takes place and TBA^+ amalgam may be involved. In agreement with this idea, fluorobenzene has only a small effect on the "background" voltammogram obtained by using 0.1 M $(TBA)BF_4$. This can be explained if the reaction rate is controlled mainly by the rate of reduction of TBA^+ and the following reaction with fluorobenzene is not fast enough to influence the current. 1,3-Difluorobenzene does increase the "background" voltammogram current. This could arise from a more rapid reaction of 1,3-difluorobenzene with "amalgam" or by competing direct electron transfer to the fluoro compound at mercury.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. $TBA{\cdot}BF_4$, 429-42-5; $DMP{\cdot}BF_4$, 69444-51-5; fluorobenzene, 462-06-6; 1,3-difluorobenzene, 372-18-9.

Magnetic Isotope Effects in Photochemical Reactions. Observation of Carbonyl ^{17}O Hyperfine Coupling to Phenylacetyl and Benzoyl Radicals. ^{17}O-Enrichment Studies

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The photochemistry of ^{17}O-enriched (at C=O) dibenzyl ketone (DBK), benzoin methyl ether (BME), and deoxybenzoin (DB) has been studied on porous silica and in homogeneous solution with the aim of enriching the recovered ketones with ^{17}O [separation of magnetic (^{17}O) from nonmagnetic (^{16}O, ^{18}O) isotopes]. ^{17}O enrichment occurs with modest efficiencies on porous silica ($\alpha \leq 1.12$); photolysis in aqueous micellar solution occurs but is complicated by oxygen exchange with water thereby obviating quanitative analysis of the enrichment. Steady-state ESR spectra are reported in toluene at 165 K. Hyperfine coupling of phenylacetyl and benzoyl radicals to the carbonyl oxygen is observed, with $a(^{17}O) = 16.1 \pm 0.5$ G.

Introduction

Previous studies from these laboratories[1-4] have shown that ^{13}C may be efficiently separated from ^{12}C in dibenzyl ketone (DBK) (1), and in other ketones,[5] via photolysis in

$PhCH_2C^*(=O)CH_2Ph$ C* encirhced with ^{13}C
1

micellar solution and subsequent recovery of the unreacted ketone. The principle of the method[1-4] involves taking advantage of the difference in hyperfine-induced (hfi) intersystem crossing rates from the triplet radical pair intermediate to a singlet radical pair between ^{13}C ($I = {}^1/_2$; a magnetic nucleus) containing molecules and those molecules that contain only ^{12}C ($I = 0$; a nonmagnetic nucleus) (Figure 1). Those triplet radical pairs possessing a ^{13}C nucleus will have larger intersystem rates (k_{isc}) and will produce the singlet radical pair more efficiently. The latter can than undergo σ-bond formation and hence return to DBK starting material. Under high conversion of the photoreaction, the recovered DBK will be enriched in ^{13}C content, essentially only at the acyl carbon if this carbon is partially enriched in the starting material.

Although a significant number of papers[1-4] have been published concerning the mechanistic detals of ^{13}C enrichment in DBK and related photochemistry, the applicability of the above principle to other nuclear systems has not been exhaustively demonstrated. There are two systems of which we are aware[6,7] that employ these principles in the separation of ^{17}O ($I = {}^5/_2$) from ^{16}O and ^{18}O (both with $I = 0$), but neither of these systems utilizes the simple photochemical behavior provided by DBK and related molecules.

Table I. Oxygen Isotopic Contents of DBK, DB, and BME Starting Materials[a]

ketone	% ^{16}O	% ^{17}O	% ^{18}O
DBK-^{16}O[b]	99.76	0.037	0.20
DBK-^{17}O[c]	44.8 ± 0.7	34.2 ± 0.5	20.9 ± 0.4
DBK-^{18}O	81.0 ± 0.5	0.0 ± 0.05	19.0 ± 0.2
DB-^{17}O[c]	51.6 ± 0.5	27.4 ± 0.4	20.9 ± 0.4
DB-^{18}O	54.5 ± 0.5	0.0 ± 0.05	45.5 ± 0.5
BME-^{17}O[c]	25.6 ± 0.3	41.1 ± 0.4	33.2 ± 0.3

[a] Determined via mass spectral analysis on a Finnigan 3300 GC/MS spectrometer (chemical ionization with methane). [b] Natural abundance material from Aldrich Chemical Co. The percent isotopic oxygen contents are taken from standard tables of isotopic contents of the elements. [c] ^{17}O-Enriched materials must necessarily contain some ^{18}O, since all commercially available $H_2{}^{17}O$ is also enriched in ^{18}O.

Therefore, it was felt that the extension of the above results for DBK-^{13}C to the oxygen nucleus of the carbonyl of DBK, and other related molecules, appears to be pertinent and warranted investigation, since a positive result will clearly demonstrate the general applicability of the above principles for isotopic separation to other nuclear systems. In addition, since the magnetic isotope of oxygen

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(1) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3886.

(2) Turro, N. J.; Anderson, D. R.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3892.

(3) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369 and references therein.

(4) Turro, N. J.; Kraeutler, B. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 6.

(5) Turro, N. J.; Anderson, D. R.; Kraeutler, B. *Tetrahedron Lett.* **1980**, 3.

(6) (a) Turro, N. J.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218. (b) Turro, N. J.; Chow, M.-F. *J. Am. Chem. Soc.* **1980**, *102*, 1190.

