Viscosity and temperature dependence of the magnetic isotope effect

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The ^{13}C enrichment observed in the first order photolytic decomposition of dibenzylketone (1,3-diphenyl-2-propanone) was studied as a function of solvent viscosity and temperature. The isotope effect is due to electron–nuclear hyperfine interactions in the free radical intermediates of the reaction. The results are explained using a continuum diffusion model and a simplified version of the radical pair theory of Chemically Induced Dynamic Nuclear Polarization (CIDNP). The isotope effect is substantially enhanced at intermediate values of viscosity.

I. INTRODUCTION

In 1971[1] the prediction was made that the same factors responsible for the production of nonequilibrium nuclear polarization in free radical reactions [chemically induced dynamic nuclear polarization (CIDNP)[2]] should also produce enrichment of isotopes of differing magnetic moment. The prediction was of a novel chemical isotope effect in that it was based on nuclear magnetic properties rather than masses.

Not long ago Buchachenko *et al.* reported observing the magnetic isotope effect for ^{13}C in the photolysis of dibenzylketone.[3] We recently corroborated this work using NMR and mass spectroscopy and further demonstrated that the effect could be substantially enhanced when the reaction is carried out at high viscosity.[4] Turro *et al.* have shown that greater enhancements of the dibenzylketone enrichment are possible by performing the reaction under conditions where the photochemistry takes place within micelles.[5] Other reports of enrichment via the magnetic isotope effect have been given for ^{13}C,[6] ^{17}O,[7] and $^{117}Sn/^{119}Sn$[8] as well as for transient isotope effects involving $^{1}H/^{2}D$.[9]

In this paper we present the results of a study of the ^{13}C enrichment in dibenzylketone over the viscosity range 6×10^{-3} to 2.7×10^{2} P and over the temperature range -60 to 25 °C. We also present a simplified model for the effect which is in good agreement with our results and which allows prediction of the optimum conditions for effecting isotope separation in other free radical reactions.

II. THEORY

The overall reaction scheme for dibenzylketone is depicted in Fig. 1. The initial excitation of the carbonyl group is most probably a transition to the $n\pi^*$ singlet state.[10] This singlet state intersystem crosses to an excited triplet which then decays via bond scission adjacent to the carbonyl group.[11] The bond scission occurs with retention of the triplet electron correlation.[12] Since bonding is not allowed when the electrons have triplet spin correlation, the radicals constitute an "inert" radical pair. If the radical pair intersystem crosses from the repulsive triplet potential energy surface to the bonding singlet potential energy surface, the parent ketone may be reformed if the radicals undergo a collision. The crux of the magnetic isotope effect is that the predominant mechanism for intersystem crossing in the radical pair is the electron-nuclear hyperfine interaction.[13]

To achieve isotope selectivity there must be competing processes for removal of the radical pairs. In this case diffusive separation of the radicals and decarbonylation of the ketyl radical serve to prevent reformation of the ketone as outlined in Fig. 1.[11,14,15] The three processes of hyperfine induced intersystem crossing, diffusion, and decarbonylation are discussed briefly below.

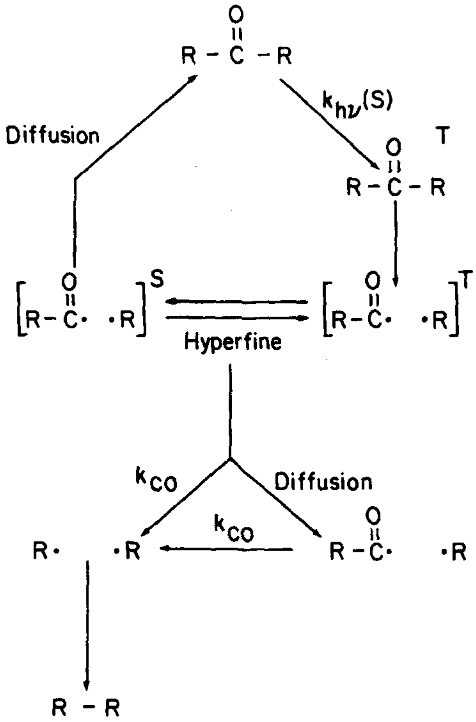

FIG. 1. Overall reaction scheme for photolysis of dibenzylketone ($R = C_6H_5CH_2$): *S* and *T* stand for singlet and triplet electron correlation, respectively; $k_{h\nu}(S)$ indicates that photolysis involves an excited singlet state; the brackets [ ] indicate radical pairs that have a finite probability of diffusive reencounter. Hyperfine couplings equilibrate *S* and *T* while diffusive encounter of singlets reforms the ketone; diffusive separation and decarbonylation (k_{CO}) form 1, 2-diphenylethane.

