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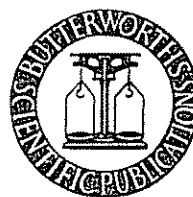
The Radiation Chemistry of Bituminous Coals in Various Atmospheres

A. Weinstein, F. Rusinko, Jr and P. L. Walker, Jr

The radiolysis of selected bituminous coals in vacuo and the reactions of the coals with oxygen, air and nitrogen in the presence of gamma and fast neutron radiation were studied. The only detectable products of radiolysis of the coals at 3.5×10^8 rads dosage were hydrogen, methane and perhaps traces of ethane. A mechanism is proposed to account for the production of hydrogen and methane. The yields of carbon oxides per unit of oxygen adsorbed by the coals irradiated in oxygen were little different from the corresponding yields for coals oxidized in the absence of radiation. The rates of desorption of adsorbed oxygen were also little affected by radiation. Radiation increased the rate of oxidation of at least one of the coals studied. All of the coals reacted with nitrogen in the presence of radiation. A mechanism is proposed for the non-radiative oxidation of the coals. There were no significant differences in the Gieseler fluidities of the irradiated and un-irradiated coals. There were also no significant differences in the rates of gas evolution or in the types of gas and coke produced by 850°C carbonization of the irradiated and un-irradiated coals.

THE effect of radiation on coal has only recently received attention. I. A. BREGER and co-workers showed that coals of various ranks were dehydrogenated[1] and probably also polymerized[2, 3] when subjected to irradiation by neutrons and alpha particles. S. ERGUN, W. F. DONALDSON and I. A. BREGER[4] suggested, from their study of uranium-bearing coalified logs, that alpha-irradiation of coal caused crosslinking of alicyclic units rather than aromatization. R. A. FRIEDEL and I. A. BREGER[3] found that the free-radical concentrations of several coals below 83 per cent carbon (moisture- and ash-free basis) were not affected significantly by nuclear reactor irradiation but that those of two coals having 89 per cent and 91 per cent carbon increased with such treatment. R. McBRIAN[5] found that the size of bituminous coal particles was reduced when the particles were irradiated in a nuclear reactor. B. I. LOSEV and co-workers[6] noted that the cobalt-60 irradiation of coals of various ranks increased the solubility of the coals in carbon tetrachloride.

No information regarding the amounts of kinds of gases liberated during irradiation of coal has been published. This information should give a clearer indication of the chemical changes occurring than ultimate analyses. Consequently, an investigation of the gases produced from selected evacuated bituminous coals as a result of gamma and fast neutron radiation was undertaken. The rates and type of gas evolved from the evacuated coals in the absence of radiation were also investigated for comparative purposes.

The effects of the presence of air, oxygen and nitrogen on the radiolyses of the coals were also of interest. In addition to studies with these gases, a comparative kinetic investigation of the oxidation of the coals in the absence of radiation was performed.

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The effect of radiation on the physical and carbonizing properties of the coals was examined after the coals had been irradiated. This contrasts with the techniques reported in a previous paper[7], in which the effects of irradiating coals during carbonization are described.

EXPERIMENTAL

Four coals (one medium volatile and three volatile A) were studied. The source, proximate and ultimate analyses for coals 167, 169, and D are given in a previous paper[7]. Coal A-A was taken from the same seam as coal A in the previous paper but at a later date. Its proximate analysis was essentially identical with that of coal A. Its ultimate analysis (on an ash-free basis) was N 2·1, S 2·0, H 5·3, C 81·0 and O 9·6 per cent.

The coals were ground to −40 mesh (U.S.) in air and were immediately evacuated at room temperature for two days. The coals were then stored under nitrogen until used.

The cylindrical Pyrex containers used to hold samples had volumes of about 100 ml and possessed two stems. One of these stems was open and partly constricted. The other stem was closed by a break-off seal.

A 35 g sample of coal was introduced into a vacuum-dried and tared container through the constricted stem. The stem was cleaned and a plug of glass wool was inserted just below the constriction. The container was then
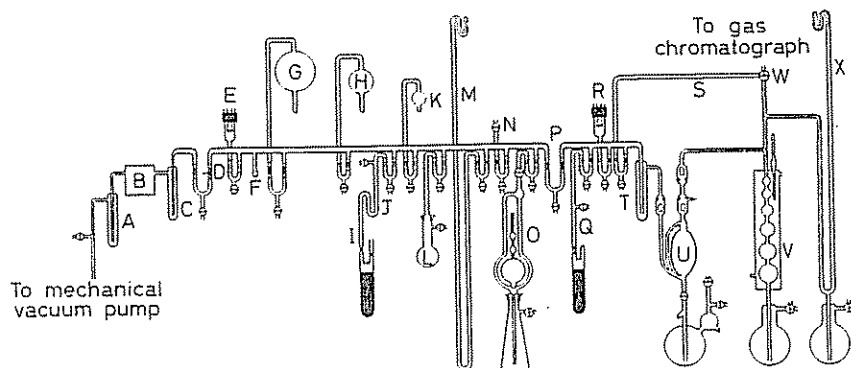

