This paper presents characteristic studies on charge transfer and hydrogen transfer in aromatic hydrocarbon molecules. Several significant articles have been referred to and discussed, covering the following items: (1) electron donor ability, (2) hydrogen donor ability of aromatic hydrocarbons, and (3) interaction of aromatic hydrocarbons with various catalysts.

The studies concentrate particularly on hydrogen bondings and aromatic π–π interactions with respect to the charge transfer between polyaromatic hydrocarbons and electron acceptors as guests. To obtain fundamental information about hydrogen transfer, the relationship between hydrogen donor ability and chemical structure of aromatics representing donor solvents is studied using experimental and computational calculation methods. Furthermore, the influence of the addition of metal oxide catalysts on transferable hydrogen in petroleum residue is studied by 1H-NMR technique. Also, the interaction of anthracene/metal chloride and petroleum/metal chloride systems was investigated by means of high temperature ESR technique. Finally, the H–D exchange reaction of hydrogen atoms attached to condensed aromatics with deuterium atom in D₂O over the catalyst was studied by means of D-NMR.

1. Introduction

Thermal and catalytic reactions of hydrocarbons have been of great interest in petroleum refining and chemical industries. Thermal cracking and reforming processes, primarily for gasoline production, dominated the industry through World War II, but they were replaced by catalytic processes in the ensuing years when the production of high octane gasoline became dominant. The industrial chemical production from petroleum began with thermal cracking processes. Such commercially available products as coke and carbon, pitch and asphalt, are all produced by thermal means. Generally, thermal and catalytic reactions involved in petroleum refining and chemical industries proceed in complex manner. Despite the many investigations made in these fields, there still remains uncertainty about reaction mechanisms and chemical structures of complex mixtures as feedstocks and as products. Novel methods of structural characterization and advanced reaction models for rationalization should be established.

Thermal and catalytic reactions of hydrocarbons are initiated by interactions of molecules themselves and by reactions between molecules and catalysts. Electron transfer and hydrogen transfer are the most fundamental phenomena associated with the reactions concerned above.

In this paper, we have studied on charge transfer and hydrogen transfer in hydrocarbons particularly aromatic compounds as probes of their structure and reactivity. Firstly, electron transfer and hydrogen transfer in simple aromatic hydrocarbons have been considered on the basis of the electronic theory of conjugated molecules and the applying various spectroscopic results. Based on the behavior of simple aromatics, we have attempted establishing “measures” or “parameters” as effective and useful characterizations for mixtures of complex hydrocarbons such as heavy residues and pitches.

2. Importance of Charge Transfer, Electron Transfer, and Hydrogen Transfer

The inter- and intra-molecular association forces have long been acknowledged as being of fundamental importance for overall physical and chemical properties of aromatic hydrocarbons. There are several types of noncovalent interactions and their relative population changes with the types of aromatic hydrocarbon structures involved. It is well known that there are three different types of noncovalent bond interactions: ionic bonds, hydrogen bonds, and aromatic π–π interactions.
Associations such as noncovalent bonding in the molecular structure of aromatic hydrocarbons have greatly shown to influence their physical behavior. In other words, hydrocarbon molecules comprise electron donor-electron acceptor associations for which intermolecular electronic charge transfer transition is usually observed. Here, we deal with interactions commonly termed “charge transfer complexes” which involve such termed electron donor-acceptor complexes and hydrogen bonding systems. Electron transfer effects the formation of a radical as described subsequently.

\[
\text{Ar}^+ + \text{H-donor} \rightarrow \text{ArH} \tag{1}
\]

The radical formed in the system abstracts hydrogen from a neighbor expressed as H-donor.

\[
\text{Ar}^- + \text{H-donor} \rightarrow \text{ArH} \tag{2}
\]

Therefore, the charge transfer (electron transfer) is closely associated with hydrogen transfer. In order to scissor the crosslinking between aromatic hydrocarbons and to obtain smaller molecules, electron and hydrogen transfers will be the key reactions.

3. Electron Donor Ability (basicity) of Aromatic Hydrocarbons

Coke formation from aromatic hydrocarbons in thermal and catalytic cracking processes represents both a loss of product and a source of heat through its combustion. It is important to know the causes of coke formation as well as its final molecular structure on the catalyst. It assumes that coke formation in thermal and catalytic cracking proceeds through intermediate aromatic structures of increasing size and complexity. The process appears to be dependent on the molecular size and molecular structure of aromatics. The coke forming tendency of many aromatics and their alkyl derivatives correlates closely with their basicity. The mechanism of coke formation has been discussed in terms of the formation of intermediate carboxonium ions. Appleby et al. have proposed a concept of basicity of aromatic hydrocarbons. Principally, basicity means the extent of electron donor ability of aromatics. We have measured spin concentration value by means of ESR spectroscopy for the aromatic host molecules with guest electron acceptor molecules such as iodine and TCNQ. The procedures and measuring method to be described in 3.4 are rather simple and easy as compared with those of Appleby et al.

3.1 Charge-transfer Complexes of Aromatics with Iodine as Electron Acceptor

It is known that iodine forms charge transfer complexes with condensed polynuclear aromatic hydrocarbons (PAC). The ability of PAC with iodine to form an iodine-PAC complex is expected to be useful in evaluating the electron donor ability of PAC.

The model compounds of petroleum pitch consisting of condensed aromatics used in this study are shown in Fig. 1. The model compounds consist of polyaromatic hydrocarbon, neutral nitrogen compound, and basic nitrogen compound. A mixture of model compounds in chloroform solution was fractionated with iodine. Figure 2 shows FID-gas chromatograph of the compounds fractionated with iodine. The figure indicates that the only basic nitrogen compound was the precipitate produced by addition of iodine under this experimental condition. The aromatic hydrocarbons and neutral nitrogen compounds were not detected in the precipitate. From this result, the compounds which interact strongly with iodine are basic nitrogen compounds such as acridine and phenanthridine.

