

PHOTOCHEMISTRY OF KETONES ADSORBED ON POROUS SILICA

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Abstract - The Photochemical reactions of several families of ketones adsorbed on various forms of silica have been investigated. The influence of surface coverage, silica average pore diameter, temperature, applied magnetic fields, and additives on the product distributions have been determined. The results are consistent with a model in which the silica surface consists of two major regions, one consisting of stronger binding sites (active silanol groups) and the other consisting of weaker binding sites (free silanol groups). The relative proportions of these two types of sites are related to the pore size of the silica, smaller pores correlating with a larger fraction of the stronger binding sites and larger pores correlating with a smaller fraction of the stronger binding sites. At low coverage, the initial location of a ketone in one of the two binding sites is an important factor in determining the product distributions. Some preliminary results are reported on the time resolved spectroscopy of ketones adsorbed on silica investigated by diffuse reflectance absorption spectroscopy.

Anisotropic Media, Thin Films, Surfaces and Interfaces

The term "anisotropic media" is not uniquely defined, so that a chemist can use his or her imagination to design systems that conform to individual's concept of the term. This article is concerned with the type of anisotropy that is exhibited by a microscopically "thin film" or a molecular "surface". The ideas that surround these systems are common to discussions of interfaces, self-organizing systems, and heterogeneous systems.¹ A microscopically thin film may be considered as an object which possesses a molecular thickness (a few atoms to a few thousand atoms), but which possesses a macroscopic breadth or extension in two dimensions. A chemical interface can be thought of as a boundary between two substances. At the molecular level an interface may be considered as resulting from a film that is so thin that it no longer has a homogeneous interior. In such cases, the properties of the interface may become very sensitive to the nature of the interior and to the proximity of the interface. There is intense current research and general interest in thin films and interfaces because of the perceived opportunities such systems present for basic research and because of the unquestioned importance such systems have in industry and in developing technologies.²

Porous Solids: Inside the World of Microscopic Surfaces and Interfaces

In mathematics and geometry a surface is a set of points having length and breadth, but no thickness. A planar surface provides an infinitely thin boundary that separates all space into two regions: "above" and "below" the plane. In chemistry a surface is not so well-defined, since it possesses a finite atomic thickness and is not necessarily planar. However, in chemistry the notion of an interface carries with it the concept of a surface that can be thought of as a common boundary between two phases.

Interface chemistry, which has played an important role in industrial and natural processes, has recently attracted the attention of photochemists³ who have become excited by the possibility that the structure of interfaces and the chemistry that occurs at interfaces can be understood in detail at the microscopic level in terms of the chemical and geometrical properties of surfaces. Furthermore, a common feature of heterogeneous catalytic systems is the existence of an interface that provides an extensive surface (high surface area to volume ratio) whose chemical and geometrical features lead to optimum reaction rates and high chemical selectivity.⁴ The existence of an extensive microscopic surface within a particle that is macroscopically solid raises immediate, exciting, intellectual challenges to attempt to conceptualize, in a scientifically precise, yet practically useful manner, the nature of surfaces at interfaces. Such conceptualization, if successful, should allow the utilization of the unique properties of interfaces or surfaces to rationally drive selected features of chemical reactions. The adsorption of molecules onto active surfaces generally produces species whose chemistry can no longer be considered in terms of the standard paradigms which have developed for reactions in homogeneous solutions. The surface/molecule must be considered as an interactive entity or as a complex with subcomponents.⁵ A particularly interesting feature of a surface that is not flat and smooth is that as it becomes more and more distorted and convoluted, it begins to fill the three dimensional space around it.

Porous solids can be imagined to possess internal surfaces that are very tortuous. The internal surface of a porous solid may be enormous. For example, surface areas of the order of 1000 m²/g are known for various forms of silica and zeolites.⁶

The acquisition of knowledge of the parameters needed to describe and characterize such surfaces is one of the major goals of interface research. It is difficult to exaggerate the potential importance of such knowledge to the modern technological world. The microelectronics technologies depend heavily on a variety of structures composed on interfaces, and the silicon based semiconductor industry relies on interface phenomena which occur between silicon and silicon dioxide. Chemically active interfaces are at the heart of heterogeneous catalysts and the refining of petroleum. The selectivity of a heterogeneous catalyst results from a complex interrelation of chemical, geometrical and dynamic features of the porous catalyst and the adsorbed substrates. The pore geometry of rocks, along with the chemical composition of the pore walls, controls the flow of liquids through porous media. An understanding of the geometrical properties of the pore network

at the microscopic level is of critical importance for a basic understanding of the factors controlling commercial and strategic processes such as oil migration, trapping, injection, storage and enhanced recovery.

From the standpoint of fundamental research, investigation of the effect of adsorption of a molecule on a porous silica surface on the products of a reaction offers a means of studying and of modelling important features of catalytic systems. Silicas are especially appropriate for such studies, since siliceous material (glass, clay, zeolites, minerals, etc.) accounts for about three quarters of the earth's matter and since catalytic processes which have occurred with the assistance of siliceous substances are implicated in processes as diverse as the construction of primordial biological molecules to the formation of the earth's petroleum reserves.⁷ In order to gain some insights concerning the possible mechanisms by which silica can modify reactivity and selectivity of a reaction sequence of adsorbed molecules we shall review information^{6,8,9} concerning the composition, structure and geometry of porous silica (in this article we shall use the term silica to apply to porous solid silica and silica gel).

Silica: Surface Composition, Structure and Geometry

The chemical composition of silica is given by the formula: $\text{SiO}_2(\text{H}_2\text{O})_x$. Information on the structure of porous silica is given in Chart 1. It is generally accepted that the structure of the "surface" of silica consists of an interconnected network of silanol (SiOH) and siloxane (SiOSi) linkages. It is convenient to classify the silanol linkages as isolated or free (1),

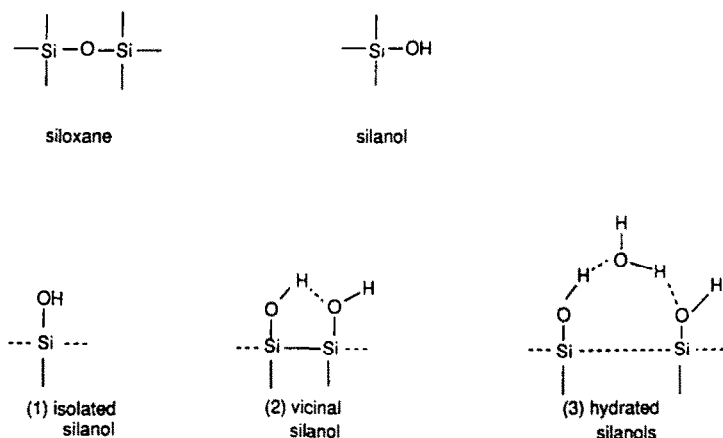


Chart 1. The chemical composition of a silica surface consists of siloxane and silanol groups. For the purposes of this paper, there are three types of silanol groups of interest: (1) the "isolated" or "free" (non-hydrogen bonded silanols that are characteristic of crystalline silica); (2) the vicinal or (hydrogen) bonded or "active" silanols that are characteristic of amorphous silica; and (3) hydrated silanols that may be the result of water binding to either free or vicinal silanols.

vicinal, active or bound (2) and hydrated (3). We shall use the term "free" for silanols of type 1, and the term "active" for silanols of type 2. The active silanols are so positioned on the silica surface so as to permit hydrogen bonding of proximate silanols. In terms of binding capability, the active silanols possess the strongest binding capacity, with the isolated silanols showing weaker binding capability and with the hydrated and siloxane linkages showing still less binding capability. The free silanol groups are characteristic of a relatively crystalline or ordered surface. The differing silanol linkages can be considered as a source of surface heterogeneity and are therefore termed surface sites. The overall rate and product distributions for surface reactions are the results of the rates and product distributions which occur at the various sites. However, catalytic activity, for example, will depend not only on the kinds of different surface sites and their number, but also the accessibility of the sites to adsorbed substrates. This accessibility is in turn related to the geometric details of the porous structure of the silica. Let us now consider the geometric implications of the pore concept briefly.

The term "porous" implies a geometry that is "sponge-like" or is composed of "microscopic holes" or "pores". Indeed, silicas are commonly characterized by "average pore sizes" which are derived from surface area measurements.¹⁰ One may view the active sites in the pores as responsible for binding in the holes and to represent a concentration that drives, in the thermodynamic sense, the adsorption of molecules into the pores, i.e., "moles of holes". The verification and elaboration of such a model is a real challenge because of the amorphous character of porous silica. Can the dimensionality of the silica surface be characterized as two dimensional? How do the ideas of reactions at an interface, or on an extended surface, or on a porous structure relate to our ordinary chemical experience with reactions in homogeneous spaces? What is the meaning of concentration for a reaction which does not occur in a three dimensional space? Does heterogeneity imply lack of reproducibility? Will there be any useful mathematical, structural and geometrical models that will drive the design and interpretation of experiments for reactions of organic molecules adsorbed on porous solids? In other words what is the meaning of a pore in terms of its chemical composition and its geometry?

