grees of freedom, n, while for cyclobutenes s is only about 40% of n. That the values of s for these reactions are considerably smaller than the total number of vibrational degrees of freedom is expected due to the nature of the approximations in the theory.[26,29,30]

The RRKM theory,[29] which has been formulated to take into account quantum effects and participation by all normal mode vibrations in intramolecular energy transfer, has been used by Elliott and Frey to predict the falloff in the rate constant with decreasing pressure for 1-methylcyclobutene.[11] In Figure 4, their predicted curve "B" for 1-methylcyclobutene is compared with the present experimental data for a temperature of 150°. The curvature of the experimental curve is well reproduced by that of the theoretical falloff curve, within the possible experimental error. The calculated curve for 1-methylcyclobutene lies about 0.3 log P_0 unit lower, however, with respect to pressure, than the present experimental curve. A similar difference was noted between their calculated curves and the experimental results for 3-methylcyclobutene and cyclobutene.[11,31] In both of the methylcyclobutene cases, the difference in log P_0 between the theoretical and experimental curves can be substantially reduced by the assumption of a smaller, but still reasonable, molecular diameter, *e.g.*, 5.9 Å as used in this work, instead of 7.1 Å as used by Elliott and Frey.[11]

The assumption of unit collisional deactivation efficiency may be an additional source of uncertainty in the calculated values,[11,32] even though there is much experimental evidence for highly efficient energy transfer for polyatomic molecules in some cases.[33] Frey has suggested that a collision efficiency factor for deactivation of about one-third would largely reconcile the theoretical and experimental curves for 3-methylcyclobutene[11] and cyclobutene.[11,31] A similar factor might be inferred then for the 1-methylcyclobutene.

Within the possible errors caused by the uncertainties discussed above, then, the RRKM theoretical falloff curves agree with the experimental curves for cyclobutene[34] and for the 1- and 3-methylcyclobutenes. In particular, the RRKM calculations of Elliott and Frey[11] have, within these possible errors, predicted the correct relative change in position of the falloff for cyclobutenes of different molecular complexity and for different positions of the methyl group on the cyclobutene ring by assuming all vibrational modes as active in the intramolecular transfer of energy, rather than some adjustable fraction of these (*i.e.*, s, in Kassel theory).

Acknowledgments. The author expresses her appreciation for the guidance and encouragement given by the late Professor W. D. Walters during the course of this research. Grateful acknowledgment is made for the assistance of Mr. Carl Whiteman in connection with the infrared and mass spectral measurements and computer calculations, and for the efforts of Mr. Joseph Male and Mr. Joseph Rearden in some of the gas chromatographic work.

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[29] R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951); G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, **37**, 1835 (1962); R. A. Marcus, *ibid.*, **20**, 359 (1952).

[30] E. W. Schlag, *ibid.*, **35**, 2117 (1961); B. S. Rabinovitch and J. H. Current, *ibid.*, **35**, 2250 (1961); M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *ibid.*, **37**, 1276 (1962).

[31] A recent experimental study and RRKM calculation published by Frey and Pope for perdeuteriocyclobutene gives a similar comparison between experiment and theory to that found for cyclobutene itself: H. M. Frey and B. M. Pope, *Trans. Faraday Soc.*, **65**, 441 (1969).

[32] *Cf.* J. D. Lambert, *Quart. Rev.* (London), **21**, 67 (1967).

[33] See, for example, the summary discussion in F. J. Fletcher, B. S. Rabinovitch, K. W. Watkins, and D. J. Locker, *J. Phys. Chem.*, **70**, 2823 (1966).

[34] With respect to the theoretical cyclobutene curve, some data of a preliminary nature obtained in the present study indicate that the rate constants observed for a 12-l. reaction vessel may give a slightly better curvature fit at low pressures than those found earlier for a 0.5-l. vessel. (In Figure XVIII of ref 1b, Appendix III, read [(log P_0) − 1] for log P_0.)

