Attempts To Trap Radicals Formed in Solution by a Magnesium Surface[1]

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The synthesis of 2,2′-azo-2-methyl-6-heptene (1) is described. Photolytic decomposition of 1 in ether gave rise to the 1,1-dimethyl-5-hexenyl radical clock (2) which yielded 1,1,2-trimethylcyclopentane (3), 6-methyl-1-heptene (4), and 2-methyl-1,6-heptadiene (5) in the ratio of 1:0.72:0.56, respectively. The ratio did not change appreciably when a well-stirred mixture of 1 and 5 equiv of magnesium powder was photolyzed. Moreover, the solution gave a negative test (2,2′-biquinoline) for the presence of Grignard reagent. Thus, it has been experimentally demonstrated that the radicals formed in solution do not react with a magnesium surface to form Grignard reagents.

Introduction

The seminal work of Paneth and Hofeditz[2] provided the foundation for free-radical chemistry when they demonstrated that *gaseous* methyl free radicals could be detected by their reaction with metallic mirrors such as lead, antimony, and zinc.[3] Subsequent work disclosed that this technique could be applied to, inter alia, various alkali and alkaline earth metals, mercury, tin, cadmium, and even lanthanum mirrors. Lagow[4] has shown that gaseous methyl free radicals will oxidize gaseous metal atoms such as bismuth, tin, mercury, cadmium, and germanium usually to their highest oxidation state, i.e., Ge to $(CH_3)_4Ge$. Lower oxidation states have also been observed[5] for the reaction of calcium and strontium vapors with gaseous methyl radicals to yield $\bullet CaCH_3$ and $\bullet SrCH_3$ radicals, respectively.

Skell and Girard[6] demonstrated that the codeposition of a variety of alkyl halides with magnesium atoms at −196 °C yielded unsolvated alkylmagnesium halides upon warming. Infrared analysis[7] of the oxidative addition reaction of magnesium atoms with methyl halides in an argon matrix supported these findings as did the gaseous-state ab initio calculations of Davis.[8] These results are consistent with the mechanism, depicted in Scheme I, which we proposed for Grignard reagent formation.[9]

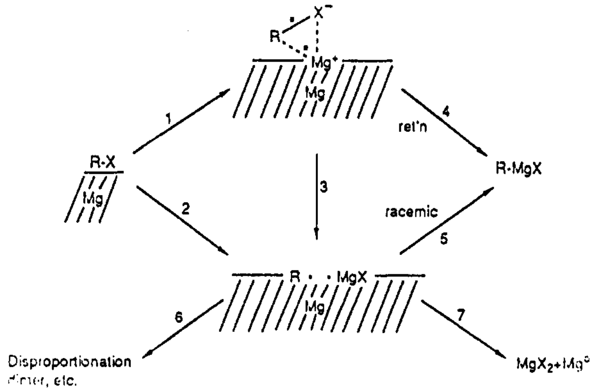
A question that has still to be answered is whether or not free radicals generated *in solution* will react with magnesium surface. The free radical we selected for this investigation is the 1,1-dimethyl-5-hexenyl radical (2) which will be generated in ether solution by the photolysis of 2,2′-azo-2-methyl-6-heptene (1). The result of this investigation is the subject of this paper.

Results and Discussion

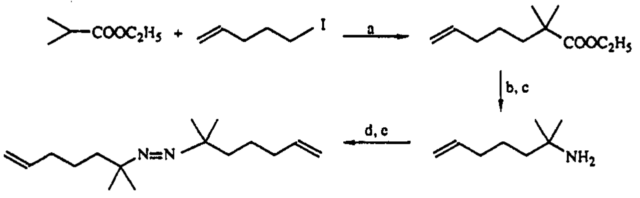
The basic ideal of our study was to generate free radicals in solution and to ascertain whether or not these radicals would interact with a magnesium surface. In essence, we wished to determine if a magnesium surface is an effective radical trap. Thus, a comparison of the behavior of radicals in solution with their behavior when generated in solution but in the presence of a magnesium surface would provide us with the answer we are seeking.