![Fig. 1 Model Electron Donor Compounds](image1)

![Fig. 2 FID-gas Chromatogram of Fractionated Compounds](image2)
In order to clarify the role of the basic nitrogen compound in its iodine complex, the basic nitrogen compound-iodine complex was analyzed by means of infrared and $^1$H-NMR spectrometers. Figure 3 shows FT-IR spectra of acridine-iodine complexes for various molar ratios. From the measurements of FT-IR for iodine complexes, it was proven that aromatic C-N stretching vibration in acridine molecule shifts to shorter wave numbers due to the formation of the complex. In the case of molar ratios 1:0.25 and above, the shift of aromatic C-N stretching vibration is observed clearly. It is considered that lone pair electrons attached to the nitrogen atom in acridine molecule play an important role in the formation of the iodine complex. Even other basic nitrogen compounds showed a similar tendency of their IR spectra. The relationship between the degree of IR shift and the molar ratio can be depicted as in Fig. 4. The degree of shift is converted to energy by equation $E=h\nu$. A similar result is observed from the measurements of $^1$H-NMR for acridine-iodine complex. From Fig. 5, it is clear that the proton nearest the nitrogen atom in acridine molecule is shifted to a lower magnetic field, while the other protons in the acridine molecule do not shift. In the case of carbazole and anthracene, their characteristic absorption shifts were not observed accompanying the formation of their iodine complexes.

In general, it is shown that a benzene-bromine complex has a sandwich structure in which the two components lie parallel to each other. The influence of sandwich structure on steric hindrance is very small. It is proposed that the complexes of neutral nitrogen compound-iodine and that of aromatic hydrocarbon-iodine also form a sandwich structure. While, the most attractive model for the basic nitrogen compound-iodine complex is an edge-to-edge model in which an iodine molecule directly attacks the binding site of the nitrogen atom. This feature for the complex is consistent with the results of Uchida who found a similar structure for the phenazine-iodine complex in crystalline using X-ray methods. From these results, it is concluded that the complex structure of basic nitrogen compounds differs...
from those of neutral nitrogen compounds and aromatic hydrocarbons.

3.2 Charge Transfer Complexes of Aromatics with TCNQ as Electron Acceptor

Tetracyanoquinodimethane (TCNQ) (I) is an electron acceptor and forms charge transfer or π-complexes with a variety of Lewis bases such as polyaromatic hydrocarbons. TCNQ forms three types of electrically conducting compounds. First, in keeping with its quinoid character, TCNQ forms crystalline π-complexes (charge transfer complexes) with aromatic hydrocarbons, amines and polyhydric phenols. These complexes are characterized by intermediate to high resistivity \((10^3 \text{ to } 10^4 \Omega \text{ cm})\) and very weak ESR absorption. In addition, TCNQ forms two series of stable, salt-like derivatives, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical \(\text{TCNQ}^-\) represented by the resonance hybrid II.

Presented by the simple salt formula \(\text{M}^{n+}(\text{TCNQ}^-)\), in which \(\text{M}\) may be a metallic or organic cation. These salts are characterized by intermediate to high resistivity \((10^4 \text{ to } 10^{12} \Omega \text{ cm})\) and weak ESR absorption in the solid state. Members of the second of the salt-like series, the complex salts represented by the formula \(\text{M}^{n+}(\text{TCNQ}^-\text{C}^-)(\text{TCNQ})\), contain a molecule of formally neutral TCNQ in addition to \(\text{TCNQ}^-\); this series is characterized by exceptionally low electrical resistivity \((10^{-2} \text{ to } 10^0 \Omega \text{ cm})\) and variable ESR absorption.

To characterize the polyaromatic hydrocarbons, TCNQ instead of iodine has been selected as an electron acceptor in the same way described in section 3.1. Carbazole as a neutral nitrogen compound in chloroform solution was readily produced a precipitate by addition of TCNQ. Some striking differences are found between the infrared spectra of carbazole alone and its TCNQ complex. These differences are observed immediately after mixing both solutions as shown in Fig. 6, which shows the spectra obtained from (a) carbazole alone and (b) from a carbazole-TCNQ complex (precipitate). Figure 6 shows some significant differences in N–H stretching, C–N stretching, and N–H transverse vibration due to the formation of the complex. In the case of acridine as a basic nitrogen compound, it is found that acridine did not quickly produce the precipitate by addition of TCNQ. However, a flock-like material was produced when the solution was allowed to stand for 10 days at room temperature. In Fig. 7, infrared spectra of the acridine-iodine complex are compared with those of the acridine-TCNQ complex (flock) in which absorption becomes broad due to the strong interaction between acridine and TCNQ. The absorption of acridine-TCNQ complex becomes broad due to the strong interaction between donor and acceptor. In other words, the interaction between acridine and TCNQ is stronger than that between acridine and iodine. Figure 7 also shows clearly the appearance of conduction electrons in the region of higher wavenumbers for the acridine-TCNQ complex. From the measurements of electronic properties, the acridine-TCNQ complex was confirmed to be incorporated into a member of electrically conducting charge transfer complexes. This significant difference in the complexes between iodine and TCNQ extends to a discrimination of covalent and/or noncovalent bonding of the aromatic...
hydrocarbons. By contrast, no remarkable changes of anthracene by addition of TCNQ were recognized, while C-H deformation band of anthracene and phenanthrene was partially split into two bands. Therefore, TCNQ acts as an electron acceptor on such special sites as positions of heteroatoms in aromatic hydrocarbon compounds. Detailed discussion will be made in terms of ESR experimentation in section 3.4.

3.3 Association Constant For Charge Transfer Complex

Complexes with aromatic π-bases are believed to have resulted from the overlapping of the respective acid and base π-orbital systems, and the magnitude of this interaction is reflected in $K$, the association constant for complex formation, and the energy of the charge transfer spectral absorption band. If the complex is assumed to be 1:1, the association equilibrium may be written as

$$A + B \rightleftharpoons C \tag{4}$$

The association constant for complex formation, $K$, then will be

$$K = \frac{(C)}{[(A) - (C)][(B) - (C)]} \tag{5}$$

where $(A)$ and $(C)$ are molar concentrations of π-acid and complex, respectively, and $[B]$ and $[C]$ are mole fractions of π-base and complex, respectively. Tetracyanoethylene (TCNE) was selected as an electron acceptor in order to simplify the operation and procedure. In Table 1, the frequency of maximum absorption, $\nu_{\text{max}}$, the base ionization potential, $I_p$, and the free energy of formation, $\Delta G^\circ$, are listed for TCNE-carbazole together with some aromatic complexes for comparison. The complex between TCNE and carbazole exhibits $\Delta G^\circ = -2,024$ cal, indicative of the strongest interaction as far as Table 1 shows.