(7) (a) Belyakov, V. A.; Mal'tsev, V. I.; Galimov, E. M.; Buchachenko, A. L. *Dokl. Akad. Nauk. SSSR* **1978**, *243*, 924. (b) Buchachenko, A. L.; Federov, A. V.; Yasina, L. L.; Galimov, E. M. *Chem. Phys. Lett.* **1984**, *103*, 405.

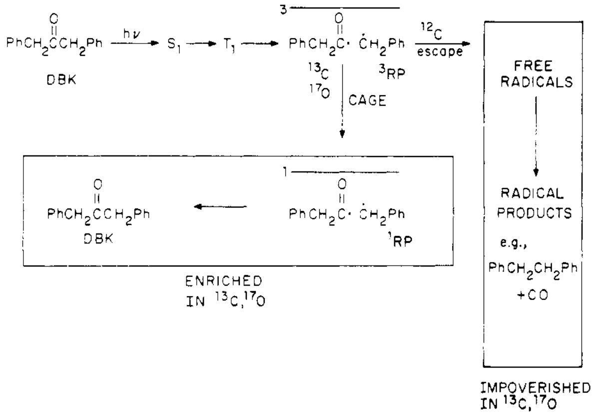


Figure 1. Working mechanism for DBK photolysis. ^{3}RP = triplet radical pair; ^{1}RP = singlet radical pair.

(^{17}O) has $I = {}^5/_2$, one may anticipate some interesting behavior with respect to the hyperfine-induced intersystem mechanism of the intermediate triplet radical pair, as information on the influence of spin systems of this kind (i.e., with $I = {}^5/_2$) in these radical pairs is presently not available.

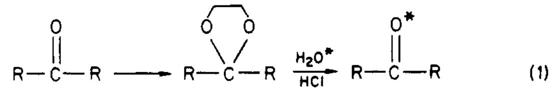
We report herein the results of the photochemistry and steady-state ESR spectroscopy of a number of ketones enriched with ^{17}O and ^{18}O, the results of which clearly demonstrate the general applicability of the above described principles for isotopic enrichment based on the magnetic isotope effect.

Results

Materials. The ketones used in this study, dibenzyl ketone (DBK), deoxybenzoin (DB), and benzoin methyl ether (BME), were purchased from Aldrich. DBK was

$PhCH_2C(=O)CH_2Ph$ $PhC(=O)CH_2Ph$
DBK DB
$PhC(=O)CH(OCH_3)Ph$
BME

purified by repeated crystallization in ether at −78 °C (dry ice bath). DB and BME were used as received. The oxygen-labeled ketones were prepared via hydrolysis of the corresponding ethylene glycol acetal with the appropriate oxygen-labeled water (eq 1). Listed in Table I are the



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R \longrightarrow R{-}C(OCH_2CH_2O){-}R \xrightarrow[HCl]{H_2O^*} R{-}\overset{\overset{\displaystyle O^*}{\|}}{C}{-}R \qquad (1)$$

appropriate percent oxygen isotropic contents as determined by mass spectral analysis on a Finnigan 3300 GC/MS system.

ESR Spectra. A necessary requirement for isotopic separation based on the principles discussed in the Introduction[1-4] is the observation of hyperfine coupling (hfc) between one (or both) of the geminate radicals (Figure 1) with the magnetic nucleus (or nuclei) concerned. Although such hfc has been well documented and correlated with the observed isotopic enrichment for ^{13}C in DBK,[1-4] no such studies are available for ^{17}O in DBK or in any other ^{17}O-enrichment system. Therefore, ESR spectra of these ketones (Table I) were taken in toluene at 165 K.

