C. Begg, P. W. Sheldon, and J. L. Foster, *ibid.*, **47**, 399 (1974); (c) J. C. Asquith, J. L. Foster, R. L. Willson, R. Ings, and J. A. McFadzean, *ibid.*, **47**, 474 (1974).
(5) K. M. Bansal and R. M. Sellers in "Fast Processes in Radiation Chemistry and Biology", G. E. Adams, E. M. Fielden, and B. D. Michael, Ed., Wiley, London, 1975, p 259.
(6) A. Henglein, *Allg. Prakt. Chem.*, **17**, 295 (1966).
(7) G. Beck, Dissertation, T.U. Berlin, 1968.
(8) A. Henglein, W. Schnabel, and J. Wendenburg, "Einführung in die Strahlenchemie", Verlag Chemie, Weinheim, W. Germany, 1969.
(9) M. Grätzel, A. Henglein, J. Lilie, and M. Scheffler, *Ber. Bunsenges. Phys. Chem.*, **76**, 67 (1972).
(10) M. Grätzel and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **77**, 2 (1973).
(11) (a) *Chem. Soc. Spec. Publ.*, **No. 17** (1964); (b) *ibid.*, **No. 25** (1971).
(12) B. Cercek and M. Ebert, *Trans Faraday Soc.*, **63**, 1687 (1967).
(13) E.g., (a) E. Hayon, T. Ibata, N. N. Lichtin, and M. Simic, *J. Am. Chem. Soc.*, **92**, 3898 (1970); **93**, 5388 (1971); (b) M. Simic, P. Neta, and E. Hayon, *ibid.*, **92**, 4763 (1970); (c) E. Hayon and M. Simic, *ibid.*, **93**, 6781 (1971).
(14) A. Samuni and P. Neta, *J. Phys. Chem.*, **77**, 1629 (1973).
(15) P. S. Rao and E. Hayon, *Biochim. Biophys. Acta*, **292**, 516 (1973).
(16) M. Simic and E. Hayon, *Biochem. Biophys. Res. Commun.*, **50**, 364 (1973).
(17) R. P. Bell, "The Proton in Chemistry", Methuen, London, 1959, p 133.
(18) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **70**, 761 (1966).
(19) K. M. Bansal, A. Henglein, E. Janata, and R. M. Sellers, *Ber. Bunsenges. Phys. Chem.*, **77**, 1139 (1973).
(20) K. M. Bansal, A. Henglein, and R. M. Sellers, *Ber. Bunsenges. Phys. Chem.*, **78**, 569 (1974).
(21) K. M. Bansal and A. Henglein, *J. Phys. Chem.*, **78**, 160 (1974).
(22) K. M. Bansal, M. Grätzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, **77**, 13 (1973).

Combination and Disproportionation of Allylic Radicals at Low Temperatures

Ralph Klein* and Richard D. Kelley

Physical Chemistry Division, National Bureau of Standards, Washington, D.C. 20234 *(Received November 1, 1974; Revised Manuscript Received May 12, 1975)*

Publication costs assisted by the National Bureau of Standards

The disproportionation–combination ratio for several allylic type radicals has been measured in the condensed phase at 90 K. Pairs of allylic radicals react exclusively by combination, with no disproportionation found within the limits of the analytical technique. Cross combination and disproportionation occurs between an allylic radical and an alkyl radical. In the cross disproportionation, the allylic radical acts exclusively as a hydrogen donor. This effect is attributed to the delocalization of the free spin, the hydrogen acceptor function being completely inhibited. Because of this, two allylic type radicals (or any radicals in which the density of the free spin is sufficiently delocalized) can only combine. The contribution of the resonant components of the allylic radicals to the combination products is found to be greatly dependent on steric effects.

Introduction

Reactions at low temperatures in a condensed phase are relatively simple because high activation energy paths are eliminated, while enthalpy developed in the reaction processes is efficiently dissipated. Advantage was taken of low temperature techniques to observe a series of alkyl radical cross disproportionation reactions.[1] In an extension of that work we consider here allylic radicals to determine the effect of the resonance structure on their combination and disproportionation reactions and contrast them with nonresonant radicals in this regard.

