many of the transits from high-energy conformations to low-energy ones appear to have relatively low barriers. Overall, then, we find these compounds to be remarkably flexible rather than rigid. The highly symmetric cyclodextrin structures portrayed in the literature are to be regarded as time-averaged structures only.

The conclusions derived from this study and the relationship to the recognition process of cyclodextrins depends on the quality of the force field used. The AMBER and MM2 force fields seem to treat hydrogen bonding in alcohols along with the anomeric effect quite well. Furthermore, both AMBER and MM2 are in qualitative agreement so the results of our study are force field independent. The question of water and its influence on cyclodextrin structure as well as its influence on inclusion complexation has not been addressed here. It is not known whether the GC phases used in chromatography are partially hydrated or completely unhydrated as we assume here. Also, with regard to the recognition process of cyclodextrins, one should consider a Boltzman distribution of the conformational states described here along with the symmetry of the included guest. To address these issues we are performing molecular dynamics simulations to derive averaged structures and energies of guest–host complexes.[22] The results of in vacuo simulations along with partially hydrated and fully solvated conditions are being examined with the CHARMM force field to understand the role of water on complexation of enantiomeric guests.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8901828) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. α-CD, 10016-20-3; β-CD, 7585-39-9; γ-CD, 17465-86-0.

Supplementary Material Available: Component energies for structures 1–3 in Table I and structures listed in Tables II–VII (7 pages). Ordering information is given on any current masthead page.

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Theoretical Studies of Radical Recombination Reactions. 4. An AM1/CI Study of Reactions of Benzylic and Allylic Radicals. An Intrinsic Barrier to Bond Formation

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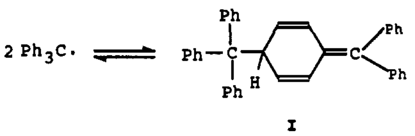
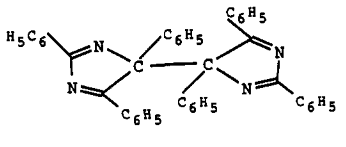
AM1/CI calculations on the reaction paths for the coupling of organic free radicals are presented. The calculations are in good agreement with previously reported experimental results for benzyl radical coupling. Selectivities for the combinations of methyl radicals with allyl, azaallyl, benzyl, and variously cyano-substituted benzyl radicals as well as seven different coupling reactions of two benzyl radicals are reported. Application of Marcus theory and a fitting to a linear equation after Leffler and Grunwald suggest the existence of an intrinsic barrier of 22 or 25 kcal/mol, respectively, for the coupling of carbon-centered free radicals.

The recombination of two free radicals to form a single covalent bond is often thought to occur without activation. This conception is probably due to analogy with the combination of two atoms, such as H, to form a covalent molecule, such as H_2. Exceptions to this idea are usually attributed to steric interactions alone. Nevertheless, experimental observations that have long been in the literature suggest that other effects, presumably electronic in nature, might also contribute to barriers to combination of radicals. In fact, the first free radical characterized, triphenylmethyl, has long been known to be in equilibrium with its dimer, which has been shown to have structure I, rather than the originally anticipated hexaphenylethane.[1]

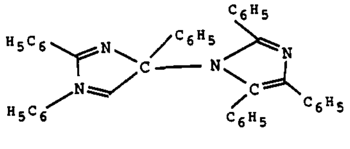


I

Also prominent among the experimental observations that support this idea are the observed selectivities for attacks at radicals that can, in principle, react at more than one site. Thus, allyl radical reacts at the terminal positions, rather than the central carbon (to give cyclopropyl products), and benzyl radicals couple predominantly at the α-carbons, rather than at the ring carbons. A particularly striking example involves the coupling of triphenylimidizoyl radicals, which combine to form two different products, one kinetically and the other thermodynamically favored.[2] The kinetically favored product, II, is clearly more sterically hindered than the thermodynamic product, III.



II



III

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[1] Lankamp; Nauta; MacLean. *Tetrahedron Lett.* **1968**, 249. Staab, Brettschneider; Brunner. *Chem. Ber.* **1970**, *103*, 1101. Voltz; Lotsch; Schnell. *Tetrahedron* **1970**, *26*, 5343. McBride. *Tetrahedron* **1974**, *30*, 2009.

