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Hydrocracking of Acenaphthene over a Sulfided Ni–Mo/Al_2O_3 Catalyst

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The selectivity of ring opening was investigated for the hydrocracking of acenaphthene under an initial hydrogen pressure of 6 MPa and in the temperature range from 390 to 450 °C. Major products were classified into the following six components: tetrahydroacenaphthylene, hexahydroacenaphthylene, perhydroacenaphthylene, ring opening products (bicyclic compounds and monocyclic compounds), alkylation products (tricyclic compounds of C_{13} or larger), and dimerization products (biacenaphthene and their hydrogenated compounds). Ring opening of acenaphthene proceeded via two routes: the direct ring opening of acenaphthene and ring opening after hydrogenation to hexahydroacenaphthylene. In the former reaction only 1-ethylnaphthalene was produced, while 1,8-dimethylnaphthalene and its hydrogenated products were not observed. In the latter reaction, on the other hand, two types of ring opening of a C–C bond adjacent to the benzene ring, the opening of a saturated five-membered ring to produce 1-ethyltetralin and the opening of a saturated six-membered ring to produce 1-propylindane, were observed.

Polycyclic aromatic compounds (PAC) are the major constituents of the heavy fraction of fossil fuels; in order to produce light fuel oils by cracking heavy fuel oil, they must first be hydrogenated and then cracked to open the polycyclic rings. On the other hand, such PAC are widely used as recycle vehicles in coal-liquefaction processes or solvents in investigating the reactivity of specific compounds. In such cases, PAC are naturally desired to be stable against such cracking reactions. In other words, a detailed understanding of the cracking reactivity for PAC is required from the standpoint of their own stability against cracking when used to promote cracking.

Generally, the hydrocracking product of PAC is a complex mixture containing a variety of isomers, which has made it difficult to fully clarify the cracking reaction process. Current developments concerning the separation and identification instruments based on capillary columns, such as GC-FID, GC-MS, GC-NPD, and GC-AED, have permitted a more exact analysis of the components of this complex mixture. The authors have succeeded in analyzing the components of such complex mixtures as petroleum heavy oil,[1—3] tar,[4,5] and coal-liquefaction products[6—8] in detail.

Naphthalene, phenanthrene, anthracene, acenaphthene, pyrene, fluorene, and fluoranthene are typical compounds of PAC which are contained in fossil fuel.[1—8] Among these compounds naphthalene (tetralin),[9—13] phenanthrene,[11—24] and pyrene[11,12,24] have been studied concerning their hydrocracking reactivity. Acenaphthene is easily converted into a liquid mixture by catalytic hydrogenation. Hexahydroacenaphthylene (abbreviated as hexahydroAcn) is expected to be an excellent hydrogen-donating solvent because it posseses a tetralin-like structure in its skeleton, whereas little information has been reported concerning its hydrocracking reactivity. In this study acenaphthene was hydrocracked over a nickel–molybdenum/alumina catalyst at temperatures ranging from 390 to 450 °C, and its hydrocracking reactivity was studied while focusing mainly on the selectivity of ring opening.

Experimental

Commercial acenaphthene was hydrogenated at 360 °C over a nickel–molybdenum/alumina catalyst, and then fractionated in order to remove both the lighter and heavier fractions to obtain the reaction feed. The composition of the feed was 27 mol% of perhydroacenaphthylene (perhydroAcn), 72 mol% of hexahydroAcn, and 1 mol% of acenaphthene. The purpose of prehydrogenation was to avoid any rapid increases in the temperature and fluctuation of the hydrogen partial pressure, and also to make it possible to handle the feed in liquid form.

A stainless-steel vibrating micro autoclave of 35 ml inner volume was used as the reactor. The catalyst was used after presulfiding with special care so as to prevent it from being oxidized again by air. An initially presulfided catalyst consisting of 0.5 g of 3 wt% NiO–15 wt% MoO_3/Al_2O_3 (Ketjen 153) and 0.025 g of powdered sulfur were packed into a quartz-glass container,[25] and placed in the stainless-steel autoclave to ensure presulfiding. After hydrogenated acenaphthene (5 ml) had been poured into another autoclave a catalyst in a glass container was quickly added to the reaction fluid to react under a hydrogen pressure of 6 MPa (cold charge) and in the temperature range of 390 to 450 °C for 10 to 80 min. The reaction temperature reached

