Organic Radical–Radical Reactions. Disproportionation vs. Combination

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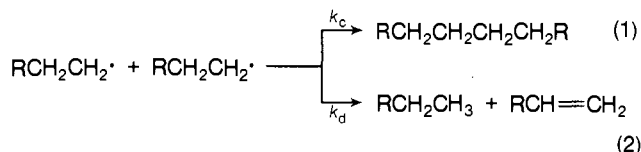
Contents

I. Introduction

When organic free radicals are produced in a reaction, these odd-electron species eventually undergo a termination reaction producing stable molecules. The paths available to a pair of radicals are combination (often called recombination or coupling), eq 1, and, if one of the original radicals bears a hydrogen atom β to the radical center, disproportionation, eq 2. Both processes are of high exothermicity ($\Delta H° = 50$ to 95 kcal/mol) and

$$RCH_2CH_2{\cdot} + RCH_2CH_2{\cdot} \quad \begin{array}{l} \xrightarrow{k_c} RCH_2CH_2CH_2CH_2R \quad (1) \\ \xrightarrow{k_d} RCH_2CH_3 + RCH{=}CH_2 \quad (2) \end{array}$$

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seemingly about as simple as any organic reaction is likely to be, yet because of their great velocity are difficult to approach directly. It is not necessary that either the radical center or the atom adjacent to it be carbon, but this review will only parenthetically mention data on noncarbon systems if it is relevant to the major discussion.

After a brief introduction listing the various modes of termination known, the first part of the review includes a discussion of methods of studying radical–radical reactions, cage processes, absolute rate constants, and theoretical approaches to these processes. The major part of the review deals with the effect of reaction variables and radical structure upon k_d/k_c ratios.

Generally, the smaller radicals have been examined both in the gas phase and in solution, while many of the interesting larger organic radicals have been studied only in condensed phases. The vast majority of organic free radical reactions are actually run in solution, where the explanation of the effects is likely to be considerably more elusive. The discussions in this review will deal with the data obtained under many sets of conditions, and we shall compare the results of these various studies and try to point out generalizations as we proceed.

The literature has been reviewed thoroughly through 1971, but early 1972 papers are also included. Earlier reviews exist,[1-3] the most recent[3] including very comprehensive gas-phase data through 1966. In the present review the most reliable (or often most recent, presumably improved) data are selected, but references to earlier work together with comments on the methods and pitfalls involved and our basis for choice of data will often be given. The data will thus be critically selected rather than exhaustive, but in all cases a real attempt has been made to indicate either primary references or reviews containing data not included. For solution studies, however, early work was often of a qualitative and descriptive nature—the data on combination and disproportionation not intended for use in detailed comparisons. These have by and large been omitted entirely except when qualitatively striking effects were evident.

II. Termination Reactions of Organic Radicals

A. General

It is useful at this stage to briefly survey the various kinds of radical destruction processes. Knowledge of termination modes together with their relative rates are of

(1) J. A. Kerr and A. F. Trotman-Dickenson, Progr. React. Kinet., 1, 105 (1961).
(2) S. W. Benson and W. DeMore, Annu. Rev. Phys. Chem., 16, 397 (1965).
(3) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," NSRDS-NBS9, U. S. Government Printing Office, Washington, D. C., 1967.

great import in predicting and interpreting radical chain kinetics and products of radical reactions in general; for example, a change from combination to disproportionation can effect a twofold change in polymer length.
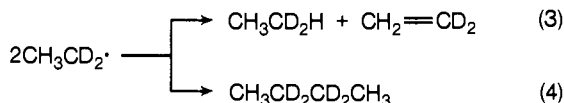
1. Combination

The simplest manner in which a seven-electron trivalent carbon species can be transformed into a diamagnetic stable compound is by the chemical bonding together of the two one-electron containing orbitals of two such species. This process, eq 1, is called radical combination, and essentially any radical pair may undergo this reaction.[4]

2. Disproportionation

When one of a pair of encountering radicals has a hydrogen atom β to the radical center, two stable molecules are produced when this hydrogen atom is abstracted by the other radical. The products are then an unsaturated molecule (from the radical abstracted from) and a molecule with a new C–H bond (eq 2). Formally, this is a radical hydrogen abstraction reaction, but it is much more exothermic than a normal hydrogen abstraction, leaving an olefin rather than another radical.

That disproportionation is entirely a head-to-tail reaction between two radicals was shown[10] by the nonmigration of deuterium in the disproportionation products of the photolysis of $\alpha,\alpha,\alpha',\alpha'$-tetradeuteriodiethyl ketone (eq 3). The labeling pattern of the butane obtained showed that recombination is cleanly a head-to-head process.

$$2CH_3CD_2\cdot \longrightarrow CH_3CD_2H + CH_2{=}CD_2 \qquad (3)$$
$$\longrightarrow CH_3CD_2CD_2CH_3 \qquad (4)$$

(4) In a few cases uncovered to date, combination takes an unusual path. For aralkyl radicals in which the radical center is benzylic, attack by another radical at the ortho or para position of the aromatic ring produces a coupled product with a methylenecyclohexadiene structure. This
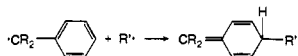

reaction occurs to the extent of 2% for two cumyl radicals[5] and is also significant for tert-butyl radical attack on a cumyl radical. These quinoids are not very stable and decompose at measurable rates to parent radicals upon warming the reaction mixture. There is also some evidence for para attack by tert-butyl radical on benzyl, α-methylbenzyl, and diphenylmethyl radicals.

The classical equilibrium between paramagnetic triphenylmethyl (and certain substituted alkyl diphenylmethyl) radicals and diamagnetic dimer is in reality an equilibrium between the radicals and a para coupling product[6] (1). Another para coupling product is the "yellow intermediate" 2 in the photolysis of benzophenone in isopropyl alcohol.[7]
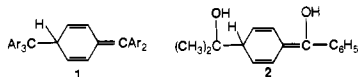
The dimerization of α-cyano radicals leads to ketenimines (3) as well as the "normal" head-to head dimers.[8,9] The ketenimines are similar to
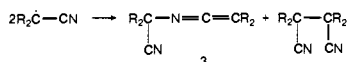
the para coupling products in that they are generally unstable and revert back to the parent radicals; some of these processes will be touched upon later in this review.

(5) S. F. Nelsen and P. D. Bartlett, J. Amer. Chem. Soc., 88, 137 (1966).

(6) H. Lankamp, W. Nauta, and C. MacLean, Tetrahedron Lett., 249 (1968).

(7) N. Filipescu and F. L. Minn, J. Amer. Chem. Soc., 90, 1544 (1968).

(8) A. F. Bickel and W. A. Waters, Recl. Trav. Chim. Pays-Bas, 69, 1490 (1950).

(9) G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, J. Amer. Chem. Soc., 81, 4878 (1959).

(10) M. H. J. Wijnen and E. W. R. Steacie, Can. J. Chem., 29, 1092 (1951).

3. Oxidation–Reduction

There are a number of metal ions (including Pb^{IV}, Mn^{III}, Ce^{IV}, Cu^{II}, Fe^{III}—with differing selectivities),[11,12] which effect the oxidation of organic radicals to cations or cation products (olefins, halides, aldehydes, etc.) in solution, and also those (typified by Cr^{II}, Fe^{II}, and Cu^{I}) effecting reduction of radicals to anion-type products (hydrocarbons, alcohols).[13,14] Some of these ions also promote radical formation from peroxides, alkyl halides, and carboxylic acids and then subsequently enter into additional electron transfers or chain decompositions of starting material. The literature here contains many very interesting and useful studies,[15] but by and large these processes will not be important in this review since the radicals are rather efficiently destroyed before encounter with potential partners.

4. Other Termination Modes

Stable radicals are often added to radical-forming reaction mixtures in order to eliminate chains or to count initiation efficiencies. Basically the destruction pathway is the same as for any radical pair reaction, but differentiation has been made here because one of the radicals has been added separately.

There are also processes in which reactive radicals are rendered very stable and do not react on a normal time scale. Physical entrainment of a radical on a surface or within a polymer is such a case, as is the chemical transformation of unstable radicals to stable ones by reaction with retarders (e.g., aromatic nitro compounds, phenols, certain olefins, and nitroso compounds).

B. Methods of Generation—Sources of Radicals

There are a large number of methods of generating free radicals,[16,17] many of these by chain decompositions which entail continuous destruction of the radicals via addition or abstraction reactions, and thus very small yields of termination products. For studies of radical-radical reactions, this situation is not too useful since it is desirable that the parent molecule be relatively stable to attack, that the solvent be unreactive, and that the termination products be formed in at least moderate yield and be easily measurable and identifiable as arising purely from termination. This has not been as easily accomplished as hoped, a good deal of data in the literature being conflicting and irreproducible between laboratories —often not because of analytical problems but rather because of incomplete understanding and control of the chemical reactions taking place.

1. Azo Compounds

Symmetrical azoalkanes and azoaralkanes decompose via eq 5. In a few cases there may be a stepwise decom-

$$R{-}N{=}N{-}R \longrightarrow R\cdot + N_2 + R\cdot \qquad (5)$$

(11) E. I. Heiba and R. M. Dessau, J. Amer. Chem. Soc., 93, 524 (1971).

(12) J. K. Kochi, J. D. Bacha, and T. W. Bethea, J. Amer. Chem. Soc., 89, 6538 (1967), and references therein.

(13) D. M. Singleton and J. K. Kochi, J. Amer. Chem. Soc., 89, 6547 (1967).

(14) C. Castro and W. Kray, Jr., J. Amer. Chem. Soc., 85, 2768 (1963).

(15) G. Sosnovsky and D. J. Rawlinson, "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 561, 585, and references therein.

(16) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957.

(17) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

position involving $RN_2\cdot$, these being for unsymmetrical azo compounds in which one of the radicals is considerably more stable than the other. Even here it is generally thought that further decomposition of the $RN_2\cdot$ to a carbon-centered radical and N_2 occurs before escape from the cage. Depending upon the structure of R in eq 5, various fractions of the radicals will recombine or disproportionate in the primary cage and never become "free" radicals. This subject will be taken up in the next section.

Most azoalkanes are not readily thermally decomposed at ordinary temperatures, but the more stable the radical after bond scission, the lower the temperature required. Thus aralkyl and tertiary α-cyano or α-carboxy azo compounds are easily used as a thermal source of radicals. Photolysis of azo compounds is in all cases very facile, proceeding via the same path as the thermolysis (eq 5).[18] Thus azoethane or azomethane (among the thermally most stable azo compounds) are readily photolyzed at low temperatures to excellent yields of ethyl and methyl radicals, respectively (with quantum yields for decomposition close to unity at low pressures).

The use of azo decompositions has some benefits and some drawbacks for the generation of radicals in termination studies. Azo compounds are not very susceptible to induced decomposition, are themselves stable, and generate only N_2 in addition to the desired radicals (so that product analysis is greatly simplified, vis-à-vis systems where other organic materials are generated). For many azo compounds the yield of radicals (free and caged) is 100%. Some azo compounds are a bit difficult to synthesize, but this is not the general case. Azo compounds in which the azo center is joined to a primary or secondary carbon atom, however, tend to rearrange to hydrazones (eq 6) if care is not taken, and in some cases the hydrazones may be more stable than the azo compounds.

$$R-N=N-CHR'_2 \longrightarrow R-NH-N=CR'_2 \qquad (6)$$
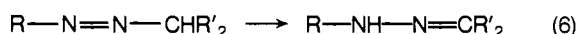
While azo compounds are among the most reliable and convenient sources for these studies, there are possible complications (section IV).

2. Peroxides

The thermal and photochemical decomposition of diacyl peroxides may give rise to two alkyl radicals and two CO_2 molecules directly, or to acyloxy radicals which can then decarboxylate to alkyl radicals. The yield of alkyl radicals is usually high overall, but the diacyl peroxides may be rather unstable and difficult to prepare.[19,20]

$$RCOOCR \longrightarrow 2RCO_2\cdot \longrightarrow 2R\cdot + 2CO_2$$
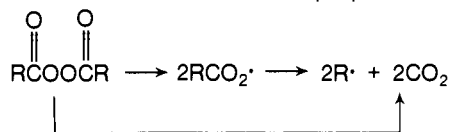
The decomposition of a perester leads to an alkoxy radical and an acyloxy radical or directly to CO_2 and an alkyl radical. Some of the data to be discussed later in this review have been obtained from perester decompositions,[21] usually the aim of the study being to examine

(18) However, see N. A. Porter, L. J. Marnett, C. H., Lochmuller, G. L. Closs, and M. Shobataki, J. Amer. Chem. Soc., 94, 3664 (1972), and references therein. This very recent report shows by CIDNP that the only effect of photolysis on trans-C_6H_5N=$NC(CH_3)_2C_6H_5$ is to convert it to the cis isomer which is thermally unstable at normal temperatures. Low-temperature photolysis of the trans compound gives cis which upon warming reverts to trans or decomposes.

(19) A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961.

(20) R. A. Sheldon and J. K. Kochi, J. Amer. Chem. Soc., 92, 4395 (1970).

(21) R. A. Sheldon and J. K. Kochi, J. Amer. Chem. Soc., 92, 5175 (1970).

$$ROOCR' \longrightarrow RO\cdot + \cdot OCR' \longrightarrow CO_2 + R'\cdot$$
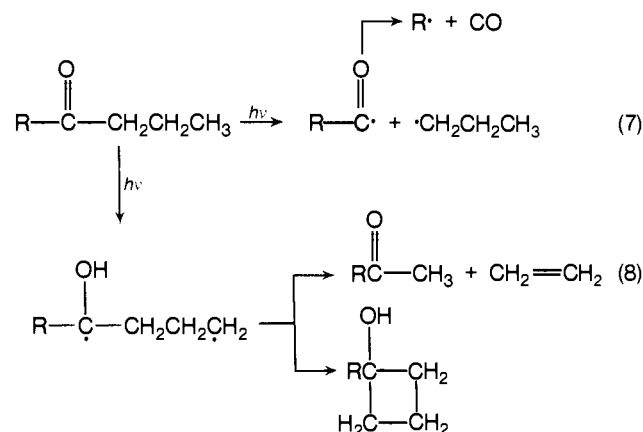$$(-RO\cdot)$$
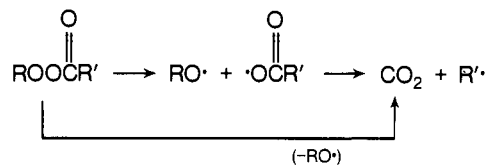
alkyl–alkoxy radical reactions. Special care must be taken in the interpretation of the disproportionation reaction here since acyloxy–alkoxy and alkyl–alkoxy disproportionations may compete, leading to the same alcohol or olefin. Again, photolysis and thermolysis are available.

## 3. Carbonyl Compounds

a. Ketone Photolyses

There are basically two modes of decomposition of ketones under the influence of uv radiation, eq 7 being the Norrish type I and eq 8 the type II process.[22] The type II

$$R-C-CH_2CH_2CH_3 \xrightarrow{h\nu} \begin{cases} R\cdot + CO \\ R-C\cdot + \cdot CH_2CH_2CH_3 \qquad (7) \end{cases}$$

$$R-\underset{OH}{\overset{\cdot}{C}}-CH_2CH_2CH_2 \longrightarrow \begin{cases} RC-CH_3 + CH_2=CH_2 \quad (8) \\ \underset{H_2C-CH_2}{\overset{OH}{RC-CH_2}} \end{cases}$$

(eq 8) process occurs only when the ketone has a hydrogen on the γ carbon atom, in which case it usually is the predominant photochemical reaction. The type I process is efficient for generating alkyl radicals with no δ hydrogens and is commonly used for producing methyl and ethyl radicals. The method has advantages in its simplicity, but there are often troublesome side reactions for vaguely complicated ketones.

b. Aldehyde Photolyses

At wavelengths above 3000 Å the major primary photochemical process is eq 9,[23] accompanied by type II abstraction if a δ hydrogen is available. At shorter wavelength eq 10 becomes increasingly important ($\Phi_{10}/\Phi_9 \approx 10^{-3}$ at 3130 Å; ≈ 0.95 at 2654 Å). It is not really clear whether eq 10 is a molecular elimination or a radical disproportionation occurring rapidly from the geminate pair formed in eq 9.

$$R-C\overset{O}{\underset{H}{\diagdown}} \xrightarrow{h\nu} \begin{cases} R\cdot + HC\cdot \qquad (9) \\ RH + CO \qquad (10) \end{cases}$$
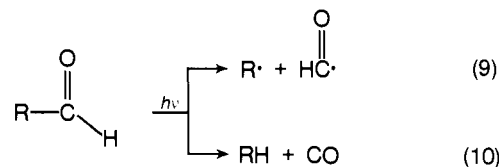
In solution or at high pressures, aldehydes decompose via a chain process involving eq 11 and 12. By and large, the aldehyde is a good hydrogen source and the chains can be long, with few radical–radical encounters occurring. Thus RH has another major source, and R(−H) must be measured as the disproportionation product. In one case olefin has been shown to arise via eq 13.[24]

(22) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

(23) Reference 22, p 368 ff.

(24) J. Grotewold and J. A. Kerr, J. Chem. Soc., 4342 (1963).

$$R—\overset{\overset{\displaystyle O}{\|}}{C}—H + R\cdot \longrightarrow R—\overset{\overset{\displaystyle O}{\|}}{C}\cdot + R—H \qquad (11)$$

$$R—\overset{\overset{\displaystyle O}{\|}}{C}\cdot \longrightarrow R\cdot + CO \qquad (12)$$

$$R_2C—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}=O + R_2\dot{C}CH_3 \longrightarrow R_2CHCH_3 + R_2\underset{\underset{\displaystyle CH_2\cdot}{|}}{C}CHO \qquad (13)$$

$$R_2\underset{\underset{\displaystyle CH_2\cdot}{|}}{C}CHO \longrightarrow \cdot CHO + R_2C{=\!=}CH_2$$
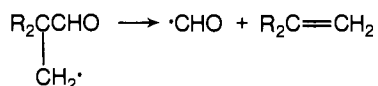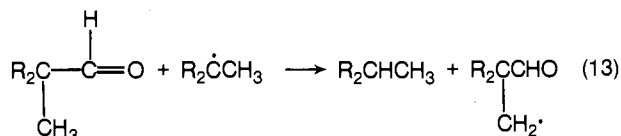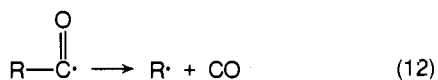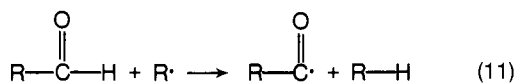
c. Formate Ester Induced Decompositions

A method involving eq 14 has been used to study a variety of alkyl radicals. The problems here include methyl radical attack at C–H bonds in R of the formate and R· attack on formate.

$$CH_3COCH_3 \xrightarrow{h\nu} 2CH_3\cdot + CO$$

$$CH_3\cdot + H\overset{\overset{\displaystyle O}{\|}}{C}OR \longrightarrow CH_4 + \cdot\overset{\overset{\displaystyle O}{\|}}{C}OR \qquad (14)$$

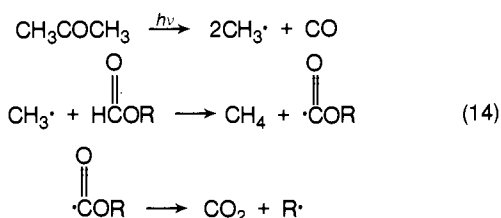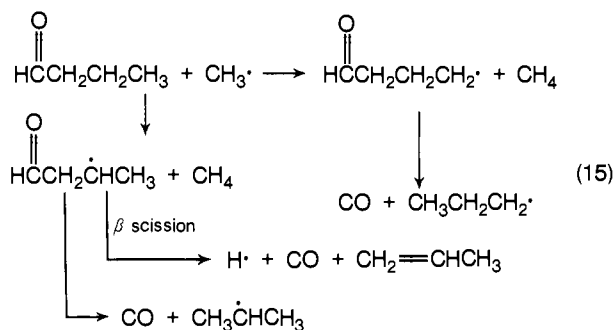$$\cdot\overset{\overset{\displaystyle O}{\|}}{C}OR \longrightarrow CO_2 + R\cdot$$

It has been suggested that the rate constant for methyl attack on n-butyraldehyde is much more like that on a hydrocarbon than on an aldehyde hydrogen.[24] Also, considerable yields of H_2 (up to one-half of the propylene) were formed in the overall reaction of this aldehyde. Equation 15 was postulated as a major side process. Thus it seems that the overall chemistry here is in doubt.

$$H\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3 + CH_3\cdot \longrightarrow H\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2\cdot + CH_4$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$H\overset{\overset{\displaystyle O}{\|}}{C}CH_2\dot{C}HCH_3 + CH_4 \qquad\qquad CO + CH_3CH_2CH_2\cdot \qquad (15)$$

$$\overset{|}{\underset{|}{\;}}\xrightarrow{\;\beta\text{ scission}\;} H\cdot + CO + CH_2{=\!=}CHCH_3$$

$$\longrightarrow CO + CH_3\dot{C}HCH_3$$

4. Organometallics

Some organometallics readily decompose to radicals thermally, the classical example being the Paneth decomposition of tetraethyllead. The yields can be good, but the syntheses and handling of the required compounds are often real obstacles. This technique is sometimes used for comparison purposes to examine the fate of radicals as a function of their generation mode, and organomercurials have been used a good deal in earlier studies. There is a major ambiguity in these decompositions in that displacement reactions can lead to apparent termination products.