[2] White, D. M.; Sonnenberg, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 3825.

Table I. Activation Energies for Combination with Methyl Radical (kcal/mol)

radical	enthalpy of activation	
	MNDO	AM1
allyl	5.5	0.3
1-azaallyl		
attack on C	3.9	0.2
attack on N	11.0	2.8
benzyl		
attack on C_α	3.0	0.8
attack on C_{ortho}	14.0	2.4
attack in C_{para}	10.0	1.6

Theoretical calculations suggest that barriers to radical recombination might exist in certain situations. MNDO/CI calculations have suggested that 1-azaallyl radical be preferentially attacked at the carbon, rather than the nitrogen,[3] and that there be a barrier to the recombination of ethyl and ethyldiazenyl radicals.[4] Ab initio and semiempirical calculations both suggest that barriers to the combination of the diamino and dihydroxylaminyl radicals should exist.[5]

In this paper we examine the coupling of benzyl radicals as well as reinvestigate the allyl system.

Methods

Although the MNDO[6] method with 3 × 3 CI (MNDO/CI) describes the bond dissociation curves of small molecules reasonably well,[7] some apparent artifacts remain. Notably, the recombination curves of two methyl radicals and an aminyl radical with a hydrogen atom have calculated barriers of 2.4 and 0.9 kcal/mol, respectively. Both of those barriers disappear[8] when the calculations are repeated by using the AM1[9] method. For these calculations, the AM1 method was used with the "biradical" procedure. In this procedure, the first excited singlet open-shell SCF orbitals are calculated by using the half-electron method.[10] The 3 × 3 CI is performed by using the ground state and doubly excited state obtained by respectively demoting and promoting an electron from the SCF state. This procedure is size consistent with the individual radicals calculated by using the same half-electron method. The AM1 method has been used with considerably success in the study of other free radical reactions such as hydrogen-transfer[11] and oxidation/reduction.[12]

The geometries of all species discussed were completely optimized in all internal degrees of freedom. Each of the transition states were characterized by calculating its force constants. One, and only one, force constant was found to be negative in each case.[13] Computations were carried out by using the AMPAC program on IBM RS/6000, DEC VAX, MICROVAX, and DECstation 3000 and Ulysses Systems I386 workstations.

Results and Discussion

Methyl–Allyl Coupling. The calculated activation enthalpies for the attack of methyl radical on allyl and 1-azaallyl radical are collected in Table I. The previously published[14] MNDO/CI values are included for comparisons. The activation energy for methyl radical attack upon allyl radical is predicted to be 0.3 kcal/mol by AM1/CI, rather than the 5.5 kcal/mol predicted by MNDO/CI. Similarly, the activation energies for attack at the C and N termini of the 1-azaallyl radical decrease to 0.2 and 2.8 kcal/mol from the previously reported MNDO/CI values of 3.9 and 11.0 kcal/mol. While the quantitative results are different, and seemingly improved for AM1/CI, the trends remain the same. In particular, attack upon the carbon terminus of 1-azaallyl is favored by both sets of calculations. AM1 seems to remove the apparently anomalous overestimation of the activation barriers in these cases, as it did for the combinations of methyl radicals and aminyl radical with hydrogen, previously mentioned.

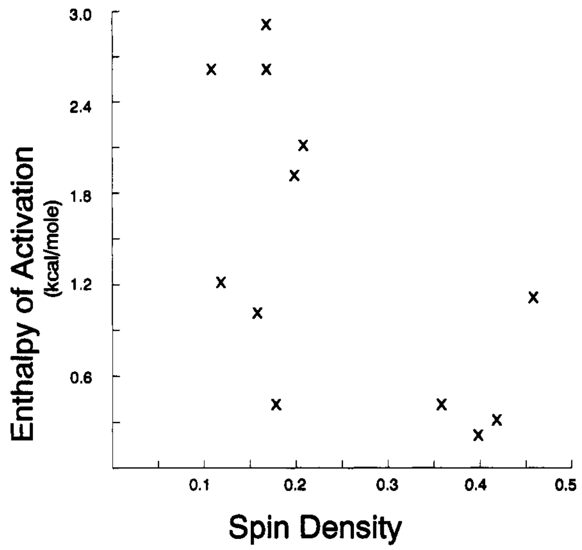

Figure 1. Plot of calculated enthalpies of activation versus spin densities on the position of the benzyl radical being attacked for the combination reactions of methyl- and cyano-substituted benzyl radicals.

