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Mechanistic investigations of iron/sulfur-catalyzed bond scission in aromatic hydrocarbons. A catalytic hydrogen atom transfer step involving a late transition state

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Abstract

The mechanism of carbon–carbon bond scission by 'iron sulfide' catalysts is explored through the use of substituted diphenylmethane model compounds. The reaction kinetics are shown to be first order in model compound with the methylene-arene carbon–carbon bond adjacent to the most substituted arene being selectively cleaved. These results are consistent with the catalyst acting as a hydrogen atom transfer agent.

Keywords: Catalysis; Hydrogen transfer; Iron; Model compounds

1. Introduction

There has been an enormous interest in the utility of nanoparticulate iron catalysts for the early stages of coal liquefaction [1]. Bench-scale liquefaction studies of iron-based catalysts (presumably nonstoichiometric iron sulfides ('FeS') have demonstrated significant enhancements in liquefaction yields [2,3]. In addition, model compound studies have demonstrated 'FeS' catalysts not only increase the rate of bond scission, but also are highly selective for the scission of strong diarylmethane carbon–carbon bonds ($ArCH_2$–Ar) [4–10]. Of particular importance is the reported selectivity for scission of $ArCH_2$–Ar in the presence of alkyl substituents [10] leading to liquefaction with minimum formation of light gases. Although there has been an abundance of model compound studies, how the catalyst induces bond scission remains a mystery.

Farcasiu and co-workers [4] suggested a mechanism in which the alkyl-arene moiety is activated to undergo bond scission by electron transfer to the catalyst, analogous to their observations using black pearls [11]. However, a key step in this pathway, unimolecular scission of the radical cation, has been argued to be kinetically and thermodynamically unfavorable [12]. We proposed a variant of the Farcasiu mechanism, a two-step electron transfer, hydrogen atom transfer pathway to generate a cationic intermediate [13]. This pathway is consistent with the observed selectivity, but recent model compound studies suggest that the formation of cationic intermediates may not occur [14].

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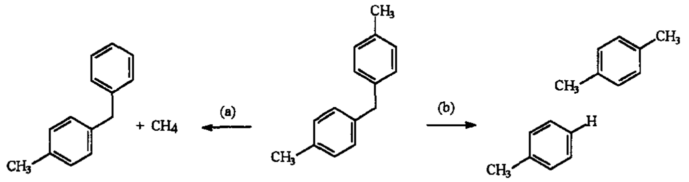
Alternative homolytic (radical) pathways have been offered by a number of workers. Malhotra and McMillen have proposed single-H atom transfer from catalytic surfaces to arene solvents to generate cyclohexadienyl radicals that in turn transfer the hydrogen by a radical hydrogen transfer (RHT) mechanism to the model compounds remote from the catalyst surface [15]. However, this is not likely because little selectivity between methyl- and benzyl-scission would have been observed if hydrogen transfer from 9-hydrophenanthryl radical by a RHT mechanism were to occur. Wei and co-workers suggested 'FeS' catalysts promote the formation of a hydrogen atom which subsequently adds to the ipso positions of C_{aryl}–C_{alkyl} bonds in dinaphthylethane ($NpCH_2CH_2Np$) and dinaphthylmethane ($NpCH_2Np$) [5–8]. The problem with this simple explanation is that although β-scission of arylmethyl radical ($NpCH_2\cdot$) is faster than β-scission of alkyl radical ($NpCH_2CH_2\cdot$), both $NpCH_2\cdot$ and $NpCH_2CH_2\cdot$ scission are significantly faster than the unimolecular scission of a hydrogen atom from the respective ipso adducts, and neither the $NpCH_2$– group nor the $NpCH_2CH_2$– group is expected to significantly stabilize the ipso-radical adduct more than the other. Thus, very little selectivity between alkyl scission and arylmethyl scission would be observed if free H-atoms are involved. Therefore, neither an ipso displacement mechanism by hydrogen atoms generated on or generated from the catalyst surface nor the transfer of hydrogen by a RHT pathway are sufficient to explain the experimentally observed selectivity trends. To address this shortcoming of the radical mechanism, McMillen recently proposed that an ipso radical adduct may be stabilized by adsorption to the catalytic surface, thereby increasing the barrier for β-scission and thus facilitating transfer of the hydrogen atom from the ipso adduct back to the catalytic surface [16].