The probe selected for this investigation was the free-radical clock which has been so effectively employed in other studies. A number of radical clocks have been calibrated, and the physical data have been collected and discussed in excellent reviews.[10,11] The 5-hexenyl and substituted 5-hexenyl cyclizable radical probes are among the most frequently used radical clocks.[12]

Scheme I



Scheme II. Synthesis of 2,2′-Azo-2-methyl-6-heptene (1)[a]



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[a] Key: (a) $(C_6H_{11}\text{-N-}i\text{-Pr})Li$; (b) $^-OH/H_3O^+$; (c) $(PhO)_2\overset{\overset{O}{\|}}{P}N_3$; (d) SO_2Cl_2; (e) NaH/*t*-BuOCl.

The method that we chose to generate the radical clock was by the decomposition of the appropriate azo compound. This method provides one with an excellent source of free radicals in solution. The chemistry of aliphatic azo

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compounds has been thoroughly investigated, and several review articles on the subject have appeared.[13,14] Unfortunately not all aliphatic azo compounds decompose smoothly. Our preliminary attempt to use a primary azo compound, azo-5-hexene, was unsuccessful. Instead of the anticipated decomposition a tautomerization took place and the corresponding hydrazone was produced. To avoid this kind of side reaction we chose a tertiary azo compound, namely 2,2′-azo-2-methyl-6-heptene, as our source of the 1,1-dimethyl-5-hexenyl radical clock (2). Tertiary azo compounds have been reported to decompose with great facility due to both the stability of the radical formed and the ground-state strain.[15,16] Moreover, they have been shown to be stable toward Grignard reagents.[17] The mechanism of decomposition of tertiary azo compounds has been established by Mill and Stringham,[18] who found that the photolysis of *trans*-azo-2-methyl-2-propane converts it to the cis isomer which decomposes thermally to give *tert*-butyl radicals. The 6-methyl-1-heptenyl radical clock (2) has been calibrated by several groups,[19] and the rate constant for cyclization has been found to be 10^6 s^{-1}.

Synthesis of 2,2′-Azo-2-methyl-6-heptene (1). The synthesis of 1 was straightforward and is outlined in Scheme II. Ethyl isobutyrate was alkylated under standard conditions with 1-iodo-4-pentene, and the product was subsequently saponified to give 2,2-dimethyl-6-heptenoic acid in 78% overall yield. The acid was then converted to the corresponding amine in 74% yield by a Curtius rearrangement using diphenylphosphoryl azide.[20] The amine was treated with sulfuryl chloride under the conditions described by van Wazer[21] to give the desired sulfamide in 60% yield. Finally, the sulfamide was oxidized to the azo compound in 58% yield by the Ohme–Engel modified hypochloride procedure.[22,23]

Our initial objective was to establish the products and product ratios formed after photolysis of azo compound 1. Photolyses of 1, at 350 μ, were carried out in diethyl ether solutions at 23 °C to give rise mainly to three hydrocarbon products: 1,1,2-trimethylcyclopentane (3), 6-methyl-1-heptene (4), 2-methyl-1,6-heptadiene (5), and several very minor products which were not isolated. The products were identified by spectral analyses, and syntheses (see Experimental Section) and product ratios, as shown in Table I, were determined by GC using 1 equiv of *n*-heptane as an internal standard reference.

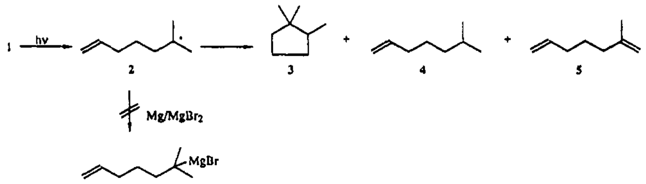

Table I. Photolysis of 1 at 350 nm in Diethyl Ether at 23 °C

entry	concn (M)	time (h)	total yield (%)	product ratio (% yield) 3	4	5
1	0.025	6	91	1 (43)	0.60 (26)	0.52 (22)
2	0.25	15	57	1 (25)	0.72 (18)	0.56 (14)
3[a]	0.25	15	56	1 (3)	12.7 (41)	3.7 (12)

[a] In the presence of 5 equiv of diphenylphosphine.