5. Mercury-Photosensitized Decomposition of Alkanes

The 2537-Å absorption of atomic Hg produces $Hg(^3P_1)$, 112 kcal/mol above the ground state.[22] This is sufficient energy to split essentially any organic C–H bond ($D°(C–H) < 102$ kcal/mol).[25] The quantum yield

$$Hg(^3P_1) + RH \longrightarrow Hg(^1S_0) + R\cdot + H\cdot$$
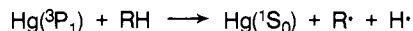
for n-butane decomposition at low pressure is unity. However, the method is of limited usefulness because of the very low specificity of $Hg(^3P_1)$, producing mixtures of all possible radicals.[26,27]

6. Hydrogen Atom Addition to Olefins

Hydrogen atoms are produced readily in a number of ways, including Hg photosensitization of H_2 ($D(H–H) = 104$ kcal/mol) and thermolysis of H_2 at a tungsten filament. The reaction of H atoms with unsymmetrical olefins is fairly selective as to direction of addition.[28] With high H_2/olefin ratios, high overall pressures, low steady-state H atom concentrations (low intensities of photolysis or low conversions and longer travel lengths in the W ribbon thermolysis), and careful product analysis, this method can yield accurate and reproducible data.[29,30] However, data from earlier studies using this technique are in serious doubt (section IV).

C. Cage vs. Encounter Reactions[31]

In any homolytic scission reaction in solution two radicals are formed in the same solvent cage. With peroxides, azo compounds, ketenimines, and other initiators, varying percentages of the radicals so formed have been shown to react together as a geminate pair in the solvent cage, never becoming "free." This gives rise to the same disproportionation and combination products as in the encounter reaction where the radicals have escaped the initial cage and do not encounter other radicals again until after many collisions with solvent. Among the reasons that a geminate radical pair process might differ from an encounter pair are the following: stereochemistry or relative orientation of one radical to the other, excess energy in the radical before it has time to thermally equilibrate, and the spin multiplicity of the pair. Each of these will be taken up in turn below, but they are not always experimentally easily separable.

1. Relative Orientation

The two radicals formed in a cage may collapse before any geometric realignment with respect to each other is possible; and if combination and disproportionation have different orientation requirements (which is indeed the case), the ratio of the two paths for a geminate pair from a particular precursor might reflect the geometry of that precursor.

Both Greene[32] and Kopecky,[33] independently studying optically active azo compounds, have found (by scaveng-

(25) The possible intermediacy of HgH has been eliminated. This reaction has been suggested to occur via energy transfer from $Hg(^3P_1)$ to RH producing vibrationally excited R–H which then decomposes to R· and H·: A. Heller, Mol. Photochem., 1, 257 (1969).

(26) P. Kebarli and M. Avrahami, Can. J. Chem., 41, 335 (1963); however, see ref 27.

(27) R. A. Holroyd and J. E. Pierce, J. Phys. Chem., 68, 1392 (1964), for a view opposing ref 26.

(28) W. E. Falconer and W. A. Sunder, Int. J. Chem. Kinet., 3, 395 (1971), and references therein.

(29) W. E. Falconer and W. A. Sunder, Int. J. Chem. Kinet., 3, 523 (1971).

(30) H. H. Georgakakos, B. S. Rabinovitch, and C. W. Larson, Int. J. Chem. Kinet., 3, 535 (1971), and references therein. These studies are also useful for easily obtaining cross k_d/k_c values between different radicals.

(31) A recent comprehensive review is J. P. Lorand in "Mechanisms of Inorganic Relations," Vol. 2, J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1972.

(32) F. D. Greene, M. A. Berwick, and J. C. Stowell, J. Amer. Chem. Soc., 92, 867 (1970).

(33) K. R. Kopecky and T. Gillan, Can. J. Chem., 47, 237 (1969).

ing all "free" radicals) that while the k_d/k_c ratios for two α-phenylethyl radicals or an α-phenylethyl radical plus a benzyl radical are the same for primary caged and encounter pairs, recombination of a geminate pair is only about 14 times faster than rotation of one of the radicals with respect to the other. This result suggests that if a molecular tumbling is required to "equilibrate" the radical so that its cage products are distributed equivalently to those from all nongeminate reaction pairs, there might be expected to be a difference between the products of the geminate and collision encounters. Indeed, this is the case in the solid (vide infra). Szwarc's group,[34,35] studying cage effects for azomethane and hexafluoroazomethane in a wide range of solvents, found that the probability of $2CH_3$ radicals combining on collision is about four times as high as that for $2CF_3$ radicals. It was suggested that this could be accounted for by the higher rate of rotation of methyl than that of trifluoromethyl radical.

However, for the 2-phenyl-3-methyl-2-butyl radical system of Bartlett and McBride,[36] it was suggested that the cage pair behaves very differently from the colliding pair, possibly an orientation effect. The evidence for this conclusion (applicable for cumyl as well) lies in the results of experiments performed in the solid state (discussed in some detail in section VIII). In frozen solids considerable differences in k_d/k_c (and alternative modes of combination) are found. It may be that the time differential is just borderline for radical equilibration and geminate termination, so that it would not be surprising to find situations where significant differences exist. An intervening stable molecule from the precursor (N_2 from an azo compound, CO_2 from a peroxide) would be expected to slow the geminate reaction with respect to equilibration of the radicals.

While this is potentially an important and very interesting aspect of these studies, so little data are available that we can only bear in mind that such things may be important for solution work.

2. Excited Species

In photochemical studies the typical situation is that the wavelength of light required to cause decomposition of precursor (because of its absorption spectrum) is much more energetic than is actually required to perform the scission. The products initially are generated with net excess energy from an electronically excited precursor. This energy will usually be distributed either into vibrational modes of the product species or into kinetic energy, and, if radical–radical reaction occurs before thermal equilibration can be attained, the radical may behave in a chemically different fashion from a ground-state species. That this occurs in photochemical systems is well known; for example, mercury photosensitized di-tert-butyl peroxide decomposition produces excited tert-butoxy radicals that cleave to methyl radicals and acetone much more readily than do the equilibrated species. Rabinovitch has studied the decomposition of activated radicals in great detail.[37] (Also, in at least a few cases, it has been found that photolysis at increasingly short wavelengths decreases the cage effect, since the radicals have greater kinetic energy.[38]) The effect would be enhanced in a geminate cage reaction since there has been less time

(and fewer collisions) to dissipate the excess energy. Section IV contains a discussion of the overall situation and the possibilities of hot radical–radical reactions in the gas phase.

By comparing overall k_d/k_c values to those when all solution radicals are scavenged, the "hot radical" effect for the cage process can be tested. The results mentioned above for two α-phenylethyl radicals which ruled out geometrical effects for the cage process also mitigate against a special cage excited radical effect. Identical k_d/k_c values have also been reported for bulk and cage products of azocumene[39] and azocyclohexane[40] decompositions.

In the study of ethyl radicals in isooctane, Dixon, Stefani, and Szwarc[41] found that both at 25 and 85° k_d/k_c ratios were unchanged by adding or removing scavenger if ethylene to butane is used as a measure of k_d/k_c. The ethane/butane ratio is much higher than the ethylene/butane ratio at all temperatures in the absence of scavenger, showing that abstraction from solvent is significant. Since k_d/k_c is constant, a geminate pair of ethyl radicals behaved identically to an encounter pair.[42]

3. Spin Multiplicity

While geminate radicals from a singlet precursor should be in a singlet state and those from a triplet precursor in a triplet state, encountering radicals (two doublets) have one chance in four of being singlet.[43,44] Lorand[31] suggests a two-in-four correction for these bulk radicals (or one-in-three for a triplet pair).[45] A fair number of experiments[39,46] have been done to examine the fate of a pair of radicals unambiguously in a triplet diradical state, but successes have been few. One effect noted was that while azobis-α-cyanocyclohexane shows no difference in cage yield upon direct or triphenylene (an efficient triplet sensitizer) sensitized photolysis, the direct decomposition of its corresponding ketenimine gave 24% 1,1'-dicyanobicyclohexyl, but 8.3% when photosensitized.[46] This has been taken to be a successful example of the lower combination probability of a triplet pair vs. a singlet pair. The general absence of a similar effect with azo precursors has been attributed to spin relaxation competing more effectively when an intervening N_2 is present. Subsequently, Bartlett and Engel[47] showed that triplet energy did not cause decomposition of azoisobutane, but that singlet energy transfer did—and furthermore that singlet transfer was generally taking place with previously used sensitizers. Thioxanthone (a very effec-

(34) O. Dobis, J. M. Pearson, and M. Szwarc, J. Amer. Chem. Soc. 90, 278 (1968).

(35) K. Chakravorty, J. M. Pearson, and M. Szwarc, J. Amer. Chem. Soc., 90, 283 (1968).

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

(37) R. F. Kubin, B. S. Rabinovitch, and R. E. Harrington, J. Chem. Phys., 37, 937 (1962).

(38) R. D. Burkhart and J. C. Merrill, J. Phys. Chem., 73, 2699 (1969).

(39) S. F. Nelsen and P. D. Bartlett, J. Amer. Chem. Soc., 88, 143 (1966).

(40) H. P. Waits and G. S. Hammond, J. Amer. Chem. Soc., 86, 1911 (1964).

(41) P. S. Dixon, A. P. Stefani, and M. Szwarc, J. Amer. Chem. Soc., 85, 2551 (1963).

(42) Kochi[20] also concluded that the relative disproportionation and combination rates are the same in a solvent cage as in free solution. This conclusion was based on a lack of change in k_d/k_c for a number of alkyl radicals generated via photolysis of diacyl peroxides in solvents giving varying cage effects. The cage effects varied from 33 to 60% in pentane to almost 100% in decalin and were determined by crossover experiments using mixtures of peroxides.

(43) R. K. Lyon, J. Amer. Chem. Soc., 86, 1907 (1964).

(44) See L. Salem and C. Rowland, Angew. Chem., Int. Ed. Engl., 11, 92 (1972), for a general discussion of the singlet–triplet diradical problem.

(45) R. D. Burkhart, J. Amer. Chem. Soc., 90, 273 (1968), found that dividing the calculated collisional rate constant by four gave values lower than the observed rate constant for reaction of bulk benzyl and pentyl radicals. Waits and Hammond[40] found that the cage effect for a triplet photosensitized geminate pair was one-third that for a pair of α-cyano radicals formed by direct photolysis (see below).

(46) J. R. Fox and G. S. Hammond, J. Amer. Chem. Soc., 86, 4031 (1964).

(47) P. D. Bartlett and P. S. Engel, J. Amer. Chem. Soc., 90, 2960 (1968).

TABLE I. Termination Rates of Alkyl Radicals In the Gas Phase

Radical	Log k_t,[a] M^{-1} sec^{-1} (T, °C)	Method[b]	Ref
$CH_3\cdot$	10.65 (125–220)	RS	48
	10.15 (175)	MS	c
$CH_3\cdot$ (and $CD_3\cdot$)	10.57 (165)	RS	d
$CH_3\cdot$	10.25[e]	e	f
$CH_3\cdot$	10.4 (20 and 127)	Abs	g
$CH_3CH_2\cdot$	11.2 − (2000 ± 1000/2.3RT) (50–150)	RS	56, h
$CH_3CH_2CH_2\cdot$	12.8[i] (100)	RS	j
$CF_3\cdot$	10.4 (127)	RS	k
$(CH_3)_2CH\cdot$	10.8 (81–169)	RS	l
$(CH_3)_2CH\cdot$	8.6 ± 1.1 (142)[m]	Comp	53
$(CH_3)_3C\cdot$	9.5 (81 and 115)	RS	n
$(CH_3)_3C\cdot$	5.6 (189)[o]	Comp	54

[a] $k_t = k_d + k_c$. [b] RS, rotating sector (light intermittency); MS, mass spectrometer; Abs, direct uv observation; Comp, competitive technique (see text). [c] K. U. Ingold and F. P. Lossing, *J. Chem. Phys.*, **21**, 1135 (1953). [d] G. B. Kistiakowsky and E. K. Roberts, *ibid.*, **21**, 1637 (1953). [e] Recalculation of data in ref 48 and footnote d. [f] A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956). [g] H. E. Van den Berg, A. B. Callear, and R. J. Norstrom, *Chem. Phys. Lett.*, **4**, 101 (1969); N. Basco, D. G. L. James, and R. D. Stuart, *Int. J. Chem. Kinet.*, **2**, 315 (1970). [h] K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc., Ser. A*, **208**, 25 (1951). [i] The authors state that k_t may be 20-fold overestimated. [j] S. G. Whiteway and C. R. Masson, *J. Chem. Phys.*, **25**, 233 (1956). [k] P. B. Ayscough, *ibid.*, **24**, 944 (1956). [l] E. L. Metcalf and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962). [m] Value for k_c alone. [n] E. L. Metcalf, *J. Chem. Soc.*, 3560 (1963). [o] Value for k_c alone. Together with pyrolysis data, the calculated $k_c = 10^{7.6}e^{-4700/RT}$.

tive triplet sensitizer) photosensitized decomposition of **4** (which cannot undergo cis–trans isomerization or dissipate energy by conformational mobility) gave more cleavage to **5** and considerably more loss of configuration in forming **6** and **7** than did thermolysis or direct pho-

(*meso* or *dl*)

4
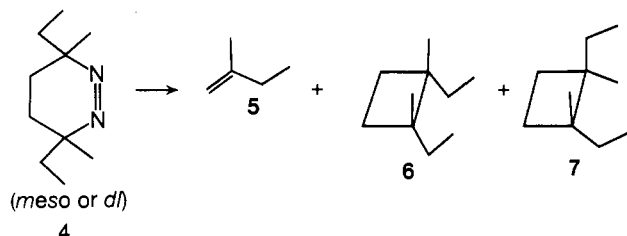
tolysis. Thus spin multiplicity can have an effect, and one might expect that geminate radicals if formed in a triplet state could show different behavior. Whether this would affect a geminate singlet pair *vs.* an encounter pair, other than the possible statistical factor, is not completely clear at this time.

Overall, the available data are not conclusive about these factors, and we can only hope that future studies will shed more light on these interesting aspects of free radical chemistry.

D. Studies of Absolute Rate Constants

It is clear that information about absolute rates of radical–radical reactions will ultimately be necessary before an understanding of the factors affecting the fate of radical pairs will be really possible. Recent results have, in fact, indicated that many previous notions will have to be discarded. Methods available for studying absolute rates of termination reactions include (a) the rotating sector method using light intermittency and either electronic absorption or electron paramagnetic resonance observation, (b) flash or flow photolysis techniques using the same observation methods, (c) mass spectrometry, and (d) competitive techniques referencing to a competing reaction of known rate constant. The next two subsections will briefly review the literature in this area.

1. Gas Phase

Since the classic rotating sector determination of the rate constant for methyl radical recombination by Gomer and Kistiakowsky,[48] the rate constants for a number of other terminations in the gas phase have been obtained by various techniques,[1,49] Table I giving selected values from these studies.

The first striking aspect of these data is the very high rate constant for the bimolecular termination reactions of the very small radicals. The collision frequency of methyl radicals in the gas phase is approximately 10^{11} M^{-1} sec^{-1}, and comparison of this with the rate constant ($\sim 10^{10.5}$) for methyl recombination reveals a very high efficiency (about one in four to six collisions) for the process.[50] The activation energy for these reactions is undoubtedly very low and the transition state "loose." The data best fit a picture of a reaction surface having a very nearly flat or actually flat profile, with recombinations (for methyl at least) generally occurring whenever a singlet pair of radicals approaches sufficiently closely to interact at all.

For ethyl and higher radicals the situation becomes quite cloudy, and it is generally agreed that a reliable set of data does not exist. For those reactions investigated repeatedly, systematic discrepancies of unknown origin appear. Waage and Rabinovitch have recently published a detailed discussion of the values (and techniques applied) for methyl recombination (and the reverse process, ethane thermal decomposition) together with a critical examination of theoretical approaches.[51] Even for this reaction, the forward rate constant (k_c for two methyls) is in disagreement with the reverse rate constant (ethane homolysis) and known thermodynamic data.

Hiatt and Benson have suggested a new competitive method using alkyl iodides to study absolute termination rates and remarked upon the poor agreement among values (and temperature dependencies) for ethyl recombinations.[52] Using this method[53] and estimating k_c(ethyl) = $10^{9.6\pm0.9}$, they find k_c(isopropyl) = $10^{8.6\pm1.1}$. The isopropyl value is significantly lower than that determined earlier by rotating sector, and the authors point out that the direct value is clearly too high in that it is greater than one-fourth the collision frequency for two isopropyls. Their analysis of all data available led them to conclude that the best values currently are k_c(methyl) = $10^{10.5}$, k_c(ethyl) = $10^{9.6}$, and k_c(isopropyl) = $10^{8.6}$ M^{-1} sec^{-1}.

Indeed, after the first draft of this review was written, McMillen, Golden, and Benson pointed out a 10^4 discrepancy between the earlier k_c value for two *tert*-butyl radicals and the measured decomposition rate of tetramethylbutane together with the thermochemistry.[54] By a competitive technique involving the pyrolysis of 2,2'-azoisobutane and the effect of HCl on this reaction, a value of $10^{5.6}$ M^{-1} sec^{-1} was found for *tert*-butyl combination at 189°. Together with the measured Arrhenius parameter for dimer homolysis and the entropy of reaction, this rate constant predicts an E_a for combination of two *tert*-butyls of ≥4.7 kcal/mol. A thermochemical treatment together

(48) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

(49) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS21, U. S. Government Printing Office, Washington, D. C., 1970. This volume contains references to original data (p 383 ff). A discussion of calculated rates is also given here (pp 23–39).

(50) Statistically, if the combination proceeds solely on the ground-state singlet potential surface, one-fourth of the collisions should be effective.

(51) E. A. Waage and B. S. Rabinovitch, *Int. J. Chem. Kinet.*, **3**, 105 (1971).

(52) R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 25 (1972).

(53) R. Hiatt and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 151 (1972).

(54) D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 4403 (1972).

TABLE II. The Recombination[a] of Alkyl Radicals (Solution)

Entry	Radical	Solvent	$10^{-9}k_t$, M^{-1} sec^{-1}	Ref
1	Methyl	Cyclohexane	4.5	63[b]
2	Propyl	Cyclohexane	1.7	58[c]
3	Pentyl	Cyclohexane	1.0	45[c]
4	n-Hexyl	Cyclohexane	1.1	63[b]
5	Cyclohexyl	Cyclohexane	0.6, 1.4	58,[c] 63[b]
6	$(CH_3)_2\dot{C}CN$	Cyclohexane	4.0	64[d]
7	tert-Butyl	Cyclohexane	1.1, 2.2	63,[b] 64[d]
8	Benzyl	Cyclohexane	2.0	58[c,e]
9	n-Propyl	Benzene	0.21	58[c]
10	Cyclohexyl	Benzene	0.36	58[c]
11	Benzyl	Benzene	1.8	58[c]
12	tert-Butyl	Benzene	0.73	64[d]
13	$(CH_3)_2\dot{C}CN$	Benzene	0.94	64[d]
14	Cumyl	Benzene	8.0	64[d]
15	p-Methylcumyl	Benzene	$(3.4)^f$	64[d]
16	p-Isopropylcumyl	Benzene	1.2	64[d]
17	p-Bromocumyl	Benzene	0.41	64[d]
18	$C_6H_5\dot{C}(CH_3)CH(CH_3)_2$	Benzene	0.23	64[d]
19	$p\text{-}CH_3C_6H_4\dot{C}(CH_2)_4\dot{C}H_2$	Benzene	0.59	64[d]
20	Ethyl	Ethane	$(1.3 \times 10^{10}$ $e^{-830/RT})$	57[g]

$^a k_t = k_d + k_c.$ ^{b} Rotating sector method with calorimetry. ^{c} Rotating sector method. ^{d} Rotating sector method photolysis in the cavity of an esr spectrometer. ^{e} R. J. Hagemann and H. A. Schwarz, *J. Phys. Chem.*, **71**, 2694 (1967), using pulsed radiolysis. ^{f} Assuming a cage effect equal to that of cumyl. ^{g} Radiolysis of liquid ethane (-177 to $-140°$) using rotating sector in the cavity of an esr spectrometer.