In the case of acridine–TCNE complex, the intensity of charge transfer absorption at 4,700 Å increases with time as shown in Fig. 8. It takes about 200 hours to attain equilibrium. The association constant for acridine–TCNE complex could not be calculated because the formation of this complex was not 1:1. Such equilibrium indicates that it takes a long time to attain a more stable structure of the complex. The long time...
required for reaching equilibrium has been supported by the flock formation of the acridine-TCNQ complex.

3.4 Evaluation of Charge Transfer Complexes by Means of ESR Spectroscopy

ESR measurement is one of the useful techniques to evaluate various charge transfer complexes. **Figure 9** shows ESR spectra of acridine complexes with three kinds of electron acceptors. The spectrum of acridine/iodine system consists of one broad line, indicative of the formation of charge transfer complex. On the other hand, acridine with a TCNE- or TCNQ-complex shows a spectrum consisting of some distinct lines. The fact suggests that electron acceptor molecules interact on definite sites of the aromatic compounds resulting in resolved spectra as illustrated in **Fig. 9**. It is thought that the spin center in acridine/iodine system stems from delocalization rather than from the acridine/TCNQ or TCNE system.

With regard to iodine as an electron acceptor, the radical concentration, $N_s$, for the aromatic hydrocarbon-iodine complexes was plotted against the ionization potential of the parent aromatic hydrocarbon as shown in **Fig. 10**. From this figure, it is clear that $N_s$ of iodine complex monotonically increases with decreasing ionization potential of aromatic hydrocarbons. This result leads to the conclusion that ESR of iodine as an electron acceptor reflects mainly on the size and shape of the aromatic rings.

On the other hand, we must consider another mechanism for the change in spin concentration of the aromatic compound-TCNQ complex. Chloroform and tetrahydrofuran (THF) were used to dissolve the electron acceptor molecule into the aromatic compound. These solvents are not absolutely neutral in terms of electron donor-acceptor interaction. **Figure 11** shows a comparison of values of spin concentration $N_s$(CHCl₃) and $N_s$(THF) for aromatic compound-TCNQ complex.
plexes. The values of $N_s$(THF) for the compounds tested are mostly similar to those of $N_s$(CHCl$_3$), except for the case of anthraflavic acid. The molecules of anthraflavic acid form a network with hydrogen bondings. A plausible interpretation for the above is that hydrogen transfer from THF molecule to the functional groups in anthraflavic acid may occur and cleave the hydrogen bonding network catalyzed by TCNQ. This causes a decrease in spin concentration of anthraflavic acid. To confirm the occurrence of hydrogen transfer reaction, a mixture of 9,10-dihydroanthracene (9,10-DHA) as a hydrogen donor and TCNQ in chloroform solution was allowed to stand for a week at room temperature. The yellow color of the solution became blue. Figure 12 shows FID-gas chromatogram of the blue solution indicating the formation of anthracene. In the reaction systems of 9,10-DHA with TCNQ in chloroform, the hydrogen transfer reaction presumably occurs through the radical anion intermediates of TCNQ.

The approach described above will give us one of the means of solving noncovalent bonding nature in heavy hydrocarbon such as pitch. When the mechanism of interaction of heavy hydrocarbons with iodine and TCNQ systems is elucidated, the strength and population of the noncovalent and hydrogen bondings will be clarified. The geometry and energetic of interactions between several polynuclear aromatic compounds and the guests will be elucidated using various methods. The ESR measurements of hydrocarbons as host with various electron acceptors as guests would be a favorable technique. One of the advantages of this technique is that it is applicable to mixtures of complex hydrocarbons as well.

3.5 Charge Transfer Fractionation of Aromatic Hydrocarbon Mixtures

Recently, Zander et al. proposed so-called "charge-transfer fractionation (CTF)" of coal tar pitch using picric acid or elementary iodine as an electron acceptors$^{14,15}$. This fractionation technique yields pitch fractions with different degrees of thermal reactivity. More recently, CTF of pitch with regard to the chemical composition of the fractions obtained has been further investigated$^{16-18}$. They revealed that resin was concentrated in the components of iodine adducts$^{16}$. The lack of detailed analysis for chemical constitution of the fractions does not allow for discussion of the mechanism of fractionation.

A novel fractionation scheme based on the knowledge obtained in sections 3.1—3.3 has been attempted. The elemental composition of the coal tar pitch used in this study is shown in Table 2. The coal tar pitch consists mainly of aromatic hydrocarbons and small amounts of nitrogen containing compounds most of which are basic nitrogen compounds (pyridine type). Concentrations of neutral nitrogen compounds (pyrrole type) are smaller than those of the basic nitrogen compounds in the sample. In order to evaluate the neutral nitrogen compound, 5wt% of indole and carbazole as two types of neutral nitrogen compounds were added to the chloroform soluble part of the coal tar pitch.

A separation scheme with iodine is shown in Fig. 13. Elemental analyses of the fractions are also shown in Table 2. The Fr-C interacts strongly with iodine effecting precipitation. It is clear that nitrogen was concentrated from 1.20 to 2.48 in Fr-C, indicating that nitrogen compounds in the pitch are concentrated in Fr-C. Figure 14 shows FID-gas chromatogram in the chloroform-soluble part of pitch(PK-E, CHCl$_3$). Fluoranthene, pyrene, and phenanthrene are major components, while five or six rings of aromatic

| Table 2 Elemental Analyses of Coal Tar Pitch and Fractionated Pitch |
|-----------------|-----|-----|-----|-----|-----|
|                 | C   | H   | N   | S   | Odi(%) |
| PK-E original   | 92.82| 4.24| 1.14| 0.38| 1.42  |
| PK-E CHCl$_3$  3-solubles | 92.73| 4.20| 1.20| 0.48| 1.38  |
| PK-E SA$^{1,2}$ | 92.47| 4.21| 1.32| 0.43| 1.38  |
| Fr-C$^{2}$      | 92.24| 3.43| 2.48| 0.44| 1.42  |

1) CHCl$_3$ free basis.
2) PK-E SA : 5 wt% of indole and carbazole are added.
3) CHCl$_3$ and iodine free basis.