Figure 1. Diagram of vacuum line. A Trap, B Mercury diffusion pump, C Trap, D Stock valve, E Thermocouple gauge tube, F Freeze-out trap, G Flask, 2 l., H Flask, 500 ml, I Sample tube side arm, J Trap, K Flask, 100 ml, L Ammonia flask, M Mercury manometer, N Gas-introducing side arm, O McLeod gauge, P Stock valve, Q Sample tube side arm, R Thermocouple gauge tube, S Side arm, T Trap, U Toepler pump, V Gasometer, W Three-way vacuum stopcock, X Mercury manometer

sealed via the stem on to the vacuum line depicted in Figure 1. The sealing operation was performed at side arm I in the manner shown.

For the vacuum radiolysis experiments, each container and its contents were evacuated for 22 or 46 hours. The container was then sealed at the constriction. It was irradiated together with six other containers in the Pennsylvania State University Nuclear Reactor for 16 h 40 min at a power level of 100 kW. Slow neutron flux into the samples was virtually eliminated

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by using a cadmium shield. The energy absorbed by the coals corresponded to about 3.2×10^8 rads of gamma radiation and 0.3×10^8 rads of fast neutrons[8]. The irradiation temperature was about 45°C.

For the radiolysis experiments with various gases, each sample container was evacuated for 22 hours as before. A measured quantity of oxygen, nitrogen or laboratory air was then introduced into the container via dry ice–acetone refrigerated trap J. The air was passed through Ascarite and Drierite before use. The oxygen used contained 0.1 per cent nitrogen as the only detectable impurity, and the nitrogen used contained 0.09 per cent oxygen. After preparation, these samples were irradiated under conditions similar to the vacuum radiolysis experiments.

For the experiments in the absence of radiation, evacuated and oxygen-containing samples were prepared by the same procedures. The samples were permitted to stand at 24° ± 3°C for periods up to 60 days. Several other evacuated and oxygen-containing samples were subjected to the following cycle of successive temperatures: 31 h at 24°C, 16 h and 40 min at 45°C, and finally 192 h and 20 min at 24°C. The total elapsed time was 10 days. This procedure was designed so that the effect of the estimated 45°C reactor operating temperature on the oxidations could be investigated.

The gases in the sample containers after treatment were analysed as follows: Each container was sealed on to the vacuum line at side arm Q in *Figure 1* via the break seal. The gases were pumped from the sample with Toepler pump U for $1\frac{1}{2}$ h. At the end of this time, the pumping rate was negligible. The gases were separated by means of liquid nitrogen and dry ice–acetone traps into three fractions. The first, containing hydrogen, oxygen, nitrogen, methane and carbon monoxide, was analysed with a 15 ft No. 5A molecular sieve column (Linde Air Products Co.) and argon carrier gas at room temperature, using a gas chromatograph described elsewhere[9]. When necessary, carbon monoxide was determined with a 6 ft silica gel column and helium carrier gas at room temperature[10].

The composition of the second fraction, which contained ethane and carbon dioxide, was determined using a 6 ft silica gel column and helium carrier gas at room temperature. The amount of this and of the previous fraction were determined in gasometer V. No other gases were detected.

The amount of the third fraction (water) was determined manometrically in a calibrated section of the vacuum line. Care was taken to ensure that the measuring pressure did not exceed the vapour pressure of water. Gas chromatographic analysis of several of these water fractions showed that no other substances were present in detectable quantities.

The Gieseler fluidities[11], BET surface areas and x-ray diffraction patterns of both the irradiated and un-irradiated coals were obtained. In addition, separate samples of the coals were coked in a quartz tube furnace to 850°C at a heating rate of 6°C/min. The rates of gas formation were measured, and the composition of the gas was determined at intervals with a gas chromatograph and with suitable absorbing fluids. The BET surface areas and x-ray