A major goal of our research investigating the photochemistry and photophysics of organic molecules adsorbed on porous solids is to develop conceptual models that will lead to answers to the above questions by providing meritorious paradigms that will serve as a guide to rationalize and to systematize known information and to drive further experimentation.

The Fractal View of Surfaces

The classical or Euclidean view of a planar surface is that of a perfectly regular, smooth, infinitely thin two-dimensional entity. If the surface becomes non-planar and

irregular, there is no simple intuitive way to characterize it in terms of classical Euclidean dimensionality. A novel approach¹¹ which has been suggested is to employ the concepts of "fractal geometry" in which surfaces of progressively higher irregularity are characterized by progressively higher fractal dimensions, D . In sharp contrast to Euclidean dimensionality, fractal dimensions may be noninteger, so that for a given surface it may be that $2 < D < 3$. The meaning of a value of D close to 2 is that the surface is very flat and smooth and therefore close to the idealized Euclidean two dimensional planar surface. The meaning of a value of D close to 3 is that the surface is very irregular and tortuous and that the surface tends to fill all the space that is near it. Thus, adsorbed molecules on a porous surface with a fractal dimension close to 3 fill space almost as efficiently as they would in filling a three dimensional volume. Although this article cannot go into the details or examples of the use of the theory of fractals to characterize porous surfaces by analysis of photochemical processes, the interested reader is referred to current pertinent literature.¹¹ At this point we can only speculate and hope that the fractal approach may eventually lead to a conceptual model that will allow the more precise use of geometry and reaction paths to replace the rather vague concept of surface area and pore size for amorphous porous solids.

Surface Dynamics of Adsorbed Organic Molecules

The rotational and diffusional motions of molecules adsorbed on surfaces can determine the rates and selectivities of reactions that occur on the surfaces. It is important, therefore, to investigate such motions, to examine how they might influence reactions, and to devise models that will be useful for both experimental design, data correlation and experimental interpretation.

The measurement of surface areas has occupied an important role in the development of the fields of interface chemistry and catalysis.^{4,5} The surface area of a porous solid is measured conventionally by adsorption of a gas such as nitrogen and by interpretation of the adsorption isotherm (the amount of gas adsorbed as a function of the equilibrium pressure) in terms of the total surface coverage of a monolayer of the gas.¹⁰ From simple geometrical models for the pore shapes (e.g., cylinders or "ink bottles", Chart 2) parameters such as an average pore volume and average pore diameter can be derived.⁸ An immediate question arises as to the physical meaning of a pore and as to the chemical and dynamic consequences of such crude geometrical models.

Models for Porous Silica Derived from Chromatography

Data from a variety of experimental probes of chromatographic behavior of silica^{8,9} has led to a model by which silica surfaces are characterized chemically by the surface silanol groups shown in Chart 1. The active silanols (2), believed to be strongly hydrogen bonded surface hydroxyls, constitute the strongest sites for adsorption of aromatic hydrocarbons and react most rapidly with hydroxyl reagents such as trimethylchlorosilane.⁹

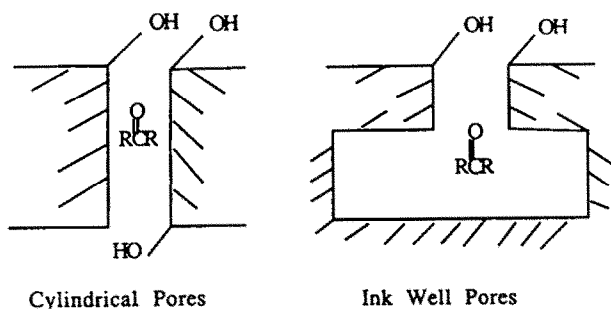


Chart 2. Two possible geometric models for the pores of silica. The cylindrical model (left) and the inkwell model (right).

Depending on the method of preparation and subsequent treatment, silica possesses a porous structure with a formal average pore diameter and a distribution of pore diameters about the average. The relative proportions of active/free (2/1) silanol groups has been shown to be correlated with the pore size of the silica. More specifically, the relative concentration of active silanols (S_a) to the total silanols (S_t) has been found to correlate with the average pore diameter (Figure 1). Thus, the smaller the pore, the larger the value of S_a/S_t , i.e., the larger the fraction of active silanols. The influence of added water on the adsorbent activity of silica as a chromatographic support is well studied.⁹ Figure 2 shows how the activities of silicas of different pore sizes are moderated as a function of added water coverage. Water presumably "titrates" the active hydroxyls first and displaces adsorbed molecules initially adsorbed to those high free energy sites to sites consisting of the free hydroxyls, all of which have comparable but lower free energy than the active silanols. Further addition of water simply results in a nonselective coverage of the free

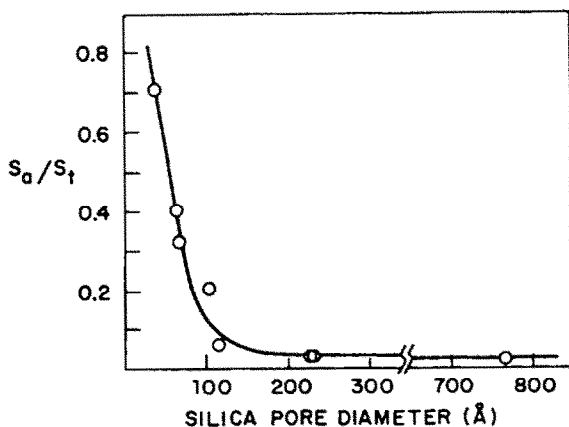


Figure 1. Correlation of active hydroxyl groups with the average pore diameters of silica.

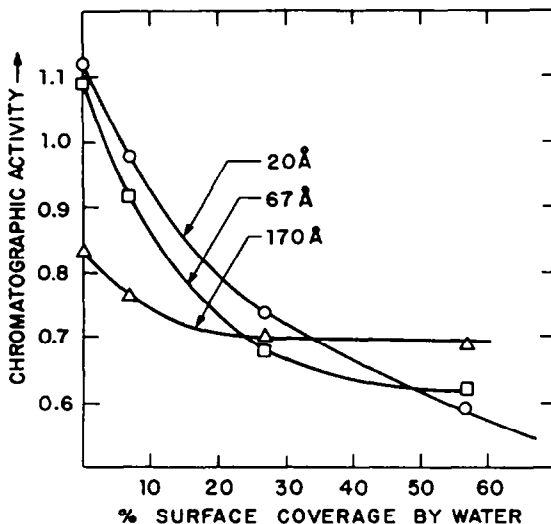


Figure 2. Variation of the chromatographic adsorbent activity or surface free energy as a function of water coverage and average pore size of the silica.

hydroxyls. Thus, there is an expected relationship between the average pore diameter and the surface chemical composition of silicas. But is there any experimental evidence that supports a relationship between the composition and pore size or any relationship between pore size and pore geometry? If pore size does have a geometric relationship, it might be expected that as one decreases the pore diameter and decreases the average radius of curvature of the silica surface, then large molecules should find increasing difficulty in adsorption because of geometric or steric factors. However, given the size of the ketones involved in this study, it is expected that geometric pore size effects will occur only with pores of diameters of 20 Å or less.

In summary, the smaller the pore diameter, the larger the fraction of active hydroxyl sites on the silica surface and the more irregular and tortuous and space filling the silica surface. Given the wide use of silica as a chromatographic material, we decided to initiate our investigations of photoreactions of ketones adsorbed on silica by employing silicas that are commonly used in the laboratory for chromatography and then, after obtaining some calibrating results, to launch into more detailed investigations employing silicas of characterized pore size.

Preliminary Investigations of the Photochemistry of Ketones on Silica: Type I and Type II Reactions on TLC and RPTLC Plates

Our first investigations of the photochemistry of ketones on silica involved very simple explorations employing silicas that are commonly available in the laboratory. The basic goal was to determine whether there would be interesting and novel observations with respect to product distributions and to reserve for a later time an analysis of the nature of the silica sample and its pore size characterization. We decided to employ the

Type I and Type II photoreactions of ketones (Chart 3), since they are well defined mechanistically,¹² as our reaction systems. For substrate systems we selected aryl alkyl ketones with structural variations of the alkyl side chain. The ketones investigated are shown in Chart 3. The purpose of the side chain structural variation was to provide a probe of conformational properties of the substrate and their impact on the photochemistry. In addition, systems were designed for which a competition between Type I and Type II reaction would provide information on the competition between diffusional separation of radical pairs produced by Type I cleavage and conformational properties of side chains which are critical for the occurrence of the Type II reaction.