Radiation-Induced Interconversion of Acetone-^{14}C and 2-Propanol-^{14}C

John G. Burr and F. C. Goodspeed

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Abstract: The yield of 2-propanol-^{14}C (IPA*) in γ-irradiated mixtures of acetone-2-^{14}C (Ac*) and 2-propanol (IPA) is a bimolecular function of the Ac* and IPA concentrations. The maximum yield is 6.9 in an equimolar mixture of components and is the same at −196° as to 40°. The yield of Ac* in irradiated mixtures of IPA* and acetone (Ac) is also a bimolecular function of the component concentrations, with a maximum yield of 4.6 in an equimolar mixture. This conversion process is more strongly affected by temperature, and the maximum yield is lower at −196° than at 40°. Neither one of these interconversion reactions could be induced by 313-nm uv light, and the yields of γ-induced 2-butene isomerization in IPA and in Ac are relatively low. These interconversions are interpreted in terms of the various possible reactions of acetone anion (formed by electron capture) and 2-propanol cation (formed by the ionizing radiation).

Yields of hydrogen (and other products) in the radiolysis of mixtures of acetone and 2-propanol were reported some time ago;[1] the presence of small amounts of acetone (1–5 vol%) effected a marked reduction in the yield of hydrogen from the 2-propanol. At the time, this effect was interpreted in terms of hydrogen atom scavenging by the carbonyl group of the ketone.

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[1] J. D. Strong and J. G. Burr, *J. Am. Chem. Soc.*, **81**, 775 (1959).

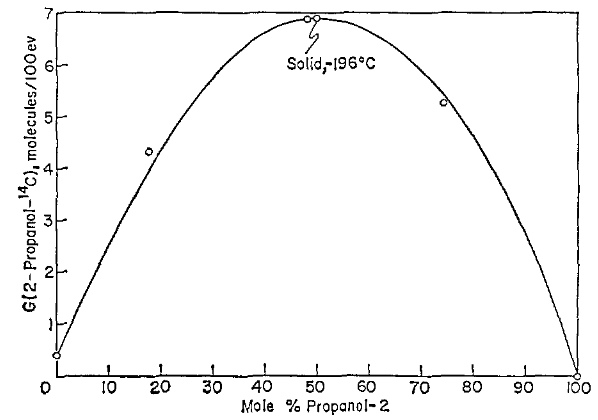

Figure 1.

It seems clear from more recent work[2] that ionic intermediates are the precursors to the radicals, and that electron scavenging as well as hydrogen atom scavenging should be considered for these radiolyses. We have endeavored to investigate the nature of the processes in the mixtures by irradiating mixtures of acetone-^{14}C with propanol-2 and of 2-propanol-^{14}C with acetone. In this way the formation of small amounts of either acetone or propanol could be detected even though a large amount of the product was already present.

Experimental Section

Materials. Acetone-^{14}C and 2-propanol-^{14}C were obtained from both U. S. Nuclear and Volk Radiochemical Co. and were diluted in a vacuum line with reagent grade acetone or 2-propanol to specific activities of about 3 μCi/mmole (40,000 cpm/mg). Samples of reagent grade acetone or 2-propanol were taken from previously unopened bottles of materials which showed free from impurities when gas chromatographed on Carbowax 20M columns in a Loenco 15B instrument. Pinacol was EK practical. It was distilled under high vacuum and the colorless distillate used as such in 2-propanol solution. Gas chromatography of this solution in a Perkin-Elmer 226 flame ionization instrument with a 100-ft Apiezon L ("Q") column at 70° showed a negligible amount of impurities present. 1-Propanol and cyclohexane were reagent grade materials from freshly opened bottles. The source of γ radiation was a Gamma cell with a dose rate of about 1.5×10^{18} eV min^{-1} ml^{-1}.

Separation Procedures. Acetone and 2-propanol were separated from each other by gas chromatography in a $^{3}/_{8}$ in. Carbowax 20M in an Aerograph Autoprep instrument, equipped with a Hamilton fraction collector. Sample size was 200–250 μl. The separated acetone and 2-propanol fractions collected from radioactive mixtures were assayed directly by counting 5–10-μl samples in a Packard Tricarb liquid scintillation counter. The completeness of the separations and the absence of important amounts of radioactive impurities in the separated components were demonstrated by the following observations. (1) The radioactivities of the separated fractions from irradiated mixtures were always compared with similar measurements made on components from unirradiated samples of the same mixtures, and only the net increase in activity reported (the nonradioactive component from an unirradiated mixture never showed activity more than slightly above background). (2) The component whose activity was important was occasionally rechromatographed and even rechromatographed in a different column—usually a Ucon column—without appreciable change in specific activity. (3) The column used for separation of radioactive mixtures was decontaminated between separations by passage of 0.5–0.8-ml samples of inactive acetone–propanol mixtures until a sample of a separated component had only background activity. (4) Samples of the separated components were shown to have negligible impurity content by analytical gas chromatography on a Loenco 15B instrument.

