

PHOTOCHEMICAL H ATOMS AS A STRUCTURAL PROBE
OF THE SURFACE OF COAL¹

by

Gilbert J. Mains, Muthu Sp. Sundaram and Joseph Solomon²
Department of Chemistry
Oklahoma State University
Stillwater, Oklahoma 74074

ABSTRACT

Hydrogen atoms, produced by the mercury photosensitization of H₂, were made to interact with coal dust, -53 to +38 microns, at 200°C in a flow reactor. Illinois No. 6, Pittsburgh Seam, and Utah-Emery coals produced a large number of products in the C₂ to C₈ range. Wyoming-Wyodak coal was considerably less reactive. The kinetic, quantitative, and structural implications of these results are discussed. Experimentation with different reactor conditions continues.

INTRODUCTION

Considerable interest in the interaction of hydrogen atoms with coal surfaces has been evident for over twenty-five years,³ resulting in a review of the literature⁴ in 1965 and recent research by N. Berkowitz, et al.⁵⁻⁶ Despite this intense interest the data are conflicting, and range all the way from reports of no reaction at ambient temperature to complete gasification. Some of these discrepancies arise from the discharge technique used to generate the H atoms; coal dust probably found its way into the discharge itself in some instances. Photochemical production of H atoms was mentioned and dismissed as being too inefficient.⁴ Because of the experimental discrepancies and their probable cause, the system H · atoms + coal was reinvestigated with photochemically generated H atoms.

EXPERIMENTAL

In work reported elsewhere in this symposium it was found that cryo-crushing was the grinding method of choice if the surface of the coal was to represent bulk coal more accurately. The grinding techniques are reported elsewhere⁷ and will not be described here. The bituminous coals

¹Based in part on data to be submitted by Muthu Sp. Sundaram as a Ph.D. Dissertation.

²On sabbatical leave, Philadelphia College of Pharmacy and Science, Philadelphia, Pa.

³V. J. Avareenko, J. Phys. Chem. (U.S.S.R) 20, 1299 (1946).

⁴F. T. Pinchin, Brit. Coal Util. Res. Assoc., Monthly Bulletin, 29, 105 (1965).

⁵Y. Sanada and N. Berkowitz, Fuel, 48, 375 (1969).

⁶K. Kobayashi and N. Berkowitz, Fuel, 50, 254 (1971).

⁷J. A. Solomon and G. J. Mains, Fuel, (accepted for publication, 1977).

were dried at 200°C in an oven through which N₂ gas was passed continuously. The sub-bituminous Wyoming-Wyodak coal was dried in a vacuum oven at 100°C. Illinois No. 6, Pittsburgh Seam, Utah-Emery, and Wyodak coal samples were then cryocrushed, sieved, and stored in a nitrogen environment. Only the -53/+38 micron fractions were used in these studies.

Fifteen grams of coal were mixed with an equal weight of ground glass, +50 micron sizes, and placed on a frit, F₁, Figure 1, for dispersal in the quartz reactor. The mercury saturator was heated to near 100°C and ambient condenser water used to produce saturation. The reactor walls were heated by passing current through the nichrome heaters. The six, meter-long, germicidal lamps, 36 watts each, were cooled with rapidly flowing, filtered air and turned on. Next, a stream of H₂ sufficient to disperse the coal dust (about 300 liters/min) was initiated. Traps T₁ and T₂, packed with 1/4" glass beads, were precooled in liquid nitrogen for ninety minutes before the experiment and were by-passed initially. When the temperature in the quartz reactor reached 200°C, the liquid-N₂-cooled traps were opened and the gas by-pass closed. Throughout this period and the remainder of the experiment, the finer coal dust, which tended to accumulate on the Millipore filter, F₄ on Figure 1, was recycled using a mechanical vibrator. At the end of an hour, during which the temperature sometimes dropped as low as 185°C, the flow was discontinued and the traps were isolated for analyses.