Photolysis of ketones 1a-1c and of ketones 2a-2c adsorbed on silica of various types was conducted at ambient temperature. "Dry" samples (thin layer chromatographic plates, TLC) were impregnated with ketone from a solvent and then the system was subjected to vacuum and maintained under vacuum during photolysis. "Wet" samples (reverse phase

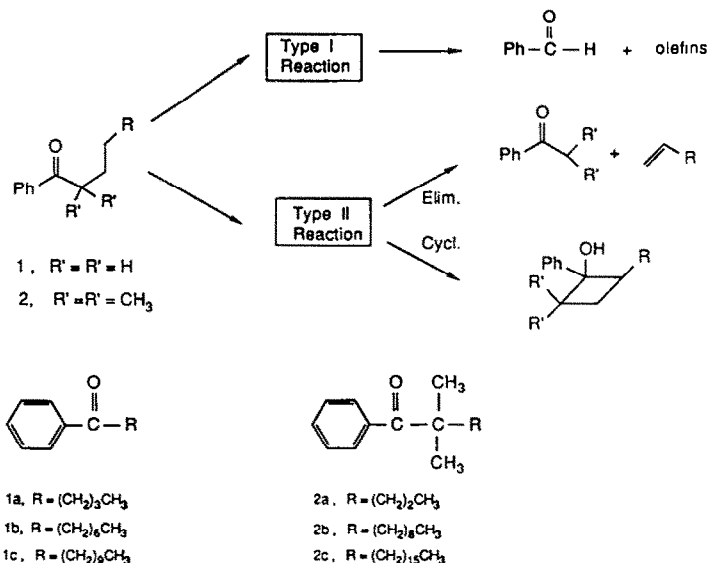


Chart 3. Ketone structures employed in the photolysis on TLC plates.

thin layer chromatographic plates (RPTLC) were impregnated with ketone and then immersed in water, nitrogen purged and then photolyzed. The results of these experiments are summarized in Tables 1 and 2.

In order to determine the effects of temperature on the photochemistry, we photolyzed 1b and 2b adsorbed on TLC and RPTLC at -125° C. In both cases Type II reaction occurs, but only the cyclization product is observed. The reaction at low temperature required a much longer irradiation time than that at ambient temperature, so the quantum yield for photolysis is evidently much lower at -125° C.

The results can be interpreted in terms of two features that were believed to be a priori general for molecules adsorbed on silica: (1) restriction of diffusional motion of radical pairs and (2) restriction of conformational motions of the alkyl side chain. The

results (Tables 1 and 2) are indeed completely interpretable in terms of these two features. For example, the ratio of Type I to Type II products for 2a-2c on silica is significantly greater than the ratio found for these ketones in t-butanol as a homogeneous standard for comparison. These results are interpreted in terms of restricted rotation of the alkyl chain, which will inhibit Type II reaction relative to Type I reaction. Thus, restriction of the rotational motion of the alkyl chain is expected to reduce the probability of triplet state ketone attaining a cisoid conformation during the triplet lifetime. Such a conformational requirement does not exist for the Type I cleavage. On the other hand, if the 1,4-biradical is

Table 1. Product distributions for the Photolysis of Phenyl Alkyl Ketones on Silicas.

<u>Ketone</u>	<u>Environment</u> ^(a)	<u>Elim/Cyc</u>
1a	RPTLC/H ₂ O	4.3
	TLC	3.7
	RPTLC	3.0
	t-Butanol	4.2
1b	RPTLC/H ₂ O	5.2
	TLC	3.8
	RPTLC	2.1
	t-Butanol	6.0
1c	RPTLC/H ₂ O	6.0
	TLC	3.9
	RPTLC	3.2
	t-Butanol	5.5

(a) Ratio of elimination to cyclization products.

Table 2. Product Distributions for the Photolysis of α,α -Dimethyl Substituted Phenyl Alkyl Ketones Adsorbed on Silicas.

<u>Ketone</u>	<u>Environment</u>	<u>Type I/Type II</u>	<u>Elim/Cyc</u> ^(a)
2a	RPTLC/H ₂ O	0.20	1.40
	TLC	0.28	0.50
	RPTLC	0.38	0.50
	t-Butanol	0.04	0.91
2b	RPTLC/H ₂ O	0.34	0.75
	TLC	0.48	0.38
	RPTLC	0.20	0.32
	t-Butanol	0.16	0.32
2c	RPTLC/H ₂ O	0.20	1.00
	TLC	0.48	0.78
	RPTLC	0.22	0.27
	t-Butanol	0.07	0.50

(a) Ratio of elimination to cyclization products.

formed from Type II abstraction, the same rotational restriction will tend to favor processes that occur in the cisoid form of the biradical. This explains the generally higher degree of cyclization relative to elimination that is observed for photolysis on silica. At low temperature, reaction only from the available cisoid conformation can occur (albeit with very low efficiency) and only cyclization is observed, a result that suggests an activation energy for conformation interconversion that is too high to be achieved at low temperature. Thus, the general conclusion from these results is that adsorption on silica can lead to significant restriction of the translational motion of radical pairs but to much smaller constraints on conformational motions of biradicals, and there is a significant temperature effect which corresponds to restriction of conformational and translational motion at low temperatures. It should be noted however, that the lifetimes of the biradicals may be much shorter than those of the radical pairs, thereby introducing a lifetime reduction of efficiency rather than a surface reduction of rate of conformational change. These results are consistent with the findings and conclusions of other groups.¹³

Magnetic Field Effects on the Photochemistry of Ketones Adsorbed on Silica

From our earlier research on the photochemistry of ketones dissolved in micelles,¹⁴ we have become accustomed to expecting magnetic field effects when radical pairs are produced in reaction spaces that restrict diffusional motion and which encourage returns of geminate radical pairs. Accordingly, we investigated the effect of an applied external magnetic field on the photochemistry of ketones adsorbed on TLC plates. The results are shown in Table 3. The magnetic field clearly favors an increase in the relative amounts of Type I to Type II reaction but does not affect the relative amount of elimination to cyclization. This result is interpreted in terms of the expected increase in the lifetime of the geminate triplet radical pair produced by Type I cleavage caused by the external magnetic field which allows for greater efficiency of radical pair separation and then, reaction.¹⁵ The magnetic field, on the other hand, is not expected to significantly influence the lifetime of a 1,4-biradical because of the large electron exchange interaction in the biradical.¹⁵

Table 3. Magnetic field effect on the product distribution for photolysis of α,α -dimethyl substituted phenyl alkyl ketones on silica gel TLC plates.^(a)

<u>Ketone</u>	<u>Field (G)</u>	<u>Type I/Type II</u>	<u>Elim/Cyc</u>
2a	0	0.28	0.50
	5000	0.35	0.46
2b	0	0.48	0.38
	5000	0.72	0.36

(a) Error limits estimated to be +/- 10%.

Photochemistry of Diastereomeric 2,4-Diphenylpentan-3-ones on Silica

In order to test more subtle effects of structure on the photolysis of ketones adsorbed on silica and to obtain more quantitative information on the efficiency of inhibition to diffusional separation, the diastereomeric system available in the 2,4-diphenylpentan-3-one (DPP) structure was investigated.¹⁴ Photochemical cleavage of this system allows a study of the rotation of radicals in the primary radical pair by measurement of the interconversion of the d,l and meso forms of the starting material. This process, in turn, is in competition with the decarbonylation of the primary geminate radical pair.

Photolysis¹⁴ of DPP on TLC plates and on RPTLC plates resulted in similar product distributions as shown in Chart 4 for two temperatures (ambient and -77° C). For comparison, photolysis of DPP at room temperature or at -77° C in homogeneous solvents such as pentane led essentially to the same result, namely nearly quantitative formation of a 1:1 mixture of the d,l and meso forms of 2,3-diphenylbutane. Evidently, on silica the primary geminate radical pair is encouraged, because of the inhibition of diffusional separation, to undergo disproportionation to 2-phenyl propionaldehyde (and styrene) and recombination reactions, the latter leading to the diastereometric isomer of the starting ketone.

