

COAL CONVERSION AT THE K/T BOUNDARY: REMNANTS OF THE HAZARDOUS WASTE

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Key Words: K/T transition, coal gasification, amino acids

ABSTRACT

The occurrence of large amounts of two nonprotein amino acids, aminobutyric acid (AIB) and isovaline (ISOVAL), in sediments near the Cretaceous/Tertiary (K/T) boundary was originally attributed to remnants of a bolide collision. However, these two amino acids are derived from the same two hydantoins that were isolated in large amounts from gasifier quench water, and we hypothesized that the K/T amino acids originated from a natural coal gasification process involving intrusion of magma into a coal seam. Condensation of the resulting gases, including carbon dioxide, ammonia, hydrogen cyanide, and ketones formed the hydantoin precursors for the amino acids. The K/T AIB/ISOVAL ratio corresponds to that observed for the corresponding hydantoins in gasifier quench water. The ratio of the ketones (acetone and 2-butanone) resulting from pyrolysis of a large variety of coals is also consistent with the AIB/ISOVAL ratio, although much larger amounts of the ketones are generated from low-rank coals.

INTRODUCTION

At the close of the Cretaceous Period, a large number of species became extinct, most noteworthy, the dinosaurs. Many theories have been suggested to explain the mass extinction at the Cretaceous/Tertiary (K/T) boundary, including climate and land mass changes as well as collisions with a massive extraterrestrial object (bolide). The occurrence of nonprotein amino acids in sediments deposited before and after the K/T boundary was interpreted as evidence for an extraterrestrial event (1). Recently I established that the assumptions that led to that conclusion were erroneous, and that a more likely explanation for the occurrence of the amino acids, aminoisobutyric acid (AIB) and isovaline (ISOVAL), is that they formed from hydrolysis of hydantoins that were produced from coal-derived gases (2). This hypothesis is based on the finding of large amounts of hydantoins, mainly 5,5-dimethylhydantoin (DMH) and 5-ethyl-5-methylhydantoin (EMH), in condensate water from a coal gasification facility (3,4). The two major hydantoins (DMH and EMH) were present in concentrations of about 2000 and 500 mg/L, respectively, in condensate water from gasification of Indian Head lignite (4). Numerous other 5-substituted hydantoins were also identified at concentrations an order of magnitude smaller (3). The two major hydantoins produced as by-products of coal gasification are in fact those that generate AIB and ISOVAL on hydrolysis. Thus the AIB and ISOVAL isolated from the sediment samples may very likely have resulted from natural thermal processing of terrestrial coal sources via hydantoin formation and subsequent hydrolysis.

The K/T transition was accompanied by extensive magmatic intrusions and volcanic activity. Magmatic intervention in a coal seam may have generated the gases that condensed and reacted to form large amounts of the hydantoins. Many examples of thermal magmatic decomposition of coal have been reported in

geological investigations of coals from various locations (5). In order to ascertain which intrusion sites might be candidates for the generation of the precursor components required for hydantoin synthesis, a relationship between the chemical evidence in the K/T or near K/T deposits and potential coal progenitors must be demonstrated. The purpose of this paper is to present data that relates to the issue of coal-derived precursors for the amino acids.

RESULTS AND DISCUSSION

The formation of hydantoins in the water from the slagging gasifier was demonstrated to have resulted from the complex Bucherer-Bergs reaction of ammonia, carbonate, hydrogen cyanide, and various ketones and aldehydes present in the gas cooling/condensing system (spray washer and tar-oil-water separator) of the gasifier and not from a high-temperature reaction in the gasifier itself (6,7). In the upper pyrolysis region of the slagging fixed-bed gasifier, hot gases produced in the high-temperature gasification zone heat the coal and release the ketones, as well as phenolics, alcohols, nitriles, and other volatile organic components. A large number of ketones are produced in coal pyrolysis, the major ones being acetone and 2-butanone, and these are present in significant concentrations in the condensate water, even after hydantoin formation has been completed (4). The ratio of acetone to 2-butanone was between 3 and 4 in the condensate water samples obtained from lignite (Indian Head, ND) gasification. This ratio corresponded closely to the DMH/EMH ratio observed in the condensate water. As much as 95% of the ketones were converted to hydantoins; but, in general, the limiting species in the Bucherer-Bergs reaction occurring in the condensate water is the hydrogen cyanide, owing to its lower solubility in water at the collection temperature. In the high-temperature gasification zone, ammonia and hydrogen cyanide are produced in about a 10 to 1 ratio (8). Carbon dioxide is generated by the reaction of oxygen with carbon in the hot zone and also by decarboxylation in the pyrolysis zone (in the case of low-rank coals).