Phase Effects. Radiolysis of liquid samples was carried out upon 0.5–1.0 ml of the mixtures or pure materials. Samples for gas-phase radiolysis were contained in 230-ml bottles, equipped with break-seals. These bottles were baked at 350–400° overnight at 10^{-7} mm before they were filled with the acetone–propanol mixture (123.3 mg; the estimated pressure at 40° was 200 mm). Solid-phase radiolyses were carried out in ampoules immersed in a dewar containing liquid nitrogen. Samples with about 75% propanol usually froze to glasses; the samples with a high acetone content usually froze to a white, apparently microcrystalline, solid.

Photolyses. The source of uv light was a 250-W ME/D medium-pressure arc, operated at about 65 V and 4 A. The 3130-Å mercury line was isolated with a Corning 7-51 filter (transmitting a band between 300 and 400 mμ), 2 cm of water to absorb heat, and three 2-mm thicknesses of Pyrex. The sample was contained in a Pyrex cell holding about 3 ml. The acetone–propanol mixture was practically black at 3130 Å. Light was absorbed in a 50:5 mixture of 2-propanol–acetone-^{14}C or of 2-propanol-^{14}C–acetone at a rate of 10^{18} quanta/min (by uranyl oxalate actinometry) for a total of 1.64×10^{20} quanta. The propanol or acetone fraction, depending on the mixture, was separated from the photolyzed mixture as above and examined for radioactivity; none was ever found. As an example, the activity in a 10-μl sample of the propanol from a photolyzed propanol–acetone-^{14}C mixture was 370 cpm and that in a 10-μl propanol sample from the unphotolyzed mixture was 400 cpm. The activity of a 10-μl sample of the acetone was 270,000 cpm.

Pinacol Measurements. Pinacol concentration in the irradiated solutions was measured by gas chromatography on an Apiezon L ("Q") column in a Perkin-Elmer 226 gas chromatograph with a flame ionization detector. The column at 70° gave a good separation of pinacol from the numerous radiolysis products; concentrations were estimated from peak heights. Standards were always run concurrently with the samples.

2-Butene Isomerizations. Solutions of *cis*-2-butene in various solvents were prepared in a vacuum line by distilling the appropriate volume of 2-butene from a pipet into an ampoule of degassed and dried (usually over BaO) solvent. This ampoule was then sealed off and irradiated. After the irradiation, the ampoule was opened *in vacuo* in the line; the butenes were toeplered off and analyzed gas chromatographically for the *cis*/*trans* 2-butene ratio. The consumption of butene was negligible under our conditions. The amount of isomerization was much higher in slightly wet solvents than in absolutely dry solvents.

Results and Discussion

The product yields from mixtures of acetone-2-^{14}C and 2-propanol are shown in Tables I and II and in Figure 1. The yield of 2-propanol-^{14}C from pure acetone-2-^{14}C was small; the yields from the various mixtures of this with 2-propanol were those to be expected from a bimolecular reaction: $G(\mathrm{IPA}^*) = k(\mathrm{Ac}^*)(\mathrm{IPA})$, where Ac* = acetone-2-^{14}C, IPA* = 2-propanol-^{14}C, and IPA = 2-propanol. The high yields, shown in Figure 1, are unique to mixtures of acetone and 2-propanol, since the yield of IPA from a 50 vol% mixture of acetone and 1-propanol was 1.95, and from a 50 vol% mixture of acetone and cyclohexane was 1.25. Furthermore the bimolecular process responsible for IPA* formation was observed to be as efficient at −196° as it was at 40°.

The maximum yield of Ac* from Ac + IPA* mixtures (Tables I and II and Figure 2) is lower than the maximum yield of IPA* from Ac* + IPA mixtures, and is more strongly affected by temperature and/or phase (Figure 2). The yield of Ac from IPA (which is high even in pure IPA at 40°) is enhanced at −196° (3.03 *vs.* 1.8 at 40°), but this enhanced low-temperature yield of Ac is increased only a little in Ac + IPA* mixtures at this temperature (Figure 2).

