutants in *Salmonella typhimurium* according to the methods of Skopek et al. (*13,14*). In this system several concentrations of extract were incubated with *S. typhimurium*, strain TM677, for 2 hr in the presence of 5% Aroclor-induced rat liver post-mitochondrial supernatant (PMS) and an NADPH-generating system. In a typical experiment, extracts were tested at 10, 30, 100, and 300 μg/mL. The cell suspension was then plated in the presence of 8-azaguanine to measure induced mutant frequency. Dilutions were plated in the absence of selective agent to measure cell survival following treatment. All extract concentrations were incubated in duplicate and plated in triplicate. Each experiment also included a negative (DMSO) and positive (benzo[a]pyrene) control incubation. After a 44-hr incubation,

Table 1. Characterization of coal studied.[a]

	%C[b]	%H[b]	%N[b]	%S[c]	%O[b]	%VM[d]	H/C[e]	O/C[e]	Heating value[f]
Montana lignite	69.97	6.36	1.13	1.08	22.54	36.20	1.091	0.242	8,809
Montana Rosebud subbituminous	77.63	4.88	1.27	1.12	16.22	35.16	0.734	0.157	11,050
Pittsburgh HVB[g] (PSOC 997)	85.86	5.97	1.89	1.72	6.22	36.98	0.836	0.054	15,303
Primrose anthracite (PSOC 869)	95.73	1.77	0.79	0.54	1.69	3.32	0.222	0.013	14,705

[a]Assays performed by the Pennsylvania State Coal Sample Bank.
[b]Dry, mineral-free basis.
[c]Dry, ash-free basis.
[d]Volatile materials on an as-received basis.
[e]Atomic (Parr).
[f]Btu/lb; dry, mineral-free basis (Parr).
[g]High volatile bituminous.

the colonies were counted and mutant frequency and survival calculated.

There is no single parameter that can adequately describe the complex, usually sigmoidal, dose-response relationship between extract concentration and the induced mutant frequency. However, it is necessary to use a simple quantitative measure of mutagenicity to compare the activities of the numerous extracts examined here. We have chosen to use the maximum dose-response slope to describe the mutagenic activity of each extract in this paper with the full knowledge that this simple parameter may obscure important aspects of the mutagenic activity of the samples.

Partition of extractable organics between char, soot, and vapor is a function of the collection temperature. At low collector temperatures, organics tend to be found on particles, while at high collector temperatures, the organics tend to remain in the vapor phase. The relative amounts of mutagenic activity in the three forms is thus a function of collector temperature and does not shed light on the pyrolytic process itself. Therefore, we have mathematically combined the mutagenic activities of soot, char, and XAD-2 resin extracts into a single unit according to the following formula:

$$M_t = (1/W_t)\,[(M_s)(W_s) + (M_c)(W_c) + (M_x)(W_x)]$$

where M_t, M_s, M_c, and M_x are the maximum mutagenic slopes of the total, soot, char, and XAD-2 extracts, respectively, and where W_s, W_c, and W_x are the total weights of soot, char, and XAD-2 extracts, respectively. W_t is the sum of the soot, char, and XAD-2 extract weights.

It should be appreciated that the partition of toxic materials between vapor and solid phase is of enormous importance to the public health. Particle-borne PAC remain in the lung considerably longer than free PAC and therefore have more opportunity to do harm. In our studies, a small, practically negligible fraction of the PAC was collected with the char. The distribution between soot and XAD-2 extracts depended upon collector temperature, with the higher molecular weight compounds being found in higher concentration in the soot extract, as expected (*11*).

Results

The specific mutagenic activity of emissions from the laminar flow drop tube furnace varied with coal type, furnace temperature, and duration of pyrolysis.

Effect of Coal Composition

Figure 1 shows that, for a particle residence time of roughly 300 msec, the specific activity of emissions from each of the four coals increased with pyrolysis temperature to 1500K. At 1700K, however, the specific activity declined substantially.