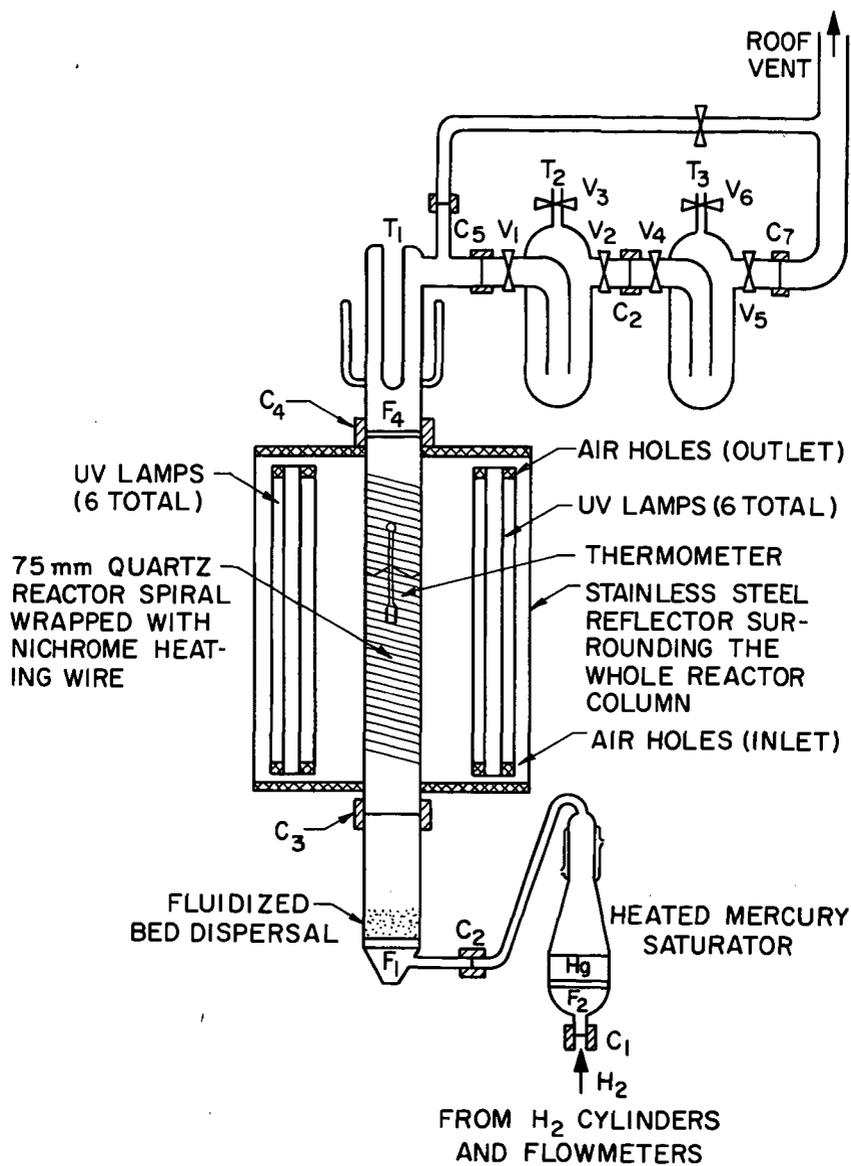
In the actinometry experiments, the identical procedure was followed except that the coal was omitted and the carrier gas contained 2% ethylene.

The traps were disconnected from the apparatus and the excess H₂ was pumped away at liquid nitrogen temperature. The residual gases, after the traps were warmed to ambient temperature for several hours, were sampled with a 25-cc sample loop and injected on to a gas chromatographic column at 60°C, 1/8" x 10', packed with n-C₁₈/Porasil C, in a Perkin-Elmer Model 990 gas chromatograph equipped with a thermal conductivity detector using 8% H₂ in He carrier gas. The resultant gas chromatograms are reproduced in Figures 2 through 5, inclusive.

