# Disproportionation *vs.* Combination of Secondary α-Aryl Alkyl Radicals from the Thermolysis of Azo Compounds in Solution[1]

Morton J. Gibian* and Robert C. Corley

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. Received July 21, 1971

Abstract: A study of the ratios of rate constants for self-disproportionation to combination (k_d/k_c) of a series of secondary aralkyl radicals (p-XC$_6$H$_4$CHR) as a function of structure and conditions was carried out by thermal decomposition of the appropriate symmetrical azo compounds. At 118° and for R = CH$_3$, variation of X including CH$_3$, H, and OCH$_3$ had a small effect on k_d/k_c, but for the p-Cl radical the ratio doubled. Benzene, acetonitrile, and N,N-dimethylaniline as solvents gave very similar results for the unsubstituted and p-methyl-α-phenethyl radicals (R = CH$_3$). For X = H, variation of R over a range of groups produced significant changes in k_d/k_c at 118° with little obvious correlation with either the number of β hydrogens available for abstraction or with the stability of olefin to be formed in disproportionation (*i.e.*, primary, secondary, tertiary, and various substituted secondary centers β to the benzylic radical). Comparison of PhĊHCH$_3$ to PhĊHCD$_3$ radicals showed that (k_d/k_c)(H)/(k_d/k_c)(D) = 1.87. It is concluded that this must be largely a primary kinetic isotope effect on disproportionation. The k_d/k_c ratios for PhĊHCH$_3$, PhĊHCD$_3$, PhĊHCH$_2$CH$_3$, and PhĊHCH(CH$_3$)$_2$ were measured at three temperatures, yielding fairly linear inverse temperature *vs.* log (k_d/k_c) relationships. The respective data are: $\Delta H_c{}^\ddagger - \Delta H_d{}^\ddagger$ = 1.47, 0.80, 1.89, and 2.60 kcal/mol; $\Delta S_c{}^\ddagger - \Delta S_d{}^\ddagger$ = 8.4, 7.7, 9.2, and 13.0 eu. Statistical factors, olefin (from disproportionation) stability, geometric requirements, and solvent have significant effects on the fate of caged radicals, and any or all of these factors may cause profound variations in k_d/k_c.

R adical–radical terminations proceed by either disproportionation (eq 1) or combination (eq 2).

$$2RCH_2CH_2\cdot \xrightarrow{k_d} RCH{=}CH_2 + RCH_2CH_3 \qquad (1)$$
$$\xrightarrow{k_c} RCH_2CH_2CH_2CH_2R \qquad (2)$$
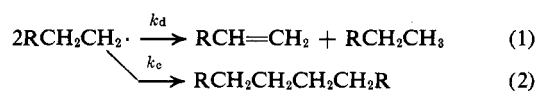
These reactions are of very high exothermicity, and occur in almost all radical systems. The disproportionation process may be considered as the abstraction of a hydrogen atom β to the radical center by another radical. These processes are seemingly about as simple as any organic reactions are likely to be, yet because of their great velocity are rather difficult to approach directly. Since each path has a very low activation energy and the same collisional process may lead to either product, it has been of considerable interest to determine the structural and environmental parameters which lead to particular radical pairs proportioning between the two pathways.

A generalization that was proposed a good while ago on the basis of the butyl radical series is that for aliphatic radicals, k_d/k_c, by and large, varies statistically with the number of available β hydrogens for the abstraction leading to disproportionation products.[2,3] Subsequent reinvestigations of several of these radicals in a number of careful studies have shown the original data to be inaccurate, and the reasons have been noted.[4] It is clear that this generalization does *not* hold for the

aliphatic series, and had long been recognized to not hold for the aralkyl series. Major problems in making generalizations from the literature are that many of the data upon which current generalizations are based have been obtained in systems which we now recognize as likely to give misleading results (usually producing disproportionation products by side reactions), and that even in the absence of such predictable situations, comparisons between laboratories are not very reliable.

Rather recently, careful and internally consistent studies have been reported for the ethyl radical,[5] for cumyl radical,[6] and a few other systems in solution. Absolute rate constants for termination reactions ($k_c + k_d$) as a function of structure and environment are also being approached.[7]

We have chosen to examine a series of closely related secondary aralkyl radicals to generate direct competition data from the decomposition products of a series of azo compounds.

$$(3)$$
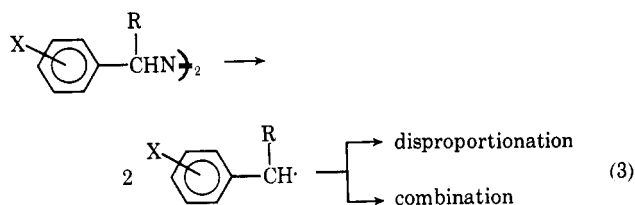
Results

α-Arylethyl Radicals (R = CH$_3$). As detailed in the Experimental Section, the azo compounds corresponding to the desired radicals were synthesized, purified, and decomposed under conditions detailed in the appropriate tables in the text. The overall reactions here

(1) (a) Taken in part from the Ph.D. dissertation of R. C. C., University of California, Riverside, 1971. Support by the Air Force Rocket Propulsion Laboratory (R. C. C.) and the Intramural Fund of the University of California is gratefully acknowledged. (b) Part of this work was presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12–18, 1971.

(2) J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, **79**, 5921 (1957).

