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A THEORETICAL STUDY OF HYDROGEN-ATOM ABSTRACTION BY METHYL RADICAL

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Abstract– The activation energies for the abstraction of a hydrogen atom from each of several hydrocarbons has been calculated using the AM1 molecular orbital method. The calculated barrier for the abstraction from methane is 15.5 kcal./mole, in good agreement with experiment. Calculated barriers for other abstractions are reasonably good. They are much improved when the calculated intrinsic barrier is used together with the experimental heats of reaction in a modified formulation of Marcus theory.

Hydrogen abstractions by free radicals are important processes for many aspects of organic and polymer chemistry. Previous attempts to model these reactions using molecular orbital methods have not led to satisfactory results.[1] Small basis set ab initio calculations cannot adequately describe the differences between the reactants and products. Small basis sets are insufficient due to the arbitrary nature of their description of the differing number of bonding interactions in the transition state as compared to the reactants. If the basis set is augmented to better describe the partial bonding in the transition state, one needs to also use the additional basis functions in the calculation of the reactants. When the basis is not complete, the arbitrariness in placing these functions near the (separated) reactants leads to a parallel arbitrariness in the energy of the reactants and, consequently, the activation energy. This problem has been discussed previously.[1] The second problem is due to the electron correlation error. The extent of electron correlation will vary with the extent of bonding between the species. For example, Hartree–Fock calculations give very poor descriptions of the energetics for bond cleavage. Extended configuration interaction or MCSCF calculations are generally necessary for reasonably accurate ab initio calculations. The passage from the transition state to reactant or product in a hydrogen abstraction reaction is very much like a bond cleavage as one of the (partially) bonding interactions is eliminated.

Previous attempts at using semiempirical methods to describe hydrogen abstraction reaction have not met with much success. The reasons for the failure lie in the methodology. In particular, the MNDO method overestimates the repulsive interactions involving hydrogens, which, presumably, is the major reason for its gross overestimation of the activation energy for hydrogen abstraction reactions. The advent of the AM1 method,[2] which was conceived with a specific goal of correcting these repulsion errors, and which is reported to give reasonable descriptions of hydrogen bonding, has encouraged us to reinvestigate hydrogen abstraction reactions.

METHODS

This work was performed using the AM1 approximation to molecular orbital theory. The hal electron method[3] was used in these calculations as it is thought to give better heats of formation than the (less expensive) UHF procedure. The reaction path for each abstraction reaction was obtained using the distance between the methyl radical and the hydrogen to be abstracted as the reaction coordinate. All geometrical parameters were optimized for each stepped value of the reaction coordinate. After a good approximation to the transition state was obtained by this procedure, the transition states were directly and completely optimized. The only exception to the above was the study of abstraction from toluene, where the aromatic ring was kept planar.

RESULTS

The results of the calculations are presented in tables 1–4. The activation energy for the abstraction from CH_4 is calculated to be 15.5 kcal./mole. This value is sufficiently close to the experimentally measured values that it is worthwhile to consider the various experimental determinations of this reaction in the gas phase. Most experimental determinations have used isotopically labeled methane and/or methyl radical. The various experimental and calculated enthalpies of activation for different combinations of protiated and deuterated methyl radicals and methane are collected in table 1. These values were calculated by correcting the activation energies by the appropriate differences in zero point energy calculated from vibrational analyses using the AM1 enthalpy surfaces. As can be seen from table 1, the calculated activation energies are very close to the experimental values. The calculated effect of perdeuteration on the methyl radical is to lower the activation energy by about 0.5 kcal./mole, while the effect of perdeuterating the methane is calculated to raise the activation enthalpy by 2.2 kcal./mole. One should note that the comparison is with experimental *enthalpies of activation*, which were (necessarily) derived from rates measured over a range of temperatures. The effect of tunneling upon the overall rate will appear in the preexponential factor. Rather, it can be treated as a modification of the transmission coefficent, κ, in transition state theory.[4] Tunneling should have no effect upon the enthalpies o activation.

The heats of formation of alkyl radicals have been recently reinvestigated by several groups.[5,6] Despite the fact that experimental errors up to 2.0 kcal./mole are common, it is clear that the heats of formation of most unconjugated alkyl radicals are somewhat underestimated by AM1. While, these errors tend to cancel for abstractions by methyl radical from alkanes, this artifact results in incorrect estimates of the activation energies for several reactions, especially the abstractions from toluene and propene.

Table 1

Reaction	Activation Energy calc.	Activation Energy exper.
$CH_3 + CH_4 \text{-->} CH_4 + CH_3$	15.5	14.9
$CH_3 + CD_4 \text{-->} CH_3D + CD_3$	17.7	
$CD_3 + CH_4 \text{-->} CD_3H + CH_3$	15.0	14.1,14.3
$CD_3 + CD_4 \text{-->} CD_4 + CD_3$	17.2	18.4

all energies are in kcal./mole

Table 2

Substrate	Heat of reaction	$\Delta H^{\ddagger}$ calc	$\Delta H^{\ddagger i}$ calc
CH_4	0.0	15.5	15.5
C_2H_6	–4.5	14.5	16.6
C_3H_8 (sec)	–9.1	13.9	18.1
C_4H_{10} (tert)	–13.4	13.6	19.6
$CH_2{=}CHCH_3$	–4.0	14.7	16.6
$phCH_3$	–3.4	16.6	18.2
cyc–C_3H_6	4.5	17.2	14.9
cyc–C_4H_8	–1.5	15.5	15.9

all energies are in kcal./mole

A reasonable test of the capacity of AM1 to model the transition states despite the fact that the heats of reaction are in error is to apply a modification of Marcus theory,[7] (equation 1) which has been thoroughly discussed by Murdoch,[8] and applied with success to other studies.[9,10] The intrinsic barrier can be calculated for each reaction studied by substituting the appropriate values for the calculated activation energies and heats of reaction in equation 1. If the marcus relationship works and all of the reactions occur through analogous reaction paths, then the intrinsic barriers calculated should all be similar. These are presented in table 2. The intrinsic barriers are reasonably similar for most of the reactions where the abstraction is from a carbon.