From the standpoint of the public health, the specific biological activity of emissions is of less interest than the total activity emitted, i.e., the specific activity times

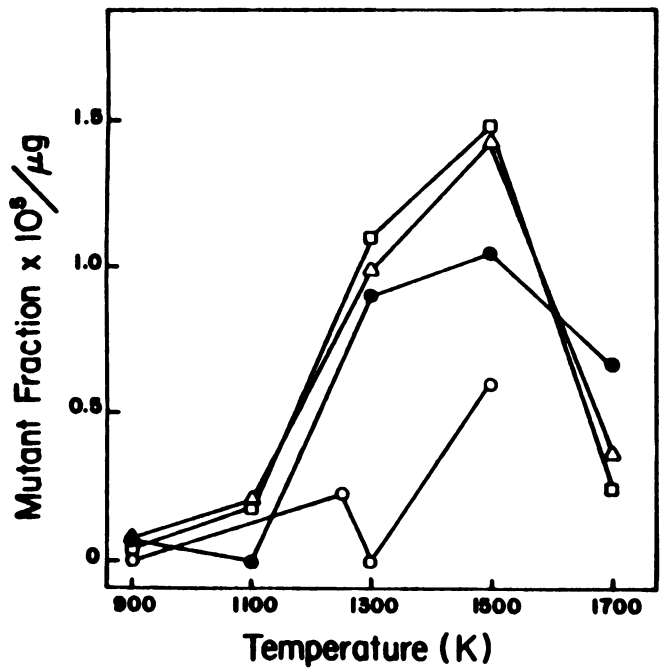

FIGURE 1. Specific mutagenic activity of methylene chloride extracts of soot, char, and material collected on XAD-2 resin at 15.2 cm as a function of furnace temperature. Mutagenic activity is displayed in terms of the maximum slope taken from dose-response curves. Coals: (●) Montana lignite, (□) Montana Rosebud subbituminous, (△) PSOC 997 Pittsburgh high volatile bituminous, (○) PSOC 869 Primrose anthracite.

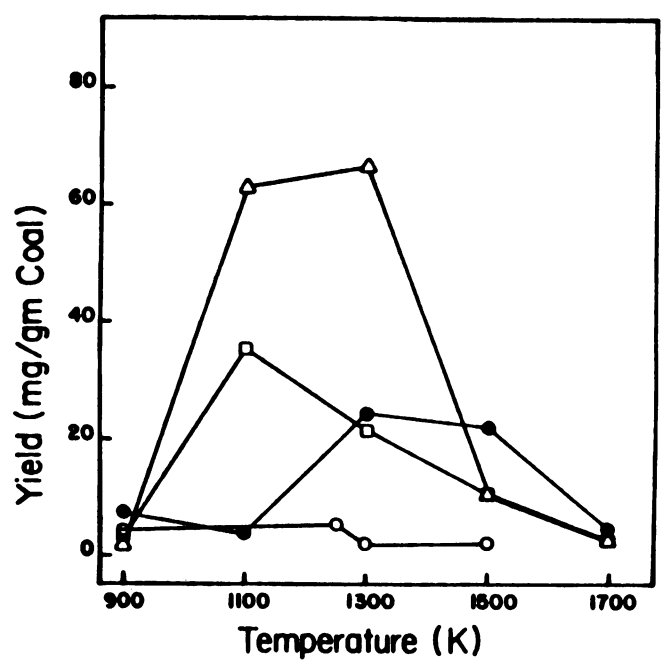

FIGURE 2. Weight of extracted organics per gram of coal injected as a function of furnace temperature. Coals: (●) Montana lignite, (□) Montana Rosebud subbituminous, (△) PSOC 997 Pittsburgh high volatile bituminous, (○) PSOC 869 Primrose anthracite.

the total weight emitted. As shown in Figure 2, for all four coals, the weight of extractable material per gram of coal consumed increased with pyrolysis temperature, reaching a maximum between 1100K and 1300K. At higher temperatures yield declined. Thus the total extractable emission yield reached peak values at somewhat lower temperatures than peak specific activity. Multiplying the specific activity shown in Figure 1 by the yields in Figure 2 generates the total emitted mutagenicity per gram of coal pyrolyzed (Fig. 3). For two coals, the high volatile bituminous and the subbituminous, the greatest mutagen emissions were found at 1500K for a 300 msec (15.2 cm) residence. Peak total activity for lignite was found at 1500K while anthracite mutagenicity was negligible at all temperatures. In all cases total mutagen yield declined to near zero if the 300 msec (15.2 cm) pyrolysis took place at 1700K.

Effect of Residence Time and Pyrolysis Temperature

To examine the effects of pyrolysis temperature and time, it is illustrative to focus on the high volatile bituminous coal, which exhibits both the highest specific mutagenicity and the highest extractable yield of the coals studied. The yield of extractable chemicals per gram of coal varied markedly with the duration of pyrolysis. Figure 4 shows that maximum yield was achieved at progressively shorter residence time as furnace temperature increased.