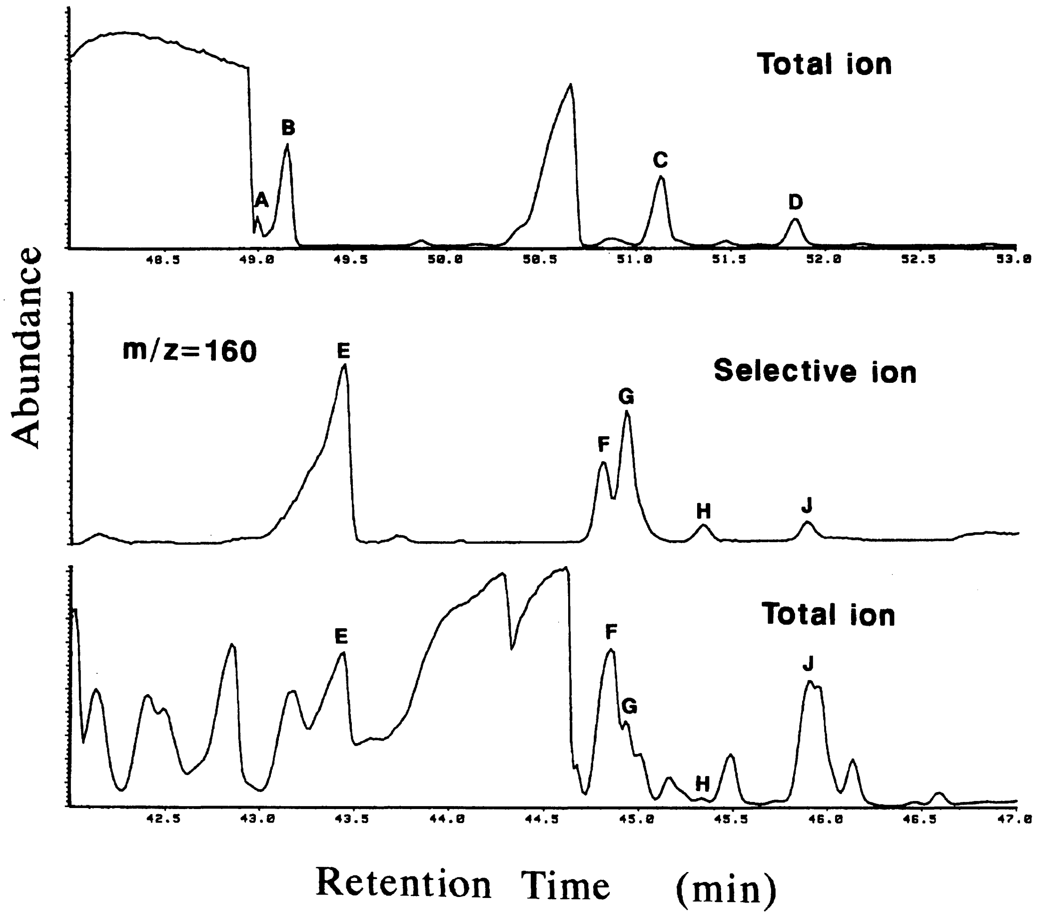

Fig. 1. GC-MS chromatogram of produced oil at 450 °C.

±3 degrees of the expected temperature approximately two minutes after initiating the reaction by means of preheating the electric furnace to 35 to 40 degrees higher than the reaction temperature.

The products were identified using a gas chromatograph (Hewlett-Packard 5880A) and a mass-selective detector (Hewlett-Packard 5970), employing a fused-silica capillary column (OV-1, 0.25 mm×50 m). Most of hydrogenated products of acenaphthene and alkylnaphthalenes are not available as commercial reagents; their mass spectra are also not available in mass-spectra libraries, such as the NBS library. Therefore, acenaphthene, 1- and 2-methylnaphthalene, 1- and 2-ethylnaphthalene, and ten isomers of dimethylnaphthalene were hydrogenated under various conditions on a Pt/Al_2O_3 or $Ni–Mo/Al_2O_3$ catalyst in order to obtain the standard compounds for analysis. The products of the reaction investigated in the present study were identified by comparing the mass-spectra and the column retention time with these synthesized compounds.