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A. Hyperfine induced intersystem crossing

In a classical picture the unpaired electron on each radical of the pair precesses due to the presence of nuclei in the radical with nonzero magnetic moments (electron–nuclear hyperfine interaction). Since the two unpaired electrons experience different magnetic environments on the two radicals, they precess differently, and consequently the spin correlation between the two electrons is destroyed.[16] This loss of correlation is equivalent to establishing a mixture of singlets and triplets having started with a pure triplet system. Quantum mechanically, this corresponds to a system oscillating between singlet and triplet since neither is an eigenstate. However, when many nuclear spins are present, the rephasing time for the electron spins becomes long, and the process resembles relaxation more than coherent oscillation. Thus, we treat the electron spins as a system approaching equilibrium (i.e., 25% singlet, 75% triplet) with the hyperfine couplings serving as the driving terms.

We define k_+ as the singlet to triplet intersystem crossing rate constant and k_- as the triplet to singlet term. At zero magnetic field $k_+ = 3k_-$. Defining $k_+ + k_-$ as the electron dephasing (intersystem crossing) rate, we wish to relate this quantity to the hyperfine interactions present in the radical pair. We assume rapid tumbling of the radicals in solution and consider only the isotropic hyperfine interaction. In high magnetic field the precession rate of an electron coupled to a single nucleus is ma, where m is the magnetic quantum number and a is the hyperfine interaction of the nucleus. Ignoring differences in electron g factors, the difference in precession rate $\Delta\nu$ for the two electrons at high field is

$$\Delta\nu_{\mathrm{HF}} = \left| \sum_i^a m_i a_i - \sum_j^b m_j a_j \right| , \tag{1}$$

where the sums are over the two radicals for a given nuclear spin state. Assuming only spin-$\frac{1}{2}$ nuclei are present, at zero field the electron–nuclear coupling becomes a rather than ma. By analogy we define for zero field:

$$\Delta\nu_0 \equiv \left| \sum_i^a n_i a_i - \sum_j^b n_j a_j \right| , \tag{2}$$

where $n = \pm 1$ for each nucleus. By averaging over all possible nuclear spin states, one can calculate the average difference $\overline{\Delta\nu}$. Since a 180° dephasing interconverts singlet and triplet, for zero field we set $k_+ + k_-$ equal to $2\overline{\Delta\nu_0}$.

The isotropic hyperfine interaction for each nucleus is directly proportional to (1) the magnetic moment of the nucleus and (2) the spin density (s-orbital character) of the electron at the nucleus. For dibenzylketone photolysis the relevant radical pair along with the known hyperfine constants is shown in Fig. 2. ^{12}C with spin 0 has no hyperfine interaction. For the ^{13}C-containing radical pair we estimate

$$^{13}k_+ + {}^{13}k_- = 7 \times 10^8 \text{ Hz}$$

and for ^{12}C,

$$^{12}k_+ + {}^{12}k_- = 1.1 \times 10^8 \text{ Hz} .$$

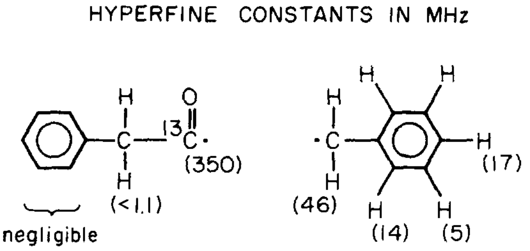

FIG. 2. Hyperfine constants for the radical pair formed by photolysis of dibenzylketone. All values are taken from Ref. 17.

B. Diffusion

Using $\rho(\mathbf{r}, t)$ to represent the probability per unit volume for finding the two members of the radical pair at a relative separation $\mathbf{r}$ and assuming no long range interactions between the radicals, $\rho(\mathbf{r}, t)$ is described by the simple diffusion equation

$$\frac{\partial\rho}{\partial t}(\mathbf{r}, t) = D_R \nabla^2 \rho(\mathbf{r}, t) , \tag{3}$$

where D_R is the relative diffusion coefficient. Since decarbonylation is fast enough to prevent formation of the ketone from radicals of different radical pairs, we need only consider the evolution of a single ensemble-averaged pair of radicals. Thus, $\rho(\mathbf{r}, t)$ is the normalized probability function for all radical pairs in solution.

C. Decarbonylation

The first order rate constant k_{CO} for decarbonylation of the ketyl radical into a benzyl radical

$$C_6H_5CH_2\dot{C}O \xrightarrow{k_{\mathrm{CO}}} C_6H_5\dot{C}H_2 + CO$$

has been reported for two temperatures -116[18] and 25 °C.[15] From these literature values k_{CO} is given by

$$k_{\mathrm{CO}} = 10^{13} \exp(-E_a/RT)\ \mathrm{sec}^{-1} ,$$

with $E_a = 7.3$ kcal/mole.