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hydrocarbons and nitrogen compounds are the minor components in the fraction.

Figure 15 shows FID-gas chromatograms of the fractionated pitches. The peaks marked with an arrow in Fig. 15 correspond to nitrogen containing compounds which are confirmed by FTD-gas chromatography. The majority of nitrogen containing compounds in Fr-C are basic nitrogen compounds, although basic nitrogen compounds are rarely found in the parent pitch sample. Many basic nitrogen compounds, for example, phenanthridine, azapyrene, and azachrysene can readily be detected. This means that the basic nitrogen compounds are concentrated in Fr-C.

On the other hand, the pattern of Fr-A chromatogram was similar to that of the parent pitch. The peak intensities of neutral nitrogen compounds were almost unchanged. Such neutral nitrogen compounds as indole and carbazole were not concentrated as precipitates by addition of iodine. In other words, the interaction between neutral nitrogen compounds and iodine was weak.

Figure 16 shows the FID-gas chromatogram of Fr-B. If the components of Fr-B were due to the contaminants from those in the mother liquid, the pattern of chromatogram might be the same as...
that of Fr-A. However, the distribution pattern differed clearly from both those of Fr-A and Fr-C, indicating that the components in Fr-B are not due only to the contaminants in the mother liquid. Let us look more closely at the components in Fr-B which consist mainly of polyaromatic hydrocarbons. Comparing the chromatogram of Fr-A with that of Fr-B, the components of Fr-B are concentrated aromatic hydrocarbons of five or six rings, for example, benzo[\(\alpha\)]pyrene and perylene. The interaction of the components in Fr-B with iodine is presumably intermediate between the components in Fr-C and Fr-A.

From the above results, the compounds in the chloroform-solubles in coal tar pitch can be separated into three types by difference in the extent of their interactions with iodine. 
1) The compounds which interact strongly with iodine are basic nitrogen compounds such as azapyrene and azachrysene.
2) The compounds which interact moderately with iodine are five or six rings aromatic hydrocarbons such as benzo[\(\alpha\)]pyrene and perylene.
3) The compounds which interact weakly with iodine are aromatic hydrocarbons with less than four rings and with neutral nitrogen compounds, for example, pyrene, phenanthrene, indole, and carbazole.

The electron affinity of the acceptor molecule of iodine is constant. The formation of the charge transfer complex of an aromatic hydrocarbon depends on the ionization potential of the electron donor molecule. In other words, the smaller the ionization potential of a donor molecule, the easier is the formation of a charge transfer complex. Ionization potentials for the selected compounds were calculated by the Hückel method, and the results obtained are shown in Table 3. First, for polyaromatic hydrocarbons, the larger the aromatic ring, the smaller is its ionization potential. The relation between charge transfer complex and ionization potential of electron donor molecule has been supported by experimental data of Fr-B. The degree of interaction of the aromatic hydrocarbons studied with iodine can be explained by the ionization potential of the donor molecule. However, for nitrogen compounds, the degree of interaction cannot be explained by its ionization potential. The strong interaction of basic nitrogen compounds with iodine is presumably due to the lone pair electrons attached to the nitrogen atom, while neutral nitrogen compounds have no such lone pair electrons.

The technique of CTF with iodine has a potential for isolating and concentrating the basic nitrogen compounds in tar pitch.

4. Hydrogen Donor Ability of Aromatic Hydrocarbons

According to the free-radical mechanism, donor effectiveness of molecules is related to the availability of abstractable hydrogen atoms and is strongly dependent upon the chemical structure of molecules. It has been suggested that hydrogen transfer is important in hydrocracking of coal. The form of ‘hydrogen-shuttling’, associated with hydrogen donor ability has been recognized in the carbonization process of heavy hydrocarbons such as pitch. This is because hydrogen stabilizes the radicals formed during pyrolysis and the viscosity of the system at high temperatures in consequence lower. However, a detailed mechanism of this hydrogen transfer has not yet been established.

4.1 Relationship between Hydrogen Donor Ability and Chemical Structure of Aromatic Hydrocarbons

In this section, the primary objectives are to
elucidate the hydrogen transfer reaction by: (1) evaluating the hydrogen donor and the acceptor ability of the model compounds, and (2) relating the hydrogen donating ability to the chemical structure of the model compounds. We have selected the following hydrocarbons for this purpose: decalin, tetralin, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene.

In general, the dehydrogenation reaction of a hydroaromatic compound (H₂A) during pyrolysis can be written as:

\[ \text{H}_2\text{A} \overset{\Delta}{\rightarrow} \text{HA}^- + \text{H}^+ \]  

where HA⁻ is the radical species of the hydroaromatic compound. Here, it is assumed that the ease of dehydrogenation of a hydroaromatic compound is related to the difference in the binding energies (ΔE) of H₂A and HA⁻, i.e., the reaction compounds having smaller values of ΔE form radicals proceed more readily than those having larger values of ΔE. Thus, it appears that ΔE represents the bond dissociation energy of the hydrogen atom at any given position.

To establish the validity of this assumption, computation calculations were carried out using the INDO method and empirical force field calculation.

Many methods are currently used for determination of molecular structures. However, to avoid the difficulties usually involved in the experimental determination of molecular structures, the force-field, i.e., the molecular mechanics method has been introduced by Allinger. This method is constructed from a set of equations and parameters derived from classical mechanics: a molecular model of the donor compound is constructed and approximate co-ordinates of atoms and details of the bonds (bond lengths and angles, etc.) obtained from the molecular model are input in a computer program. The energy of the molecule with co-ordinates corresponding to the initial geometry is calculated and then, energy minimization is carried out to obtain the final steric energy and the most stable structure. The INDO (intermediate neglect of differential overlap) method is based on the semi-empirical molecular orbital (MO) theory, and it has often led to good results for spin density in the system (particularly, the radical). Askari et al. have carried out an ab initio MO calculation using the co-ordinates calculated using the force field method and obtained the results which best fit the experimental results. Accordingly, the precise geometries of the donor compounds obtained using the force field method were used for input data of the INDO method.

Table 4 summarized the binding energies of the donor compounds, their radicals, and their energy differences calculated using the INDO method. It is evident that the binding energy difference, ΔE, is largest for decalin and smallest for 1,4-DHN, i.e., decalin > tetralin > 1,2-DHN > 1,4-DHN.

