

A THEORETICAL AND EXPERIMENTAL STUDY OF UNIMOLECULAR  
AND BIMOLECULAR RADICAL HYDROGEN TRANSFER REACTIONS

Tom Autrey, Gerald J. Gleicher, Donald M. Camaioni, Kim F. Ferris and  
James A. Franz

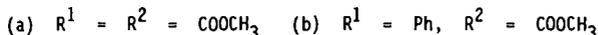
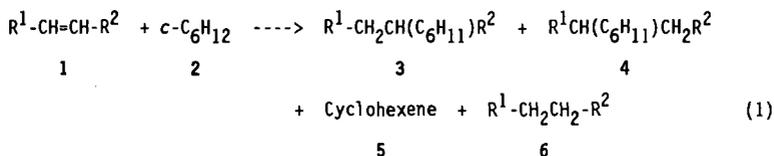
Pacific Northwest Laboratory(a)  
P. O. Box 999 Richland, WA 99352

Keywords: Radical Hydrogen Transfer, RHT, AM1, Semiempirical Quantum Chemical Calculations

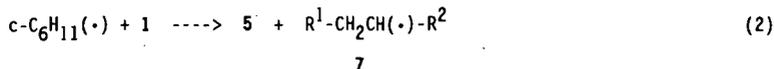
INTRODUCTION

The bimolecular transfer of hydrogen atom from an organic radical to an olefin or aromatic system, known as the radical hydrogen transfer (RHT) reaction, has been proposed as an important pathway for hydrogen transfer in liquid phase pyrolysis reactions and as an important pathway for selective bond cleavage in coal liquefaction.<sup>1-5</sup>

Experimental observation of the RHT reaction was apparently first reported by Metzger,<sup>6</sup> followed almost simultaneously by a study of Billmers et al.<sup>7</sup> In Metzger's work, the radical addition of cyclohexane to dimethylfumarate and methyl cinnamate at 250 to 400 °C was examined:

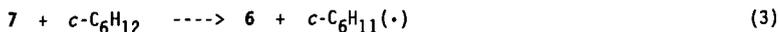


The reaction, which exhibits a chain length of 100, is initiated by hydrogen transfer from cyclohexane to 1. Reversible addition of cyclohexyl radical to 1 followed by abstraction from 2 leads to 3 and 4. The formation of reduced product 6 is suggested to occur via the RHT reaction of cyclohexyl radical with 1:



(a) Operated for the U. S. Department of Energy by Battelle Memorial Institute.

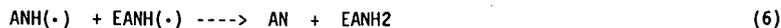
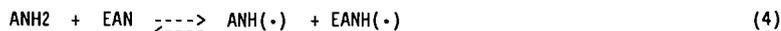
Chain propagation occurs by reaction of 7 with cyclohexane to produce the RHT product, 6:



Chain propagation also occurs by abstraction of hydrogen atom from cyclohexane by the adducts of cyclohexyl radical to 1. An alternate mechanism for formation of 6, the scission of hydrogen atom from cyclohexyl radical and addition of the H atom to 1, leading to 6, was ruled out, based on the observed first order dependence on 1 for the formation of 6. Unfortunately, hydrogen (H<sub>2</sub>), which would have revealed the production of H·, was not analyzed in the reaction mixture. From the chain length of the reaction, the yield of 6 produced in the initiation step was suggested to be insignificant.

Metzger's results<sup>6</sup> are indeed surprising, since they imply a very low barrier for the RHT reaction. The rate of  $\beta$ -scission of hydrogen from cyclohexyl radical is given by  $k_{\beta} = 5 \times 10^{13} \exp(-36000/RT)$ , or  $k_{\beta} = 1.2 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$  at 400 °C. For RHT transfer of hydrogen to the olefin, to occur 10 times faster than  $\beta$ -scission of free hydrogen at the  $5 \times 10^{-3} \text{ M}$  concentrations of 1 employed, an RHT barrier of only 9.7 kcal/mole would be required. For RHT to occur 100 times faster than free hydrogen atom production requires an RHT barrier of only 6.6 kcal/mole. This assumes a typical bimolecular A-factor of  $10^{8.5} \text{ M}^{-1}\text{s}^{-1}$  for RHT.