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[2] (a) J. J. J. Myron and G. R. Freeman, *Can. J. Chem.*, 43, 1484 (1965), and references cited therein. (b) An excellent review of the relative importance of ionic and other intermediates in carbinol radiolyses can be found in the review by R. A. Holroyd, in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Publishers, New York, N. Y., 1968.

Table I. Product Yields in Irradiated Liquid Mixtures of Acetone and 2-Propanol^{a}

Mole % acetone	Mole % 2-propanol	G-(acetone)	G(2-propanol)	G(pinacol)
100	0		0.39^{c}	
100 ^{14}C	0		0.84^{b}	
74.0 ^{14}C	26.0		5.25	
48.1 ^{14}C	51.9		6.85	
17.6 ^{14}C	82.4		4.36	
53	47 ^{14}C	4.14		0.66,^{c} 0.63^{c}
49	51 ^{14}C	4.55		
0	100 ^{14}C	1.85^{b}		0.51^{b} (0.46)^{c}

^{a} Dose: 15.5 × 10^{20} eV/g, 40°. *G* values are based on energy absorbed by the whole mixture. ^{b} Determined by isotope dilution. ^{c} Determined by gas chromatography.

Table II. Effect of Phase on Product Yields

Labeled component, mole %	G(product) and identify	Phase	Temp, °C
2-Propanol, 100	1.85 (acetone)	Liquid	50
2-Propanol, 100	3.03 (acetone)	Solid	−196
2-Propanol, 51	4.55 (acetone)	Liquid	40
2-Propanol, 40	2.16 (acetone)	Solid (crystal)	−196
2-Propanol, 75	2.77 (acetone)	Solid (glass)	−196
2-Propanol, 50	1.33 (acetone)	Gas, 200 mm	40
Acetone, 48.1	6.85 (2-propanol)	Liquid	40
Acetone, 50	6.92 (2-propanol)	Solid	−196

These observations can be summarized by saying that in an equimolar mixture of acetone and 2-propanol, the IPA is oxidized to acetone with a *G* value of 4.5, and acetone is reduced to IPA with a *G* value of 6.9 Both interconversions are bimolecular; the acetone reduction is unaffected by temperature or phase over the temperature range of −196–40°, whereas the IPA oxidation is more sensitive to these factors.

It is probable that these interconversion reactions can best be considered in terms of the reactions of the electron and of the hydrogen atom (species which are labile at −196°), and of the positive ions, negative ions, and free radicals consequent upon formation and capture of the electrons and the hydrogen atoms. The unimportance of excited molecules as intermediates in these interconversion reactions is suggested by both the failure of near-uv light to induce the interconversions (thus probably excluding excited acetone species) and the low yield of 2-butene isomerization both in acetone and in various carbinols as well as in IPA (Tables III and IV).

Table III. Isomerization of *cis*-Butene-2 in Irradiated Acetone Solution^{a}

Mole % butene	Number of determinations	G(cis–trans)
0.10	2	0.055
0.25	2	0.17 ± 0.04
0.50	4	0.64 ± 0.02
1.0	2	0.67 ± 0.04^{b}

^{a} Total dose, 1.5 × 10^{22} eV/g. ^{b} This corresponds to a yield of triplets of about 1.4, compared to the value of 1: *Discussions Faraday Soc.*, **36,** 111 (1963).

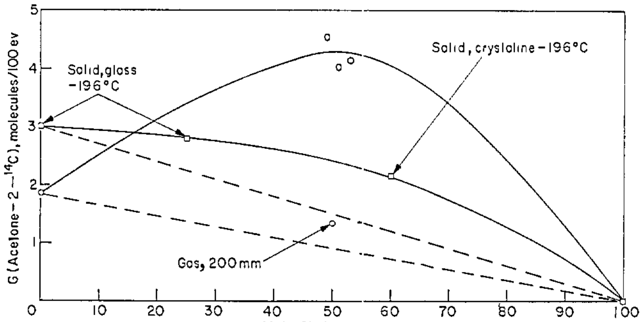

Figure 2.