TABLE III. Rate Constants for the Thiol–Triethyl Phosphite Reaction[a]

Radical	Solvent	$10^{-4}k_p$,[b] M^{-1} sec^{-1}	$10^{-9}k_t$,[c] M^{-1} sec^{-1}
Benzyl	Benzene	2.2	1.8
Cyclohexyl	Benzene	3.0	0.36
n-Propyl	Benzene	3.0	0.21
Benzyl	Cyclohexane	2.3	2.0
Cyclohexyl	Cyclohexane	39	0.6
n-Propyl	Cyclohexane	290	1.7

^{a} From ref 58. ^{b} The overall precision was estimated by the author to be $\pm 10\%$. ^{c} The overall precision was estimated by the author to be $\pm 25\%$.

with data for neopentane pyrolysis predicts an E_a of ~ 2.5 kcal/mol for the cross-combination of methyl with tert-butyl. Direct kinetics at varying temperatures was not feasible in this study, but it was stated that experiments are under way to ascertain combination rate constants over wide temperature ranges and the detailed nature of the process. The $10^{5.6}$ M^{-1} sec^{-1} value for tert-butyl continues the trend noted above for decreasing combination rate constants with increasingly substituted radicals.[55]

Direct observations on ethyl radical disappearance have given $E_a = 2.0$ kcal/mol in the gas phase[56] and 0.8 kcal/mol in liquid ethane.[57] The situation is thus far from clear, and new carefully documented studies would be helpful.

2. Solution Phase

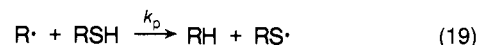When charges are being made or destroyed (or for highly polar reactions), the solvent effects involved are
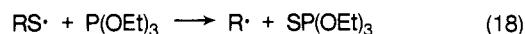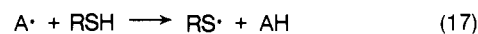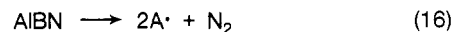
(55) The sharp disagreement between indirect and direct kinetic data for *tert*-butyl radicals means that one of these methods is subject to gross errors. McMillen, Golden, and Benson[54] suggest that rotating sector experiments are particularly dangerous in regards to the assumption of the nature of the termination process and the assumption that bimolecular termination alone controls any decay of radicals greater than first order.

(56) A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, **26**, 1020 (1957).

(57) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

large and fairly amenable to analysis and prediction, but for nonpolar reactions the effects of medium (presumably small) are still rather mysterious. This section reviews the situation for termination reactions in solution, Table II being a collection of rate constants for many of the small carbon-centered radicals. The various studies will be discussed in turn below.

Burkhart[45,58] examined radical–radical reactions as a function of structure and solvent using the thiol–triethyl phosphite reaction (eq 16–20), both k_p (eq 19) and k_t

$$AIBN \longrightarrow 2A\cdot + N_2 \tag{16}$$

$$A\cdot + RSH \longrightarrow RS\cdot + AH \tag{17}$$

$$RS\cdot + P(OEt)_3 \longrightarrow R\cdot + SP(OEt)_3 \tag{18}$$

$$R\cdot + RSH \xrightarrow{k_p} RH + RS\cdot \tag{19}$$

(eq 20) being determined by rotating sector experiments (Table III). The value of k_p in benzene is not very sensi-

$$2R\cdot \xrightarrow{k_t} products \tag{20}$$

tive to the type of radical involved, whereas in cyclohexane there is a real spread. For k_t, it is in cyclohexane that there is less sensitivity to radical structure. Burkhart describes the benzene behavior of k_t as a "leveling" effect, suggesting that the alkyl radicals interact with benzene to form a complex involving delocalization of the unpaired electron into the aromatic nucleus.[59] Thus the effect of R· structure is diminished greatly in eq 19 (k_p) for benzene as opposed to cyclohexane as solvents. For cyclohexane, presumably not solvating, k_p reflects thermochemistry as in the gas phase. The k_t values are close in cyclohexane since diffusion coefficients and encounter diameters should not differ greatly among these radicals, while in benzene the degree of solvation affects

(58) R. D. Burkhart, *J. Phys. Chem.*, **73**, 2703 (1969).

(59) This type of solvent effect was first postulated by G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, **77**, 4031 (1955), and subsequently verified by Russell.[60]

(60) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

TABLE IV. Proportioning of the Rate Constants for Disproportionation and Recombination in Benzene
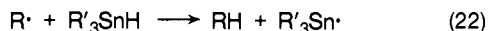
Radical	k_d/k_c	$10^{-8}k_d$, M^{-1} sec^{-1}	$10^{-8}k_c$, M^{-1} sec^{-1}	Ref
Cumyl	0.054	4	76	5
p-Methylcumyl	0.06	2	32	109
p-Isopropylcumyl	0.1	1.4	11	109
p-Bromocumyl	0.3	1	3	109
2-Phenyl-3-methyl- 2-butyl	0.3	0.6	1.8	36
tert-Butyl	4.6	6.0	1.3	36
2-Cyano-2-propyl	0.1	0.9	8.5	8
Cyclohexyl	1.1	1.8	1.7	a
Propyl	0.15	0.3	1.8	112

^{a} W. A. Cramer, J. Phys. Chem., 71, 1171 (1967).

these parameters. Benzyl radical, the most stable of the series, shows a negligible solvent effect in either reaction.

Rather recently, Burkhart, et al., examined a series of 1-alkyl radicals in cyclohexane,[61] measuring k_t values by the same method and also, using a photochemical space intermittency technique, their diffusion rates (k_{diff}). Significantly, the latter values were all considerably smaller than for the corresponding hydrocarbons, indicating some kind of radical solvation in this solvent. Through n-$C_{12}H_{25}\cdot$, the k_t values agreed reasonably well with the k_{diff} data, but for the octadecyl radical k_t was about seven times smaller. Thus the long-chain species either do not react on every encounter, or, more likely, the radical end is partially buried in the coiled chain so that geometric restrictions become important.[62]

Carlsson and Ingold studied the kinetics of the chain reaction of alkyl halides with organotin hydrides in cyclohexane (eq 21–24″).[63] For alkyl bromides termination

$$In \longrightarrow \longrightarrow R\cdot \qquad (21)$$

$$R\cdot + R'_3SnH \longrightarrow RH + R'_3Sn\cdot \qquad (22)$$

$$R'_3Sn\cdot + RX \longrightarrow R'_3SnX + R\cdot \qquad (23)$$

$$2R\cdot \longrightarrow \qquad \qquad (24)$$
$$R\cdot + R'_3Sn\cdot \longrightarrow \} \text{ termination} \qquad (24')$$
$$2R'_3Sn\cdot \longrightarrow \qquad \qquad (24'')$$

was almost entirely by eq 24 and for chlorides by eq 24″ (because of the relative efficacy of eq 23). Rate constants for these steps were obtained by calorimetry combined with quenching and rotating sector methods for measuring initiation rates. Some of the termination data are included in Table II and are in fair agreement with other studies. The methyl value being rather high, Ingold suggested that such small radicals may have unusually high diffusion coefficients (k_{diff} was calculated as 8.0 × 10^9 for all these radicals). Three possible reasons for the discrepancy between k_t's (all except methyl being in the range 0.7–1.8 × 10^9 M^{-1} sec^{-1}) and k_{diff} were given as (1) the diffusion radius is not equal to the reaction radius, (2) orientation of the radicals is important (rotational diffusion), and (3) a spin correction must be applied.

Weiner and Hammond[64] photolyzed a series of azo compounds in the cavity of an esr spectrometer and determined the overall rate constants for bimolecular decay of the radicals. The data are also included in Table II. The results on the cumyl series (entries 14–17) show that para substituents apparently have a marked effect on the rate constant. Hammond ruled out the following possible explanations: (1) variable amounts of para coupling, since Nelsen and Bartlett[5] found that unsubstituted cumyl radical gave a maximum of 2.2% abnormal coupling, and para substitution should diminish this process; (2) pure electronic effects, since the difference between k_t for p-methyl and p-isopropyl (15 vs. 16) is as large as the other differences and also because the esr hyperfine splitting constants show only small perturbations of the overall spin distribution; (3) relative stabilities of the radicals, since cumyl radicals decay at a rate 11 times faster than do tert-butyl radicals (14 vs. 12) and also benzyl radicals (entry 11).

Combining the k_t data with the separately measured values of k_d/k_c allows the dissection of the rate constant into the contributions from disproportionation and coupling (Table IV). It appears that k_c is varying with structure more than is k_d; particularly striking is the comparison between cumyl and tert-butyl. For the 85-fold change in k_d/k_c, k_d has increased about 1.5-fold and k_c decreased some 58-fold on going from cumyl to tert-butyl. These data present the problem of accounting for very different behavior of the same radical pair in the two highly exothermic reactions. The possibility of some form of solvation and/or solvent shell relaxation was proposed by Hammond.

Fujisawa, Monroe, and Hammond examined the rates of termination (largely coupling) of ketyl radicals in isopropyl alcohol.[65] The rates range from 5 × 10^7 to 5 × 10^8 M^{-1} sec^{-1}, showing no obvious correlation with structure of the particular ketyl. Both in benzene and isopropyl alcohol there was a substituent effect for substituted benzophenone ketyls which disappears in saturated hydrocarbon solvents.[66] It thus seems that k_t is primarily responding to solvation of the radical and that reorganization of the solvent cages has a profound effect on the rate.

The termination rates of a few other kinds of organic radicals have been measured in solution; references to these can be found in some of the recent references given here.[67,68]

Finally, it would be quite desirable to compare gasphase to solution results for these termination rate constants—a literally Sisyphean task at this date since neither of the lists of data (Tables I and II) seems to have much stability. For methyl radical the k_t in solution is about tenfold smaller than the gas-phase value, a result qualitatively reasonable considering encounter frequencies. For reactions proceeding more slowly than the diffusion-controlled rate and in the absence of solvent effects (the latter being, probably, an almost unattainable condition), the rate is expected to be independent of the viscosity of the medium. Several authors have addressed themselves to this point in recent years, some with the

(61) R. D. Burkhart, R. F. Boynton, and J. C. Merrill, J. Amer. Chem. Soc., 93, 5013 (1971).

(62) It also is worth noting that 1-pentyl had an anomalously low k_t and k_{diff}. Presumably the chemistry was still clean, and it was suggested that some sort of specific effect of caged pairs of a particular size is involved.

(63) D. J. Carlsson and K. U. Ingold, J. Amer. Chem. Soc., 90, 7047 (1968).

(64) S. A. Weiner and G. S. Hammond, J. Amer. Chem. Soc., 91, 986 (1969).

(65) T. Fujisawa, B. M. Monroe, and G. S. Hammond, J. Amer. Chem. Soc., 92, 542 (1970).

(66) G. S. Hammond and S. A. Weiner, Intra-Sci. Chem. Rep., 3, 241 (1969).

(67) D. J. Carlsson and K. U. Ingold, J. Amer. Chem. Soc., 89, 4891 (1967), and C. Walling and V. P. Kurkov, ibid., 89, 4895 (1967), have both measured k_t for tert-butoxy radicals, but see C. Walling and J. A. McGuinness, ibid., 91, 2053 (1969).

(68) K. U. Ingold, Accounts Chem. Res., 2, 1 (1969); various terminations of peroxy radicals.

specific object of examining the difference between a process in an "absolutely inert" solvent and in the gas phase. It is clear that there is a profound change upon changing the phase; however, the origin (or description) of this effect is unclear. Given the large solvent effects along with the discrepancies among laboratories for processes in both gas and liquid phases, the remainder of this review (and indeed the bulk of the data in the field) focuses on the *relative rates* of combination to disproportionation. It will not be until reliable both absolute and relative rate data are in hand that there will be any certainty about the factors causing differences in the path of reaction for different radical pairs.

III. Theoretical Approaches to Disproportionation and Combination

The theoretical approach to this subject has been one of some interest and has been discussed in several reviews.[1,2,69-71] This section will only briefly outline the approaches taken and the general conclusions. As described before, preexponential (A) factors for both combination and disproportionation are approximately 10^{11} M^{-1} sec^{-1}. Disproportionation is formally a radical abstraction process, but these typically have A values of about 10^8, so that the analogy is obviously misleading. Data on temperature dependencies in the gas phase are scarce, except for a methyl radical pair.

Early pictures of radical–radical termination assumed a common activated complex for the two processes.[1] Using ethyl radicals as an example, one proposal involved head-to-head dimer formation leading to an activated butane which could then either be deactivated to stable butane in a third body collision or undergo a four-centered elimination to disproportionation products (eq 25). This model is ruled out by a number of observations,

$$2CH_3CH_2 \cdot \longrightarrow$$
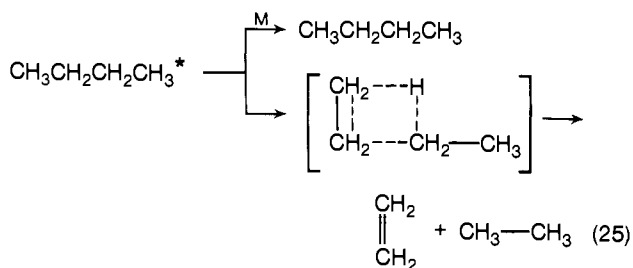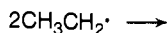
including the relatively small effects of pressure or solvent (third bodies), the fact that with *tert*-butyl radical disproportionation is greatly favored (the four-centered transition state for two *tert*-butyls is extremely hindered), and it is ruled out directly by data from the pyrolysis of mixtures of n-C_4H_{10} and n-C_4D_{10} which shows that even when most of the thermally generated ethyl radicals are scavenged by NO, the products have the same isotopic composition as in the uninhibited system.[71] This experiment eliminates the excited butane common path since the intramolecular elimination of C_2H_6 and C_2H_4 from excited C_4H_{10} is of negligible import with respect to homolysis and since recombination (and disproportionation) is ordinarily efficient, and excited butane cannot arise by a dimer–elimination path.

For similar reasons another early model that proposes a single four-centered activated complex which leads to dimer or alkane and alkene is also not attractive. Bradley

and Rabinovitch suggested two slightly different four-centered processes such as that shown here (eq 26) for disproportionation and combination.[72]

$$2CH_3CH_3 \cdot \longrightarrow$$
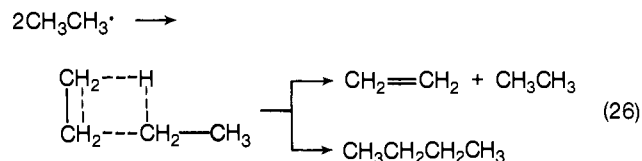
One particularly useful approach has come from the consideration that recombination is the reverse of the unimolecular decomposition of the alkane dimer, implying an unusually high Arrhenius A factor for the decomposition since the recombination is very efficient. This, in fact, has been at least qualitatively borne out by experiment ($A_{decomp} \approx 10^{16}$ sec^{-1} for ethane).[51,71]

Benson analyzed the required very "loose" transition state for $C_2H_6 \rightleftarrows 2CH_3 \cdot$ and concluded that a purely homolytic (covalent) picture is incompatible with the A factors.[2] He postulated a partial ionic bonding, for example, 8, for combination. On the basis that disproportiona-

8
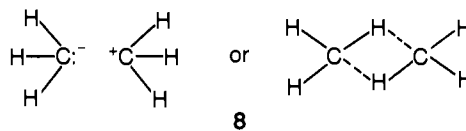
tion has a very similar A factor, and also a loose complex, contributions such as 9 and 10 were considered necessary to make up the activated complex for this process.

9

10
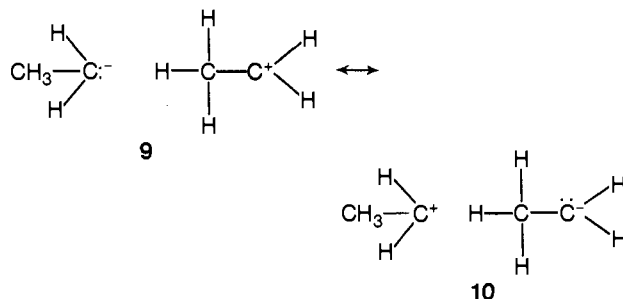
In their detailed analysis of the methyl radical–ethane system, Waage and Rabinovitch used the RRKM approach (considering vibrational frequencies of energized species and the activated complex explicitly) to compare experiment and theory.[51] The theory adequately treats the decomposition and combination data separately, but there was not good agreement either experimentally or theoretically between the forward and reverse reactions when treated together as a reversible system (equilibrium assumption). It was concluded that further experimental data are required to really test the approach.

The very small temperature dependence of the k_d/k_c ratio for alkyl radicals led to the suggestion of an empirical relationship between k_d/k_c and the entropy change of the processes.[73] This was expressed as eq 27, where a

$$\log (k_d/k_c) = a\Delta S + b \tag{27}$$

and b are constants, and ΔS is the entropy of the products of disproportionation minus the entropy of the products of combination. Using data available at the time (pre-1967) for the alkyl radical series, it was found that a and b were fairly constant.[74-76] These were taken as

(69) A. F. Trotman-Dickenson, *Annu. Rep. Chem. Soc.*, **55**, 36 (1958).

(70) J. G. Calvert, *Annu. Rev. Phys. Chem.*, **11**, 41 (1960).

(71) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(72) J. N. Bradley and B. S. Rabinovitch, *J. Chem. Phys.*, **36**, 3498 (1962).

(73) J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

(74) R. A. Holroyd and G. A. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

purely empirical constants with no fundamental significance, but the regularity of the relationship reinforced the original assumption that the k_d/k_c ratio was entirely entropically determined.

It has been pointed out that one may assign a physical significance to a and b.[77] For competitive reactions between the two same species, one may show easily that

$$\log (k_d/k_c) = (\Delta G_c^{\ddagger} - \Delta G_d^{\ddagger})/2.3RT$$

The usual linear free energy relationship then is expressed as

$$\log (k_d/k_c) = \beta(\Delta G_c^{\circ} - \Delta G_d^{\circ})/2.3RT + \text{constant}$$

or

$$\log (k_d/k_c) = \beta(\Delta H_c^{\circ} - \Delta H_d^{\circ})/2.3RT +$$

$$\beta(\Delta S_d^{\circ} - \Delta S_c^{\circ})/2.3R + \text{constant} \quad (28)$$

Equation 27 defined ΔS as $\Delta S_d^{\circ} - \Delta S_c^{\circ}$, so that with eq 28

$$a = \beta/2.3R$$

$$b = \beta(\Delta H_c^{\circ} - \Delta H_d^{\circ})/2.3RT + \text{constant}$$

Clearly, b is constant only if $(\Delta H_c^{\circ} - \Delta H_d^{\circ})$ is either zero or constant throughout the series. While it was originally thought that $\Delta \Delta H$ was zero, more recent investigations have cast doubt on this as a generality (vide infra). The actual value of this difference is very small and might be hard to ascertain experimentally from the data.[78]

A very recent replotting of $S_d^{\circ}-S_c^{\circ}$ using a wide range of data shows that while a general qualitative trend for certain kinds of radicals may hold, there is a great deal of scatter.[30] Those reactions forming 1-olefins in disproportionation together with single alkene-forming reactions form a deviant group, as do reactions giving trans internal olefins. Larger branched radicals deviate from small radicals. It is doubtful if the entropy generalization is adequate to explain k_d/k_c ratios.[81]

IV. Effect of Mode of Generation of Radicals on Disproportionation–Combination Ratios

To obtain k_d/k_c for a given radical pair, both the coupling and at least one of the disproportionation products must be measured with some care. It must be shown that the measured amounts of the products truly represent the termination process and neither arise in any other way nor are destroyed during the course of the reaction. This is usually not a difficult problem with regard to the coupling product. Disproportionation, however, produces an alkane which may be derived from the original radical by any hydrogen abstraction reaction and to an alkene which may arise from the radical by disproportionation with other than the desired radical. The alkene, usually highly susceptible to attack by other radicals, for most sets of conditions is destroyed as the reaction progresses, especially since by design (to maximize

the yields of termination products) only very poor radical traps or transfer agents are present. The most thorough studies measure all three products at the outset, at various times during the reaction, and over a range of initial concentrations or pressures. If alkane is formed only from disproportionation and alkene is attacked by radicals to give products without attacking either dimer or alkane, the reaction initially produces equal amounts of alkane and alkene and later diminishing amounts of alkene relative to alkane, but during all this the alkane to dimer ratio is constant. Particularly for early gas-phase studies (but in more recent solution studies as well) alkene rather than alkane was measured for the disproportionation yield since it was clear that alkane was being formed by abstraction from other molecules in the medium. The alkene yields were assumed to be correct. Reinvestigations have shown in several cases that these assumptions are poor, and major discrepancies exist.

There are also studies in which the chemistry is just not well defined. Section II reviewed a number of chemical problems for particular precursors as well as certain potential complications in some physical modes of generation. The data of sections VI–VIII have been chosen to eliminate questionable values, or, in some cases, footnotes will remark on possible problems.