Table II. AM1 Energies for the Combination of Methyl Radical with Substituted Benzyl Radicals

radical	position	ΔH_{act}	spin
benzyl	α	0.7	0.48
	ortho	2.4	0.17
	para	1.6	0.19
p-CN	α	0.3	0.42
	ortho	1.0	0.16
	para	2.1	0.21
o,*o*-di-CN	α	0.2	0.40
	ortho	2.9	0.17
	para	0.4	0.18
o,*o*,*p*-tri-CN	α	0.4	0.36
	ortho	2.6	0.17
	para	1.9	0.20
α,α-di-CN	α	1.1	0.46
	ortho	2.6	0.11
	para	1.2	0.12

Methyl–Benzyl Coupling. The activation enthalpies for the combination of methyl and benzyl radicals to form products IVa, Va, and VIa are collected in Table II. The reaction is favored at the α, rather than ortho or para, position on the benzyl radical. From these results, as well as those previously discussed for the combination of methyl and the allylic radicals and experimental reports relating

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(3) Dannenberg, J. J.; Tanaka, K. *J. Am. Chem. Soc.* **1985**, *107*, 671.

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(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* *107*, **1985**, 3902.

(10) Dewar, M. J. S.; Hashwall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* *90*, **1968**, 1953.

(11) (a) Lluch, J. M.; Bertran, J.; Dannenberg, J. J. *Tetrahedron* **1988**, *24*, 7621. (b) Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

(12) Wayner, D. D. M.; Sim, A. B.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

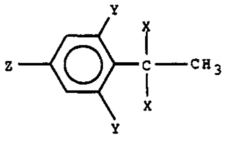
(13) This could not be accomplished when the activation energy was close to zero, i.e., when there was no transition state.

(14) Dannenberg, J. J.; Tanaka, K., *J. Am. Chem. Soc.* **1985**, *107*, 671.

Table III. AM1 Energies for the Dimerization of Benzyl Radicals (kcal/mol)

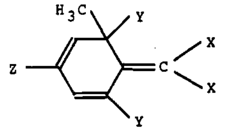
dimerization	ΔH_f(TS)	ΔH_{act}-(AM1)	$\Delta H°$-(AM1)	C–C bond (Å)
α–α, VIIa		0.0	−68.0	
α–ortho, VIIIa	107.9	3.7	−39.3	2.33
α–para, IXa	107.2	3.2	−40.8	2.33
para–para, Xa	120.7	16.7	−14.7	2.07
ortho–para, XIa	122.3	18.3	−13.0	2.10
ortho–ortho, XIIa,b				
RR	121.7	17.7	−12.9	2.09
RS	122.6	18.7	−10.7	2.10

spin densities to radical stability,[15] one might suspect that the relative ease of reaction at a particular position might be related to the spin density at that position. To test that hypothesis, we located the transition states for the reaction of methyl radical with benzyl radicals that have been variously substituted with cyano groups to form products IVb–e, Vb–e, and VIb–e. The cyano groups were used to perturb the spin densities of the parent benzyl radical. The calculated activation barriers and spin densities are also collected in Table II. Figure 1 shows a plot of the calculated enthalpies of activation versus the spin densities for the appropriate positions of the corresponding radicals. The correlation is clearly quite poor. The obvious conclusion is that polarization of the spin of the reacting radical must be reasonably facile process. As such, it contributes little to the activation energy.



