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The Reaction of Bituminous Coals with Ammonia in the Presence of Radiation

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Seven bituminous coals were irradiated in the presence of ammonia to a dosage of $3{\cdot}5 \times 10^8$ rads. The amounts of hydrogen produced were greater than those produced from vacuum-irradiated coals. The lack of corresponding increases in the yields of nitrogen produced indicated that the excess hydrogen did not originate merely from the radiolysis of ammonia. The reaction of amine radicals with the coals was postulated to explain the results. No significant changes in the Gieseler fluidities or free-radical concentrations of the coals irradiated in ammonia were found.

AN INVESTIGATION of the reactions of bituminous coals with ammonia in the presence of nuclear reactor radiations was undertaken as part of the preliminary work reported in a companion paper[1]. Ammonia was chosen for this work because of the ease with which its breakdown products (hydrogen and nitrogen) could be removed from the coals and analysed. The ratio of these two gases was expected to give information regarding any reactions taking place. Ultimately, it was hoped that irradiation of coals with gases such as ammonia, oxygen[1] and nitrogen[1] would provide a unique and useful method of modifying the properties of coal.

EXPERIMENTAL

The ground samples of coals 166, 167, 169, A, B, C and D used by J. A. HAMMOND and P. L. WALKER, Jr[2] were used in this work. The Pyrex sample containers and vacuum system used were essentially the same as those described[1], except that the volume of the containers was about 135 ml.

A 35 g sample of each coal was weighed into a container and evacuated for 22 h. The coal was permitted to take up ammonia (Matheson, 99·99 per cent purity) which had previously been dried further by the method of R. T. SANDERSON[3]. This sorption was conducted at room temperature for about two hours, after which the sorption rate was quite slow. The container was then isolated from the vacuum system and the gas phase ammonia was frozen into the container with liquid nitrogen. Any residual gases left in the container were then pumped away, and the container was sealed *in vacuo* with the liquid nitrogen bath still in place.

The sample container was then thawed and the coal was irradiated to $3{\cdot}5 \times 10^8$ rads in the manner described[1]. Following irradiation the samples were sealed on to the vacuum line and the hydrogen, nitrogen and methane in the containers were transferred into the gasometer through a liquid nitrogen-refrigerated trap. This trap removed the ammonia. The gases were then analysed gas chromatographically[1].

For comparison, samples of pure ammonia at various pressures were irradiated in identical containers and in the same fashion. The amounts of hydrogen and nitrogen produced were determined as before.

The Gieseler fluidities of the ammonia-irradiated and the original (un-irradiated) coals were then determined[1]. The free-radical concentrations of the coals were also determined with the E.P.R. spectrometer described by R. A. FRIEDEL and I. A. BREGER[4] at a frequency of 9·5 kMc/s and a magnetic field strength of about 3300 gauss.

RESULTS AND DISCUSSION

The results of irradiating the pure ammonia samples are given in *Table 1*. One salient feature was the nearly constant 3:1 ratio of the amounts of hydrogen and nitrogen produced. This, and the linear dependence of the total gas yield on ammonia pressure (*Figure 1*), agreed with results obtained with other types of radiation[5–8].

The results of irradiating the coal-ammonia samples are presented in *Table 2*. The hydrogen yields for the ammonia-irradiated coals were much

Table 1. Yields of product gases from the radiolysis of pure ammonia

Amount of ammonia introduced, ml (s.t.p.)	*Pressure of ammonia in container, mm Hg at 24°C*	*Amount of product gases found after irradiation, ml (s.t.p.)*	*Composition of product gases, vol. %*		*% Ammonia decomposed*
			N_2	H_2	
132·3	795	0·735	23·2	76·8	0·278
129·5	775	0·997	27·0	73·0	0·385
62·2	387	0·434	27·2	72·8	0·349
61·8	375	0·469	26·5	73·5	0·380
12·7	76	0·112	24·8	75·2	0·441