RESULTS AND DISCUSSION

Because the vapor pressure of Hg was high, probably near a millitorr, most of the 2537A resonance radiation was absorbed within 0.2 cm of the quartz wall. However, the resultant excited ³P₁ Hg atoms, τ₀ ≈ 10⁻⁷ sec, were essentially completely quenched by the atmosphere of H₂ and thus generated two H atoms per photon in this 240 cm³ zone. The extent to which the rapidly moving H atoms attained a uniform concentration throughout the vessel is not known, nor is the rate at which they were removed at the quartz reactor surface by recombination. When 2% ethylene was added to the flow stream in the absence of coal and the resultant butane, ethane, ethylene mixture analyzed, a rate of H atom formation of 2.90 x 10¹⁸ atoms/sec in the reactor was indicated. If these were uniformly distributed, 5.4 x 10¹⁴ atoms/cc/sec was the stationary state rate of hydrogen atom production and an overall steady state concentration of about 2 x 10¹³ H atoms/cm³ can be calculated, which compares well with those generated by discharge techniques.

Although no coal dust deposited on the walls of the quartz reactor, it did collect on the pyrex thermometer, the Millipore filter paper, F₄, and in the lower un-irradiated zone. This deposition precluded a quantitative



THE PHOTOREACTOR

Figure 1

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF ILLINOIS NO. 6 COAL

AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

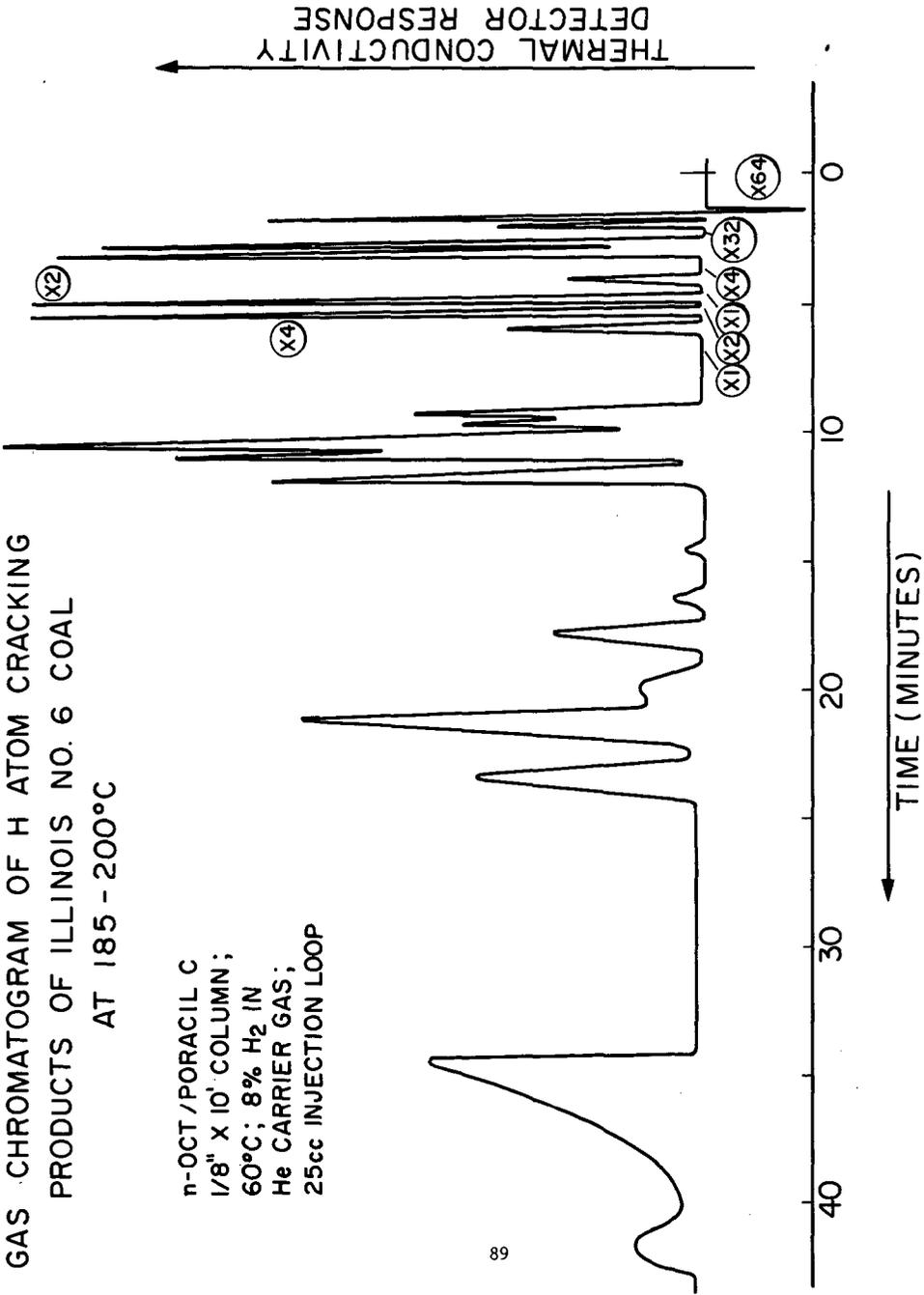
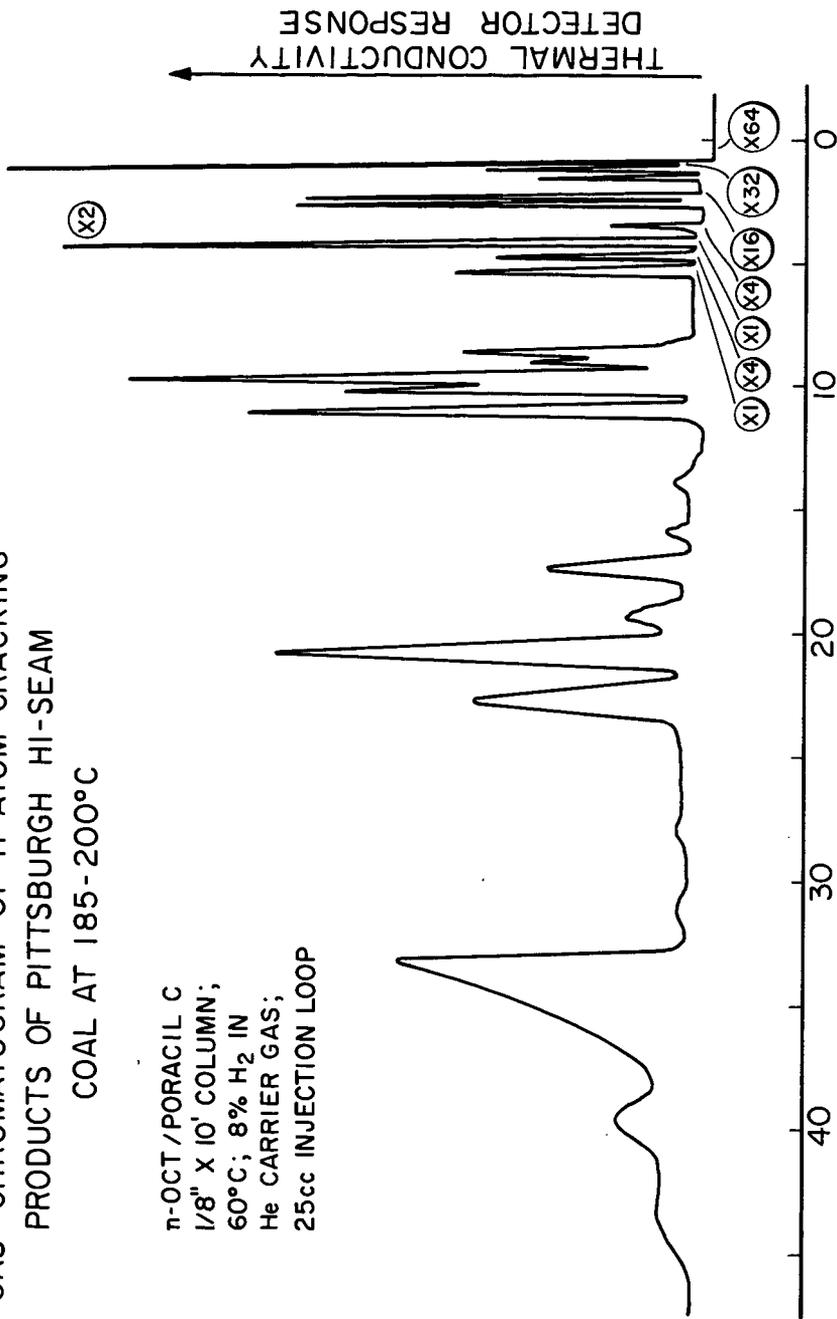