Results and Discussion

Ring Opening Products. The predominant hydrogenated products of acenaphthene were hexahydroAcn and perhydroAcn, which were described in a previous report.[5] Twelve isomerized compounds of perhydroAcn were recognized, although they were lower in yield. Compounds with a molecular weight (MW) of 156 are considered to be produced when ring opening of acenaphthene proceeds without ring hydrogenation. A GC-MS analysis of the products revealed that actually four compounds (**A**, **B**, **C**, and **D** shown in Fig. 1) with an MW of 156 were produced. HexahydroAcn, on the other hand, produces molecules with an MW of 160 as a result of ring opening; five molecules (**E**, **F**, **G**, **H**, and **J** shown in Fig. 1) with this MW were recognized.

Figure 2 shows the mass spectra of four compounds with an MW of 156. Compound **B** was revealed to be 1-ethylnaphthalene from its mass spectrum and column retention time. The mass spectra and retention times of **A**, **C**, and **D**, however, do not coincide with any ethyl- or dimethyl-substituted naphthalenes. All of the compounds exhibit two ions, a parent ion and an ion with a valency one less than the parent. These compounds as well as acenaphthene, which has similar characteristics, are considered to be tetrahydroacenaphthylene (tetrahydroAcn).

Figure 3 shows the mass spectra of five compounds with an MW of 160. From their mass spectra and the retention times, compounds **G** and **H** were identified to be 1-ethyl-1,2,3,4-tetrahydronaphthalene (1-ethyltetralin) and 2-ethyltetralin. No compounds corresponding to 5- or 6-ethyltetralin were produced. Compound **E** is considered to be 1-propylindane based on its mass spec-