If the AIB and ISOVAL in the K/T boundary sediments resulted from natural coal gasification via DMH and EMH, then the AIB/ISOVAL ratio should match the acetone/2-butanone ratio in the products from pyrolysis of the type of coal that was heated at the K/T transition. Pyrolysis products from a number of coal samples of different ranks were collected and analyzed in a pyrolysis/devolatilization project at the University of North Dakota Energy Research Center (9). Data from these analyses are given in Table 1. The ratio of acetone to 2-butanone from pyrolysis of the various coals is between 3 and 4 and is not rank dependent. The ratio of AIB to ISOVAL found in the sediment layers above and below the iridium layer at Stevns Klint was 3 and 4, respectively (1). This means that either a bituminous or lower rank coal could have been the source of the ketones which formed the amino acids found in the sediments.

A terrestrial coal source can account for production of a very large amount of amino acids. The total quantity of acetone and 2-butanone produced from coal pyrolysis is significantly large and is rank dependent (Table 1). Low-rank coals gave three times more ketones than bituminous coals. Thus the yield of hydantoins from 1 kg of lignite could have been as high as 4 g, if all the acetone and 2-butanone produced in pyrolysis were converted via a Bucherer-Bergs reaction in a condensed phase. Geothermal or volcanic gasification of a small coal seam of 1 km² by 10 m thickness could have generated 6×10^7 kg of hydantoins.

A possible mechanism for natural coal gasification is suggested here. Since a low-rank coal may contain as much as 40% water and a high percentage of oxygen that could be converted to carbon dioxide, a source of intense heat is the main requirement for pyrolytic generation of ammonia, hydrogen cyanide, ketones, and carbon dioxide, which are the precursors for the hydantoins. However, ground or stream water may have played a role in furnishing steam, which could have effectively driven the gasification, and also in furnishing a coolant for the gas produced, so that the condensed gases could react to form the hydantoins. A second possibility is discharge and collection of gases into natural water reservoirs overlying the magma intrusion into the coal seam. Hydrolysis of hydantoins to the amino acids may have been microbially catalyzed or may have occurred over a long time period. Utilization of the 2-substituted amino acids by microorganisms is not likely, resulting in high stability for these compounds. Actually, the method for analysis of the sediments involved conditions that may have hydrolyzed hydantoins to the amino acids; therefore, we cannot rule out their existence in the sediments.

The location and extent of the natural coal gasification promises to be as interesting as the search for the alleged bolide collision site has been. One very important fact must be considered. Whereas the iridium anomaly specifically requires a mantle type of volcanic activity (or bolide), any kind of volcanic or magmatic intrusion into a coal field could have been responsible for the amino acid anomaly. Evidence was recently presented for a tectonic uplifting activity (10) and mantle hot-spot doming in the North Atlantic at the K/T transition (11). Alternatively the magmatic event may have been associated with the North American Laramide magmatic trend, such as the Raton, Colorado, area, where large quantities of char were observed (5). Natural coal gasification may have occurred in several localities, since coal deposits as well as geothermal activity were plentiful in the northern hemisphere.

Natural coal gasification may be only indirectly related to the extinctions that occurred at the K/T transition through volcanism or magmatic intrusions that accompanied a general climatic or sea level change scenario. The complex sequence of extinctions related to volcanism, sea level changes, and other global trends was recently reviewed by Officer (12). There is also a possibility that coal gasification may be related to extinctions during a period of intense volcanic activity. Drawing from the Lake Nyos disaster which involved conversion of a relatively small amount of carbon and evolution as carbon dioxide, we could speculate on another possible relationship. Many of the compounds generated as a result of coal gasification are highly toxic. Besides the ammonia and hydrogen cyanide discussed above, hydrogen sulfide is produced in copious amounts; however, the major component of coal gas by weight is carbon monoxide. Toxic compounds such as phenols and carcinogens such as polynuclear aromatics and amines are also formed. Hydantoins are well known as hypnotics and suspected carcinogens. Many of the organic products would have persisted for a long time. Thus the toxicity of coal gasification gases or other products may offer an alternative explanation for some of the extinctions that occurred in this period.

Table 1 Yields of Ketones (micrograms/gram maf coal) from Pyrolysis of Coals

Coal	%C maf	%O (dif.)	Acetone	2-Butanone
Gascoyne Blue	59.8	32	1600	510
Center	70.0	23	1480	440
Indian Head	72.0	22	1420	400
Rosebud	76.3	16	930	320
Sufco	79.2	14	750	250
Illinois #6	77.2	11	500	120

Pyrolysis conditions were the following: heating rate of 45°C/min, max. 850°C, helium atmosphere, -60-mesh particle size, 5-g sample size (9).

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