In this paper, we address this issue of selectivity and reversible hydrogen transfer by specifically proposing hydrogen atom transfer from the catalytic surface (perhaps a sulfhydryl group, Fe–S–H) to the arene to generate cyclohexadienyl radical/catalyst radical pair. The fate of the cyclohexadienyl radical adduct depends upon competing back-hydrogen transfer and β-scission pathways. Our nonionic, reversible hydrogen atom transfer hypothesis assumes little effect from surface adsorption for the diphenylmethane series of model compounds and is consistent with both experimental observations and conventional thermochemical wisdom.

2. Results and discussion

Previously, we reported the structure–reactivity relationships for the catalytic-induced decomposition of a series of mono-, di-, and trimethyl substituted diphenylmethanes. With the catalyst 'FeS' in 9,10-dihydrophenanthrene (DHP), we observed high selectivity for benzyl group displacement [10]. (The catalyst, 'FeS' was derived from the in situ reaction of ferric oxyhydroxysulfate (OHS) and elemental sulfur under reducing conditions.) On the other hand, the noncatalytic thermolysis of these model compounds yields both benzyl and methyl scission. For example, thermolysis of 4,4′-bismethyldiphenylmethane (4,4′-Me_2DPM) in 9,10-dihydrophenanthrene (DHP) leads to both methyl and benzyl radical displacement (Scheme



Scheme 1.

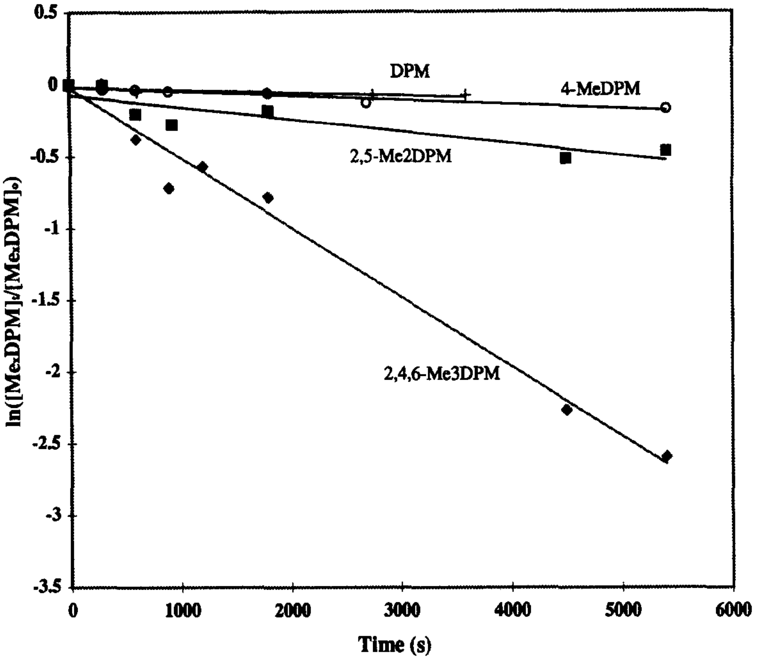


Fig. 1. Observed first-order rate of model compound bond scission in 9,10-dihydrophenanthrene using 6-line ferrihydrite at 390°C: (+) diphenylmethane, (○) 4-methyldiphenylmethane, (■) 2,5-dimethyldiphenylmethane, (▲) 2,4,6-trimethyldiphenylmethane.

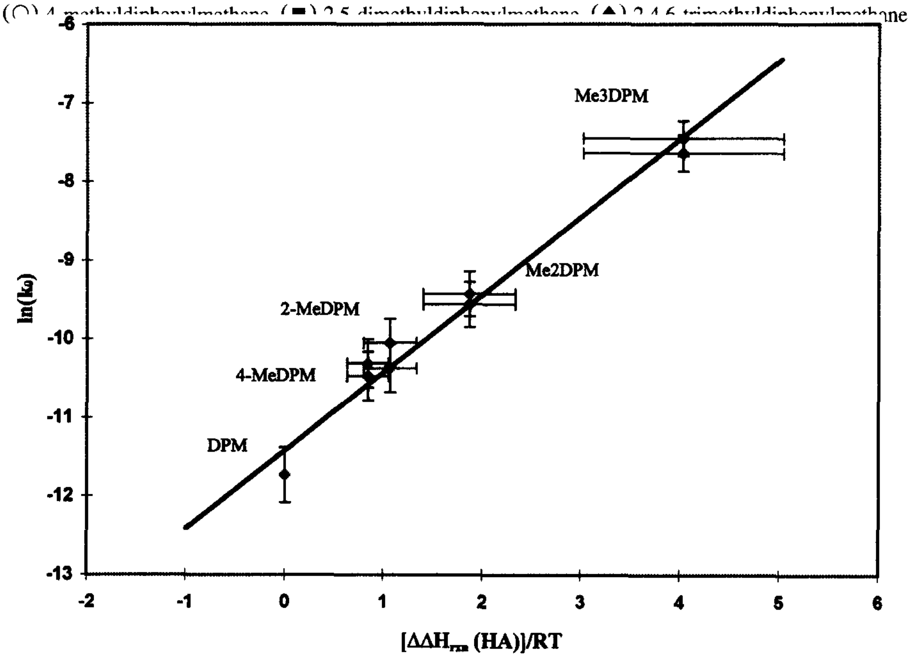
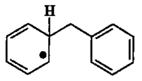
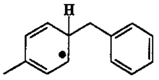
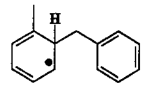
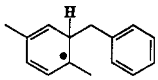
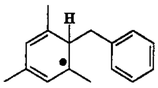