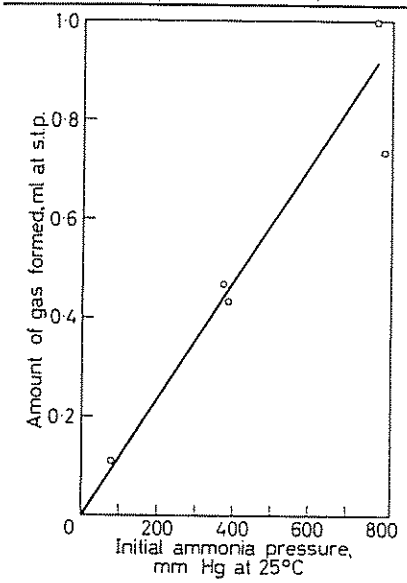

Figure 1. Dependence of radiative yield of gas on ammonia pressure

higher than those for the vacuum-irradiated coals. The nitrogen yields were more erratic, due to the fact that the vacuum-irradiated samples were not evacuated in exactly the same fashion as were the samples to which ammonia was later added. It has been shown[1] that the nitrogen yield is quite sensitive to the evacuation procedure and time.

Table 2. Yields of gases from coals irradiated in ammonia

Coal†	Initial conditions*			Amounts of gases found after sample irradiation, ml (s.t.p.)		
	Total amount of ammonia introduced, ml (s.t.p.)	Pressure of ammonia in container, mm Hg at 24°C	Amount of ammonia adsorbed on coal, ml (s.t.p.)	H_2	N_2	CH_4
166-V[9]	—	—	—	0·60	0·12	0·03
166-NH_3	160	430	105	3·24	0·33	0·057
167-V[1]	—	—	—	2·00	0·039	0·041
167-NH_3	185	630	105	6·32	0·35	0·13
169-V[1]	—	—	—	3·40	0·11	0·051
169-NH_3	210	570	140	7·27	0·22	0·15
A-V[9]	—	—	—	3·6	0·46	0·07
A-NH_3	185	630	105	8·97	0·21	0·17
B-V[9]	—	—	—	2·8	0·42	0·06
B-NH_3	205	610	130	9·27	0·20	0·23
C-V[9]	—	—	—	1·5	0·27	0·24
C-NH_3	220	560	150	8·28	0·15	0·62
D-V[1]	—	—	—	4·72	0·17	0·093
D-NH_3-1	200	590	130	9·23	0·23	0·51
D-NH_3-2	203	600	132	9·64	0·27	0·42

* All values for the amounts of ammonia are estimated to be accurate to ± 20 per cent.
† All numbers followed by -V indicate vacuum-irradiated samples. The superscripts are the references from which these values were obtained. All numbers followed by -NH_3 indicate samples irradiated with ammonia. D-NH_3-1 and -2 are duplicates.

The high yields of hydrogen from the ammonia-irradiated coals cannot be explained merely as the result of decomposition of ammonia. For example, 0·21 ml of nitrogen was found with ammonia-irradiated coal A (code A-NH_3). Even if all of this nitrogen had been produced from ammonia decomposition, an increase in hydrogen yield of only 0·63 ml would be expected (3:1 ratio). This increase was only a fraction of the 5·4 ml increase actually observed. The same point can be demonstrated for all of the coals.

A reaction such as

$$NH_2^{\cdot} + \text{coal} \rightarrow NH_2\text{–coal} \qquad \ldots\ [1]$$

can explain these results. The formation of amine radicals in irradiated ammonia is an accepted phenomenon, and the formation of aniline and other nitrogenous compounds from benzene irradiated with ammonia has been observed[10–13]. The excess hydrogen atoms from the ammonia can react by abstraction to form hydrogen molecules[1]. The formation of hydrazine, which could also account for the high hydrogen to nitrogen ratio, has never been observed in a static system.

The methane yields of the ammonia-irradiated samples were higher than those of the vacuum-irradiated samples. This agreed with a trend already discussed[1] toward increase in methane yield with increase in hydrogen yield.

The free-radical concentrations and Gieseler fluidities of the coals were little different before and after irradiation in ammonia. The former were somewhat higher and the latter somewhat lower after the irradiation, but all values were within the limits of reproducibility of the equipment used.

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