Table 1. Yields of gases from coals irradiated in oxygen and in vacuo

Initial conditions		Amounts of gases found after sample irradiation, ml (s.t.p.)								Time between preparation and irradiation of sample, days	Total time between preparation and analysis of sample, days
Time evacuated h	Amount of oxygen introduced, ml (s.t.p.)	H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O		
Coal No. 167											
22	0	2·00	0	0·039	0·041	0·011	T*	0·085	5·14	10	39
46	0	1·49	0	0·021	0·036	0	T	0·066	2·17	8	42
22	3·77	1·75	0	0·062	0·040	0	T	0·19	15·8	10	40
22	10·41	1·69	0	0·072	0·043	0·073	T	0·36	2·11	14	42
22	25·32	3·16	0	0·098	0·064	0·26	T	0·80	2·28	18	45
Coal No. 169											
22	0	3·40	0	0·11	0·051	0·012	0·11	0·19	7·20	13	40
46	0	3·05	0	0·052	0·045	0·015	0·090	0·19	7·82	8	38
22	3·50	3·31	0	0·23	0·051	0·035	0·099	0·32	21·5	12	40
22	9·38	3·09	0	0·23	0·054	0·091	0·098	0·50	7·57	13	43
22	23·62	5·46	0	0·24	0·080	0·25	0·060	0·96	8·78	11	41
Coal No. A-A											
22	0	7·79	0	0·17	0·16	0·080	0·011	0·44	2·62	36	67
46	0	7·16	0	0·040	0·13	0·068	0·011	0·40	4·44	34	66
22	2·68	6·31	0	0·19	0·095	0·10	0·009	0·62	7·62	32	54
22	11·85	7·01	0	0·18	0·11	0·16	0·009	0·79	3·80	14	37
22	25·04	7·07	0	0·21	0·11	0·26	0·009	1·13	6·08	21	43
Coal No. D											
22	0	4·72	0	0·17	0·093	0·13	0·052	0·62	0·79	11	41
46	0	2·53	0	0·048	0·049	0·084	0·059	0·49	3·20	9	43
22	3·76	4·85	0	0·15	0·088	0·14	0·059	0·69	4·36	25	55
22	10·59	4·78	0	0·21	0·079	0·23	0·048	0·94	5·31	25	55
22	21·80	5·20	0	0·20	0·088	0·43	0·047	1·28	11·0	17	51

* T indicates a trace (<0·003 ml of ethane at s.t.p.).

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diffraction patterns of the cokes produced were also examined, as were the reactivities of the cokes in air at 400°C.

RESULTS

The yields of gases from the oxygen- and vacuum-irradiated coals are shown in *Table 1*. Duplicates were run only for the samples to which oxygen had been added. The mean of the average deviations of the results was about 25 per cent.

The ratios of the yield of methane to that of hydrogen were approximately constant for each coal regardless of treatment. The average values of these ratios were 0·022, 0·016, 0·015 and 0·018 for coals 167, 169, A-A and D, respectively. The yields of ethane were more constant than those of methane but, unlike the latter, could not be correlated with hydrogen yields. Since oxygen did not affect these yields, oxidative side reactions were negligible.

The time of evacuation affected only the nitrogen yields in a consistent and marked manner. Longer evacuation reduced the nitrogen yield by 50 to 75 per cent. This was the first indication that the nitrogen was residual and was not formed by radiolysis of the coal. With coal 167, the amounts of nitrogen were small enough to be influenced by the nitrogen present as an impurity in the added oxygen.

The yields of carbon oxides increased approximately linearly with increase in the amount of oxygen added. The ratios of carbon dioxide to carbon monoxide fell in the range of about 2:1 to 4:1.

Much more difficulty was experienced with the reproducibility of the water determinations than with that of the other gases. This was probably due to the adsorption of water by the coals during their introduction into containers. Despite the poor reproducibility, two conclusions could be reached. First, the complete lack of correlation between the hydrogen and water yields indicated that hydrogen was not produced in any significant quantities by radiolysis of water. Secondly, a rough material balance showed that most of the oxygen added to the coals became adsorbed on the surface, even assuming that all of the water originated from the oxygen added.

The results of allowing evacuated 35 g coal samples to stand at room temperature for various times are shown in *Table 2*. Comparison of these results with those for the 22 h vacuum-irradiated samples in *Table 1* permitted the conclusion to be drawn that only hydrogen and methane were products of coal radiolysis *in vacuo*, for the following reasons.

First, hydrogen was found only in trace quantities* with the un-irradiated and evacuated coals and in thousandfold greater quantities with the vacuum-irradiated coals. This great increase could only be ascribed to the production of hydrogen from the coal itself. This was not surprising, since all organic materials containing hydrogen liberate this gas in varying quantities when

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* These quantities of hydrogen (<0·004 ml at s.t.p.) may have been residual or may have been formed by carbonization of the coal particles which clung inside the neck of the containers. These particles could not be completely removed after introduction of the coal samples into the containers, and were carbonized during sealing of the neck.

they are irradiated[12]. The G values for hydrogen, defined as the number of hydrogen molecules produced per 100 eV (1.6×10^{-10} erg) of energy absorbed, were in the range of 0.005 to 0.03. Methane was also found in much larger quantities with the irradiated samples and could therefore also be described as a radiolysis product.