A convenient method for preparation of radicals is the hydrogen atom addition to an appropriate olefin.[2] The condensed olefin, either with or without a diluent such as propane, is present as a layer on the bottom of a flask immersed in a refrigerant such as liquid oxygen. Hydrogen atoms are produced by thermally dissociating molecular hydrogen on a heated tungsten filament. The atoms bombard the condensed layer and react with the olefin by addition to form radicals. These diffuse away from the surface, where they are formed, and undergo radical–radical reactions.[3]

To prepare allylic radicals, conjugated dienes are used. Thus, H atom addition to 1,3-butadiene gives the methylallyl radical. Higher homologs may possess isomers of the cis and trans variety. These are useful for assessing rotation in the allylic radical by way of the diene-radical–product path. A substantial activation energy barrier for rotation exists, one estimate being 70 kJ/mol.[4] Sustman and Trill,[5] using a flow system and ESR spectroscopy, found a value of 34–42 kJ/mol for an allyl radical containing CN and isobutyl groups. Doering and Beasley[6] gave 75 kJ/mol for the cis–trans isomerization of some hexatrienes via the allylic radical. Rotation of allylic radicals, as evidenced by a cis–trans isomerization, would not be expected to be observed in the low-temperature region. The preparation of the allylic radicals at low temperatures, as noted, is through hydrogen atom addition to a diene. The exothermicity of the process is approximately 209 kJ/mol and consideration must be given to the question of whether or not configuration is retained. We give here the results of several observations that are pertinent.

A further purpose of this paper is to determine some of the disproportionation–combination characteristics of allylic radicals, particularly in the low temperature region. Nelsen and Bartlett[7] first pointed out the striking difference between cumyl radicals and *tert*-butyl radicals in their disproportionation–combination reactions. Cumyl radicals combine to an extent of 94% at 20° whereas *tert*-

butyl radicals combine to an extent of only 20%. Nelsen and Bartlett suggested that the anomolous behavior with regard to the low disproportionation rate may be associated with the benzylic delocalization of the free electron. They also noted, however, that a lowering of the combination rate might have also been expected on this basis and no prediction could have been made. Engel and Bishop[8] reported that for the methylallyl radical, there was less than 2% disproportionation relative to combination. James and Kambanis[9] found that the ratio of combination to disproportionation for the radical pair allyl and cyclohexadienyl is 91 to 9, confirming the propensity of allyl type radicals to favor combination. Al-Sader and Crawford[10] showed that in the interaction of allyl radicals, 1,5-hexadiene is produced with only a trace of propene. Again, the major, if not exclusive, process is combination.

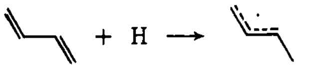
Previous work has shown that there is a temperature effect in the disproportionation–combination ratio[15] for alkyl radicals,[3] lower temperatures favoring disproportionation. For *sec*-propyl radicals, for example, $k_d/k_c = 0.6$ at 300 K and $k_d/k_c = 5.5$ at 90 K. Disproportionation for the allylic radicals would, by analogy, be enhanced at low temperatures, and it might be expected that disproportionation would be observed.

Experimental Section

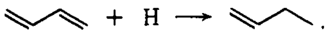
Experimental details of the low-temperature technique have been published previously.[1] Following the reaction, the film is warmed and transferred to the inlet of a gas chromatograph. Analysis of the entire film, typically 0.5×10^{-3} mol, was accomplished by chromatographically separating the mixture into three fractions: (1) diluent; (2) reactant and disproportionation products; and (3) radical dimer products. A squalane column was used for the initial separation. A 10 m, 20%, 3,3′-oxydipropionitrile (saturated with $AgNO_3$) column was used at 25° for the analysis of the second fraction, while a 4-m version of this column was used at 35° for the third fraction. Standard samples were used wherever possible to verify that these procedures yield accurate quantitative results.

Results

Allylic–Allylic Radical Reactions. H atom addition to 1,3-butadiene at a concentration of 0.3% in propane at 90 K yields the methylallyl radical


(1)

It will be shown that the alternate reaction


(2)

is negligible. If both disproportionation and combination reactions of these radicals occur, C_4 and C_8 compounds would be produced. A precise indication of the amount of disproportionation is available through the C_4 analysis. Disproportionation of methylallyl would necessarily yield 1-butene or 2-butene. Neither of these compounds was detected in the reaction products following the H-atom addition to 1,3-butadiene. The product analysis from a typical experiment is given in Table I. The distribution of the C_8 diene products (given in Table V) indicates that the only radical present in this system is methylallyl and therefore that reaction 2 is not significant. Consideration of the absence of four carbon products and the equivalence of C_8 diene with the depleted reactant requires us to conclude that greater than 99% of the reaction of methylallyl with methylallyl at 90 K is by way of combination.