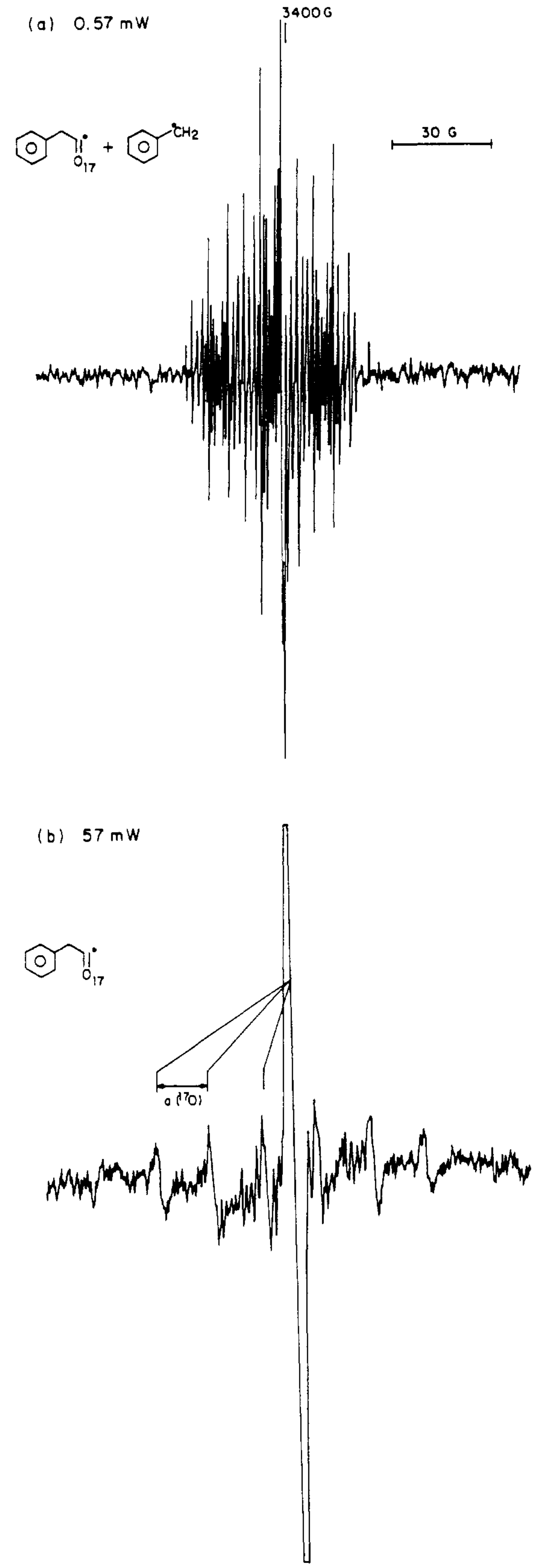


Figure 2. (a) ESR spectra of photogenerated phenylacetyl and benzyl radicals from DBK-^{17}*O* in ethanol at 180 K; (b) same sample, but at higher microwave power; a (^{17}O) = 16.1 ± 5 G.

Photolysis of solutions (10^{-2} M) of DBK-^{17}O and BME-^{17}O yielded benzyl radicals (the parent benzyl and α-methoxybenzyl) and the phenylacetyl and benzoyl radicals, respectively. Under low microwave power (0.57 mW) both the benzyl radical and the phenylacetyl and benzoyl radicals are observed in the ESR spectrometer (Figures 2a and 3a). At high microwave power (~57 mW) the benzyl radical resonances disappear (due to a saturation effect), leaving only the phenylacetyl and benzoyl resonances (g = 2.0007). At high spectrometer sensitivity new resonances are observed which are assigned as due to ^{17}O hyperfine coupling (Figures 2b and 3b). There are a total of six lines

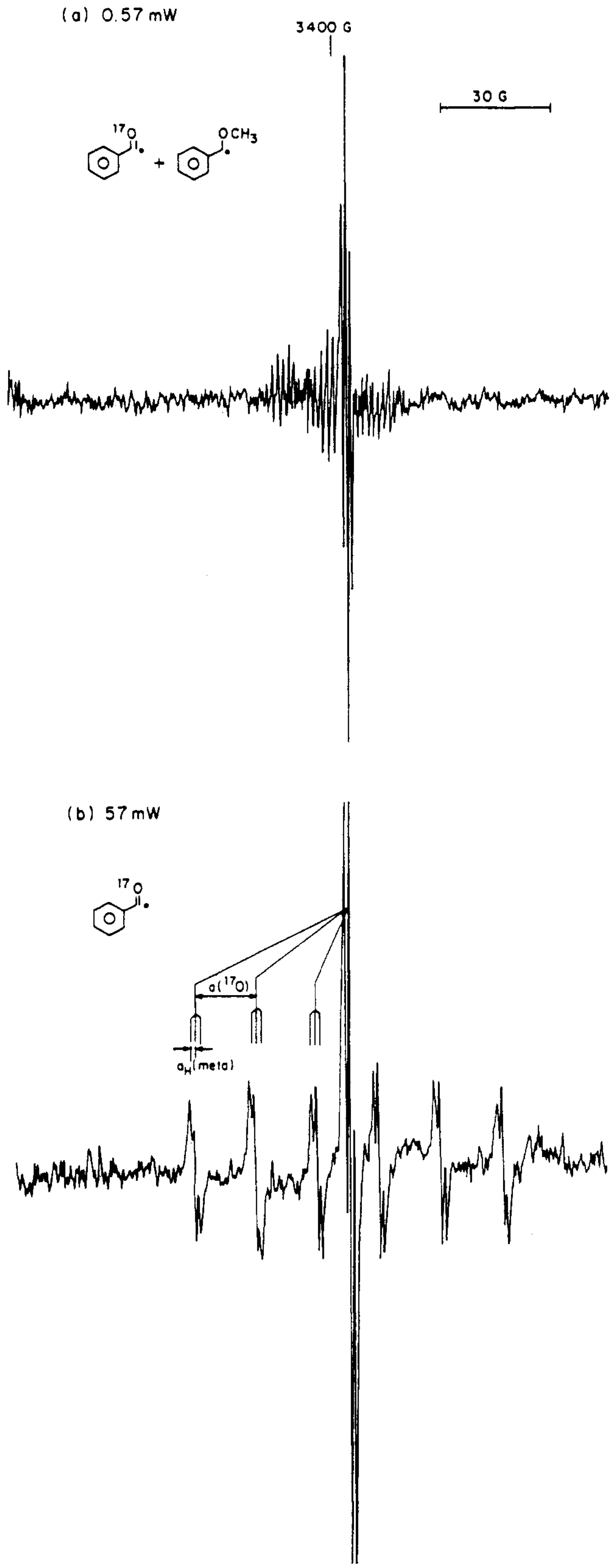


Figure 3. (a) ESR spectra of photogenerated benzoyl and methoxy benzyl radicals from BME-^{17}O in toluene at 223 K; (b) same sample, but at higher microwave power; $a(^{17}O) = 16.6 \pm 0.2$ G, a_H(meta) = 1.3 ± 0.2 G.

($I = {}^5/_2$) for both the phenylacetyl and the benzoyl radical; the magnitude of the observed ^{17}O hyperfine coupling (hfc) in the phenylacetyl spectra is $a(^{17}O) = 16.1 \pm 0.5$ G. For the benzoyl radical the observed hfc is 16.5 ± 0.2 G; in addition, the hfc to the meta hydrogens of the benzene ring is also observed with $a(^{17}O) = 1.3 \pm 0.2$ G.