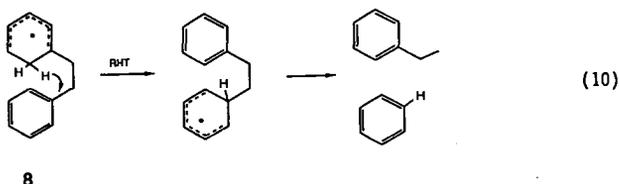
The study of Billmers et al.,<sup>7</sup> examined the transfer of hydrogen from 9,10-dihydroanthracene (ANH<sub>2</sub>) to 2-ethylanthracene (EAN) to form 9,10-dihydro-2-ethylanthracene (EAH<sub>2</sub>) and anthracene (AN). The kinetic order of the non-chain reaction and the observed Arrhenius dependence were consistent with a mechanism involving rate-determining reverse radical disproportionation (RRD) (eq. 4). Other key steps include production of EANH(·) by RHT, eq 5, and formation of the product EANH<sub>2</sub> is by disproportionation (eq. 8) or abstraction (eq. 9).



Billmers et al.<sup>7</sup> found that the rate of formation of EANH<sub>2</sub> was decreased by increasing the ratio AN/ANH<sub>2</sub> at fixed concentrations of ANH<sub>2</sub> and EAN in the initial reaction mixture. This is presumed to be due to the reverse of eq. 5. From an analysis of the reduction of the rate of production of EANH<sub>2</sub> with increasing AN/ANH<sub>2</sub>,  $k_{-5}$  was estimated to be  $120 \text{ M}^{-1}\text{s}^{-1}$  at 350°C, or  $E_{-5} = 18.3 \text{ kcal/mole}$ .

In a related study of hydrogen transfer between 9,10-dihydrophenanthrene and anthracene, computer modeling of the observed kinetics led to an "RHT" rate constant  $k = 7.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 350 °C, corresponding to  $E_a = 13.3$  kcal/mole. If correct, this is a surprisingly low activation barrier, since the barrier was lowered fully as much as the enthalpy change for the reaction compared to the thermoneutral transfer between anthracenes, -5 kcal/mole. This corresponds to an Evans-Polanyi factor of ca. 1 for the reaction, whereas hydrogen atom metathesis reactions usually exhibit Evans-Polanyi factors of 0.5 or less. The authors point out that the reaction kinetics are suggested to be equally well represented by a 3-step sequence of addition of hydrophenanthrenyl radical to anthracene, intramolecular hydrogen atom transfer, and radical scission to give phenanthrene and 9-hydroanthracenyl radical, without postulating the unconventional RHT reaction.

In recent work,<sup>9</sup> we examined the intramolecular RHT reaction of the 2-(2-phenylethyl)cyclohexadienyl radical, **8**, (eq. 10). Intramolecular hydrogen shift from the cyclohexadienyl ring to the *ipso* position of the phenyl ring, followed by  $\beta$ -scission would have given benzene and ethylbenzene as products.



Competing with this reaction is  $\beta$ -scission to give benzyl radical and isotoluene, or hydrogen loss to give bibenzyl. No detectable RHT occurred at 235 °C for this near-thermoneutral reaction. The ratio of H• loss (or the isoenergetic  $\beta$ -scission) to RHT, determined by product detection limits, was greater than 100:1. The predicted A-factor for intramolecular RHT,  $A_1 = 10^{10.8} \text{ M}^{-1} \text{ s}^{-1}$ , and the predicted rate constant for H atom loss,  $7.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , results in a minimum barrier for the intramolecular RHT reaction of 23 kcal/mole for the slightly endergonic hydrogen transfer ( $\Delta H^\circ = 0.5$  kcal/mole). In research currently under way, we are preparing exothermic analogues of intramolecular RHT to attempt to unambiguously observe, in a stereochemically restricted system, a "true" RHT reaction with no possibility of free H atom involvement.