Fig. 2. Selectivity of hydrogen transfer. Correlation between increase in the stability of radical adduct ($\Delta\Delta H_{\mathrm{rxn}}$ HA addition) and the increase in the observed rate of carbon–carbon bond scission (■, OHS) (◆, 6-line ferrihydrite). The solid (—) line is the least squares best fit (α ca. 0.98 ± 0.11, $r^2 = 0.95$).

Table 1

Observed first-order rate of MeDPM bond scission (s^{-1}) by OHS and 6-line ferrihydrite versus calculated heat of reaction $(\Delta\Delta H_{rxn})/RT$ for the addition of a hydrogen atom to MeDPM at 390°C

Diphenyl-methane	Radical adduct	$\Delta\Delta H_{rxn}$ (HA add'n (kcal/mol)	$k_{observed} \times 10^4$ (s^{-1}) OHS	6-line
DPM		0	0.08	0.08
4-MeDPM		1.1	0.33	0.28
2-MeDPM		1.4	0.43	0.31
2,5-Me$_2$DPM		2.5	0.7	0.8
2,4,6-Me$_3$DPM		5.3	5.8	4.8

1, paths a and b) and is significantly slower [1] than the catalytic decomposition (Scheme 1, path a only). Table 1 shows the radical intermediates leading to the observed scission products, the calculated heat of hydrogen atom addition, and our experimentally measured rate of decomposition. The rate of catalyst-induced bond scission for this series of methyl-substituted diphenylmethanes was found to be first order over the temperature range investigated, 310–390°C. The time-dependent consumption of the model compounds at 390°C is shown in Fig. 1. Given that catalytic hydrogen transfer is first order in substrate, and pseudo zero order in DHP, overall first-order kinetic behavior is observed. Formation of the ipso adduct, at the benzyl position, by H-transfer from catalyst to arene is probably rate limiting because scission of benzylic radicals is fast compared to scission of a hydrogen atom. If the observed rate constant for cleavage is proportional to the rate constant for H-atom transfer from catalyst to arene to form ipso adducts, an analysis of how the H-transfer rate constant depends on the enthalpy of reaction could provide insight into the nature of the transfer reaction and its transition state (TS) structure [2]. As shown in Fig. 2, the rate of catalytic-induced carbon–carbon bond scission correlates directly with the calculated heat of reaction for addition of a hydrogen atom to the arene, ΔH_{rxn} (HA) [3]. The least-squares fit to the data yields a line with unit slope for reactions between catalysts derived from both OHS and 6-line ferrihydrite and five different methyl-substituted diphenylmethanes. This result explicitly shows that an increase in the stability of the ipso radical adduct,i ΔH_f°, (ArH·), leads to an equal decrease in the E_a. The Evans–Polanyi factor, derived from the slope of Fig. 2, may be interpreted as a measure of the position of the TS relative to the reactants or products. According to the Hammond postulate, an α near 1 requires the TS bear close