(3) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, **1**, 107 (1961).

(4) (a) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **46**, 664 (1968); (b) D. H. Slater, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **90**, 268 (1968); (c) D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **65**, 175 (1969).

(5) (a) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 2551 (1963); (b) P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 3345 (1963); (c) A. P. Stefani, *ibid.*, **90**, 1694 (1968).

(6) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966).

(7) (a) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969); (b) R. D. Burkhart, *ibid.*, **90**, 273 (1968); (c) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

Table I. Rate Constant Ratios and Product Balances for α-Arylethyl Radicals[a]

Entry	p-XC₆H₄ĊHCH₃ X	Solvent	No. of samples[b]	Concn azo, M	k_d/k_c[c]	Yield[d] of combination + disproportionation products, %
1	H	C₆H₆	8	0.05	0.097 ± 0.002	95 ± 2
2	H	CH₃CN	3	0.05	0.098 ± 0.002	96 ± 2
3	H	C₆H₅N(CH₃)₂	2	0.05	0.109 ± 0.001	90 ± 1
4	H	o-C₆H₄Cl₂	16	0.01-0.5	0.090 ± 0.006	e
5	CH₃	C₆H₆	4	0.05	0.089 ± 0.002	99 ± 1
6	CH₃	CH₃CN	2	0.05	0.094 ± 0.001	98 ± 1
7	CH₃	C₆H₅N(CH₃)₂	2	0.05	0.091 ± 0.001	100 ± 2
8	CH₃	o-C₆H₄Cl₂	2	0.05	0.097 ± 0.001	e
9	H	C₆H₆	2	0.02	0.093 ± 0.001	102 ± 1
10	H	C₆H₆	2	0.05	0.100 ± 0.001	99 ± 1
11	H	C₆H₆	2	0.09	0.095 ± 0.001	96 ± 1
12	H	C₆H₆	2	0.17	0.097 ± 0.002	77 ± 1
13	H	None	2	Neat	0.17 ± 0.03	76 ± 1
14	OCH₃	C₆H₆	4	0.05	0.084 ± 0.002	99 ± 1
15	Cl	C₆H₆	4	0.05	0.176 ± 0.009	50 ± 2[f]

[a] From decompositions of the appropriate azo compounds at 118° in sealed ampoules degassed three times. [b] Each sample was analyzed in duplicate. [c] Glpc corrected (α-arylethane/2,3-diarylbutane). [d] Vs. 0.1 M biphenyl internal standard. [e] The dichlorobenzene (and chlorobenzene) low product balance is discussed in detail by Corley and Gibian,[10] and is due to a polar side reaction. The data given here are for the radical portion of the reaction, and also for reaction mixtures in which the side reaction was avoided. These values are in adequate agreement with each other and with those in other solvents. [f] Based on starting azo compound. Immediately after opening only very high boiling material, in addition to combination and disproportionation products, was present. After 1 day in air, the yields of the radical products were unchanged, but 49 ± 2% p-chloroacetophenone was present (based on azo), thus accounting for all the material. The side reaction appears to be the same as for chlorinated solvents.

may be described as in Scheme I. Table I lists the

Scheme I
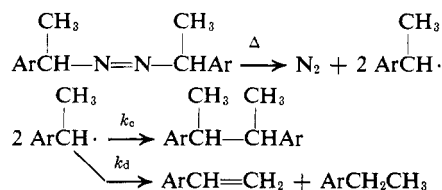
k_d/k_c ratios, along with conditions and product balances, for this series at 118°. The value for the α-phenethyl radical is in reasonable agreement with other recent determinations of this number.[8]

Examination of entries 1–4 and 5–8 of Table I shows a small (but outside experimental error) variation of k_d/k_c for the α-phenethyl and α-(p-methylphenyl)ethyl radicals with various solvents. This variation does not follow any obvious pattern, and is probably due to a rather specific solvation effect. Entries 9–13 represent a study of k_d/k_c vs. concentration in benzene. From 0.02 to 0.17 M the ratio for the α-phenethyl radical is essentially constant, but for pure azo compound there is an almost twofold increase. As concentration increased, the total yield decreased, possibly a consequence of induced decomposition beginning to be significant at about 0.2 M. It was decided to standardize conditions for all other work at 0.05 M azo compound in benzene.

Entries 1, 5, 14, and 15 are for para-substituted α-phenethyl radicals under identical conditions. The first three reveal a small dependency of k_d/k_c upon sub-

stitution (this ratio slightly decreasing with increasing electron-donating substituents), but the halogen substituent exhibits a dramatic increase in the ratio. A similar small trend (but of the opposite order) along with the same dramatic increase for a para-halogen substituent was noted in a study of alkyl-substituted cumyl radicals.[9] While rearrangement to hydrazone[10] accounts entirely for the lower yield of radical products here, the origin of the ratio variation is unclear at this time.