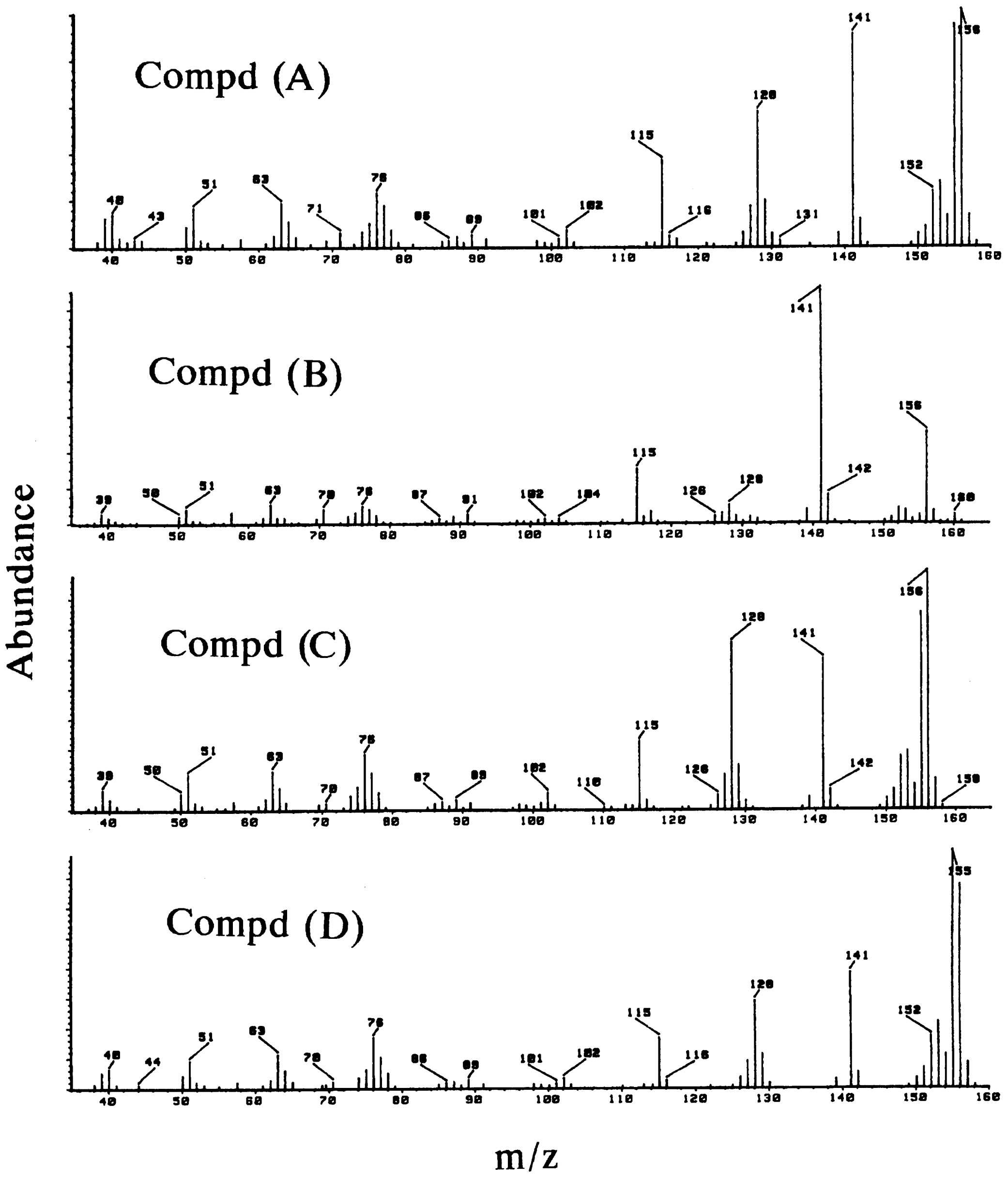

Fig. 2. Mass spectra of compounds with MW of 156.

trum, while the structures of **F** and **J** can not be identified.

Figure 4 shows the correlation between the yields and the reaction temperatures for the four compounds with an MW of 156 and the five compounds with an MW of 160. Among the former compounds, the yield of compound **B** increased with the reaction temperature, while **A**, **C**, and **D** decreased, suggesting that these compounds were partially hydrogenated products of acenaphthene. The yields of compounds **F**, **G**, **H**, and **J** increased along with a rise in the temperature; this supports the assumption that they were products formed by ring opening. Since **F**, **H**, and **J** were produced only under higher temperatures, it is thought that **E** and **G** were the original products of the ring opening reaction, while the others were formed by isomerization of these initial products.

Secondary Cracking of Ring Opening Products. Bicyclic compounds with carbon numbers of 9 to 11 and monocyclic compounds with carbon numbers of 6 to 10 were recognized as secondary cracking products of the original ring opening products. Figure 5 shows the correlations between the yields and the reaction temperatures for these products according to their carbon numbers. When bicyclic compounds were compared, it was found that the yield of C_{11} was less than that of C_{10} compounds, suggesting that dealkylation occurs with greater ease than cracking the side chain. The major components of C_{10} compounds were naphthalene, tetralin and 1-methylindan, while that of C_{11} were 1- and 5-methyltetralin and a small quantity of 1-methylnaphthalene.