D. Enrichment factor

To describe the system fully it is necessary to introduce two probability functions $\rho_S(\mathbf{r}, t)$ and $\rho_T(\mathbf{r}, t)$, one for singlet radical pairs and one for triplet radical pairs, respectively.[19] With these two quantities the system is described by the following equations:

$$\frac{\partial\rho_S}{\partial t}(\mathbf{r}, t) = D_R \nabla^2 \rho_S(\mathbf{r}, t) - k_{\mathrm{CO}}\, \rho_S(\mathbf{r}, t) - k_+ \rho_S(\mathbf{r}, t) + k_- \rho_T(\mathbf{r}, t) , \tag{4}$$

$$\frac{\partial\rho_T}{\partial t}(\mathbf{r}, t) = D_R \nabla^2 \rho_T(\mathbf{r}, t) - k_{\mathrm{CO}}\rho_T(\mathbf{r}, t) + k_+ \rho_S(\mathbf{r}, t) - k_- \rho_T(\mathbf{r}, t) . \tag{5}$$

The following boundary conditions are introduced:

$$\rho_S(\mathbf{r}, t) , \quad \rho_T(\mathbf{r}, t) \to 0 \text{ as } |\mathbf{r}| \to \infty , \tag{6a}$$

$$\rho_S(\mathbf{r}, t) = 0 , \quad |\mathbf{r}| = r_c , \tag{6b}$$

$$\hat{r} \cdot \nabla \rho_T(\mathbf{r}, t) = 0 , \quad |\mathbf{r}| = r_c . \tag{6c}$$

Condition (6a) holds since there are a finite number of radical pairs. Condition (6b) states that all singlets are absorbed when the interradical separation $|\mathbf{r}|$ equals r_c, the collision radius. Condition (6c) states that all triplets are reflected when the radicals reach the collision radius. The initial conditions placed on the system are

$$\rho_S(\mathbf{r},0)=f_S\,\delta(\mathbf{r}-\mathbf{r}_0)\ , \tag{7a}$$

$$\rho_T(\mathbf{r},0)=(1-f_S)\,\delta(\mathbf{r}-\mathbf{r}_0)\ , \tag{7b}$$

where f_S is the fraction of singlets present at $t=0$, and $\mathbf{r}_0$ is the initial interradical separation.

The fraction R of radical pairs which recombine is equal to the flux of singlets into the reaction zone $|\mathbf{r}|=r_c$ integrated over all time[20]:

$$R=\int_0^\infty dt\int dA\,D_R\,\frac{\partial\rho_S}{\partial r}(\mathbf{r},t)\ , \tag{8}$$

$$|\mathbf{r}|=r_c\ .$$

Integrating Eqs. (4) and (5) over all time and solid angle, recognizing the solutions as zeroth-order modified spherical Bessel functions, and imposing the boundary and initial conditions, the following expression is obtained for R:

$$R=\frac{r_c}{r_0}\,\frac{(1+\beta r_c)\exp[-\alpha(r_0-r_c)]+[f_S(1+k_+/k_-)-1]\,(1+\alpha r_c)\exp[-\beta(r_0-r_c)]}{(1+\beta r_c)+(1+\alpha r_c)k_+/k_-}\ , \tag{9}$$

where the following quantities have been introduced:

$$\alpha=(k_{\mathrm{CO}}/D_R)^{1/2}\ , \tag{10}$$

$$\beta=([k_{\mathrm{CO}}+k_++k_-]/D_R)^{1/2}\ . \tag{11}$$

All of the isotope dependence is contained in k_+ and k_- (see Sec. II.A).

Since we are interested in a differential effect between ^{13}C and ^{12}C (references to ^{13}C and ^{12}C in the Discussion below will always pertain to the carbonyl position), it is necessary to define an enrichment factor which allows direct comparison between theory and experiment. We define the enrichment factor ϵ as equal to the differential loss between ^{12}C and ^{13}C radical pairs relative to the loss of ^{12}C:

$$\epsilon=\frac{(1-{}^{12}R)-(1-{}^{13}R)}{1-{}^{12}R}=1-\frac{1-{}^{13}R}{1-{}^{12}R}\ . \tag{12}$$

For dibenzylketone $f_S=0$, and we assume that both radicals have the same self-diffusion constant D_{self} so that $D_R=2D_{\mathrm{self}}$.[21] The collision radius r_c equals the sum of the radii of the ketyl and benzyl radicals. We take r_c to be twice the molecular radius σ of toluene since the toluene molecule is intermediate in size to the two radicals. From the molecular density of toluene we estimate

$$\sigma\simeq 3\times10^{-8}\ \mathrm{cm}$$

and

$$r_c\simeq 2\sigma\ .$$

The initial interradical separation r_0 depends upon the exothermicity of the bond scission[22] and upon the microscopic structure of the solvent.[23] Treating r_0 as a phenomenological parameter, a value of ~9 Å gives good agreement between theory and experiment (see Fig. 6). ϵ is plotted in Fig. 3 as a function of D_{self}.