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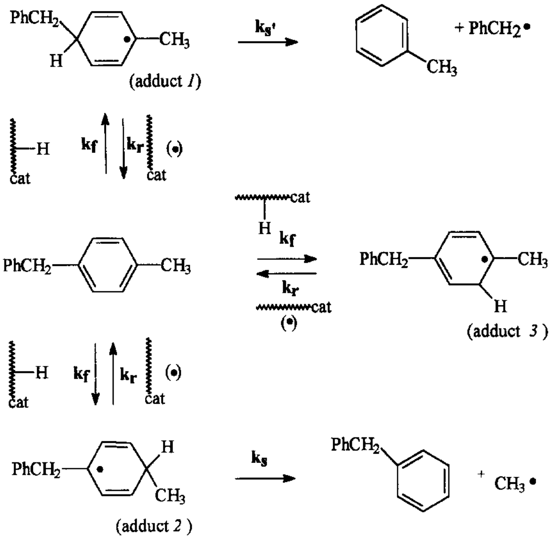
[1] Ln k ca. −13.2, thermolysis of 4,4′-DPM in DHP 400°C see [10]. Catalytic decomposition of 4,4′-DPM follows first order dependence over the experimental reaction time 60 min, 350–400°C, Ln k ca. −9.8.

[2] This treatment assumes little difference between Arrhenius A-factors for each of the individual methyldiphenylmethanes. We believe this is a valid assumption (1) given that the rate of catalytic induced bond scission of the *ortho*- and the *para*-substituted methyldiphenylmethane are the same and (2) the rate of catalytic induced bond scission of 4,4′-dimethyldiphenylmethane is twice the rate of 4-methyldiphenylmethane.

[3] The heat of reaction for hydrogen atom addition, ΔH_{rxn} (HA), was calculated as follows: ΔH_{rxn} (HA) = [ΔH_f° (arene) + δH_f° (H·)] − ΔH_f° (ArH·). ΔH_f° (H·) = 52.1 kcal/mol. The experimental ΔH_f° of the methylated benzenes are available from the literature [17]. We assumed that ΔH_{rxn}° for hydrogen atom addition would not be significantly different for methyl and benzyl-substituted benzenes. AM1 [18] and macro-incremenatation methods [19] were used to calculate the ΔH_f° (ArH·). [Ar(H·) (AM1/mac-inc) (ΔH_f° kcal/mol)], [DPM(H·) (37.1/42.9)], [4-MeDPM(H·) (28.6/33.6)], [2-MeDPM(H·) (28/33.6)], [2,5-Me$_2$DPM(H·) (18.9/25.4)], [2,4,6-Me$_3$DPM(H·) (8.0/17.2)]. We calculated the $\Delta\Delta H_{rxn}$ (HA) for both AM1 and macro-incrementation methods and used the average value and average deviation for the correlation with our measured rates of disappearance of the methyldiphenylmethane.



Scheme 2.

structural resemblance to the products [20]. This result is important because it implies that if catalytic bond scission occurs by the radical pathway, then transfer of a hydrogen atom occurs very late along the reaction coordinate, i.e. hydrogen transfer by a reverse radical disproportionation (RRD)-like pathway [4].

The RRD-like pathway not only provides a rational explanation for the selective preference of $PhCH_2\cdot > CH_3\cdot$ displacement from the methyldiphenylmethane series of model compounds, it also predicts that transfer of a hydrogen atom occurs to the arene that will stabilize the radical adduct most effectively. The RRD-like pathway explains the absence of alkyl ($CH_3\cdot$) displacement, when consideration is given to the accompanying radical disproportionation-like (RD) back-hydrogen atom transfer pathway, Scheme 2. Given the expected decrease in diffusion and the low efficiency of escape of the radical adduct away from the catalytic surface, a RD-type pathway is a reasonable candidate for back hydrogen transfer. In our series of model compounds, the observed rate of decomposition is defined as the sum of benzyl displacement, $k'_o = k_f/k_r(k'_s)$ and methyl displacement, $k_o = k_f/k_r(k_s)$, where k_f is the rate of hydrogen transfer from the catalyst to methylated diphenylmethane (DPM) [5]; k_s and k'_s are the rates of β-scission of the methyl radical and the benzyl radical, respectively; and k_r is the rate of back-hydrogen transfer (RD) from the radical adduct to the catalyst. In the catalytic decomposition $k'_o > k_o$, and in the thermal decomposition, $k'_o \approx k_o$. Therefore, when the stabilities of the ipso adducts are approximately equal, the key step governing the observed selectivity is competition between back hydrogen transfer, k_r, and β-scission of the alkyl group, k'_s. The competing back-hydrogen transfer step, k_r, to regenerate the DPM must occur at a rate faster than methyl scission. For example, in the catalytic decomposition of 4-methyldiphenylmethane (CH_3PhCH_2Ph), all adducts, 1, 2 and 3 (Scheme 2), are expected to be formed with near-equal probability. However, RD (k_r) of adduct 2 with the catalyst radical (Cat(·)) is faster than β-scission of the methyl radical; therefore, little demethylation occurs, and RD (k_r) of adduct 3 is faster than hydrogen abstraction; therefore, few reduced products form. On the other hand, β-scission of benzyl radical, from adduct 1, is at least competitive with RD (k_r) and therefore leads to carbon–carbon bond scission. A competing back-hydrogen transfer step explains both the observed selectivity and the absence of reduction products.