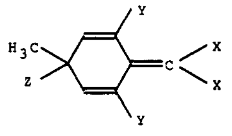
IV

	X	Y	Z
a	H	H	H
b	H	H	CN
c	H	CN	H
d	H	CN	CN
e	CN	H	H



V

	X	Y	Z
a	H	H	H
b	H	H	CN
c	H	CN	H
d	H	CN	CN
e	CN	H	H



VI

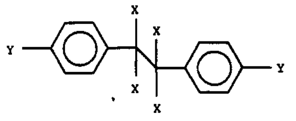
	X	Y	Z
a	H	H	H
b	H	H	CN
c	H	CN	H
d	H	CN	CN
e	CN	H	H

Benzyl–Benzyl Coupling. Calculation of the combination of pairs of benzyl radicals at various positions gives the activation enthalpies collected in Table III. The favored combination to form 1,2-diphenylethane, VIIa, has no enthalpic barrier. However, the calculations predict small but significant barriers of 3.7 and 3.1 kcal/mol, respectively, for the attacks of the α-carbon of one benzyl radical upon the ortho or para position of the other to form VIIIa and IXa. Couplings at the ortho or para position of both rings have barriers between 16.7 and 18.7 kcal/mol. There are seven possible products (excluding attack at the meta carbons): α–α, VIIa; α–ortho, VIIIa; α–para, IXa; para–para, Xa; ortho–para, XIa; and two diastereomers of ortho–ortho, XIIa–b. Significantly, the calculated activation enthalpies predict face selectivity in the formation of the ortho–ortho coupling product XIIa–b. Further theoretical studies of face selectivity are currently in progress.

Table IV. Experimental Ratio of Different Coupling Products of Benzyl Radicals at Various Temperatures[a]

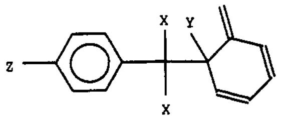
T (°C)	αp/αα	αo/αα	αo/αp
−18	0.061	0.048	0.79
−9	0.088	0.071	0.81
+2	0.095	0.086	0.90
+12	0.102	0.099	0.97
+20	0.102	0.098	0.96
+28	0.103	0.107	1.04
+36	0.095	0.105	1.10
+45	0.086	0.104	1.21
+54	0.077	0.102	1.33
+62	0.071	0.109	1.54

[a] From ref 16.



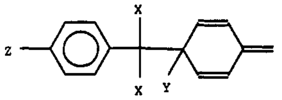
VII

	X	Y
a	H	H
b	CN	H
c	H	CN



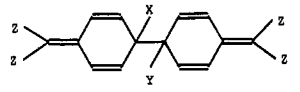
VIII

	X	Y	Z
a	H	H	H
b	CN	CN	H



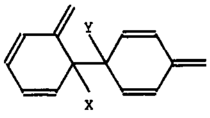
IX

	X	Y	Z
a	H	H	H
b	CN	CN	H



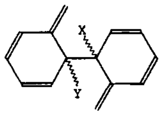
X

	X	Y	Z
a	H	H	H
b	CN	CN	H
c	H	H	CN



XI

	X	Y
a	H	H
b	CN	CN



XII

	X	Y	Conformation
a	H	H	d,l
b	H	H	meso
c	CN	CN	d,l
d	CN	CN	meso

Fischer and Langhals[16] have reported experimental product ratios for the diffusion-controlled coupling of benzyl radicals to form three products: VIIa (α–α coupling), VIIIa (α–ortho coupling), and IXa (α–para coupling). The products of ortho–ortho, ortho–para, and para–para coupling, Xa, XIa, and XIIa,b, were not observed. The experimental results (see Table IV) cover ten different temperatures over a range of 100°. In order to evaluate the AM1 results reported here, we correlated the calculated and experimental results in the manner described below. It was not possible to calculate predicted product ratios simply on the basis of enthapies of activation since that value is zero for α–α coupling, indicating that the entropy must contribute significantly to the free

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[16] Langhals, H.; Fischer, H. *Ber.* **1978**, *111*, 543.

