

## INTRINSIC BARRIERS FOR H-ATOM TRANSFER REACTIONS

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Hydrogen transfer reactions play a well recognized role in coal liquefaction. While H-abstraction reactions between radicals and H-donors have been well studied, understanding of structure-reactivity relationships remains surprisingly incomplete. The Bell-Evans-Polanyi relationship<sup>1</sup> expressed by Equation 1 is used routinely to correlate and predict rates of H-abstraction from a homologous series of donors.

$$E_a = \alpha \Delta H_r + C \quad 1)$$

The constant, C, is interpreted as the activation barrier if the reactions were to occur with zero enthalpy change. For hydrocarbon radicals, the value of C is usually assigned the barrier for the identity reaction of methyl plus methane with justification being that the few identity reactions that have been measured are all within a few kcal/mol of this value. However, uncertainties of this amount when combined with uncertainties in the reaction enthalpy can lead to orders of magnitude errors in rate estimates.

Another form of hydrogen transfer known as radical hydrogen transfer (RHT)<sup>2,3,4,5,6</sup> is currently the subject of much speculation with respect to its role in coal liquefaction. RHT is unusual in that the radical donates a  $\beta$ -hydrogen to an acceptor molecule rather than abstracting hydrogen from a donor molecule. RHT is known to take place readily between ketones and ketyl radicals.<sup>6</sup> But in hydrocarbon systems, it remains controversial due to a lack of information about its activation barrier. The reaction is thought to be important in high temperature liquid-phase reactions of hydrocarbons<sup>3,4c</sup> and in coal liquefaction<sup>4c,5</sup> where it provides a simple route for migration of hydrogen from hydroaryl to aryl structures and for cleavage of aryl-alkyl bonds. However, multi-step reaction pathways to the same products are usually possible. For RHT to be important, its activation barrier must be sufficiently low to compete with these alternative pathways. In particular, RHT must compete with unimolecular scission of H-atom from the radical and subsequent rapid reactions of free H atoms. Thus, RHT remains controversial due to the lack of information about activation barriers for RHT reactions.

Marcus Theory<sup>7</sup> has been shown to be applicable to atom transfer reactions in the form of Equation 2 but it has received little attention until recently.<sup>8,9,10</sup>

$$E_a = \Delta E^\ddagger_1 \left( 1 + \frac{\Delta E_r}{4\Delta E^\ddagger_1} \right)^2 \quad 2)$$

Marcus theory<sup>7</sup> defines the intrinsic barriers as above and equates it with one-fourth of the bond reorganization energy for forming the transition state (TS) structure. Marcus theory also recognizes that the intrinsic barrier may depend on both the attacking radical and the H donor, and defines the intrinsic barriers for unsymmetrical reactions as the average of the barriers for contributing symmetrical identity reactions. Finally, the Marcus equation simplifies to the Bell-Evans-Polanyi equation when Equation 2 is expanded and the quadratic term is negligible (*i.e.*, reactions that exhibit small exothermicities and large intrinsic barriers). Nonetheless, the possibility that intrinsic barriers are unique for each set of radical and donor should not be neglected.

Recent theoretical<sup>8,11,12</sup> studies of H-abstraction reactions of simple hydrocarbons and functionalized methanes have shown significant variation in intrinsic barrier heights and essentially have validated the assumption of Marcus theory that the intrinsic barrier for cross reactions are approximately the average of that for the two contributing identity reactions. However, a complete understanding of structural effects is still incomplete: for although these studies have shown how the effects of alkyl and heteroatom functional groups attached to the reaction site effect the intrinsic barrier, the effects of delocalizing groups such as vinyl and aryl groups on intrinsic barriers for H-abstraction remain to be examined. Since no kinetic data are available for hydrocarbon RHT reactions, theory-based insights to rate-controlling factors are needed to aid experimental verification and elucidation of this pathway.

**COMPUTATIONAL METHODOLOGY.** MNDO-PM3<sup>13</sup> calculations of TS geometries and energies ( $\Delta H^\ddagger$ ) were performed using MOPAC (Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN; QCPE No. 455 ver. 6.0). Geometries of transition states for H-atom transfer reactions were optimized using the Hartree-Fock (RHF) half-electron Hamiltonian. TSs for identity reactions were located using the default optimizer by forcing the breaking/forming C-H bonds to have equal lengths. TS geometries for nonidentity reactions were optimized using one or more of the following methods available in MOPAC ver. 6: Bartel's nonlinear least squares minimization routine, McIver-Komornicki gradient minimization routine, and the eigenvector follower optimizers. Force calculations were performed to