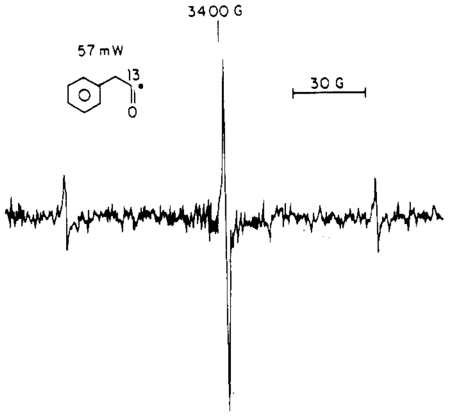


Figure 4. ESR spectra of phenylacetyl (^{13}C, 29.8%) at high microwave power (165 K, toluene); ^{13}C satellites, with $a = 128 \pm 5$ G.

As control experiments, the ESR spectra of DBK-^{16}*O* and DBK-^{13}*C* (~30% ^{13}C at the carbonyl) were also taken under similar conditions. DBK-^{16}*O* failed to give any additional hfc while DBK-^{13}*C* ($I = {}^1/_2$) gave a well-defined triplet (Figure 4), with $a(^{13}C) = 128 \pm 5$ G. This value is in agreement with previously reported [$a(^{13}C) = 125$ G] values.[8] We have confirmed the intermediacy of benzyl radicals on silica by ESR spectroscopy. At room temperature the ESR spectra reveal broad and sharp features which imply a wide range of radical mobility.

DBK-^{17}*O* Enrichment Studies. Although the existence of hfc between the acyl radical and the carbonyl ^{17}O is a necessary requirement for ^{17}O enrichment to take place via a magnetic isotope effect, it is not a sufficient condition. Previous work[1,2] from these laboratories has shown that photolysis of DBK-^{13}*C* in toluene, benzene, or *n*-dodecane results in only a small amount of ^{13}C enrichment in the recovered DBK-^{13}C. When photolysis was carried out in micelles, however, substantially larger ^{13}C enrichments were observed. α values[9] increased from ≤1.03 in benzene to 1.4 in hexadecyltrimethylammonium chloride (HDTCl) micelles.[1,2]

Initially we carried out DBK-^{17}*O* photolysis in benzene and in HDTCl micelles. The sodium dodecyl sulfate (SDS) micelle was not used since it was found that this micelle catalyzed ^{17}O exchange with water rapidly enough ($t_{1/2} \approx$ 10 min at room temperature) to wash out any possible ^{17}O enrichment. In photolysis experiments carried out to >80% conversion in benzene, no ^{17}O enrichment was observed (Table II). In HTDCl micelles, however, ^{17}O enrichment was detected, with α values of ca. 1.04 under optimum conditions. Although ^{17}O enrichment was demonstrated in aqueous micelles, we were not satisfied with the low α values obtained and, more importantly, with the difficulty in optimizing the ^{17}O-enrichment efficiency. Thermal ^{17}O exchange does take place in HDTCl micelles, although to a much less extent than in SDS micelles, and it is this small amount of exchange that appears to be responsible for giving "depressed" α values. As a result, we developed a new strategy, namely, to conduct the photolysis in a "supercage" environment that mimics

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(8) Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

(9) Since ^{13}C (and ^{17}O) enrichment depends on the extent of conversion, the parameter α, which is the single-stage isotope separation factor,[10] is used to measure the efficiency of isotope separation.[1,2]

(10) Bernstein, R. B. *J. Phys. Chem.* **1952**, *56*, 893.

(11) (a) Sullivan, P. D.; Bolton, J. R.; Geiger, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 4176. (b) Gulick, W. M.; Geske, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 4119. (c) Broze, M.; Luz, Z.; Silver, B. L. *J. Chem. Phys.* **1967**, *46*, 4891. (d) Rieker, A.; Scheffler, K. *Tetrahedron Lett.* **1965**, 1337.

Table II. Isotopic Oxygen Contents for Recovered DBK after Photolysis on Porous Silica[a]

DBK	conditn[b]	conversn	recovered DBK % ^{16}O	recovered DBK % ^{17}O	recovered DBK % ^{18}O	α[c]	% enrichment[d]
DBK-^{16}O	2.5% coverage	96%	99.6 ± 0.4	0.0 ± 0.05	0.2 ± 0.1	*e*	*e*
DBK-^{18}O	2.5% coverage	99%	80.1 ± 0.5	0.0 ± 0.05	19.9 ± 0.3	$\alpha(^{18}O) \le 1.03$	≤5 (^{18}O)
DBK-^{17}O	2.5% coverage	97%	39.4 ± 0.3	41.5 ± 0.3	19.0 ± 0.2	$\alpha(^{17}O) = 1.12^{g}$	21 (^{17}O)
DBK-^{17}O	5% coverage	94%	40.7 ± 0.3	39.3 ± 0.2	20 ± 0.5	$\alpha(^{17}O) = 1.09^{g}$	15 (^{17}O)
DBK-^{17}O	2.5% coverage, 2 kG	95%	41.4 ± 0.3	38.7 ± 0.3	20 ± 0.5	$\alpha(^{17}O) = 1.05^{g}$	13 (^{17}O)
DBK-^{17}O	benzene	70–90%	43.6 ± 0.4	34.7 ± 0.3	21.6 ± 0.2	$\alpha(^{17}O) \le 1.03$	≤2 (^{17}O)