An example of a source effect in solution which may have serious implications for all azo decompositions comes from a study of medium-ring cycloalkyl radicals.[82] The decomposition of dicyclooctylmercury proceeded smoothly to give high yields of the products expected for two cyclooctyl radicals, k_d/k_c being approximately 0.4. Azocyclooctane gave a k_d/k_c ratio of approximately 0.6 along with some bicyclo[3.3.0]octane. The corresponding mercury and azocyclodecyl compounds gave k_d/k_c values of approximately 1.0, with the azo compound again giving considerable bicyclic product. For both precursors photolysis results differed significantly from pyrolysis results. The most probable explanation advanced for the formation of bicyclic products was one-bond scission on the azo compound followed by α-hydrogen abstraction to produce a diazo compound, which would then undergo transannular carbon–hydrogen insertion along with α-insertion to give olefin. This kind of process does not have to be limited to medium-ring azo compounds, but was noted here because of the transannular reaction (see Scheme I).

The only real effect of radical source upon the combination to disproportionation competition, of course, will be if the radicals are not equilibrated with their environment before they react. In section II.C the problem of geminate reaction between excited radicals was discussed. Terminations involving nonequilibrated but nongeminate radicals have been reported in a number of photolytic gas-phase studies, manifest as a pressure-dependent k_d/k_c ratio leveling off at a thermally equilibrated limit at high pressures (although the third-body problem was not considered as an alternative explanation).

For the mode of generation involving hydrogen atom addition to olefins, the hot radical effect must be seriously considered since this reaction is very exothermic ($\Delta H \approx -40$ kcal/mol),[83] and vibrationally excited radicals are generated that may not equilibrate before reaction. The potential problems include not only formation of any of the products by hot radical reaction, but also possible formation of alkane disproportionation product via attack of R· on HgH or on the various alkanes and alkenes

(75) P. Gray, R. Shaw, and J. C. Thynne, Progr. React. Kinet., 4, 90 (1967).
(76) J. O. Terry and J. H. Futtrell, Can. J. Chem., 45, 2327 (1967).
(77) R. S. Konar, Int. J. Chem. Kinet., 2, 419 (1970).
(78) The original criticism of the ΔS treatment,[77] while analytically in error,[79] is still valid if $\Delta \Delta H$ is not zero.[80] This linear free energy relationship differs from most others in that entirely independent values of ΔS are used, and so, even if enthalpy–entropy compensation were to occur in the reaction, the data plots would diverge from linearity.
(79) K. J. Laidler, Int. J. Chem. Kinet., 3, 377 (1971).
(80) R. S. Konar, Int. J. Chem. Kinet., 3, 379 (1971).
(81) It was proposed[30] that steric effects are a manifestation of energy barriers in disproportionation (or vice versa). This proposal will be discussed below and seems to have experimental verification.

(82) A. C. Cope and J. E. Englehart, J. Amer. Chem. Soc., 90, 7092 (1968).
(83) L. E. Reid and D. J. Leroy, Can. J. Chem., 46, 3275 (1968).

SCHEME I
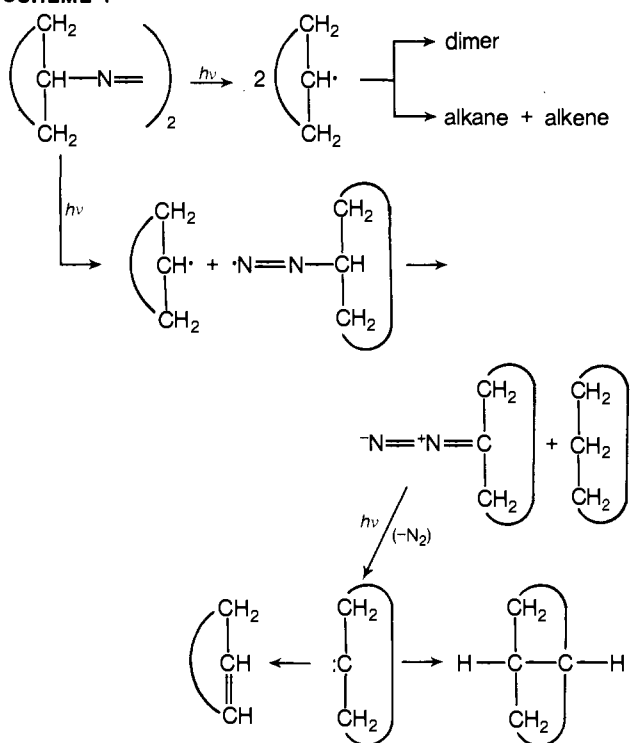
present; additionally, the reaction of H· with radicals leading to apparent disproportionation products has been shown to occur. While extensive studies employing this reaction have often given poor agreement with other methods,[24,84-88] very recently the system has been very carefully analyzed and conditions have been arranged so that the serious complications are avoided.[29,30] Auto and cross ratios for ethyl, both propyls, and n- and sec-butyl radicals were in good agreement with the most generally agreed upon, or most recent, data. However, the auto tert-butyl value (3.1)[29] was in agreement with values from photolysis of di-tert-butyl ketone and pivaldehyde (3.2),[89] and in disagreement with two recent independent values from photolysis of t-BuN=N-t-Bu (2.3).[87,90,91] There is thus still uncertainty over the value for the small and simple tert-butyl radical, and it must be that there still remain systematic errors in some of these methods that are unrecognized. Falconer and Sunder[29] suggested that the blame lies with the azo decomposition, involving either molecular elimination of dimer and N_2 or t-Bu· attack on parent azo compound to give high yields of dimer (but the latter seems unlikely from the study by James and Stuart[87] in which the rate constant for this process was found to be very low).

This is one of the few cases in which it is claimed that there is an anomalous route to dimer and that higher k_d/k_c values are correct. In general, azo decompositions (both symmetrical and unsymmetrical and also mixtures of azo compounds) give lower k_d/k_c values than other

(84) P. J. Boddy and J. C. Robb, Proc. Roy. Soc., Ser. A., 249, 518, 532, 547 (1959).

(85) J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 1609 (1960).

(86) R. N. Birrell and A. F. Trotman-Dickenson, J. Chem. Soc., 4218 (1960).

(87) D. G. L. James and R. D. Stuart, Trans. Faraday Soc., 65, 175 (1969).

(88) A. B. Callear and W. P. D. Pereira, Trans. Faraday Soc., 59, 2758 (1963).

(89) J. A. G. Dominquez, J. A. Kerr, and A. F. Trotman-Dickenson, J. Chem. Soc., 3357 (1962).

(90) J. O. Terry and J. H. Futtrell, Can. J. Chem., 46, 664 (1968).

(91) The value of Georgakakos, et al.,[30] is 2.7.

TABLE V. Disproportionation–Combination of Ethyl Radical as a Function of Solvent,[a] 65°

Solvent	Scavenger	k_d/k_c
Gas phase	None	0.14
Isooctane	None	0.144 ± 0.003
Isooctane	Styrene	0.145 ± 0.007
Limonene	None	0.158 ± 0.005
Ethylbenzene	None	0.156 ± 0.001
m-Xylene	None	0.165 ± 0.003
Toluene	None	0.167 ± 0.003
2-Butanol	None	0.168 ± 0.003
2-Propanol	Styrene	0.178 ± 0.001
1-Propanol	Styrene	0.181 ± 0.003
Aniline	Styrene	0.195 ± 0.001
Acetonitrile	None	0.200 ± 0.006
Acetonitrile	Styrene	0.208 ± 0.006
Ethylene glycol	None	0.241 ± 0.003

[a] From ref 92. By photolysis of azoethane.

methods, this usually having been taken to be the result of a cleaner reaction. The next most reliable method has usually been assumed to be ketone or aldehyde photolysis. These reviewers are in agreement with this generalization, but the new values from H· plus alkene reactions show that recent data here can probably be considered fairly reliable when care was exercised in arranging conditions.

V. Effect of Medium

In section II.C.2 the effect of solvent on termination rates was discussed, it having been concluded that there are profound, but as yet largely unexplained, variations with medium. A priori, the relative rates of k_d and k_c could be expected to be rather insensitive to solvent change since the ratio would eliminate any absolute factors affecting radical approach or interaction. On the other hand, if specific complexing or solvent-shell relaxation rates are the determining factors, a very rapid collapse of the two radicals (both having relaxed shells) to combination and disproportionation products could cause the ratio to be dependent upon their relative geometries at the time.

From Table II, it appears that the absolute rate constants vary more than do their ratios. For example, propyl radicals show an eightfold change in overall termination rate on going from cyclohexane to benzene, but alkyl radicals in general show only a small (~10%, Table V) change in k_d/k_c. Most radicals (see section VII.B, Table XII) show only small changes in k_d/k_c with solvent variation.[92]

On the basis of combination and disproportionation involving the same reacting species and having at least very similar transition states, and also since the results are measured as a ratio of rate constants, in a general examination of the effect of phase on free radical processes, Mayo concluded that there would be essentially no (or very small) effects of phase change on the k_d/k_c value.[93] For alkyl radicals, comparing gas phase to small hydrocarbon solvent, this prediction seems approximately true. Unfortunately there are insufficient really reliable and internally consistent data (see section VII) to make meaningful comparisons. Careful studies in one laboratory should be able to aid here significantly.

In contradiction to the above, profound effects were reported in one carefully examined system, Table V giv-

(92) A. P. Stefani, J. Amer. Chem. Soc., 90, 1694 (1968).

(93) F. R. Mayo, J. Amer. Chem. Soc., 89, 2654 (1967).

ing the data of Stefani for the ethyl radical.[92] In this same study the temperature was varied for several solvents, and it was found that the k_d/k_c ratio was also temperature dependent. The two results (solvent and temperature dependencies) were interpreted as being interrelated, the temperature variation presumably actually being a preexponential variation (not in the E_a difference) affecting the solvent properties (this will be discussed in more detail in the next section). The k_d/k_c ratio was suggested to be a function of the internal pressure of the solvent, implying that the volume of activation[94] for disproportionation is smaller than that for combination. Originally, these same data were interpreted in terms of solvation of the radicals,[41] but Stefani subsequently ruled this out because there was no obvious correlation with the dielectric properties of the solvent. It has been pointed out,[20] however, that the real variations in Table V arise in unsaturated and polar solvents, and that solvation may still be the major factor.[98]

In an investigation of a wide variety of alkyl radicals,[20] Kochi found that the hydrocarbon solvents pentane, decalin, and Nujol all gave basically the same results within the experimental error, although the "internal pressure" varies widely in the series. He concluded that Stefani's solvent effects were primarily specific solvations or polar solvations of the radicals, thus affecting their chemical behavior.

The general conclusions seem to be that medium effects on termination rate constants are significant, but that effects on the k_d/k_c rate ratios are quite small. The available data, however, are far from extensive.

VI. Effect of Temperature Variation

This section will be concerned with temperature effects on the actual k_d/k_c ratios for organic radicals. Considered artifactual in this context (and discussed elsewhere in this review) is temperature effecting (1) a phase change, (2) an increase in rate of some side reaction leading to one or more termination products, and (3) a change in collisional deactivation or generation of excited radicals such that their reactions alter the observed combination–disproportionation product ratios.

Assuming that these "anomalous" effects have been eliminated, preexponential as well as exponential temperature dependencies might be expected to be observed for reactions of such high exothermicity and low activation energy requirements as are under consideration here. For condensed phases, in addition to the gas-phase preexponential dependence, viscosity (affecting diffusion rates and fractions of geminate termination) and solvation of the radicals (affecting freedom of interaction, stereochemistry, and polarity) could have a temperature dependence manifest in either or both the preexponential and exponential terms. For the small radicals, the experimental temperature dependencies are generally small, mak-

ing it virtually impossible to meaningfully treat the data in terms of separating T^n from $\exp(E_a/RT)$ behavior.

A. Gas Phase

Rate constants for recombination of small alkyl radicals are generally 10^{10}–10^{11}, fairly close to the collision frequencies.[99] If the efficiencies are so high, clearly the activation energies are low, and one conclusion reached by a number of workers is that $E_{a(c)}$ is in general zero. Since disproportionation effectively competes with coupling, having similarly large A factors, the $E_{a(d)}$ for disproportionation must also be quite low, and the difference between the two activation energies must be indeed very small. Temperature independent k_d/k_c values have been reported for gas-phase cyclopentyl (26 to 250°),[100] n-propyl (18–150°),[101] ethyl (50–215°,[102] although this result is in disagreement with that of Szwarc, et al.[41,92]), n-butyl (20–130°),[103] isobutyl (25–168°[104] and 26–124° [105]), and tert-butyl (100–320°) [106] radicals.

Discontinuities in the temperature dependence of k_d/k_c, possibly due to vibrationally nonequilibrated radicals, have been reported for n-butyl radicals above 127°,[103] and for isobutyl radicals above 168°.[104,105] An apparent $E_{a(c)} - E_{a(d)}$ of 1.3 for n-butyl radicals over the range 61 to 229° was observed by Kerr and Trotman-Dickenson,[107] and an apparent $E_{a(c)} - E_{a(d)} = 0.25$ kcal/mol for two tert-butyl radicals (24–127°) has also been reported.[87]

It is a fact that in some of these studies complete material balances were not performed, and it is known that at higher temperatures radical abstraction from starting material (among other things) becomes significant. The chronologically later studies have usually been more carefully done; for tert-butyl the James and Stuart result ($\Delta E_a = 0.25$ kcal/mol) seems the most likely correct. It is not surprising that discontinuities are observed at higher temperatures for many systems.

The most carefully studied system is that of two ethyl radicals. For the photolysis of azoethane at 44, 0, and −65° Szwarc found an Arrhenius plot to give $E_{a(c)} - E_{a(d)} = 0.3$ kcal/mol, and a plot of log k_d/k_c vs. log T to give a slope of −0.7.[41] Subsequently, Stefani added +80° data to this study and found that increasing the volume of the reaction vessel caused an increase in k_d/k_c, this effect being the greatest at the lowest temperature.[92] It was concluded that the termination is at least partly heterogeneous. At two high temperatures (259 and 320°, the values at these points being well within experimental error of each other) Reid and Leroy found high k_d/k_c values for two ethyl radicals[83] (this is in the direction contrary to Szwarc's results). Considering the effect to be an exponential one, these workers plotted log (k_d/k_c) vs. $1/T$ (including the 25° value) to obtain $E_{a(d)} - E_{a(c)} = 0.91$ kcal/mol. Varying amounts of inert gas (CO_2) were added to show the absence of a hot radical effect

(94) It has been reported[95] that k_d/k_c increases with increasing pressure for ethyl radicals in solution. A similar trend has recently been found for two cyclohexyl radicals[96] and for two cumyl radicals.[97] Many systems show dramatic increases in disproportionation upon examination in the solid state (section VIII), a phenomenon probably associated with geometry of the precursor (and the original radical pair). The effect of pressure may be analogous.

(95) M. Szwarc, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. POLY-83.

(96) R. C. Neuman, Jr., and M. J. Amrich, J. Amer. Chem. Soc., 94, 2730 (1972).

(97) R. C. Neuman, Jr., and M. J. Amrich, unpublished data.

(98) The "internal pressure" correlation was discussed by Neuman (R. C. Neuman, Jr., J. Org. Chem., 37, 495 (1972), and personal communication) who pointed out that actually cohesive energy densities were used and, furthermore, that a recalculation of the fit showed very little correlation (in fact, the alcohols and acetonitrile formed a separate set from the hydrocarbon solvents).

(99) However, see section II.D for recent results indicating that this longstanding generalization may be limited to only the very small radicals.

(100) H. E. Gunning and R. L. Stock, Can. J. Chem., 42, 357 (1964).

(101) J. Grotewold and J. A. Kerr, J. Chem. Soc., 4337 (1963).

(102) J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 1611 (1960).

(103) W. E. Morganroth and J. G. Calvert, J. Amer. Chem. Soc., 88, 5387 (1966).

(104) D. H. Slater, S. S. Collier, and J. G. Calvert, J. Amer. Chem. Soc., 90, 268 (1968).

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

(106) E. L. Metcalfe and A. F. Trotman-Dickenson, J. Chem. Soc., 5072 (1962).

(107) J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 1602 (1960).

TABLE VI. Temperature Dependencies of k_d/k_c for Radicals in Solution

Radical	Solvent	$\Delta H_c{\ddagger} - \Delta H_d{\ddagger}$ $(E_{a(c)} - E_{a(d)})$, kcal/mol	Temp range, °C	Ref
$2C_2H_5\cdot$	Isooctane	0.32^a	-191 to 85	41
$2C_2H_5\cdot$	2-Propanol	0.44^a	-191 to 85	41
$2C_6H_5\dot{C}HCH_3$	Benzene	1.47	98 to 148	108
$2C_6H_5\dot{C}HCH_2CH_3$	Benzene	1.89	98 to 148	108
$2C_6H_5\dot{C}HCH(CH_3)_2$	Benzene	2.60	98 to 148	108
$2C_6H_5\dot{C}HCD_3$	Benzene	0.80	98 to 148	108
$2C_6H_5\dot{C}(CH_3)_2$	Benzene	0.0^b	20 to 60	5
$2p\text{-}RC_6H_4\dot{C}(CH_3)_2$ (R = H, CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$, and t-C$_4$H$_9$)	Toluene	0.0^c	46.5 and 64	109
$2p\text{-}BrC_6H_4\dot{C}(CH_3)_2$	Toluene	3.8^c	46.5 and 64	109
$2C_6H_5\dot{C}(CH_3)CH(CH_3)_2$	Chlorobenzene	-2.0	0 to 100	36

^{a} Stefani[92] has discussed this result as a possible $T^{0.3}$ preexponential dependence (section V). ^{b} Nelsen and Bartlett[5] found E_a(diffusion) $- E_a$ (cage reaction) $= 1.3$ kcal/mol and, estimating E_a(diffusion) as 2.6 kcal/mol, estimated $E_{a(c)} = E_{a(d)} = 1.3$ kcal/mol. ^{c} The p-bromocumyl result was calculated by us using Shelton's data. The p-alkylcumyl radicals showed no dependency.

(the method of radical generation was $Hg(^3P_1)$ sensitization of H_2 decomposition in the presence of ethylene), but it may be that other side reactions are occurring here.

In sum, the temperature dependencies of k_d/k_c for the small radicals in the gas phase is very small—but seemingly real. Most of those reported show inverse dependencies (k_d/k_c decreasing with increasing temperature), meaning a stronger dependence of k_c than k_d.

B. Liquid Phase

Table VI contains data on the temperature dependence of k_d/k_c for a variety of radicals in solution. While in all cases examined thus far the temperature dependence of the product ratio is quite small, in over half the total reported cases a reproducible and regular dependence was found that gave reasonably linear log k_d/k_c vs. $1/T$ plots. (It is in general extremely difficult to judge these dependencies as to their linearity because of their rather small slopes and the temperature ranges to which they are limited. That is, for close numbers, $\Delta \log A \sim \Delta A$.) If one takes the results in toto, with the exception of one case[36] (discussed below), the trend is uniformly to *decreasing k_d/k_c ratios with increasing temperature.*[108] which implies a greater temperature dependence for combination than for disproportionation. This same result was noted above for the few gas-phase studies available.
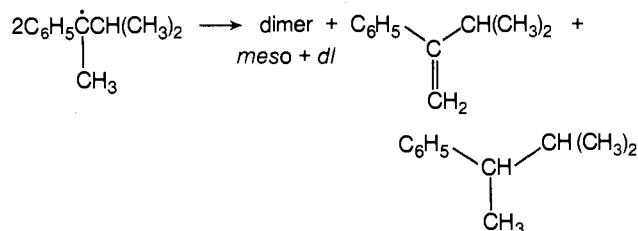
If these are exponential effects, $E_{a(c)}$ is greater than $E_{a(d)}$. They could be effects primarily on the solvent structure or macroscopic properties that in turn affect geometry or solvation of the radicals or radical pairs. This would be in accord with the restriction generalization from solvent and pressure effects, since, if disproportionation has a more restricted activated complex, as the solvent becomes looser (higher T) k_c becomes increasingly more favorable.

For ethyl, the $\Delta\Delta H\ddagger$ ($\Delta H_c\ddagger - \Delta H_d\ddagger$) value is between 0.1 and 0.4 kcal/mol,[41] while for α-aryl radicals (with the exceptions noted) the values are between 1.0 and 3.8 kcal/mol.[108,109] While the alkyl radical data may be fit to low-order T^n dependencies, this is not reasonable in general for the α-aryl series. (For the α-phenylethyl series the exponent would have to be between -2 and -3.4.) The $\Delta\Delta H\ddagger$ values for the 1-phenylethyl, 1-phenylpropyl, 1-phenyl-2-methylpropyl, and the [2,2,2-^{2}H]-1-phenylethyl

(108) M. J. Gibian and R. C. Corley, *J. Amer. Chem. Soc.*, **94**, 4178 (1972).