establish that optimized geometries actually were saddle points for H transfer (only one negative vibrational frequency). The TS energies for twenty H-abstraction reactions were correlated with experimental energies (obtained by summing experimental  $\Delta H_f^\circ$  of the abstracting radicals and hydrogen donors, and experimental activation enthalpies). The least squares fit yielded the following equation and statistical parameters:  $\Delta H_f^\circ(\text{expt}) = 1.14\Delta H_f^\circ(\text{calc}) - 8.1$  kcal/mol;  $r^2 = 0.9984$ ; standard error  $\Delta H_f^\circ(\text{calc.}) = 1.9$  kcal/mol.  $\Delta H_f^\circ$  for radicals and donors were obtained from the literature<sup>14</sup> or derived from standard estimation methods<sup>14</sup> when experimental data were unavailable. Rate data for H-abstraction reactions are from the literature.<sup>15,16</sup> For reactions in which temperature-dependent rate data are lacking, Arrhenius activation energies ( $E_{a,x}$ ) were estimated using Equation 3, which equates the difference in activation energies between the reaction of interest and a basis reaction of known activation energy with the log of the relative rate constant at a known temperature and statistically corrected for the number of donatable-hydrogens.

$$E_{a,2} - E_{a,1} = n_1/n_2 \cdot \ln(k_2/k_1) \quad 3)$$

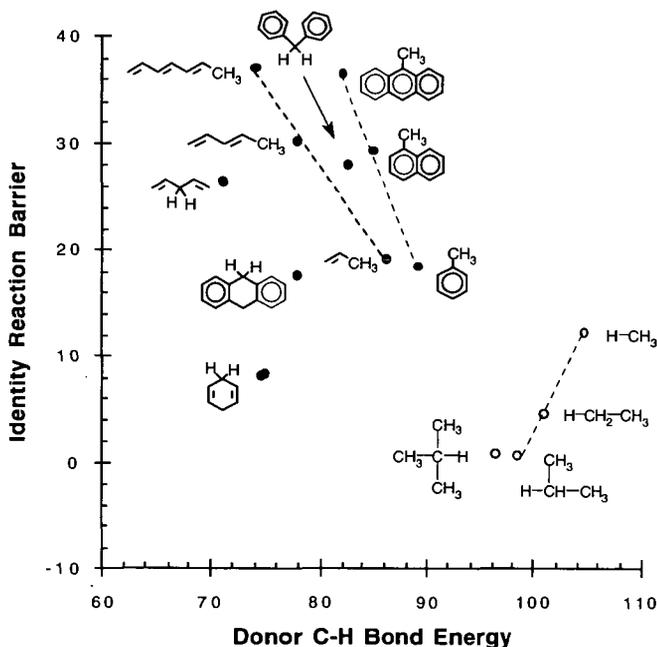
**RESULTS. Analysis of Errors in the MNDO-PM3 Method.** PM3 yields  $\Delta H_f^\circ$  that differ systematically from experimental values with different errors for different structural classes.<sup>17</sup> For example, experimental  $\Delta H_f^\circ$  for polycyclic aromatic hydrocarbons show a linear correlation with PM3 heats. The fit to benzene, naphthalene, phenanthrene and anthracene is excellent ( $r^2 = 0.99993$ ). Inclusion of higher aromatic hydrocarbons gives a very good fit as well, except for benz[a]phenanthrene, triphenylene, pyrene and tetracene data which are sufficiently far from the line to warrant skepticism about their accuracy. An important feature of the fit is that it has non-unit slope and non-zero intercept. Thus, agreement between theory and experiment differs according to the magnitude of a compound's  $\Delta H_f^\circ$ . In the case of radicals, the errors are systematic for families of structurally-related radicals. For example, primary, secondary and tertiary radicals each exhibit an excellent correlation, deviating -12, -16, and -18 kcal/mol from experiment. We find that experimentally-determined H-abstraction TS energies correlate with PM3 calculated energies, too. The linear correlation between experimental<sup>18</sup> and calculated TS enthalpies is surprisingly good, especially considering that the data base includes reactions of methyl, ethyl, benzyl, and diphenylmethyl radicals with alkane, alkene and aromatic donors and reaction enthalpies range from thermoneutral to -20 kcal/mol. Unlike the correlation for alkyl radicals, a simple offset correction will not suffice to reproduce experimental data. The least squares fit (see Methodology section) to the data yields a non-unit slope of 1.15 and a negative intercept. Therefore, calculated TS energies may be lower than experiment, approximately equal to experiment, or higher than experiment depending on the magnitude of the TS energy.