Table II. Photolysis of 1 at 350 nm in Diethyl Ether in the Presence of Magnesium

run	concn (M)	time (h)	total yield (%)	product ratio (% yield) 3	4	5
1[a]	0.025	6	91	1 (43)	0.61 (26)	0.52 (22)
2[b]	0.25	15	25	1 (11)	0.72 (8)	0.55 (6)
3[c]	0.25	15	58	1 (26)	0.69 (18)	0.54 (14)
4[d]	0.25	15	59	1 (27)	0.68 (18)	0.54 (14)
5[e]	0.25	15	52	1 (23)	0.65 (15)	0.60 (14)

[a] In the presence of 5 equiv of magnesium powder which was activated by stirring under argon.[26] [b] In the presence of 5 equiv of magnesium activated by ethylene bromide (0.5 equiv of $MgBr_2$). [c] In the presence of 5 equiv of magnesium powder activated by ethylene bromide and the magnesium bromide was washed out. [d] In the presence of magnesium which was activated by MeI and the MeMgI was washed out. [e] In the presence of Rieke magnesium.[27]

As can be seen in Table I, the total yield, as expected, is much lower in the case of a high concentration of 1 due to the formation by dimerization and/or polymerization of some nonvolatile products. Although the yields are lower at the higher concentrations they are more in line with the concentrations normally used in Grignard reagent formation. Hence in our study, for the most part, the higher concentrations will be used. However, it should be noted that product ratios do not change appreciably at the different concentrations. It can also be seen that the photolysis of 1 does indeed give rise to the 1,1-dimethyl-5-hexenyl radical (2) since it could be trapped by diphenylphosphine as evidenced by the large reduction of cyclized product 3. This observation is in good agreement with the rate of abstraction of hydrogen from diphenylphosphine[24] being in excess of 10^7 s^{-1} and the rate of cyclization[19] of 2 being about 10^6 s^{-1}. Also, the close correspondence in the yields of 4 and 5 would indicate that these products arose largely by disproportionation of the intermediate radical 2.

Effect of Magnesium Surface on the Rearrangement of Free Radicals Generated in Solution. In order to establish the effect that the magnesium surface has on the rearrangement of free radicals in solution the photolysis of 1 was performed under the same conditions but in the presence of magnesium which had been activated in a variety of ways (Table II). In each case (runs 1–5, Table II), after total consumption of 1 by photolysis, the reaction mixture was checked for Grignard reagent by addition of 2,2-biquinoline,[25] and in each case a negative result was obtained. Under our conditions if 1% of Grignard reagent had been formed it would have been detected. The mixtures were analyzed using the same techniques that we described above.

As can be seen in run 1, Tables I and II, the yield and ratio of products are identical whether 1 was photolyzed

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in the presence or absence of a magnesium surface. Furthermore, regardless of how one attempted to activate the surface of the magnesium including the use of the highly reactive Rieke magnesium[27] the results were the same (runs 2–6). Moreover, they are almost identical to the product ratios obtained in the absence of a magnesium surface. We have calculated (see Experimental Section) that in the case of Rieke magnesium that all the radicals are generated with 1500 Å of the surface of the magnesium. We may reasonably assume that at these distances one should observe some interaction of these radicals with the magnesium surface. It has been calculated that the *n*-octyl radical can travel as far as 17 000 Å into the solution and still have a 40% chance of getting back to the surface of magnesium before reacting with ether solvent.[28] We may reasonably assume that the tertiary radical 2 or the (2,2-dimethylcyclopentyl)carbinyl radical we generate should react even slower with the solvent than do *n*-octyl radicals. Since our radicals are generated, in the case of Rieke magnesium, about 10 times closer to the magnesium surface they should have a perfect chance to reach the surface and form Grignard reagent. Yet, they do not! These results provide compelling evidence that under these conditions magnesium *does not* behave as an effective radical trap.

Experimental Section

All the reagents were purchased from Aldrich, except for dicyclohexylphosphine which was purchased from Strem. THF and ether were dried by refluxing and distilling from sodium–potassium alloy. All experiments were conducted in a dry argon atmosphere. All melting points and boiling points are uncorrected.

IR spectra were taken on a Perkin-Elmer 257 spectrophotometer. UV spectra were recorded with a Cary 219 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz with $CDCl_3$ as solvent unless noted otherwise, with Me_4Si and $CHCl_3$ (7.26 ppm) was internal standard. Mass spectra and GC–MS analyses were performed using a Finnigan 4500 automated gas chromatograph/EI-CI mass spectrometer equipped with a DB-5 fused silica capillary column (J&W Scientific). Microanalyses were performed by Beller Laboratories, Göttingen, Germany.

Reaction products were analyzed on a Varian 3300 gas chromatograph using a capillary column DX4-30N (30 m × 0.25 mm, film thickness 0.25 μm) at 40 °C, with helium as a carrier gas and a flame ionization detector.