TABLE I: Product Analysis from Methylallyl + Methylallyl at 90 K

Product	mol × 10^9
n-C_4H_{10} 1-C_4H_8 2-C_4H_8	<1
1,2-C_4H_6	<1
Δ(1,3-C_4H_6)[a]	160 ± 5%
C_8H_{14}	156

[a] Δ(1,3-C_4H_6) is the 1,3-butadiene depleted by reaction with H atoms. The quantity indicated represents approximately 10% conversion.

In another example, the radical 1,3-dimethylallyl

was prepared by the H atom addition to *cis*-1,3-pentadiene diluted to 0.3% with propane at 90 K. Disproportionation of these radicals would yield 1- and 2-pentenes. These compounds were not detected in the products within the limits of the chromatographic technique. The quantity of C_{10} diene observed indicates that the C_{10} dimer to pentene ratio exceeds 100.

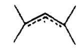
The disproportionation–combination reactions of alkyl radicals show steric effects for branched chain radicals markedly favoring disproportionation. The k_d/k_c ratio for isobutyl at 90 K is approximately 500. Whether the effect of branching is applicable to allylic radicals was determined with


I

Not only is this radical branched, but there are seven "donor" hydrogens associated with each of the "free spin" carbons. These characteristics should be especially favorable to disproportionation. The preparation of I was by H atom addition to 2,4-dimethyl-1,3-pentadiene in a 0.1% solution in propane at 90 K. The reactions of the allylic radicals were followed by the formation of the C_{14} dimers and the diminution of the parent olefin. More than 99% of the reaction is combination. Table II summarizes the disproportionation–combination data for these allylic radicals. Included are related data for radicals derived from unconjugated dienes and a C_5 olefin. The 4-penten-2-yl radical and the 2-pentyl radical were generated at 90 K in propane films by the H atom addition to 1,4-pentadiene and 1-pentene, respectively.[1] The disproportionation to combination ratio for 4-penten-2-yl is given by the product ratio, 1-$C_5H_{10}/C_{10}H_{18}$ while that of 2-pentyl is given by n-$C_5H_{12}/C_{10}H_{22}$. In both cases, these product ratios were found to be constant, within 5%, for a series of six runs with each radical. The difference between the allylic and these nonallylic radicals is striking. Clearly, a generalization may be adduced, that allylic–allylic radical reactions are exclusively combination, and that disproportionation does not occur.

Allylic–Alkyl Radical Reactions. The question arises as to whether or not the absence of disproportionation is characteristic of allylic radical reactions in general or only in those reactions where both radicals are allylic. The results

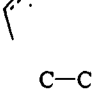
TABLE II: Autodisproportionation–Combination Ratios at 90 K for Several Allylic and Alkyl Radicals[a]

Radical	k_d/k_c
	<0.01
	<0.01
	<0.01
	7.6
	6.4

[a] The radicals are produced by the H atom addition to an appropriate olefin or diolefin highly diluted in propane. See text for experimental details of these measurements.

of James and Troughton[11] show that disproportionation for an allylic radical occurs provided it reacts with an alkyl radical. The reaction between allyl and ethyl at 410 K showed 85% combination, and 15% disproportionation. 73% of the disproportionation involved allyl as the H atom acceptor and 27% as the donor radical. These experiments were done in the temperature range 137–175°. The preparation of ethyl and allyl radicals involved photolysis of a mixture of diethyl ketone and diallyl at 3130 Å. Conclusions with regard to disproportionation between ethyl and allyl depend on the assumption that propylene and allene arise exclusively from disproportionation of ethyl and allyl. The complexity of the generating system would dictate caution in this regard, however.