**Barriers for H-Transfer Identity Reactions.** The above findings indicate that energy minima and maxima on PM3 potential energy surfaces for H-transfer correlate with experiment. With this insight, reliable structure-barrier trends can be obtained for H-transfer identity reactions provided that the necessary corrections are applied to the reactant energies when the barrier is obtained by taking the difference between TS and reactant energies. We have opted to use experimental data for reactants in our calculations because it reduces the number of structures to be calculated and eliminates the need to determine reactant errors. Barriers so obtained reproduce experimental trends qualitatively.

**Barriers for H-Abstraction Identity Reactions.** Figure 1 shows results for alkyl radical systems. Intrinsic barriers for H-abstractions decrease in the order: methyl > ethyl  $\approx$  *t*-butyl > *i*-propyl.<sup>19</sup> The barriers for methyl, ethyl and *i*-propyl correlate well with the decrease in bond dissociation energies (BDE) of the R-H bond as expected from ab initio calculations and valence-bond curve-crossing models.<sup>11</sup> We think that the *t*-butyl system is anomalous because PM3 overcompensates for methyl group repulsions that develop in the pyramidal TS. Support for this explanation is found in comparisons of the calculated and experimental energies for the isomeric alicyclic butanes and pentanes.<sup>14</sup> PM3  $\Delta H_f^\circ$  errors parallel the degree of branching. The calculated  $\Delta H_f^\circ$  for *n*-butane is 1.3 kcal/mol larger than the experimental value whereas isobutane is larger by 2.9 kcal/mol. For the pentanes, the calculated  $\Delta H_f^\circ$  are larger by 0.6 kcal/mol for *n*-pentane, 2.4 kcal/mol for isopentane, and 4.5 kcal/mol for neopentane. Allowing for this error, the overall trend in alkyl radical H-abstraction identity barriers is in keeping with experiment<sup>20</sup> and higher level theory.<sup>11</sup> *The downward trend in intrinsic barriers with methyl group substitution shows that the effect of branching at the reaction site stabilizes the TS more than the reactants.*

The effect of conjugation with the reaction site operates in the opposite direction. Results for systems involving  $\pi$ -delocalizing aryl and vinyl groups also appear in Figure 1. Intrinsic barriers for phenyl substitutions increase in the order: ethyl < benzyl < diphenylmethyl. This effect was first noted by Stein<sup>21</sup> who compared the reactivity of methyl, benzyl and diphenylmethyl radicals. A similar effect is calculated for alicyclic polyenyl and arylmethyl systems with intrinsic barriers for increase the order: allyl < pentadienyl < heptatrienyl and benzyl < 1-naphthylmethyl < 9-anthrylmethyl. Good linear correlation with R-H BDEs are obtained for these homologous series, especially when uncertainties associated with radical  $\Delta H_f^\circ$  and BDEs are taken into consideration. *These consistent trends indicate that the TS is stabilized less than the reactants by  $\pi$ -delocalization.*

Interestingly, cyclic donors have lower intrinsic barriers than acyclic polyenyl and arylmethyl systems. Barriers for cyclohexadienyl-plus-cyclohexadiene and hydroanthryl-plus-dihydroanthracene systems are substantially lower than barriers for 1,4-pentadien-3-yl plus 1,4-pentadiene and diphenylmethyl plus diphenylmethane. This trend is attributed to the release of strain in the TS that is present in the cyclic donors but not in the acyclic donors. Cyclic hydroaromatic donors are better than arylalkyl donors for coal liquefaction. Having lower intrinsic barriers for donating H is probably an important but unrecognized contributing factor.

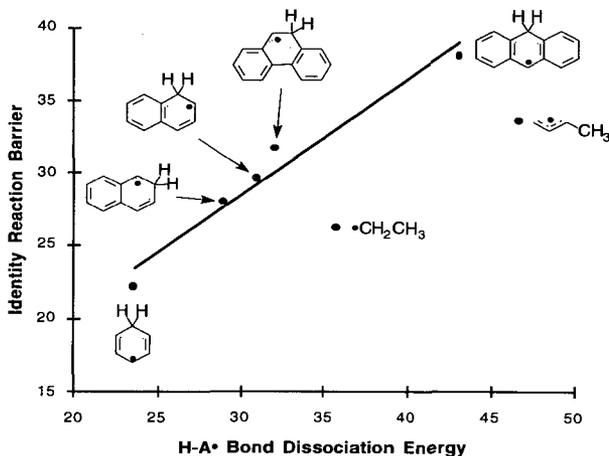


**Figure 1.** The effects of radical-site branching and conjugation on calculated barriers for H-abstraction identity reactions of hydrocarbon systems: barriers for alkyl systems (o) decrease with donor C-H bond dissociation energy; barriers for conjugated systems (\*) show the opposite trend.