Variation of the β Group. Table II gives data for several further azo compounds of general structure

Table II. Rate Constant Ratios and Product Balances for Various Secondary α-Alkylbenzyl Radicals[a]

Entry	C₆H₅ĊHR R	No. of samples[b]	k_d/k_c[c]	Yield[a] of combination + disproportionation products, %
16	CH₃	4	0.097 ± 0.002	94.5 ± 2
17	CH₂CH₃	4	0.107 ± 0.003	98 ± 2
18	CH₂CH(CH₃)₂	4	0.095 ± 0.002	98 ± 1
19	CH₂C₆H₅	5	0.113 ± 0.004	104 ± 5
20	CH(CH₃)₂	3	0.037 ± 0.001	79 ± 10
21	CD₃ (88% D)[d]	3	0.057 ± 0.002	95 ± 4
22	CD₃ (94.5% D)[d]	2	0.055 ± 0.004	94 ± 5
23	CD₃ (100%)[e]		0.052 ± 0.003	

[a] From decomposition of the appropriate 0.05 M azo compound in C₆H₆ at 118° with 0.1 M biphenyl internal standard. [b] Each sample was analyzed in duplicate. [c] Glpc corrected alkane disproportionation product/combination product. [d] See Experimental Section for preparation and analyses of these materials. The k_d/k_c ratio reported is the total experimental value, uncorrected for isotope purity. [e] Calculated from purity data from entries 21 and 22.

(C₆H₅CHRN=)₂ in which the β C–H of the radical being attacked in the disproportionation was varied

(8) F. D. Greene, M. A. Berwick, and J. C. Stowell, ibid., 92, 867 (1970). These authors have shown by the use of scavengers that the cage effect in benzene for azobis-α-phenylethane at 105° is 32%, and that the products generated by azo decomposition are identical with those formed from generation of α-phenethyl radicals by radical abstraction from ethylbenzene. In our study exactly equal amounts of glpc-separated meso and d,l diastereomers were formed from each azo compound. This agrees with Greene's result for the diastereomeric azo compounds in the absence of scavengers and for the ethylbenzene generated system.

(9) J. R. Shelton, C. K. Liang, and P. Kovacic, ibid., 90, 354 (1968).
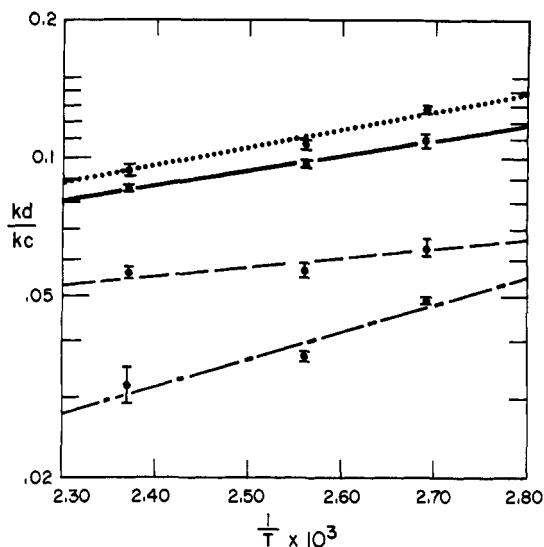(10) R. C. Corley and M. J. Gibian, J. Org. Chem., in press.

Figure 1. Inverse temperature dependence of log k_d/k_c for a series of radicals generated from 0.05 M azo precursors in benzene $vs.$ 0.1 M biphenyl as internal standard: (· · · ·) $C_6H_5\dot{C}HC_2H_5$; (——) $C_6H_5\dot{C}HCH_3$; (– – –) $C_6H_5\dot{C}HCD_3$; (–·–·) $C_6H_5\dot{C}HCH(CH_3)_2$. The vertical bars indicate experimental error from at least triplicate runs, each analyzed twice.

from primary (entry 16) to simple secondary (entry 17), more hindered secondary (entry 18), secondary benzylic (entry 19), and tertiary (entry 20). For the three β secondary H compounds the k_d/k_c values are fairly close, but also close to the overall value for the CH_3 compound. Statistically these values would be $^2/_3$ the value for CH_3, and thus the trend is an *increase* in the disproportionation on a per H basis. The β tertiary H radical, however, shows a *decrease* in the k_d/k_c value. Compared to the β primary H compound it is lower by a factor of almost 3, the statistical value. These values were very carefully checked, and the starting materials and products showed no anomalies that we could ascertain.

The processes for entry 16 $vs.$ 17 should not differ significantly except for an increase in 1,4-butane steric interactions in the combination reaction coordinate that would be minimized in disproportionation. It might then be that replacement of CH_2CH_3 by CH_2-$CH(CH_3)_2$ would magnify this difference, and show a further increase in the k_d/k_c ratio. The data in Table II, entry 18, show that if there is any effect, it might be a decrease. Entry 19, producing stilbene by disproportionation, shows a k_d/k_c value quite similar to those of the other CH_2R radicals.

Substitution of β Deuterium. The last three entries of Table II are for phenethyl radicals with deuterium at the β (abstractable) position. The parent azo compounds of entries 21 and 22 were two entirely separate preparations. The values given in the k_d/k_c column are based on the total yields (H and D containing) of disproportionation and combination products. The k_d/k_c ratio for the CD_3 species (correcting for the CH_3 impurity) is calculated to be 0.052 ± 0.003 upon combining the two separate determinations (entry 23). This leads to a deuterium kinetic isotope effect on the ratio ($[k_d(H)/k_c(H)]/[k_d(D)/k_c(D)]$) of 1.87.[11] The mag-

(11) Attempts to extend this part of the study to secondary and tertiary β C–D radicals met with serious difficulties in the synthesis of the deuterated azo compounds (see Experimental Section), and were discontinued.

nitude of this isotope effect is well within that observed for primary kinetic isotope effects. There is the possibility of a β secondary deuterium isotope effect, but the magnitude, from all prior experience, would have to be considerably lower than 1.87 (and probably less than 1.0; see Discussion). It seems not unreasonable to conclude that the isotope effect is a primary one on the disproportionation step.