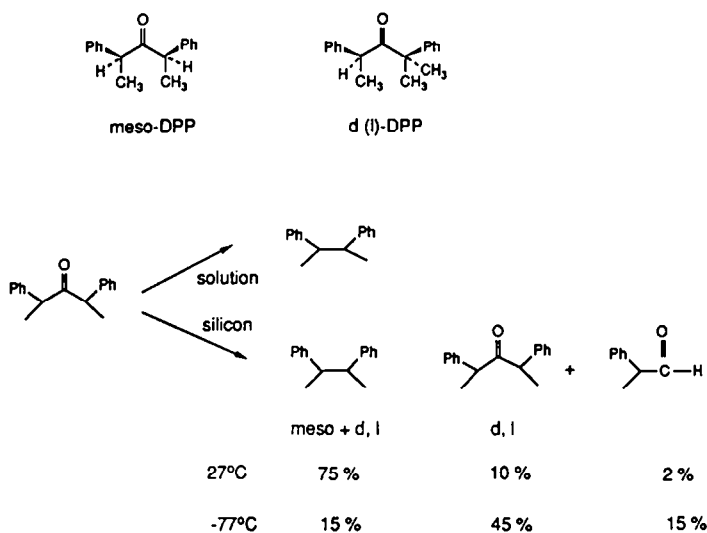


Chart 4. Reactions scheme for the competing Type I and Type II processes.

In order to obtain a more quantitative measurement of the silica adsorption effect, the percent of stereoisomerization relative to the percent disappearance of DPP was measured. The slope of such a plot, *s*, is a measure of the fraction of reacted DPP that undergoes isomerization. For example, *s* = 0.01 for the photolysis of either d,l-DPP or meso-DPP in homogeneous solvents, i.e., the photoisomerization is only of the order of 1% of the total reaction. In contrast, *s* is of the order of 0.2 for photolysis of either d,l-DPP or meso-DPP adsorbed on silica, i.e., the extent of photoisomerization relative to the net reacting ketone is

of the order of 20%. It was also found that there is, in general, a significant magnetic field effect on the value of s , the application of an external field causing a decrease in the value of s . This result is interpreted to mean that there is a competition between the return of the primary geminate radical pair (to cause stereoisomerization) and diffusional separation (to encourage reactions other than stereoisomerization).¹⁵ The applied magnetic field reduces the rate of intersystem crossing of primary radical pairs and thereby decreases the fraction of pairs that can recombine to cause isomerization of the starting material.

All of the above results suggested that adsorption of ketones on silica could indeed vary significantly the product distribution relative to those for homogeneous solution, and that magnetic field effects are potentially general for radical pair reactions on silica in the same way that they have been shown to be for radical pair reactions in micelles.¹⁴ This, in turn, suggests the concept of a "super cage" or a restricted geometry which constitutes the reaction space of a microscopic reactor. Therefore, we next decided to investigate the influence of surface area (pore size) and surface coverage on radical pair reactions with a new goal in mind, namely to use silica as a possible environment to explore magnetic isotope effects that could lead to isotope separation.

Correlation of Cage Effects and Magnetic Field Effects with Pore Size and Surface Coverage in the Photolysis of p-Me Dibenzyl Ketone

The theory of the magnetic isotope effect on the chemistry of radical pairs suggests that both the restriction to diffusion (termed the microviscosity) and the size and shape (geometry) of the reaction space (termed the microscopic reactor or super cage) are critical features in determining the efficiency of separation of magnetic isotopes.¹⁵ We decided to explore the microscopic viscosity of silica and the ability of silica to serve as a microscopic reactor by studying the magnetic field effect and magnetic isotope effect on the photochemistry of p-methyl dibenzyl ketone (p-MeDBK) adsorbed on silica as a function of temperature, silica pore size and ketone coverage.¹⁷

Under our conditions the major products (Chart 5), formed in the photolysis/pMeDBK adsorbed on silica were the three diphenylethanes AA, AB and BB. The ratios of products were used to determine the cage effect according to eq. 1. The cage is usually defined as the percent of geminate pair combination that occurs when a radical pair is produced by homolytic cleavage of a radical pair precursor.¹⁸ In the asymmetric ketone, ACOB, the cage effect can be evaluated by simply measuring the three possible products resulting from decarbonylation, i.e., AA, AB and applying eqn 1.

$$\% \text{ Cage Effect} = \frac{(AB) - (AA + BB)}{AA + AB + BB} \times (100) \quad (1)$$

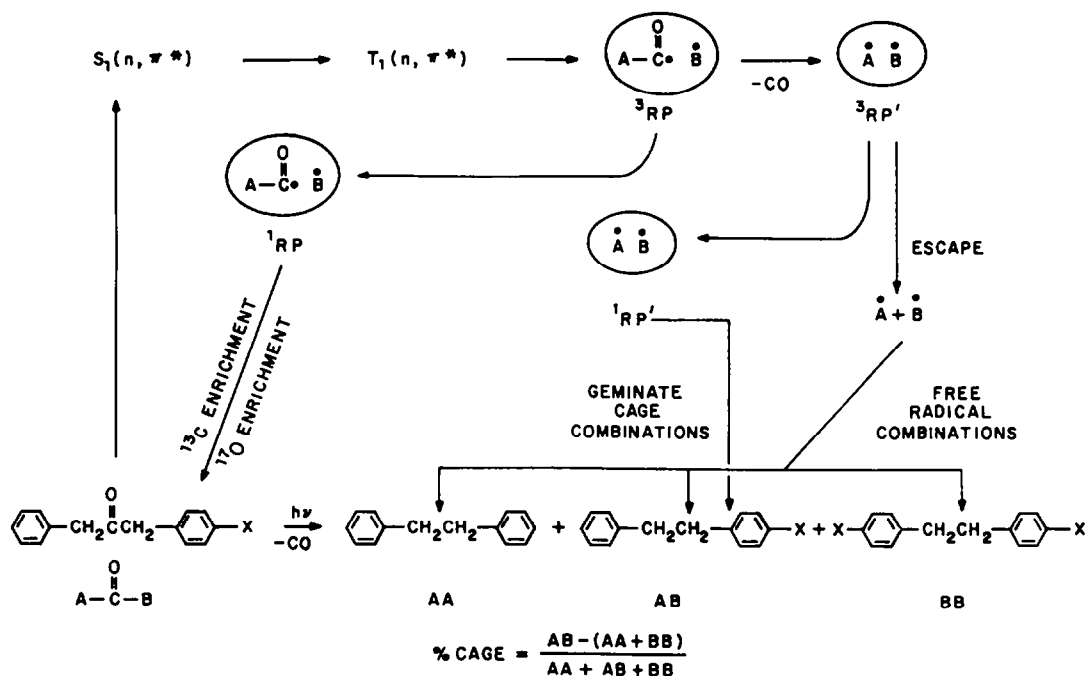


Chart 5. Structures and products from the photolysis of DPP.

For example, if the asymmetric molecule AB is the only product, then the cage effect is positive and equal to 100%. If the ratio of AA:AB:BB is 1:2:1 then the cage effect is 0% (i.e., is typical of random coupling). As long as AA, AB and BB are the major products of photolysis of ACOB, the cage effect can be calculated from eqn. 1 and may achieve values ranging from 100% to 0%. Since excellent mass balances (>90%) were obtained in all of the reported cases, the molar ratios of the products (AA, AB and BB) determined by vpc analysis may be employed to obtain the cage effect.

High purity silica of known surface area and of fairly narrow pore size distribution (Figure 3) was employed for the photolysis. The % cage was determined for the photolysis of pMeDBK as a function of coverage on the various silicas (Figure 4). For comparison, a sample of commercial silica was analyzed for its pore size distribution and was employed for photolysis. In some cases low yields of isomers of the starting ketone were formed; these products are analogous to the primary radical pair products formed in the photolysis of DPP described above, but will not be considered in this article.¹⁶ An investigation of the effect of conversion on the cage effect revealed little difference between high and low conversions. For example, the cage effect for ca 32% conversion and for 100% conversion for 22 Å silica was found to be 21% and 22%, respectively. For each of the silicas investigated the profile of % cage as a function of coverage (Figure 4) is qualitatively similar and consists of two distinct regions: (Region I) for "low" coverage (<5%) the % cage is substantial and decreases slowly with increasing coverage, and (Region II) for "high" coverage (>5%) the % cage reaches a limiting value, which is maintained to higher coverages. Significantly, the family of curves

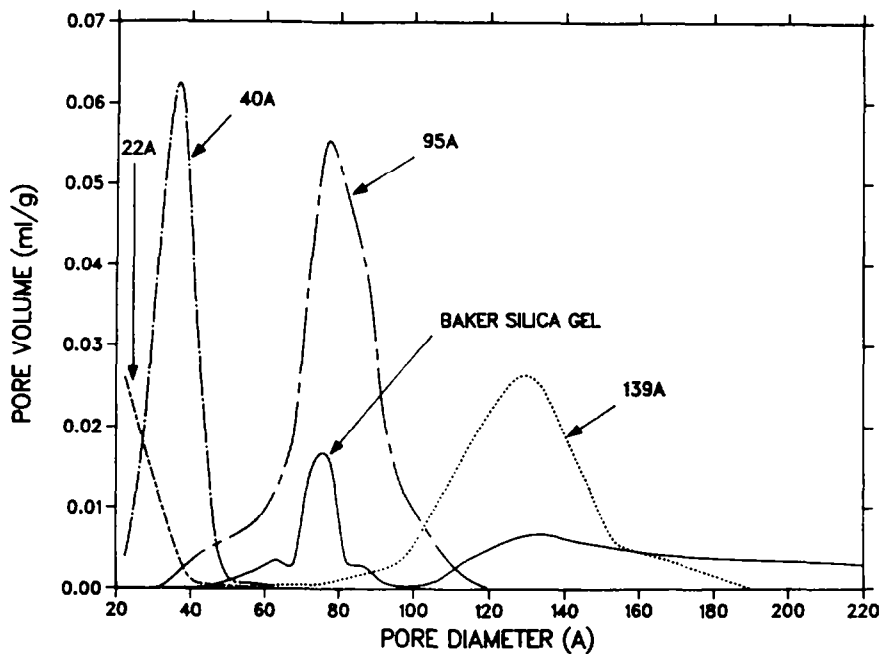


Figure 3. Pore diameter profiles of the freeze-formed silicas employed in the described photolysis.