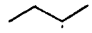
We have investigated the alkyl–allyl type radical–radical reaction of 2-butyl with 1,3-dimethylallyl. The reactions were at 90 K and the radicals were generated by exposure to gas phase atomic hydrogen of a condensed phase consisting of *cis*-1,3-pentadiene, *cis*-2-butene, and propane in a ratio of 10:1:3000. Hydrogen atom addition generates 1,3-dimethylallyl and 2-butyl. These react via biradical encounters. The 1,3-pentadiene is in considerable excess of the *cis*-2-butene so there will be an excess of 1,3-dimethylallyl over 2-butyl. Auto 2-butyl reactions are hence minimized. The experimental results are shown in Table III. Several significant conclusions may be drawn. The absence of 3,4-dimethylhexane shows that 2-butyl–2-butyl reactions are negligible. Thus, essentially all 2-butyl radicals react by cross disproportionating or cross combining with the dominant radical, 1,3-dimethylallyl. The cross disproportionation reactions possible are

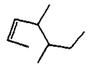


$$+$$

$$\begin{aligned}
\mathrm{C{-}C{-}\dot{C}{-}C} &\longrightarrow \mathrm{C{=}C{-}C{-}C + C{-}C{=}C{-}C{-}C}\\
&\longrightarrow \mathrm{C{=}C{-}C{-}C + C{=}C{-}C{-}C{-}C} && (3)\\
&\longrightarrow \mathrm{C{-}C{=}C{-}C + C{-}C{=}C{-}C{-}C}\\
&\longrightarrow \mathrm{C{-}C{=}C{-}C + C{=}C{-}C{-}C{-}C} && (4)\\
&\longrightarrow \mathrm{C{-}C{-}C{-}C + C{=}C{-}C{=}C{-}C}\ (\text{cis}) && (5)\\
&\longrightarrow \mathrm{C{-}C{-}C{-}C + C{=}C{-}C{=}C{-}C}\ (\text{trans}) && (6)\\
&\longrightarrow \mathrm{C{-}C{-}C{-}C + C{-}C{=}C{=}C{-}C} && (7)
\end{aligned}$$

Previously it was noted that when 2-butene was formed from 2-butyl in reactions at 90 K where 2-butyl acted as a hydrogen donor, the 2-butene was 98% trans.[3] The advantage of using *cis*-2-butene as the 2-butyl source is that products are distinguishable from reactants. For the reaction between 1,3-dimethylallyl and 2-butyl, the ratio n-C_4H_{10}/(1-C_4H_8 + *trans*-2-C_4H_8) is greater than 25. The ratio n-butane/4,5-dimethyl-2-heptene, a measure of k_{da}/k_c where the k's refer to the cross radical process, is equal to 1 ± 0.2. Where butene is formed in the cross disproportionation, equal amounts of 2-pentene (reactions 3 and 4) must be produced. The ratio of n-butane/2-pentene = 100. The small amount of C_4 monoolefin products found were extraneous to the cross disproportionation reaction and probably arose from a small amount of 2-butyl + 2-butyl reaction.

TABLE III: Products from the Reaction of  and  at 90 K[a]

Product	Relative yield
n-C_4H_{10}	25
1-C_4H_8	<0.5
t-2-C_4H_8	<0.5
t-1,3-C_5H_8	<0.1
2,3-C_5H_8	<0.1
3,4-Dimethylhexane	<0.1
	25
C_{10} diene	4,000

[a] Film composition C_3H_8:*cis*-1,3-C_5H_8:*cis*-2-C_4H_8 = 3000:10:1.

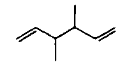
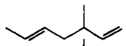
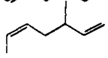
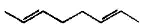
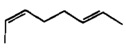
TABLE IV: Product Analysis from 1,3-Dimethylallyl + 2-Methyl-2-butyl at 90 K

Product	Relative yield
2-Methylbutane	1.0
2-Methyl-1-butene	<0.01
n-Pentane 1-Pentene 2-Pentene	<0.02
$C_{10}H_{20}$	1.7
$C_{10}H_{18}$	250

In a similar manner we investigated the cross-disproportionation of 2-methyl-2-butyl with 1,3-dimethylallyl (in great excess). The reaction products from one run are indicated in Table IV. The reaction produced 2-methylbutane (from the reaction analogous to (5)). However, 2-methyl-1-butene, 2-pentene, and 1-pentene (from reactions analogous to (3) and (4)) were not detected. Thus, the 1,3-dimethylallyl radical reacts by cross disproportionation in the same way with both of these alkyl radicals. The outstanding feature, and the point to be emphasized, is that in the cross disproportionation reaction of the allylic radical, the radical acts only as a hydrogen donor. Because allylic type radicals cannot function as hydrogen acceptors, in allylic–allylic radical reactions only combination is possible.