**Barriers for RHT Identity Reactions.** Due to the complete lack of rate data for RHT reactions, a correlation for TS energies cannot be demonstrated. However, a rigorous ab initio calculation has been carried out on the prototypical reaction, ethyl plus ethylene. The barrier (26.9 kcal/mol) we calculate using PM3 agrees well with the ab initio barrier (27.2 kcal/mol),<sup>22</sup> provided that the PM3 barrier is obtained from the calculated TS energy and the experimentally-derived  $\Delta H^\ddagger$  for ethyl and ethylene. PM3 also reproduces the salient features of the ab initio transition structure (linear C-"inflight H"-C bond angle, planar carbons  $\beta$  to inflight H, pyramidal carbons  $\alpha$  to "inflight H").<sup>23</sup>

Calculations of TS energies for higher homologs were performed to elucidate structure-reactivity trends for the RHT reaction. In all cases, RHT barriers were obtained from the difference between PM3 TS energies and experimental reactant energies. Barriers for RHT identity reactions were calculated for a series of hydroaryl-plus-arene systems as well as 1-methylallyl plus butadiene. Figure 2 shows trends for conjugated systems plotted against donor radical (HA $\cdot$ ) C-H bond energies (estimated from thermochemical data<sup>14</sup> as follows: cyclohexadienyl, 25; 1-hydronaphthyl, 31; ethyl, 36; 9-hydroanthryl, 43; 1-methylallyl, 46). The barriers for hydroaryl radicals increase in the series: cyclohexadienyl < 2-hydronaphthyl < 1-hydronaphthyl < 9-hydroanthryl < 9-hydroanthryl. The barriers correlate well with the C-H bond strengths for the AH $\cdot$  donor radicals indicating that the BDE is an indicator of the relative RHT barrier heights for aromatic systems. A similar trend is apparent for ethyl and methylallyl radical donors. BDEs for AH $\cdot$  increase because the radicals derive more resonance energy than the olefins or arenes from  $\pi$ -delocalizing benzo and vinyl groups. Similarly, RHT barriers increase because the reactants (mainly the radicals) are being stabilized more than the TS by conjugation effects.

**DISCUSSION.** It is most noteworthy and surprising that RHT barriers are a substantial fraction (~80% for ethyl-plus-ethylene) of the  $\beta$ -C-H bond energy. In contrast, H-abstraction reactions occur with barriers that are a small fraction (~15% for ethyl-plus-ethane) of the donor C-H bond energy. Our calculations indicate clearly that RHT is intrinsically more difficult than H abstraction. Furthermore, they show that barriers vary significantly with structure such that a single or average intrinsic barrier cannot be used to estimate H-transfer reaction rates accurately. Inspection of the TS geometries calculated for H-abstraction and RHT reactions provides fundamental insight to both the noted effects of  $\pi$ -delocalizing groups and the substantial difference between H-abstraction and RHT barriers. TS structures for H abstraction resemble an H atom in transit between two alkyl groups, not alkyl radicals. A radical  $sp^2$  carbon exhibits a relatively low barrier to pyramidal distortion compared to that for planar distortion of alkyl  $sp^3$  carbon.<sup>24</sup> Consequently, most of the structural reorganization occurs at the radical carbon. Overlap with adjacent  $\pi$ -delocalizing groups is diminished in the TS with the net result being that the reactants are most effected by  $\pi$ -stabilization. For the RHT reaction, the radical site remains planar because it is remote to the carbons that are transferring the H atom. Carbons with greater reorganization energies,  $sp^3$  alkyl and  $sp^2$  alkene/arene, are at the reaction site and must deform to achieve the TS geometry. The  $sp^3$  carbon that is donating the H-atom deforms substantially towards  $sp^2$  character to achieve the TS. Thus, the RHT TS resembles an H atom interacting with the termini of two olefinic or aromatic moieties. With these insights, the greater barriers for RHT compared to H-abstraction are not surprising. The increase in barrier with benzannulation of the cyclohexadienyl-plus-benzene and vinylogous homologation of the ethyl-plus-ethylene systems is also consistent with these insights. Radicals derive relatively more stabilization from conjugation than olefins and arenes. Otherwise, the HA• BDEs would not increase with conjugation. The loss of radical character and development of olefin/arene character on forming the RHT TS causes the reactants to be stabilized more by conjugation; which explains why RHT barriers correlate so well with the AH• BDEs.



**Figure 2.** Barriers for radical hydrogen transfer identity reactions of conjugated systems increase with degree of conjugation. The effect correlates well with the bond dissociation energies of homologous radicals.

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  19. If the barriers are obtained using PM3 energies for the reactants, then an opposite and erroneous trend is obtained: methyl, 11.7; ethyl, 13.5; isopropyl, 14.7; *t*-butyl, 18.6.
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