Figure 2

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF PITTSBURGH HI-SEAM
COAL AT 185-200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP



TIME (MINUTES)

Figure 3

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF EMERY-UTAH COAL
AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

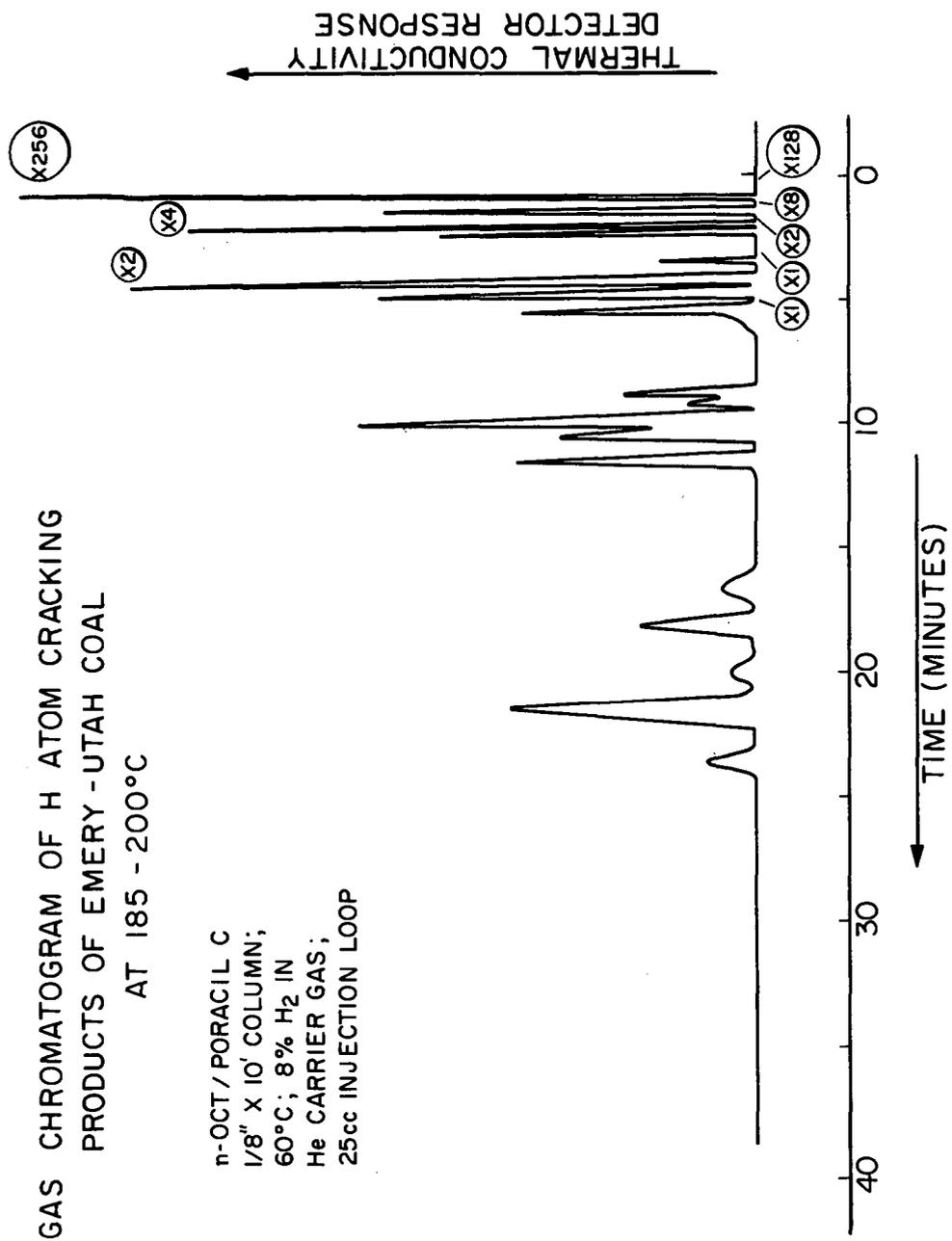


Figure 4

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF WYOMING-WYODAK COAL
AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

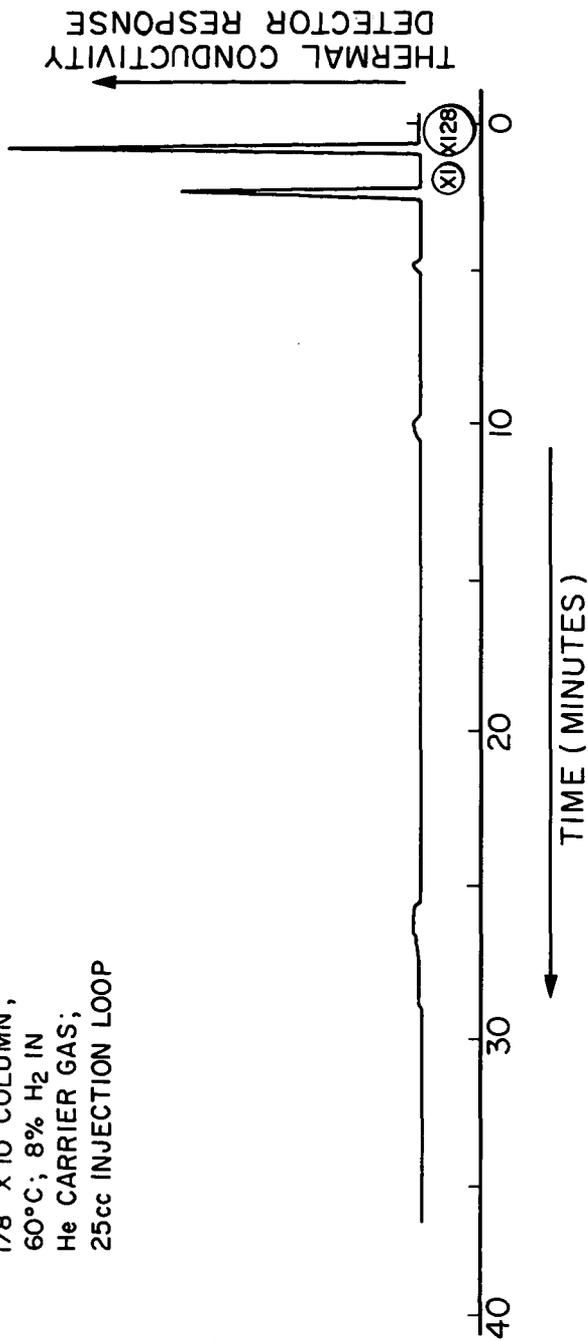


Figure 5

determination of the particle concentration. Swirling coal dust in the reactor zone is visible to acute eyes and is inferred readily by light scattering when He-Ne laser beam is directed through the reactor. A coarse (and, probably, high) estimate of the particle concentration can be made if one assumes that 0.01% of the coal is dispersed in the flowing H₂ at any given time; making this admittedly poor assumption, we calculate 6 x 10⁶ coal particles/cc in the reactor. This suggests about Avogadro's Number of collisions per second between atomic H and coal dust, and the yields suggested in Figures 2 to 4 are consistent with the formation of 10¹⁴-10¹⁵ product molecules per second. This suggests a collision efficiency of the order of 10⁻⁹ to 10⁻⁸ which is below the 10⁻⁷ value observed by Snelson⁸ for graphite; the estimated coal particle concentration must be far too high and/or the profile of atomic hydrogen not uniform across the reactor. Based on the overall product yield estimates and the actinometry for the entire reactor, the product efficiency per hydrogen atom must be in the 10⁻² to 10⁻³ range. Clearly, further experimentation, especially product identity and quantification, is required to decrease the uncertainty in the yield per H atom.