[a] Porous silica samples were provided by Dr. W. Mahler[11] (mean pore diameter = 20 Å; surface area = 888 m^2/g). Experiments performed in earth's magnetic field (~0.5 G) unless otherwise indicated. [b] All experiments on porous silica at different coverages unless otherwise noted. [c] Single-stage isotope separation factor (see text). [d] Relative percent increase in ^{17}O or ^{18}O content. [e] No detectable enrichment in ^{17}O or ^{18}O.

micelles and for which carbonyl oxygen exchange can be avoided. We report here an environment is provided by porous silica.[12]

Porous silica samples (22-Å medium pore diameter)[13] were rigorously dried (~200 °C; 10 h) prior to use. Photolysis of DBK-^{17}O adsorbed on silica and subsequent analysis of the recovered material showed substantial ^{17}O enrichment, with an optimum α value of 1.12 ± 0.03 at a loading capacity of 2.5% of the total available surface area of the silica. The results of several runs with DBK-^{16}O, DBK-^{17}O, and DBK-^{18}O are summarized in Table II. The α values for DBK-^{17}O are substantially higher than those observed in HDTCl micelles. Additionally, experiments performed with DBK-^{18}O on silica resulted in essentially no ^{18}O enrichment under similar conditions, thus showing the requirement of a magnetic nucleus in the system. In other words, the enrichments observed for ^{17}O are much larger than those that could be ascribed simply to a mass isotope effect (which have $\alpha \le 1.03$).

The mass spectral analysis of recovered DBK-^{17}O cannot distinguish between ^{13}C and ^{17}O enrichment since both would give increased (M + 1) values on the mass spectrometer. Although we have demonstrated that the enhanced (M + 1) peak can be "exchanged off" by mixing the photolyzed sample with aqueous acid and analyzing the subsequently recovered material, we sought additional evidence that enrichment was indeed at the carbonyl oxygen and not at other nuclei (C or H) of other nuclei (C or H) of the molecule. Corroborative evidence was provided by IR spectroscopy of the samples. Thus, prior to photolysis, the DBK-^{17}O sample (in $CHCl_3$ solution) showed $\bar{\nu}(C{=}^{16}O) = 1717 \pm 3\ cm^{-1}$ and $\bar{\nu}(C{=}^{17}O) = 1705 \pm 3\ cm^{-1}$, with the $C{=}^{16}O$ stretch in greater intensity. The $C{=}^{18}O$ peak cannot be discerned in the DBK-^{17}O sample. However, using DBK-^{18}O, we can assign the $C{=}^{18}O$ stretch at 1690 ± 3 cm^{-1}.

After photolysis (~80–90% conversion), the IR spectrum of the recovered photolysate, which consists of unreacted DBK-^{17}O and diphenylethane (DPE), was obtained. The single most striking change is the increased intensity of the $C{=}^{17}O$ stretch relative to that of $C{=}^{16}O$, indicating ^{17}O enrichment of the carbonyl. The amount of enrichment can be roughly estimated to be about 10–20% (relative percent), which is in agreement with values calculated via mass spectrometry (Table II). When this sample was stirred in acidified acetonitrile, and the IR taken of the recovered organic material (Figure 3), only the $C{=}^{16}O$ stretch is observable. The spectrum is that of essentially pure DBK-^{16}O, both ^{17}O and ^{18}O being readily exchanged off. These results clearly demonstrate that the enrichments observed via mass spectrometry can be unambiguously assigned to be due to ^{17}O enrichment at the carbonyl of DBK-^{17}O.

Application of a 2 kG magnetic field during the photolysis of DBK-^{17}O on porous silica gave $\alpha = 1.05 \pm 0.04$, which is a small but measurable decrease from the value of 1.12 ± 0.03 at "zero" field (earth's field of ~0.5 G). The decrease in α is in accord with the theory of isotopic separation based on the CIDNP theory of radical pairs[1-4] and will be firther discussed in the Discussion.

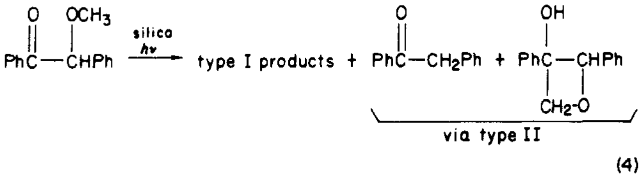
DB-^{17}O and BME-^{17}O Enrichment Studies. Since both DB and BME are known to undergo efficient α cleavage via T_1 (eq 2 and 3), to give triplet radical pairs,[14]

$$\underset{\text{DB}}{PhC({=}O)CH_2Ph} \xrightarrow{h\nu} PhC({=}O)\cdot\ \cdot CH_2Ph \rightarrow PhC({=}O)C({=}O)Ph + PhCH_2CH_2Ph \quad (2)$$

$$\underset{\text{BME}}{PhC({=}O)C(OCH_3)HPh} \xrightarrow{h\nu} PhC({=}O)\cdot\ \cdot C(OCH_3)HPh \rightarrow PhC({=}O)C({=}O)Ph + PhC(OCH_3)HC(OCH_3)HPh + PhCHO \quad (3)$$

the principles established for ^{13}C and ^{17}O enrichment for DBK should be equally applicable to DB and BME. Additonally, we have already observed ^{17}O hyperfine coupling of the carbonyl oxygen to the benzoyl radical in photolysis at 165 K. To complete the present study, we have examined the ^{17}O-enrichment efficiencies for both DB-^{17}O and BME-^{17}O on porous silica.

