# Surface Photochemistry: Radical Pair Combination on a Silica Gel Surface and in Micelles

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*Summary* Photolysis of a benzyl phenylacetate and a dibenzyl ketone generates a radical pair, singlet and triplet respectively, which has been used to demonstrate both a cage effect and translational motion, intra- and/or inter-particulate, on a silica gel surface.

VIRTUALLY all photochemical experimentation from the beginning of the century up to the present has involved the use of homogeneous solutions or the gas phase with, recently, minor incursions into the crystalline state. We have become interested in the photochemistry of adsorbed molecules, and have shown that limited translational movement may precede recombination in a singlet radical pair (Photo–Fries rearrangement) generated on dry silica gel, *i.e.*, that a quasi-cage effect was operative.[1] We now report the observation of a much greater degree of translational movement in radical pairs on silica gel; for comparison, the results obtained with the same substrates in micelles are described.

$p$-$MeOC_6H_4CH_2C(:O)OCH_2C_6H_4Me$-$p$

**(1)**

$p$-$R^1C_6H_4[CH_2]_2C_6H_4R^2$-$p$

**(2)** **a**; $R^1 = R^2 = Me$
**b**; $R^1 = Me, R^2 = OMe$
**c**; $R^1 = R^2 = OMe$

$p$-$MeOC_6H_4CH_2C(:O)CH_2C_6H_4Me$-$p$

**(3)**

The photolysis in solution of the ester (**1**) has been studied extensively by Givens;[2] carbon dioxide is eliminated, and the bibenzyls (**2a**—**c**) are obtained with a distribution ranging from 1:2·5:1 (statistical = 1:**2**:1) in dioxan ($\eta$ = 1·087 × $10^{-3}$ N s m$^{-2}$) to 1:5·07:1 in isopropyl alcohol ($\eta$ = 1·765 × $10^{-3}$ N s m$^{-2}$), a marked cage effect being noted in the solvents of higher viscosity. We have found that photolysis in potassium dodecanoate micelles (0·08 M) led to a sharp increase in the formation of (**2b**) derived from geminate pair combination (Table 1); at 0·76 mM (**1**) ($\bar{N}$ = 0·64) 97% of the bibenzyl mixture is (**2b**). Evidently a micelle, in localising the radical pair until reaction occurs, is acting as a super-cage, a fact to which attention has now been drawn.†

TABLE 1. Photolysis of ester (**1**) and ketone (**3**) in 0·08 M potassium dodecanoate micelles.[a]

| | | Bibenzyl ratio[b] | | |
|---|---|---|---|---|
| | Conc./mM | (**2a**) | (**2b**) | (**2c**) |
| (**1**) | 0·76 | 1·0 | 72 | 1·1 |
| | 1·21 | 1·4 | 44 | 1·0 |
| | 1·51 | 1·0 | 31 | 1·0 |
| | 2·02 | 1·2 | 26 | 1·0 |
| | 2·52 | 1·0 | 23 | 1·4 |
| | 3·00 | 1·1 | 15 | 1·0 |
| (**3**) | 0·60 | 1·4 | 14 | 1·0 |
| | 0·83 | 1·2 | 7·5 | 1·0 |
| | 1·01[c] | 1·0 | 6·4 | 1·2 |
| | 1·01[d] | 1·0 | 48 | 1·0 |

[a] Micelle solutions of (**1**) and (**3**) were nitrogen-purged and irradiated at 254 nm. [b] From v.p.c. analysis at *ca.* 50% conversion, based on recovered ester and ketone. [c] $\bar{N}$ = 0·85. [d] 0·16 M surfactant; $\bar{N}$ = 0·35.

Photolysis of (**1**) on dry silica gel gave the results indicated in Table 2. At 10% monolayer coverage‡ the distribution of bibenzyls resembles that found in isopropyl alcohol solution. It is not increased at 50% coverage, indicating that molecules of (**1**) are not interfering with translational movements. Lowering the temperature does decrease such motion and at −50 ± 5 °C (**2b**) represents *ca.* 95% of the bibenzyls.