Table V. Calculated Selectivities of Benzyl Radical Couplings[a]

couplings	$\Delta\Delta H_{act}$ (kcal/mol)	$\Delta\Delta S_{act}$ (eu)	statistical factor *g*
αp/αα	3.1	2.4 (3.8)	2
αo/αα	3.8	3.4 (4.8)	4
αo/αP	0.7	1.0	2

[a] Values in parentheses are before correction of 1.4 eu for the differences in rotational number of TSs.

Table VI. AM1 Energies for the Cyanobenzyl Radical (kcal/mol)

dimer	position	ΔH_{act}	BDE	C–C bond (Å)
VIIb	α–α	17.4	19.3	2.59
VIIc	α–α	0.0	68.5	
VIIIb	α–ortho	14.9	9.2	2.23
IXb	α–para	13.9	12.1	2.24
Xb	para–para	27.3	−1.7	2.09
Xc	para–para	23.9	6.5	2.01
XIb	ortho–para	26.7	−4.2	2.08
XII	ortho–ortho:			
XIIc	d,l	28.5	−7.3	2.09
XIId	*meso*	29.6	−8.5	2.09

energy of activation. Instead, we compared the theoretical and *all* of the experimental results using eq 1 where f_2/f_1

$$\frac{f_1}{f_2} = \frac{g_1}{g_2} e^{-(\Delta\Delta H_{act} - T\Delta\Delta S_{act}/RT)} \qquad (1)$$

is the ratio between two products, g_2 and g_1 are the appropriate statistical weighting factors, and $\Delta\Delta H_{act}$ and $\Delta\Delta S_{act}$ the differential enthalpies and entropies of activation. The experimental product ratios and the theoretical enthalpies of activation are assumed to be correct. A least-squares fit of the data accumulates all the errors into the differential entropies of activation. The differential entropies of activation are then corrected for the fact that the α–α transition state has one 2-fold rotational axis, while the other transition states have none. If these differential entropies of activation are small, the correspondence between theory and experiment is good. The total range of (corrected) differential entropies of activation is 3.4 eu, which corresponds to 1.0 kcal/mol at 300 K. Thus, the calculated and experimental values seem to be in good mutual agreement (see Table V).

The relatively high activation energies and low bond energies calculated for the o–o, o–p, and p–p coupling of benzyl radicals suggest the possibility of making kinetically stable compounds containing a C–C bond whose BDE is negative. We have previously discussed compounds with N–N and C–N bonds that have negative BDEs.[5b] For this reason we calculated the BDEs and activation energies for coupling and dissociation for several dimers of cyanobenzyl radicals, VIIb–c, VIIIb, IXb, Xb,c, XIb, and XIIc,d. As the cyano group generally stabilized unsaturated and radical relative to saturated centers, we hoped that the products that result from the coupling of cyanobenzyl radicals at their substituted positions would give in compounds that contained a C–C bond with a negative BDE. The relevant data are collected in Table VI. As anticipated the p–p dimer of the *p*-cyanobenzyl radical Xb, the o–p dimer of the *o*-cyano- and *p*-cyanobenzyl radicals XIb, and the o–o dimers of the *o*-cyanobenzyl radical XIIc,d have negative bond energies, yet are predicted to be kinetically stable species. In principle, compounds of this type could be prepared in the laboratory (using preparatory procedures other than coupling). Measurement of the ΔH_{act} and BDEs of these species would provide convincing evidence concerning our suggestions regarding barriers for radical coupling reactions.

Table VII. Activation Enthalpies of Benzyl Radical Couplings from the Marcus Equation

dimerization	$\Delta H_{act}{}^i$	ΔH_{act}	ΔH_{act}(Marcus eq)
α–α		0.0	1.1
α–ortho	18.0	3.7	6.6
α–para	17.6	3.1	6.2
ortho–ortho			
RR	23.7	17.7	15.8
RS	23.7	18.7	16.8
ortho–para	24.4	18.3	15.8
para–para	23.5	16.7	15.1
average	21.8		

Intrinsic Barrier. The results presented in this paper strongly suggest the existence of an intrinsic or natural barrier for the coupling of two carbon-centered radicals. We define such a barrier as the activation energy required to form (or break) a C–C bond whose BDE is zero. One can evaluate the magnitude of such a barrier in several manners. We have chosen the Marcus equation and a linear equation after Leffler and Grunwald.