Rotation about a C—C bond in an allylic radical moiety presents a 40 to 80 kJ/mol activation barrier. Rotation at low temperatures, for example 90 K, would not be expected. However, in a sequential reaction series, where the initial preparative step is highly exothermic, uncertainty exists as to the retention of configuration. Information in this

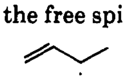
TABLE V: Combination Products of Methylallyl Radicals at 90 K

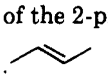
Product		% total dimer		
		90 K[a]	398 K[b]	
	Meso	8.4 ± 0.15	M	17.2
	Rac	7.5 ± 0.16	M	
	Trans	43.5 ± 0.53	28.7	47.1
	Cis	<0.1	18.4	
	Trans, trans	40.5 ± 0.63	12.2	35.8
	Cis, trans	0.22 ± 0.03	17.5	
	Cis, cis	<0.1	6.1	

[a] Source of the methylallyl radicals is the H atom addition to 1,3-C_4H_8 (0.3% in propane at 90 K). The uncertainty is one σ for 14 determinations in which the conversion was varied by more than 10-fold. The gc analysis was accomplished with a 4-m 20% 3,3′-oxydipropionitrile (saturated with $AgNO_3$) column. [b] R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Am. Chem. Soc.*, **93**, 3810 (1971).

regard can be obtained from the data in Table III in which the products of the H atom addition to *cis*-1,3-pentadiene (in large excess) and *cis*-2-butene are given. In the cross disproportionation of 1,3-dimethylallyl with 2-butyl, 1,3-dimethylallyl acts exclusively as the hydrogen donor, and the 1,3-pentadiene is re-formed. Rotation in the allylic radical would result in the formation of *trans*-1,3-pentadiene. In the experiments where the 1,3-dimethylallyl radical was in excess, butane formation indicated that a cross disproportionation reaction had occurred, but no trace of *trans*-1,3-pentadiene was found. The sensitivity of the analysis was such that 1 part of *trans*-1,3-pentadiene out of 250 parts of *n*-butane would have been detected. Clearly, the exothermic heat of H atom addition to the 1 position of *cis*-1,3-pentadiene is dissipated to the condensed phase sufficiently rapidly that the energy equivalent to the rotation barrier is not accumulated at the 3 position.

The cross combination of 2-propyl with the methylallyl radical is interesting because there is a secondary as well as a primary carbon in the methylallyl radical capable of combination with the free spin carbon of the 2-propyl radical:

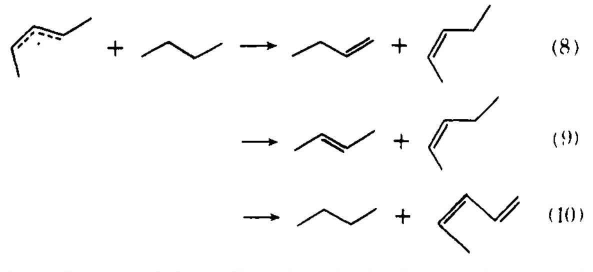

A


B

The radicals were prepared by exposing an equimolar mixture of propene and 1,3-butadiene in propane (olefin concentration 1%) at 90 K to H atoms in the gas phase. The reaction products, 3,4-dimethyl-1-pentene and 5-methyl-2-hexene (B + 2-propyl), were measured in several runs in which the conversion of the reactants varied considerably. The ratio 5-methyl-2-hexene to 3,4-dimethyl-1-pentene was found to be 4 and constant for conversions up to 10%. Favoring of B in the cross combination with *sec*-propyl over that of A by a factor of 4 may be explained on the basis of steric hindrance. Engel and Bishop[8] considered an analogous problem involving the autocombination of unsymmetrical allylic radicals. They noted that neither relative spin densities nor product stabilities were determining factors for the combination distribution. Steric effects seemed to be the most likely explanation for their results on the combination of 1,1-dimethylallyl radicals. With the tertiary carbon of the 1,1-dimethylallyl radical designated as the H (head) end and the terminal allylic carbon as the T (tail) end, Engel and Bishop found the distribution of dimers to be HH-16, HT-30, and TT-54. The TT dimer, showing the least steric hindrance for the approach of the two carbon atoms to be bonded, is highly favored.