In summary, studies to date suggest a barrier for thermoneutral hydrogen transfer in the RHT reaction between aromatic systems of ca. 18 kcal/mole. None of the studies of RHT or equivalent mechanisms have attempted to directly observe H<sub>2</sub>, and direct determination of Arrhenius parameters and a detailed examination of the pathway of the hydrogen transfer process remains to be carried out.

To better understand the structural and energetic aspects of RHT, we have carried out a semiempirical molecular orbital study of bimolecular and intramolecular RHT reactions for a variety of aromatic systems. We also examined in detail the energetics of hydrogen transfer between ethyl radical

and ethylene via RHT, an addition/metathesis/scission pathway, and a hybrid "concerted" pathway.

## RESULTS AND DISCUSSION

AM1/RHF<sup>10</sup> transition states were located for hydrogen transfer reactions from the cyclohexadienyl radical to benzene, the *ipso* position of toluene, the 1-position of naphthalene, and the 9-position of anthracene. In addition, RHT transition states were located for thermoneutral hydrogen transfer between naphthalenes (1-positions) and anthracenes (9-positions), and the thermoneutral RHT reaction between ethyl radical and ethylene was examined. In each case, the hydrogen is caused to migrate to the olefinic or aromatic carbon.

Table I lists activation barriers for thermoneutral transfer of hydrogen between pairs of benzene, naphthalene, and anthracene rings. AM1 calculations often result in barriers that are higher than experimental values for reactions involving stretched bonds in open-shell systems. However, hydrogen abstraction barriers predicted by AM1 are often in good agreement with experimental values. For example, AM1/RHF predicts a barrier of 18 kcal/mole for the symmetric hydrogen abstraction reaction from cyclohexadiene by the cyclohexadienyl radical, in good agreement with thermoneutral abstraction reactions of alkyl radicals from alkanes, which, in the absence of steric effects, exhibit barriers of ca. 14 kcal/mole.<sup>11</sup> Thus, it was surprising to find that the nominally similar RHT reactions gave substantially higher barriers. Table II presents results for transfer of hydrogen from cyclohexadienyl to aromatic systems. For purposes of comparison, Table III gives calculated and experimental values of C-H bond dissociation energies and activation barriers for hydrogen loss from hydroaryl and ethyl radicals. Although a totally satisfactory calibration of the AM1 method for the present category of reactions is not possible, the overestimations of C-H bond dissociation energies for hydroaryl radicals suggest that the calculated AM1/RHF RHT barriers are 25 to 50% higher than the actual values. Finally, in Table IV, barriers for intramolecular RHT reactions are presented for 2-, 3-, and 4-carbon bridging linkages.

Although the AM1 method has obvious limitations, some interesting observations are possible: (1) RHT barriers for thermoneutral hydrogen transfer reactions are predicted to be closely spaced, with a slight increase in barrier going from benzene to anthracene. Thus, the hydroaryl radicals that have the strongest C-H bonds correspond to the aromatic systems best able to stabilize the liberated hydrogen atoms. (2) The predicted barriers drop dramatically as the hydrogen transfer reactions become more exothermic, such that the barrier for transfer between cyclohexadienyl and anthracene is low enough for the reaction to be observable at moderate (< ca. 250°C) temperatures. The dramatic drop is reminiscent of the drop in barrier for hydrophenanthrenyl H<sub>2</sub> transfer to anthracene vs. thermoneutral transfer between anthracenes.<sup>7</sup> (3) In every case, the activation barrier for RHT is below that of free hydrogen atom production. Finally, (4) intramolecular RHT with 2-, 3- and 4-carbon bridges between the two benzenoid aromatic systems results in closely spaced activation barriers, higher by 2 to 4 kcal/mole than thermoneutral intermolecular RHT reactions. The question becomes whether RHT

will compete with free H<sub>2</sub> reaction or with the more conventional addition/transfer/scission pathway for hydrogen transfer.