Variation of the Temperature. The k_d/k_c ratios of the three simplest secondary aralkyl radicals in which primary (CH_3), secondary (CH_2CH_3), and tertiary (CH-$(CH_3)_2$) β hydrogens are abstractable, along with the CD_3 compound, were studied at 98, 118, and 148°. All these data were for thermal decompositions in benzene, and Figure 1 presents the four sets of values plotted $vs.$ the inverse absolute temperature. These plots are not over as wide a temperature range as might be desired, since the slopes are small.[12] At face value, these plots might be showing curvature or not, but the linear fit is not bad.[13] Table III gives the activation parameters

Table III. Activation Parameter Differences between Disproportionation and Combination for Secondary Aralkyl Radicals with Varying β Groups

$C_6H_5\dot{C}HR$ R	$\Delta H_d{}^{\ddagger} - \Delta H_c{}^{\ddagger}$, kcal/mol	$\Delta S_d{}^{\ddagger} - \Delta S_c{}^{\ddagger}$, eu	$D(C_6H_5$-$\dot{C}HCR_1$-R_2–H), kcal/mol
CD_3	-0.80 ± 0.24	-7.66 ± 2.28	50
CH_3	-1.47 ± 0.06	-8.43 ± 0.34	48
CH_2CH_3	-1.89 ± 0.18	-9.20 ± 0.87	45
$CH(CH_3)_2$	-2.60 ± 0.40	-13.05 ± 2.02	44

for the four series assuming a linear relationship between log (k_d/k_c) and $1/T$. The data for the R = CH_3, CH_2CH_3, and $CH(CH_3)_2$ radicals seem to show a regular trend of larger differences as substitution at the β carbon is increased. The CD_3 compound shows a significantly smaller apparent $\Delta\Delta H^{\ddagger}$ than does the CH_3 compound. The $\Delta\Delta S^{\ddagger}$ values also show an apparent regular trend to increasing differences in the series. This kind of compensation is rather common for series of similar reactions, and may be partially reflecting the higher density of energy states for a higher total energy system.

Discussion

Examination of Tables I and II (k_d/k_c data at 118°), ignoring for now the deuterium compounds, leads to little that might be used to generalize at this point about the effect of structure on the competition between combination and disproportionation. While the differences are apparently real, any general conclusions would be unwarranted.

Sheldon and Kochi,[14] on the basis of detailed studies, have recently concluded that, in addition to statistics, there are significant factors operating upon the disproportionation step that are primarily a function of the structure of the radical being abstracted from.

(12) We did not obtain data at 25° by photolysis (and would be a bit hesitant to include these on the same plot).

(13) The temperature dependence is too high for a reasonable fit to a T^n plot (the values of n determined are much higher than those in Stefani's[6c] work on ethyl radicals).

(14) R. A. Sheldon and J. K. Kochi, $J. Amer. Chem. Soc.$, **92**, 4395 (1970); **92**, 5175 (1970).

Hammond and Weiner[7a] found that the variations in the overall rate constants for termination for a series of alkyl and aralkyl radicals are seemingly very large. Combining their data with product ratio data[9] led to approximate absolute values for k_c and k_d, with the conclusion that k_c's were varying much more dramatically than k_d's.[15] Bartlett and McBride[16] found that cage effect data (for cage reactions of radical pairs *vs.* diffusion as measured with scavengers) were incompatible with reported recombination rate constants for a series of radicals. They presented indications that the cage effect data are likely the more reliable, but in light of the more recent conclusions of Hammond about radical association and very large solvation effects on k_t, it is not improbable that the two kinds of experiments (absolute *vs.* competitive rate constants) may be measuring different things.[17]

Activation Parameters. Examination of the temperature dependencies for the β primary, secondary, tertiary CH and CD_3 (Table III) compounds leads to apparent higher activation enthalpies for combination ($\Delta H_c^{\ddagger}$) than for disproportionation ($\Delta H_d^{\ddagger}$). Reported temperature variations for other radicals include ethyl ($\Delta H_c^{\ddagger} - \Delta H_d^{\ddagger} = 300$ cal/mol),[5] isopropyl ($\Delta H_c^{\ddagger} - \Delta H_d^{\ddagger} \approx 100$ to 200 cal/mol),[18] *sec*-butyl ($\Delta H_c^{\ddagger} - \Delta H_d^{\ddagger} \approx 350$ cal/mol),[19] cumyl ($\Delta\Delta H^{\ddagger} \approx 0$),[6] and α,α-methylisopropylbenzyl ($\Delta H_d^{\ddagger} - \Delta H_c^{\ddagger} \approx 2000$ cal/mol).[16] In all, the differences are generally small, and it has often been found that within experimental error $\Delta\Delta H^{\ddagger}$ (or ΔE_a) is essentially nil. If, as seems to be the case here, the two processes have distinct reaction paths, there seems no simple way to predict which would have a larger activation enthalpy.

