Surface photochemistry of alkyl aryl ketones: energy transfer and the effect of a silica-gel surface on electronic states of excited molecules

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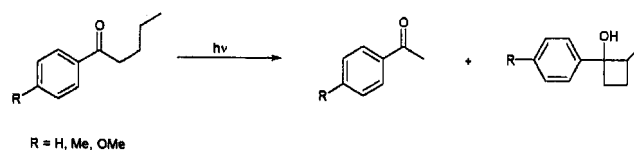Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184-8501, Japan

ABSTRACT: Alkyl aryl ketones undergo Type II photoreaction both on a silica-gel surface and in solution. The amount of acetophenone produced from valerophenone increases linearly with increase in the amount of valerophenone loaded at coverage below *ca* 60%. The effect of the alkyl chain length on the Type II photoreactivity of alkyl phenyl ketones on the surface is weak. The relative quantum yields Φ_{MeAP}/Φ_{AP} and Φ_{MeOAP}/Φ_{AP} on the surface are lower than those in benzene containing 0.5 M pyridine. A silica-gel surface provides a polar reaction medium that makes the energy difference between the lowest n,π* and the upper π,π* triplet states small and may cause the inversion of the nearby n,π* and π,π* triplet states. The filter effect is trivial in surface photochemistry when all loaded molecules are in the monomolecular layer. The energy transfer processes are observed in the valerophenone–*p*-methylvalerophenone and valerophenone–*p*-methoxyvalenophonone systems in which the internal filter effects are so strong that the energy transfer processes cannot be observed directly in solution. Although the Stern–Volmer quenching kinetics would be applicable to the photoreaction on the surface, a correction for the probability of excitation of a molecule should be made. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: surface photochemistry; Type II reaction; alkyl aryl ketones; silica gel; Stern–Volmer quenching kinetics; energy transfer

INTRODUCTION

Photochemical processes of organic molecules have been widely studied and a growing understanding of the underlying mechanisms has greatly stimulated developments in organic photochemistry. Although the synthetic value of photoreactions is now well recognized,[1] selectivity in the reactions is still an important problem in synthetic and industrial chemistry. Recently, photochemical interest has been focused on the behavior of molecules in a crystalline state[2] and on a solid surface.[3–6] Non-reactive solid surfaces, such as silica gel or alumina, provide an ordered two-dimensional environment for effecting and controlling chemical reactivity as a function of the polarity or molecular associations enhanced or inhibited by the microscopic surface.[4] The conformation of organic molecules may be distorted and conformational flexibility may be restricted by adsorption on the surface.[7,8] Although the types of most

photoreactions observed on the surface are fundamentally the same as those seen in solution,[9] large differences in product distributions have been observed in some cases[8,10] and a few examples of novel photoreactions unique to the non-homogeneous environment have been reported.[11–14] However, a general rule for the prediction of novel photoreactions has not been established because the origin of the novel photoreactivity has not yet been completely clarified. There must be more than one factor involved in the origin, and some might govern the behavior of excited molecules[11–14] whereas others might control the activity of intermediates.[12,13] The photochemistry of alkyl aryl ketones in solution has been widely studied and is now well understood.[15] Thus, the Type II photoreaction of the ketones has been used as a surface probe. We report here the effect of the polarity of a silica-gel surface causing a change in the property of the lowest excited state of adsorbed ketone molecules and the energy transfer between the ketones.

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R = H, Me, OMe

RESULTS AND DISCUSSION

Dependence of molecular coverage on the extent of acetophenone formation from the Type II photoreaction of valerophenone

Valerophenone (VP) undergoes a Norrish Type II reaction to give acetophenone (AP) and 2-methyl-1-phenylcyclobutanols in solution[16] and on a dry silica-gel surface.[9d,10g] The molecular coverage of the surface is an important factor for surface photoreactions because the character of the reaction environment should change dramatically at 100% coverage. Monolayer coverage has been determined from the Langmuir adsorption isotherm[10abe,13] or by calculation based on the surface area of silica gel used and the area occupied by one molecule estimated from space-filling models.[9c,10be,12–14] A photoreaction on the surface can also be used for the determination of monolayer coverage.[12,14] The values of the coverage obtained from these different methods generally show good agreement.[10be,12,13] Thus, the monolayer coverage of VP was determined from its Type II reaction on the surface.