The present data do not permit a rigorous analysis of the role of adsorption of the radical intermediates to the catalytic surface. The physical interaction between the ipso radical adduct

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[4] We utilize the molecular mechanistic terms 'RRD-type' and 'RD-type' carefully, only to provide a semi-quantitative descriptive picture of the hydrogen transfer step from the catalyst surface to the arene.

[5] Hydrogen transfer to non-ipso positions is shown in Scheme 1. The catalyst is not expected to be selective for ipso attack. Thermochemical estimates predict non-ipso attack to be more favorable than ipso attack. For further discussion see [14]. Reduction products are formed at an apparently lower rate if there is no leaving group, see [10].

and the surface may well decrease the rates of β-scission of both methyl and benzyl radical as previously proposed [16]. A physical interaction between the catalyst surface and the radical adducts may explain the low selectivity (approximately 8) for –A– bond scission relative to –B– bond scission in 4-(1-naphthylmethyl)bibenzyl (NBBM) [9]. We expect selectivity to be much higher than observed given the ca. 6 kcal/mol difference between the radical adduct formed by the hydrogen atom addition to 1-methylnaphthalene and *p*-xylene. Perhaps adsorption plays a role in lowering the selectivity in NBBM bond scission.

3. Conclusions

Provided that arguments against the ionic hydrogen transfer pathways hold true, hydrogen transfer from the catalyst to the arene by a late hydrogen transfer pathway, with competing back-hydrogen transfer, explains several key observations ranging from the absence of significant reduction or dealkylation to the observed preference for displacement of arylmethyl substituents. Two factors influence the selectivity of 'FeS' catalytic-induced bond scission: first and foremost, the stability of the ipso radical adduct, and second, the stability of the displaced radical, arylmethyl $\gg$ alkyl. The competing back hydrogen transfer controls the catalytic preference for the scission of strong diarylmethane bonds and likely prevents the formation of light oils and gases in coal liquefaction reactions.

The direct relationship between the decrease in activation barrier with increase in radical adduct stability provides a compelling argument for direct H-atom transfer at the catalytic surface by a RRD-like pathway. Given the parallel trends between the model compound results and the coal liquefaction experiments, i.e. little formation of light oils or gases, it is reasonable to assume that hydrogen can be transferred directly from the catalytic surface to coal in the early stages of liquefaction. The selectivity also argues against any contribution from the proposed two-step pathway, transfer of hydrogen from the catalyst to the solvent, followed by the solvent donating a hydrogen atom by a RHT pathway to the arene.

If an RRD-like pathway is responsible for the rate-limiting catalytic hydrogen transfer step, it may be from a hydrogen-terminated edge or defect in the solid catalyst surface, such as an iron hydride [21] [6] or FeX-H where X may be S and/or O. Further work is in progress to test this hypothesis and address the role of physical interactions between the catalytic surface and model organic compounds.

4. Experimental

Dichloromethane (capillary GC grade), benzyl alcohol, toluene, *p*-xylene, and mesitylene were purchased from Aldrich and used as received. The 2-methylbenzophenone, 4-methylbenzophenone, and 2,5-dimethylbenzophenone were purchased from Lancaster Synthesis and used as received. The 9,10-dihydrophenanthrene (9,10-DHP) (Aldrich, 94%) was distilled and recrystallized from methanol prior to use. Final purity of 9,10-DHP was > 99% by GC. The methylated diphenylmethanes were produced by either acid-catalyzed benzylation [10] or Clemenson reduction of the appropriate benzophenone [22], distilled under vacuum and eluted with pentane over silica gel on a Harrison Research Chromatotron® to yield colorless oils > 98% pure by GC.

The catalyst precursors, 6-line ferrihydrite, and ferric oxyhydroxysulfate were synthesized using the RTDS method as described previously [23–25]. The solid catalyst precursors (−325

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[6] A metal hydride bond may be weak enough to transfer hydrogen by this pathway. HMn(CO)5 + 9,10-dimethylanthracene.

mesh) were combined with elemental sulfur in a 1:1 by weight ratio, a 1:2 Fe:S molar ratio, prior to use.