Table 2. Rates of gas release from evacuated coals at 24°C in the absence of radiation

Time days*	Amounts of gases found at stated time, ml (s.t.p.)							
	H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O
	Coal No. 167							
10	0†	0	0.037	0	T‡	0	0.026	0.92
30	0	0	0.045	0	0	0	0.045	2.58
60	0	0	0.037	0	0.015	0	0.088	1.40
	Coal No. 169							
10	0	0	0.20	0	T	0.061	0.065	4.18
30	0	0	0.19	0	T	0.033	0.091	5.10
60	0	0	0.18	T	T	0.095	0.22	4.59
	Coal No. A-A							
10	0	0	0.19	0	T	T	0.068	6.09
30	0	0	0.18	0	0.028	T	0.13	2.04
60	0	0	0.065	T	0.056	T	0.30	3.88
	Coal No. D							
10	0	0	0.12	0	0.015	0.030	0.10	4.78
30	0	0	0.17	0.0095	0.025	0.068	0.20	3.61
60	0	0	0.13	T	0.048	0.040	0.29	3.07

* Samples were evacuated for 22 h, sealed *in vacuo*, and then permitted to stand at room temperature for the stated time.
† Hydrogen was found in most of these samples in quantities not exceeding 0.004 ml (s.t.p.). The presence of this hydrogen was felt to be due to the procedure used in sealing the sample containers (see text).
‡ T indicates a trace (<0.005 ml of carbon monoxide or <0.003 ml of methane or ethane at s.t.p.).

The yields of nitrogen and ethane were approximately the same for the irradiated and un-irradiated samples. With coals 167 and A-A, the yields of ethane were somewhat higher for the irradiated samples. However, the amounts of ethane observed were so close to the detection limit of the chromatograph that it was impossible to decide whether the differences were significant. If ethane was produced by radiolysis, it was produced in much smaller quantities than were observed either for hydrogen or methane.

The yields of the carbon oxides liberated from the evacuated coals were time-dependent. This dependency is shown to be approximately linear in *Figures 2* and *3*. The amounts of carbon monoxide found for coals 167 and 169 were too close to the detection limits to afford results which could be plotted. It did not seem likely that this time-dependency was due to the slow diffusion of the carbon oxides from the pore systems of the coals, since large molecules such as ethane reached diffusive equilibrium in equal periods of time. It was reasonable to conclude that the time-dependency was due to the reactions:

$$C(O_2) \rightarrow CO_2 \qquad \dots\, [1]$$

$$C(O) \rightarrow CO \qquad \dots\, [2]$$

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These reactions indicated conversion of the adsorbed oxygen into the gaseous oxides. This adsorbed oxygen was present because the coals had been ground in air.

The approximate linearity of the curves in *Figures 2* and *3* indicated a reaction order close to zero. Since the lines converged at or near the origin, it could also be deduced that the amounts of the residual carbon oxides (the amounts not removed by pumping) were small.
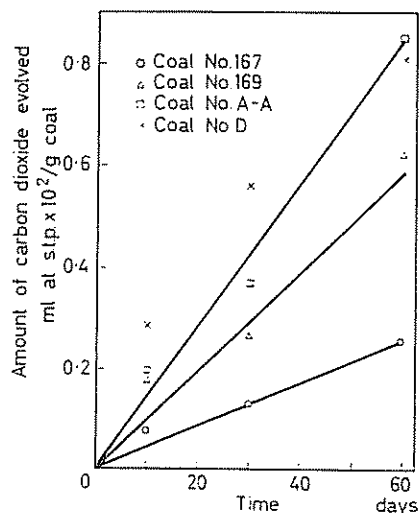

Figure 2. Rates of carbon dioxide release from evacuated coals at 24°C in the absence of radiation
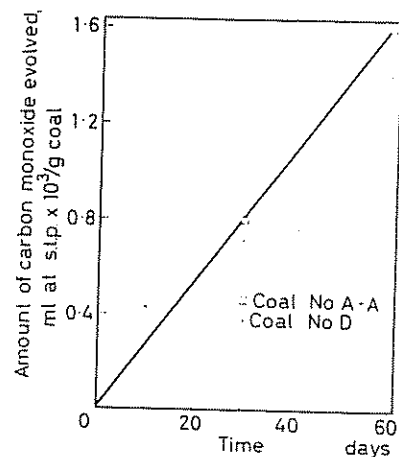
Figure 3. Rates of carbon monoxide release from evacuated coals at 24°C in the absence of radiation

Finally, comparison of the yields of carbon oxides in *Table 2* with the corresponding 22 h vacuum-irradiated samples in *Table 1* revealed the latter to be somewhat higher. For example, in *Table 1*, 0·085 ml of carbon dioxide was obtained for the vacuum-irradiated sample of coal 167. This amount was found after 39 days after preparation of the sample. Reference to *Table 2* revealed that the amount of carbon dioxide found after 39 days should have been *ca.* 0·058 ml. This small difference was probably due to the higher temperature seen by the sample in the reactor, rather than radiation, as will be shown later.