A simple thermochemical calculation leads to the bond dissociation energies of the β CH in $C_6H_5\dot{C}H$-CHR_1R_2 to be as shown in Table III. If we guess that k_c is almost constant in this very similar series, we might ascribe much of the $\Delta\Delta H^{\ddagger}$ variations to a decrease in $\Delta H_d^{\ddagger}$ as $D(\beta$ C–H) decreases. The regular trend between the two sets of values is rather suggestive of such an origin for the variation. A regular increase in $\Delta H_c^{\ddagger}$ with substitution would be an alternative explanation.

The actual magnitudes of the activation parameter differences, and especially the $\Delta\Delta S^{\ddagger}$ values, are quite large. While the activation enthalpy requirement is larger for combination than for disproportionation, the entropic differences suggest a considerably more restricted transition state for disproportionation. This restriction conclusion is similar to that of Szwarc[20] in a high pressure study of ethyl radicals, which showed a smaller volume of activation (more restricted) for disproportionation than that for combination (this same

conclusion has been suggested as the origin of the solvent effects for the ethyl radical).[5a,c]

Kinetic Isotope Effect.[21] The kinetic isotope effect may be expressed as in eq 4.

$$[\Delta H_c^{\ddagger}(H) - \Delta H_c^{\ddagger}(D)] + [\Delta H_d^{\ddagger}(D) - \Delta H_d^{\ddagger}(H)] \cong 0.7 \text{ kcal/mol} \quad (4)$$

It is quite unlikely that the recombination reaction would have a kinetic isotope effect of the magnitude observed here. Any isotope effect on coupling would be of the secondary variety, and it ought to be an inverse one. Seltzer[26] has reported a value of 1.108 for k_H/k_D in the decomposition of the parent CD_3 azo compound. Attributing this isotope effect to the change from sp^3 to a radical-like transition state with sp^2 character (and some 30–35 kcal higher in energy), we would expect a secondary isotope effect on combination for our system that was less than unity, if any at all. We shall thus assume that the isotope effect is due almost entirely to the disproportionation reaction, and that $\Delta H_d^{\ddagger}(D) - \Delta H_d^{\ddagger}(H) \cong 0.7$ kcal/mol.

The magnitude of the kinetic isotope effect and the difference in temperature dependence of k_d/k_c for the CH_3 *vs.* the CD_3 compound, measured independently, are in approximate agreement. At 118°, the k_H/k_D ratio of 1.87 amounts to 486 cal/mol (0.49 kcal/mol) for $\Delta\Delta G^{\ddagger}$. This value may be compared to that from the temperature variations of Table III ($\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger} = 400$ cal/mol).

We conclude that the isotope effect is a primary one, manifest in the disproportionation reaction. An alternate explanation is the possibility of tunneling. In the general case (including disproportionation) hydrogen abstraction by radicals is a circumstance likely to involve tunneling effects.[27] The usual macroscopic criteria for ascribing a deuterium isotope effect to tunneling, ΔE_a (or $\Delta\Delta H^{\ddagger}$) greater than the vibrational zero point energy differences, and/or A_H/A_D (or antilog $\Delta\Delta S^{\ddagger}/2.3R$) much less than unity,[28] are absent in our study.[29] This does not rule out tunneling as a possible

(15) It was tentatively suggested[7a] that the anomalous reactivity relationships observed may be the result of solute–solvent relaxation being the rate-limiting step in some of these processes.

(16) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(17) (a) Burkhart[7b] has similar findings, and very recently Bentrude[17b] observed variations in the heats of solution for di-*tert*-butyl nitroxide radical in a range of aromatic solvents. (b) W. C. Bentrude and A. K. MacKnight, *J. Amer. Chem. Soc.*, **92**, 5259 (1970).

(18) R. Klein, M. D. Scheer, and J. G. Waller, *J. Phys. Chem.*, **64**, 1247 (1960).
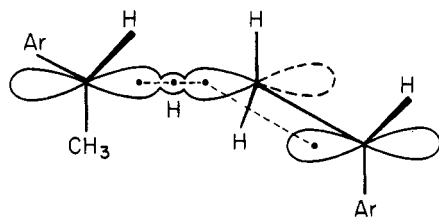
(19) R. Klein, M. D. Scheer, and R. Kelley, *ibid.*, **68**, 598 (1964).

(20) M. Szwarc, Abstracts presented at 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, paper POLY 83.

(21) Kinetic isotope effects on the k_d/k_c ratios for various radicals have been previously noted several times. These include (a) a value of approximately 1.4 for $2C_2H_5\cdot$ *vs.* $2C_2D_5\cdot$;[22] (b) 2.3 for $2C_2H_4T\cdot$ at $-210°$, k_H/k_T;[23] (c) 1.7 for $2C_3H_6T\cdot$ at $-210°$;[24] and (d) 2.0 ± 0.2 (clearly in the disproportionation step) for randomly deuterated α-cyanoisopropyl radicals at $-78°$ in the crystal.[25] The effect reported in the present study seems to be the first such observation for radicals in solution.

(22) P. J. Boddy and E. W. R. Steacie, *Can. J. Chem.*, **38**, 1576 (1960).

(23) K. W. Watkins and H. C. Moser, *J. Phys. Chem.*, **69**, 1040 (1965).

(24) H. B. Yun and H. C. Moser, *ibid.*, **69**, 1059 (1965).

(25) J. M. McBride, *J. Amer. Chem. Soc.*, **93**, 6302 (1971). We thank Professor McBride for informing us of this result prior to publication and for helpful discussions.

