

explained in terms of geometric ensemble requirements of Rh-Fe alloy formation on the Rh surface. Such a surface impedes CO dissociation, e.g. methanation, while enhancing the hydrogenation of nondissociatively chemisorbed CO into methanol. Variation in surface coverage of CO causes a frequency shift due to dipole-dipole interaction of only 10 cm^{-1} ,¹⁹ so most of the shifts in both carbonyl bands could be attributed to an electronic effect in the supported Rh-Fe catalysts, possibly by increasing the back-donation of electron density from Fe to CO adsorbed on Rh.

Conclusions

IR spectra of CO chemisorption demonstrated unusually large reduction of stretching frequencies of bridged carbonyls adsorbed on Rh in contact with oxophilic Mn, Ti, and Zr ions, e.g. $\nu_{\text{CO}} = 150\text{--}350\text{ cm}^{-1}$. This indicates that the ions of electropositive metals and/or oxygen-deficient metal oxides on the Rh particle surface provide sites at which CO is activated by a tilted CO chemisorption

mode with its carbon bonded to Rh and its oxygen to the promoter ions and/or oxygen vacancies similar to adducts with Lewis acids. These observations of IR frequency reduction suggest that the adsorbed C- and O-bonded CO dissociates to C_{ads} and O_{ads} with lower activation energies, which is reflected in the strong enhancement of CO conversion on such oxophilic metal-promoted Rh catalysts. On the other hand, we find that Fe added to Rh highly suppresses the abundance of bridged carbonyl chemisorption on Rh surface. This is basically interpreted in terms of a geometric ensemble effect where multibridged CO chemisorption is preferentially prevented by the formation of Rh-Fe alloy by clustering on the Rh particle surface, similarly with Pd-Ag and Cu-Ni alloy catalysts.

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Magnetic Isotope Effects in the Photolysis of Dibenzyl Ketone on Porous Silica. ¹³C and ¹⁷O Enrichments

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The photolysis of dibenzyl ketone (DBK) on porous silica has been investigated. Both ¹³C and ¹⁷O isotopic enrichment in the ketone remaining after partial photolysis is demonstrated. The efficiency of ¹³C enrichment was found to be relatively insensitive to the average pore diameter of the silica host, to the percent coverage by DBK, and to the application of an external magnetic field. A significant dependence of ¹³C enrichment with temperature, with a maximum in the enrichment-temperature profile, was observed. The results are interpreted in terms of the competition between pathways available to the triplet $\text{C}_6\text{H}_5\text{CH}_2\text{CO CH}_2\text{C}_6\text{H}_5$ radical pair produced by photolysis of DBK.

Introduction

We¹ and others² have shown that it is possible to obtain substantial and efficient separation of ¹³C from ¹²C based on a mechanism in which the key step involves a magnetic isotope effect (mie). The influence of the mie is found to be maximal³ when a geminate triplet pair is produced in a "supercage" environment which (1) allows diffusional separation of the radical fragments to a distance which allows reduction of electron exchange and for efficient interactions between nuclear magnetic moments and electron magnetic moments, and (2) encourages a high probability of geminate radical pair reencounters. In addition, the radical pair must possess an "escape" process which allows sorting of nuclei which differ in their magnetic properties. Under the proper conditions magnetic nuclei embedded in the triplet radical pair can enhance the rate of triplet-singlet intersystem crossing during the diffusional excursions of the radical fragments. Upon reencounter radical pairs possessing magnetic nuclei have a higher probability of being in a singlet state than do radical pairs which do not contain magnetic nuclei. Since, in general, only singlet radical pairs are capable of undergoing cage reactions (combination and disproportionation), a mechanism is available for enriching nuclei via a mechanism based on differences in nuclear magnetic properties.