Table 3 lists the results of the non-radiative kinetic studies of the oxidation of coals 167, 169 and A-A. A more extensive study was undertaken with coal D, and these results are listed separately in *Table 4*. All of the coals reacted relatively rapidly with oxygen. This point had an important bearing on the results with the coals irradiated in oxygen. These coals (*Table 1*) had been held at room temperature for periods of 8 to 34 days before being irradiated, which had been necessitated by reactor time schedules. In these periods of time, many of the samples had reacted with all of the oxygen present. The rate of oxidation of coal 167, at least, was increased in the presence of radiation (compare *Tables 1* and *3*).

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Table 3. *Kinetic data and gas yields for the oxidation of coals 167, 169 and A-A at 24°C in the absence of radiation*

Amount of oxygen introduced*, ml (s.t.p.)	Oxidation time, days	Amounts of gases found at stated time, ml (s.t.p.)							
		H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O
					Coal No. 167				
11·09	10	0†	7·69	0·060	T‡	§	T‡	0·10	1·50
11·69	30	0	6·18	0·079	0	0·094	T	0·19	3·14
12·18	60	0	1·79	0·080	0	0·15	0	0·43	1·79
					Coal No. 169				
11·52	10	0	1·67	0·20	0	0·13	0·042	0·24	1·66
12·43	30	0	0	0·25	0	0·17	0·034	0·36	4·00
9·89	60	0	0	0·19	T	0·15	0·038	0·41	4·36
					Coal No. A-A				
11·96	10	0	1·35	0·23	0	0·12	T	0·23	5·92
11·34	30	0	0	0·19	0	0·14	T	0·36	6·36
12·25	60	0	0	0·18	0·0075	0·17	T	0·51	5·14

Table 4. *Kinetic data and gas yields for the oxidation of coal D at 24°C in the absence of radiation*

Amount of oxygen introduced*, ml (s.t.p.)	Oxidation time, days	Amounts of gases found at stated time, ml (s.t.p.)							
		H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O
4·34	10	0†	1·09	0·17	0	0·078	0·033	0·19	6·99
11·49	10	0	5·45	0·20	0	0·11	0·031	0·24	3·52
23·30	10	0	15·22	0·22	0	0·17	0·031	0·33	4·38
3·67	30	0	0	0·21	T‡	0·087	0·023	0·27	2·78
10·93	30	0	1·28	0·26	T	0·18	0·023	0·42	5·10
23·00	30	0	6·80	0·22	T	0·25	0·021	0·58	5·33
3·51	60	0	0	0·14	T	0·11	0·047	0·42	2·84
11·83	60	0	0	0·12	T	0·25	0·011	0·68	2·21
23·63	60	0	0·018	0·19	0·0096	0·46	0·043	1·11	6·31

* All samples were evacuated for 22 h prior to the addition of oxygen.
† Hydrogen was found in most of these samples in quantities not exceeding 0·004 ml (s.t.p.). The presence of this hydrogen was felt to be due to the procedure used in sealing the sample containers (see text).
‡ T indicates a trace (<0·003 ml of methane or ethane at s.t.p.).
§ Carbon monoxide could not be determined for this sample due to experimental difficulties.

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The corrected carbon oxide yields for the non-radiative oxidations are shown in *Figures 4* and *5*. These yields were computed by subtracting the 'blank' values in *Table 2* from those listed in *Tables 3* and *4* at the same time of reaction. Within the limits of reproducibility, the corrected yields of carbon oxides for the radiative oxidations were about the same. This probably resulted in part from the fact that all or much of the oxygen reacted with the samples before the latter were irradiated. The effect of radiation on this reacted (adsorbed) oxygen will be shown to have been small or non-existent.
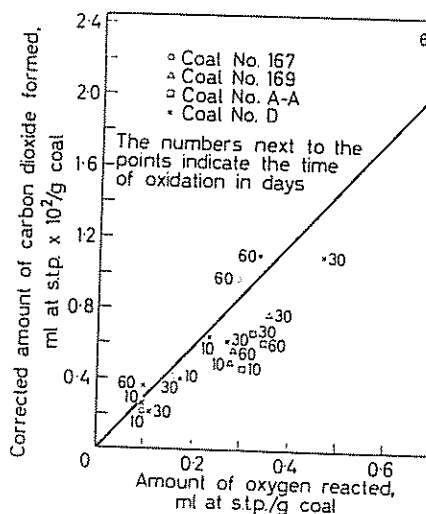