Figure 1 shows the relationship between the amount of VP loaded on 1 g of silica gel and the amount of AP formed from the Type II reaction of VP under the same irradiation conditions. The amount of AP initially increased with increase in the amount of VP loaded and then levelled off to a constant value. The coverage must be 100% when 5.7×10^{-4} mol of VP was loaded on 1 g of the silica gel. When multiple layers are formed on the surface, the VP molecules in the outermost layer should be responsible for the photoreaction. The filter effect should be trivial when all loaded VP molecules are in the monomolecular layer. The surface area of the silica gel used is 477 m^2g^{-1}, so that the area occupied by one VP molecule is 1.4×10^{-18} m^2. This value was in accord with that obtained from calculation on the basis of a space-filling model (1.4×10^{-18} m^2).
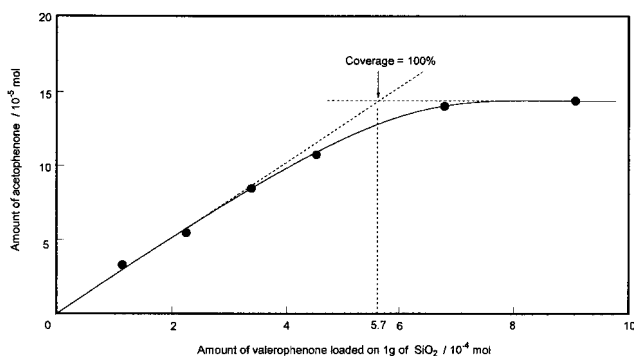
Figure 1. Dependence of the extent of acetophenone formation on amount loaded in the surface photoreaction of valerophenone
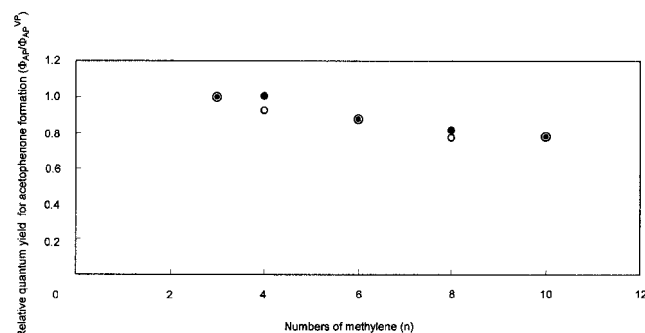
Figure 2. Relative quantum yields for production of acetophenone from alkyl phenyl ketones PhCO(CH$_2$)$_n$CH$_3$ in benzene containing 0.5 M pyridine (○) and on a silica-gel surface (●)

Conformational flexibility of alkyl phenyl ketones on a silica-gel surface

Conformational flexibility is an important factor for determining the photoreactivity of alkyl phenyl ketones in solution[17] and may be a critical factor for molecules adsorbed on the surface.[8] The relative quantum yields for AP production from the Type II reaction of caprophenone (CP), octanophenone (OP), decanophenone (DP) and laurophenone (LP) with respect to that of VP (Φ_{AP}/Φ_{AP}^{VP}) were determined in order to clarify the effect of the alkyl chain length on the Type II photoreactivity of the alkyl phenyl ketones on the surface. The results are shown in Fig. 2. The relative quantum yields on the surface were similar to those in benzene containing 0.5 M pyridine. A Lewis base such as pyridine is known to maximize the Type II quantum yield by suppressing reverse hydrogen transfer in the 1,4-biradical intermediate, thus ensuring that product ratios are actually equal to the ratios of the reaction rates from the triplet states.[16b] As the absorption coefficients of the alkyl phenyl ketones were nearly equal to each other and within an experimental error both in benzene ($\epsilon_{313} = 50$–53) and in methanol ($\epsilon_{313} = 73$–76), the ratios of the relative quantum yields on the surface should be equal to the ratios of the reaction rates from their triplet states as in solution. Reverse hydrogen transfer is prevented on the surface as well as in benzene containing pyridine. The surface provides a strong polar reaction medium. Leermakers *et al.* reported that silica gel approximates to methanol on the Kosower Z scale.[18] Despite the surface having strong polarity, the effect of the alkyl chain length on the Type II photoreactivity of the alkyl phenyl ketones on the surface is weak and is nearly the same as that in solution.