#### The Addition/Transfer/Scission Pathway

The AM1/RHF barrier for the RHT reaction between ethyl radical and ethylene, 40.0 kcal/mole, is found to be less than the barrier for hydrogen scission, 52 kcal/mole, but remains a high energy pathway. To examine an alternative pathway to RHT, that of addition, metathesis, and scission, we examined the reaction of ethyl + ethylene. The results of a map of several possible surfaces is depicted in Figure 1. Throughout the calculation, the C4-C3 and C1-C2 bonds were constrained to be planar. The lower path shows the energy profile for addition of ethyl to ethylene to yield an eclipsed butyl radical (the trans conformer is calculated to be 5 kcal/mole more stable). The upper surface in Figure 1 shows the energy as a function of the C2-C3 distance, with equal C1-H-C4 distances at the position of maximum energy, corresponding to the energy barrier for hydrogen migration from C1 to C4. The energy gap labeled A shows the barrier for 1,4-hydrogen transfer, which is less than that of  $\beta$ -scission. The energy gap B corresponds to RHT via a cyclic transition state structure. It is calculated to be 1 kcal/mole lower than the acyclic transition state structure in which C2 and C3 do not interact. The energy gap C corresponds to H atom elimination. It is energetically the least favored reaction path. This calculation suggests that conventional addition/transfer/scission pathways may be favored by enthalpy over the direct RHT path, and that the RHT barrier is reduced (B in Figure 1) by the interaction of the two pi systems. Also, the position of the upper curve between 1.5 to 1.8 Å below the  $\beta$ -scission transition state energy raises the possibility that the addition/transfer/scission pathway might become concerted at suitably high temperatures. Further work to examine similar effects with RHT between aromatic systems is underway.

Finally, the lower predicted barriers for addition/metathesis/scission in this system may mean that intramolecular RHT reactions that are stereochemically precluded from the addition/metathesis pathways (and are true "RHT" reactions) may actually be significantly higher energy pathways. We are currently synthesizing model intramolecular RHT systems to observe exothermic RHT reactions to attempt to unambiguously observe and characterize RHT reactions.

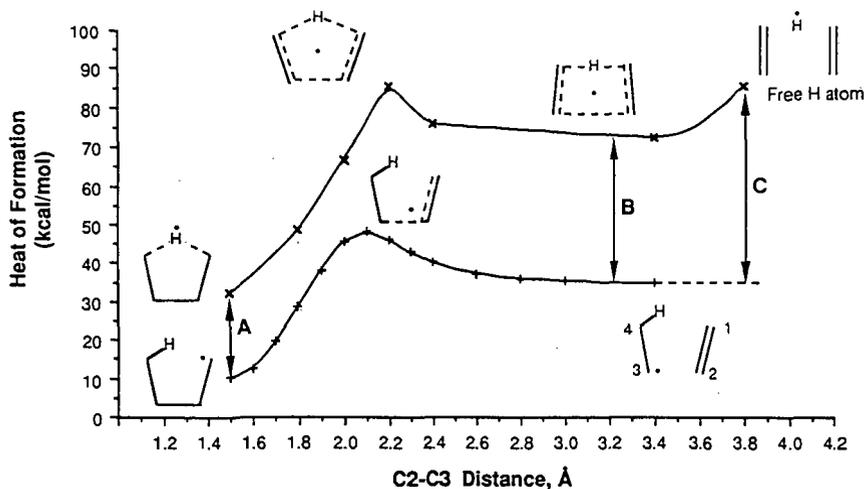
#### REFERENCES

- 1) D. F. McMillen, W. C. Ogier, S.-J. Chang, R. H. Fleming and R. Malhotra, Proc. Intl. Conf. on Coal Science, Pittsburgh, PA 15-19 August, 1983, p. 199.
- 2) D. F. McMillen, R. Malhotra, S.-J. Chang, and S. E. Nigenda, Am. Chem. Soc., Div. Fuel Chem Preprints, 1985, 30(4), 297.
- 3) D. F. McMillen and R. Malhotra, Proc. 1987 Intl Conf. Coal Science, Maastricht, The Netherlands, 26-30 October, 1987.
- 4) D. F. McMillen, R. Malhotra, S.-J. Chang, W. C. Ogier, E. Nigenda and R. H. Fleming, Fuel, 1987, 66, 1611.