Photolysis of DB on silica results in benzil and diphenylethane (eq 2) as the only products. Benzil readily decomposes on silica and can only be detected at low conversion. Photolysis of BME on silica results in additional products in addition to those observed in solution (eq 3). In addition to the type I reaction, type II reaction also takes place on silica, as had been reported by deMayo et al.[15] These additional products are shown in eq 4. In



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our ^{17}O enrichment study of BME-^{17}O, the isotopic oxygen contents of BME-^{17}O starting material and deoxybenzoin

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(12) (a) Baretz, B. H.; Turro, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 1309 and references therein. (b) Turro, N. J.; Cheng, C.-C.; Mahler, W. *J. Am. Chem. Soc.* **1984**, *106*, 5022.

(13) Porous silica samples were generously provided by Dr. W. Mahler of the Du Pont Co. The synthesis of these materials is given in: Mahler, W.; Bechtold, M. L. *Nature (London)* **1980**, *285*, 97.

(14) (a) Heine, H.-G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. W.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691. (b) Lewis, F. D.; Hoyle, C. H.; Magyar, J. G. *J. Org. Chem.* **1975**, *40*, 488. (c) Lewis, F. D.; Lauterbach, R. T.; Heine, H.-G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519.

(15) deMayo, P.; Nakamura, A.; Tsang, P. W. K.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 6824.

Table III. Isotope Oxygen Contents for Recovered DB and BME and DB Product from BME Photolysis on Porous Silica[a]

compd	conditn	conversn	oxygen isotopic content in recovered DB or BME			α[b]
			% ^{16}O	% ^{17}O	% ^{18}O	
DB-^{17}O	5% coverage	80%	49.3 ± 0.4	30.3 ± 0.3	20.5 ± 0.3	$\alpha(^{17}\mathrm{O}) = 1.10$
DB-^{17}O	2.5% coverage	84%	48.8 ± 0.4	31.2 ± 0.3	19.7 ± 0.4	$\alpha(^{17}\mathrm{O}) = 1.13$
DB-^{17}O	benzene	70–90%	51.1 ± 0.4	26.9 ± 0.3	20.4 ± 0.4	$\alpha(^{17}\mathrm{O}) \leq 1.02$
DB-^{18}O	2.5% coverage	80–90%	54.2 ± 0.5	0.0 ± 0.05	46.8 ± 0.4	$\alpha(^{18}\mathrm{O}) \leq 1.03$
BME-^{17}O	2.5% coverage	93%	25.3 ± 0.2[c]	42.5 ± 0.4[c]	33.9 ± 0.5[c]	$\alpha(^{17}\mathrm{O}) = 1.03$
			22.9 ± 0.2[d]	43.9 ± 0.4[d]	33.1 ± 0.4[d]	$\alpha(^{17}\mathrm{O}) = 1.04$
BME-^{17}O	benzene	70–90%	25.4 ± 0.3	41.3 ± 0.4	33.6 ± 0.5	$\alpha(^{17}\mathrm{O}) \leq 1.02$

[a] Porous silica was provided by Dr. W. Mahler[13] (mean pore diameter = 20 Å; surface area = 888 m^2/g). All experiments in earth's magnetic field (0.5 G). [b] Single-stage isotopic separation factor.[1,2,9,10] Estimated error in quoted values ±0.03. [c] Recovered BME. [d] DB product.

product (via type II) were analyzed and their corresponding α's calculated. Results for DB-^{17}O and BME-^{17}O and BME-^{17}O enrichment studies are summarized in Table III. The α values for DB-^{17}O (recovered material) are similar to those found for DBK-^{17}O, with perhaps a modest increase in efficiency. For BME-^{17}O photolysis on silica, we find the recovered BME-^{17}O and DB product are both enriched in ^{17}O (α = 1.03 and 1.04, respectively). Noteworthy is that neither DB-^{17}O nor BME-^{17}O gave detectable ^{17}O enrichment when photolyses were carried out in benzene. Photolysis of DB-^{18}O on silica gave only a slight enrichment in ^{18}O, due presumably to a mass isotope effect.

Discussion

The results of this work has clearly demonstrated that the method of isotopic separation developed for DBK-^{13}C based on magnetic isotope effects[1-4] is equally applicable to ^{17}O-labeled DBK and other similar molecules. The ^{17}O enrichments observed (as measured by α) are not as large as for ^{13}C at the carbonyl but are sizable nevertheless. More importantly, the observed $\alpha(^{17}\mathrm{O})$'s are significantly larger than those observed, which can be ascribed to a mass isotope effect ($\alpha(^{18}\mathrm{O}) \leq 1.03$). Additional evidence that the mechanism for isotopic separation is due to a magnetic isotope effect is the effect of an applied magnetic field on α. For DBK-^{17}O, it is found that α drops to a value of 1.05 from 1.12 upon application of the external field. The decrease in α is in full accord with a mechanism involving hfi intersystem crossing of the geminate radical pair (Figure 1) as responsible for ^{17}O separation from ^{16}O and ^{18}O.[1-4] Corroborative evidence is provided by the observation of hyperfine coupling of the phenylacetyl and benzoyl radicals to the carbonyl ^{17}O, with $a(^{17}\mathrm{O})$ = 16 G. Previous studies[1-4] with DBK-^{13}C have shown that the magnitude of the single-stage isotopic separation factor (α) depends critically on the magnitude of the corresponding hyperfine coupling of the carbon concerned with the free electron. Thus, for the carbonyl carbon, the largest $\alpha(^{13}\mathrm{C})$ is observed (α = 1.4), which corresponds with the largest ^{13}C hyperfine coupling (a = 125 G) with the free electron. The α-carbon of DBK has a = 50 G and gave $\alpha(^{13}\mathrm{C})$ = 1.2. The lower enrichment efficiencies observed ($\alpha \approx 1.1$) for ^{17}O are therefore not surprising considering that the hyperfine coupling to the free electron is much lower than observed for the C_1 and C_2 positions of the phenylacetyl radical. A more quantitative relationship between the magnitude of the hyperfine a and the corresponding single-stage isotopic separation factor α is desirable but has yet to be attempted for any magnetic isotope.