Effect of the surface on photoreactivity of *para*-substituted phenyl alkyl ketones

The photoreactivity of *para*-substituted phenyl alkyl

ketones depends on the properties of their lowest excited states. Ketones having the lowest n,π^* state undergo the Type II photoreaction with moderate to high quantum efficiency, whereas ketones having the lowest π,π^* state undergo the reaction with low efficiency. The Type II quantum yield of the ketones in which the energy gap between the lowest n,π^* and the upper π,π^* triplet state is small in non-polar solvents depends on the solvent polarity because the polarity affects the energy level of the triplet states. Polar solvents may produce an inversion of the n,π^* and π,π^* triplet state because the π,π^* state is more polar and the n,π^* state less polar than the ground state in terms of changes in dipole moment.[19a] Since a silica-gel surface provides a strong polar environment, the surface should cause changes in the properties of the lowest excited state.[10a] The deviation of the photoreactivity of organic compounds on the surface from that in solution may be responsible for the change in the properties of the lowest excited state. Hence the photoreactivity of *para*-substituted phenyl alkyl ketones was studied.

Valerophenone, *p*-methylvalerophenone (MeVP) and *p*-methoxyvalerophenone (MeOVP) underwent the Type II photoreaction to give the corresponding acetophenone both in solution[19] and on a silica-gel surface. The quantum yield for the formation of *p*-methylacetophenone (MeAP) from MeVP in benzene containing 0.5 M pyridine was equal to that for AP formation from VP ($\Phi_{MeAP}/\Phi_{AP} = 1$). However, the Φ_{MeAP}/Φ_{AP} values for the photoreaction in methanol and on the surface were less than unity (Table 1). On the other hand, the quantum yield for the formation of *p*-methoxyacetophenone (MeOAP) from MeOVP was lower than that for AP from VP even in benzene containing 0.5 M pyridine. The Φ_{MeOAP}/Φ_{AP} value was only 0.2. The low photoreactivity of MeOVP is responsible to the π,π^* character of its lowest excited state. The Φ_{MeOAP}/Φ_{AP} values for photoreactions in methanol and on the surface were low (Table 1). These results can be reasonably explained in terms of the polar medium effect. The character of the lowest triplet state of MeVP should change from n,π^* to π,π^* when the solvent is changed from benzene to methanol. The Type II photoreaction should occur from
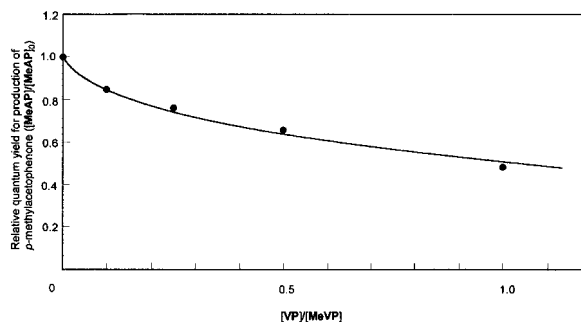
Table 1. Relative quantum yields for acetophenone formation