(26) S. Seltzer and E. J. Hamilton, Jr., *ibid.*, **88**, 3775 (1966).

(27) (a) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 3 (1965); (b) H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, **83**, 1 (1961).

(28) (a) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 205 ff, 211. (b) A recent example is E. S. Lewis, J. M. Perry, and R. H. Grinstein, *J. Amer. Chem. Soc.*, **92**, 899 (1970).

(29) The zero point energy difference considering only vibration of the C–H *vs.* C–D bonds is approximately 1.2 kcal/mol. $\Delta\Delta H^{\ddagger}$ (or ΔE_a) here is 0.7 kcal/mol, well below the maximum. For X–H *vs.* X–D the ratio of collision theory preexponential factors A_H/A_D (or the equivalent antilog $\Delta\Delta S^{\ddagger}/2.3R$ in transition state theory terms) is predicted to be between $2^{1/2}$ and 0.5 for zero point energy differences being the sole cause of the kinetic isotope effect. If tunneling is important this ratio is predicted, and has been found, to be significantly less than unity.[27b,28] From Table III, $[A_d/A_c(H)]/[A_d/A_c(D)] = 0.85$, within normal bounds.

origin of the observations, but is just a lack of evidence. Trotman-Dickenson[27a] has considered the possible import of such factors in studies of hydrogen abstraction reactions, but it has not yet been possible to construct the required potential surfaces with sufficient accuracy for any solution system to compare the experimental data. Our system is another such case, and for the present it would seem most appropriate to discuss the results in the more usual manner.

Conclusions

For the secondary aralkyl radicals, we would like to tentatively suggest comparative pictures of the two processes in which combination is a rather enthalpically limited process, and disproportionation an entropically limited process. Referring to the original postulates of a rather restricted geometric alignment of the atoms in a hydrogen abstraction reaction (*i.e.*, disproportionation), we may postulate a rather "loose" angular dependence for the presumed sp^2-sp^2 odd electron approach in combination. A further restriction for disproportionation is a partial freezing of a rotation about the C_1-C_2 bond in order to have p–p overlap in the incipient olefin. Taken in all, we con-

clude that for α-phenethyl radicals there are separate transition states for disproportionation and combination, that solvent and structural variations have significant effects on the fate of a pair of caged radicals, that in this case combination has a higher energy barrier but a smaller geometric restriction than disproportionation, that the bond dissociation energy of the β hydrogen (or π overlap of the incipient olefinic bond) is a factor (but not the sole one) in determining the pathway of reaction, and that various factors may dominate the apparent ratio of disproportionation to combination in diverse systems.

Experimental Section

General. Reagent grade benzene, *o*-dichlorobenzene, and hexane were purified by thoroughly shaking with sulfuric acid, distilled water, saturated sodium bicarbonate, and saturated sodium sulfate solution, then dried over Na or P_2O_5, and distilled. *N*,*N*-Dimethylaniline was treated with acetic anhydride (to remove monomethyl impurities) and distilled.[30] Acetonitrile was refluxed over P_2O_5 and distilled, and pyridine was dried over KOH for 1 day, decanted onto fresh KOH for another day, and distilled.

Ir spectra (CH_2Cl_2) were recorded using a Perkin-Elmer 137 spectrometer. Nmr spectra were recorded at ambient temperature using a Varian A-60D spectrometer. Except where otherwise noted, samples were run as dilute solutions in deuterated chloroform with TMS as internal reference. All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are corrected.

Standards for Glpc. (a) *meso-* and *dl*-2,3-Diphenylbutane. α-Bromoethylbenzene was dimerized with Mg in ether. The solid product was recrystallized from methanol (mp 125–126°, lit.[31]

mp 123–124° for the meso isomer). The solution from which the meso isomer first crystallized was distilled to give a colorless liquid, bp 100–105° (2 mm) for the *d,l* pair.

(b) 1,2,3,4-Tetraphenyl-2,3-butanediol. Deoxybenzoin was photolyzed in isopropyl alcohol to produce the pinacol. The insoluble α form was recrystallized from methanol, mp 212–214°.[32,33]

(c) 1,2,3,4-Tetraphenylbutane. The above pinacol was reduced in ethyl acetate on Pd–C in a Paar apparatus at 60 psi H_2 for 5 days (tlc monitoring). The product (an oil) was chromatographed on alumina (Wohlm activity 3). The first two fractions gave a white solid of mp 182–184° (lit.[34] mp 183–185°).

Ketones. (a) Deuterio Compounds. Acetophenone (10 g), Na_2CO_3 (0.4 g), and D_2O (20 ml) were refluxed in 70 ml of THF (distilled from sodium) for 24 hr after which the THF layer was salted out and the procedure repeated two more times. Finally the ketone was distilled, bp 200–202°. Nmr indicated 97.5% D incorporation.

Following the same procedure, 10 g of propiophenone was converted to 7 g of the α-dideuterio ketone (96% D incorporation, bp 216–218°). The same procedure met with failure on isobutyrophenone. The best method for exchange of the tertiary hydrogen was NaH in dry THF to prepare the enolate, then neutralization with D_2O. This method produced 99% α-deuterated compound, bp 221–222°.