The kinetics of the hydrogenolysis reactions were followed by removing reaction tubes from a fluidized sand bath at appropriate times. After the tubes were removed from the sand bath and air cooled, they were processed as described previously [23]. The reaction tubes were sealed under vacuum after filling with the model compound in solution with biphenyl (a nonreacting internal GC standard), 9,10-dihydrophenanthrene (100 mg), and a 1:1 mixture of the catalyst precursor and elemental sulfur (6 mg total). In a typical experiment, the catalyst precursor/sulfur mixture was weighed into the reaction tube. Then, 10 μl of a biphenyl:model compound (1:2 by weight) solution was added by syringe into a melting point capillary tube, open at both ends, and placed in the reaction tube (this avoided depositing the sample along the side of the thermolysis tube). The DHP was added and the tube sealed under vacuum.

AM1 calculations of energies were performed using MOPAC (Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN; QCPE no. 455, version 6.0).

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References

[1] See the first 21 papers in Energy Fuels, 8 (1994) and references therein.
[2] F.V. Stohl, K.V. Diegert and D.C. Goodnow, Am. Chem. Soc., Div Fuel Chem. Preprints, 40(2) (1995) 335.
[3] F.V. Stohl, K.V. Diegert, D.C. Goodnow, K.R.P. M Rao, F. Higgins and G.P. Huffman, Proc. Coal Liquefaction Gas Coversion Contractors Conference, Pittsburgh, PA, 1994, p. 605.
[4] M. Farcasiu, C. Smith, V.R. Pradhan and I. Wender, Fuel Proc. Technol., 29 (1991) 199.
[5] X.-Y. Wei, E. Ogata and E. Niki, Bull. Chem. Soc. Jpn., 65 (1992) 1114.
[6] X.-Y. Wei, E. Ogata and E. Niki, Chem. Lett., (1991) 2199.
[7] X.-Y. Wei, E. Ogata, E. Niki and Z-M. Zong, Energy Fuels, 6 (1992) 868.
[8] X.-Y. Wei and Z.-M. Zong, Energy Fuels, 6 (1992) 236.
[9] J.C. Linehan, D.W. Matson and J.G. Darab, Energy Fuels, 8 (1994) 56.
[10] J.C. Linehan, D.W. Matson, J.G. Darab, S.T. Autrey, J.A. Franz and D.M. Camaioni, Am. Chem. Soc., Div Fuel Chem. Preprints, 39(3) (1994) 720.
[11] M. Farcasiu and C. Smith, Energy Fuels, 5 (1991) 87; (b) M. Farcasiu and S.C. Petrosius, Am. Chem. Soc., Div Fuel Chem. Preprints, 39(3) (1994) 723.
[12] J.H. Penn and J. Wang, Energy Fuels, 8 (1994) 421.
[13] J.A. Franz, D.M. Camaioni, M.S. Alnajjar, S.T. Autrey and J.C. Linehan, Am. Chem. Soc., Div Fuel Chem. Preprints, 40(2) (1995) 203.
[14] T. Autrey, J.C. Linehan, D.M. Camaioni, T.R. Powers, E.F. McMillan and J.A. Franz, Am. Chem. Soc., Div Fuel Chem. Preprints, 40(4) (1995) 973.
[15] R. Malhotra and D.F. Mc Millen, Energy Fuels, 7 (1993) 227.
[16] D.F. McMillen and R. Malhotra, Am. Chem. Soc., Div Fuel Chem. Preprints, 40(2) (1995) 221.
[17] S.G. Lias, J.E. Bartmass, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, J. Phys. Chem. Ref. Data, 17 (1988) 1.
[18] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902.
[19] J.F. Liebman, in Macroincrementation Reactions: A Holistic Estimation Approach for the Properties of Organic Compounds in Molecular Structure and Energetics, Vol. 3, VCH, Weinheim, 1986.
[20] G.S. Hammond, J. Am. Chem. Soc., 77 (1955) 334.
[21] R. Sweany, S.C. Butler and J. Halpren, J. Organomet. Chem., 213 (1981) 487.
[22] E.L. Martin, Organic Reactions I, New York, 1942, p. 155.
[23] D.W. Matson, J.C. Linehan and R.M. Bean, Mater. Lett., 14 (1992) 222.
[24] D.W. Matson, J.C. Linehan and M.E. Geusic, Part. Sci. Technol., 10 (1992) 143.
[25] D.W. Matson, J.C. Linehan, J.G. Darab and M.F. Buehler, Energy Fuels, 8 (1994) 10.