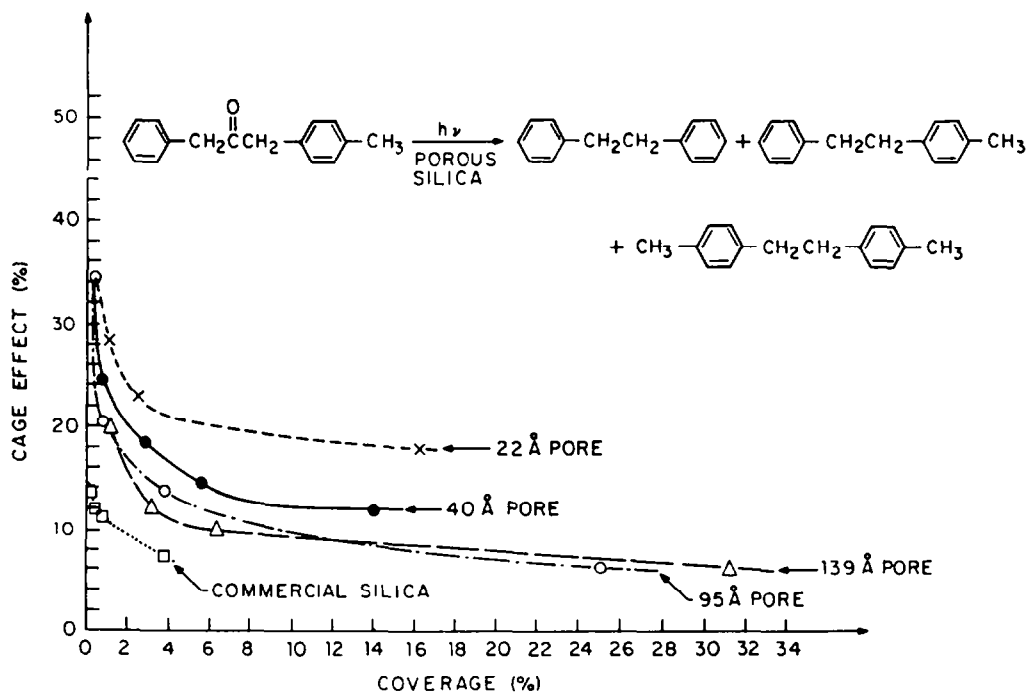


Figure 4. Cage effect as a function of coverage for the photolysis of p-MeDBK as a function of silica pore size.

produced by a plot of % cage vs. coverage is correlated with pore size. The smaller the median pore size, the higher the limiting % cage at high coverage. For comparison, commercial Baker silica is found to behave more similarly to the largest pore silicas investigated. The curves shown in Figure 4 bear a striking similarity to the plots of chromatographic activity versus coverage with water (Figure 1). The latter curves are interpreted in terms of deactivation of the strongest adsorbing sites by water. When all of the active silanols have been deactivated with water, only free silanol sites remain and further addition of water results in nonselective coverage of these groups. The net result is to produce an activity-coverage profile which shows a sharp initial decrease for low coverage followed by a "plateau" region for which the activity is relatively insensitive to further coverage. The situation is somewhat different for the smallest pore size silicas, because of the relatively high (ca 50%) percentage of active silanols. These groups are not of uniform energy because they are associated with an amorphous surface. Recall from the above discussion that upon addition of small portions of water, the strongest binding sites are covered selectively, but there remains a range of site energies in the remaining uncovered surface. Further incremental addition of water again selectively covers the strongest of the remaining sites and so on until the residual sites are mainly composed of free silanols.

An analogous interpretation can be made for Figure 4. At low coverage, pMeDBK molecules are selectively adsorbed in (small) pores containing active silanol groups. Ketone molecules bind tighter to these sites than they do in (large) pores containing mainly free silanol groups. The large pores begin to be filled with ketones only after the small pores containing the active silanols are filled. Since the free energy change for filling pores containing free silanols is comparable, binding is more or less random.

An additional elaboration of the interpretation of the results in Figure 4 is also possible by assuming there is a geometric interpretation possible for the silica pores; i.e., the smaller the pore size the greater the efficiency of geminate return because of reflectings of the radicals off the pore walls, and the larger the pore size, the lower the efficiency of return of geminate pairs to a common space which is needed for cage recombination and the more efficient escape of radicals from an initial pore. Once geminate radical pairs escape the pore in which they were generated, they become awash in a sea of free silanols and are equivalent to "free radicals" in a homogeneous solution and, accordingly, they combine in a random fashion corresponding to 0% cage. Thus, we postulate that not only are the ketones bound more strongly in the smaller pores, but so are the radical pairs produced by photolysis. Furthermore, the smaller pores provide a "super cage" effect which encourages geminate radical combination independently of the effects of binding. The stronger binding and smaller cage size of the radical pairs (lower coverage and smaller pore size) implies less mobility, more efficient reflection of geminate radical pairs and higher cage effects. The weaker binding of the ketones by the free silanols is matched by a weaker binding of the radical pairs and smaller cage effects for high coverage and larger pore size. As the pore

sizes reach 100 Å the % active silanols approaches a limiting value, the cage walls become shallow and non-reflecting and the % cage approaches a limiting value. This limit represents a surface consisting of only free silanol groups (as is the case in crystalline, non-porous silica, such as glass). An implication of this interpretation is that the net cage effect for the large pore silicas represents (after subtraction of the contribution due to the smaller pore in the pore size distribution) a true restriction of radical pair translational motion resulting from adsorption on free silanols, but one which is not due to a geometrical effect.

It can be seen by inspection of Figure 4 that a plot of the cage effect for the plateau regions versus pore size will produce a graph that is similar in shape to that of Figure 2 for which the fraction of active hydroxyls is plotted versus pore size. Thus, there is a striking analogy between the relationships between chromatographic activity and coverage (Figure 1) and the relationship between the cage effect and coverage (Figure 4) and between the relationship between the fractions of active hydroxyls and pore size (Figure 2) and the limiting cage effect versus pore size (Figure 4).

Influence of Temperature on the Cage Effect

The influence of temperature on the cage effect was investigated for a small pore (22 Å) and a larger pore (95 Å) silica. The results are shown in Figure 5. In both cases the cage effect increases as the temperature decreases. Since the pore structure of silica is expected to be temperature independent, we attribute the temperature effect to an increase in surface viscosity, i.e., there is an activation energy to motion of the radicals on the surface. The pore size effect is assigned to the larger initial viscosity of the smaller pore system

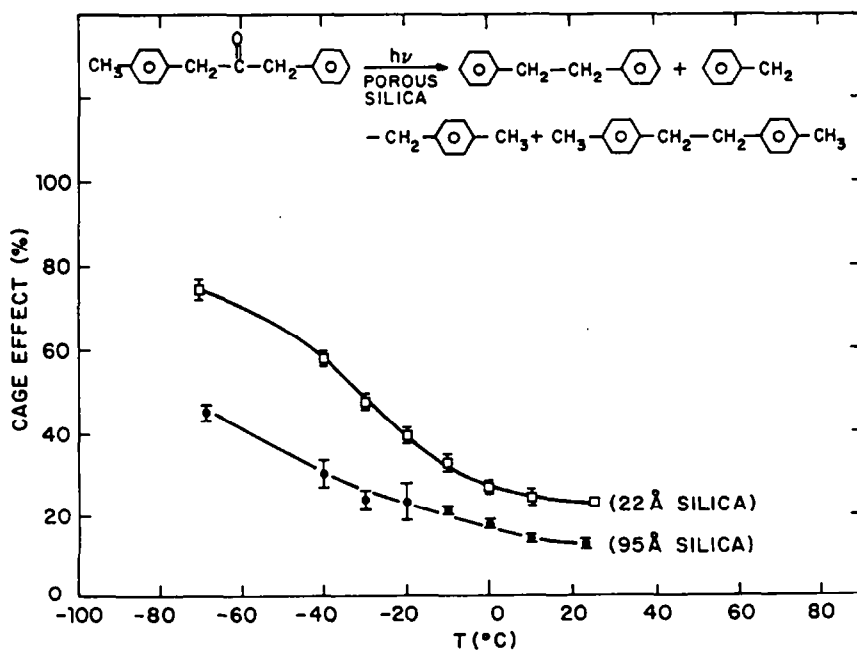


Figure 5. Effect of temperature on the cage effect of p-MeDBK adsorbed on silica.