Discussion

The unusual features of reactions of allylic radicals is that, in the reaction of an allylic radical pair, combination is essentially quantitative. Disproportionation can occur between an allylic radical and alkyl radical, but the former functions only as a hydrogen donor. The fact that the allylic radical is not a hydrogen acceptor implies that an allylic–allylic radical interaction can only be of the combination type. James and Suart,[14] in studies of disproportionation reactions of the cyclohexadienyl radical and methyl, ethyl, 2-propyl, and isobutyl radicals, noted that the cyclohexadienyl radical did not accept a hydrogen atom. The explanation proposed by them was based on energetic grounds. If the cyclohexadienyl radical acted as a hydrogen acceptor, in which case cyclohexadiene either in the 1,3 or 1,4 configuration is formed, a considerable fraction of the stabilization energy of 104 kJ/mol would be lost compared to the situation where cyclohexadienyl is the hydrogen donor and benzene results. Since, as we have shown, allylic radicals also react in this manner, i.e., they function exclusively as the donor radical in cross disproportionation reactions with alkyl radicals, the resonance energy suggestion is not convincing. The enthalpy change in the cross-disproportionation reactions 8–10 of the 1,3-dimethylallyl and the 2-butyl radicals are $(\Delta H_8)_{298K} = -230$ kJ/mol; $(\Delta H_9)_{298K} = -243$ kJ/mol, $(\Delta H_{10})_{298K} = -251$ kJ/mol.[16] Our observation is that reaction 10 predominates while reactions 8 and 9 occur, if at all, to a negligible extent. It is unlikely that the course of these highly exothermic reactions would be deter-

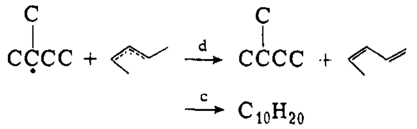
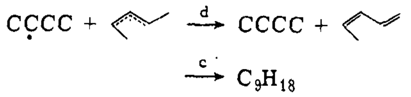


mined by differences of a few percent in the total enthalpy change. In fact, the autodisproportionation reaction of the 2-butyl radical producing 1-C_4H_8 and n-C_4H_{10} [ΔH_{298K} = −229 kJ/mol] is favored over that producing t-2-C_4H_{10} [ΔH_{298K} = −280 kJ/mol]. If the overall exothermicity were controlling, the opposite result would be found.

Disproportionation of two alkyl radicals is characterized by a near zero activation energy and hence is mechanistically unrelated to hydrogen abstraction reactions where a 25 to 40 kJ/mol activation energy is usual. The "head to tail" transition complex has been widely accepted as a basis for consideration of the disproportionation reaction. The transfer of hydrogen in a disproportionation reaction is concerted. The p electron of the free radical carbon interacts with the C–H σ bond, the acceptor radical changing from sp^2 to sp^3 hybridization. The donor radical simultaneously develops the π bond characteristic of the olefin. Allylic radicals, as we have shown, do not disproportionate with other allylic radicals, and when disproportionating with alkyl radicals, function exclusively as hydrogen donors. Their activity as hydrogen acceptors is absent. It is suggested that this characteristic is attributable to the electron delocalization in the allylic radical. The free electron has a probability of ½ of being associated with an end carbon of the allylic radical grouping. This contrasts with a probability of 1 for the appropriate alkyl radical carbon. The smaller effective charge density on the carbon available as a potential acceptor in allylic type radicals inhibits the interaction with the σ C–H bond of the counterradical so that allylic type radicals (or resonance type radicals in general where the free electron density is reduced) no longer function as H atom acceptors in disproportionation. The donor effectiveness of the allylic radical is unaffected by these considerations.