The photolysis of dibenzyl ketone (DBK) in a micellar environment is a prototype system for ¹³C isotopic enrichment.^{1,3} The conventional mechanism is outlined in Figure 1. According to

TABLE I: ¹³C and ¹⁷O Enrichment of Dibenzyl Ketone Recovered from Photolysis on Silica at Room Temperature

isotopic enrichment factor	pore diameters		
	22 Å	40 Å	95 Å
α_{13}^a	1.21 ± 0.03 (1.18 ± 0.02) ^c	1.22 ± 0.02	1.21 ± 0.01
α_{17}^a	1.10 ± 0.02^b (1.05 ± 0.02) ^c	1.08 ± 0.03^b	1.06 ± 0.03^b

^a Conversions were typically 30-80% without significant variation in α . The coverage by ketone was 2.5%. (At 10% coverage there was no significant variation in α .) The initial DBK was 30% enriched in ¹³C at the carbonyl carbon for measurement of α_{13} . The initial DBK was 34% enriched in ¹⁷O at the carbonyl oxygen for measurement of α_{17} . The values of α_{13} are the average of four points. ^b Average value of coverage below 5%. ^c In 2-kG magnetic field.

this mechanism, ¹⁷O isotopic enrichment should also be possible (¹⁶O and ¹⁸O have no nuclear spin, ¹⁷O possesses spin 5/2). However, we found that technical problems hampered a definitive

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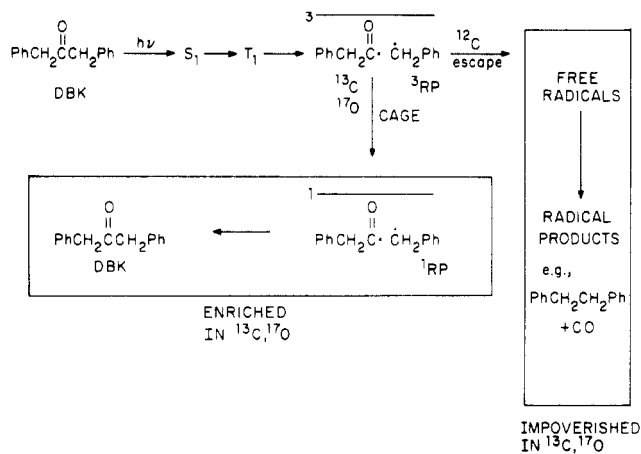


Figure 1. Standard scheme for the photolysis of dibenzyl ketone. A magnetic isotope effect occurs at the stage which the triplet radical pair produced by cleavage of the triplet ketone undergoes either intersystem crossing to a singlet radical pair or escape (diffusional separation and/or decarbonylation). At this stage either ^{13}C or ^{17}O hyperfine-induced intersystem crossing causes faster formation of singlet pairs and enrichment in ^{13}C and ^{17}O in the coupled products.

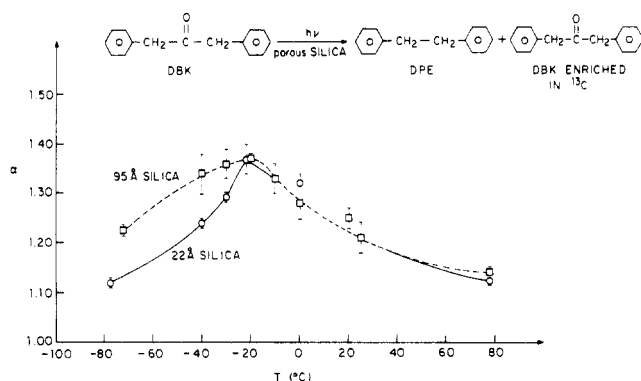


Figure 2. Temperature dependence of the ^{13}C enrichment efficiency of recovered DBK photolyzed on 22- (circles) and 95-Å (squares) silica.

demonstration of ^{17}O enrichment via the photolysis of DBK in micellar systems.⁴ Accordingly, we sought an alternative "supercage" environment which would allow a definitive testing of the prediction of ^{17}O enrichment and would serve as an alternative to micelles. We report here that porous silica⁵ provides an environment for the efficient enrichment of ^{13}C and ^{17}O by photolysis of DBK.

DBK was deposited on porous silica and photolyzed to various conversions.⁶ The isotopic composition of the recovered DBK was determined by GC/MS analysis. The results are shown in Table I, in terms of the enrichment efficiency factor α (α_{13} for ^{13}C enrichment and α_{17} for ^{17}O enrichment). The value of α_{13} is found to be somewhat lower than the maximum values (ca. 1.4) found for photolysis of DBK in micelles¹ and is found to be insensitive to the degree of coverage (up to 10% coverage).⁷ In

(4) Significant exchange of ^{16}O from the bulk aqueous phase and the ^{17}O of the DBK occurs during the photolysis and/or workup.