which contains more active hydroxyls. The similarity of the shape of the two curves suggests that, in the main, the mechanisms of the temperature effect, i.e., increase in viscosity, is the same for the two pore systems. These results are consistent with the interpretation of the results for other systems discussed above and related reports in the literature.¹³

The temperature dependence of the photolysis of DPP on 22 Å and 95 Å silica was briefly investigated by measuring the s value as a function of temperature. The value of s makes a large jump from ca 0.17 at ambient temperature to 0.8 at -40 °C, i.e., the extent of recombination of the primary geminate radical pair reaches values of 80% at low temperatures.

Influence of Coadsorbates on the Cage Effect

Strong binding coadsorbates, such as water and alcohols, are expected to influence radical pair mobility in several ways: (1) the coadsorbate could displace the adsorbed ketone from a strong (active silanols) binding site to a weaker (free silanols) binding site, thereby enhancing translational motion of the photochemically produced radical pairs and reducing the magnitude of the cage effect; (2) molecules of the coadsorbate could cluster at the mouth of an "ink bottle" pore openings (Chart 2) faster than they displace ketone molecules from the interior of the pore, thereby "entombing" the ketone within the pore and increasing the cage effect; (3) the coadsorbate could cause a variation in the substrate distribution of the ketones on the surface.

We have found evidence for mechanisms (1) and (2) for the addition of water as a coadsorbate. Table 4 shows the effect of added water on the cage effect for silicas of varying pore size. For the smaller size pores the cage effect appears to be unaffected by the added water, whereas for the larger pores, the cage effect undergoes a drastic decrease when water is added. These results are consistent with the operation of mechanism (1), the entombment of ketone molecules in "inkwell" pores (Chart 2) by water, for the smallest (22 Å) pore silica and with the operation of mechanism (2), the displacement of ketones to areas of the surface that allow greater translational mobility, for the larger pore silica. These ideas are consistent with the qualitative result that the rate of photolysis is slower for small

Table 4. Influence of Water on the Cage Effect for Silicas of Various Pore Sizes.

<u>Pore Size</u>	<u>22 Å</u>	<u>95 Å</u>	<u>139 Å</u>	<u>255 Å</u>
"Dry" ^a	33%	28%	9%	13%
"Wet" ^b	32 %	3%	4%	2%

(a) Degassed, nitrogen pruged, photolyzed.

(b) Degassed, exposed to water vapor, photolyzed.

pores than for the larger pores (Rel. rates for $<20 \text{ \AA}$, 22 \AA , 40 \AA , 95 \AA and 122 \AA are ca 1.0, 1.2, 1.5, 2.0 and 2.0, respectively).

A preliminary investigation of alcohol additives revealed a significant structural effect: for 22 \AA silica at low ($<1\%$) coverage by ketone, the cage effect increased upon addition of an excess of 1-adamantanol but decreased upon addition of an excess of 1-tetradecanol. We speculate that the caged alcohol served to cap inkwell pores (Chart 2) containing adsorbed ketone, while the chain alcohol caused displacement of the ketone from a small pore site to a larger pore site.

Although an early, pioneering investigation of the mobility of radicals adsorbed on silica claimed that (from product analysis) the adsorbed radicals underwent restricted rotation and little translational motion,¹⁹ a latter investigation of the same system and other systems¹³ have indicated that rotational motion is not restricted for dry silica, but that translational motion is clearly restricted relative to non-viscous homogeneous solutions as standards of comparison. By and large, our results are consistent with the latter work.

Analogy between the Cage Effect for Molecules Adsorbed on Silica and Molecules Solubilized in Micelles.

The notions of a "super cage" environment that encourages geminate pair combinations is reminiscent of the effect of solubilization of geminate radical pairs in micelles.¹⁴ One of the consequences of the analogy between micelles and silica pores is the expectation that the % cage will be magnetic field dependent. The expectation is realized experimentally in the photolysis of DBK on silica (Figure 6).²⁰ Significantly, a large magnetic field effect was found only in region I (coverage less than 1 %). For both 22- and 95- \AA pores, the magnetic field effect becomes less significant for coverage above a few %. There is only an insignificant magnetic field effect on the cage effect in region II (coverage greater

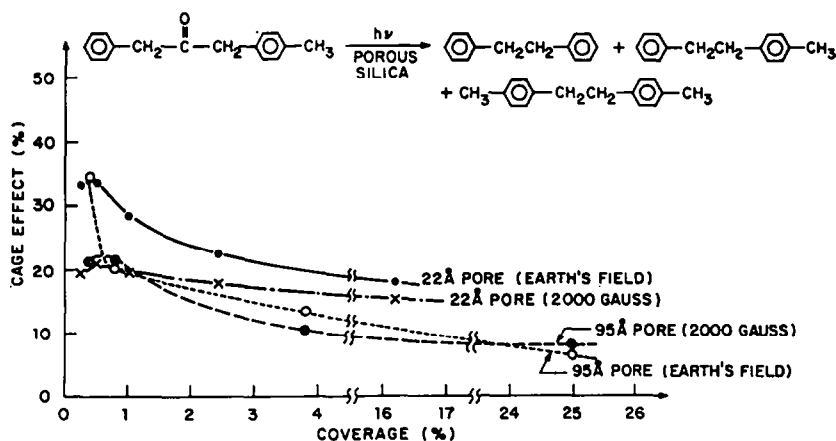


Figure 6. Magnetic field effect on the cage effect of p-MeDBK adsorbed on silica.

than a few %). It was found that there is no significant effect at any coverage for commercial silica. Thus, our results may again be simply interpreted in terms of a two-site model as discussed above for the cage effect in the photolysis of adsorbed pMeDBK on silica which shows behavior characteristic of regions I and II, respectively. Magnetic effects are observed in region I because of the super cage effect of encouraging geminate radical pair combinations. The effects are absent in region II because only the weaker viscosity effect operates, and it is known that in homogeneous solution magnetic effects on radical pair reactions are very weak.²¹

In a related investigation¹³ the photolysis of a p-methyl, p-methoxy dibenzyl ketone on commercial silica failed to reveal an appreciable change in the cage effect for coverages from 1% to 50%. Among the possible reasons suggested for the lack of a coverage effect were that the presence of adventitious water which filled the active surface sites or that the benzyl radicals produced by photolysis may not find themselves in an active surface site. Our results suggest a third possibility that the polydisperse nature of commercial silica may lead to a mixture of active sites, all of which are relatively large pore in nature and therefore relatively insensitive to coverage effects (Figure 4). These authors¹³ objected to the description of the silica surface as a super cage because they note: "usage of the word "cage" referring to a surface is somewhat misleading since, on the surface, a radical is not surrounded by a solvent "wall" (or anything else) as it is in solution. If a functional analogy be required...recourse may be had to the relationship of flies to flypaper as more adequately representing the relationship of an adsorbed molecule to the adsorbent surface." Actually, we like the fly paper analogy and believe it is acceptable for high coverage or large pore silicas, but it does not appear to reflect the whole story, especially for low coverages and small pore size, since in the latter, geometrical effects may operate.

Magnetic Isotope Effects in the Photolysis of Dibenzyl Ketone on Silica, C-13 and O-17 Isotope Separations.