Conditions	Φ_{MeAP}/Φ_{AP}	Φ_{MeOAP}/Φ_{AP}
In benzene containing 0.5 M pyridine[a]	1.0[c]	0.2
In methanol[a]	0.5	0.004
On the silica-gel surface[b]	0.5	0.003

[a] The solution contained 0.05 mol dm^{-3} of VP, MeVP, or MeOVP.
[b] The amount of VP, MeVP or MeOVP loaded on silica gel was 1.64×10^{-4} mol (1g of SiO$_2$)$^{-1}$ (coverage *ca* 25%).
[c] The quantum yield for disappearance of VP was unity and formation of AP (Φ_{AP}) was 0.85 in benzene containing a Lewis base.[19b]

Figure 3. Effect of added valerophenone (VP) on relative quantum yields for formation of MeAP from 0.05 M MeVP in benzene containing 0.5 M pyridine. The curved line was obtained from the equation [MeAP]/[MeAP]$_0$ = ε_{MeVP}/(ε_{MeVP} + ε_{VP}[VP]/[MeVP]), where [MeAP]$_0$ = 1.63, ε_{VP} = 51 and ε_{MeVP} = 72

its upper n,π^* triplet state.[20] As the polarity of the silica-gel surface is fairly high, the energy difference of the two triplet states becomes large and the contribution of the photoreactive upper triplet state in excited molecules becomes low on the surface.

Energy transfer between ketones on a silica-gel surface

The change in the energy level might affect the rate of the bimolecular energy transfer. If two kinds of photoreactive ketones co-exist in solution and absorb the same irradiation line, each of the ketones acts as an internal filter for the photoreaction of the other.[16b,21] Figure 3 shows the internal filter effect of VP on the production of MeAP from MeVP. The experimental results fit the curve obtained from calculation assuming the internal filtering by VP. The internal filter effect may be trivial in surface photochemistry when all loaded molecules are in the monomolecular layer, and the process of energy transfer
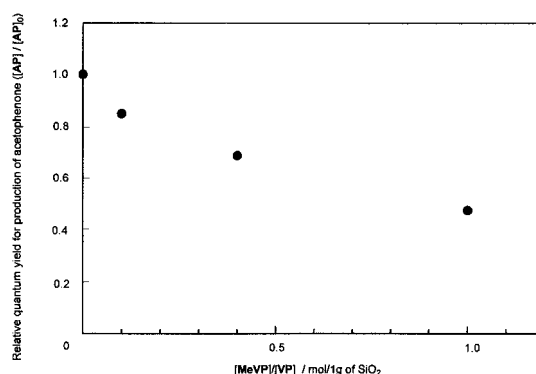
Figure 4. Relative quantum yields for production of acetophenone in the Type II reaction of VP on a silica-gel surface in the presence of MeVP. In all runs 1.64×10^{-4} mol of VP were loaded on 1 g of silica gel. The surface coverage of VP is *ca* 25%
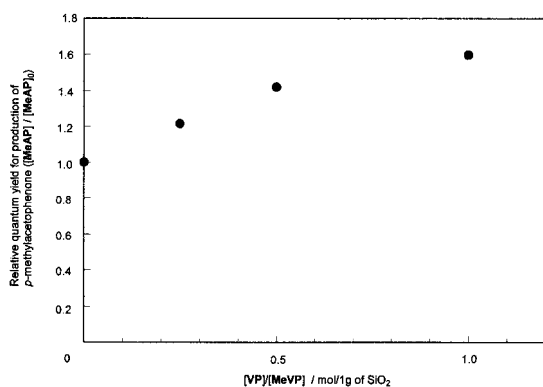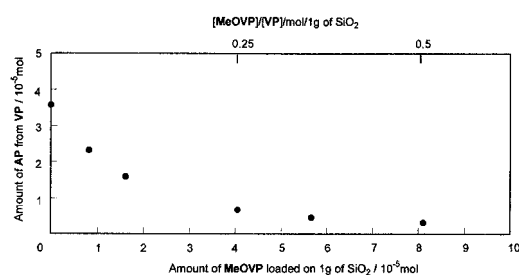
Figure 5. Relative quantum yields for production of MeAP in the Type II reaction of MeVP on a silica-gel surface in the presence of VP. In all runs 1.64×10^{-4} mol of MeVP were loaded on 1 g of silica gel. The surface coverage of MeVP is *ca* 25%