The reactions involved in forming the electron and hydrogen atom are presumably those shown in eq 1 and 2.[2] The initial yield of electrons in these substrates

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2CHOH^+ + e_s \quad (1a)$$

$$(CH_3)_2{}^*CO \longrightarrow (CH_3)_2{}^*CO^+ + e_s \quad (1b)$$

$$(CH_3)_2CHOH^+ + (CH_3)_2CHOH \longrightarrow$$
$$(CH_3)_2CHOH_2^+ + [(CH_3)_2CHO \rightleftharpoons (CH_3)_2COH] \quad (2a)$$

$$(CH_3)_2CHOH_2^+ + e_s \rightleftharpoons (CH_3)_2CHOH + H \quad (2b)$$

(IPA, 1-propanol, acetone, cyclohexane) can be estimated from the value of *W* (gas phase) for these molecules. The appropriate *W* values are given by Adler and Bothe[3] (in eV per ion pair), with the corresponding values for *G* (electrons) in parentheses: IPA, 24.2 (4.1); Ac, 25.5 (3.9); PrOH, 24.5 (4.1); c-C_6H_{12}, 22.7 (4.4). These values are, of course, larger than the yields of free (solvated) electrons which are functions of the dielectric constant.[2b] For alcohols,[4] the yields of solvated electrons appear to be about $G(e_s) = 1.0$–1.2. The free electron cannot be observed in acetone, but the yield is calculated from the dielectric constant[2b] to be about 0.9. The yield of free electron is about 0.1 in cyclohexane.[2a] The correlation of initial electron yields with gas-phase *W* values depends upon a number of assumptions, but existing data justify this as a means for an initial guess. The yield of electrons in cyclohexane, measured by reaction with N_2O or CH_3I, is about 4.[2b] The measured value for $G(e_s)$ in water ($W = 29.9$[3]), 2.8, compares reasonably well with that corresponding to the *W* value. In ethanol, Russell and Freeman[5] estimate the initial yield of electrons to be 3.1, compared to the value of 4 which corresponds to the *W* value. Acetone is a much more efficient scavenger of electrons,[6a] $K_{(e_s+Ac)} = 5 \times 10^9$, than is IPA[6b] ($K_{(e_s+IPA)} = 1.5 \times 10^6$).

Table IV. Isomerization of *cis*-Butene-2 in Irradiated Alcohols

Alcohol	% butene	G(cis-butene → trans-butene)
Methanol	0.5	0.94
Ethanol	0.5	0.96
2-Propanol	0.5	0.87
2-Methyl-2-propanol	0.5	2.1^{a}
Acetone	0.5	0.64
Benzene	0.36	0.85

^{a} This alcohol may have been a little wet.

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[3] P. Adler and H. K. Bothe, *Z. Naturforsch.*, *A*, **20,** 1700 (1965).

[4] (a) M. C. Saher, S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, **42,** 708 (1965); (b) J. C. Russell and G. R. Freeman, *J. Phys. Chem.*, **71,** 755 (1967).

[5] J. C. Russell and G. R. Freeman, *ibid.*, **71,** 755 (1967); **72,** 816 (1968), give initial electron yield of 4.0 in ethanol.

[6] (a) W. V. Sherman, *ibid.*, **69,** 4053 (1965); (b) *ibid.*, **70,** 677 (1966).

With these considerations in mind the longest lived intermediates present in the Ac + IPA mixtures are likely to be the ions Ac^- (from electron capture by Ac) and $Me_2CHOH_2^+$ (from reaction 2). If the semipinacol radical, $Me_2C\text{–}OH$, is always the intermediate in the reduction (*i.e.*, H_2 transfer does not occur), then the maximum probable yield of IPA* from an Ac* + IPA mixture would be equal to one-half of the maximum yield of *Ac^-. Each of the two most probable pathways (3a or b) leads to this stoichiometry. Naturally other

$$Ac^- + Me_2CHOH^+ \longrightarrow [2Me_2C\text{–}OH] \longrightarrow Me_2CO + Me_2CHOH \quad (3a)$$

$$Me_2CHOH^+ + Me_2CHOH \longrightarrow Me_2CHOH_2^+ + [Me_2CHO \rightleftharpoons Me_2C\text{–}OH] \quad (3b)$$