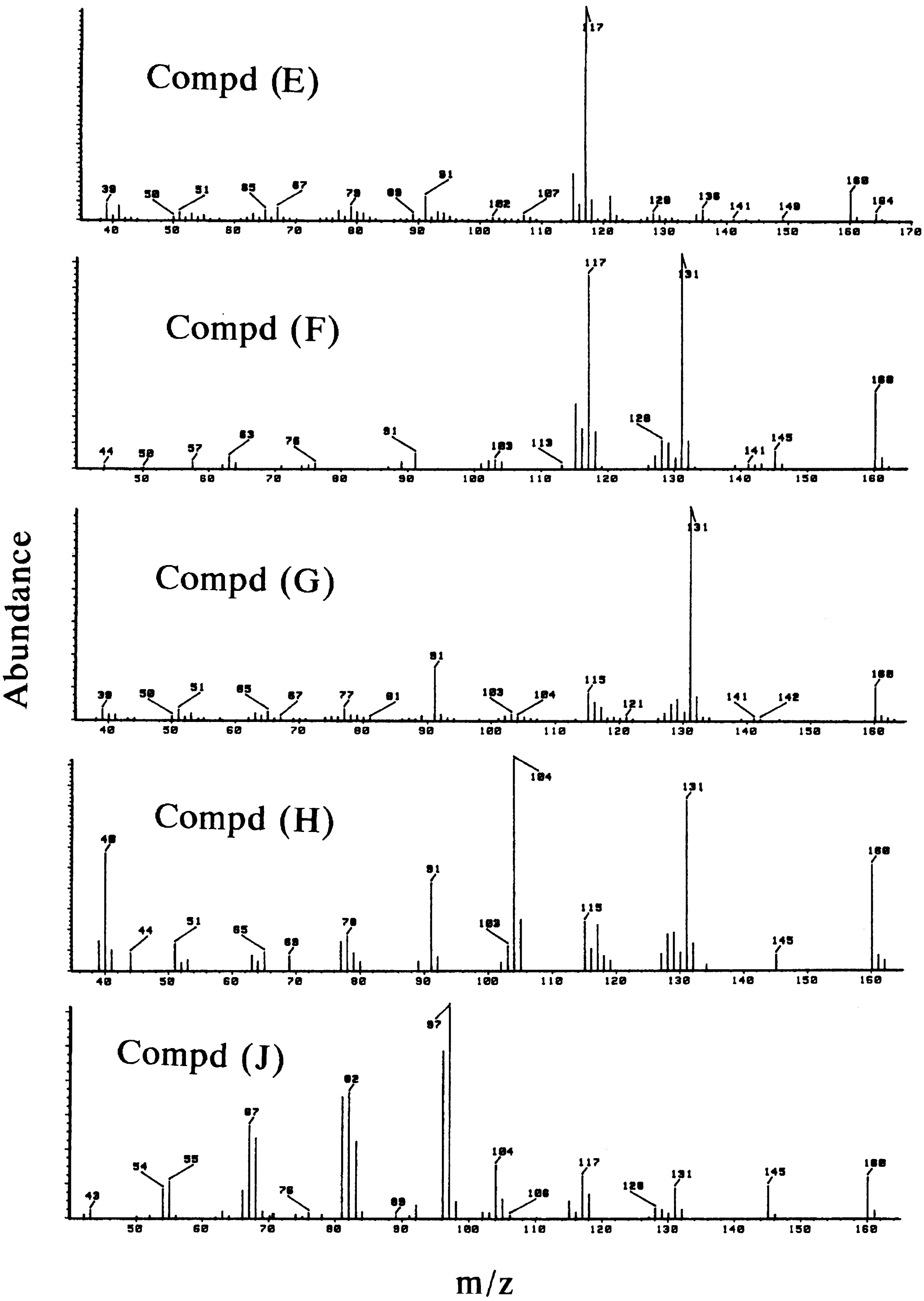

Fig. 3. Mass spectra of compounds with MW of 160.

Upon comparing monocyclic compounds it was found that the yields of C_6 and C_7 compounds were the highest, followed by C_{10} compounds, while that of C_8 and C_9 compounds were low. The major components of the C_6, C_7, and C_{10} compounds were methylcyclopentane, toluene, and butylbenzene, respectively; it is thought that butylbenzene was produced by a ring opening of tetralin.

Other Reactions. The addition reaction of acenaphthene or its hydrogenated products to form compounds with an MW of 306 to 314 is also recognized. These compounds are recognized as addition products between acenaphthene or its hydrogenated derivatives. The fact that small amounts of such addition products are preferably produced on a Ni–Mo/Al_2O_3 catalyst has also been observed in the hydrodesulfurization of thiophenes and benzothiophenes.[26,27]

In addition, the production of small quantities of alkylacenaphthenes and its hydrogenated derivatives with C_{13} or larger was also recognized. This is considered to be caused by the addition of cracked fragments of the alkyl side chain of bicyclic or monocyclic compounds to acenaphthene.

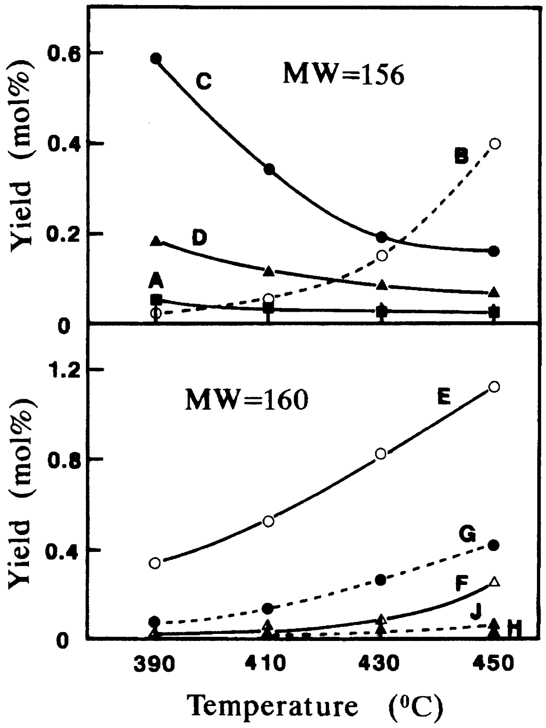

Fig. 4. Correlation between yields and temperatures for compounds with MW of 156 and 160.