(b) Other Ketones. Isovalerophenone was synthesized by the Friedel–Crafts reaction of isovaleric acid and benzene. Isobutyrophenone was synthesized from the Grignard of bromobenzene and isobutyronitrile followed by hydrolysis. All other starting ketones were commercially obtained.

Azines. Acetophenone (60 g, 0.5 mol) and hydrazine hydrate (12.5 g, 0.25 mol) were dissolved in 110 ml of absolute ethanol containing 1 ml of acetic acid and warmed on a steam bath. Within 1 min the colorless solution turned deep yellow, and within 10 min a copious quantity of yellow solid had formed. This was filtered, washed with cold methanol and recrystallized from dioxane to give yellow prisms, mp 123–124° (lit.[35] mp 123–124°), yield 56.1 g (95%).

The procedure above was duplicated with isobutyrophenone; however, the solid was white, not yellow (even though the solution was yellow).[36] *Anal.* Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.59. Found: C, 82.28; H, 8.57; N, 9.46.

To test the possibility of using nondeuterated reagents and solvents without proton exchange, 1.3 g (0.01 mol) of acetophenone-d_3 (97.5% D), 0.1 ml of anhydrous hydrazine, 10 ml of ethanol, and 1 drop of acetic acid were warmed on a steam bath for 5 min, by which time the solution was deep yellow. The solution was immediately chilled and produced a yellow solid azine, 400 mg, mp 122–124° (lit.[26] mp 123–124°). Nmr integration showed 97% CD_3 in the product. This was repeated on a fourfold larger scale and 3.3 g (90% yield) of azine, again 97% CD_3, was obtained.

Following the same procedure, 5.7 g of the deuterated propiophenone was converted to 3.7 g of the desired azine, mp 66–68°. All attempts to convert this compound to the desired azo compound met with failure. The reduction procedures outlined below did not work with this azine. Attempts to prepare deuterated isobutyrophenone azine failed because this material underwent H and D exchange.

Following the standard procedure, 14.5 g (0.1 mol) of *p*-cyanoacetophenone was converted to the azine (14.3 g, quantitative yield, mp 225–235°). Recrystallization from 4:1 methanol–chloroform raised the melting point to 239–241°: nmr τ 2.1 (m, 4 H), 7.65 (s, 3 H). *Anal.* Calcd for $C_{18}H_{14}N_4$: C, 75.47; H, 4.93; N, 19.57. Found: C, 75.24; H, 5.19; N, 19.30.

Table IV summarizes the data on the remainder of the azines, all of which were prepared by the same technique as acetophenone azine. Yields were greater than 90% in all cases.

Hydrazines. (a) Hydrochloride Salts. The procedure of Schulze and Lochte,[37] hydrogenation of azine over PtO_2 in acetic

(30) Although the pure liquid is yellow, vacuum degassing resulted in loss of color. Opening the clear liquid to air resulted in a change back to yellow.

(31) H. J. Barber, R. Slack, and A. M. Woolman, *J. Chem. Soc.*, 99 (1943).

(32) F. Bergmann and Y. Hirshberg, *J. Amer. Chem. Soc.*, **65**, 1429 (1943).

(33) H. M. Crawford, M. E. Saeger, and F. E. Warneke, *ibid.*, **62**, 2862 (1940).

(34) D. P. Wyman, *J. Org. Chem.*, **27**, 3712 (1962).

(35) S. G. Cohen, S. J. Groscos, and D. B. Sparrow, *J. Amer. Chem. Soc.*, **72**, 3947 (1950).

(36) D. S. Malament and J. M. McBride, *ibid.*, **92**, 4591 (1970). We thank Professor McBride for helpful discussions in interpretation of the spectra for this compound, which shows a mixture of the stereoisomeric azines.

Table IV. Azines and Azo Compounds

R	X	(XC₆H₄CR=N-)₂ azine Mp,[a] °C	(XC₆H₄CR=N-)₂ azine Lit. mp, °C	(XC₆H₄CHRN=)₂ azo Mp,[a] °C	(XC₆H₄CHRN=)₂ azo Lit. mp, °C
CH₃	H	123–125	123–124[b]	72–73	72–73[b]
CH₃	CH₃	137–139	137–138[b]	78–80	78–79[b]
CH₃	OCH₃	201–202	200–202[b]	92–94	91–92[b]
CH₃	Cl	153–155	150–153[b]	110–112	108–109[b]
CH₂CH₃	H	68–70	66–67[b]	58–60	58–59[b]
CH₂CH(CH₃)₂	H	70–72	68–70[b]	84–86	83–84[b]
CH₂C₆H₅	H	162–164	161[c]	138–140	d
CH(CH₃)₂	H	80–83	74–75,[e] 78–80[f]	58–60	d
CD₃	H	122–124	123–124[g]	71–73	72–73[g]
CH₃	CN	239–241	d		

[a] Thomas-Hoover capillary melting point apparatus, corrected melting points. [b] Reference 35. [c] S. Goldschmidt and B. Acksteiner, *Chem. Ber.*, **91**, 502 (1958). [d] New compounds. [e] J. Elguero, R. Jacquier, and C. Marzin, *Bull. Soc. Chim. Fr.*, 713 (1968). [f] Reference 36. [g] Reference 26.

acid–dioxane, was followed to isolate a pure, solid hydrazine derivative of acetophenone which was recrystallized from methanol, mp 186–188° (lit.[37] mp 188°), wt 8.0 g (59% yield).