For comparing the computation results, evaluations of hydrogen donor ability by gas chromatography are available. A relation between the amount of hydrogen evolved, as determined by g.c.(TCD), and the heat-treatment temperature (HTT) for donor compounds is shown in Fig. 17. The order of the model compounds of capable of releasing hydrogen is: decalin > tetralin > 1,2-dihydronaphthalene(1,2-DHN) ≤ 1,4-dihydronaphthalene(1,4-DHN).

Determination of hydrogen transfer by ¹H-NMR has been also attempted. Hydrogen transfer can be monitored using the extent of 9,10-dihydroanthracene(9,10-DHA) formation from anthracene as

| Table 4 Binding Energy of Model Compounds, Radicals, and Their Binding Energy Difference |
|---------------------------------|---------------------------------|-----------------|
| H₂A  | HA⁻  | ΔE         |
| (-11.9434) | (-11.6265) | 0.3174 |
| (7,490.26) | (7,291.21) | (199.1) |
| (-10.7882) | (-10.4753) | 0.3129 |
| (6,765.50) | (6,569.27) | (196.2) |
| (-10.3707) | (-10.0657) | 0.3050 |
| (6,503.67) | (6,312.40) | (191.3) |
| (-10.3558) | (-10.0576) | 0.2982 |
| (6,494.33) | (6,307.32) | (187.0) |

* A.U. = 6.2712×10² kcal/mol.
1) The energy level of β-radical from donor compound was found to be higher than that of α-radical.
2) Value in the bracket is unit in kcal/mol.
Here, various combinations of hydrogen donor and acceptor were heat-treated. NMR spectra of CDCl₃-soluble materials prepared by heat-treatment of 1,4-DHN with anthracene at 623, 673 and 723 K are shown in Fig. 18 (a)-(c), respectively. Significant changes in the peak intensity of 9,10-protons (3.87 ppm) occur, i.e., the amount of hydrogen transferred increases with increasing HTT. Acenaphthylene, also used as the hydrogen acceptor, produced acenaphthene having ethano-bridge protons (3.35 ppm).

Figure 19 shows the relative amount of 9,10-DHA and that of acenaphthene as measured using ¹H-NMR. Here, the relative amount represents the ratio of the proton peak intensity of 9,10-protons in 9,10-DHA and the ethano-bridge protons in acenaphthene versus tetramethylsilane (TMS) (0.5 wt% TMS in CDCl₃). Figure 19 (a) shows that the order of the model compounds in terms of their ability to transfer hydrogen to anthracene is: 1,4-DHN > 1,2-DHN > tetralin. For 1,4-DHN, it was not possible, through peak separation, to distinguish the ethano-bridge protons of acenaphthene from a certain proton of 1,4-DHN itself. With phenanthrene as the hydrogen acceptor, a hydrogenated derivative, e.g., 9,10-dihydrophenanthrene, was not observed in any of the donors at any HTT. It may be concluded qualitatively that the order of the model compounds in terms of ease of hydrogenation is phenanthrene < anthracene < acenaphthylene. This order is in good agreement with that in terms of the frontier electron density at any given
position in the compounds.

The experimental results are satisfactorily interpreted by theoretical prediction. Furthermore, these results appear to be in good agreement with the results reported by King et al.\textsuperscript{28} that the bond dissociation energy of 1,4-DHN is less than that of 1,2-DHN. Also, the binding energy of 1,2-DHN radical \( \cdot \) is smaller than that of 1,4-DHN radical \( \cdot \) (i.e., \( \cdot \) is more stable than \( \cdot \)) in agreement with the prediction made previously.

\textbf{4.2 Hydrogen Transfer of Petroleum Residues and Pitches at High Temperatures}\textsuperscript{29}

The amounts of transferable hydrogen, \( H_{\text{DHA}} \), in vacuum residues heated at 673 K are summarized in Fig. 20. Vacuum residues such as Venezuela(VZ) and Wafra(WF) gave a small amount of transferable hydrogen and yield cokes with fine mosaics of anisotropic optical texture. The size of the anisotropic units of the cokes increases with increasing amount of \( H_{\text{DHA}} \). Samples which show a larger amount of transferable hydrogen yield cokes exhibiting a large flow-type anisotropy. It is clear that there is a very close relation between the optical texture of the coke and the amount of transferable hydrogen in the vacuum residue.

Taking account of the results above and previous studies\textsuperscript{30–32}, we propose a model of carbonization shown in Fig. 21. Homolysis of covalent bonds in pitch or in vacuum residue at high temperatures gives radicals. When the radicals are not stabilized, but are carbonized further in a viscous state, they may recombine with other species to form non-graphitizable carbon(char) having an isotropic or fine mosaic optic texture. Let us assume that if the radicals are stabilized by hydrogen transfer, thermal fragments are turned into stable low molecular species. These smaller species maintain the relatively low viscosity of the carbonization system, leading to carbon network layers, which are capable of stacking themselves up in parallel, being able to stack parallel each other with a greater optical texture.

\textbf{Table 5} shows the variation of transferable hydrogen in petroleum residues with metal oxide catalysts. For the samples so far tested, all of the solid catalysts decreased transferable hydrogen for both WF- and Taching(TK)-vacuum residues. The transferable hydrogen in petroleum residues decreases in the presence of silica gel as an inert material. It is conceivable that the addition of solid catalyst acts as an inhibitor to spatially restrict hydrogen transfer in the carbonization system, resulting in the reduction in optical texture. By contrast, \( \text{SeO}_2 \) markedly promotes hydrogen transfer in vacuum residues, resulting in a substantial increase in optical texture for WF-VR.

Therefore, hydrogen transfer is one of the important key steps for production of graphitizable carbon.