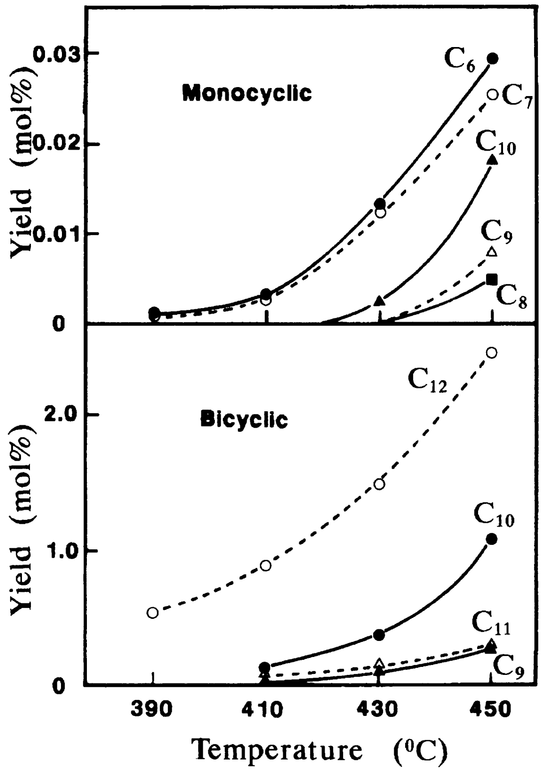

Fig. 5. Correlations between yields and temperatures for products according to their carbon numbers.

The above-mentioned reactions can be summerized as follows: Major products can be roughly classified into tetrahydroAcn, hexahydroAcn, perhydroAcn, ring opening products, alkylation products, and addition products. In order to provide an outline of the reaction, the relation between the reaction temperatures and the yields of these six fractions and acenaphthene are presented in Fig. 6. As the temperature rises, the yields of the hydrogenated derivatives of acenaphthene decrease, and the yield of acenaphthene increases as a result. This suggests that these compounds are in a near-equilibrium concentration with respect to hydrogenation in the temperature range studied.

The yields of ring opening products and alkylation products increased with increasing temperature, while that of the addition products decreased. The addition products are thought to decompose again when the reaction temperature is raised.

Reaction Network. In Fig. 7 the yields of the major products with an MW of 156 and 160 are plotted versus the reaction time. The nomenclature used in this figure coinsides with those compounds shown in Fig. 1. The yields of compounds **B**, **E**, and **G** increase with the reaction time, while **C** decreases, suggesting that the former compounds are ring-opening products and that latter compound is a partially hydrogenated product of acenaphthene, as mentioned above.

The selectivity in the ring opening of polycyclic compounds has been studied concerning several compounds,

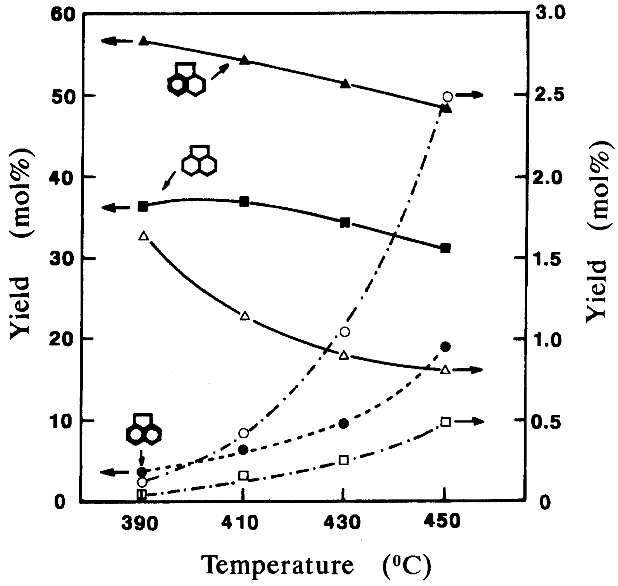

Fig. 6. Relation between temperatures and yields of six fractions produced. ○; Ring-opening product, △; Addition product, □; Alkylation product, ●; 1, ▲; 2, ■; 3.