2,2-Dimethyl-6-heptenoic Acid. *n*-Butyllithium (1.6 M, 62.5 mL) was added to a mixture of THF (100 mL) and freshly distilled *N*-isopropylcyclohexylamine[29] (0.1 mol, 16.5 mL), at −70 °C. The dry-ice/acetone bath was removed, the temperature was allowed to rise 0 °C, and the reaction mixture was maintained at this temperature for 0.5 h. The solution was cooled to −70 °C, and ethyl isobutyrate (0.095 mol, 11.4 g) was added dropwise. Stirring was continued for 1 h at −70 °C, and then a solution of 5-iodo-1-pentene[30] (0.095 mol, 18.4 g) in HMPA (15 mL) was added. The stirring was continued overnight at ambient temperature, and the reaction mixture was poured into ice/water containing 10 mL of concentrated HCl. The product was then extracted with diethyl ether (3 × 50 mL), and the combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was distilled to afford 15 g (86%) of colorless liquid (135–140 °C/aspirator): ^{1}H NMR 1.15 (s, 6 H), 1.23 (t, 3 H, J = 7.0 Hz), 1.2–1.28 (m, 2 H), 1.44–1.56 (m, 2 H), 1.97–2.07 (bq, 2 H), 4.11 (q, 2 H, J = 7.0 Hz), 4.9–5.04 (m, 2 H), 5.7–5.86 (m, 1 H) ppm.

The distillate was disolved in methanol (100 mL), 20% aqueous sodium hydroxide was added (25 mL), and the solution was refluxed for 2 h. After being cooled, the mixture was diluted with water (100 mL), extracted once with diethyl ether (50 mL), and then acidified with 10% hydrochloric acid (60 mL) with cooling (ice/water bath). The product was extracted with diethyl ether (3 × 70 mL), and the combined extracts were washed with water and brine and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue distilled to give 11.5 g (78% yield from iodide) of the acid (95–100 °C (0.1 mmHg)): IR (film) cm^{-1} 3069, 2972, 2934, 2677, 1696, 1634 cm^{-1}; ^{1}H NMR 1.17 (s, 6 H), 1.3–1.42 (m, 2 H), 1.5–1.6 (m, 2 H), 1.99–2.09 (bq, 2 H), 4.91–5.05 (m, 2 H), 5.72–5.87 (m, 1 H) ppm. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.18; H, 10.35.

6-Amino-6-methyl-1-heptene. Diphenylphosphorazidate[20] (21.7 g, 79 mmol) was added with external cooling to a stirred solution of 2,2-dimethyl-6-heptenoic acid (11.5 g, 74 mmol) and triethylamine (11 mL, 79 mmol) in dry benzene. A slightly exothermic reaction commenced and was completed after about 1 h. Stirring was continued for an additional 1 h at room temperature followed by refluxing for 3 h (evolution of nitrogen). The solution was cooled and washed with water (3 × 100 mL), and the benzene phase was separated and dried over anhydrous sodium sulfate. The solvent was evaporated, and a mixture of 15% hydrochloric acid (20 mL) and acetic acid (20 mL) was added. After about 10–15 min of stirring at room temperature a rapid evolution of a gas took place, and stirring was continued overnight. The mixture was added dropwise to a cooled 10% aqueous solution of sodium hydroxide (200 mL) and extracted with diethyl ether (3 × 70 mL), and the combined extracts were washed with water and brine and dried over potassium hydroxide. The solvent was evaporated, and the residue was distilled to give 7 g (74% yield) of the amine (collected at 160–170 °C): IR (film) 3340, 3260, 1630, 1590 cm^{-1}; ^{1}H NMR 1.08 (s, 6 H), 1.22–1.48 (m, 4 H), 2.0–2.1 (bq, 2 H), 4.91–5.05 (m, 2 H), 5.74–5.9 (m, 1 H) ppm. Anal. Calcd for $C_8H_{17}N$: C, 75.52; H, 13.47. Found: C, 75.49; H, 13.59.