$$\Delta H^{\ddagger} = \Delta H^{i} + \Delta H_{reaction} + (\Delta H_{reaction})^2/(16\Delta H^{i}) \qquad (1)$$

Another useful application of Marcus theory is to recalculate the activation energies using the intrinsic barrier and the experimental heats of reaction. This allows the modelling procedure to overcome the errors due to the incorrect description of the heats of formation of the radicals and consequent erroneous heats of reaction. Table 3 compares the activation enthalpies calculated using three different sets of experimental radical heats of formation (those used by Dewar, Golden, and Griller) with the experimental values.[11] The activation parameters are in reasonably good agreement with the experimental values when calculated in this manner. The agreement would be improved i one were to add 0.5 kcal./mole to the experimental values to correct for the fact that the abstractions were measured using $CD_3{}^{\cdot}$, rather than $CH_3{}^{\cdot}$. This illustrates the utility of using Marcus theory in conjunction with MO calculation to model important reaction series.

Table 3

		Enthalpy of activation			
Substrate	calc.	Method A	Method B	Method C	exper.
CH_4	15.5	15.5	15.5	15.5	14.9
C_3H_6	14.5	12.4	12.0	13.5	12.2 D
C_3H_8 (2•)	13.9	10.9	10.5	11.6	10.3 D
C_4H_{10} (3•)	13.6	10.1	8.6	10.7	8.2 D
$CH_2{=}CHCH_3$	14.7	7.5	6.4	7.9	7.7 D
$phCH_3$	16.6	8.1		8.4	8.3 D
cyc$-C_3H_6$	17.2	16.1			12.9 D
cyc$-C_4H_8$	15.5	11.5			10.1 D

Calculation of Enthalpies of activation using the intrinsic barrier calculated for CH_4 + $CH_3{}^{\cdot}$ and heats of reaction calculated as described below.

All energies are in kcal./mole

Method A uses radical heats of formation from McMillen and Golden, reference 6.

Method B uses heats of formation from Dewar and Thiel[12]

Method C uses radical Heats of formation from Griller et al. reference 5.

D (in exper) means abstraction by CD3, all values from reference 11.

Complete optimization of the reaction paths and transition states may be extremely costly for many reaction processes. If one can establish that the Marcus equation works properly within a reasonable sampling of reactions that presumably follow similar reaction paths, then one can use the intrinsic barrier extracted from these calculations together with simple thermochemical data for the additional reactions in question to calculate their activation parameters. The thermochemical data may be obtained in whatever manner is most appropriate or available, either experimentally or theoretically.

Table 4 shows the C−H distances and bond orders for the bonds being formed and broken. The C−H−C angle was 180° in all cases. As expected, the optimized transition states have bond lengths and bond orders characteristic of structures that increasingly resemble the products as the reactions become more endothermic. In this table the calculated (rather than experimental) heats o reaction are used for comparison with the calculated transition states.

Marcus theory can be used in another manner to interpret the reaction paths. The calculated intrinsic barriers increase in a regular manner as the abstracted hydrogen is changed from that in methane to 1•, 2• and 3• H's (see table 2). This can be taken as an indication that the intrinsic barrier increases with increasing steric crowding in the transition state. Kreevoy has also observed modifications of the intrinsic barriers of atom-transfer reactions with structural changes in the reagents.[13] This behavior seems consistent with an intrinsic barrier that corresponds to a transition state of almost constant geometry except for the added methyl groups. In such a case, one would expect a small increase in repulsion (in the transition state) for each methyl group added. It is not completely clear whether this is the only cause of the increase in intrinsic barrier. Another possibility is that some of the overestimation of the repulsions between H's and other atoms that was corrected for in the modification of the MNDO formalism that distinguishes the two methods remains in AM1. A last complication that need to be considered for the abstraction reactions involved in this study is the possibility of tunnelling. Kinetic isotope effect studies on hydrogen abstraction reactions suggest that tunnelling exerts a significant effect on the rates of these reactions. However, tunneling should affect the preexponential factor in the rate equation, not the barrier.

Table 4

Properties of Transition States

Radical (R)	R–H distance	R–H bond order	Me–H distance	Me–H bond order	Heat of reaction
CH_3	1.29	0.48	1.29	0.48	0.0
C_2H_5	1.27	0.52	1.34	0.45	−4.5
sec-C_3H_7	1.25	0.53	1.37	0.43	−9.1
t-C_4H_9	1.25	0.54	1.39	0.41	−13.4
allyl	1.27	0.51	1.33	0.46	−4.0
benzyl	1.27	0.47	1.35	0.49	−3.4
cyc-C_3H_5	1.30	0.43	1.28	0.53	4.5
cyc-C_4H_7	1.27	0.48	1.31	0.48	−1.5

(distances in Angstroms)

In conclusion, AM1 calculations give reasonably accurate descriptions of the reaction processes involved in hydrogen abstraction. The intrinsic errors in the relative heats of formation of the various radicals can be adequately corrected for using modified Marcus theory. This methodology should be extremely useful for modelling abstraction reactions involving large molecules including chain transfer processes in polymers.

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