Results for DB-^{17}O are in full accord with expectations since this molecule reacts in a very similar manner as DBK-^{17}O. The reactive state is a triplet,[12] to give a triplet radical pair from which the ^{17}O-induced intersystem crossing mechanism may operate and lead to ^{17}O separation from ^{16}O and ^{18}O isotopes. However, unlike the phenylacetyl radical in DBK, the benzoyl radical of DB (and BME) do not decarbonylate. Thus the initially generated triplet radical pair in DB-^{17}O photolysis can only either escape from each other (to give random coupling products) or recombine to give back DB starting material. Because DB-^{17}O photolysis lacks a decarbonylation pathway (which does not contribute to the enrichment process, but only depletes substrate), one might have expected ^{17}O enrichment to be more efficient for DB-^{17}O compared to DBK-^{17}O. However, the resulting indicate (Tables II and III) that DB-^{17}O and DBK-^{17}O gave essentially the same ^{17}O-enrichment efficiency, as measured by α (at the same coverage on porous silica). This result is important to future studies with the aim of designing molecules that can enhance the magnetic isotope effect for isotope separation.

Photolysis of BME-^{17}O on porous silica resulted in an additional type II pathway. This additional type II pathway presented a number of intriguing mechanistic possibilities for oxygen isotope partitioning. Although we were somewhat surprised at the low efficiencies observed, results from this work indicate that both type I and type II reaction of BME-^{17}O can lead to ^{17}O enrichment. However, the exact mode of oxygen isotope partitioning and relative efficiencies of ^{17}O enrichment in type I/type II photochemistry remains an area for additional studies.

Previous studies from these laboratories[1-4] on ^{13}C enrichment in aqueous micelles associated the major effect of the micellar detergent solution with their ability to provide extended "cages", in which the probability for recombination of the radical pairs is high. In other words, the role of the micelle may be viewed as providing a reflective boundary for the radical pair, so as to increase the time in which magnetic isotope effects can operate to "separate" magnetic from nonmagnetic isotopes. Drawing on this analogy, porous silica which behaves as a "supercage" medium for photogenerated radical pairs, and for ^{17}O-enrichment studies, provides a crucial medium for carrying out the enrichment. Additional studies are in process to delineate the mechanism of isotopic enrichment on porous silica.

Our current observation of a hyperfine coupling between the ^{17}O isotope and the radical centers is to our knowledge the first report of this type. Its existence indicates that there is considerable interaction between the carbonyl oxygen and the unpaired electron via interaction with the inpaired electron which occupies a σ orbital. There have been a number of reports[11] that have dealt with the coupling of the ^{17}O nucleus with a π-type system. The magnitude of the hyperfines in these systems (e.g., −9 to −14 G) was attributed to the presence of considerable spin density on the oxygen atom. In our systems we were not able to ascertain the sign of the hyperfine splittings due to the oxygen interaction. Since the magnitude of the hyperfine is similar for both the benzoyl and the phenacyl radical, it is conceivable that their structures are relatively similar. This conclusion is contingent on the mechanism for interaction between the oxygen and the unpaired electron being the same for both radicals.

Conclusion

Two other ^{17}O-enrichment systems based on the magnetic isotope effect are known.[6,7] The first of these[6] involves thermolysis of endoperoxides of aromatic compounds. Endoperoxides thermolyze to give a mixture of singlet and triplet molecular oxygen. In the presence of an ^{17}O isotope in the endoperoxide, and increase in the amount of ^{17}O-containing triplet oxygen is produced ("untrappable" oxygen) due to the fact that the initially formed singlet biradical (cleavage of carbon–oxygen bond in the endoperoxide) can intersystem cross more efficiently to a triplet biradical, which further fragments to give triplet oxygen. In the presence of a good singlet oxygen trap, the untrappable oxygen is enriched in ^{17}O. On the basis of the reported data,[6] we calculate $\alpha = 1.03 \pm 0.02$ for this ^{17}O-enrichment system.

The second system of ^{17}O enrichment is that developed by Buchachenko and co-workers.[7] In this system, the thermal decomposition of tetraoxides (ROOOOR) in the presence of molecular oxygen is utilized. Tetraoxides decompose to give peroxy ($RO_2\cdot$) radicals, which can either recombine with molecular oxygen to regenerate ROOOOR or undergo termination reactions (e.g., loose molecular oxygen to give alkyl radicals etc.). Recombination of two peroxy radicals with a molecule of oxygen which contains a ^{17}O isotope is more favorable, since hyperfine-induced intersystem allows for the appropriate spin pairing in order for bond formation to occur (recall that molecular oxygen is a triplet in the ground state). Thus, ^{17}O-containing oxygen molecules are selectively taken up by the peroxy radicals to regenerate the tetraoxide, which can further release the oxygen and undergo the process again. ^{16}O- and ^{18}O-containing oxygen molecules are preferentially taken up by irreversible oxidation reactions with other radicals in the system. The net result is enrichment of ^{17}O in the unconsumed oxygen. On the basis of the data presented,[7] we calculate $\alpha = 1.07 \pm 0.02$ for this system.

