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A Study of the Spin-Lattice Relaxation Time, T_1, of Coal-derived Oil

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The spin-lattice relaxation time, T_1, of carbons was measured for various types of carbons in ring-type fractions separated from coal-derived oil. The T_1 for most carbons in the coal-derived oil was less than 2 s because of the existence of free radicals, while the T_1's of aromatic non-protonated carbons in the monocyclic and bicyclic aromatics fractions were approximately 12—15 s. The effects of a relaxation reagent on the T_1 were also discussed.

In recent years, ^{13}C-NMR spectrometry has been applied to the study of coal chemistry[1–7] and has proved to be a powerful tool for the investigation of the structure of coal-derived oil, since it makes the direct observation of the hydrocarbon skeleton possible.

The determination of various structural parameters for coal-derived oil requires a quantitative NMR spectrum. The peak intensity in the FT-NMR proton decoupling spectrum is generally affected by two factors, the nuclear Overhauser enhancement (NOE) and the spin-lattice relaxation time, T_1. The former, the NOE, can be fully suppressed by the gated-decoupling technique,[6–8] whereas the latter, T_1, can not be, since it is closely related to the structure and has a definite value for each carbon in the coal-derived oil.

The FT-NMR method requires a pulse repetition time much larger than T_1 in order to avoid the progressive saturation of signals. It is necessary, therefore, to have information on the T_1 of the sample prior to the NMR spectrum measurement. Unfortunately, however, there have not yet been any reports on the T_1 of coal-derived oil, as far as we know. In the present work, the T_1's of various types of carbons and other structural information of coal-derived oil have been obtained from the partially relaxed Fourier transform (PRFT) spectra.

Experimental

The coal sample used in the present work is from Akabira, Hokkaido. The sample was hydrogenated over an Adkins catalyst at 400 °C for 60 min under the initial hydrogen pressure of 100 kg/cm^2. The hydrogenated product was extracted with hexane in a Soxhlet extractor. The extracted coal-derived oil was separated into five fractions by liquid chromatography, a modification of the Bureau of Mines-API 60 method:[9] saturates (Fr-P), monocyclic aromatics (Fr-M), bicyclic aromatics (Fr-D), tri- and tetracyclic aromatics (Fr-T), and polycyclic aromatics and polar aromatics (Fr-PP).

The coal-derived oil and ring-type fractions (Fr-M, D, T, and PP) were used for the T_1 measurement. The samples were dissolved in deuteriochloroform, and the solution was