may be observable because of separation from the internal filtering even in the case where the internal filter effect is so strong that the energy transfer process cannot be observed directly in solution photochemistry.
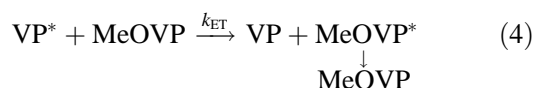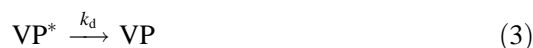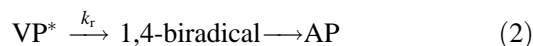
A constant amount of VP and an appropriate amount of MeVP were loaded on 1 g of silica gel and irradiated. The amount of AP from the Type II reaction of VP decreased with increase in MeVP added (Fig. 4). On the other hand, when a mixture of a constant amount of MeVP and an appropriate amount of VP on the surface was irradiated, the amount of MeAP produced from the Type II reaction of MeVP increased with increase in VP (Fig. 5). These results provide strong evidence for energy transfer from VP to MeVP on the surface. The triplet energies of VP and MeVP in an ethanol matrix are measured to be 74.5 and 73 kcal mol^{-1}, respectively[19a] (1 kcal = 4.184 kJ). The triplet energy of VP should be higher than that of MeVP on a polar silica-gel surface.

When a mixture of a constant amount of VP and an appropriate amount of MeOVP on the surface was irradiated, the amount of AP produced from VP decreased with increase in MeOVP (Fig. 6). As the photoreactivity of MeOVP is fairly low, as shown in

Table 1, and its photoreaction is negligible compared with that of VP, the following simple scheme for the photoreaction of VP can be written;

$$VP \xrightarrow{h\nu} VP^* \qquad (1)$$

$$VP^* \xrightarrow{k_r} \text{1,4-biradical} \longrightarrow AP \qquad (2)$$

$$VP^* \xrightarrow{k_d} VP \qquad (3)$$

$$VP^* + MeOVP \xrightarrow{k_{ET}} VP + MeOVP^* \qquad (4)$$
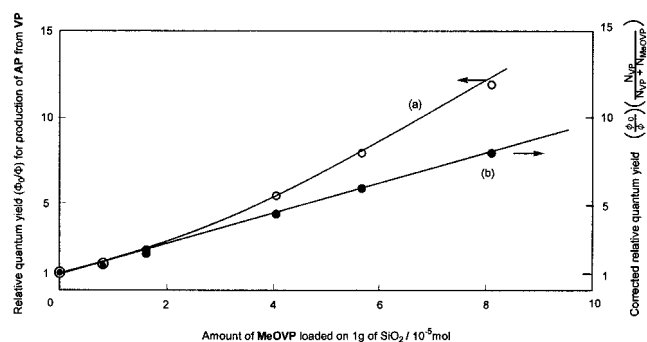$$\downarrow$$
$$MeOVP$$

An equation similar to the Stern–Volmer equation can be obtained by applying the steady-state approximation to the scheme:

$$\frac{\phi_0}{\phi} = 1 + \frac{k_{ET}}{k_r + k_d} [MeOVP] \qquad (5)$$

The concentration of MeOVP may be defined as the amount of MeOVP on a unit square[22] or a 1 g of silica gel.[22,23] The two definitions are convertible. Hence the definition based on the amount on 1 g of silica gel was adopted to analyze of the effect of MeOVP on the photoreactivity of VP.