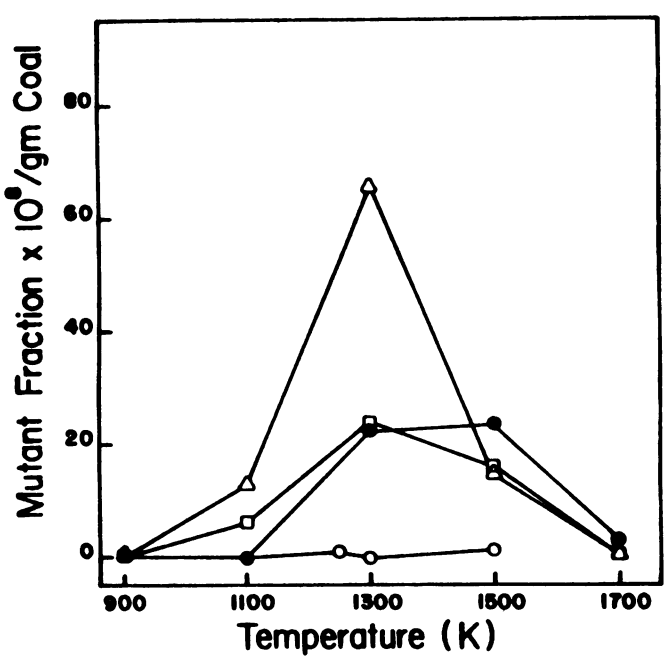

FIGURE 3. Total mutagenic activity per gram of coal injected as a function of furnace temperature. These data were generated by multiplying the slopes in Fig. 1 by the yields per gram of coal in Fig. 2. Coals: (●) Montana lignite, (□) Montana Rosebud subbituminous, (△) PSOC 997 Pittsburgh high volatile bituminous, (○) PSOC 869 Primrose anthracite.

This regular behavior was not reflected in the specific mutagenicity of the samples. Figure 5 shows that the greatest activity was found at 200 msec (11.4 cm) when pyrolysis occurred at 1100K or 1500K; while at 1700K, the specific mutagenic activity was relatively constant from 50 to 300 msec (3.8–15.2 cm).

Once again multiplying the specific mutagenicity in Figure 5 by the extractable yield in Figure 4 generates the total mutation yield per gram of coal consumed, plotted in Figure 6. A regular pattern emerges. At 1100K total mutation yield is greatest at 200 msec (11.4 cm); at 1500K, 100 msec (7.6 cm); and at 1700K, 50 msec (3.8 cm) or less. Thus, peak mutagen yield appears progressively earlier in the furnace as the temperature rises.

Discussion

Coal Type

The four traces in Figure 1 show that specific mutagenicity generally decreases in the order: subbituminous ≥ high volatile bituminous > lignite > anthracite, indicating that the chemical nature of the organic products produced in pyrolysis depends on the composition of the parent coal. Table 1 reveals no trend in element abundance that parallels that of specific mutagenicity, so we conclude that it is the chemical structure of the coal, and not just its elemental composition, that accounts for compositional differences in the pyrolysis products.

From Figure 1 and Table 1, one might observe the similarity between specific mutagenicity and the volatile matter content of the coal: the subbituminous, bituminous, and lignite are high and roughly equal; the anthracite is low. Because volatile matter results from the cleavage of weak bonds connecting substituent groups (e.g., alkyl, hydroxyl, carboxyl, etheric, amino) to the coal's aromatic clusters and the bridges (e.g., methylene, etheric) between aromatic clusters, one might speculate that the effect of temperature on mutagenic potential is a consequence of both increasing cleavage of such bonds and the parallel condensation reactions leading to higher molecular weight compounds.