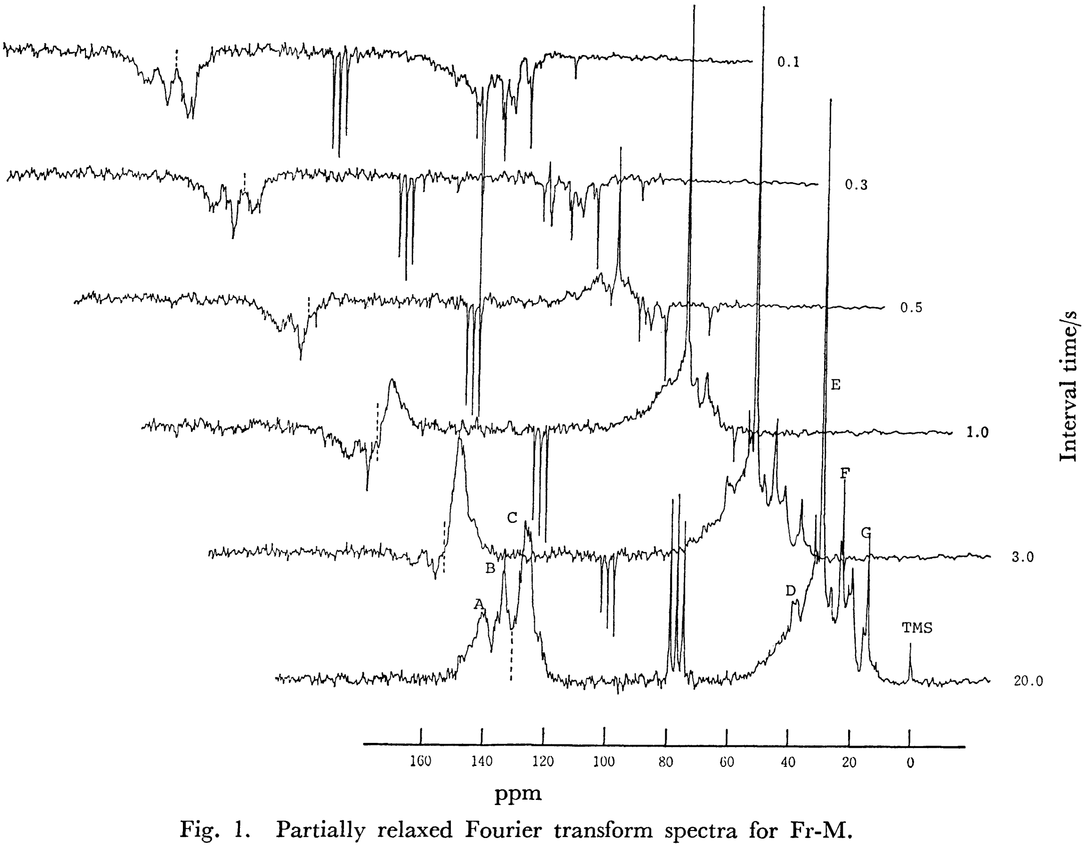

Fig. 1. Partially relaxed Fourier transform spectra for Fr-M.

Table 1. Spin-lattice relaxation times, T_1, of various types of carbons for ring-type fractions of coal-derived oil

Carbon type	Chemical shift δ/ppm	Spin-lattice relaxation time, T_1				
		Fr-M	Fr-D	Fr-T	Fr-PP	Coal-derived oil
Aromatic						
A. Substituted	138.6	12.7	10.9	2.8	1.8	1.1—1.4
B. Bridge head	131.8	12.0—13.0	12.9—14.7	4.1	1.9	1.3
C. Protonated	126.8	1.2	1.6— 2.6	0.4—0.8	0.8—1.0	0.6—1.0
Aliphatic						
D. Methylene bridge	37.9	0.7— 0.9	0.8	0.4	0.6	0.5—0.6
E. ε or further CH_2 from end	29.6	0.6— 0.7	0.9— 1.0	0.3—0.4	0.5	0.4
F. α-CH_3 to ring	21.3	1.2	1.3— 1.7	0.5—0.9	0.8—1.1	0.7—0.9
G. end-CH_3 to ring	14.0	2.4	2.1— 2.5	0.9—1.3	1.6—2.0	1.2

not degassed. Tris(acetylacetonate)chromium(III) ($Cr(acac)_3$) was used as the relaxation reagent.

The spectra were obtained with a JNM-FX60 Fourier transform spectrometer (JEOL Ltd.) and were measured over a range of 4000 Hz, with 8192 data points at 15 MHz. The T_1 measurement was performed using an inversion recovery pulse sequence $(180°\text{-}t\text{-}90°)_n$,[10] where t stands for the interval time between 180° and 90° pulses. The waiting time between pulse sequences was 20 s. The width of the 90° pulse was 16 μs. The NOE was fully suppressed by the gated decoupling technique.

Results and Discussion

In the ^{13}C-NMR method, the progressive saturation of signals should be avoided by making the excited spins completely relaxed. Therefore, a pulse-repetition time of at least five times the largest relaxation time, T_1, is needed. In general, the T_1 values for quarternary carbons of standard hydrocarbons are several decades of seconds, and the pulse-repetition time required for their quantitative spectra becomes extremely long. Fortunately, coal-derived oil contains an adequate amount of free radicals ($\approx 10^{18-19}$ spins/g),[11] and its T_1 turns out to be much smaller than those for standard chemicals. The PRFT spectra of the Fr-M fraction is shown in Fig. 1. The T_1 depends on the molecular size, the number of hydrogen atoms bonded to the carbon nucleus, the molecular motion, *etc*. Therefore, the difference in the relaxation rates of carbons can give structural information and the PRFT spectra are helpful for the assignment of signals. As can be seen in Fig. 1, the aromatic carbons are clearly divided at about 129 ppm into two groups of slowly relaxing nonprotonated and fast relaxing protonated carbons. On the other hand, the aliphatic carbons, though not conclusively, are also divided into two groups at about 22 ppm. The low-field group, for which the relaxation rate is fast, is assigned to cycloparaffinic, methylene bridge, and alkyl carbons except for the methyl and the terminal methyl groups. The T_1 values of these carbons are presumed to be relatively short because of their "rigid" structures. The high-field one is assigned to alkyl substituents (methyl, ethyl, and terminal methyl groups), and these carbons are presumed to have longer T_1 values because of their loose bondings. Thus, T_1 often provides information supplemental to the assignment of the signal.