III. EXPERIMENT

The experimental procedure was to photolyze the dibenzylketone and monitor the ^{13}C content of the compound as the reaction proceeded. For ease of analysis the ketone was prepared with the carbonyl carbon initially enriched to approximately 30% ^{13}C.

An AH-6 mercury lamp (Illumination Industries, Inc.) was used for the photolysis, and the reaction progress was followed using gas chromotography to monitor the relative amounts of the ketone and the decarbonylation product 1, 2-diphenylethane.

The isotopic analysis was performed with two different methods: mass spectrometry and NMR spectroscopy. In the former method a mass spectrum is taken for the molecular ion of the dibenzylketone. The spectrum is then analyzed by assuming natural abundance isotopes at all positions except for the carbonyl carbon. Although mass spectrometry is more accurate, NMR has the advantage of monitoring the isotopic content at the carbonyl position directly. A carbonyl ^{13}C splits the proton resonance at the adjacent methylene position by 6.3 Hz. By observing the proton NMR spectrum and comparing the integrated areas of the ^{13}C satellites to the unsplit methylene resonance, the percent ^{13}C is obtained. One set of results where the NMR analysis is performed

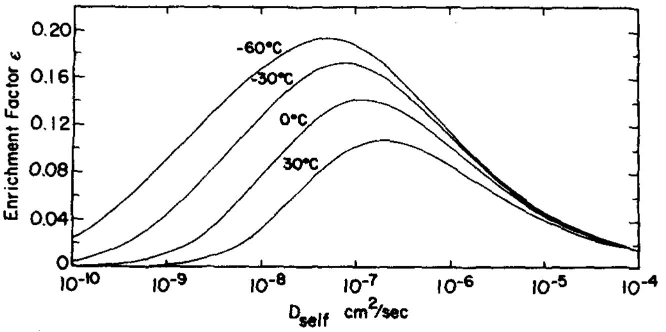

FIG. 3. Calculated dibenzylketone enrichment factor as a function of temperature and self-diffusion coefficient. The enrichment factor ϵ is the differential loss between ^{12}C and ^{13}C relative to the loss of ^{12}C for a single stage of photolysis.