The relationship between the relative quantum yield (ϕ_0/ϕ) and the amount of MeOVP on 1 g of silica gel is shown in Fig. 7 [line (a)]. The gradient of line (a) increases from its initial value. Hence the linear relationship expected from Eqn. (5) could not be observed. Most VP molecules are in the monomolecular layer at less than 100% coverage and the amount of AP produced from VP increases linearly with increase in the amount of VP loaded on the silica gel and reaches a constant value as shown in Fig. 1. The molecular length of MeOVP is nearly the same as that of VP, so the coverage must be less than 40% under the experimental conditions and

Figure 6. Relationship between the amount of AP from the Type II reaction of VP on a silica-gel surface and the amount of co-present MeOVP. In all runs 1.64×10^{-4} mol of VP were loaded on 1 g of silica gel. The surface coverage of VP is *ca* 25%

Figure 7. Dependence of relative quantum yields for production of AP from the Type II reaction of VP (○) and its corrected from (●) on the amount of co-adsorbed MeOVP. In all runs 1.64×10^{-4} mol of VP were loaded on 1 g of silica gel. The surface coverage of VP is *ca* 25%

multiple layers must not be formed. Molecules in the monomolecular layer would be expected not to act as a filter for each other. Therefore, the filtering effect should not be responsible for lowering the photoreactivity of VP.

Similar upward curves have been observed in the Stern–Volmer plots of the fluorescence quenching of pyrene adsorbed on silica gel by 2-bromonaphthalene.[23] Upward curvature of the Stern–Volmer plots seems to be essential in surface photochemistry. There must be a process other than normal quenching and it lowers the photoreactivity of molecules on the surface by quencher molecules. There may be fewer strong-binding sites available for the quencher at a high concentration. This may result in an increase in quenching rate as implied by the upward curvature of the Stern–Volmer plot.[23]

However, the upward tendency is observed even at low quencher concentration as in Fig. 7. There seems to be a factor involved other than the availability of strong-binding sites. The probability of excitation of molecules on a surface would be different from that in solution. Silica gel particles may be regarded as impenetrable spheres. When VP molecules on a hemisphere are irradiated, the molecules on the other hemisphere should be in the dark. Then, the probability of excitation of a molecule should be proportional to the probability of occupying a special site where the molecule absorbs light. If the molecular lengths and strength of adsorption of molecules are nearly the same, the probability should be defined as the ratio of the numbers of molecules under consideration to the whole numbers of molecules presented. The following equation can be written for the VP–MeOVP system:

$$\frac{\phi_0}{\phi} = \left(\frac{N_{\mathrm{VP}} + N_{\mathrm{MeOVP}}}{N_{\mathrm{VP}}}\right)\left(1 + \frac{k_{\mathrm{ET}}}{k_{\mathrm{r}} + k_{\mathrm{d}}}[\mathrm{MeOVP}]\right) \quad (6)$$

where N_{VP} and N_{MeOVP} are the numbers of VP and MeOVP molecules, respectively.

When the corrected relative quantum yields [$N_{\mathrm{VP}}/(N_{\mathrm{VP}} + N_{\mathrm{MeOVP}})$] ($\phi_0/\phi$) were plotted against the amount of MeOVP on 1 g of silica gel, a linear relationship was observed [line (b) in Fig. 7]. The slope of line (b) was 8.53×10^4 [mol (1g of SiO$_2$)$^{-1}$]$^{-1}$. This result strongly indicates that a correction for the probability of excitation is needed for the Stern–Volmer equation for surface photoreactions.

CONCLUSION

A silica gel surface provides a polar reaction medium that makes the energy difference between the lowest n,π^* and the upper π,π^* triplet states small and may cause the inversion of the nearby n,π^* and π,π^* triplet states. The surface may bring about new reactions that are not

observed in solution because of the inversion. The internal filter effect is trivial in surface photochemistry when all loaded molecules are in the monomolecular layer, and the process of energy transfer is observable even in the case when the internal filter effect is so strong that the energy transfer process cannot be observed directly in solution photochemistry. Although the Stern–Volmer quenching kinetics would be applicable to the photoreaction on the surface, a correction for the probability of excitation of a molecule should be made.