TABLE 2. Photolysis of ester (**1**) and ketone (**3**) on dry silica gel.[a]

| | | | Bibenzyl ratio[b] | | |
|---|---|---|---|---|---|
| | Coverage/% | T/°C | (**2a**) | (**2b**) | (**2c**) |
| (**1**) | 1 | 20 | 1·0 | 6·1 | 1·0 |
| | 10 | 20 | 1·4 | 5·5 | 1·0 |
| | 50 | 20 | 1·0 | 4·1 | 1·1 |
| | 10 | −50 | | >96% | |
| (**3**) | 1 | 20 | 1·2 | 3·7 | 1·0 |
| | 10 | 20 | 1·0 | 3·2 | 1·0 |
| | 50 | 20 | 1·0 | 3·1 | 1·0 |
| | 2 | −50 | 1·2 | 9·0 | 1·0 |
| | 10 | −50 | 1·0 | 6·3 | 1·0 |
| | 50 | −50 | 1·0 | 6·2 | 1·0 |
| | 10 | −165 | trace | >95% | trace |

[a] Silica gel (35—70 mesh) was heated to 200 °C (0·03 mmHg) for at least 5 h immediately before use. Samples were degassed to <$10^{-5}$ mm Hg and irradiated either *in vacuo* (20 °C experiments) or under nitrogen (low temperature experiments) at 254 nm (ester, 20 °C) or >220 nm (ketone; ester, −50 °C). Sample mixing was accomplished by rotation of the sample tube. [b] V.p.c. analysis.

Photolysis of ketone (3) in isopropyl alcohol gave a product distribution of 1:2:1, in contrast with that obtained with (**1**). In micelles (Table 1), as with the ester, *ca.* 96% of (**2b**) could be obtained, again indicating a strong localising influence. On dry silica gel at from 1 to 50% coverage (Table 2) a distribution resulted which was closer to statistical than that obtained from the ester. At these coverages the mean separation of molecular centres is from *ca.* 130 to *ca.* 20 Å. Cooling to −50 °C gave a ratio of 1:*ca.* 6:1 indicating less restriction than with (**1**).

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† After this portion of the work was completed, Turro reported the first of his extensive micellar studies of dibenzyl ketone photolysis (N. J. Turro and W. R. Cherry, *J. Am. Chem. Soc.*, 1978, **100**, 7431; N. J. Turro, B. Kraeutler, and D. R. Anderson, *ibid.*, **1979**, **101, 7435**).

‡ Determined from a Langmuir isotherm and by calculation.

Further lowering to −165 °C§ gave >95% of (**2b**), a ratio comparable with that obtained with (**1**) at the higher temperature.

The above leads to the conclusion that on the surface of silica gel translational motion, intra- and/or inter-particulate, competes more effectively with recombination in (**3**) than (**1**). The radicals formed from (**1**) and (**3**) are the same; only the distance between the radical centres and their multiplicities differ. A radical pair formed with greater separation, as in (**1**), should have more opportunity to diffuse apart. The opposite is observed so we favour an explanation based on multiplicity. The decomposition of (**3**) is established as being *via* a triplet;[3] that for (**1**) is not known, but related esters[4] are believed to follow a singlet pathway. The change in ratio from 1:5:1 for (**1**) to 1:2:1 for (**3**) in solution in isopropyl alcohol with the formation of the same radicals in the same solvent must, similarly, involve a difference in spin multiplicity; namely, the singlet radical pair recombines faster than does the triplet pair. The "cage" properties of the silica gel surface are indicated by the increase in the non-statistical distribution of products from both (**1**) and (**3**) with lowered temperature. In the "supercage" micelles the effect of multiplicity is much smaller.

The similar distribution of products with both low and high coverage (1—50%) from (**1**) and (**3**) suggests that the environment of the once-formed radicals is much the same at these coverages, *i.e.*, that for this system, and over this coverage range at room temperature, all sites of attachment are effectively equal. This conclusion differs from that drawn in a study of the decomposition of azocumene on silica gel.[5]

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§ At this temperature on the time-scale of the experiment the ketone itself is presumably translationally immobile; the derived radicals may also be so, but on warming become mobile between this temperature and −50 °C when the product distribution requires movement.

[1] D. Avnir, P. de Mayo, and I. Ono, *J. Chem. Soc., Chem. Commun.*, 1978, 1109.
[2] R. S. Givens and W. F. Oettle, *J. Org. Chem.*, 1972, **37**, 4325.
[3] P. S. Engel, *J. Am. Chem. Soc.*, 1970, **92**, 6074.
[4] B. Matuszewski, R. S. Givens, and C. Neywick, *J. Am. Chem. Soc.*, 1973, **95**, 595; R. S. Givens, personal communication.
[5] J. E. Leffler and J. J. Zupancic, *J. Am. Chem. Soc.*, 1980, **102**, 259.