- 5) D. F. McMillen, R. Malhotra, G. P. Hum, and S.-J. Chang, Energy & Fuels, 1987, 1(2), 193.
- 6) J. O. Metzger, Angew. Chem. Int. Ed. Engl. 1986, 25, 80.
- 7) R. Billmers, L. L. Griffith and S. E. Stein, J. Phys. Chem. 1986, 90, 517.
- 8) R. Billmers, R. L. Brown, and S. E. Stein, Int. J. Chem. Kinetics, 1989, 21, 375.
- 9) Tom Autrey and James A. Franz "A Search for the Radical Hydrogen Transfer Pathway in Coal Liquefaction," Prepr. Fuel Div. Am. Chem. Soc. 1990, 35(2), 381.
- 10) MOPAC Molecular Orbital Program, Quantum Chemistry Program Exchange, Program No. 455, version 5.0, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University.
- 11) J. A. Franz, M. S. Alnajjar, R. D. Barrows, D. A. Kaisaki, D. M. Camaioni, and N. K. Suleman, J. Org. Chem. 1986, 51, 1446.

#### ACKNOWLEDGEMENT

The authors thank Dr. J. O. Metzger for useful discussions. This work was supported by the Office of Basic Energy Sciences, U. S. Department of Energy, under contract DE-AC06-76RLO 1830.



**Figure 1.** Reaction paths for ethyl radical + ethylene calculated with AMI/RHF. A: Barrier for 1,4-hydrogen atom shift from eclipsed butyl radical (*trans*-butyl radical conformation is 5 kcal/mole lower in energy). B: Barrier for radical hydrogen transfer (RHT). The Z-shaped or alicyclic TS structure with non-interacting termini is calculated to be 1 kcal/mole higher in energy. C: Barrier for H-atom elimination-addition reaction.

Table I. AMI/RHF Barriers for Thermoneutral Hydrogen Transfer From Hydroaryl Radicals to Aromatic Rings and the Ethyl + Ethylene Reaction

Reaction	$\Delta H^\ddagger$ , kcal/mole
Cyclohexadienyl + Benzene	32.7
1-Hydronaphthyl + Naphthalene	34.5
9-Hydroanthracenyl + Anthracene	36.6
Ethyl + Ethylene	40.0

Table II. AMI/RHF Barriers for Hydrogen Transfer From Cyclohexadienyl Radical to Aromatic Rings

Reaction	$\Delta H^\ddagger$ , kcal/mole <sup>a</sup>	$\Delta H^\circ$ , kcal/mole <sup>b</sup>
Cyclohexadienyl + Toluene ( <i>ipso</i> position)	36.4	0.4
Cyclohexadienyl + Benzene	32.7	0.0
Cyclohexadienyl + Naphthalene	25.6	-7.5
Cyclohexadienyl + Anthracene	16.4	-18.8

<sup>a</sup>AMI/RHF calculation

<sup>b</sup>Experimental heat of reaction for the hydrogen atom transfer reaction

Table III. Hydrogen Atom Scission from Hydroaryl and Ethyl Radicals

Reaction	$\Delta H^\ddagger$ , kcal/mole <sup>a</sup>		$\Delta H^\circ$ , kcal/mole <sup>b</sup>	
	expt	calc	expt	calc
Cyclohexadienyl ---> benzene + H	28.7	44	25.7	34.8
1-Hydronaphthyl ---> naphthalene + H	37	--	35	39.9
9-Hydroanthracenyl ---> Anthracene + H	45	58	43	50.3
Ethyl ---> Ethylene + H	38	52	35.6	49.4

<sup>a</sup>AMI/RHF calculation

<sup>b</sup>Experimental heat of reaction for the hydrogen atom transfer reaction

Table IV. AMI/RHF Barriers for Intramolecular RHT Reactions<sup>a</sup>

Ground State Radical	$\Delta H^\ddagger$ , kcal/mole
2-(2-phenylethyl)cyclohexadienyl, 8	38.2
2-(2-phenylpropyl)cyclohexadienyl	40.8
2-(2-phenylbutyl)cyclohexadienyl	39.4

<sup>a</sup>The hydrogen is transferred to the *ipso* position of the appended ring. See, e.g., eq. 10