Figure 4. Yields of carbon dioxide from the oxidation of coals at 24°C in the absence of radiation (corrected for blank values from the corresponding evacuated coals)
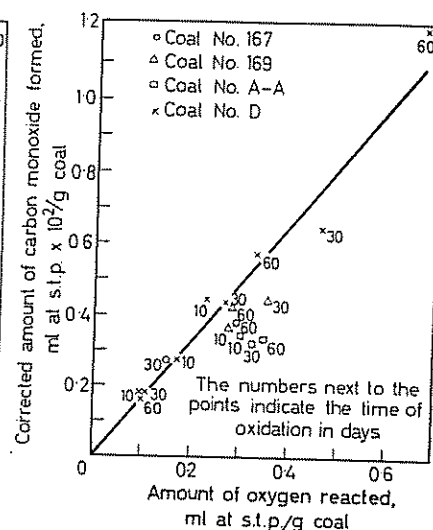
Figure 5. Yields of carbon monoxide from the oxidation of coals at 24°C in the absence of radiation (corrected for blank values from the corresponding evacuated coals)

Figures 4 and *5* also show that the corrected yields of carbon oxides depended linearly on the amounts of oxygen consumed, and were independent of the rates of oxidation. This was clearly shown whether the results for each coal were inspected separately or grouped together.

The rate of oxidation of coal D could be very closely described by the Elovich equation

$$dq/dt = Ae^{-Bq} \qquad \dots [3]$$

where q is the quantity of oxygen adsorbed in time t, and A and B are constants. With q expressed in units of ml of oxygen at s.t.p./g coal, the constants had the values $A = 0.0313$ and $B = 2.71$ for the samples with initial oxygen concentrations of *ca.* 0.66 ml/g coal. For the samples with initial oxygen concentrations of *ca.* 0.3 ml/g coal, the constants had the values $A = 0.0446$ and $B = 9.86$. There was no obvious relationship between the constants at the various concentrations, but there were not enough data to permit evaluation of the constants for the samples with initial oxygen concentrations of *ca.* 0.1 ml/g coal.

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Table 5 shows the effect of the 24°C–45°C–24°C cycle on the evacuated samples and on the oxygen-containing samples. This temperature cycle was designed to investigate the effect of the estimated 45°C reactor operating temperature on the oxidations and the rates of gas release. The effect on the latter may be seen by comparing the gas yields of the evacuated samples in *Table 5* with those of the 10-day samples in *Table 2*. The amounts of carbon

Table 5. *Effect of 24°C–45°C–24°C cycle on the oxidations and rates of gas release from coals in the absence of radiation**

Amount of oxygen introduced†, ml (s.t.p.)	Amounts of gases found after 10 days, ml (s.t.p.)							
	H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O
Coal No. 167								
0	0‡	0	0·025	0	T‖	T	0·046	1·62
11·31	0	6·83	0·061	0	§	T	0·13	1·82
Coal No. 169								
0	0	0	0·13	0	0·017	0·052	0·085	0·83
11·45	0	0·12	0·22	0	0·15	0·032	0·33	3·31
Coal No. A-A								
0	0	0	0·14	0	0·024	T	0·19	6·04
11·73	0	0·086	0·16	0	0·20	T	0·48	6·82
Coal No. D								
0	0	0	0·12	0	0·027	0·030	0·16	2·50
11·06	0	3·95	0·20	0	0·145	0·030	0·33	5·0?

* The samples were treated in the following cycle of successive temperatures: 31 h at 24°C, 16 h 40 min at 45°C and finally 192 h 20 min at 24°C. The total elapsed time was 10 days.
† All samples were evacuated for 22 h prior either to the addition of oxygen or to sealing *in vacuo*.
‡ Hydrogen was found in most of these samples in quantities not exceeding 0·004 ml (s.t.p.). The presence of this hydrogen was felt to be due to the procedure used in sealing the sample containers (see text).
§ Carbon monoxide could not be determined for this sample due to experimental difficulties.
‖ T indicates a trace (<0·005 ml of carbon monoxide or <0·003 ml of ethane at s.t.p.).

oxides desorbed increased for all of the coals treated at the higher temperature by factors of 1/3 to 3. This implied high activation energies for the desorption processes listed as equations 1 and 2. These temperature-promoted increases in carbon oxide yields accounted for the somewhat higher yields of the oxides found with the vacuum-irradiated samples. Thus radiation did not significantly affect reactions 1 and 2. When the 'blank' values for the carbon oxides in *Table 5* were subtracted from the amounts of carbon oxides formed in the presence of oxygen, the corrected yields shown in *Figure 6* resulted. The lines drawn are the same as those in *Figures 4* and *5* (for the oxidations at 24°C) so that the reasonably good agreement between the two sets of results may be seen. Thus, the higher temperature did not affect the corrected yields of carbon oxides very greatly.

The yields of gases from samples of coals irradiated in air and nitrogen are shown in *Table 6*. The hydrogen and methane yields were within the range of values observed for the oxygen and vacuum-irradiated samples. The yields of gases other than nitrogen were also about as expected, except for the anomalous carbon dioxide yield for coal 169 irradiated with nitrogen. The amounts of water found with all of the nitrogen- and air-irradiated samples were much lower than those with the other samples.