Table VI shows the disproportionation–combination ratio of 2-butyl with dimethylallyl and of 2-methyl-2-butyl with dimethylallyl, though they differ by a factor of 2, are nevertheless both considerably lower than that of alkyl–alkyl radical ratios. The lowest k_d/k_c ratio found for alkyl radicals under cryogenic conditions is that of 2-propyl-2-propyl with a value of 5.5. The value for 2-butyl + 2-butyl is 9.5 and for 2-methyl-2-butyl + 2-methyl-2-butyl is 1500. The cross reactions of allylic radicals with alkyl radicals favor combination relative to alkyl with alkyl reactions. This is true even considering the absence of H atom transfer to the allylic radical which would account for only a factor of about 2. The notably low value of the k_d/k_c ratio for cross allylic–alkyl radical reactions could be accounted for by assuming that the H atom transfer to the alkyl radical is inhibited. The rationale for such an assumption is not evident. It is more likely that the combination reaction is favored with respect to H atom transfer to the alkyl radical because the delocalization of the free electron in the allylic radical furnishes two reactive centers for combination.

TABLE VI: Disproportionation–Combination Ratios[a]

Reaction	k_d/k_c
	1.7 ± 0.2
	1.0 ± 0.2

[a] In the condensed phase at 90 K. The k_d/k_c values are derived from the data given on Tables III and IV.

Data for the k_d/k_c ratio for several pertinent radical pairs may be seen in Table II. The absence of disproportionation between allylic radicals, and the favoring of combination in cross reactions between allylic and alkyl radicals, has been noted. The autodisproportionation–combination of 4-pentene-2-yl, with k_d/k_c = 7.6, shows clearly that the presence of a simple olefinic bond in the radical has no effect on the k_d/k_c ratio, the value of 7.6 being "normal" for alkyl radicals. The values of 9.5, 35, and 1500 for the pairs (2-butyl, 2-butyl), (2-butyl, 2-methyl-2-butyl), and (2-methyl-2-butyl, 2-methyl-2-butyl) show clearly that there is no simple relationship among the k_d/k_c ratios (for example, that the cross reaction ratio is the geometric mean between the two autoreaction ratios). In the three pairs (dimethylallyl, dimethylallyl), (dimethylallyl, 2-butyl), and (2-butyl, 2-butyl), the k_d/k_c ratios are ~0, 1, and 9.5, respectively.

Summary

Allylic radicals are found to react in a remarkably different manner than alkyl radicals. Low temperature reactions of pairs of allylic radicals occur by combination, with no disproportionation observed. In contrast, alkyl radicals react predominantly by disproportionation. However, cross disproportionation as well as combination with alkyl radicals can occur. In the cross disproportionation between an allyl and an alkyl radical, the allylic radical acts exclusively as a hydrogen donor. This effect is attributed to the inhibition of the hydrogen acceptor function by the delocalization of the free spin. Because of this, two allylic type radicals (or any radicals in which the density of the free spin is sufficiently delocalized) can only combine. The contribution of the resonant components of the allylic radicals to the combination products is greatly dependent on steric effects.

References and Notes

(1) R. D. Kelley and R. Klein, *J. Phys. Chem.*, **78**, 1586 (1974).
(2) R. Klein and M. D. Scheer, *J. Phys. Chem.*, **62**, 1011 (1958).
(3) R. Klein, M. D. Scheer, and R. D. Kelley, *J. Phys. Chem.*, **68**, 598 (1964).
(4) D. M. Golden, *Int. J. Chem. Kinet.*, **1**, 127 (1969).
(5) R. Sustman and H. Trill, *J. Am. Chem. Soc.*, **96**, 4343 (1974).
(6) W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973).
(7) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).
(8) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **94**, 2148 (1972).
(9) D. G. L. James and S. M. Kambanis, *Trans. Faraday Soc.*, **65**, 2081 (1969).
(10) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).
(11) D. G. L. James and G. E. Troughton, *Trans. Faraday Soc.*, **62**, 145 (1966).
(12) R. J. Crawford, J. Hamelin, and B. Strehlke, *J. Am. Chem. Soc.*, **93**, 3810 (1971).
(13) J. C. Aston, G. Szasy, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).
(14) D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **64**, 2735 (1968).
(15) The ratio k_d/k_c is defined as the ratio of the sum of the rate constants of the possible disproportionation reactions to that of the possible combination reactions.
(16) Although ΔH_{90K} will differ from ΔH_{298K}, the latter values nevertheless give a valid indication of the relative ordering for the three reactions.