We²² and others²³ 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 maximal²¹ 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. As discussed earlier,^{15,21} 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 ^{13}C isotopic enrichment.²² The conventional mechanism is outlined in Chart 7. From the standpoint of the micelle, the key starting point is the primary geminate triplet radical pair that is generated by homolytic cleavage of the triplet ketone. This electron spin correlated pair has two processes available to it: (1) it may undergo diffusional separation to generate free radicals and (2) it may undergo chemical reaction (decarbonylation) to produce a new geminate pair. Recombination to regenerate the starting ketone or an isomer of the starting ketone is not an option, because triplet radical pairs cannot undergo direct bond formation, i.e., intersystem crossing must occur prior to bond formation. In order to undergo intersystem crossing, the radical spin centers must separate to a distance of about 10 \AA so that the hyperfine interactions with the magnetic nuclei can induce triplet to singlet conversion. Thus, during diffusional separation ^{13}C and ^{17}O nuclei can cause triplet to singlet intersystem crossing. If the geminate singlet pairs thereby produced can return to a region of space in which they become collision partners, combination processes to regenerate the starting ketone can occur. Since the geminate pairs possessing ^{12}C or $^{16}\text{O}/^{18}\text{O}$ nuclei have an alternate process, decarbonylation, available to them, a set of competing processes (hyperfine induced intersystem crossing and decarbonylation) provide a means of separating and enriching isotopes.²²

Indeed, significant ^{13}C enrichment has been demonstrated by the photolysis of DBK in micellar environments,²² where the micelle served as a sort of "super cage" environment to encourage geminate pair reencounters after separation and intersystem crossing occurred. ^{17}O isotopic enrichment should also be possible (^{16}O and ^{18}O have no nuclear spin, ^{17}O

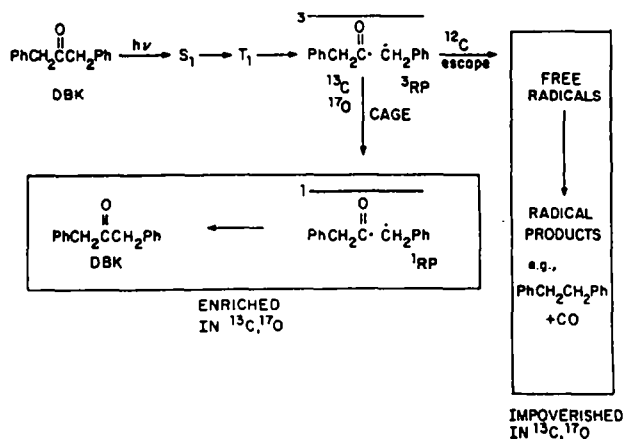


Chart 7. Paradigm for the photolysis of DBK for isotopic enrichment.

possesses spin 5/2) by photolysis of DBK in micellar solution. However, technical problems (^{16}O exchange during photolysis during reaction and workup) hampered a definitive demonstration of ^{17}O enrichment via the photolysis of DBK in micellar systems. 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. From the above results, porous silica was expected to provide such an environment for the efficient enrichment of both ^{13}C and ^{17}O by photolysis of DBK.²⁰

As a test of these ideas, DBK was deposited on porous silica and photolyzed to various conversions. The isotopic composition of the recovered DBK was determined by GC/MS analysis. The results are shown in Table 5, in terms of the enrichment efficiency factor α (α_{13} for ^{13}C enrichment and α_{17} for ^{17}O enrichment). For calibration, an α value of 1.05 would correspond to a large mass isotope effect for ^{13}C . Thus, values of >1.1 are much larger than those expected for mass isotope effects. In micelles²² the values of α are of the order of 1.4. The value of α_{13} for photolysis of DBK on silica is found to be somewhat lower than the maximum values (ca. 1.4) found for photolysis of DBK in micelles and is found to be insensitive to the degree of coverage (up to 10% coverage). In 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 7).

Table 5. ^{13}C and ^{17}O Enrichment of Dibenzyl Ketone Recovered from Photolysis on Silica At Room Temperature.

Enrichment	Pore Diameter		
	22 Å	40 Å	95 Å
α_{13}	1.21	1.22	1.21
α_{17}	1.10	1.08	1.06

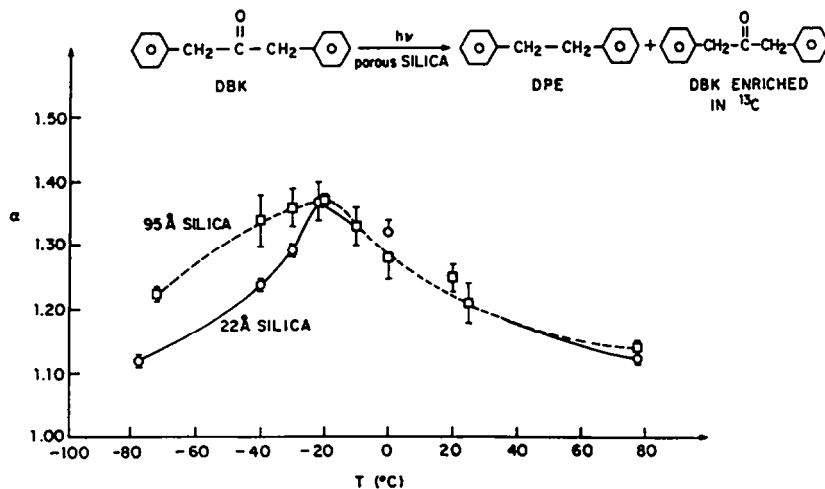


Figure 7. Temperature dependence of the efficiency of isotopic enrichment for the photolysis of DBK on silica gel.

If hyperfine-induced intersystem crossing is temperature insensitive and if there exists a competition between diffusion of radical pairs (a function of viscosity and the geometry of the restricted space) and decarbonylation of radical pairs (a function of temperature), a maximum in the profile of enrichment efficiency vs. temperature is expected from the theory²⁴ of the mie. 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 are 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. These results should be considered relative to the temperature effect on the cage effect for photolysis of pMeDBK adsorbed on silica (Figure 5). The latter results proved a clear indication of the operation of viscosity effects on the translational diffusion of the secondary radical pair.

It was desirable to demonstrate convincingly that the isotopic changes involved in our ¹⁷O investigations were due to selective enrichment of ¹⁷O in the recovered DBK. This was accomplished by infrared spectroscopy, since the carbonyl stretching frequencies of C=O¹⁶, C=O¹⁷, and C=O¹⁸ are at 1717, 1705, and 1690 cm⁻¹, respectively. Photolysis of a sample of ¹⁷O enriched DBK on 22-Å silica, followed by recovery of the residual DBK, showed an increase (ca. 10-20%) of ¹⁷O in the latter as determined by IR spectroscopy (Figure 8). The enrichment agrees with the value measured by mass spectrometry (Figure 9).

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 ¹⁷O nucleus (16G) compared to the carbonyl ¹³C nucleus (125 G).²⁵ Photolysis of ¹⁸O-enriched DBK results in an insignificant enrichment in ¹⁸O in the residual DBK α (ca 1.03), demonstrating that a mass isotope effect cannot explain the photochemical results.

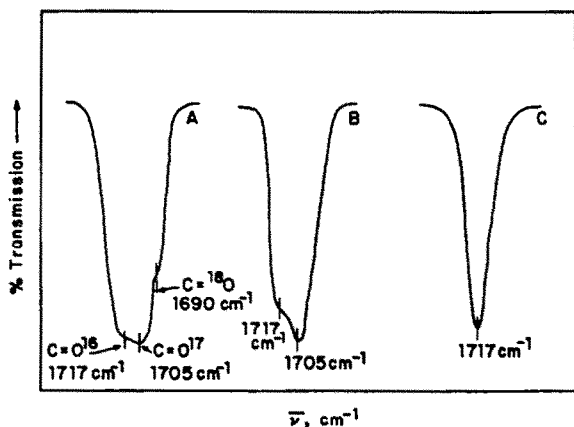


Figure 8. Infrared determination of the ¹⁷O enrichment in the photolysis of DBK on silica. A is starting DBK. B is DBK recovered after 95% conversion. C is recovered DBK allowed to undergo oxygen exchange in 0.50 M H₂SO₄. Spectra recorded on a Perkin-Elmer 983 spectrometer in CHCl₃ solution (1.0 mm NaCl cells).

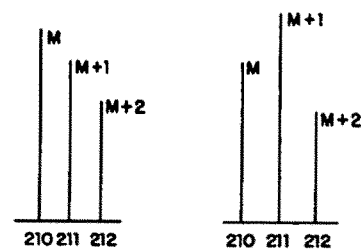


Figure 9. Mass spectrometric determination of the ¹⁷O enrichment. Left: masses corresponding to the molecular ion of starting DBK, synthetically enriched with ¹⁷O. Right: masses corresponding to the molecular ion of DBK recovered after 90% conversion.

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.¹⁷ In the latter instance the percent cage 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 $C_6H_5CH_2CO-CH_2C_6H_5$ and $C_6H_5CH_2-CH_2C_6H_5$ 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. The general conclusions reached for the photolysis of DBK are also valid for the photolysis of DPP. For example, for 22 Å silica the s value (for low conversions) decrease with ketone coverage: $s = 0.17, 0.14$ and 0.12 for 0.25, 2% and 12% coverage, respectively. On a larger pore (95 Å) silica the same trend is found. Similar conclusions have been reached by other workers who have studied the enrichment of DBK resulting from its photolysis on silica.²³

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.