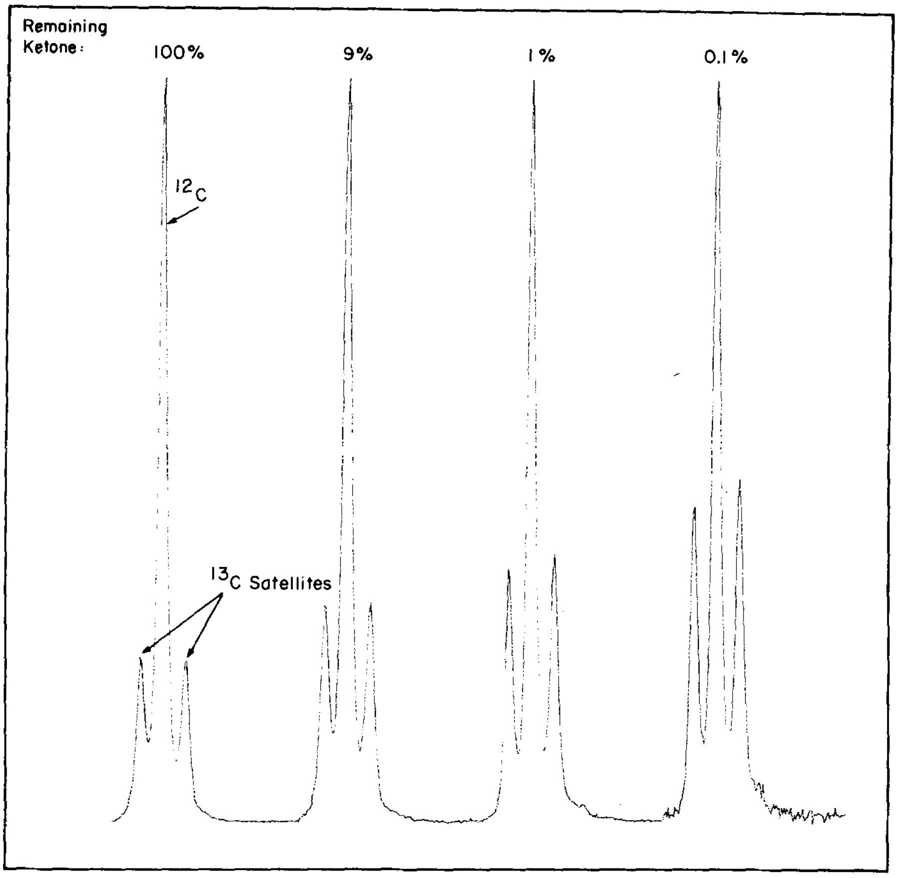

FIG. 4. Methylene proton NMR signal as a function of remaining ketone for photolysis of dibenzylketone in cyclohexanol at 0 °C. In the absence of ^{13}C the methylene resonance is a single line. With ^{13}C at the carbonyl position the resonance is split by 6.3 Hz. Isotopic analysis by curve fitting the three lines gives: 100% ketone, 29% ^{13}C; 9% ketone, 36% ^{13}C; 1% ketone, 40% ^{13}C; 0.1% ketone, 47% ^{13}C. Total photolysis time is 409 min.

as a function of the percent of ketone remaining is shown in Fig. 4.

IV. RESULTS

The aim of this study was to optimize the ^{13}C enrichment by manipulating the diffusion and decarbonylation rates through viscosity and temperature changes, respectively. In Fig. 5 we show the increase in ^{13}C relative to ^{12}C as a function of remaining ketone for three different solvents. The effect of viscosity on the enrichment is evident. We wish to cast these results in a form for comparison with the previously defined enrichment factor.

Defining $k_{h\nu}$ as the rate constant for photolytic production of triplet radical pairs, we obtain for the disappearance of ^{13}C and ^{12}C-containing dibenzylketone

$$[^{13}\mathrm{C}] = [^{13}\mathrm{C}]_0 \exp[-(1 - {}^{13}R)k_{h\nu}t] \tag{13}$$

and

$$[^{12}\mathrm{C}] = [^{12}\mathrm{C}]_0 \exp[-(1 - {}^{12}R)k_{h\nu}t] , \tag{14}$$

where $[^{13}\mathrm{C}]$ and $[^{12}\mathrm{C}]$ are the concentrations of dibenzylketone with ^{13}C and ^{12}C at the carbonyl position, respectively. From the above equations it is easily seen that

$$\ln([^{13}\mathrm{C}]/[^{13}\mathrm{C}]_0) = -(1 - {}^{13}R)k_{h\nu}t \tag{15}$$

and

$$\ln([^{12}\mathrm{C}]/[^{12}\mathrm{C}]_0) = -(1 - {}^{12}R)k_{h\nu}t \tag{16}$$

so that

$$\ln([^{13}\mathrm{C}]/[^{13}\mathrm{C}]_0) = \frac{(1 - {}^{13}R)}{(1 - {}^{12}R)} \ln([^{12}\mathrm{C}]/[^{12}\mathrm{C}]_0) . \tag{17}$$

Plotting $\ln([^{13}\mathrm{C}]/[^{13}\mathrm{C}]_0)$ versus $\ln([^{12}\mathrm{C}]/[^{12}\mathrm{C}]_0)$, the slope $(1 - {}^{13}R)/(1 - {}^{12}R)$ may be obtained, and the enrichment factor ϵ equals (1 − slope) [see Eq. (12)]. ϵ is calculated for the data shown in Fig. 5 and presented in Table I. For the theoretical calculation of ϵ we estimate the self-diffusion coefficient D_{self} of the radicals from the Stokes–Einstein equation with a factor of 1/4 to correspond to "slip" boundary conditions[23]:

$$D_{\mathrm{self}} = \frac{1}{4} \frac{kT}{\pi\sigma\eta} , \tag{18}$$

where $\sigma \simeq$ toluene molecular radius $\simeq 3\times10^{-8}$ cm and η = solvent viscosity in poise. The theoretical values are given in Table I.