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(6) A calibrated amount of DBK in *n*-pentane was added to a sample of porous silica which was soaking in a minimum amount of *n*-pentane. The solvent was evaporated slowly to produce a solid which was placed in a quartz cell and degassed at ca. 2×10^{-4} torr. The sample was maintained under vacuum and tumbled during photolysis (312 nm). The products were worked up by extraction with CH_2Cl_2 and removal of filtrated solvent by rotoevaporation. The organic residue was dissolved in anhydrous ether and then subjected to gc/ms analysis.

contrast to the insensitivity of α_{13} to conversion and to coverage (up to ca. 10% coverage), this parameter was found to be significantly influenced by temperature (Figure 2).⁸

A maximum in the profile of enrichment efficiency vs. temperature is expected from the theory of Pines et al.,^{2a} who showed that such an occurrence is expected if hyperfine-induced intersystem crossing is temperature insensitive and there exists competition between diffusion of radical pairs (a function of viscosity) and decarbonylation of radical pairs (a function of temperature). Qualitatively, if diffusion or decarbonylation is fast relative to intersystem crossing, there will be no differentiation between isotopically different radical pairs, because no DBK will be regenerated. Similarly, if diffusion or decarbonylation is too slow relative to intersystem crossing, there will be no differentiation between isotopically different radical pairs, because DBK will be regenerated so efficiently that no escape route for one of the isotopes exists.

It was desirable to demonstrate convincingly that the isotopic changes involved in our ^{17}O investigations were due to selective enrichment of ^{17}O in the recovered DBK. This was accomplished by infrared spectroscopy, since the carbonyl stretching frequencies ($\pm 3 \text{ cm}^{-1}$) of $\text{C}=\text{O}$,¹⁶ $\text{C}=\text{O}$,¹⁷ and $\text{C}=\text{O}$ ¹⁸ are at 1717, 1705, and 1690 cm^{-1} , respectively. Photolysis of a sample of ^{17}O enriched DBK on 22-Å silica, followed by recovery of the residual DBK, showed an increase (ca. 10–20%) of ^{17}O in the latter as determined by IR spectroscopy. The enrichment agrees with the value measured by mass spectrometry.

The values of α_{17} (ca. 1.1) are consistently lower than those of α_{13} (ca. 1.2). This result is consistent with the smaller hyperfine interaction of the carbonyl ^{17}O nucleus (16 G) compared to the carbonyl ^{13}C nucleus (125 G).⁹ Photolysis of ^{18}O -enriched DBK results in an insignificant enrichment in ^{18}O in the residual DBK ($\alpha < 1.03$), demonstrating that a mass isotope effect cannot explain the photochemical results.

The results reported here contrast with those found for the percent cage coupling of geminate pairs produced by photolysis of an asymmetrical DBK on porous silica.^{5c} In the latter instance the percent cage was highest for smallest pore sizes and for a given pore size was highest at lowest coverage. The percent cage was also influenced (decreased) by an application of an external magnetic field with the magnetic influence being more pronounced for lower coverage. The striking differences in the behavior of the $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_2\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ geminate pairs may reflect differences in the time domain for the reactions of the pairs. We suspect that the former persists for a shorter period of time than the latter. As a result, diffusion and pore characteristics probably play a lesser role for the pair leading to isotopic enrichment.

Our results are in contrast in two important respects to a recent investigation of the ^{13}C enrichment of DBK on commercial silica.^{5a} The latter study did not employ silicas of known pore size and did not observe a maximum in the α vs. temperature profile.

In summary, the photolysis of DBK to partial conversion on porous silica is found to result in both ^{13}C and ^{17}O isotopic enrichment of the residual DBK. The efficiency of ^{13}C enrichment is not sensitive to pore size, DBK coverage, or applied magnetic field, but is strongly sensitive to temperature.

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(7) The surface areas of 22-, 40-, and 95-Å silica were 888, 703, and 571 m^2/g , respectively. Surface coverage was calculated based on the assumption of a surface area of 84 \AA^2 for the DBK molecule.

(8) As the photolysis of temperature dropped below 0 °C, isomers of 1,2-diphenylethane (DPE) began to form in detectable amounts (i.e., phenyl-*p*-tolylmethane and phenyl-*o*-tolylmethane in 3:1 ratio). The yield of these products relative to DPE increased as the temperature decreased. At ca. -70 °C they constituted ca. 10% of the yield on both 22- and 95-Å silica.