***N,N'*-(2-Methyl-6-hepten-2-yl)sulfamide.** Freshly distilled sulfuryl chloride (2.17 g, 27 mmol) was added dropwise with stirring to the solution of 6-amino-6-methyl-1-heptene (7 g, 55 mmol) and triethylamine (8.4 mL, 61 mmol) in dry diethyl ether (150 mL) at −70 °C. Stirring was continued for 2 h at −70 °C, and the mixture was kept overnight at −20 °C. Ether (50 mL) was added, and the suspension was poured into water. The organic phase was separated, washed with water and brine, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, hexane–ethyl acetate (10:1)) to give 5.2 g (60% yield) of a waxy solid, mp 46–47 °C: RI (Nujol) 3310, 1630, 1300, 1130 cm^{-1}; ^{1}H NMR 1.33 (s, 6 H), 1.36–1.61 (m, 4 H), 2.0–2.1 (bq, 2 H), 3.95 (bs, 1 H), 4.93–5.06 (m, 2 H), 5.72–5.87 (m, 1 H) ppm. Anal. Calcd for $C_{16}H_{32}N_2O_2S$: C, 60.72; H, 10.19. Found: C, 60.70; H, 10.15.

2,2'-Azo-2-methyl-6-heptene (1). *N,N'*-(2-Methyl-6-hepten-2-yl)sulfonamide (5.2 g, 16.4 mmol) was dissolved in dry hexane (100 mL) and added to a suspension of sodium hydride (0.8 g, 33 mmol) in dry hexane (100 mL). The mixture was stirred at room temperature for 3 h and cooled to 0 °C (ice bath), a solution of *tert*-butyl hypochlorite (4 mL, 33.5 mmol) in dry hexane (10 mL) was added slowly, and the mixture was stirred overnight at room temperature. Water was carefully added with external cooling (ice bath), and after stirring for 0.5 h the hexane layer was separated, washed with water, and dried over anhydrous calcium chloride. The solution was filtered through a thin layer of silica gel, the solvent was evaporated, and the residue was distilled (100–120 °C (0.05 mmHg)). The distillate was purified by chromatography (silica gel/hexane-ethyl acetate (100:1)). After evaporation of solvent the product was distilled in vacuo (Kugelrohr 100–110 °C (0.05 mmHg)) to give 2.4 g (58% yield) of the title compound: UV ($CHCl_3$) λ_{373} ϵ 19.7; ^{13}C NMR (75 MHz) 23.13, 24.43, 34.20, 40.05, 68.24, 114.44, 139.18; ^{1}H NMR 1.08 (s, 6 H), 1.23–1.35 (m, 2 H), 1.57–1.66 (m, 2 H), 1.96–2.06 (bq, 2 H), 4.88–5.03 (m, 2 H), 5.71–5.86 (m, 1 H) ppm. Anal. Calcd for $C_{16}H_{30}N_2$; C, 76.74; H, 12.07; N, 11.19. Found: C, 76.88; H, 12.06; N, 11.15.

Photolysis of 2,2'-Azo-2-methyl-6-heptene (1). All experiments were carried out in a Rayonet photochemical reactor equipped with 16 ultraviolet lamps, Model RPR-3500 Å. The jacketed reaction vessel was cooled with constantly flowing water to maintain the internal temperature at 23 ± 0.5 °C. All reactions were carried out under an argon atmosphere and stirred with a

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magnetic stirrer. Before the irradiation started the samples had been degassed by passing argon through the solution. Reactions were carried out for 6 h at the concn of 0.025 M and for 15 h at the concn of 0.25 M. After addition of the standard (1 mmol of *n*-heptane per 1 mmol of the initial azo compound), aliquots were analyzed by capillary GC.

Preparation of 2-Methyl-1,6-heptadiene (5). A commercially available (Aldrich) mixture of methyltriphenylphosphonium iodide with sodium amide (4.2 g, giving 10 mmol of the ylide upon dissolving) was added to a solution of 1.12 g (10 mmol) of 6-hepten-2-one in ether at −20 °C, and the reaction mixture was stirred overnight at room temperature. The mixture was filtered, and the ether was removed by distillation using a spinning band column. The residue was diluted with pentane (25 mL), filtered, and passed through a short pad of silica gel. Pentane was removed by distillation through a spinning band column, and the residue was distilled at atmospheric pressure to give 0.6 g (55%) of 2-methyl-1,6-heptadiene[31] (bp 105 °C): IR (film) 1635 cm^{-1}; ^{1}H NMR 1.42–1.55 (m; 2 H), 1.67 (s; 3 H), 1.95–2.05 (m; 4 H), 4.62–4.70 (m; 2 H), 4.90–5.02 (m; 2 H), 5.75–5.87 (m; 1 H) ppm.