The Marcus equation[17] has been applied to many reactions other[18] than the electron-transfer processes originally treated. This topic has been discussed at length by Murdoch[19] and Kreevoy[20] and used previously in connection with molecular orbital calculations. A useful application of the marcus equation involves calculating the intrinsic barrier from the theoretically determined activation enthalpies and heats of reaction by using the Marcus equation in the form shown in eq 2. If the individual reactions have a common mechanism, one might expect the intrinsic barriers calculated from them to be similar in magnitude. We have previously used this application in a theoretical study of hydrogen-atom transfer reactions.[21] The intrinsic barriers calculated in this manner are included in Table VII.

$$\Delta H_{act} = \Delta H_{act}{}^i + \frac{\Delta H^\circ}{2} + \frac{(\Delta H^\circ)^2}{16\Delta H_{act}{}^i} \qquad (2)$$

Following Leffler and Grunwald,[22] we have also fitted the data to a linear equation (3). For this purpose we have

$$\Delta H_{act} = 24.51 - 0.520\text{BDE} \qquad (3)$$

used all the data for bonds with BDEs < 48 kcal/mol, as bonds with BDEs > 48 kcal/mol would all give negative predicted barriers by using such a linear relationship. These results are also included in Table VIII.

Using Marcus theory, the intrinsic barrier calculated from the average of the couplings between the ring carbons is 23.8 kcal/mol, while that calculated from the average of the α-ring carbon couplings is 17.8 kcal/mol (the α–α coupling has no barrier). The overall average is 21.8 kcal/mol. The three higher barrier reactions are much less exothermic than the couplings involving the α-carbons. They also involve the loss of aromaticity in two rather than one (in the case of α-ring coupling) or none (in the case of α–α coupling). It is possible that the $\Delta H_{act}{}^i$ for the ring–ring couplings should differ from that for the ring-α coupling, which, in turn, would differ from that for α–α coupling. The activation barriers for all the reactions were

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Table VIII. Comparison of Enthalpies of Activation Calculated with AM1, the Marcus Equation, and Linear Regression

	enthalpies of activation		
dimer	AM1	Marcus	linear regressn
	Benzyl Radical Dimer		
VIIa	0.0	1.1	0.0
VIIIa	3.7	6.6	4.1
IXa	3.1	6.2	3.3
Xa	16.7	15.1	16.8
XIa	18.3	15.8	17.8
XIIa (*d,l*)	17.7	15.8	17.8
XIIb (*meso*)	18.7	16.8	19.0
	Cyanobenzyl Radical Dimer		
VIIb	17.4	13.2	14.5
VIIc	0.0	1.0	0.0
VIIIB	14.9	17.4	19.7
IXB	13.9	16.2	18.2
Xb	27.3	22.7	25.4
Xc	23.9	18.7	21.2
XIb	26.7	23.9	26.7
XIIc (*d,l*)	28.6	25.6	28.3
XIId (*meso*)	29.6	26.3	28.9
	Methyl + Cyanobenzyl Radicals		
IVb	0.3	0.4	0.0
IVc	1.0	4.3	0.0
IVd	2.1	5.5	2.0
IVe	0.2	0.5	0.0
Vb	2.9	5.8	2.6
Vc	0.4	4.3	0.0
Vd	0.4	0.5	0.0
Ve	2.6	5.8	2.5
VIb	1.9	5.7	2.4
VIc	1.1	2.4	0.0
VId	2.6	5.4	1.8
VIe	1.2	4.9	0.8
	Methyl + Benzyl Radicals		
IVa	0.7	0.5	0.0
Va	2.4	4.4	0.0
VIa	1.6	4.2	0.0

recalculated by using the overall average value of 21.8 kcal/mol for $\Delta H_{\mathrm{act}}{}^{\mathrm{i}}$, with the results indicated in Table VIII. As can be seen, the agreement is reasonably good, even with the combinations involving α-carbons. However, the use of the Marcus equation may not be entirely appropriate for bond dissociation/recombination surfaces, as it is predicated on the assumption of overlapping wells on the potential energy surface. One of the consequences of this formulation is the inverted effect described by Closs.[23] Clearly, there is no well-defined minimum on the potential surface for the separated radicals, so the model may not apply here. We believe that the apparent inconsistency of the intrinsic barriers calculated from the benzyl–benzyl data with the methyl–allyl and methyl-benzyl data is due to this problem.