Figure 2 demonstrates the ranking of coal type with respect to extractable organic yield: high volatile bituminous >> subbituminous = lignite >> anthracite. Yield differs more pronouncedly with coal type than dose specific mutagenicity, so total mutagenicity (as plotted in Fig. 3) displays the same coal type ordering as organic yield. It should be noted, however, that at high temperatures (≥ 1500K), total mutagenicities differ only slightly. Thus, even though the high volatile bituminous coal produces extractable material of no higher specific mutagenicity than the subbituminous and lignite coals, its larger yield makes it more harmful from the standpoint of public health. The anthracite, a

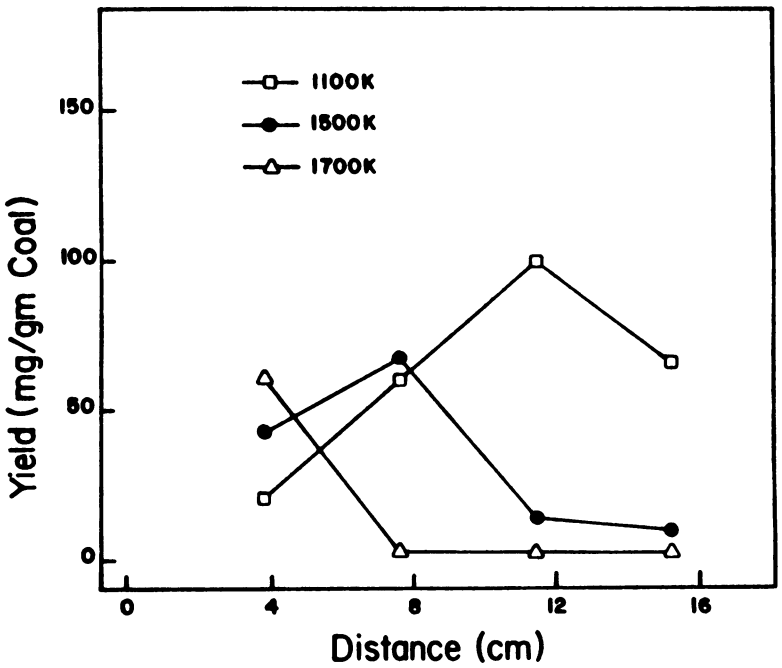

FIGURE 4. Weight of extracted organics per gram of PSOC 997 high volatile bituminous coal injected as a function of distance between injector and collector. The correspondence between distance and residence time is not linear. It is estimated that the residence time at 3.8 cm is < 50 msec, for 7.6 cm: 100 msec, 11.4 cm: 200 msec, and 15.2 cm: 300 msec.

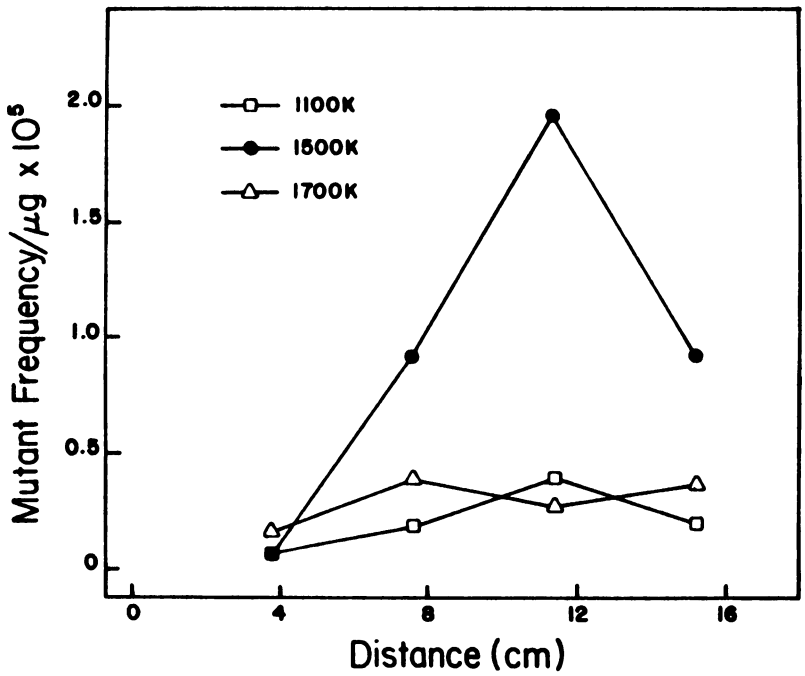

FIGURE 5. Specific mutagenic activity of methylene chloride extracts as a function of injector to collector distance.