\textbf{5. Interaction of Aromatic Hydrocarbons with Various Catalysts by ESR}

In order to clarify the difference in the nature of

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Sample & \( H_{\text{DHA}} \) (mg-H2/g-sample) & \\
\hline
A240 & 0.24 & 0.12 \\
FCC-DO & 0.23 & 0.11 \\
ETP & 0.20 & 0.10 \\
SH-VR & 0.14 & 0.07 \\
WF-VR & 0.06 & 0.03 \\
VZ-VR & 0.04 & 0.02 \\
\hline
\end{tabular}
\caption{Transferable Hydrogen(HDHA) in Sample}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Catalyst & WF-VR & TK-VR \\
\hline
VR alone & 0.110 & 0.076 \\
VR/\text{SiO}_2-\text{Al}_2\text{O}_3 & 0.082 & 0.058 \\
VR/\text{MoO}_3-\text{Ti}_2\text{O}_5 & 0.077 & 0.048 \\
VR/\text{Al}_2\text{O}_3 & 0.076 & 0.041 \\
VR/\text{SiO}_2 gel & 0.074 & — \\
VR/\text{SeO}_2 & 0.540 & 0.610 \\
\hline
\end{tabular}
\caption{Transferable Hydrogen(HDHA) in WF- and TK-VR/Metal Oxide Systems}
\end{table}

* The unit is (mg-H2/g-VR).

HTT 673 K, no soaking period, 10 K/min.
Lewis acidity of various catalysts with respect to the radical formation in the condensed aromatics, ESR studies at different temperature levels have been carried out using anthracene and petroleum pitch.

5.1 ESR Spectra in Pyrolysis of Anthracene/Catalyst Systems

Figure 22 (a) shows the ESR spectrum of anthracene with SbCl₃ heat-treated for 47 min at 428 K. The spectrum shows equally spaced hyperfine lines superimposed on a broad background line. The peak to peak width for the hyperfine lines is 1.5 G. The broad background signal increases with reaction time. The spectrum broadening might be attributed to a magnetic dipolar broadening mechanism. Anthracene in concentrated H₂SO₄ produces anthracene cation radicals. The movement of the radicals can be restricted by lowering the temperature below 283 K as illustrated in Fig. 22 (b).

Examination of the temperature dependence of the spectra of anthracene/H₂SO₄ identifies the radical species for anthracene/SbCl₃ systems as being anthracene cation radicals, because the spectrum derived from anthracene/H₂SO₄ (low temperature) is strikingly similar to that from anthracene/SbCl₃ with respect to the number of hyperfine lines and peak positions. A similar spectrum was observed when anthracene was pyrolyzed with AlCl₃ at 341 K.

The ESR spectrum for anthracene-derived radicals in a weak Lewis acid(ZnCl₂) is quite different from that for those radicals in a strong Lewis acid(SbCl₃), as shown in Fig. 23. Although the spectrum of the anthracene/ZnCl₂ system shows poor resolution, it comprises about 9 lines with the same interval of 2.5 G and spreads over about 24 G.

Furthermore, each hyperfine line seems to consist of a quartet. It is not simple to describe the radical derived from anthracene/ZnCl₂ because of poor resolution. The even lines of the hyperfine structure can be explained in terms of the interaction with the odd hydrogen nuclei, but the elucidation of the type of radical species in the anthracene/ZnCl₂ system requires further study.

Figure 24 shows the ESR signal amplitude for two radicals in the anthracene/SbCl₃ system (a broad line radical and a radical with hyperfine lines) (see Fig. 22 (a)) heated at 248 K as a function of time. The intensity of the broad line gradually increased monotonically with reaction time, but the relative intensity of the hyperfine spectral lines first increased reaching a maximum in about 10 min and then decreased with further reaction time.

The existence of a maximum for the hyperfine radical concentration seems to indicate that this radical is one of the intermediates of the reaction species. Thus, there is a possibility of a reaction pathway via cation radical species in the pyrolysis...
of anthracene/catalyst systems.

5.2 ESR Spectra from Pitch/Catalyst Systems at Pyrolysis Temperature

Changes in the spin concentration of pitch with several metal chlorides at 693 K are shown in Fig. 25. The pronounced increase in the spin concentration was observed for the pitch/ZnCl₂ and pitch/SnCl₂ systems. On the other hand, the increase in the spin concentration of the pitch with a strong Lewis acid such as SbCl₃ and AlCl₃ was almost identical with that of the pitch alone and much less than for ZnCl₂ and SnCl₂. From the figure, we can divide these systems into two groups with respect to their profiles of spin concentration increase. The first includes the pitch with relatively weak Lewis acid (ZnCl₂ and SnCl₂) systems; and the second with strong Lewis acid (SbCl₃ and AlCl₃) systems.

By the usual ESR technique, relatively stable free radicals are available for observation. The radicals detected in the present study, therefore, may result from the stable cation π radicals and/or σ radicals with relatively long life. The former radicals have been reported to be produced in the complex between ZnCl₂ and polynuclear aromatics. As for σ radicals, observations of some transient radicals occurring during the pyrolysis of aromatic hydrocarbons have been reported by Livingston et al. The reason for the importance of a suitable strength of Lewis acidity for producing free radicals has been explored by observing the interaction between a metal chloride and anthracene selected as a model compound.

5.3 Exchange of Hydrogen Attached to Condensed Aromatics with Deuterium in Heavy Water over Catalysts

The H-D exchange reaction of hydrogen atoms attached to condensed aromatics with deuterium atoms in D₂O over various catalysts for getting information at the initial stage of reaction of aromatic hydrocarbons has been studied by means of D-NMR. MoO₃/ZrO₂, MoO₃/SiO₂, Fe₂O₃·SO₄²⁻, SbCl₃ and ZnCl₂ showed a significant catalytic activity for the exchange reaction. The H-D exchange ability was discussed in terms of the acidic properties and concentration of Mo⁵⁺ catalyst supports.

5.3.1 Molybdenum Containing Catalyst Systems

Several metal oxide catalysts with different acidities were tested with respect to the H-D exchange reaction. The D-NMR spectrum of the product from the anthracene/MoO₃-ZrO₂/D₂O system which was allowed to react at 573 K for 15 min is shown in Fig. 26 (a). It is apparent that the D-H exchange reaction takes place over an acidic catalyst, MoO₃-ZrO₂. Assignment of deuterium atoms attached to anthracene is made by comparison with the proton chemical shifts of anthracene. A similar spectrum was observed when MoO₃-SiO₂ was used. On the other hand, no significant exchange reaction was observed for the basic catalyst MoO₃-MgO, as shown in Fig. 26 (b).