EXPERIMENTAL

Silica gel (Merck Kieselgel 60, Art. 7734) was used as received. Benzene was washed with sulfuric acid and then water, dried and fractionally distilled over phosphorus pentoxide. Pyridine was dried over potassium hydroxide and then fractionally distilled. Alkyl aryl ketones were prepared by Friedel–Crafts acylation according to the method given in the literature.[24] A Taika 100 W high-pressure mercury lamp was used as an irradiation source. A potassium chromate filter solution was used for isolation of the 313 nm line.[25] Gas–liquid chromatographic (GLC) analysis was performed with a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector which was connected to a Shimadzu C-R6A Chromatopac integrator, using a 2 m column containing 15% propylene glycol succinate on Uniport B. Hexadecane was used as a calibrant for the GLC analysis.

Photolysis of VP on silica gel at different coverages. A 1 g amount of silica gel and 5 cm^3 of dichloromethane containing appropriate amounts of VP were placed in a 50 cm^3 round-bottomed flask. The mixture was sonicated for 5 min and then the solvent was evaporated under reduced pressure. The coated silica gel was placed in an 18 × 180 mm Pyrex culture tube. The tubes were rotated and irradiated with 313 nm radiation from a 100 W high-pressure mercury lamp. After the irradiation, 4 cm^3 of acetone containing a known amount of hexadecane as a calibrant were added and the mixture was sonicated for 10 min. The supernatant solutions were analyzed to determine the amounts of AP. The results are shown in Fig. 1.

General procedure for determination of relative quantum yields for formation of AP from alkyl phenyl ketones in benzene containing 0.5 M pyridine. Benzene containing 0.5 mol dm^{-3} pyridine solutions of a mixture of *ca* 0.05 mol dm^{-3} of an alkyl phenyl ketone (VP, CP, OP, DP or LP) and a known concentration of hexadecane (*ca* 0.0025 mol dm^{-3}) as a calibrant were placed in 15 × 150 mm Pyrex culture tubes. The tubes were degassed by three freeze–pump–thaw cycles and then sealed. Irradiation with 313 nm radiation was

performed on a 'merry-go-round' apparatus with an Ushio 450 W high-pressure mercury lamp. The amounts of AP formed were determined from the results of GLC analyses. The relative quantum yields are shown in Fig. 2.

General procedure for determination of relative quantum yields for production of AP from alkyl phenyl ketones on a silica-gel surface. After 5.0×10^{-5} mol of an alkyl phenyl ketone (the surface coverage for LP is *ca* 25%) had been loaded on 1.0 g of silica gel and irradiated at 313 nm, the amount of AP was determined as described in the procedure for the photolysis of VP on silica gel at different coverages. The relative quantum yields for the formation of AP from alkyl phenyl ketones are shown in Fig. 2 together with those in solution. In the case of the determination of the relative quantum yields for the formation of acetophenones from *para*-substituted alkyl phenyl ketones, 1.64×10^{-4} mol of the ketones were loaded on 1.0 g of silica gel. The relative quantum yields are shown in Table 1.

General procedure for determination of relative quantum yields for production of Type II cleavage product from alkyl aryl ketones on a silica gel surface in the presence of the second ketone. After a mixture of 1.64×10^{-4} mol of VP or MeVP and an appropriate amount of the second ketone (MeVP or MeOVP for VP, VP for MeVP) had been loaded on 1.0 g of silica gel and irradiated at 313 nm, the amount of AP or MeAP was determined as described in the procedure for the photolysis of VP on silica gel at different coverages. The relative quantum yields for the formation of AP or MeAP from VP or MeVP with respect to the ratio of VP or MeVP to the second ketone, respectively, are shown in Figs. 4–7.

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