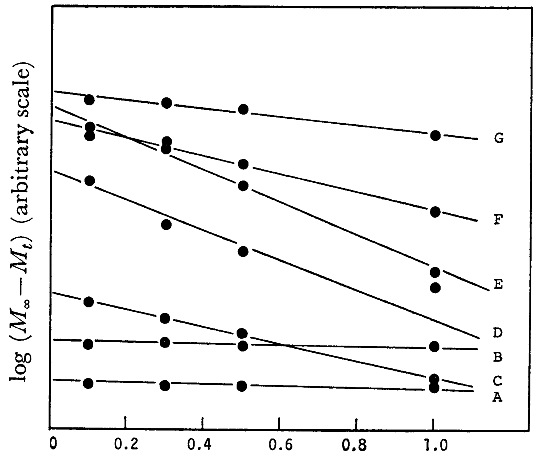

Fig. 2. Relationship between $\ln(M_\infty - M_t)$ and interval time.

T_1 is calculated by means of the following equation:

$$\ln(M_\infty - M_t) = \ln 2M_\infty - t/T_1$$

where M_∞ is the signal intensity when the carbon nucleus is completely relaxed. In the spectrum of a multi-component mixture such as coal-derived oil, the relation between $\ln(M_\infty - M_t)$ and the interval time generally has a tendency to deviate from a straight line, for each signal in the spectrum corresponds to some carbons with various T_1 values and the change in the signal intensity with the interval time may show the overall relaxation rates of these carbons. Therefore, the T_1 value calculated from the gradient of the straight line in Fig. 2 often varies the range of interval time

Table 2. Change in the aromaticity (f_a) of coal-derived oil with the pulse-repetition time

Pulse-repetition time/s	Aromaticity (f_a)
0.7	0.53
1.0	0.57
2.0	0.60
4.0	0.61
6.0	0.61
25.0	0.61

Table 3. Change in the spin-lattice relaxation time, T_1, with the amount of $Cr(acac)_3$ added

Carbon type	Chemical shift δ/ppm	Spin-lattice relaxation time, T_1			
		None	10 mg[a]	20 mg[a]	30 mg[a]
Aromatic					
A. Substituted	138.6	1.1—1.4	0.3—0.4	0.3	0.2
B. Bridge head	131.8	1.3	0.4—0.6	0.3—0.4	0.1—0.2
C. Protonated	126.8	0.6—1.0	0.2—0.3	0.2—0.3	0.2
Aliphatic					
D. Methylene bridge	37.9	0.5—0.6	0.4—0.5	0.5	0.2—0.4
E. ε or further CH_2 from end	29.6	0.4	0.3—0.5	0.2	0.2
F. α-CH_3 to ring	21.3	0.7—0.9	0.5—0.7	0.2—0.4	0.2—0.4
G. end-CH_3 to ring	14.0	1.2	0.7—0.8	0.3	0.2—0.4

a) Amount of $Cr(acac)_3$ added to about 0.5 g of coal-derived oil in 0.53 ml of deuteriochloroform.