The fact that MoO₃-ZrO₂ and MoO₃-SiO₂ are more active than MoO₃-MgO for the H-D exchange reaction might be explained by the greater ability of ZrO₂ and SiO₂ to reduce MoO₃ to form lower bonding stages of Mo, such active species as Mo⁶⁺, Mo⁴⁺ and so on. Since Mo⁵⁺ is a paramagnetic species, it is detectable by ESR spec-

Fig. 25 Spin Concentration vs. Time of Pyrolysis

![Spin Concentration vs. Time of Pyrolysis](image)

Fig. 26 D-NMR Spectra of Products from Anthracene/Catalyst/D₂O System

(a) anthracene/MoO₃-ZrO₂/D₂O at 573 K for 15 min,
(b) anthracene/MoO₃-MgO/D₂O at 573 K for 15 min.
troscopy. Table 6 shows the correlation between the proportion of the deuterium atoms incorporated in anthracene by the H–D exchange reaction and the Mo\(^{5+}\) spin concentration in Mo-containing catalysts. The presence of reduced form Mo species may be responsible for the H–D exchange reaction.

### 5.3.2 Iron Oxide Catalyst Systems

Fe\(_2\)O\(_3\) is one of the most promising catalysts for coal liquefaction process, because iron oxides and iron ore are disposable catalysts. One modification of Fe\(_2\)O\(_3\) catalyst was attempted by including SO\(_4^{2-}\) ions. The Fe\(_2\)O\(_3\)-SO\(_4^{2-}\) catalyst showed higher activity and selectivity than those of pure Fe\(_2\)O\(_3\) catalyst\(^{40}\) for liquefaction of both Akabira coal and Taiheiyo coal.

The effect of SO\(_4^{2-}\) ion in Fe\(_2\)O\(_3\) catalyst on coal liquefaction may partly be due to the increased acid strength of the catalyst. Therefore, it can be expected that SO\(_4^{2-}\) ion in the Fe\(_2\)O\(_3\) catalyst influences the H–D exchange reaction of the anthracene/Fe\(_2\)O\(_3\)/D\(_2\)O system. In fact, some evidence of such influence on the exchange reaction was obtained from the D–NMR spectrum of the product from the Fe\(_2\)O\(_3\)-SO\(_4^{2-}\)/anthracene/D\(_2\)O system reacting at 573 K for 15 min.

On the other hand, no evidence of the H–D exchange reaction could be obtained for pure Fe\(_2\)O\(_3\) catalyst system.

### 5.3.3 Lewis Acid Catalyst System

Available evidence about metal chloride catalysts suggests that Lewis acid is first converted to Bronsted acid in the presence of water\(^{40}\). Therefore, one can easily invoke a direct adduct of Lewis acid and anthracene as the intermediate allowing the H–D exchange. This consideration was confirmed directly by means of D–NMR for Lewis acid catalysts (SbCl\(_3\), ZnCl\(_2\)) with anthracene.

The D–NMR spectrum of the product from the anthracene/ZnCl\(_2\)/D\(_2\)O system reacting at 483 K for 15 min is shown in Fig. 27 (a). It can be seen that the deuterium atoms are especially concentrated at (9,10) positions of anthracene. Figure 27 (b) indicates that a significant H–D exchange reaction also takes place over the SbCl\(_3\) catalyst, mainly at (9,10) and (1,4,5,8) positions of the nuclei of anthracene. The deuterium distribution clearly differs from that of the ZnCl\(_2\) catalyst.

The D–NMR investigation of the H–D exchange reaction was extended to various polynuclear aromatics such as perylene, pyrene, phenanthrene, benz[\(a\)]anthracene, and naphthacene. Among the hydrocarbons so far tested, phenanthrene had the highest degree of H–D exchange reaction with respect to ZnCl\(_2\) catalyst.

### 6. Concluding Remarks

The association forces in heavy hydrocarbons play important roles in determining physical properties such as solubility, viscosity, boiling point and apparent molecular weight. The abilities of charge transfer and hydrogen transfer of polyaromatic hydrocarbons have been measured by means of various spectroscopic techniques and theoretical calculations. These abilities relate to the association forces such as hydrogen bonding and aromatic \(\pi-\pi\) interactions in heavy hydrocarbons and provide probes of structure and reactivity.

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Table 6 Catalytic Activity of MoO\(_3\) over Metal Oxides for H–D Exchange Reaction on Anthracene and Their Mo\(^{5+}\) Concentration

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Exchanged product[%]</th>
<th>Mo(^{5+}) spin concentration[spins/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO(_3)/ZnO</td>
<td>8.3</td>
<td>2.52\times10(^{10})</td>
</tr>
<tr>
<td>MoO(_3)/SiO</td>
<td>8.2</td>
<td>1.42\times10(^{10})</td>
</tr>
<tr>
<td>MoO(_3)/MgO</td>
<td>0.0</td>
<td>0.77\times10(^{10})</td>
</tr>
</tbody>
</table>

(a) anthracene/ZnCl\(_2\)/D\(_2\)O, 483 K, 15 min, (b) anthracene/SbCl\(_3\)/D\(_2\)O at 418 K for 15 min.

Fig. 27 D–NMR Spectra of Products from Anthracene/Lewis Acid Catalyst/D\(_2\)O System
References
要旨

多芳香族炭化水素の電荷移動及び水素移動
—化学構造と反応性に対するプローブ—

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多芳香族炭化水素の熱的および触媒反応は石油精製、化学工業の分野において非常に興味深い。石油から得られる製品には熱的反応によってつくられるものが多くある。熱および接触反応は、分子間または分子と触媒との相互作用で起こり、このような反応を考える上で、電子移動、水素移動は最も基本的な反応である。本論文では、多芳香族炭化水素の電荷移動（電子移動）および水素移動について考察した。

電子受容体である芳香系、多芳香族炭化水素（PAH）と電荷移動錯体を形成することはよく知られており、PAHとヨウ素の電荷移動錯体を形成する能力は、PAHの電子供与能を評価する上で有用なパラメーターである。

ピチのモデル化合物（Fig. 1）の混合法流に添加するため、塩基性の塩素化合物の選択的な沈殿剤を生成することが明らかになった（Fig. 2）。そのIRスペクトルは芳香性C-N伸縮振動帯が大きく変化していることを観察した（Fig. 3）。さらに1H-NMRから塩基性塩素化合物の塩素原子に最も近いプロトンのケミカルシフトが、より素と錯体を形成することにより大きく変化することも示した（Fig. 5）。他の電子供与体（芳香族炭化水素、中性塩素化合物）では反応の変化は認められなかった。これらのことを考慮して、生成した錯体の構造について検討した結果、塩基性塩素化合物-ヨウ素錯体は、サンドイッチ構造ではなく、edge-to-edge modelであれば考えられる。