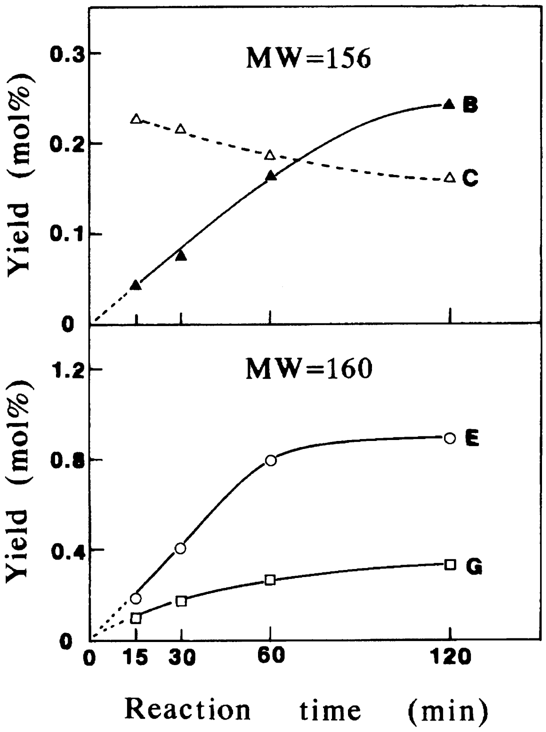

Fig. 7. Relation between yields and reaction time for products with MW of 156 and 160.

though few papers have been presented regarding that of acenaphthene. Although it is easy to cleave the CH_2–CH_2 bond in the pentane ring of perhydroindene on a reduced nickel–alumina catalyst,[28)] it is difficult to open the ring over acidic catalysts.[29,30)] In the thermal cracking of indane and tetralin, two types of ring opening have been reported: The opening of a C–C bond adjacent to the benzene ring (α ring opening) and the opening of a C–C bond not adjacent to the benzene ring (β ring opening).[31)] Opening of the central ring has been observed with 9,10-dihydrophenanthrene[14,24,32)] and fluorene.[33,34)] In the cracking of 1,2,3,4-tetrahydrophenanthrene, α ring opening of the saturated terminal ring was observed as a major reaction;[14,32)] in some cases the β ring opening of that was observed as a minor reaction.[32)]

In this experiment, the ring opening of acenaphthene proceeded through two routes: a direct opening of acenaphthene and ring opening after hydrogenation of acenaphthene to hexahydroAcn. In direct ring opening, only 1-ethyl-naphthalene was produced, while 1,8-dimethylnaphthalene and its hydrogenated products were not observed. In the latter reaction route, on the other hand, two types of α ring opening, ring opening of a saturated five-membered ring and that of a saturated six-membered ring, were observed.

All of the above-mentioned products show that the only α ring opening proceeds under these reaction conditions. The cracking mechanism shown in Fig. 8 is proposed. One of the reasons why ring opening is rather

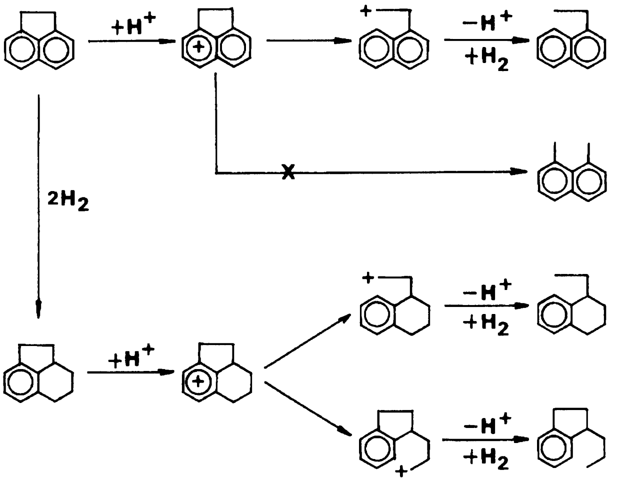

Fig. 8. Cracking mechanism of acenaphthene.

difficult to proceed seems to be because the reaction involves a primary carbonium ion.

Recently, there seems to be some expectation to obtain 1,8-dimethylnaphthalene from acenaphthene as a chemical resorce; however, the data given here show that this is very difficult as long as this type of catalyst is used.

References

1) Y. Miki, S. Yamadaya, M. Oba, and Y. Sugimoto, *Kagiken Hokoku*, **80**, 361 (1985).

2) Y. Sugimoto, Tunnukji, Y. Miki, and S. Yamadaya, *Sekiyu Gakkaishi*, **35**, 339 (1992).

3) Y. Sugimoto, Y. Miki, Y. Niwa, Tunnukji, and S. Yamadaya, *Sekiyu Gakkaishi*, **35**, 349 (1992).

4) Y. Miki and Y. Sugimoto, *Nippon Kagaku Kaishi*, **1983**, 697.