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For the air-irradiated samples, about 10 per cent of the nitrogen originally introduced was not recovered. This trend was exhibited by all the coals, and it indicated that nitrogen probably had reacted with the samples[*]. To check this possibility, two coal samples were irradiated in nitrogen. The results of these irradiations confirmed the observations with the air samples.

Table 6. Yields of gases from coals irradiated in air and nitrogen

Amount of air introduced*, ml (s.t.p.)	Amount of nitrogen introduced†, ml (s.t.p.)	Amounts of gases found after sample irradiation, ml (s.t.p.)							
		H_2	O_2	N_2	CH_4	CO	C_2H_6	CO_2	H_2O
					Coal No. 167				
38·6	30·1	3·91	0	27·6	0·070	‡	T§	0·24	<0·5
0	63·3	3·11	0	61·8	0·049	‡	T	0·13	1·08
					Coal No. 169				
33·3	26·0	5·00	0	23·8	0·07	0·11	0·044	0·57	0·92
0	61·8	4·98	0	58·8	0·07	‡	0·077	0·47	3·05
					Coal No. A-A				
35·5	27·7	7·10	0	25·5	0·10	0·13	0·010	0·63	1·42
					Coal No. D				
39·3	30·7	6·62	0	28·5	0·11	0·21	0·025	0·60	<0·5

* All samples were evacuated for 22 h prior to addition of a gas.
† The amount of nitrogen present in the air samples was calculated from the known composition of air by assuming perfect gas behaviour and correcting the air composition to a carbon dioxide-free basis. This led to amounts of N 78·08, O 21·00 and A 0·93 per cent. The amount of argon introduced was subtracted from the amount of gases found after the samples had been irradiated.
‡ Carbon monoxide could not be determined for these samples because of experimental difficulties.
§ T indicates a trace (<0·003 ml of ethane at s.t.p.).

Figure 6. Yields of carbon oxides from the oxidation of coals treated in the 24°C–45°C–24°C cycle in the absence of radiation (corrected for values from the corresponding evacuated coals)
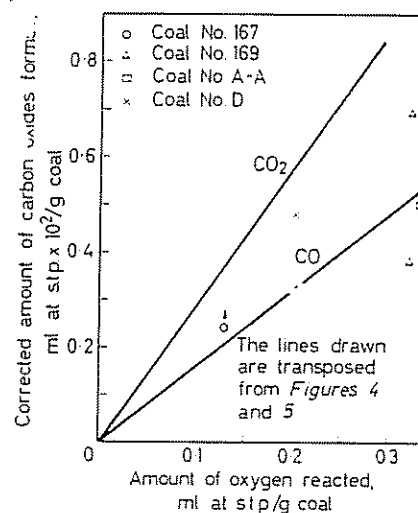
There were no significant differences in irradiated and un-irradiated coals coals investigated by means of x-ray diffraction patterns, BET surface areas, Gieseler fluidities, and 850°C carbonization. There were also no significant differences in the x-ray diffraction patterns, BET surface areas and reactivities in air at 400°C of cokes from the irradiated and un-irradiated coals.

* The reaction between nitrogen and oxygen results in low yields of nitrogen oxides under the conditions used here[13].

DISCUSSION

(a) *Radiolysis products*

It has been shown that hydrogen, methane and perhaps ethane are radiolysis products of bituminous coals. The magnitudes of the hydrogen yields for for the coals (G_{H_2} = 0·005 to 0·03) are in the range of those observed for aromatic compounds[14-16]. In contrast, aliphatic compounds give G_{H_2} values in the range of 1 to 6 under similar conditions[12]. Thus, the hydrogen yields are consistent with the known aromatic structure of coal.
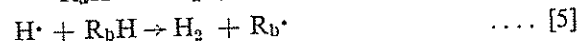
One aspect of these yields, the constant ratio of methane to hydrogen, requires some explanation. Based on accepted principles[17-20], the reactions which are primarily involved in the production of molecular hydrogen during irradiation of coal are probably the following:

$$R_aH \rightsquigarrow R_{\dot{a}} + H\cdot \qquad \dots. [4]$$

$$H\cdot + R_bH \rightarrow H_2 + R_b\cdot \qquad \dots. [5]$$

$$H\cdot + A \rightarrow HA\cdot \qquad \dots. [6]$$

R_aH and R_bH are any hydrogen-containing groups in the coal, and A is any aromatic group in the coal. It can be seen from this scheme that the amount of molecular hydrogen produced from coal should be a linear function of radiation dosage (at the dosage used). This is so because a relatively small amount of hydrogen is removed from the coal, and the concentrations of R_aH, R_bH and A remain effectively constant. The number of hydrogen molecules produced should therefore be a constant fraction of the number of H atoms formed in reaction 4.