一方、電子受容体が7,7,8,8-トリアゾノキノジメタン（TCNQ）の場合、中性塩素化合物であるカルバゾールがもっとも沈殿剤を生成し、そのIRスペクトルもN-Hに関する吸収が大きく変化することが明らかになった（Fig. 6）。また塩基性塩素化合物であるアクリジンはTCNQ添加後、約10日後に紫斑の沈殿剤（ブロック）を生成し、そのブロックのIRスペクトルから電子の吸収が認められるようになった（Fig. 7）。

そこで電子受容体にテトラシアノエチレン（TCNE）を用いた錯体の会合定数の計算を行った。錯体の自由エネルギー（ΔG°）の値は中性塩素化合物であるカルバゾール他の芳香族炭化水素よりも大きい値を示すことがわかり（Table 1）。このことはカルバゾール-TCNQ錯体が強く相互作用するという先の結果を支持するものである。一方、アクリジン-TCNE錯体の電荷移動吸収は時間とともに変化し（Fig. 8）、かつ錯体形成が1:1ではなくΔG°を求めることはできなかった。

触媒の電子受容体とアクリジン錯体のESR測定の結果、ヨウ素はプロードなシグナルを示すのに対し、TCNE、TCNQは比較的锐い分光したピークが観測された（Fig. 9）。PAH-ヨウ素錯体のラジカル濃度は、PAHの電子結合と触媒に密接関係し、イオン化ポテンシャルにて整理ができる（Fig. 10）。TCNQは本素結合を形成する能力のある有機塩素化合物を組み合わせた場合、高いラジカル濃度を示し、用いる溶媒によってその値が変化することが観察された（Fig. 11）。THF溶液のところ錆体のラジカル濃度が減少するのに対して、TCNQの存在下で溶媒より水素移行が起こるためと考えられる。そこで、水素供与体として9,10-ジヒドロアントラセン（9,10-DHA）、溶媒にクロロホルムを用いTCNQの混合溶液を1週間、室温で放置した結果、アントラセンが生成していることが明らかになった（Fig. 12）。したがって、TCNQ-PAH-α-錆体を形成するとともに、9,10-DHAのような水素供与体から室温で水素引き抜き反応を起こす能力を持っていることがわかる。

この考察を応用して、ヨウ素を用いた多芳香族化合物の混合溶液であるピチの分離方法について検討した。ヨウ素を添加して分離されたものの内には、塩基性塩素化合物が濃縮されており（Fig. 14）、モデル化合物の実験を支持する結果が得られた。しかしながら分離物には、5,6 環の多芳香族炭化水素が含まれていた（Fig. 16）。ピチ中には、5,6環の芳香族炭化水素の酸成分であり、このことは5,6環の芳香族炭化水素を塩素の添加により濃縮することへの応用にもできるだろう。芳香族炭化水素だけに限定すると、電荷移動錯体の沈殿物生成の挙動は炭化水素のイオン化ポテンシャルの値を説明することが可能である（Table 3）。

水素移動の基礎的知見を得るために、モデル化合物の水素供与能と化学構造との関係を検討した。モデル化合物の水素供与能は、テトラシアノチレンと1,2ジヒドロアントラセンと1,4ジヒドロアントラセンの順である（Fig. 17）。

INDO法により計算されたモデル化合物とそのラジカルの結合エネルギーを密接に相関することが明らかになった（Table 3）。石油残油中の移動可能水素を定量した。その量は0.1〜0.5 mg/g 程度で水銀に大きく依存する（Fig. 20）。石油系残油の移動可能水素に及ぼす金属酸化物触媒の影響を「H-NMRを用いて検討した。SiO2-Al2O3, MoO3-TiO2, β-Al2O3, SiO2-Al2O3, MoO3-TiO2, β-Al2O3, SiO2-Al2O3, MoO3-TiO2, β-Al2O3等の固体触媒はワフラ減圧残油の移行可能水素を減少させ、一方、SiO2は減圧残油における水素移行反応を大きく促進した（Table 5）。SiO2は移行水素に対して高活性を示し、石油系残油の炭化に良好な触媒となり得ることが結論される。

炭化反応における金属塩化物触媒の役割を明らかにするためには、高温ESRを用いてピチとそのモデル化合物触媒について、金属塩化物触媒の相互作用をラジカルの挙動に着目してin-situでモニターした。アントラセン/AIOCl, アントラセン/ShCl₂系からは、高温のもとでカチオンラジカルが生成することが判

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明した（Fig. 22）。しかし、アントラセン/ZnCl₂系から生成するラジカルの超微細構造は単なるカチオンラジカルとは異な
る ESR スペクトルを示した（Fig. 23）。また、アントラセン
/StCl₂系では、カチオンラジカルが反応中間体であることが
Fig. 24 によって明らかになった。ZnCl₂、SnCl₂、触媒はピッ
チのラジカル濃度を著しく増加させるが、AlCl₃、SbCl₃、触媒
は顕著な変化を示さなかった（Fig. 25）。
種々の触媒について、重水中の芳香族炭化水素の H-D 交換反応の触媒能を D-NMR を用いて評価した。MoO₃/ZrO₂、
MoO₃/SiO₂、Fe₂O₃-SO₄²⁻、SnCl₂、ZnCl₂ は交換反応に関し
て良好な触媒である（Figs. 26、27）。触媒の H-D 交換能力は
Mo³⁺ の濃度で評価が可能である（Table 6）。
以上総括すると、重質炭化水素類の配合剤は、種々の物理的
性質を決定する重要な役割を果たしている。種々の分析法は
は理論的計算により、多環芳香族炭化水素の電荷移動およ
び水素移動の評価が可能である。これらの能力は重質炭化水素
類を支配している水素結合、芳香族 π-π 相互作用に関係し、
そしてそれらの能力は化学構造と反応性のプローブとなる。

Keywords
Noncovalent bond, Charge transfer, Electron transfer, Hydrogen transfer, Electron acceptor

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