Preparation of 1,1,2-Trimethylcyclopentane (3). This compound was isolated from a mixture of olefin **4**, cyclopentane **3**, and diene **5** formed in a ratio of 1.28:1.77:1 after photolysis of 2,2′-azo-2-methyl-6-heptene. The mixture (900 mg) was mixed with pentane (100 mL) and concentrated sulfuric acid (100 mL) and stirred vigorously at room temperature for 14 h. The pentane layer was separated, washed with a solution of potassium carbonate, dried over magnesium sulfate, and filtered through silica gel. The pentane was removed by distillation through a spinning band column, and the residue was distilled using a Buchi Kugelrohr to give the desired authentic sample which gave the same spectral properties as reported:[32] ^{1}H NMR 0.72 (s; 3 H), 0.82 (d; 3 H; J = 7.2 Hz), 0.94 (s; 3 H), 1.27–1.57 (m; 7 H) ppm; MS M$^+$, 112.

Preparation of 6-Methyl-1-heptene (4). Isoamyl lithium was prepared at −70 °C by mixing a solution of 3-methyl-1-bromobutane (7.2 mL, 60 mmol) in dry ether and a solution of t-butyl lithium (100 mL, 120 mmol, 1.2 M in hexane). After stirring for 45 min the mixture was added via cannula and under an argon atmosphere to a suspension of CuBr·Me$_2$S (6.8 g, 33 mmol) in ether. The mixture was stirred at −40° for 1 h and an ether solution of allyl bromide (1.7 mL, 20 mmol) was added. The reaction mixture was allowed to warm to 0 °C and then quenched with a mixture composed of 10% concentrated NH$_4$OH/saturated aqueous NH$_4$Cl solution. The mixture was extracted with ether (3 × 50 mL) and the ether extract was washed with water and dried over magnesium sulfate. The solvent was removed using a spinning band column and the crude residue was purified by distillation using a Buchi Kugelrohr (bp 100 °C) to give **5** (1.2 g, 54% yield). The NMR spectrum of the product isolated was identical to that reported.[33] ^{1}H NMR 0.87 (d; 6 H; J = 6.6 Hz), 1.2–1.6 (m; 5 H), 2.05 (m; 2 H), 5 (m; 2 H), 5.8 (m; 1 H) ppm. MS: M$^+$: 112.

Table III

distance L (Å)	total vol of soln within spheres (mL)	fraction of radicals generated within spheres (%)
250	0.40	4.0
500	1.19	11.9
750	2.49	24.9
1000	4.42	44.2
1250	7.12	71.2
1500	10.71	107.1

Calculation of the Distance that Radicals Are from the Surface of Rieke Magnesium. We use for our calculations the average particle size of Rieke magnesium which is reported[27c] to be 0.1 μm (10^{-5} cm). The radius of this particle, assuming that it is a sphere, is $r = 5 \times 10^{-6}$ cm and the calculated volume of such a particle is 5.23 × 10^{-10} cm^3.

Magnesium, 12.5 mmol (0.3 g), was used in the experiment. The density of magnesium is 1.74 g/cm^3, and the total volume of magnesium is calculated to be 0.17 cm^3. The number of Rieke magnesium particles is calculated by dividing the total volume of magnesium by the volume of magnesium particles and equals 3.25 × 10^{14}.

Let us now calculate the volume of a solution within a sphere extending from the magnesium surface to a point L Å beyond the surface into the solution. The volume of such a sphere is calculated by substracting the volume of the magnesium particle from the total volume of magnesium particle and the solution around it. The latter is a ball whose radius is equal to the sum of the radii of magnesium particles and the distance L ($r + L$). By multiplying the volume of the sphere around magnesium by the number of magnesium particles one can obtain a total volume of the solution around the magnesium particles. This volume is subsequently compared to the total volume of the solution (10 mL) to calculate how many radicals are generated close to the magnesium surface.

Since it is not known how far radicals can diffuse into the solution we will assume reasonable values to be several hundred to tens of thousands of Å, and these values will be used for the distance L in our calculations. The results of these calculations are shown in Table III. These simple calculations indicate that in the case of Rieke magnesium all the radicals are generated close to the magnesium surface (within the sphere L = 1500 Å).

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