In order to study the enrichment over a large viscosity range we chose to use 70/30 and 80/20 weight/weight mixtures of cyclohexanol and isopropanol as solvents and vary the temperature. Although the decarbonylation rate changes with temperature, it does not change as rapidly as the viscosity. Thus, although both factors enter into the enrichment factor (and are included in our computation of ϵ), the main features in the temperature dependence are due to viscosity changes. The temperature dependence of the enrichment factor for photolysis in 70/30 cyclohexanol/isopropanol solvent is shown in Fig. 6 along with theoretically predicted curves. In contrast to the data shown in Fig. 5 where the enrichment factor

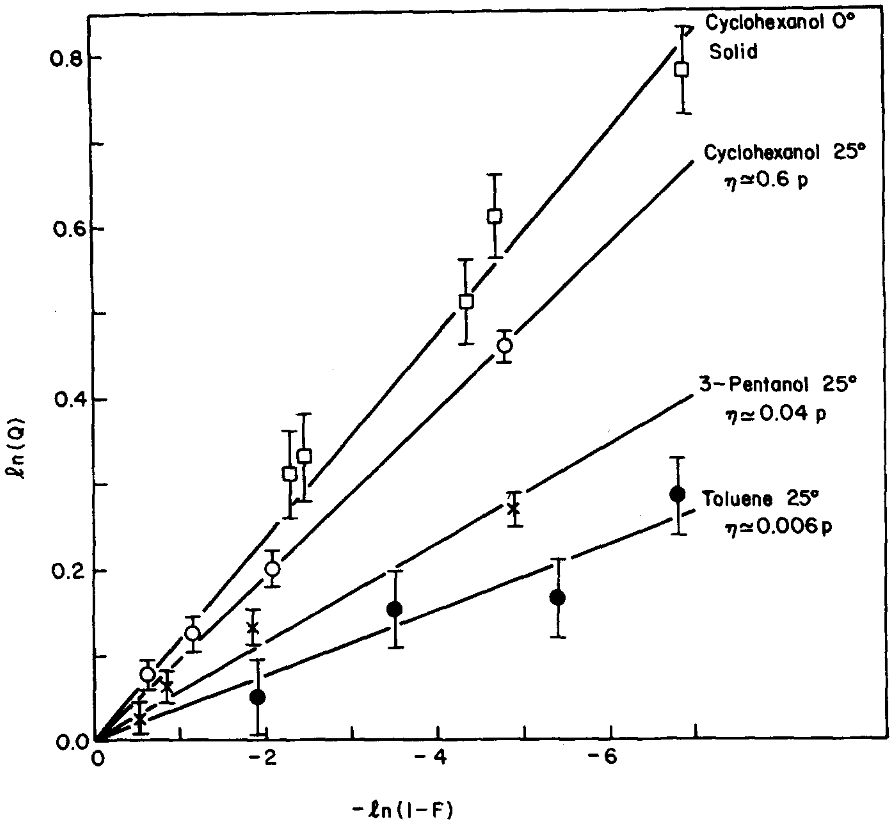

FIG. 5. ^{13}C enrichment of dibenzylketone for photolysis in three different solvents. η is the viscosity with units of poise. The form of the plot corresponds to the analysis (valid for small enrichment factors) proposed by Bernstein.[24] Q is the ratio of ^{13}C to ^{12}C in the ketone relative to the ratio at zero photolysis. F is the fraction of ketone which has decarbonylated.

TABLE I. Dibenzylketone enrichment ϵ as a function of viscosity and temperature.

Solvent	Viscosity[a] (P)	Temperature[b] (°C)	ϵ, experimental[c]	ϵ, theoretical[d]
Toluene	0.006	25	0.038 ± 0.003	0.031
	0.008	0	0.061 ± 0.003	0.040
3-Pentanol	0.04	25	0.056 ± 0.002	0.069
Cyclohexanol	0.6	25	0.093 ± 0.002	0.114
	Solid[e]	0	0.112 ± 0.003	...
70% Cyclohexanol/ 30% isopropanol, *w/w*	0.2 (?)	3	0.073 ± 0.002	0.112
	3.8	−35	0.166 ± 0.002	0.163
	11	−45	0.168 ± 0.003	0.144
	18	−50	0.138 ± 0.006	0.131
	32	−55	0.105 ± 0.003	0.117
80% Cyclohexanol/ 20% isopropanol, *w/w*	36	−45	0.086 ± 0.007	0.099
	270	−60	0.088 ± 0.008	0.050

[a] The viscosities are all approximate. Viscosities for the neat solvents were interpolated from the tables in Ref. 26. For the 70/30 and 80/20 cyclohexanol/isopropanol (weight/weight) solvents the viscosities were measured with a falling ball viscosimeter. The 3 and − 35 °C viscosities for 70/30 cyclohexanol/isopropanol were extrapolated (using an Arrhenius law) from data measured from − 60 to − 40 °C.

[b] Temperatures are average values over the course of a photolysis and typically varied by ± 3 °C. Photolysis times varied from 1 h at 25 °C (1% ketone remaining) to 50 h at − 60 °C (25% ketone remaining).

[c] The enrichment factor ϵ is the differential loss between ^{12}C and ^{13}C relative to the loss of ^{12}C for a single stage of photolysis. The experimental determination of ϵ is described in Sec. IV.