(109) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968).

radicals follow the order of decreasing bond dissociation energy for the β C–H (or C–D) bond,[108] and probably reflect a dependence of k_d for this very similar series upon the strength of that bond (or olefin stability, essentially the same thing).

It appears that combination is largely energetically limited, having the higher exponential dependence, and that disproportionation is entropically limited, having a lower $\Delta S\ddagger$ (or A factor).

The exception to the trend of the apparent $\Delta H_c\ddagger - \Delta H_d\ddagger$ being positive is for the 2-phenyl-3-methyl-2-butyl radical, studied by Bartlett and McBride,[36] which is anomalous also in that the disproportionation apparently leads solely to α-isopropylstyrene as opposed to the

$$2C_6H_5\underset{\underset{CH_3}{|}}{\dot{C}}CH(CH_3)_2 \longrightarrow dimer + C_6H_5\underset{\underset{CH_2}{\|}}{\overset{CH(CH_3)_2}{C}} +$$
$$meso + dl$$

$$C_6H_5\underset{\underset{CH_3}{|}}{CH}CH(CH_3)_2$$

more stable trimethylstyrene. Evidently the primary hy-

$$C_6H_5\underset{\underset{CH_3}{|}}{C}{=}C(CH_3)_2$$
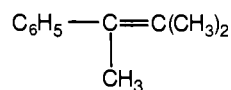
drogen is abstracted overwhelmingly more often than the tertiary, an unusual result (see section VII).

Since methods for studying absolute rate constants in solution are now available, and these may be used to measure temperature dependencies, data should be forthcoming that may be used to give separate k_d and k_c values when combined with product ratio information. We have already discussed the few such examples available, noting that solvation effects are very important. It is likely that there is a very close balance between the activated complex energetics for combination and disproportionation, and that subtle structural as well as solvation factors will be manifest in the relative rates. For small changes in product distribution (indeed perhaps even for large changes), a preexponential vs. an exponential temperature dependence is not easily discernible. A solvent effect may be manifest as an exponential effect rather than a preexponential one, so that the available data will have to be significantly expanded before these effects can be sorted out.

TABLE VII. Auto Disproportionation–Combination Ratios for Carbon Radicals in the Gas Phase[a]

Entry	Radical	k_d/k_c	Δ/β_H	Source, $T(°C)$	Ref
1	$CH_3CH_2\cdot$	0.13 ± 0.02	0.022	Wide variety	10, 29, 41, 76, 84
2	$CH_3CH_2CH_2\cdot$	0.15 ± 0.01	0.038	Wide variety	24, 76, 101, 112–114
3	$C_2H_5CH_2CH_2\cdot$	0.14^b	0.035	c, 20–127	97
4	$(CH_3)_2CHCH_2\cdot$	0.076 ± 0.02^d	0.037	c, 25–168	90, 104
5	$CH_3\dot{C}HCH_3$	0.66 ± 0.02	0.055	e, 100; f, <200; e, 25; g, 25	29, 76, 89, 113
6	$CH_3CH_2\dot{C}HCH_3$	$0.63,^h 0.77$	0.063	g, −78 and 25	37, 29
7	$(CH_3)_3C\cdot$	$2.3,^i 3.1, 2.7$	0.13	c, 25–100; g, 25	29, 30, 87, 90
8	$Cyclo\text{-}C_5H_9\cdot$	~ 1.0	~ 0.13	j, 26–250	100
9	$Cyclo\text{-}C_6H_{11}\cdot$	~ 0.5	~ 0.062	j, 29	116
10	$(CH_3)_2CH\dot{C}HCH_3^k$	$(\Delta_1)\ 1.11$ $(\Delta_2)\ 0.39$	0.18 0.20	g, 25 g, 25	29, 120[l]
11	$CH_3CH_2\dot{C}(CH_3)_2^k$	$(\Delta_1)\ 1.6$ $(\Delta_2)\ 0.6$	0.13 0.15	g, 25 g, 25	29, 123[l]
12	$(CH_3)_3CCH_2\dot{C}HCH_3^k$	$(\Delta_1)\ 1.11$ $(\Delta_2)\ 0.38$	0.18 0.10	g, 25 g, 25	29
13	$(CH_3)_2CHCH_2\dot{C}(CH_3)_2^k$	$(\Delta_1)\ 2.8$ $(\Delta_2)\ 0.84$	0.23 0.21	g, 25 g, 25	29
14	$ClCH_2CH_2\cdot$	<0.05	<0.012	m, 0–58	129
15	$CH_3O\cdot$	$9.3, >60$	$1.6, >10$	n, 25; o, 25	117, 119
16	$CH_3CH_2O\cdot$	12	3	n, 25	117

^{a} Data for this table were chosen as near 25° as possible. Section VI discusses temperature dependencies of these values. ^{b} Other values ranging from 0.5 to 0.95 have been shown to be incorrect[107,111] (W. J. Moore and L. A. Wall, J. Chem. Phys., 17, 1325 (1949)). ^{c} Photolysis of the azo compound. ^{d} Earlier values[105,106] were shown to be incorrect. ^{e} Photolysis of ketone. ^{f} Alkyl formate decomposition. ^{g} Addition to H· to olefin. ^{h} Earlier values are not in agreement[84,105] (M. Miyoshi, et al., J. Chem. Phys., 36, 3019 (1962); B. S. Rabinovitch, et al., ibid., 30, 735 (1959)), and are all considerably higher than the one above. Several were noted to be "maximum values." The values quoted in the table agree best with the isopropyl figure. The ratio of 1-butene/2-butene has been reported as 1.5,[30,37] the statistical value, and also as 1.1,[29] a preference for the internal olefin. Reference 37 discusses the various data for this radical. ^{i} Again, a number of higher values were reported earlier[86,89,105] (H. M. Frey, Proc. Chem. Soc., London, 385 (1959)). These have been discussed in the reference given. ^{j} Mercury photosensitized composition of RH. ^{k} For unsymmetrical radicals, Δ_1 connotes the ratio of 1-olefin/dimer and Δ_2 that of internal olefin/dimer. The total k_d/k_c (Δ_{tot}) is the sum of these values. ^{l} Some of the values given were later recalculated.[29] ^{m} Photolysis of $CCl_4 + C_2H_4$. ^{n} Photolysis of $RI + O_2$. ^{o} Photolysis of azo compound + O_2.

Looking at all the gas and solution data, we would say that one-temperature k_d/k_c determinations are qualitatively valuable since dependencies are low, but the ratios are not really temperature independent. Conclusions about structural or medium effects drawn from relatively close k_d/k_c values, even when the individual determinations are extremely accurate, are inherently tenuous at best.

VII. Disproportionation vs. Combination as a Function of Structure

One of the most successful techniques (also replete with its own set of pitfalls) available to an experimentalist studying reaction mechanisms is to examine a series of related species or compounds in the same reaction while holding all other variables constant, and by competitive or comparative techniques arrive at conclusions about mechanism from the known structural variations. This approach, especially fruitful as a diagnostic in free radical chemistry, has been central in the development of information and notions about the fate of radical pairs.

Data here and in all tables in this section have been chosen as near to 25° as possible, the varying observations on the effect of temperature changes having already been discussed. The values given are those judged by the current authors as the most reliable either on the basis of agreement among laboratories using different methods or (when a limited number of independent studies is available) that value obtained by the most reliable technique or most recently if the workers have shown where earlier studies incurred experimental errors affecting the observed k_d/k_c.[110]

(110) The symbol Δ is used interchangeably with k_d/k_c and $\Delta/\beta H$ is Δ divided by the total number of hydrogens available for abstraction (for an autoreaction this is twice the number of β hydrogens on the radical). $\Delta(R_1\cdot, R_2\cdot)$ connotes the ratio of $R_1H + R_2(-H)$ to R_1-R_2, and in parts

A. Gas Phase

1. Auto Reactions

Table VII presents the available data for pairs of the same radicals in the gas phase. A generalization[105] that has been often quoted (and seems to still persist) is that for alkyl radicals Δ varies with the number of β H's available for abstraction in the disproportionation reaction. Early values for k_d/k_c of tert-butyl, isobutyl, and sec-butyl radicals generated by photolysis of the respective symmetrical ketones at 100° were 4.6, 0.42, and 2.3, respectively. These are in the ratio 10/0.9/5.0, quite close to the number of β H's, 9/1/5. Also, the disproportionation of sec-butyl produced the statistical ratio of 1- to 2-butenes, 3 to 2. A subsequent determination of 0.70 for the k_d/k_c of n-butyl (by photolysis of n-valeraldehyde) led Kerr and Trotman-Dickenson[107] to question the generalization (the value predicted was 0.9), particularly since they also found a temperature dependence (section VI.A) of the ratio. In 1962, a value of 0.95 was reported for n-butyl.[111]

Calvert later noted[103] that these values (found and predicted) for n-butyl radical were all very high compared to generally agreed-upon k_d/k_c's for ethyl,[10,29,41,76,84] n-propyl,[24,76,101,112–114] and n-pentyl[115] (all ca. 0.15) and reinvestigated the n-butyl value by photolytically decom-

of the text (especially in Table XI and the following discussion) $\Delta'(R_1\cdot, R_2\cdot)$ will signify $\Delta(R_2\cdot, R_1\cdot)$, connoting the ratio of $R_2H + R_1(-H)$ to R_1-R_2. For a radical with two different kinds of abstractable hydrogens (two different olefins formed when it is the H donor in disproportionation), Δ_1 will be for formation of the less substituted olefin and Δ_2 for the more substituted olefin.

(111) J. C. Thynne, Trans. Faraday Soc., 58, 1533 (1962).
(112) P. Ausloos and E. Murad, J. Amer. Chem. Soc., 80, 5929 (1958).
(113) J. C. Thynne, Trans. Faraday Soc., 58, 676, 1394 (1962).
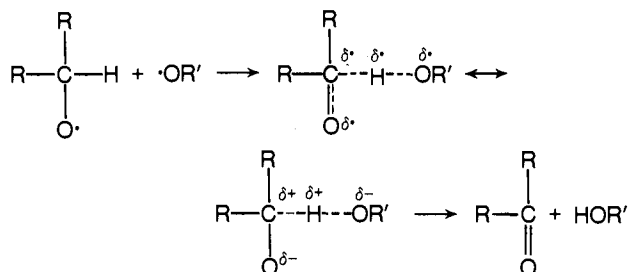(114) J. A. Kerr and A. F. Trotman-Dickenson, Trans. Faraday Soc., 55, 572 (1959).
(115) M. H. J. Wijnen, J. Amer. Chem. Soc., 83, 3752 (1961).

posing the symmetrical azo compound $(n\text{-}C_4H_9\text{-}N{=}N\text{-}C_4H_9\text{-}n)$. Very careful and thorough product analysis gave $k_d/k_c = 0.14$, constant from 20 to 130°C. The previous experiments and generalization were thus seriously questioned. Subsequently, the isobutyl radical was reinvestigated by Terry and Futtrell[90] and by Calvert, et al.,[104] both via azo compound photolysis, and the much lower value of 0.076 (originally 0.4) was found in both studies. For sec-butyl, the best value seems to be about 0.7 (see footnote h to Table VII), although there is still some doubt here. The tert-butyl radical also has been revised downward based on two careful studies using azo compound photolysis[87] and hydrogen atom addition to isobutylene (see footnote i, Table VII).[29,30]

Two salient considerations emerge from this historical summary. First, there is no basis for the purely statistical generalization for even simple alkyl radicals in the gas phase, and we certainly expect to see additional complications for more complex radicals or for medium changes. Second, the trend is that side reactions producing interfering products usually give high, rather than low, k_d/k_c values. This is because there are few side reactions of starting materials or radicals that lead to dimers (k_c), but a number leading to either disproportionation product (k_d).

Discussion of the structural determinants and of the few branched and larger alkyls will be deferred to the next subsection and treated with the cross-reaction gas-phase data. We may note from Table VII at this stage that there is no constancy of $\Delta/\beta H$ for primary, secondary, or tertiary radicals, even for abstraction of primary, secondary, or tertiary hydrogens if the group next to the hydrogen to be abstracted is varied. While cyclohexyl[116] is about normal for a secondary radical, the cyclopentyl[100] value seems a bit high. This latter k_d/k_c was obtained via mercury photosensitized decomposition of cyclopentane and is suspect.

It is clear that alkoxy radicals give very high fractions of disproportionation,[21,117–119] this having been attributed to increased polar contributions to the transition state for disproportionation.[119] Gray[75] has collected k_d/k_c data for

$$R{-}\underset{\underset{O\cdot}{|}}{\overset{\overset{R}{|}}{C}}{-}H \;+\; \cdot OR' \;\longrightarrow\; R{-}\underset{\underset{O^{\delta\cdot}}{|}}{\overset{\overset{R}{|}}{C}}\overset{\delta\cdot}{\cdots}H\overset{\delta\cdot}{\cdots}OR' \;\longleftrightarrow$$

$$R{-}\underset{\underset{O^{\delta-}}{|}}{\overset{\overset{R}{|}}{C}}\overset{\delta+}{\cdots}H\overset{\delta-}{\cdots}OR' \;\longrightarrow\; R{-}\overset{\overset{R}{|}}{\underset{\underset{O}{\|}}{C}} \;+\; HOR'$$

alkoxy radicals in the gas phase and generalized that $\Delta(X,Y)$ values (X abstracts from Y) lie in three groups: $\Delta(NO,CH_3O\cdot) \sim \Delta(NO,CH_3CH_2O\cdot) \sim \Delta(NO_2,CH_3O\cdot$ or $CH_3CH_2O\cdot)$ is between 0.1 and 0.5; $\Delta(\text{alkyl,alkoxy}) \sim \Delta(\text{alkoxy,alkyl})$ is between 1 and 3; $\Delta(\text{alkoxy,alkoxy})$ is close to 10. He pointed out that the Δ data for alkoxy radicals clearly do not follow the Bradley relationship involving only ΔS.

Unfortunately, few carbon-centered radicals other than the small alkyls have been studied in the gas phase, although Rabinovitch has recently reported several studies

on branched large alkyl[30,120–123] radicals. It would be valuable to have data for the α-aryl and nitrile groups, since comparison among H, alkyl, C_6H_5, and CN substituents at the α position in the gas phase would be much more interpretable than in solution, and would allow for comparing the results in the two phases.

2. Cross Reactions

Table VIII presents the available data for gas-phase reactions between different radicals. The table is arranged first in order of increasing complexity of the abstracting radical (given first) and then the radical being abstracted from.

When the abstracting radical is constant, there is only a very rough correlation with the number of β H's, clearly a dependence upon the structure of the second radical being abstracted from or combined with. For methyl radical abstracting from ethyl, isopropyl, and tert-butyl in each case a methyl group is being abstracted from, but the product olefin is increasingly stable in the series. While it is not clear whether there should be steric differences in the abstractions, there is clearly a steric variation in the combinations. Both energetically and sterically the Δ values should increase in the series, as is observed. This same trend is manifest several places in Table VIII. Cursory examination of the table also reveals a variation for a series of $R_1\cdot$ radicals abstracting from or combining with the same $R_2\cdot$.

In order to compare those cases for which data are available for abstraction from vs. combination with one radical $(R_2\cdot)$ by a series of others $(R_1\cdot)$, some of the values given in Tables VII and VIII have been combined in Table IX. These data suffer somewhat from their inter-laboratory character, and there are many blank spaces, but it is worthwhile to examine the situation as it stands. A complete and reliable set of data here, at least for the small radicals, would be valuable.

As we go down a column in Table IX (one $R_2\cdot$), there is an increasing tendency for the more substituted radicals $R_1\cdot$ to abstract rather than combine. This trend seems to be distinctly more pronounced than the trend going across a row (neglecting the last $R_2\cdot$ entry, cyclohexadienyl) in which a given radical $(R_1\cdot)$ either abstracts from or recombines with increasingly substituted $R_2\cdot$'s. This is not the result expected from simple considerations of olefin stability since all $R_2\cdot$ entries in a column produce the same olefin, while going across a row produces increasingly stable olefins. Basically, the recombination energetics are very similar for either series (down or across). This all amounts to the generalization that secondary and tertiary radicals seem to be better abstractors than abstractees. For example, the pair tert-butyl $(R_1\cdot)$ and ethyl $(R_2\cdot)$ give a larger per βH fraction of isobutane and ethylene than ethyl $(R_1\cdot)$ and tert-butyl $(R_2\cdot)$ give ethane and isobutylene. Indeed, the former process has almost the same $\Delta/\beta H$ as for two tert-butyl radicals. It is almost inescapable to conclude that steric hindrance is the determining factor. A more detailed analysis along these lines is presented later.

Included in Tables VII and VIII are a number of variously substituted 2-alkyl radicals (mostly studied in Ra-

(116) P. W. Beck, D. V. Kneibes, and H. E. Gunning, J. Chem. Phys., 22, 672 (1954).

(117) J. Heicklen and H. S. Johnston, J. Amer. Chem. Soc., 84, 4030, 4394 (1962).

(118) J. C. Thynne and P. Gray, Trans. Faraday Soc., 59, 1149 (1963).

(119) D. F. Dever and J. G. Calvert, J. Amer. Chem. Soc., 84, 1362 (1962).

(120) C. W. Larson, B. S. Rabinovitch, and D. C. Tardy, J. Chem. Phys., 47, 4570 (1967).

(121) C. W. Larson and B. S. Rabinovitch, J. Chem. Phys., 52, 5181 (1970).

(122) C. W. Larson, E. A. Hardwidge, and B. S. Rabinovitch, J. Chem. Phys., 50, 2769 (1969).

(123) C. W. Larson and B. S. Rabinovitch, J. Chem. Phys., 51, 2293 (1969).

TABLE VIII. Cross Disproportionation–Combination Reactions in the Gas Phase
(the first radical abstracts from the second in disproportionation)