5) Y. Miki and Y. Sugimoto, *Nippon Kagaku Kaishi*, **1983**, 704.

6) Y. Miki and Y. Sugimito, *Nenryou Kyokai-shi*, **63**, 28 (1984).

7) Y. Sugimoto, Y. Miki, S. Yamadaya, and M. Oba, *Nippon Kagaku Kaishi*, **1984**, 755.

8) Y. Sugimoto, Y. Miki, M. Oba, and S. Yamadaya, *Bull. Chem. Soc. Jpn.*, **63**, 967 (1990).

9) S. Yamadaya, M. Oba, and Y. Miki, *Bull. Chem. Soc. Jpn.*, **50**, 79 (1977).

10) C. J. Read, S. Schwarz, and M. T. Klein, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **37**, 207 (1992).

11) R. F. Sullivan, C. J. Egan, and G. E. Langlois, *J. Catal.*, **3**, 183 (1964).

12) H. W. Haynes, *Ind. Eng. Chem. Process Des. Dev.*, **22**, 401 (1983).

13) E. Kikuti, N. Shibahara, A. Tsunoda, and Y. Morita, *Sekiyu Gakkaishi*, **27**, 369 (1984).

14) Wen-Lung Wu and H. W. Haynes, Jr., *ACS Symp. Ser.*, **20** (Hydrocracking Hydrotreat.), 65 (1975).

15) S. A. Qader, *ACS Symp. Ser.*, **20** (Hydrocracking Hydrotreat.), 82 (1975).

16) R. Badilla-Ohlbaum, K. C. Pratt, and D. L. Trimm, *Fuel*, **58**, 309 (1979).

17) E. Kikuti, N. Shibahara, A. Tsunoda, and Y. Morita, *Sekiyu Gakkaishi*, **27**, 296 (1984).

18) C. Song, K. Hanaoka, T. Ono, and M. Nomura, *Bull. Chem. Soc. Jpn.*, **61**, 3788 (1988).

19) J. L. Lemberton, M. Touzeyidio, and M. Guisnet, *Appl. Catal.*, **54**, 91 (1989).

20) J. L Lemberton, M. Touzeyidio, and M. Guisnet, *Appl. Catal.*, **54**, 101 (1989).

21) K. Ueda, H. Matsui, C. Song, and Wei-Chun Xu, *Sekiyu Gakkaishi*, **33**, 413 (1984).

22) T. Kabe, K. Sawahiraki, S. Watanabe, Y. Imai, K. Yamamoto, and H. Kameyama, *Nenryou Kyokai-shi*, **69**, 940 (1990).

23) R. N. Landau, S. C. Korre, K. M. Neurock, and M. T. Klein, *Prepr. Pap.–Am. Chem. Soc., Div. Fuel Chem.*, **37**, 1871 (1992).

24) Y. Nakatsuji, T. Kubo, M. Nomura, and S. Kikkawa, *Bull. Chem. Soc. Jpn.*, **51**, 618 (1978).

25) Y. Kuriki, M. Yumura, S. Oshima, M. Kawamura, F. Ikazaki, and Y. Miki, *Sekiyu Gakkaishi*, **35**, 288 (1992).

26) Y. Miki, Y. Sugimoto, and S. Yamadaya, *Sekiyu Gakkaishi*, **35**, 332 (1992).

27) Y. Miki, Y. Sugimoto, and S. Yamadaya, *Sekiyu Gakkaishi*, **36**, 32 (1993).

28) Y. Miki, S. Yamadaya, and M. Oba, *Sekiyu Gakkaishi*, **23**, 287 (1980).

29) Y. Miki, S. Yamadaya, and M. Oba, *Sekiyu Gakkaishi*, **23**, 291 (1980).

30) Ye. I. Bagrii, T. N. Dolgopolova, and P. L. Sanin, *Neftekhimiya*, **10**, 475 (1970).

31) J. M. L. Penninger and H. W. Slotboom, *Recl. Trav. Chim. Pay-Bas*, **92**, 513 (1973).

32) J. L. Lemberton and M. Guisnet, *Appl. Catal.*, **13**, 181 (1984).

33) W. D. Constant, G. L. Price, and E. McLaoghin, *Fuel*, **65**, 8 (1986)

34) A. T. Lapinas, M. T. Klein, and B. C. Gates, *Ind. Eng. Chem. Res.*, **30**, 42 (1991).