Time Resolved Investigations of Organic Molecules Adsorbed on Silica

The technique of time resolved diffuse reflectance absorption spectroscopy allows,²⁶ in principle, the direct observation of transients that are photochemically produced from organic molecules adsorbed on silica. This method nicely complements the emission method²⁷ that has been very profitably employed to investigate photophysical processes on silica. We describe briefly here two types of systems that have been investigated by the diffuse reflectance technique: the Type II reaction of aryl alkyl ketones²⁸ and the triplet energy transfer between benzophenone and naphthalene.²⁹

Figure 10 shows the diffuse reflectance transient absorption spectra produced upon pulsed laser excitation of acetophenone, valerophenone and diphenylbutyrophenone adsorbed on 255 Å pore silica.²⁸ From quenching experiments and comparison of the observed spectra with standards, it was concluded that the transients, whose non-exponential decay is of the order of microseconds, are the triplet states of the ketones, and not the biradicals (in the case of valerophenone and the butyrophenone). This result contrasts sharply with results in solution for which only the biradicals are observed by nanosecond laser spectroscopy because the ketones persist for only nanoseconds.³⁰ In effect, adsorption on silica has changed the rate determining kinetics from hydrogen abstraction (in solution) to conformational dynamics (on silica). Evidently, conformational restrictions dramatically increase the lifetime of the triplet state, but not on the lifetime of the biradical (which is relatively long-lived in solution). The results are selfconsistent; however, since only one conformation is appropriate for the hydrogen abstraction process, whereas many conformations may allow intersystem crossing in the triplet biradical, which,

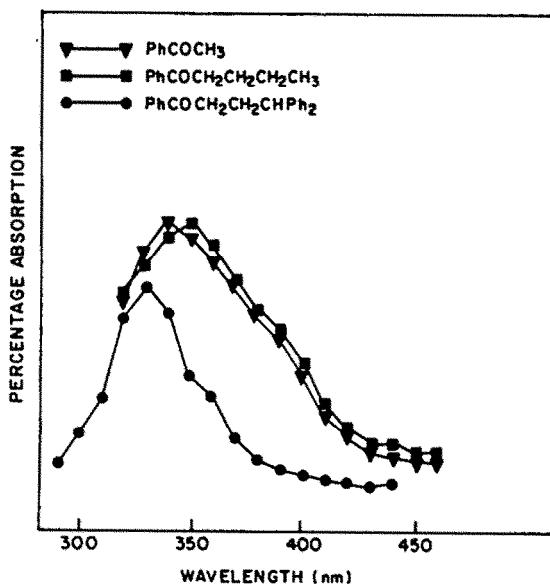


Figure 10. Transient absorption spectra obtained from laser excitation of several ketones adsorbed on silica.

upon undergoing intersystem crossing to the singlet undergoes rapid reaction. The same conformational restrictions that slow down the achievement of the correct geometry for hydrogen abstraction may prevent the biradical from achieving conformations in which it is less reactive and therefore more stable. An interesting spinoff of the quenching studies was the observation that oxygen is much less efficient than 1,3-butadiene as quencher of ketone triplets although both quenchers are comparably efficient in solution. The exact mechanistic basis for this difference in quenching behavior is not known, but it is clear that the processes that control quenching in solution and on silica are different.

Figure 11 shows the transient absorption produced by pulsed laser excitation of benzophenone on silica in the presence and in the absence of naphthalene.²⁹ Figure 12 shows the behavior of the decay of benzophenone triplet as a function of added naphthalene, and Figure 13 shows the behavior of the decay of benzophenone as a function of added 1-methoxynaphthylene. In both cases a considerable amount of static quenching is observed. However, in the case of naphthalene as a quencher, this is a component of dynamic quenching, whereas in the case of 1-methoxynaphthalene only static quenching is observed. Although the exact mechanistic basis for the observed difference is not known, it is clear as it was from the above described study, that dynamic processes can be strongly affected by variation of silica parameters. Further studies are necessary to understand the influence of pore sizes on the quenching processes. Mixes of dynamic and static quenching have been noted in other investigation of quenching on silica surfaces.²⁷

Conclusions

The photochemical reaction of ketones adsorbed on silica display a number of effects that are different from those observed in a solution phase of comparable chemical

composition, e.g., alcohols. The differences are interpreted to result from the nature of the silica surface which causes interface effects and from the porous structure of the surface which provides geometrical effects. The interface effects may be broken down into site effects (free silanols *versus* active silanols) and viscosity effects. The former is responsible for the variation of surface activity and its associated effects on rotational and translational motion as a function of coverage (at coverages well below a monolayer), and the latter is responsible for temperature effects on translational and rotational motion. The geometric effects of pore size are only apparent for small pore sizes of relatively low dispersion. The silica surface provides the photochemist with an anisotropic medium (hydroxys on the surface side, a gas or vacuum on the other side), which can serve as an environment for the investigation of unusual photoprocesses (unusual product distributions, magnetic field effects, magnetic isotope effects, enhanced lifetimes of reactive intermediates, etc.) which result from the anisotropic nature of silica surfaces. In the future, studies of the effects of additives on photoreactions in small pore silicas and the development of quantitative models that relate relative rates and product distributions to the nature and geometry of the small pores are in order.

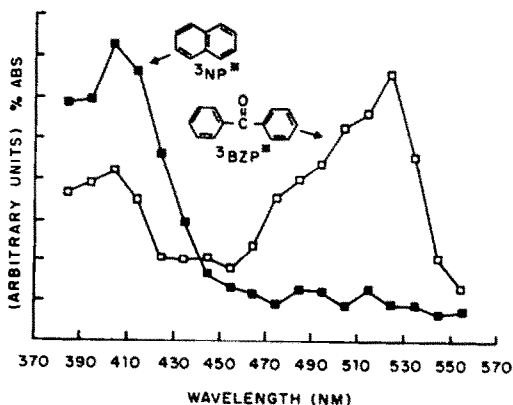


Figure 11. Transient absorption spectra obtained from irradiation of benzophenone on 95Å silica at 400 ns after a laser pulse (open squares). Transient absorption spectrum obtained from irradiation of benzophenone and naphthalene on 95Å silica 5 micro-sec after the pulse (closed squares).

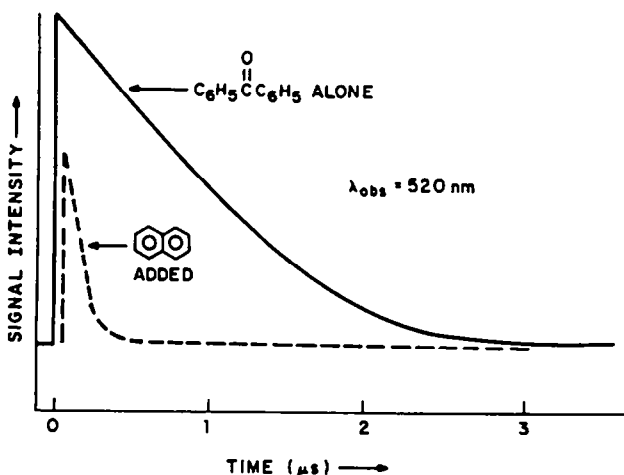


Figure 12. Plot of the benzophenone triplet decay rate in the presence and absence of naphthalene. Note that the decay consists of a static component (decrease in the intensity at zero time) and of a dynamic component (decrease in the rate of decay in the presence of naphthalene relative to the decay in the absence of naphthalene).

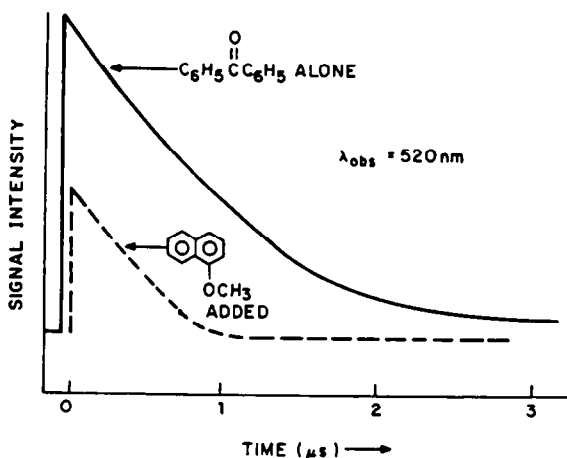


Figure 13. Plot of the benzophenone triplet decay rate in the presence and absence of 1-methoxynaphthalene. Note that the decay consists entirely of a static component (decrease in the intensity at zero time with no change in the rate of decay in the presence or absence of 1-methoxynaphthalene).

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the diffuse reflectance laser flash photolysis apparatus. They are thanked for their outstanding intellectual and experimental contributions to the original research reported in this paper. The support of this research was generously provided by the Air Force Office of Scientific Research, by the National Science Foundation and by the IBM Corporation.

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