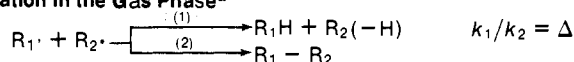| Entry	Radicals R_1	R_2	k_d/k_c (Δ)	$\Delta/\beta H$	Source, T (°C)	Ref
1	$CH_3\cdot$	$CH_3CH_2\cdot$	0.039^a	0.013	Wide variety	76, 101, 24
2		$CH_3CH_2CH_2\cdot$	$(0.033)^b$ 0.058	(0.016) 0.029	c, 118–144; d, 25	76, 101, 24
3		$CH_3CH_2CH_2CH_2\cdot$	$(0.15)^e$	(0.075)	f, 75–186	111
4		$CH_3CH_2CH_2CH_2CH_2\cdot$	$(\sim0.1)^e$	(~0.05)	g, 63 and 91	115
5		$CH_3\dot{C}HCH_3$	0.163^h	0.027	d, 25	76
6		$CH_3CH_2\dot{C}HCH_3$	$(0.3)^{i,j}$ 0.08^j	(0.06) 0.016	k, −103–25; l, 107–168	k; l
7		$(CH_3)_2CH\dot{C}HCH_3$	0.18^m	0.045	n, 25	120
8		$(CH_3)C\cdot$	$(0.70,^e 0.85)^o$	(0.078, 0.094)	g, 80–188; p, 20–60	p
9		Cyclo-$C_6H_7\cdot^{ff}$	0.27	0.135	q, 23–117	124
10		$CH_3O\cdot$	1.51	0.50	r, 124–155	118
11	$C_2H_5\cdot$	$CH_3CH_2CH_2\cdot$	0.066^s	0.033	d, 25	76
12		$CH_3CH_2CH_2CH_2\cdot$	0.08	0.04	t, 0–25	27
13		$(CH_3)_2CHCH_2\cdot$	0.04^u	0.04	n, 25	120
14		$(CH_3)_2CH\cdot$	0.20^v (0.4)	0.033 (0.067)	d, 25 and w, 25 (g, 48–112)	76, 74, 89
15		$(CH_3)_3C\cdot$	0.52^x	0.058	d, 25; w, 25; g, 75; n, 25	90, 74, 89, 120
16		$CH_3CH_2\dot{C}(CH_3)_2$	0.60^y	. . .	w, 25	74
17		$(CH_3)_3C\dot{C}HCH_3$	0.21	0.07	w, 25	74
18		$CH_3CH_2\dot{C}HCH_3$	0.23^y	. . .	w, 25	74
19		$(CH_3)_3CCH_2\dot{C}HCH_3$	(Δ_1) 0.28 (Δ_2) 0.10	0.093 0.05	n, 25	30
20		Cyclo-$C_5H_9\cdot$	0.26	0.065	w, 25	74
21		Cyclo-$C_6H_7\cdot^{ff}$	0.38	0.19	z, 34–118	124
22		$CH_2{=}CHCH_2\cdot$	0.047	0.047	aa, 134–175	aa
23	$CH_3CH_2CH_2\cdot$	$CH_3CH_2\cdot$	0.058	0.019	d, 25; c, 61–127	76; 101
24	$(CH_3)_2CHCH_2\cdot$	$CH_3CH_2\cdot$	0.04	0.013	d, 25	90
25	$(CH_3)_3CCH_2\cdot$	$(CH_3)_3CCH_2CH(CH_3)\dot{C}HCH_3$	0.32^y	. . .	n, 25	122
26	$CH_2{=}CHCH_2\cdot$	$CH_3CH_2\cdot$	0.13	0.043	aa, 134–175	aa
27		Cyclo-$C_6H_7\cdot^{ff}$	0.10	0.050	bb, 130–190	bb
28	$(CH_3)_2CH\cdot$	$CH_3CH_2\cdot$	0.16	0.053	g, 48–112	76, 89
29		$CH_3CH_2\dot{C}HCH_3$	$(0.4)^y$	. . .	cc	84
30		$CH_3CH_2CH_2\cdot$	0.41	0.20	d, 25; n, 25	76, 29
31		$(CH_3)_3C\cdot$	0.7	0.08	g, 75	89
32		$(CH_3)_2CHCH(CH_3)\dot{C}HCH_3$	0.54^y	. . .	n, 25	120
33		$(CH_3)_2CHCH_2\dot{C}(CH_3)_2$	(Δ_1) 0.95 (Δ_2) 0.23	0.16 0.12	n, 25	30
34		Cyclo-$C_6H_7\cdot^{ff}$	0.52	0.26	z, 27–100	124
35	$CH_3CH_2\dot{C}HCH_3$	$(CH_3)_2CH\cdot$	(0.4)	(0.067)	cc	84
36		$CH_3(CH_2)_2CH_2\cdot$	0.45	0.22	n, 25	29
37		$(CH_3)_3C\cdot$	(0.23)	(0.026)	cc	84
38	$(CH_3)_3CCH_2\dot{C}HCH_3$	$CH_3CH_2\cdot$	0.23	0.077	n, 25	30
39		$(CH_3)_3C\cdot$	0.81	0.09	n, 25	30
40	$CH_3CH_2C(CH_3)_2CH_2\dot{C}HCH_3$	$CH_3CH_2\dot{C}(CH_3)_2$	(Δ_1) 0.9 (Δ_2) 0.4	0.15 0.2	n, 25	123
41	$(CH_3)_2CHCH(CH_3)\dot{C}HCH_3$	$(CH_3)_2CH\cdot$	0.40	0.067	n, 25	120
42	$(CH_3)_3CCH(CH_3)\dot{C}HCH_3$	$(CH_3)_3C\cdot$	0.7	0.078	n, 25	121
43	$CH_3CH_2CH_2C(CH_3)_2\dot{C}HCH_3$	$CH_3CH_2\dot{C}(CH_3)_2$	(Δ_1) 0.9 (Δ_2) 0.1	0.15 0.05	n, 25	123
44	$(CH_3)_3C\cdot$	$CH_3CH_2\cdot$	0.32^{dd}	0.10	d, 25; g, 75; n, 25	30, 89, 90
45		$(CH_3)_2CH\cdot$	0.67	0.11	g, 75	89
46		$CH_3CH_2\dot{C}HCH_3$	(2.0)	(0.4)	cc	84
47		$(CH_3)_3CCH_2\dot{C}HCH_3$	(Δ_1) 0.67 (Δ_2) 0.21	0.22 0.10	n, 25	30
48		$(CH_3)_3CCH(CH_3)\dot{C}HCH_3$	1.4^y	. . .	n, 25	121
49		Cyclo-$C_6H_7\cdot^{ff}$	1.33	0.67	g, 27–100	124
50	$CH_3CH_2\dot{C}(CH_3)_2$	$CH_3CH_2CH_2C(CH_3)_2\dot{C}HCH_3$	1.0	0.33	n, 25	123
51		$CH_3CH_2C(CH_3)_2CH_2\dot{C}HCH_3$	1.0^y	. . .	n, 25	123
52	$(CH_3)_2CHCH_2\dot{C}(CH_3)_2$	$(CH_3)_2CH\cdot$	0.89	0.15	n, 25	30
53	$ClCH_2CH_2\cdot$	$CH_3CH_2\cdot$	0.22	0.073	ee	129
54	$Cl_3C\cdot$	$CH_3CH_2\cdot$	0.22	0.073	ee	129
55		$ClCH_2CH_2\cdot$	0.14	0.070	ee	129

TABLE VIII (Footnotes)

[a] Average of a large number of values collected in ref 101. Two determinations (ref 113 and C. A. Heller, J. Chem. Phys., **28**, 1255 (1958)) disagree with a dozen or so others and have been criticized.[76] [b] References 24 and 76 discuss earlier values, some of which are in disagreement.[112,113] Values in parentheses are either questionable because of technique used but are the only data available for that pair, or, if more data are also shown, they disagree with the other values and seem the less preferred. Values that have been shown to be incorrect have been omitted from the table. [c] Mixed ketone and RN_2R photolysis. [d] Mixtures of azo compounds and mixed azo compounds, photolysis. [e] For systems in which the data have been redetermined and compared with other methods of generation, these techniques usually have been found to give higher values of k_d/k_c. [f] Mixed acetone and alkyl formate photolysis. [g] Ketone photolysis. [h] References 85 and 113 give higher values. [i] The value for 2-sec-butyl by B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys., **30**, 375 (1959), upon which this cross k_a/k_d is dependent, was later changed by these authors. [j] Total disproportionation (to give 1- and 2-butene, cis and trans). [k] From H· addition to 2-butene, giving some CH_3· by decomposition and subsequent reaction with olefin: B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys., **30**, 735 (1959). [l] Thermolysis of di-tert-butyl peroxide with propylene: M. Miyoshi and R. K. Briton, ibid., **36**, 3019 (1962). [m] Statistical removal of primary and tertiary hydrogens. [n] H· addition to olefin. Much more reproducible data than in cc (ref 84). [o] This study gave a very high value for $2(CH_3)_3C$·, and also involved a reaction $(t\text{-}BuOO\text{-}t\text{-}Bu \rightarrow 2t\text{-}Bu\cdot + O_2)$ which, if actually occurring, is likely to give rise to excited radicals. Photolysis, short wavelength, of di-tert-butyl peroxide with acetylene: H. M. Frey, Proc. Chem. Soc., London, 385 (1959). [q] Photolysis of RN_2R and cyclohexadiene. [r] Dimethyl peroxide decomposition with methyl formate. [s] Reference 27, using mercury-sensitized alkane photolysis, is in close agreement, and ref 101 (ketone photolysis) is fairly close; J. C. J. Thynne, Proc. Chem. Soc., London, **18**, 68 (1961), shows two other methods in disagreement with each other and with other studies. [t] Photolysis at 1849 Å of Hg and RH, with $^{14}C_2H_4$. [u] Reference 27, using Hg-photosensitized alkane decomposition, gives a value of 0.02 ± 0.02 for this cross reaction. [v] Other determinations group around 0.2 (R. O. Brinton and E. W. R. Steacie, Can. J. Chem., **33**, 1840 (1955), and ref 84, or about 0.4 (J. C. Thynne, Proc. Chem. Soc., London, **18**, 68 (1961). [w] Photolysis at >2000 Å of Hg and RH, with $^{14}C_2H_4$. [x] Reference 84 gives 0.3. [y] Both disproportionation products together. [z] Photolysis of ketone and cyclohexadiene. [aa] Photolysis of $(C_2H_5)_2CO$ plus biallyl: D. G. L. James and G. E. Troughton, Trans. Faraday Soc., **62**, 145 (1966). [bb] Thermolysis of $C_6H_7CO_2CH_2CH=CH_2$ (see footnote ff). D. G. L. James and S. M. Kambanis, ibid., **65**, 2081 (1969). [cc] H· addition to olefins. Much of these data are of questionable accuracy owing to competing processes and excited

radicals. [dd] Reference 84 gives 1.7 for this ratio (Hg*, H_2, alkene). [ee] Photolysis of CCl_4, C_2H_6, and C_2H_4. [ff] Cyclo-C_6H_7 = ⬡ .

TABLE IX. Combination–Disproportionation in the Gas Phase[a]

$$R_1\cdot + R_2\cdot \begin{array}{c} \xrightarrow{\quad(1)\quad} R_1H + R_2(-H) \\ \xrightarrow{\quad(2)\quad} R_1 - R_2 \end{array} \qquad k_1/k_2 = \Delta$$

					$\Delta/\beta H$			
$R_1\cdot$	$R_2\cdot = CH_3CH_2\cdot$	$RCH_2CH_2\cdot$	$(CH_3)_2\text{-}CHCH_2\cdot$	$(CH_3)_2CH\cdot$	$(CH_3)_3\text{-}C\dot{C}HCH_3$	$(\dot{C}H_3)_3C\cdot$	$(CH_3)_3CCH_2\text{-}\dot{C}HCH_3$	Cyclo-$C_6H_7\cdot$,[b]
$CH_3\cdot$	0.013	0.03		0.03		0.08		0.14
$C_2H_5\cdot$	0.022	0.04	0.04	0.03	0.07	0.06	$\Delta_1 = 0.09$ $\Delta_2 = 0.05$	0.19
$CH_3CH_2CH_2\cdot$	0.019	0.035						
$(CH_3)_2CHCH_2\cdot$	0.013		0.04					
$(CH_3)_2CH\cdot$	0.053	0.20		0.06		0.06		0.26
$(CH_3)_3C\cdot$	0.10			0.11		0.13	$\Delta_1 = 0.22$ $\Delta_2 = 0.10$	0.67
$(CH_3)_3CCH_2\dot{C}HCH_3$	0.077					0.09	$\Delta_1 = 0.18$ $\Delta_2 = 0.10$	

[a] Data are from Tables VII and VIII. [b] Cyclo-$C_6H_7\cdot$ = ⬡ .

TABLE X. Ratios of 1- to 2-Olefin from α-Methyl Radicals in the Gas Phase[a]

Entry	$R_1\cdot$	$R_2\cdot$	Δ_1/Δ_2	$(\Delta_1/\beta H_1)/(\Delta_2/\beta H_2)$[b]
1	⌇	⌇	1.5 (1.1)[c]	1.0 (0.7)[c]
2	$CH_3\cdot$	⌇	3.1	1.03
3	⌇	⌇	2.8	0.93
4	⌇	⌇	2.2	0.7
5	⌇	⌇	2.7	0.90
6	⌇	⌇	4.0	1.3
7	⌇	⌇	3.3	1.1
8	$C_2H_5\cdot$	⌇	2.8	1.9
9	⌇	⌇	3.0	2.0
10	⌇	⌇	3.2	2.1

[a] All values are from Tables VII and VIII. [b] $(\Delta_1/\beta H_1)/(\Delta_2/\beta H_2) = (\Delta_1/\Delta_2)/(\beta H_1)/(\beta H_2) = (\Delta_1/\Delta_2)/(\text{statistically expected ratio})$. [c] See footnote h of Table VII.

binovitch's laboratory) that upon disproportionation as $R_2\cdot$ may produce either a 1-olefin by loss of an H from a CH_3 or a 2-olefin by loss of an internal H. The ratio of 1-olefin to 2-olefin, and the same value divided by the number of β H's, is given in Table X. These data represent solely the relative propensities for abstraction at the two positions because k_c is cancelled out in the ratio of ratios. For the cases where the internal H is relatively unhindered by substitution β to it in $R_2\cdot$, the result is generally close to statistical abstraction or shows a small preference for internal olefin formation (entries 1–5, Table X). Entries 6 and 7, for 2,4-dimethyl-2-pentyl, are intermediate, while for 4,4-dimethyl-2-pentyl (entries 8–10) there is a twofold preference for abstraction from the CH_3. The site adjacent to the internal CH_2 group in the last case is quaternary, leading to the conclusion that the increased Δ_1/Δ_2 arises from hindrance to approach by $R_1\cdot$ at the CH_2.

Data on trans/cis ratios for those olefins capable of such stereoisomerism when formed in disproportionation were omitted from the previous tables. Rabinovitch has found that for ethyl, tert-butyl, and 4,4-dimethyl-2-pentyl radicals abstracting from 4,4-dimethyl-2-pentyl radical the ratios of trans/cis 2-olefin are 33, 29, and 28, respectively. Apparently this ratio is independent of the $R_1\cdot$ and is the result of a steric effect that is a manifestation of an energy barrier in the abstraction. The autodisproportionation of 2-butyl radicals produces a trans/cis ratio

TABLE XI. Disproportionation Competitions in the Gas Phase^a

Entry	R$_1$•	R$_2$•	Δ/Δ'^{b,c}	(Δ/βH)/(Δ'/βH')^d
1	CH$_3$CH$_2$•	CH$_3$CH$_2$CH$_2$•	0.066/0.058 = 1.14	0.033/0.019 = 1.74
2	CH$_3$CH$_2$•	(CH$_3$)$_2$CHCH$_2$•	0.04/0.04 = 1.00	0.04/0.013 = 3.08
3	CH$_3$CH$_2$•	(CH$_3$)$_2$CH•	0.20/0.16 = 1.25	0.033/0.05 = 0.62
4	CH$_3$CH$_2$•	(CH$_3$)$_3$C•	0.52/0.32 = 1.62	0.058/0.10 = 0.58
5	CH$_3$CH$_2$•	CH$_2$=CHCH$_2$•	0.047/0.13 = 0.36	0.047/0.043 = 1.09
6	CH$_3$CH$_2$•	(CH$_3$)$_3$CCH$_2$ĊHCH$_3$	(Δ$_1$/Δ') 0.28/0.23 = 1.22 (Δ$_2$/Δ') 0.10/0.23 = 0.44 (Δ$_{tot}$/Δ') = 1.66	0.093/0.077 = 1.21 0.05/0.077 = 0.65 1.00
7	(CH$_3$)$_2$CH•	(CH$_3$)$_3$C•	0.7/0.67 = 1.04	0.08/0.11 = 0.73
8	(CH$_3$)$_2$CH•	(CH$_3$)$_2$CHCH$_2$Ċ(CH$_3$)$_2$	(Δ$_1$/Δ') 0.95/0.89 = 1.07 (Δ$_2$/Δ') 0.23/0.89 = 0.26 (Δ$_{tot}$/Δ') = 1.33	0.16/0.15 = 1.07 0.12/0.15 = 0.80 1.00
9	(CH$_3$)$_2$CH•	(CH$_3$)$_2$CHCH(CH$_3$)ĊHCH$_3$	(Δ$_{tot}$/Δ') 0.54/0.40 = 1.35	0.14/0.067 = 2.09
10	(CH$_3$)$_3$C•	(CH$_3$)$_3$CCH$_2$ĊHCH$_3$	(Δ$_1$/Δ') 0.67/0.81 = 0.83 (Δ$_2$/Δ') 0.21/0.81 = 0.26 (Δ$_{tot}$/Δ') = 1.09	0.22/0.09 = 2.44 0.10/0.09 = 1.11 1.96
11	(CH$_3$)$_3$C•	(CH$_3$)$_3$CCH(CH$_3$)ĊHCH$_3$	1.4/0.7 = 2.0	0.35/0.078 = 4.49
12	(CH$_3$)$_2$ĊCH$_2$CH$_3$	C$_2$H$_5$C(CH$_3$)$_2$CH$_2$ĊHCH$_3$	(Δ$_{tot}$/Δ$_1$') 1.0/0.9 = 1.11 (Δ$_{tot}$/Δ$_2$') 1.0/0.4 = 2.5 (Δ$_{tot}$/Δ'$_{tot}$) 1.0/1.3 = 0.77	0.2/0.15 = 1.33 0.2/0.2 = 1.0 1.23
13	(CH$_3$)$_2$ĊCH$_2$CH$_3$	n-C$_3$H$_7$C(CH$_3$)$_2$ĊHCH$_3$	(Δ/Δ$_1$') 1.0/0.9 = 1.11 (Δ/Δ$_2$') 1.0/0.1 = 10.0 (Δ/Δ'$_{tot}$) = 1.0	0.33/0.15 = 2.20 0.33/0.05 = 6.60 2.67^e

^{a} Data from Table VIII. ^{b} Δ/Δ' = $(k_d/k_c)/(k_d'/k_c)$ = k_d/k_d', where k_d is for formation of R$_1$H + R$_2$(−H), and k_d' is for the process giving R$_1$(−H) + R$_2$H. ^{c} For unsymmetrical radicals with two different kinds of β H's (two olefins possible), Δ$_1$ is for abstraction of primary H (to give 1-olefin), Δ$_2$ for abstraction of internal H (to give 2-olefin). Δ$_{tot}$ is for the total olefin formation in cases where the two products were not reported separately. ^{d} Each Δ is divided by the number of β H's to give that olefin. For cases with two olefins formed, if measured separately, Δ$_1$/βH$_1$ and Δ$_2$/βH$_2$ are given; if not separated Δ$_{tot}$/βH$_{tot}$ is given (for statistical abstraction, this ratio is 1.0.). ^{e} (Δ$_{tot}$/βH$_{tot}$)/(Δ'$_{tot}$/βH'$_{tot}$).

of approximately 3. The $\Delta\Delta H_f°$ values between cis and trans olefins for 4,4-dimethyl-2-pentene and 2-butene are, respectively, about 4.1 and 1.2 kcal/mol, qualitatively in the direction of the ratios found in the reaction. While awaiting temperature dependence studies in these systems, Rabinovitch reiterated his earlier position that the transition states for combination and disproportionation are different and suggested that there may be real energy barriers in these reactions. Subsequent more direct work (sections III and VI), especially by Benson, confirms this conclusion.

To construct tables of intermolecular Δ ratios such that k_c values cancel out requires a large amount of very accurate data, but the cases for which values are available have been so treated in Table XI. For the last column, a ratio greater than unity shows preferential (greater than statistical) abstraction by R$_1$• from R$_2$•. For example, entry 1 indicates that a secondary β H of n-propyl radical is 1.7 times as prone to abstraction by ethyl as is a primary β H of ethyl to abstraction by n-propyl. A ratio less than unity indicates the reverse situation; i.e., in entry 3 an ethyl primary H is 1.6 (1/0.62) times more prone to removal by isopropyl than is an isopropyl primary H to removal by ethyl.

Entries 1 and 2 show both n-propyl (secondary β H) and isobutyl (tertiary β H) being preferential H donors to ethyl while entries 3 and 4 show that isopropyl and tert-butyl preferentially abstract from the primary β H of ethyl radical rather than be donors to it (they are also primary β H donors). This same effect is also manifest by tert-butyl being a more effective abstractor from isopropyl than the reverse (entry 7). For the simple radicals, then, we see again by this analysis the preference for abstraction by, rather than from, the more α-substituted radical — in the direction opposed to that giving the more stable olefin. Also following this generalization is the pair 2-methyl-2-butyl radical with 4,4-dimethyl-2-hexyl (Δ$_1$' and Δ$_{tot}$ ratios > 1, entry 12). Comparing this latter result

with that for 2-methyl-2-butyl and 3,3-dimethyl-2-hexyl (entry 13), there is another twofold overall increase in preference for attack by the same tertiary radical upon the more hindered secondary radical, as opposed to the reverse process.

The cross-disproportionation between the two secondary radicals, isopropyl and 3,4-dimethyl-2-pentyl (entry 9 of Table XI), shows a twofold preference for abstraction by isopropyl rather than from it. Unfortunately Δ$_1$/Δ$_2$ data are not available here, but based on the similar 3-methyl-2-butyl radical (entry 3 of Table X) the ratio is likely approximately statistical or with a preference for abstraction at the CH$_3$ of 3,4-dimethyl-2-pentyl. The preference for abstraction by isopropyl is very unlikely to be an energetic effect, but rather steric.

Finally, we may note the high value for tert-butyl with 4,4-dimethyl-2-pentyl (entry 10) and the largest effect of the entire table, tert-butyl with 3,4,4-trimethyl-2-pentyl (entry 11). In the former, abstraction from the methylene position is hindered by a neighboring tert-butyl group, while in the latter case this effect is accentuated by the addition of another methyl substituent on the large branched radical, but the net effect is to cause increases in abstraction by tert-butyl and diminish abstraction by the larger radical upon tert-butyl. This observation is in accord with the generalization noted in relation to the small radicals of Table IX, in which increasing substitution caused a preference for hydrogen atom acceptance, rather than donation, in disproportionation.