[d] The theoretical description of ϵ is given in Sec. II. D. All values assume $r_0 = 9$ Å.

[e] Cyclohexanol forms a plastic crystal from − 10 to 24 °C.[25]

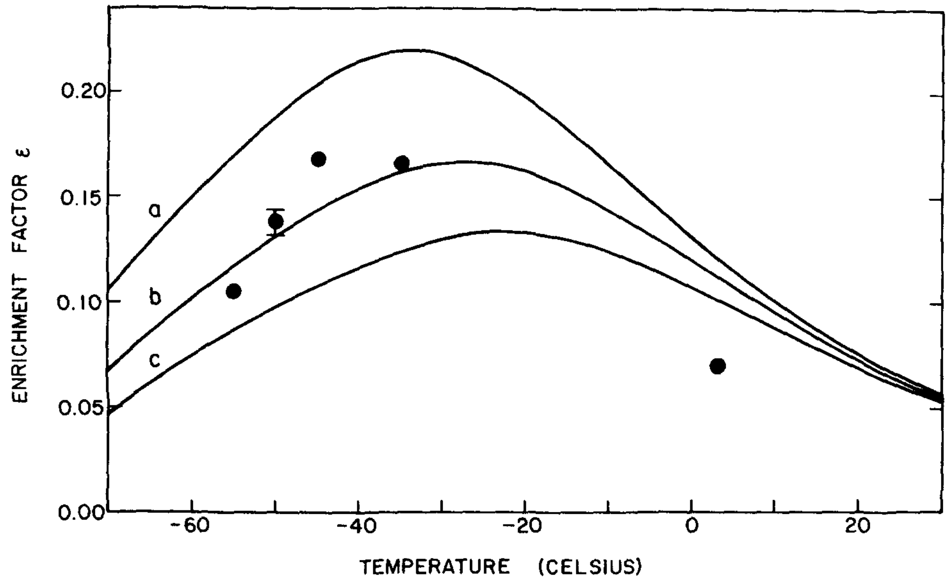

FIG. 6. Enrichment factor as a function of temperature for photolysis of dibenzylketone in a 70/30 cyclohexanol/isopropanol weight/weight solvent. The viscosities of the data points are given in Table I. Uncertainities are given by error bars or size of point. The theoretical curves follow the analysis of Sec. II. D and are calculated for different values of r_0, the radical–radical separation immediately after scission of the ketone: (a) $r_0 = 8$ Å, (b) $r_0 = 9$ Å, (c) $r_0 = 10$ Å. For the theoretical curves the measured viscosities were fitted to an Arrhenius expression.

increases with viscosity, the data in Fig. 6 show that at very high viscosity the enrichment factor begins to fall off. The experimental and theoretical values for the 70/30 cyclohexanol/isopropanol solvent are tabulated in Table I along with two values for the 80/20 solvent at higher viscosity.

V. CONCLUSION

The nuclear magnetic isotope effect as demonstrated in the photolysis of dibenzylketone has been shown to depend strongly on viscosity. We have shown that the viscosity and temperature dependence of the enrichment is in accordance with a simple model treating hyperfine induced intersystem crossing as a first order process. Our model which includes the full viscosity and temperature dependence of diffusion and decarbonylation allows prediction of the optimum conditions for observing the enrichment.

It is hoped that this work will aid in extending such studies into the realm of isotopes with much bigger hyperfine couplings (as in organometallic chemistry) where much larger enrichment factors may be possible.[8] In the future, optimal conditions will most likely involve larger hyperfine couplings and controlled temperature and viscosity, and will also make use of solvents of restricted volume (i.e., micelles) or restricted dimensionality (i.e., liquid crystals, bilayers). In order to show the effect of restricted volume, the treatment of the enrichment factor was carried out as in Sec. II.D but with the added constraint of a reflecting boundary at $r_b (r_b > r_0)$:

$$\hat{r}\cdot\nabla\rho(\mathbf{r},t)=0\ , \qquad |\mathbf{r}|=r_b\ . \tag{19}$$

The results of this calculation are shown in Fig. 7, and the enhancement of the enrichment factor with decreasing volume is quite evident. The complete expression for the total recombination yield R under these conditions is given in the Appendix.

