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# PHOTOCHEMISTRY OF 1,2-DIPHENYL-2,2-DIMETHYL-PROPANONE-1 IN MICELLAR SOLUTIONS. CAGE EFFECTS, ISOTOPE EFFECTS AND MAGNETIC FIELD EFFECTS.

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The cage reaction resulting from photolysis of $PhCOC(CH_3)_2Ph$ and $PhCOC(CD_3)_2Ph$ in micellar solution is shown to be subject to substantial magnetic field and magnetic isotope effects.

## Introduction

Photolysis of 1,2-diphenyl-2,2-dimethyl-propanone-1[1] 1 in benzene solution[2] results in the formation of products expected from free radicals produced by escape of PhCO and $C(CH_3)_2Ph$ radicals from the primary solvent cage. We report here an investigation of the photolysis of 1 in micellar solution with the goal of comparing "cage effects" for homogeneous organic solvents with those in micellar solution.

## Chemical products and quantum yield measurements

Table 1 summarizes the products formed when 1 is photolyzed under various conditions and Scheme 1 presents a proposed mechanism to explain the observed products. In homogeneous organic solvents ($C_6H_6$, $CH_3CN$, $CH_2Cl_2$), the following products have been reported[2] and have been observed in this work: 3 (∿4%), 4 (∿15%), 5 (∿19%), 7 (∿8%) and traces of 6. The quantum yields for disappearance of 1 is ∿0.9 in organic solvents.

In micellar solution (Table 1) the major products of photolysis are 3 (∿23%) and 4 (∿23%). Trace amounts of 5 and 6 were detectable by vpc analysis. However, 7 could not be detected, even in trace amounts. The quantum yields for disappearance of 1 in ionic micellar solution are high (∿0.7), but somewhat lower than the values for homogeneous organic solvents ($\gtrsim$0.9).

The following aspects of our results in cationic micelles such as HDTCl micellar solution are noteworthy: (1) the yields of 3 and 4 are experimentally identical and (2) the yields of 5 and 6 (important products in organic homogeneous solvents) are nearly negligible.

Scavenging experiments. Micellar cage effects.

Addition of $Cu^{2+}$ ions (as $CuCl_2$) to micellar solutions of HDTCl is found to lead to the following results: (1) the quantum yield for disappearance of 1 is found to be comparable to that observed in the absence of $Cu^{2+}$; (2) the quantum yields for formation of 3 and 4 in the presence and absence of $Cu^{2+}$ are experimentally identical; (3) the trace products 5, 6 and 7 are completely absent when $Cu^{2+}$ is present; (4) substantial formation of three new products, 8a, 8b and 9 is observed when $Cu^{2+}$ is present.[3] These results allow the conclusion that in HDTCl 3 and 4 are formed nearly exclusively in micellar "cages," whereas the other products are formed as a result of radical escape from micellar cages.

From the $Cu^{2+}$ results we calculate the "cage effects" for HDTCl micelles as ∿30%, i.e., the absolute yield of 3 (or 4) relative to 1 reacted in the presence of $Cu^{2+}$ (Table 2). The mass balance for $Ph\dot{C}(CH_3)_2$ radicals is ∿80%, whereas for $Ph\dot{C}O$ radical it is ∿60%.[4]

Deuterium isotope effects on quantum yields and cage efficiency.

The influence of deuterium substitution (1 → 2) on quantum yields and cage efficiency in micellar photolysis was investigated. The major products from micellar photolysis of 2 in HDTCl solution are PhCDO (10) and $PhC(CD_3)=CD_2$ (11). Confirming the conclusion that the aldehyde and styrene products are cleanly produced via cage disproportionation.

The quantum yield for formation of the cage products drops from 0.16-0.18 (∿30% cage effect) for 1 to ∿0.12 (∿23% cage effect) for 2 (Table 2). The origin of this substantial isotope effect on the extent of cage reaction may be ascribed to a competition of diffusion of radicals out the micelle cage and either (1) disproportionation of $Ph\dot{C}O$ and $Ph\dot{C}(CD_3)_2$ radicals in a primary micelle cage or (2) intersystem crossing of a triplet radical pair to a singlet radical pair (followed by disproportionation). Since only the latter possibility would be sensitive to the application of laboratory magnetic fields, a study of the cage effect of 1 and 2 as a function of external magnetic field strength was undertaken.

Magnetic field effects on cage effects.

It has recently been demonstrated that a laboratory magnetic field can dramatically decrease the extent of micellar cage reaction.[5] Qualitatively, the lowered cage effect is ascribed to removal of the degeneracy of the $T_+$ and $T_-$ sublevels of the triplet radical pair and the singlet radical pair. When the strength of the applied field is greater than the hyperfine interaction which causes ISC in the triplet radical pair, $T_+$ and $T_-$ undergo only inefficient intersystem crossing to S (relative to zero field). Thus, it is expected that the relative yield of 3 and 4 (cage products) will be substantially reduced when photolysis is conducted in the presence of an applied magnetic field. Table 2 presents data which confirms this expectation. The cage effect for 1 is decreased from 30% at 0.5 Gauss (earth's magnetic field) to 20% at 200 Gauss. Further increase in field strength to 10,000 Gauss does not result in a further substantial decrease. The cage effect is also substantially decreased as a result of deuterium substitution. The observation that the cage effect decreases significantly for 2 upon going from 0.5 Gauss to 200 Gauss demonstrates that the decreased cage effect for 2 relative to 1 is substantially due to a magnetic isotope effect, i.e., since D has a smaller hyperfine interaction than H, ISC will be slower for $^3$RP from 2 than for $^3$RP from 1 and radical escape will compete more efficiently with cage reaction.