Referring back, now, to Table VIII, the series of reactions 9, 21, 34, and 49 represent large excesses of alkyl radicals (methyl, ethyl, isopropyl, and tert-butyl) reacting with cyclohexadienyl radical (thus avoiding autocyclohexadienyl reactions).[87,124] No cyclohexadiene (by cyclohexadienyl abstraction from alkyl radical) was formed from any of these reactions. All the Δ values are high,

(124) D. G. L. James and R. D. Stuart, Trans. Faraday Soc., 64, 2735 (1968).
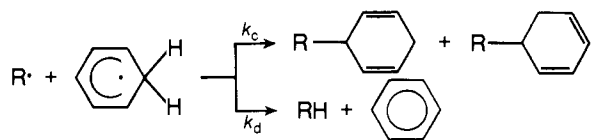
presumably reflecting the stability of the incipient aromatic system in the disproportionation step. This must be reflecting, in turn, an energy barrier for the process. Arguing against the four-centered common transition state for disproportionation and combination, James and Stuart interpreted the regular increase in the series in terms of the Benson approach using ionic configuration contributions to the transition state. They assumed that the ionic contribution is greater for the disproportionation than the combination process (but no rationalization for this proposal is offered). Since the ionization potentials of the radicals decrease monotonically in the series methyl, ethyl, isopropyl, tert-butyl while the electron affinities are close to constant, and also since the cyclohexadienyl anion is a much weaker base than the alkyl anion, the conclusion was that the alkyl radicals are electron donating and cyclohexadienyl electron accepting in the transition state in this system. Reaction 27, allyl plus cyclohexadienyl, gave a low (compared to alkyl plus cyclohexadienyl) k_d/k_c value (and also generated 1–3% cyclohexadiene). This result is similar to the observation in solution for all cumyl and α-cyano radicals that two highly stabilized and delocalized radicals seem to give unusually high combination yields (this will be discussed in the following section).

Finally, with data such as discussed in this section Rabinovitch reexamined the log k_d/k_c vs. $S_d°-S_c°$ relationship,[30] the result of which study was discussed in section III. At this time, there is no general way of correlating or predicting k_d/k_c values in the gas phase, although the more limited generalizations offered at different stages of the above discussion will likely hold.

B. Liquid Solution

Table XII presents the available data in solution.[125] These data have been selected using the criteria given at the beginning of section VII, but for studies in which solvent and temperature were extensively varied, we have in some cases omitted some of the experiments. Values as close as possible to room temperature were selected.

Here we have a much broader range of radicals and, with our current limited understanding of solvation, a much more difficult situation to analyze. It is again clear that, for a given medium, there is a dependence upon more than just the statistical number of β H's. Studying autoalkyl radical reactions at 30° in n-pentane and decalin, Kochi noted that $\Delta/\beta H$ tended to group around 0.03 for primary radicals (ethyl, n-propyl, n-butyl), 0.1 for secondary radicals (isopropyl and sec-butyl), and 0.4 for tertiary (tert-butyl).[20] These generalizations are based on rather limited data, however, and the last value is almost certainly incorrect. From the sec-butyl radical, the ratio of 1-butene to trans- to cis-2-butene is 5 to 3 to 1, close to the thermodynamically expected value for the 2-butenes, but with more 1-butene than expected thermodynamically.

Within Table XII there are some striking substituent

effects to be noted. With the exception of the very hindered 3,3-dimethyl-2-cyanobutyl radical (entry 15),[125a] all the α-CN alkyl radicals give very low $\Delta/\beta H$ values in comparison to tertiary alkyl radicals. Secondary aryl-substituted radicals (entries 21–30) also show a *decreased* disproportionation yield compared to, e.g., sec-butyl or isopropyl. A major substituent effect, noted originally by Nelsen and Bartlett,[5] is the striking change from two tert-butyl radicals (entry 6; Δ = 4.5, $\Delta/\beta H$ = 0.25) to two cumyl radicals (entry 31; Δ = 0.054, $\Delta/\beta H$ = 0.0045), the former value fairly close to that in the gas phase. On a per H basis, this represents a 50-fold decrease in k_d/k_c upon substitution of a phenyl for a methyl group. The same substitution of a phenyl for a methyl comparing an isopropyl pair ($\Delta/\beta H$ = 0.10) to an α-phenylethyl pair ($\Delta/\beta H$ extrapolates to 0.029 at 30°) shows only a three- to fourfold decrease. Looking at this effect another way, while replacement of an α-hydrogen with a methyl group (isopropyl ($\Delta/\beta H$ $\approx$ 0.10) vs. tert-butyl radical ($\Delta/\beta H$ $\approx$ 0.25)) results in a two- to threefold *increase*, qualitatively in agreement with all the gas-phase data, the same replacement for aralkyl radicals (α-phenylethyl ($\Delta/\beta H$ $\approx$ 0.03) vs. cumyl ($\Delta/\beta H$ = 0.0045)) shows a sixfold *decrease*.

This unique behavior of cumyl radicals has been speculated about by a number of recent workers. Bartlett, focusing on the comparison with tert-butyl, suggested delocalization of the odd electrons as an explanation but could not rationalize the fact that disproportionation selectively is retarded. Hammond[64] considered a solvation effect. Neuman,[126] noting that the effect is peculiar to a *pair* of cumyl radicals (i.e., the cyclohexyl-cumyl cross reactions, entries 38 and 39, are about "normal") postulated a sandwich complex of two cumyls that geometrically favors coupling. The delocalization of cumyl, however, is not much greater than that of α-phenethyl which does not show the low k_d/k_c, and it is hard to envision the proposed complexing being so specific for cumyl to the exclusion of the other α-aralkyl radicals. It is interesting to note that it is those radicals which give abnormal coupling (i.e., by attack at the para position of cumyls and at the nitrogen of α-cyano radicals[9,96,127,128]) that give the low k_d/k_c values in solution.

For the secondary α-aralkyl radicals there is no obvious pattern for $\Delta/\beta H$ variation with structure at 118°, but as discussed in section VI a trend emerges upon examination of the temperature dependencies. It would be interesting to have reliable and self-consistent data for the cycloalkyl radicals, only a few having been measured, and these from different kinds of precursors.

By photolysis of various peresters, Kochi[21] measured the cross-reaction k_d/k_c values for alkoxy-alkyl radical pairs in solution. Combination to form ether and disproportionation to give olefin and alcohol were found to be exclusively cage processes (as opposed to the alkyl-alkyl pairs from diacyl peroxide photolysis which gave varying percentages of nongeminate combination and disproportionation, depending on the particular radical (Scheme II). The data (Table XII, entries 40–48) show that for each alkoxy radical (each R') k_d/k_c increases as R varies from methyl (no alcohol possible) to ethyl to isopropyl to tert-butyl. Comparison of these data to alkyl-alkyl reactions reveals that (as in the gas phase) alkoxyl radicals have a higher propensity for disproportionation (the k_d/k_c

(125) Qualitative and semiquantitative data have been omitted from this table. Much of the pioneering and very interesting work of Overberger was usually reported in terms of isolated yields of products without total analyses, so that comparisons with the other data could be misleading: (a) C. G. Overberger, et al., J. Amer. Chem. Soc., 74, 3293 (1952); (b) ibid., 78, 1638 (1956); (c) ibid., 81, 1194 (1959), and references therein; (d) "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., 1966.

(126) R. C. Neuman, Jr., and E. S. Alhadeff, J. Org. Chem., 35, 3401 (1970).

(127) C. S. Wu, G. S. Hammond, and J. M. Wright, J. Amer. Chem. Soc., 82, 5386 (1960).

(128) J. M. McBride, J. Amer. Chem. Soc., 93, 6302 (1971).

TABLE XII. Disproportionation–Combination Ratios in Solution

Entry	Radical		k_d/k_c (Δ)	$\Delta/\beta H$	Solvent	Conditions	Ref
1	$2CH_3CH_2\cdot$		0.15, 0.12	0.025, 0.020	n-Pentane, decalin	a, 30°	20
			0.19, 0.17	0.032, 0.028	Toluene	b, 0°, 65°	41
			0.20, 0.18	0.033, 0.030	2-Propanol	b, 0°, 65°	41
			0.26, 0.23	0.043, 0.038	Ethylene glycol	b, 0°, +85°	41
			0.18, 0.16	0.030, 0.027	Isooctane	b, 0°, 25°	41
			0.15, 0.14	0.025, 0.023	Isooctane	b, 45°, 85°	41
2	$2CH_3CH_2CH_2\cdot$		0.15, 0.13	0.038, 0.032	n-Pentane, decalin	a, 30°	20
3	$2CH_3CH_2CH_2CH_2\cdot$		0.14, 0.13	0.035, 0.032	n-Pentane, decalin	a, 30°	20
4	$2(CH_3)_2CH\cdot$		1.2	0.10	Decalin	a, 30°	20
5	$2CH_3CH_2\dot{C}HCH_3$		1.0, 1.1	0.10, 0.11	n-Pentane, decalin	a, 30°	20
6	$2(CH_3)_3C\cdot$		7.2^c	0.40	n-Pentane	a, 30°	20
			4.5	0.25	Benzene	b, 20–60°	5
7	$CH_3\cdot + CH_3CH_2\cdot$		0.062, 0.054	0.021, 0.018	Isooctane	d, 0°, +85°	41
			0.092, 0.084	0.031, 0.028	Glycol	d, 0°, +85°	41
8	$2CH_2\!\!=\!\!CH(CH_2)_3CH_2\cdot$		0.12	0.03	Nujol	a, 30°	20
9	$2Cyclo\text{-}C_4H_7\cdot$		0.45, 0.50	0.056, 0.062	n-Pentane, decalin	a, 30°	20
10	$2Cyclo\text{-}C_6H_{11}\cdot$		1.1	0.14	Cyclohexane	e, 33°	e
11	$2Cyclo\text{-}C_8H_{15}\cdot$		$0.4, 0.6^f$			g	82
12	$2Cyclo\text{-}C_{10}H_{19}\cdot$		$0.8, 6.4^f$			g	82
13	$2Cyclo\text{-}C_5H_9CH_2\cdot$		<0.1	<0.05	Nujol	a, 30°	20
14	$2(CH_3)_2\dot{C}CN$		~0.1	~0.008	Toluene	h, 111°	8
15	$2(CH_3)_3C\dot{C}(CN)CH_3$		~11	~1.8	Benzene	h, 80°	125a
16	2α-Cyanocyclohexyl		0.14	0.018	Chlorobenzene	h, 100°	96, 127
17	$2(CH_3CH_2)_2\dot{C}CN$		<0.05	<0.0062	Benzene	b, 30°	128
18	$2(CH_3)_2\dot{C}CO_2H$		~0.5	~0.042	Toluene	h, 111°	8
19	$2CH_2\!\!=\!\!CH\dot{C}(CH_3)_2$		(~0)		o-Dichlorobenzene	h, 49°	i
20	$2CH\!\!\equiv\!\!C\dot{C}(CH_3)_2$		(~0)		Carbon tetrachloride	h, 42°	i
21	$2C_6H_5\dot{C}HCH_3$		0.14	0.023	Benzene	h, 105°	32
			0.097, 0.098	0.016, 0.016	Benzene, acetonitrile	h, 118°	108
			0.109, 0.090	0.018, 0.015	N,N,-Dimethylaniline, o-dichlorobenzene	h, 118°	108
22	$2p\text{-}CH_3C_6H_4\dot{C}HCH_3$		0.089, 0.094	0.015, 0.016	Benzene, acetonitrile	h, 118°	108
			0.091, 0.097	0.015, 0.016	N,N-Dimethylaniline, o-dichlorobenzene	h, 118°	108
23	$2p\text{-}CH_3OC_6H_4\dot{C}HCH_3$		0.084	0.014	Benzene	h, 118°	108
24	$2p\text{-}ClC_6H_4\dot{C}HCH_3$		0.176	0.029	Benzene	h, 118°	108
25	$2C_6H_5\dot{C}HCH_2CH_3$		0.107	0.027	Benzene	h, 118°	108
26	$2C_6H_5\dot{C}HCH_2CH(CH_3)_2$		0.095	0.024	Benzene	h, 118°	108
27	$2C_6H_5\dot{C}HCH_2C_6H_5$		0.113	0.028	Benzene	h, 118°	108
28	$2C_6H_5\dot{C}HCH(CH_3)_2$		0.037	0.018	Benzene	h, 118°	108
29	$2C_6H_5\dot{C}HCH_2CH(C_6H_5)CH_2CH_3$		<0.04	<0.01	Bromobenzene	h, 89 and 114°	125b
30	$2C_6H_5\dot{C}HCD_3$		0.052	0.0087	Benzene	h, 118°	108
31	$2C_6H_5\dot{C}(CH_3)_2$		0.054	0.0045	Benzene	b, 20°; h, 40–60°	5
			0.064, 0.066	0.0054, 0.0056	Toluene	h, 44.5°, 64°	109
32	$2p\text{-}CH_3C_6H_4\dot{C}(CH_3)_2$		0.060	0.0050	Toluene	h, 44.5°, 64°	109
33	$2p\text{-}C_2H_5C_6H_4\dot{C}(CH_3)_2$		0.084, 0.070	0.0070, 0.0058	Toluene	h, 44.5°, 64°	109
34	$2p\text{-}(CH_3)_2CHC_6H_4\dot{C}(CH_3)_2$		0.076, 0.056	0.0064, 0.0046	Toluene	h, 44.5°, 64°	109
35	$2p\text{-}(CH_3)_3CC_6H_4\dot{C}(CH_3)_2{}^j$		0.122, 0.106	0.0102, 0.0088	Toluene	h, 44.5°, 64°	109
36	$2p\text{-}BrC_6H_4\dot{C}(CH_3)_2{}^k$		0.224, 0.220	0.0186, 0.0184	Toluene	h, 44.5°, 64°	109
37	$2C_6H_5\dot{C}(CH_3)CH(CH_3)_2$		0.2–0.6	0.03–0.1	Benzene, toluene	b, 100–0°	36
38	$Cyclo\text{-}C_6H_{11}\cdot + C_6H_5\dot{C}(CH_3)_2$		1.1	0.18	Cumene	l, 110°	126
39	$C_6H_5\dot{C}(CH_3)_2 + Cyclo\text{-}C_6H_{11}\cdot$		0.24	0.06	Cumene	l, 110°	126
40	$(CH_3)_3CO\cdot$	$CH_3CH_2\cdot$	0.32	0.11	Decalin	m, 30°	21
41		$(CH_3)_2CH\cdot$	2.4	0.40	Decalin	m, 30°	21
42		$(CH_3)_3C\cdot$	19	2.1	Decalin	m, 30°	21
43	$CH_3CH_2C(CH_3)_2O\cdot$	$CH_3CH_2\cdot$	0.33	0.11	Decalin	m, 30°	21
44		$(CH_3)_2CH\cdot$	1.8	0.30	Decalin	m, 30°	21
45		$(CH_3)_3C\cdot$	27	3.0	Decalin	m, 30°	21
46	$(CH_3)_2CHC(CH_3)_2O\cdot$	$CH_3CH_2\cdot$	0.25	0.08	Decalin	m, 30°	21
47		$(CH_3)_2CH\cdot$	2.7	0.45	Decalin	m, 30°	21
48		$(CH_3)_3C\cdot$	23	2.6	Decalin	m, 30°	21

^{a} Photolysis of $RCOO_2COR \rightarrow 2R\cdot + 2CO_2$ at 2537 Å. ^{b} Photolysis of $RN\!\!=\!\!NR$. ^{c} This value may be too high, according to authors, because of the occurrence of a polar decomposition of the parent peroxide giving the same products as those from disproportionation. ^{d} Photolysis of $CH_3N_2C_2H_5$. Runs were also performed between 0 and $-191°$. See temperature dependence section. ^{e} Photolysis of $(C_6H_5)_2Hg$ at 2537 Å: W. A. Cramer, J. Phys. Chem., 71, 1171 (1967). ^{f} See discussion of these data, section IV. ^{g} R_2Hg + azo compound. ^{h} Thermal decomposition of azo precursor. ^{i} P. S. Engel and D. J. Bishop, J. Amer. Chem. Soc., 94, 2148 (1972). ^{j} The workers found a lower (~85%) total yield of products for this compound than for the other alkyl-substituted cumyls. In flash-esr experiments, di-p-tert-butylazocumene (in contrast to the other azocumenes) did not give observable substituted cumyl radicals, but rather a spectrum consistent with $R_2N\dot{N}R$. ^{k} The overall yield of termination products is 77% at 46°, 87% at 64°. At 46°, p-bromo-α-methylstyrene was in >50% excess over p-bromocumene—a very unusual result. The k_d/k_c given above is based on the cumene. The workers chose the apparent sum of olefin and alkane as their k_d yield (essentially this averages the two values), and interpreted the data as a temperature dependence of k_d/k_c with $E_{a(c)} > E_{a(d)}$; see, however, R. C. Corley and M. J. Gibian, J. Org. Chem., 37, 2910 (1972). ^{l} Thermolysis of the mixed azo compound. ^{m} Photolysis of perester giving ether (k_c) and alcohol plus olefin (k_d).

TABLE XIII. k_d/k_c Values for Alkyl-Alkyl and Alkoxy-Alkyl Radicals Pairs[a,b]

R·	k_d/k_c (relative)		
	$2R·^c$	t-BuO· + R·[c]	$CH_3·$ + R·[d]
$CH_3CH_2·$	1.0	1.0	1.0
$(CH_3)_2CH·$	8.0	7.5	5.5
$(CH_3)_3C·$	30	60	17.5

[a] This table is an adaptation of Table VI, ref 21. We have used, however, the best values from Tables VIII and XII for the alkyl-alkyl data. [b] k_d/k_c $(2C_2H_5·)$ = 1. [c] From Table XII, in solution. [d] From Table VIII, gas phase.

SCHEME II
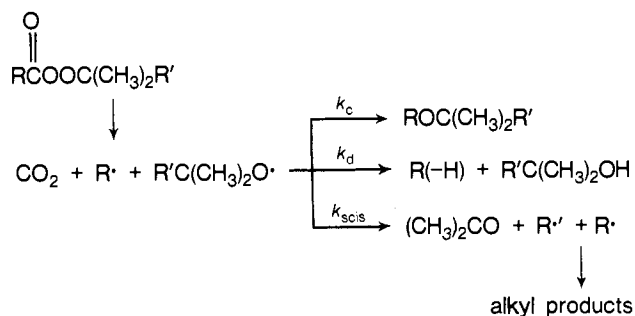
values here are at least twice the auto k_d/k_c values for the same alkyl radical). Kochi points out that k_d/k_c for alkoxy-alkyl ratios increase in parallel for the series R = ethyl < isopropyl < tert-butyl (Table XIII), attributing the variations to k_d. The reason for the parallel values was interpreted as being due to little bond breaking in the transition state for disproportionation (since alkoxy radicals show different selectivities in abstraction reactions). We submit, however, that the selectivities were not really tested in this series (all abstractions were from C–CH_3 in disproportionation) and that the alkoxy pairs and α-haloalkyl radicals[129] examined in the gas phase do show considerably changed k_d/k_c values. This is another area that might shed light on the entire subject if further investigated.

The Δ values in solution show no dramatic general change from those obtained in the gas phase for those few radicals studied under both sets of conditions. The absolute $\Delta/\beta H$ data for the alkyl radicals are similar and qualitatively seem to follow the trends discussed in relation to Tables IX and XI. Much of the information on the effects of solvation was discussed in previous sections, but it would be very interesting to make comparisons between gas and solution data. This will have to await more extensive investigations on simple radical-radical reactions, especially cross reactions, in solution.

VIII. Solid-Phase Studies

The few studies involving solid-phase radical-radical reactions have yielded some intriguing observations. This is an area of some current attention and promises to be fruitful over the next few years.

While it has been most often found that k_d/k_c of solid-state radicals is significantly higher than in solution, there are exceptions to this generalization. Among the variety of states generally referred to as "solid" are glasses, frozen mixtures or solid solutions, pure crystalline solids, and partly frozen crystalline or glassy states with pockets of highly concentrated solution. In addition, these materials may be in bulk phase or in a thin film. There is no

(129) B. C. Roquitte and M. H. J. Wijnen, J. Amer. Chem. Soc., **85**, 2053 (1963).

reason to expect the behavior of each of these media to be identical, or even more similar to each other than to fluid solutions, except that often (but not always) these studies are carried out at low temperatures where molecular translational motion is quite restricted.

The earliest studies involved allowing H atoms (generated gaseously by thermolysis at a tungsten ribbon) to react with films containing propylene together with varying amounts of n-butane at less than $-173°$ (mostly $-195°$).[130] The dominant process is addition of H· to propylene to give isopropyl radicals, which then react. Over a range of conditions, the yield of propane relative to 2,3-dimethylbutane (the usual measure of k_d/k_c) is rather constant at approximately 8, compared to 0.5 in the gas phase at 25°. The three possible explanations considered for the high value were (a) "hot" isopropyl radicals (because of the exothermicity of the reaction generating them) giving high disproportionation percentages, (b) isopropyl radical reacting with H· to give propane, (c) $E_{a(c)} - E_{a(d)}$ = 0.3 kcal/mol. Upon further investigation using cis-2-butene as the olefin together with varying amounts of 3-methylpentane (which makes a "very rigid" matrix) as inert diluent,[131] evidence for both the hot radical process (a) and for the radical–hydrogen atom reaction (b) was obtained. The same workers also photolyzed azobisisopropane at $-195°$ and obtained a k_d/k_c of 1.6, and upon varying the temperature found k_d/k_c = $0.4e^{-260/RT}$. The conclusion was that $E_{a(c)} - E_{a(d)}$ = 260 cal/mol for isopropyl radical. Similar behavior was found for sec-butyl ($E_{a(c)} - E_{a(d)}$ = 350 cal/mol in this study).