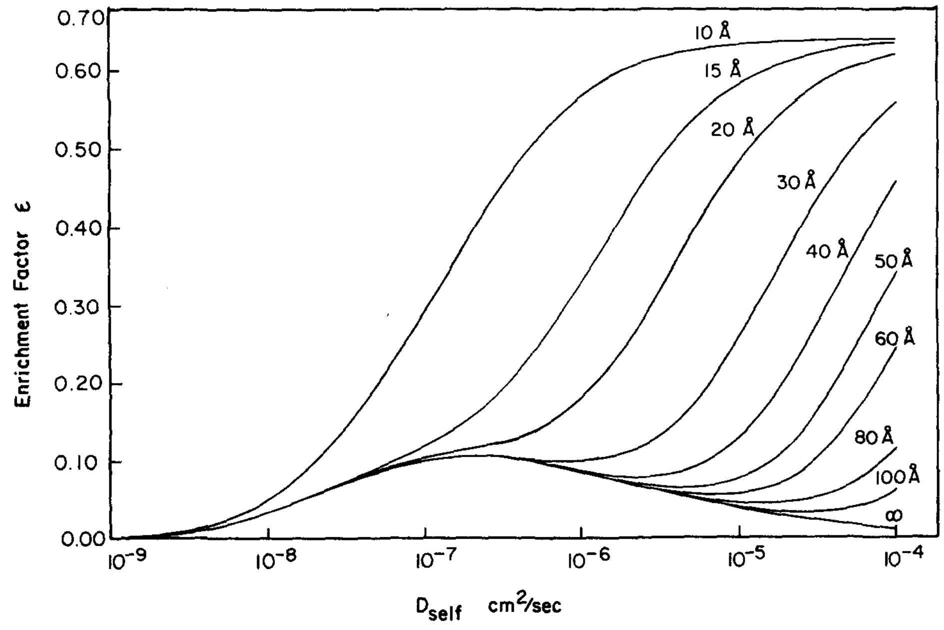

FIG. 7. Enrichment factor for photolysis of dibenzylketone within a sphere with a reflecting wall (e.g., a micelle). The curves are labeled by the radius of the sphere in angstroms. For experimental results of dibenzylketone photolysis within a micelle see Turro *et al.*[5]

In addition, the generalization of this reaction scheme to other systems is not limited by the requirement of a feature such as decarbonylation. Any reaction which involves bond scission into two different radicals introduces symmetric coupling products which serve as competitive channels to prevent reformation of the starting material, or radicals may be removed by the use of scavengers.

ACKNOWLEDGMENTS

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APPENDIX: RECOMBINATION IN A RESTRICTED VOLUME

Equations (4)–(7b) and (19) are solved in a straightforward fashion, and the recombination yield R is then computed from Eq. (8). We find that

$$R=\frac{1}{r_0}\left\{\frac{\Delta_3(\Phi_2\Delta_2-\Phi_1\Delta_4)}{\Delta_1\Delta_4-\Delta_2\Delta_3}+r_c\cosh\left[\alpha(r_0-r_c)\right]+\frac{1}{\alpha}\sinh[\alpha(r_0-r_c)]\right\}, \tag{A1}$$

where

$$\Delta_1\equiv\exp[\alpha(r_0-r_c)]-\frac{(1+\alpha r_b)}{(1-\alpha r_b)}\exp[\alpha(r_0+r_c-2r_b)], \tag{A2}$$

$$\Delta_2\equiv\frac{\gamma}{k}\left\{\exp[\beta(r_0-r_c)]-\frac{(1+\beta r_b)}{(1-\beta r_b)}\exp[\beta(r_0+r_c-2r_b)]\right\}, \tag{A3}$$

$$\Delta_3\equiv\frac{(1+\alpha r_b)(1-\alpha r_c)}{(1-\alpha r_b)}\exp[\alpha(r_0+r_c-2r_b)]-(1+\alpha r_c)\exp[\alpha(r_0-r_c)], \tag{A4}$$

$$\Delta_4\equiv\frac{\gamma}{k_+}\left\{(1+\beta r_c)\exp[\beta(r_0-r_c)]-\frac{(1+\beta r_b)(1-\beta r_c)}{(1-\beta r_b)}\times\exp[\beta(r_0+r_c-2r_b)]\right\}, \tag{A5}$$

$$\Phi_1\equiv\frac{-1}{\alpha}\sinh[\alpha(r_0-r_c)]-\frac{\gamma}{\beta k_-}\sinh[\beta(r_0-r_c)], \tag{A6}$$

$$\Phi_2\equiv r_c\cosh[\alpha(r_0-r_c)]+\frac{1}{\alpha}\sinh[\alpha(r_0-r_c)]-\frac{\gamma}{k_+}\left\{r_c\cosh[\beta(r_0-r_c)]+\frac{1}{\beta}\sinh[\beta(r_0-r_c)]\right\}, \tag{A7}$$

$$\gamma\equiv f_S(k_++k_-)-k_-. \tag{A8}$$

Using Eq. (A1) for R, the enrichment factor ϵ is calculated as in the text and shown in Fig. 7.

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