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## References.

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(3) J. Kochi, "Free Radicals," John Wiley, New York, 1973.

(4) In presence of Cu$^{2+}$ the free radical product of PhCO· is benzoic acid 9. 9 was detected as its ethyl ester by vpc-analysis.

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Scheme I.

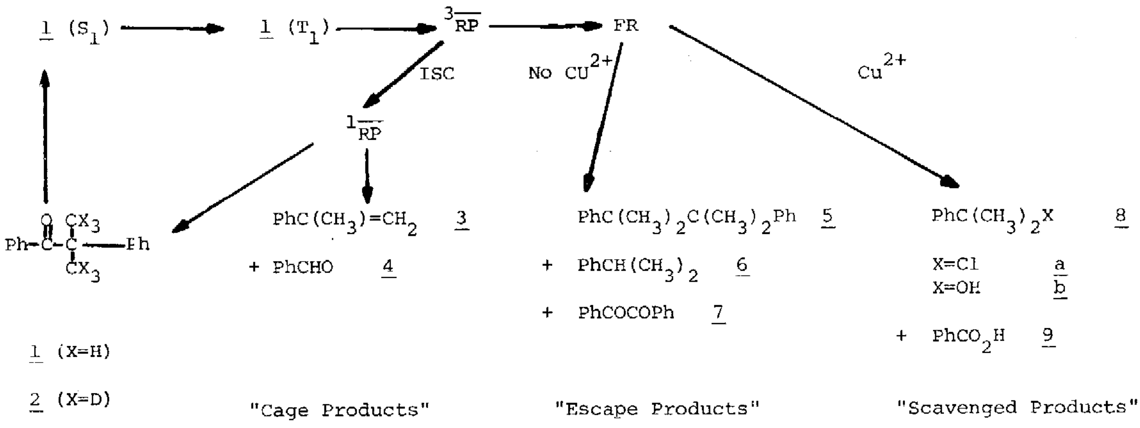

Table 1. Chemical and quantum yields of the photolysis of 1 on homogeneous and micellar solutions.(a)

| Solution(b) | 1(c) | 3 | | 4 | | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Φ | Yld. | Φ | Yld. | Φ | Yld. | Φ | Yld. | Φ | Yld. | Φ |
| $C_6H_6$ | 0.85 | 3.4 | 0.03 | 15 | 0.14 | 21 | 0.18 | (d) | (d) | 8.0 | 0.07 |
| $CH_2Cl_2$ | 0.97 | 6.1 | 0.06 | 18 | 0.18 | 18 | 0.18 | 0.8 | 0.008 | 7.1 | 0.07 |
| $CH_3CN$ | 0.95 | 3.3 | 0.03 | 10 | 0.10 | 18 | 0.17 | (d) | (d) | 9.2 | 0.09 |
| HDTCl | 0.73 | 23 | 0.16 | 22 | 0.16 | 2.2 | 0.02 | 0.8 | 0.006 | - | |
| HDTBr | 0.73 | 23 | 0.16 | 27 | 0.19 | 3.5 | 0.03 | 1.0 | 0.008 | - | |
| DDTCl | 0.75 | 15 | 0.11 | 24 | 0.17 | 4.0 | 0.03 | 1.3 | 0.009 | - | |
| SDS | 0.67 | 17 | 0.11 | 30 | 0.19 | 2.8 | 0.02 | 1.3 | 0.008 | - | |
| Brij 35 | 0.88 | 17 | 0.15 | 22 | 0.19 | 2.6 | 0.02 | 0.9 | 0.008 | - | |

[a] Quantitative vpc analyses were carried out using a SE-30 column (10% on Gas-Chrom Q) and biphenyl as internal standard. The chemical yields (Yld.) are related to disappearance of 1 = 100%. Light intensities were measured with valerophenone in t-BuOH as actinometer.

[b] Concentration of 1 in homogeneous and micellar solutions = 5 mM. Micellar solutions contain 100 mM detergent in water. All solutions were degassed with nitrogen.
HDTCl (HDTBr) = hexadecyltrimethylammonium chloride (bromide).
DDTCl = dodecyltrimethylammonium chloride.
SDS = sodium dodecyl sulfate.
Brij 35 = polyoxyethylene (23) lauryl ether.

[c] Disappearance of 1.

[d] 6 is formed only in traces in benzene and acetonitrile.

Table 2. Magnetic field effects on cage effects.(a)

| Field Strength (Gauss) | 0.5 | 100 | 200 | 500-10,000 |
|---|---|---|---|---|
| 1 (DPMP-$h_6$) | 30 | 24 | 20 | 19 |
| 2 (DPMP-$d_6$) | 23 | 17 | 15 | 13 |

[a] The cage effect is defined as moles of 3 (or 4) formed/moles of 1 (or 2) consumed times 100.

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