$$Ac^- + Me_2CHOH \longrightarrow Me_2C\text{–}OH + Me_2CHO^-$$

$$Me_2CHO^- + Me_2CHOH_2^+ \longrightarrow 2Me_2CHOH$$

$$2Me_2C\text{–}OH \longrightarrow Me_2CO + Me_2CHOH$$

pathways can be conceived, *e.g.*, those in which not all electrons are captured by the acetone, but some neutralize the $Me_2CHOH_2^+$ to give hydrogen atoms, but these also lead to the same predicted maximum yield. The low yield of IPA from pure acetone means that Ac^- does not abstract an H^+ from another acetone molecule (although it can from IPA, PrOH, or $c\text{-}C_6H_{12}$).

The magnitude of the yield of IPA from the Ac + 1-propanol mixture (1.95) is consistent with an Ac^- yield of 4, if the Ac^- disappears by a proton-transfer process, leading to a yield of semipinacol radical of 4.

$$Ac^- + PrOH \longrightarrow Me_2C\text{–}OH + PrO^-$$

The lower yield of IPA from the Ac + cyclohexane mixture (1.25) reflects the lower availability of the electron in cyclohexane because of the lower dielectric constant and thus the lower yield of Ac^-. The yield of acetone from pure IPA (1.85) is also consonant with path a or b.

The role of acetone in Ac + IPA mixtures is thus that of an electron capturer; its presence prevents the neutralization reaction (2b) and substitutes for it a proton-transfer process (pathway 3a or b), preventing the formation of hydrogen atoms (eq 2). The effect of acetone in reducing the hydrogen yield from 2-propanol[1] is probably caused then by scavenging of the precursor of the hydrogen atom rather than by scavenging of the hydrogen atom itself.

An electron-scavenging process of a similar sort is probably also responsible at least in part for the γ-ray-induced pinacolization of benzophenone in IPA solution,[7] although direct excitation of the benzophenone

$$(C_6H_5)_2CO^- + Me_2CHOH^+ \longrightarrow (C_6H_5)_2C\text{–}OH + Me_2C\text{–}OH$$

triplet is a likely process because of the high yield of pinacol. Triplet-excited solutes have been observed in several γ-irradiated solutions,[8] and the yield of benzophenone semipinacol radicals, 6.6, is greater than would be expected from simple electron scavenging. Both benzophenone anion and triplet-excited benzophenone may be involved in the formation of the pinacol.

The mechanism thus described does account for the main features of our observations, but it does not account for several aspects of the data; the system is really more complicated. The unusually high value (6.9, compared to the expected value of 2) for the yield of IPA* from the Ac* + IPA mixtures and the equally unusually high yield of Ac* from the Ac + IPA* mixtures (4.5 compared to the expected value of 2) both indicate that there must be pathways for the interconversions other than those described above. The magnitudes of these values even suggest short chains, although we have not been able to propose any reasonable chain carriers. It is perhaps more likely that energetic excited species (with higher energy content than those produced by 313-nm photons) are formed by the γ rays, and that these species contribute to the interconversions. We have a more comprehensive study of the photochemistry of this system in progress now.

It is also not clear why the yield of Ac from IPA is larger at −196° than it is at 40°, or why the acetone reduction is less sensitive to temperature and phase than is the IPA oxidation. These changes in temperature and phase should be reflected presumably in the reactions of the semipinacol radicals since the disproportionation/recombination ratios of several alkyl radicals are sensitive to temperature.[9] However, it has been observed[10] that the pinacol formed by photolysis of a mixture of acetone-d_6 and IPA was composed 60% of pinacol-d_0 and 40% of pinacol-d_{12} and thus did not arise from random recombination of semipinacol radicals. It seems possible that semipinacol radicals only disproportionate.

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[7] J. G. Burr and J. D. Strong, *J. Phys. Chem.*, 63, 873 (1959).

[8] E. J. Land and A. J. Swallow, *Trans. Faraday Soc.*, 64, 1247 (1968); J. W. Hunt and J. K. Thomas, *J. Chem. Phys.*, 46, 2954 (1967).

[9] H. A. Gillis, *J. Phys. Chem.*, 71, 1089 (1967).

[10] G. Kolzenburg, K. Gorzney, and G. O. Schenck, personal communication.