Examination of Figures 2, 3, and 4 shows that the gas chromatographic traces are extremely similar for the hydrogenation products from Illinois No. 6, Pittsburgh Seam, and Utah-Emery coals. Although all three are indeed bituminous coals, they are physically very different and one would be surprised if they had identical surface compositions. The "fingerprints" do show subtle differences, but in view of the uncertainties just discussed, one is struck more by their similarity than anything else. (At this writing, only a few of the peaks have been identified. It is hoped that GC-MS identification will be made on every peak this summer.) Either the surface structures which can be "cracked off" by H atoms at 185°-200°C are the same for these three coals or all the products represented by peaks have common precursors which are liberated from the coals in the experiment, e.g., BTX and naphthalenes. Worth mentioning is one experiment in which He carrier gas was used instead of H₂. Only very small yields of benzene (20 minute elution time) and the product with 35-minute retention time were found in the traps, presumably photo-detached from the coal surface. The yields were far too small to account for all the other products by hydrogen atom cracking of these compounds. Blank experiments using H₂ but leaving the ultraviolet lights off gave no detectable products in an hour. While considerable experimentation remains to be done, the similarity of the products from the three bituminous coals suggest the following mechanism:



⁸A. Snelson, A.C.S. Div. Fuel Chem. Proc. 18, 101 (1973).

In other words, the similarity of the product distributions from the different bituminous coals is proposed to be a result of the similarity of secondary H atom cracking of the product precursors from reaction (3) under the identical reactor conditions, rather than an indication that these three coals, with different histories and different physical properties, have surfaces that are similar. At this point, the only likeness in surface that can be inferred is the ability of H atoms to liberate the hydrogenation precursors from the surface of Illinois #6, Pittsburgh Hi-Seam, and Utah-Emery bituminous coals. Reaction (3) must be similar in rate and reaction products to account for the similarity of Figures 2, 3, and 4. Kinetic information about reaction (4) is appearing⁹⁻¹⁰ and should aid in the interpretation of future experiments involving more uniform concentrations.

Finally, the failure of Wyoming-Wyodak coal to react under identical conditions must be attributed to a slowness of reaction (3). A greater diversity of products from a sub-bituminous coal might have been expected since its organic structures had been subjected to less stringent coalification conditions. Since Figure 5 looks remarkably similar to results from experiments early in this program using Illinois #6 coal at ambient temperature, one might expect a greatly enhanced ESR spectrum such as was observed then. That is, a result of H atom bombardment is the production of nonvolatile free radicals. Further work is clearly warranted.

Nonetheless, it has now been demonstrated that photo-produced H atoms do interact with the surface of bituminous coals at 200°C to yield C₂ to C₈ hydrocarbons. However, the authors feel that further experiments, some altering the steady state H atom concentration and adding suspected precursors, are required to elucidate the mechanisms. Also, an accurate method for determining coal particle concentrations in the photoreactor needs to be found before reliable rate data can be forthcoming. Finally, other sub-bituminous coals need to be examined to see if the Wyodak results, reproduced several times, are common to this rank of coal. Whether H atoms will prove an effective coal surface probe remains to be proven. These preliminary results are encouraging in some respects.

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- ⁹P. Kim, J. Lee, R. Bonnano and R. Timmons, J. Chem. Phys., 59, 4593 (1973).
¹⁰A. Amano, O. Horie, and W. Hanh, Int. J. Chem. Kinetics 8, 321 (1976).