(b) Hydrazine Derivatives. The purified hydrochloride salt, suspended in benzene, was neutralized with concentrated KOH solution to obtain the free base.

Azo Compounds. Considerable difficulty was encountered in reproducing literature methods[35,26] for oxidation of hydrazines to azo compounds. Most successful was a modification of Robertson's method[38] of oxygen oxidation which gave high yields of azo compound even when using crude hydrazine oil.

Acetophenone azine (23.6 g, 0.1 mol) was reduced in 400 ml of acetic acid with 200 ml of PtO₂, worked up as above, and the crude yellow oil set aside in an open flask in the dark. After 3 days, the entire mass had solidified. It was triturated with 10 ml of methanol and the yellow solution decanted off and discarded leaving 17.3 g (73% yield based on starting azine) of the white solid azo compound, which was recrystallized from methanol (mp 72–73°, lit.[35] 72–73°).

Deoxybenzoin azine (7 g, 0.18 mol) was reduced and reoxidized as above. We obtained 4.5 g (65% yield, based on starting azine), mp 138–140°: nmr τ 2.8 (s, 10 H), 3.05 (s, 10 H), 5.3 (t, 2 H), 6.78 (dd, 4 H). *Anal.* Calcd for C₂₈H₂₆N₂: C, 86.11; H, 6.71; N, 7.18. Found: C, 85.92; H, 6.83; N, 7.30.

Isobutyrophenone azine (7.0 g) in 100 ml of acetic acid was reduced with 70 mg of PtO₂ at 72 psi H₂ pressure. Work-up yielded a yellow oil which upon oxidation gave a very pale yellow solid which was dissolved in methanol, treated with activated charcoal, filtered, and chilled to yield 2.6 g of a white solid, mp 53–56°. The yellow filtrate was concentrated and chilled to give an additional 3.0 g of white solid, mp 52–57°. Both crops of crystals were contaminated with some material which persisted as a solid up to 70°. Also, tlc showed a large, major spot with another spot (much smaller) having about one-half the R_f of the major component. Three recrystallizations of the combined crops of crystals produced no further purification. The solid was chromatographed on 80 g of neutral alumina with benzene as eluent. Solvent was removed and the remaining solid recrystallized from methanol (mp 58–60°, 4 g, 57% yield based on starting azine, one spot on tlc): nmr τ 2.68 (m, 10 H), 5.82 (dd, 2 H), 7.45 (m, 2 H), 8.95 to 9.4 (complex multiplet, 12 H). *Anal.* Calcd for C₂₀H₂₆N₂: C, 81.58; H, 8.89; N, 9.53. Found: C, 81.82; H, 8.95; N, 9.76.

(37) W. A. Schulze and H. L. Lochte, *ibid.*, **48**, 1030 (1926).

(38) J. A. Robertson, *Chem. Abstr.*, **45**, 1384; U. S. Patent 2520339, Aug 29, 1950, to Du Pont.

Attempts to prepare and isolate the p-cyano azo compound failed. The hydrogenation proceeded smoothly, but each method of oxidation produced a mixture (determined by tlc) from which no azo compound could be isolated.

The data for the remaining azo compounds are summarized in Table IV. Yields varied from 43 to 82%.

Thermal Decomposition Studies. (a) Sample Preparation. Azo decompositions were performed in sealed ampoules after three freeze–thaw degassings at 10⁻⁶ mm. Half-lives of the azo compounds studied were approximately 3 hr[35] at 118°. After 0.5 hr heating, analysis showed the alkene and alkane disproportionation products to be present in about equal amounts. When heating was over a 24-hr period, the alkane:alkene ratio was greater than 1, and when the heating was over a 3-day period, only traces of olefin remained. The alkane disproportionation (to combination) product yields remained constant over the three different time periods, and therefore alkane yields were selected to be data points for calculating k_d/k_c ratios. It is assumed that olefin disappearance was due to polymerization. Typical reactions were run for 24–48 hr (8–16 half-lives) at 118°, with adjustments for different temperatures.

(b) Analyses. Analyses of the products from the thermal decomposition of azo compounds were performed by glpc. The product yields were determined using biphenyl as internal standard and standardization plots as described below.

Standard solutions containing a known amount (0.1 M) of the internal standard biphenyl, and concentrations of the pure compounds corresponding to the products ranging from 0.002 to 0.4 M were used to generate the standardization plots. The data were plotted as (area of product)/(area of biphenyl) vs. (moles of product)/(moles of biphenyl). All plots were linear with slopes near unity. A large amount of care was taken to ensure reproducibility and accuracy of glpc analyses.

(c) Errors. Experimental errors given in the text are the average deviations obtained from the average values. In developing the correction lines, it was found that duplicate glpc analyses gave a mean deviation of 2% or less, and periodic analysis of standard solutions came within 2% of the value previously determined.

There are errors associated with calculation of absolute yield which cancel when determining k_d/k_c ratios. In general, a 20–25 mg sample of azo compound was weighed and transferred to the reaction ampoule. The biphenyl standard was added as 1 ml of 0.2 M solution, then washed down with pure solvent past the constricted point where the tube would eventually be sealed. This results in weighing and pipetting error sources, but both products are affected identically. Therefore, an occasional total yield is as high as 116% or as low as 75%, but the ratio of products remained constant within experimental error.