In their comprehensive study of ethyl radical recombinations (sections V and VI), Dixon, Stefani, and Szwarc[41,92] noted that plots of log k_d/k_c vs. log T or $1/T$ showed biphasic behavior such that when two straight lines were drawn through the data, they intersected at the melting point of the solvent being used, isooctane or toluene. A temperature dependence remained in solid isooctane ($T^{-0.33}$), but of lower magnitude than in solution ($T^{-0.86}$). Similar behavior was found for the methyl–ethyl cross reaction.[132] While the pure crystalline azo compounds also gave very high k_d/k_c values, a peculiarity was that azoethane in liquid methane at $-184°$ behaved the same as in frozen media (in both studies frozen toluene, isooctane, glycol, and mixed propanols gave similar results in the "solid," but very different results in fluid solution). These effects were discussed later in terms of "internal pressure" (section VI).

Watkins and Moser,[133] studying ethylene reactions with H and T atoms at $-210°$ on a solid film of olefin, obtained k_d/k_c values of 0.8 for two ethyl radicals. This is significantly higher than extrapolation of Szwarc's data would predict, and the authors suggest a medium effect as the rationale. A value of 5.5 for the k_d/k_c of two isopropyl radicals was found under similar conditions.[134]

In their study of azocumene, Nelsen and Bartlett[5] found that k_d/k_c for two cumyls ($\sim$0.05 in benzene solution, temperature independent from 20 to 60°) dramatically rose to 0.99 $\pm$ 0.06 at $-8°$ in frozen benzene. This is clearly a phase, rather than a temperature, effect. To eliminate the possibility of the reaction occurring primari-

(130) R. Klein, M. C. Scheer, and J. G. Waller, J. Phys. Chem., **64**, 1247 (1960).

(131) R. Klein, M. D. Scheer, and R. Kelley, J. Phys. Chem., **68**, 598 (1964).

(132) P. S. Dixon, A. P. Stefani, and M. Szwarc, J. Amer. Chem. Soc., **85**, 3345 (1963).

(133) K. W. Watkins and H. C. Moser, J. Amer. Chem. Soc., **69**, 1040 (1965).

(134) H. B. Yun and H. C. Moser, J. Amer. Chem. Soc., **69**, 1059 (1965).

ly in frozen pockets, a toluene solution of azocumene was photolyzed while it was kept well below its freezing point of $-95°$. Observed k_d/k_c values ranged from 1.48 to 3, with the reacting radicals almost certainly being primary cage partners. The explanation offered for this solid effect on k_d/k_c was that disproportionation can occur from many more relative orientations of two cumyl radicals than can combination, and since rotational motion is much less restricted than is translation as the temperature decreases, k_d/k_c continually increases.

A similar effect was reported by Bartlett and McBride[36] for the 2-phenyl-3-methyl-2-butyl radical (section VI.B). The k_d/k_c ratio regularly decreases with decreasing temperature in all solvents from $100°$ (~ 0.6) to approximately $0°$, but it reaches a minimum at $4°$ in benzene (~ 0.25) and rises rapidly until at $-40°$ the ratio is over 1.0, where it levels off. While both meso and dl starting azo compounds in solution gave equal meso and dl dimer, in frozen benzene meso azo compound gave meso/dl ratios that rose rapidly with the distance below the melting point of solvent. At $-195°$ meso azo compound gave pure meso product, and dl azo compound gave dl product. This is indicative of essentially a 100% cage effect in the solid, with 0% in solution. The authors used this conclusion to estimate the k_d/k_c ratio for caged frozen radicals at intermediate temperatures as a function of temperature. Plotting log k_d/k_c vs. $1/T$, a linear relationship resulted, showing $E_{a(d)}$(cage) $-$ $E_{a(c)}$ (cage) $= 1$ kcal/mol (this value was 2 in solution). However, $\Delta S\ddagger$ in the cage favors disproportionation (as opposed to combination in solution) as previously noted for cumyl radicals. Although the frozen benzene and chlorobenzene solutions appeared polycrystalline, the stereochemical and k_d/k_c behavior implies a medium of increasing viscosity with decreasing temperature, and possible physical explanations were offered by the authors. This study also reported the successful epr observation of geminate N_2-separated triplet radical pairs at $-196°$.

Very recently, McBride has reported that two 2-cyano-2-propyl radicals (photolysis of AIBN), which in solution give 5% disproportionation ($k_d/k_c = 0.053$), give 95% disproportionation in the crystalline state ($k_d/k_c = \sim 19$).[128] The kinetic isotope effect (see section IX) in the crystal indicated competition between H and D on one methyl group but no effect either when only one of two geminate radicals was deuterated or between geminal methyls. This indicates that methyl rotation is rapid, but motion of one radical relative to its partner is slow compared to the hydrogen abstraction. For 3-cyano-3-pentyl radicals (from azobis-3-cyano-3-pentane, ACP),[135] however, the fluid and crystalline products were very similar (<5% disproportionation). Indeed, crystallographic analysis indicated that while AIBN forms a very ordered structure, the ACP crystals are disordered.[136] Besides this difference in total disproportionation to combination yields, the ratio of the two coupling products from 2-cyano-2-propyl radicals (tetramethylsuccinonitrile and ketenimine) changes dramatically in the crystal. Yet different behavior was found in glassy media.
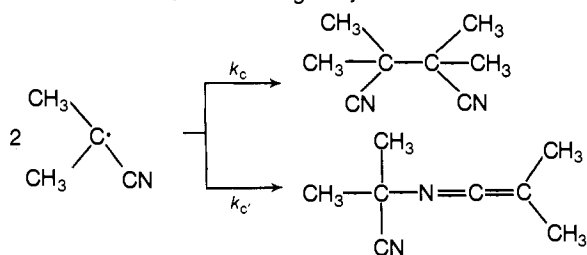
The explanation for the dichotomy of effects for the two compounds was suggested by McBride to be due to a polarity effect in crystalline AIBN that favors reactions that keep the dipoles correctly aligned and disfavors reactions requiring the reorganization of dipoles. The solid-phase results discussed in the earlier part of this section will probably not be really interpretable in the absence of information regarding molecular alignments of individual compounds in the respective solid media, a formidable barrier.

IX. Kinetic Isotope Effects

Of the two modes of radical–radical termination only disproportionation involves an atom transfer and could manifest a primary kinetic isotope for replacement of a β hydrogen by deuterium or tritium. On the other hand, either process might be subject to a secondary kinetic isotope effect for either α or β isotopic substitution.

The origin of the kinetic isotope effect lies in the difference in bond energies and vibrational strengths between starting materials and transition state.[137-141] Detailed calculations have been done for some simple radical abstraction processes and compared with experimental gas phase values with some degree of success.[140,142] It is beyond the scope of this review to embark on a discussion of theoretical treatment, and we shall rather treat the available data phenomenologically.

Expressing the primary effect as

$$k_H/k_D = A_H/A_D[e^{-(E_{a(H)}-E_{a(D)})/RT}]$$

it is usually assumed in organic chemistry that A_H/A_D is close to unity, and that k_H/k_D represents primarily differences only in the symmetrical stretching frequency of the transition states for H and D (the "maximum" k_H/k_D being obtained when these frequencies are equal and the full zero-point energy differences are manifest). However, the reactions under consideration here are extremely exothermic, and the usual interpretation of E_a (and the assumption of a temperature independent A) is questionable.

A. Empirical Predictions

Isotopic substitution on the carbon adjacent to the radical center can, in principle, lead to a β secondary isotope effect upon combination (eq 29), a primary isotope effect on disproportionation (eq 30), or, if a β H is abstracted, both a β (for going to alkane) and an α (for going to olefin) secondary isotope effect on disproportionation (eq 31). In the following discussion we shall attempt to estimate the expected maximum magnitudes of the secondary effects for each of these processes.

Seltzer has compared the decompositions of azo compounds with D substitution at the α carbon to their proton analogs and has also measured ^{15}N and α-^{13}C primary effects.[143] Azobis-α-phenylethane (($C_6H_5CD(CH_3)N=$)$_2$),

(135) A. B. Jaffe, J. J. Skinner, and J. M. McBride, J. Amer. Chem. Soc., 94, 8510 (1972).

(136) A. B. Jaffe, D. S. Malament, E. P. Slisz, and J. M. McBride, J. Amer. Chem. Soc., 94, 8515 (1972).

(137) J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

(138) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(139) F. H. Westheimer, Chem. Rev., 61, 265 (1961).

(140) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 351 ff.

(141) A recent and rather thorough discussion of k_H/k_D values for abstraction by CH_3· and CF_3· is given by P. Gray, A. A. Herod, and A. Jones, Chem. Rev., 71, 247 (1971).

(142) H. S. Johnston and D. Rapp, J. Amer. Chem. Soc., 83, 1 (1961).

$$(29)$$

$$(30)$$

$$(31)$$
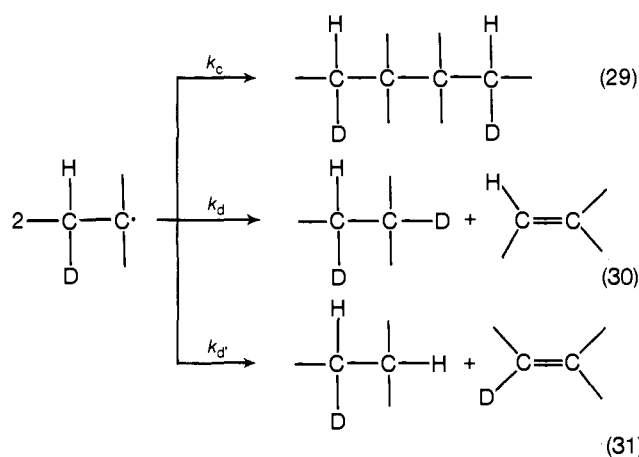
generally agreed to decompose *via* simultaneous homolytic scission of both C–N bonds, gives a k_H/k_D value of 1.27 for the dideuterated species.[144] α-Phenylethylazomethane $(C_6H_5CD(CH_3)N\!=\!NCH_3)$, which decomposes in two discrete steps to first give α-phenylethyl and methyldiazenyl radicals and then N_2 and methyl, gives a k_H/k_D of 1.13 for deuterium substitution on the phenylethyl moiety,[145] close to the per H value for the former species. The process for the symmetrically substituted compound is conversion of sp^3 carbon to an activated complex of very close to completely dissociated geometry (*i.e.*, planar sp^2 about the α-C), since the E_a is close to the bond dissociation energy. In eq 31, the α secondary effect involves conversion of sp^3 C–D to olefinic sp^2 C–D when H is abstracted from this carbon. The maximum effect from this portion would be 1.13 per D, but since the activated complex is in all likelihood still quite far from completely reorganized to planar geometry about this carbon, the k_H/k_D contribution should be considerably less than 1.13.

Seltzer also examined the decomposition of the β-deuterated symmetrical compound $(C_6H_5CH(CD_3)N\!=\!)_2$, finding a k_H/k_D of 1.108 for 6 D's (1.017 per D) for this β secondary effect.[146] Again, this is for conversion of sp^3 CD_3C–X to almost completely radical $CD_3C\cdot$, presumably sp^2, and is likely a maximum value compared to a highly activated reaction. The β secondary isotope effect in eq 31 and the effect in eq 29 are for $CD_3C\cdot$ radicals going to CD_3C–X covalent species and would reasonably exhibit an *inverse* effect. The maximum effect (minimum k_H/k_D) for these would be $1/1.017 = 0.983$ per D atom (that for eq 29 would be $1/1.035 = 0.966$ per D atom for the radical as written). This is all assuming completely additive effects, probably a not unreasonable assumption. For eq 31 then, we have predicted opposing maximum effects of 1.13 and 0.983 per D, which will tend to cancel (presumably multiplicatively to a maximum of 1.11 per D), and for eq 29 an inverse effect of 0.983 per D (or 0.966 for one β D on each radical).

Equation 30, the possible primary effect for D abstraction, could in principle be any value from 1 to 8 or so (the latter being that value calculated for complete loss of zero-point vibrational energy difference between H and D), but probably should be nearer the minimum.

(143) S. Seltzer and S. G. Mylonakis, *J. Amer. Chem. Soc.*, **89**, 6584 (1967).

(144) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2625 (1961).

(145) S. Seltzer and F. T. Dunne, *J. Amer. Chem. Soc.*, **87**, 2628 (1965).

(146) S. Seltzer and E. J. Hamilton, Jr., *J. Amer. Chem. Soc.*, **88**, 3775 (1966).

B. Results and Discussion

Much of the rather meager data for this area have been gathered for radical–radical processes in the solid phase, and all of it is in terms of $(k_d/k_c$ (H)$)/(k_d/k_c$ (D)$)$ ratios except for one very recent study. This last is the work of McBride[128] on the crystalline phase photolysis of AIBN at Dry Ice–acetone temperature, analyzed by very careful nmr integration of product peaks. When the precursor (and hence the 2-cyanopropyl radicals) was specifically unsymmetrically labeled as in **11**, the dispro-

11
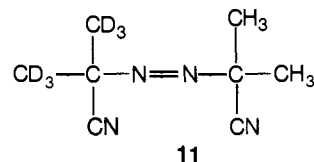
portionation products (the major path; see section VIII) showed no kinetic isotope effect, *i.e.*, no discrimination between H and D. However, when 73% randomly deuterated AIBN was decomposed in the crystal, an intramolecular isotope effect (for competition between H and D on the same methyl) of 2.0 ± 0.2 was observed. This is clearly on the disproportionation step, eq 30. Together, this is evidence that all radical–radical reactions are geminate in this crystal, and that molecular movement is severely restricted. The $k_{d(H)}/k_{d(D)}$ is 2.0.

Moser has also done product analyses at low temperatures ($-210°$) allowing films of ethylene and ethylene-d_4 to react with T atoms, yielding $CTH_2CH_2\cdot$ and $CTD_2CD_2\cdot$, respectively.[133] The overall k_d/k_c ratio for both species was 0.76, but for $2CTH_2CH_2\cdot$ the ratio of C_2H_5T/C_2H_3T was found to be 1.44. This ratio is expected to be 2.0 for purely statistical abstraction from the $-CTH_2$ group by $C_2H_4T\cdot$, or 1.0 if T is never abstracted. The experimental value thus represents a k_H/k_T primary isotope effect of 2.3 ± 0.5,[147] while for $CTD_2CD_2\cdot$, k_D/k_T is 1.5 ± 0.2. By division, the calculated k_H/k_D for $CDH_2CH_2\cdot$ is 1.5 per D. A similar experiment using propylene to give tritiated isopropyl radicals led to k_H/k_T here of 1.7 ± 0.2 per T atom.

Boddy and Steacie simply measured the k_d/k_c of $C_2D_5\cdot$ in the gas phase from 25 to 150° by photolysis of $C_2D_5COC_2D_5$.[148] The k_d/k_c was 0.0985, while for $C_2H_5\cdot$ their value was 0.13, leading to a k_H/k_D of 1.41. It was pointed out that this ratio is the same as the ratios of the C–H *vs.* C–D stretch in C_2H_6 and C_2D_6, and the isotope effect was attributed to a preexponential effect.

Recently, the present authors examined the k_d/k_c values of $C_6H_5CHCH_3$ and $C_6H_5CHCD_3$ in benzene solution *via* azo compound decompositions.[108] The k_d/k_c at 118° was 0.052 for 100% CD_3 *vs.* 0.097 for CH_3. The k_H/k_D, then, is 1.87 at this temperature. The k_d/k_c for a sample of $C_6H_5CHCD_3$ (88% D) was measured also at 148 and 98°, the logs of the three values being plotted *vs.* $1/T$. The slope for the deuterated material gave an apparent $E_{a(c)} - E_{a(d)} = 800 \pm 24$ cal/mol, compared to 1470 ± 60 cal/mol for the hydrogen compound, a difference of about 700 cal/mol for the activation energy (or enthalpy) differences. The ratio of preexponentials $((A_d/A_c$ (H)$)/(A_d/A_c$ (D)$))$ was 0.85.

At the beginning of this section the likely magnitudes of the kinetic isotope effects for each of the three modes of reaction were discussed. *From the data presented, it is clear that in the gas, liquid, and solid phase there is a significant kinetic isotope effect that must be a primary*

(147) From just the k_d/k_c values for $2C_2H_5\cdot$ *vs.* $2C_2H_4T\cdot$, a k_H/k_T of 1.7 was calculated.

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

one on the disproportionation. The magnitudes of these effects are surprisingly large for reactions of such low activation energies.

One aspect of the primary effect on disproportionation that must be seriously considered is proton tunneling.[142,149,150] This arises quantum mechanically, from the much higher probability of a hydrogen than any heavier atom to cross an energy barrier without having the apparent potential or kinetic energy. Hydrogen abstraction by radicals meets all the criteria likely to involve tunneling effects, and it has been concluded that tunneling should be a major contributor to abstraction rates.[149] Most studies have tended to ignore this, primarily because the *experimental* criteria for tunneling have been observed in only a very few cases.

The most striking experimental evidence for tunneling is a very high k_H/k_D value, several having been reported for a variety of reactions in recent years.[151-153] This is probably so seldom observed because tunneling raises the apparent activation energy difference and lowers the ratio of preexponential factors, to a first approximation tending to be cancelling effects.[154] By determining k_H/k_D as a function of temperature these latter two criteria may be examined,[150] it being indicative of tunneling if (1) A_H/A_D (the ratio of preexponentials) is less than 0.5, the classical lower limit, or (2) $E_{a(D)} - E_{a(H)}$ is greater than the zero-point energy differences, approximately 1.2 kcal/mol for C–D vs. C–H. None of these criteria are evident in the data thus-far for radical–radical processes, and indeed out of a very large number of examples only a very few hydrogen abstractions by radicals show tunneling experimentally.[155,156]

(149) A. F. Trotman-Dickenson, *Advan. Free Radical Chem.*, 1, 3 (1965).

(150) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 205 ff, 211.

(151) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc. Ser. A*, 294, 273 (1966).

(152) E. S. Lewis and L. H. Funderbunk, *J. Amer. Chem. Soc.*, 89, 1287 (1967).

(153) E. S. Lewis, J. M. Perry, and R. H. Grinstein, *J. Amer. Chem. Soc.*, 92, 899 (1970).

(154) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, 23, 1535 (1955).

(155) Johnston and Rapp[142] have performed calculations which include quantum mechanical tunneling and obtained good agreement between theory and experiment for $CH_3\cdot$ attack on hydrocarbons. Gray, et al.,[141] p 287, examining a very large number of $CH_3\cdot$ and $CF_3\cdot$ reactions, found only two results displaying the criteria discussed above, and these in cases where the experimental validity of the data were questioned for reasons not involving the isotope effects results. These authors tend to adopt, as does Trotman-Dickenson,[149] a "moot" approach to the subject, it not being a question of whether tunneling occurs, but whether the data show statistically significant contributions from this effect.

At this stage, we can only take the isotope effect data at face value and ascribe its origin to a classical primary effect involving competition between C–H and C–D breaking in disproportionation *vs.* the combination reaction. This implies two different activated complexes.

X. Summary

A large number of combination to disproportionation ratios have been measured in the gas phase as a function of structure, but many fewer in solution. The data indicate dependence upon radical structure, and in ways that suggest that both steric and energetic effects are operating. While only some really reliable temperature dependency studies have been done, a number of these (most of those examined in solution, about half of the gas phase data) indicate a real dependence, and this is usually an increase in k_d/k_c as temperature is decreased (apparent $\Delta H_{(c)}\ddagger > \Delta H_{(d)}\ddagger$ and $\Delta S_c\ddagger > \Delta S_d\ddagger$). The effect of medium is not large in solution, but solid-phase studies show very intriguing orientation effects. In all three phases the k_d/k_c ratio shows a kinetic isotope effect for β-D substitution of about 2 for various radicals, and in the solid this is clearly a primary kinetic isotope effect on disproportionation.

Very recently, more direct kinetics on radical terminations have been forthcoming, and it is clear that many of the rates are much slower than encounter controlled and probably involve activation energies. The review contains a number of suggestions for generalizations about the effects of structure, phase, solvation, and mode of generation on k_d/k_c proportioning as well as critical analyses of existing data.

(156) Wiberg[140] (p 360) has suggested that the deuterium–tritium effect would be worth examining in this light, the tunneling correction here being much smaller than for hydrogen–deuterium because of the greater masses. Indeed, the data of Watkins and Moser[133] show a k_D/k_T that is reasonably consistent with the k_H/k_T and k_H/k_D effects.