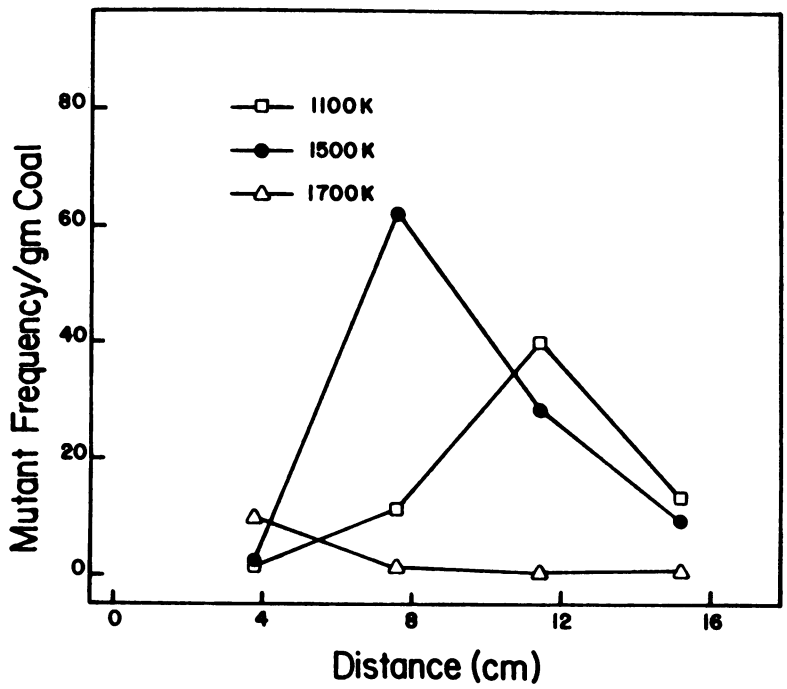

FIGURE 6. Total mutagenic activity per gram of coal injected as a function of injector to collector distance. These data were generated by multiplying the slopes in Fig. 5 by the yields per gram of coal in Fig. 4.

highly graphitized coal with little substitution, produces small quantities of barely active mutagenic material.

Pyrolysis Temperature and Time

Figure 1 shows that for all four coals (at a drop distance of 15.2 cm), specific mutagenicity exhibits a gradual rise then fall with increasing temperature, peaking near 1500K. Figures 2 and 3, however, reveal that the overriding effect of extractable organic yield, which peaks at a lower temperature of 1300K, causes the total mutagenicity to reach its highest value at the same temperature of 1300K. This behavior illustrates the importance of the competition between formation and destruction reactions of the aromatics. Between 900K and 1300K, the mutagen formation reactions predominate. At temperatures higher than 1300K, the destruction reactions prevail, but these reactions show slight partiality to the nonmutagenic species since total mutagenicity does not drop quite as steeply as yield.

Figures 4 through 6 display the influence of temperature and drop distance on the mutagenicities and yield of the organics from the most mutagenically active coal, PSOC 997. Figure 5 shows the specific mutagenicity to be insensitive to residence time at the lowest and highest temperatures, 1100K and 1700K. Specific mutagenicity is much higher at 1500K, however, and peaks at an intermediate distance of 11.4 cm.

Yield behaves differently from mutagenicity, displaying peak values at successively shorter distances for successively higher temperatures. Because of its dominant effect, yield determines the shapes of the total mutagenicity curves in Figure 6. The huge specific mutagenicities of the 1500K samples, however, contribute somewhat to the large amplitude of the corresponding total mutagenicity curve.

Again, the conflicting influences of the mutagen formation and destruction reactions are evident. As demonstrated in Figure 6, at low temperature (1100K), formation reactions prevail, gradually producing more mutagenic species with longer time until 11.4 cm, when destruction reactions take over. A higher temperature (1500K) accelerates both formation and depletion reactions, so peak yield is seen at shorter distance (7.6 cm). At 1700K, reactions are so fast that formation of mutagens is almost instantaneous, and the dominant picture is one of destruction. Hence, total mutagenicities of the 1700K samples are essentially negligible.

Mutagens

A provocative feature of these data is the lack of correspondence between the temperature dependence of specific mutagenic activity (Fig. 1) and that of organic yield (Fig. 2). Peak specific mutagenic activity for subbituminous and high volatile bituminous coals was shifted to higher temperatures vs. peak organic yield. As a function of residence time, peak specific mutagenic activity (Fig. 5) appeared later than peak organic yield, at 1500K (Fig. 4).

These data support the notion that pyrolysis products undergo chemical transformations from relatively non-

mutagenic to more mutagenic species with increased residence time or temperature. The nature of these changes awaits the identification of the mutagens involved.

Conclusions

The mutagenicity of coal pyrolysis products depends on three factors: the chemical structure of the parent coal, pyrolysis temperature, and residence time, as a consequence of the differences in both specific mutagenicity of the pyrolysis products and their yields.