Experimental Section

Materials. DBK, DB, and BME (natural abundance materials) were purchased from Aldrich. DBK was purified by repeated crystallization in ether at −78 °C (dry ice/acetone), to give colorless crystals at room temperature. DB and BME were used as received. The oxygen-labeled materials (^{17}O or ^{18}O) were synthesized by hydrolysis of the corresponding ethylene glycol acetals in CH_3CN/labeled water. A general procedure is provided as follows: the ketone was refluxed with 3 equiv of ethylene glycol in 200 mL of toluene and 3–5 drops of concentrated H_2SO_4 in a Dean–Stark apparatus (5–8 h). Sodium bicarbonate was then added to neutralize excess acid. After several washings with aqueous bicarbonate, the toluene was distilled off on a rotary evaporator, to give a slightly yellow solid. For both DB and DBK, the yield of the acetal was >90%. For BME, the unreacted ketone (~40%) was separated from the acetal by crystallization at −78 °C; the pure acetal crystallizes, leaving unreacted ketone in solution.

For the hydrolysis, a 3-fold excess of labeled water was used and a minimum amount of dried acetonitrile (sufficient to effect solution of the mixture at reflux) was added. HCl (g) was bubbled into the refluxing solution as the catalyst. The hydrolysis was followed by GC and as usually over after 30 min. Extraction of the mixture with CH_2Cl_2 gave the crude labeled ketone, which in all cases was purified by crystallization in ether at −78 °C. ^{1}H and ^{13}C NMR spectra of the labeled materials were identical with those of the natural abundance substances; no ^{17}O couplings were observed. However, both MS and IR showed the presence of isotopic oxygen (vide infra).

^{17}O- and ^{18}O-labeled water was obtained from KOR Isotopes or MSD Isotopes. The ^{17}O isotopic content of the water used was >40%, so as to provide ketones with high ^{17}O content for ease of measurement of enrichment. In general, it was found that ~90% of the oxygen label is transferred to the ketone in the overall synthesis.

Porous silica samples[13] were generously provided by Dr. W. Mahler of E. I. du Pont de Nemours and Co., Inc., Wilmington, DE. The samples were activated at ~200 °C for 10 h and stored in a desiccator prior to use.

ESR Spectra. Electron spin resonance spectra were obtained on a IBM-Bruker ER-100D spectrometer. Typically, 10 mM solutions of the starting ketone in the appropriate solvent were deoxygenated with either argon or nitrogen. The sample chamber in the ESR cavity was cooled to the appropriate temperature (223 K for BME in toluene; 180 K for DBK in ethanol) by using thermostated liquid N_2 boil-off. The solution was flowed through the cavity at a flow rate of ≤1 mL/min. The sample cell was a 2 mm × 4 mm × 20 mm i.d. flat Suprasil cell with inlet and exit ports. With these flow rates the temperature could be stabilized to ±1 K (although signal intensity suffered slightly).

Irradiation of the sample was achieved with a 1000-W Hg–Xe arc lamp using a $NiSO_4$ solution to isolate the $n \rightarrow \pi^*$ transition. This configuration provided the optimum signal to noise ratio for the duration of the experiments.

Photolysis Procedure. Photolyses were carried out in Pyrex vessels (compartment size, 2.5 × 1.5 cm) equipped with a vacuum stopcock and a 5-cm neck. Silica samples for photolysis were prepared by adding a solution of the ketone in CH_2Cl_2 (dried, kept over sodium bicarbonate) to a preweighed amount of silica in a small round-bottom flask. After the majority of the solvent was removed under aspirator vacuum, the sample was transferred to the photolysis vessel and pumped down to 10^{-4} to 10^{-5} mmHg before sealing. A Hanovia 450-W Hg lamp was used for irradiation; the Pyrex vessel was kept as close to the lamp well as possible, which also allowed continuous tumbling during the photolysis (to ensure homogeneous irradiation). After photolysis, the samples were extracted with CH_2Cl_2, which gave material balances >90%.

Analyses of Oxygen Isotopic Contents. Oxygen istopic contents were determined via mass spectrometry using a Finnigan 3300 GC/MS system (chemical ionization with methane, multiple ion detection). The isotopic peaks of the molecular ion (DBK and DB) were corrected for natural abundance ^{13}C content before calculation of oxygen isotopic composition. For BME, the molecular ion (in CI/methane) was very weak and the ($M^+ - OCH_3$) fragment was used as the base peak instead.

For DBK-^{17}*O*, qualitative determination of the oxygen isotopic contents were also carried out using IR spectroscopy, monitoring the carbonyl absorption region. IR's were taken in $CHCl_3$ with NaCl capillary cells on a Perkin-Elmer 8600 spectrometer. Use of IR spectroscopy for DB and BME was problematic due to the additional absorptions of benzil and benzaldehyde of the photolysate.

Conversions and product analyses were determined on a Varian Aerograph Model 3700 gas chromatograph (Se-30 capillary column). Products were identified by comparison with authentic samples, where required.

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Registry No. DBK-^{17}*O*, 95676-04-3; BME-^{17}*O*, 95676-05-4; DB-^{17}*O*, 95676-06-5; $PhCH_2\dot{C}^{17}O$, 95676-07-6; $PhCH_2\cdot$, 2154-56-5; $Ph\dot{C}^{17}O$, 95676-08-7; $Ph\dot{C}HOMe$, 21793-39-5; ^{17}O, 13968-48-4.