A Study of the Structure of Pyridine Extracts from Coals by High Resolution Nuclear Magnetic Resonance Spectroscopy

By Gen TAKEYA, Mitsuomi ITOH, Akira SUZUKI and Susumu YOKOYAMA

(Received April 30, 1963)

Hitherto, various studies of hydrogen distribution in coals have been made by such methods as infrared[1] and broad-line NMR spectroscopy.[2] Of these analytical methods, although it would seem that the high resolution NMR method has some important advantages, only a few papers[3] have been published reporting on studies of the constitution of coal or coal-like materials made using it.

The present report deals with the constitution of the pyridine extracts of some Japanese coals, a study based upon their hydrogen distribution. The pyridine extracts of Yubari, Taiheiyo, Sumiyoshi and Sohya coal were separated from the solvent, dried and redissolved into deutero-pyridine, C_5D_5N. The C_5D_5N solutions (18~20%) of the coal extracts thus prepared were examined by NMR spectroscopy at 60 Mc. with a JNM-3H-60 NMR spectrometer.

The distribution of hydrogen was estimated from the intensities of the three different NMR bands. $\mathbf{H}_a$ represents the aromatic hydrogen atom which was situated ca. 7.5 p.p.m. from the tetramethyl silane peak in the NMR spectra; $\mathbf{H}_\alpha$, the hydrogen atom at α-positions to the aromatic rings (ca. 2.6 p.p.m.), and $\mathbf{H}_o$, the hydrogen on the other saturated carbon atoms (ca. 1.5 p.p.m.). It has been confirmed by Ikenoue that the resonance peak for phenolic hydrogens in a pyridine solution appeared at a far lower position of the applied magnetic field than 8.5 p.p.m.[4]

From the contents of the different types of hydrogen atoms and the elementary analysis, the structural parameters: f_a (carbon aromaticity), σ (the measure of the substitution of the aromatc systems) and $\mathbf{H}_{au}/\mathbf{C}_a$ (the aromatic hydrogen-to-carbon ratio of the hypothetical unsubstituted aromatic material) which were introduced by Brown et al.[3a] have been calculated for the pyridine extracts of coals. A new parameter of the length of the aliphatic carbon chain is proposed by the present authors

TABLE I. ANALYTICAL AND STRUCTURAL DATA OF THE PYRIDINE EXTRACTS

Coal sample		Yubari	Taiheiyo	Sumiyoshi	Sohya
Yield of extract (d. a. f.)		18.5	16.7	15.8	16.6
Pyridine extract analysis (d. a. f.)*	C	83.73	80.28	78.05	76.78
	H	6.39	7.13	6.51	6.42
	O	9.88	12.59	15.44	16.80
C/12 ($\propto$ **C**)		6.98	6.69	6.50	9.40
H/1 ($\propto$ **H**)		6.39	7.13	6.51	6.42
O/16 ($\propto$ **O**)		0.62	0.79	0.95	1.05
Hydrogen distribution (fraction)	$\mathbf{H}_a/\mathbf{H}$	0.151	0.053	0.064	0.105
	$\mathbf{H}_\alpha/\mathbf{H}$	0.224	0.183	0.195	0.191
	$\mathbf{H}_o/\mathbf{H}$	0.625	0.764	0.741	0.704
Structural parameters	f_a	0.61	0.50	0.53	0.55
	σ	0.58	0.79	0.79	0.71
	$\mathbf{H}_{au}/\mathbf{C}_a$	0.54	0.55	0.58	0.66
	$\mathbf{H}_o/\mathbf{H}_\alpha$	2.9	4.2	3.8	3.7
Numbers of aromatic condensed ring		6	6	5~6	4
Length of aliphatic C-chain		4	5	5	5

* These data are revised by substraction of phenolic hydrogen.

1) For example, D. W. van Krevelen, "Coal", Elsevier, Amsterdam (1961), pp. 363-372.
2) Ibid., pp. 382—391.
3) a) J. K. Brown, W. R. Ladner and N. Sheppard, *Fuel*, 39, 79 87 (1960). b) J. F. M. Oth and H. Tschamler, *Brennstoff-Chem.*, 42, 378 (1961); 43, 177 (1962).
4) Private communication from Dr. T. Ikenoue (Tohoku University, Sendai).

on the basis of the following relation: $\mathbf{H}_o/\mathbf{H}_\alpha=(\mathbf{H}_o/\mathbf{H})/(\mathbf{H}_\alpha/\mathbf{H})$. In the derivation of the above four parameters, nitrogen and sulfur (less than 2% d. a. f.-basis) in coal constituents have been disregarded. Furthermore, two assumptions were made regarding the constitution of coal: (1) all oxygen elements are attached directly to the aromatic systems; i. e., practically all oxygen occurs as phenolic OH and quinone groups, and (2) the aromatic rings are not directly linked by a C–C bond.[3a]

Assumption 1 may be accepted on the basis of our experimental results,[5] which show that more than 60% of the oxygen involved in the four parent sample coals appears as phenolic OH and quinone groups; assumption 2 is reasonable since a high degree of C–C crosslinking between aromatic systems is unlikely because of the large steric interactions of the aromatic systems involved. A realistic value for x and y in Brown's relations appears to be close to 2, as Brown et al. have set forth.[3a]

The structural parameters, f_a, σ, $\mathbf{H}_{au}/\mathbf{C}_a$ and above $\mathbf{H}_o/\mathbf{H}_\alpha$, calculated on the above assumptions, together with the features for the mean structure which are inferred from these parameters, are given in Table I.

Faculty of Engineering
Hokkaido University
Sapporo

5) G. Takeya et al., the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April 4, 1961.