Total mutagenicity exhibits the following order with coal type: high volatile bituminous > subbituminous ≥ lignite >> anthracite. This order, which is similar to that of volatile matter in the parent coals, reflects the comparative yields of extractable material from the pyrolysis of these coals. Total mutagenicity peaks in a temperature range of 1300K to 1500K for all four coals and generally parallels the temperature and residence time trends of aromatic yield. Mutagens form faster and are destroyed faster at higher temperatures.

Specific mutagenicity varies with coal type and pyrolysis conditions, but differences exhibit only a secondary effect on total mutagenicity. Specific mutagenic activity reaches peak values at higher temperatures and longer residence times than does organic yield.

There is a competition between mutagen formation and mutagen destruction reactions that evinces itself in the residence time/temperature trends of total mutagenicity. Formation reactions prevail at low temperatures and short times; destruction reactions prevail at high temperatures and long times. The resulting products reflect the relative dominance of one set over the other.

This work was supported by the National Institute of Environmental Health Sciences Center Grant # NIH-2P30-ES02109-06A1 and National Institute of Environmental Health Sciences Program Project Grant # NIH-2P01-ES01640-06. We wish to thank Barbara Andon, Alexandra Hawiger, Joany Jackman, and Margarita Klibanov for carrying out the bioassays described here. The authors are grateful to the Pennsylvania State Coal Sample Bank, Pennsylvania State University, University Park, PA, for supplying the coals and their elemental analysis.

REFERENCES

1. Hoffman, D., and Wynder, E. L. Air Pollution, Volume II. Academic Press, New York, 1977.
2. Guerin, M. R. Polycyclic Hydrocarbons and Cancer. Academic Press, New York, 1978.
3. Lee, M. L., Prado, G. P., Howard, J. B., and Hites, R. A. Source identification of urban polycyclic aromatic hydrocarbons by gas chromatography mass spectrometry and high resolution mass spectrometry. Biomed. Mass Spectrom. 4: 182–186 (1977).
4. Seeling, M. G., and Benignus, E. L. Coal smoke soot and tumors of the lung in mice. Am. J. Cancer 28: 96–111 (1936).
5. Kennaway, E. L., and Kennaway, N. M. A further study of the incidence of cancer of the lung and larynx. Br. J. Cancer 1: 260–298 (1947).
6. Braun, A. G., Busby, Jr., W. F., Liber, H. L., and Thilly, W. G. Chemical and toxicological characterization of residential oil burner emissions: II. Mutagenic, tumorigenic and potential teratogenic activity. Environ. Health Perspect. 73: 235–246 (1987).
7. Farmayan, W. F., Toqan, M., Yu, T-U., Teare, J. D., and Beér, J. M. Reduction of NO_x emission from natural gas flames by staged fuel injection. 1985 Joint Symposium on Stationary Combustion NO_x Control, Boston, MA, 1985.
8. Badzioch, S., and Hawksley, P. B. W. Kinetics of thermal-decomposition of pulverized coal particles. Ind. Eng. Chem. Process. Des. Dev. 9: 52–57 (1970).
9. Kobayaski, H., Howard, J. B., and Sarofim, A. F. Coal devolitilization at high temperatures. In: Proceedings of the Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1977, pp. 411–425.
10. Nenniger, R. D. Aerosols Produced from Coal Pyrolysis. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1986.
11. Mitra, A., Bar-Ziv, E., and Sarofim, A. F. Evolution of polycyclic aromatic hydrocarbons during the pyrolysis of coal. Presented at the 8th International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October, 1983.
12. Mitra, A., Bar-Ziv, E., and Sarofim, A. F. The influence of coal type on the evolution of polycyclic aromatic hydrocarbons during coal devolitilization. Aeros. Sci. Tech., in press.
13. Skopek, T. R., Liber, H. L., Krolewski, J. J., and Thilly, W. G. Quantitative forward mutation assay in *Salmonella typhimurium* using 8-azaguanine resistance as a genetic marker. Proc. Natl. Acad. Sci. (U.S.) 75: 410–414 (1978).
14. Skopek, T. R., Liber, H. L., Kaden, D. A., and Thilly, W. G. Relative sensitivities of forward and reverse mutation assays in *Salmonella typhimurium*. Proc. Natl. Acad. Sci. (U.S.) 75: 4465–4469. (1978).