The Leffler–Grunwald treatment seems to give a better fit to the data. In contrast to the Marcus treatment, this equation seems reasonably general for all the cases studied. For example, one can assume that the intrinsic barrier for coupling is the sum of two intrinsic half-barriers, one for each radical. Using only the benzyl–benzyl data, the intrinsic barrier is calculated to be 24.5 kcal/mol. By symmetry, the half-barrier for benzyl is half the intrinsic barrier or 12.3. If one uses this value for the benzyl half-barrier to calculate the methyl half-barrier from only the benzyl–methyl data and the same slope, one obtains 12.8, hardly different from the benzyl–benzyl half-barrier. Thus, the data imply that there be one intrinsic barrier for carbon–carbon bond dissociation or recombination (in the absence of steric or other specific complications).

The implications of this result are that the intrinsic barrier for the coupling of carbon radicals may be as high as about 24.5 kcal/mol and that the low (often zero) ΔH_{act} values often encountered are due primarily to the large exothermicities of most observed combination reactions (eq 3 predicts no barrier for combinations forming bonds stronger than 48 kcal/mol).

It is worthy of note that the intrinsic barrier has been calculated to be 21.5 kcal/mol for the coupling of substituted aminyl radicals,[5b,24] in agreement with ab initio calculations[25] and in reasonably good agreement with the results presented here.

The prediction of a significant intrinsic barrier for radical coupling reactions might seem counterintuitive at first. However, (as mentioned above), the activation energies for radical–radical coupling to form bonds with BDEs of 48 kcal/mol or greater will be insignificant.

The implications of this result are potentially significant. First of all, the intrinsic barrier suggests that compounds containing carbon–carbon bonds that have zero or negative BDEs are potentially isolable under the right conditions. Secondly, it implies that selectivities in the radical–radical coupling reaction can be observed and predicted. Both of these implications present exciting new challenges for experimental chemists.

Conclusion

AM1/CI calculation provide a reasonably accurate manner in which to calculate the reaction paths involved in the coupling of carbon-centered free radicals. These calculations, which are in good agreement with the experimentally observed selectivities for the combination of benzyl radicals, predict an intrinsic barrier of about 22 kcal/mol from Marcus theory (which may not be appropriate) and 25 kcal/mol from a best fit to a linear equation following Leffler and Grunwald. These results suggest that organic compounds containing C–C bonds that have zero or negative BDEs might be synthesized and isolated and that selectivities in radical recombinations can be understood and exploited.

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Registry No. **VIIb**, 7077-64-7; **VIIc**, 4381-02-6; **VIIIb**, 136060-88-3; **IXb**, 136060-89-4; **Xb**, 136060-90-7; **Xc**, 136088-40-9; **XIb**, 136060-91-8; **XIIc**, 136060-92-9; **XIId**, 136060-93-0; $H_2C{=}CHNH^{\bullet}$, 50614-03-4; 2,6-$C_6H_3CH_2^{\bullet}$, 136060-86-1; 2,4,6-$C_6H_2CH_2^{\bullet}$, 136060-87-2; 4-$CNC_6H_4CH_2^{\bullet}$, 4939-73-5; α,α-$(CN)_2C_6H_4CH_2^{\bullet}$, 7141-74-4; $CH_3^{\bullet}$, 2229-07-4; $H_2C{=}CHCH_2^{\bullet}$, 1981-80-2; $PhCH_2^{\bullet}$, 2154-56-5.

Supplementary Material Available: Drawings and archive files for each of the 14 transition states optimized for the benzyl or cyanobenzyl dimerizations VIIa–XIId, except products VIIa and VIIc, whose reactions do not have activation barriers (42 pages). Ordering information is given on any current masthead page.

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