employed. We calculated the T_1 values from the gradient in the range of interval time from 0.1 to 1.0 s. The T_1 values of various types of carbons in the ring-type fractions of coal-derived oil are summarized in Table 1. The T_1 of aromatic non-protonated carbons is the longest among the T_1's of all the types of carbons. In particular, their T_1 values for the Fr-M,D fractions are much longer than those for Fr-T,PP. The great difference in the T_1 values of various types of carbons between the Fr-M,D and Fr-T,PP fractions may be attributed not only to their molecular sizes but also to the concentration of free radicals contained in the fractions. The components in the Fr-M,D fractions are presumed to be sufficiently hydrogenated compared with those in Fr-T,PP. The T_1 of coal-derived oil is nearly equal to that of the Fr-PP fraction. On the whole, the T_1 of coal-derived oil (hexane Soxhlet's extract) is moderately short, although some of the components have considerably long T_1 values. Table 1 shows that the pulse-repetition time required for the quantitative spectrum of coal-derived oil is approximately 5—6 s. This value is confirmed by the change in the aromaticity (f_a) of coal-derived oil with the pulse-repetition time, as is shown in Table 2. With a short pulse-repetition time, aromatic non-protonated carbons are not yet completely relaxed and f_a may have been underestimated because of the progressive saturation. Table 2 shows that the pulse-repetition time of 5—6 s is necessary to obtain a quantitative spectrum within the limits of experimental errors. This result is in good agreement with the T_1 data.

Thus, the quantitative spectrum for coal-derived oil requires a significantly long measurement time. Therefore, the addition of a relaxation reagent to samples is often used in time-effective measurements.[3,6-8] Table 3 shows the change in T_1 with the amount of relaxation reagent ($Cr(acac)_3$) added. The addition of $Cr(acac)_3$ shortens the T_1 values of all carbons considerably. With 20 mg of $Cr(acac)_3$, the T_1 of aromatic non-protonated carbons was nearly equal to those of other carbons. The addition of 10—20 mg of $Cr(acac)_3$ is found to be very effective for the reduction of T_1. However, more than 30 mg of $Cr(acac)_3$ should not be added, since such an addition will result in the broadening of the signals. In conclusion, the pulse-repetition time can be reduced from 5—6 s to about 2 s by the addition of a relaxation reagent, as can be seen in Table 3.

Finally, the NMR[12] and field desorption (FD) mass[13] spectrometric studies for the structural analysis of these ring-type fractions made it clear that alkylnaphtenomonocyclic aromatics were predominant for the Fr-M fraction; alkylnaphtenobicyclic aromatics, for the Fr-D fraction; alkylnaphtenotri- and tetracyclic aromatics, for the Fr-T fraction; and alkylpolycyclic aromatics, for the Fr-PP fraction. Thus, the Fr-M and D fractions have considerably saturated structures, that is, "mobile" structures, whereas the Fr-T and PPf ractions have "rigid" structures. The difference in ring size and chemical structure, as well as the concentration of free radicals present in the fractions, is considered to affect the T_1 values.

References

1) R. J. Pugmire, D. M. Grant, K. W. Zilm, L. L. Anderson, A. G. Oblad, and R. E. Wood, *Fuel*, **56**, 295 (1977).

2) Y. Maekawa, T. Yoshida, Y. Yoshida, and M. Imanari, *Nenryo Kyokai Shi*, **56**, 351 (1977).

3) D. L. Wooton, W. M. Coleman, L. T. Taylor, and H. C. Dorn, *Fuel*, **57**, 17 (1978).

4) P. Fischer, J. W. Stadelhofer, and M. Zander, *Fuel*, **57**, 345 (1978).

5) J. M. Dereppe, C. Moreaux, and H. Castex, *Fuel*, **57**, 435 (1978).

6) K. S. Seshadri, R. G. Ruberto, D. M. Jewell, and H. P. Malone, *Fuel*, **57**, 549 (1978).

7) W. R. Ladner and C. E. Snape, *Fuel*, **57**, 658 (1978).

8) J. N. Shoolery and W. L. Budde, *Anal. Chem.*, **48**, 1458 (1976).

9) S. Yokoyama, N. Tsuzuki, T. Kato, and Y. Sanada, *Nenryo Kyokai Shi*, **57**, 748 (1978).

10) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

11) T. Yokono and Y. Sanada, *Fuel*, **57**, 334 (1978).

12) H. Uchino, S. Yokoyama, T. Kato, Y. Sanada, and T. Yoshida, "Proceedings of the 21th Meeting, Japan Petrol. Inst. (Sapporo)," 1978, p. 96.

13) T. Yoshida, Y. Maekawa, H. Uchino, S. Yokoyama, T. Higuchi, and Y. Itagaki, *Fuel*, submitted for publication.