The most feasible scheme for the production of methane from coal is

$$H\cdot + R_c\!-\!CH_3 \rightarrow R_{\dot{c}} + CH_4 \qquad \dots. [7]$$
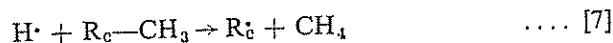
This reaction and reaction 5 predict that the yields of both methane and hydrogen will depend on the same quantity, i.e. the H atom concentration. The ratio of product gases will therefore be constant providing (as before) that $R_c\!-\!CH_3$ and R_bH remain approximately constant.

Presumably, the small differences in the methane to hydrogen ratios for the different coals are the result of structural differences. It is interesting that these ratios are inversely related to the non-radiative oxidation rates. No definite conclusions regarding structure can be reached from this relationship, however.

(b) *Reaction of coal with oxygen*

The increased rate of oxidation of coal 167 under radiative conditions indicates activation of either the coal or the oxygen. By analogy with the results of the oxidation of graphite in a radiation field[21] it is probable that the oxygen becomes activated. Radiation causes the splitting of molecular oxygen into atomic oxygen and also causes the formation of ozone. The latter two species would react faster with the coals than molecular oxygen. However, these species either produce carbon oxides in approximately the same quantities and ratios as molecular oxygen[22], or they are not present in amounts high enough to affect the results significantly. Considering that

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much of the oxygen had already reacted in many of the samples before irradiation, the latter alternative seems more probable.

The results of non-radiative coal oxidation can be considered briefly. It is interesting that the oxidation of coal D at room temperature could be described with precision by the Elovich equation for periods of time as long as 60 days. T. Wood[23] observed that the oxidation of an Australian coal containing 82·6 per cent carbon (dry, ash-free basis) also obeyed Elovich kinetics. Wood's measurements were made with initially un-oxidized samples at 40°C for a total of about four hours. However, it appears that credit must be given to G. H. Scott[24] as the first to show (1944) that coal oxidation kinetics could be described by the Elovich equation. Eleven coals ranging in rank from sub-bituminous to anthracite obeyed the equation with pure oxygen at temperatures from 100°C to 350°C and for periods up to 35 days.

The results with coal D extend the range of conditions over which the Elovich equation has been observed to describe the kinetics of coal oxidation. The results also suggest that the equation may have more widespread applicability for this purpose than has heretofore been realized. One reason for this lack of realization is that other kinetic expressions have been used[23]. Wood suggested that oxidation of the coals prior to the beginning of experiments might account for these other expressions. The results with coal D show, however, that this idea does not always apply. This is also shown theoretically elsewhere[25].

The mechanism of the formation of carbon oxides from coal is of interest. It has already been shown that part of the oxides probably arise by desorption of an adsorbed complex (reactions 1 and 2). For example, the sequence of reactions for carbon dioxide is:

$$O_2 + C \rightarrow C(O_2) \qquad \dots \text{[8]}$$

$$C(O_2) \rightarrow CO_2 \qquad \dots \text{[1]}$$
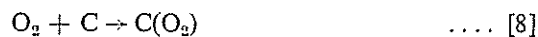
However, not all of the carbon dioxide formed can have been produced by this sequence[25]. The results obtained indicate that the other mode of formation of carbon dioxide is the one-step reaction

$$C + O_2 \rightarrow CO_2 \qquad \dots \text{[9]}$$

In this reaction, a constant fraction of the oxygen molecules which strike the surface forms gaseous carbon dioxide. This accounts for the fact that the yield of carbon dioxide formed by this process (the 'corrected' yield) depends only on the amount of oxygen adsorbed, and not on the rate of oxidation.

It is interesting to speculate on the mechanism by which reaction 9 takes place. One possible reaction involves the formation of a highly energetic intermediate complex. A constant fraction of these energetic intermediates would become detached from the surface in essentially zero time. The remainder would then lose energy to form the usual $C(O_2)$ complex. The concentration of this complex is apparently not changed much by the fresh oxygen since oxygen was adsorbed by the coals during grinding. Thus, the rate of reaction 1 is not increased greatly.

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This proposed mechanism raises several interesting questions. First, what is the nature of the fraction of the energetic intermediates which immediately detach themselves from the surface? Secondly, why is the size of the fraction relatively uninfluenced by temperature (45°C results)? One possible answer is that the fraction is a measure of the number of 'dangling' carbon atoms in the coal, i.e. atoms which are attached to other carbon atoms by very weak and sterically strained bonds. These 'dangling' or dislocated atoms could quite conceivably arise during coalification. When an oxygen molecule struck such a carbon atom, the energy released by the reaction would be more than enough to break the weak bonds. Gaseous carbon oxides would result from a successful collision of this kind.

Department of Fuel Technology,
   Pennsylvania State University,
     University Park, Pennsylvania, U.S.A.

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