The competition between δ-hydrogen abstraction and cage effects in the photochemistry of o-methyl dibenzyl ketone in various environments

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Abstract

The photolysis of *o*-methyl dibenzyl ketone (*o*-MeDBK) proceeds by two primary photochemical processes: α-hydrogen abstraction leading to a 1,5-biradical which cyclizes to an indanol and α-cleavage leading to a radical pair which, after decarbonylation, forms diphenylethane coupling products. The product distribution (in the earth's field and in a magnetic field of 2 kG) in the photolysis of *o*-MeDBK depends on the environmental conditions of the photolysis (homogeneous solutions, micellar solutions, cyclodextrin solutions and cyclodextrin solid complexes). In the presence of an external magnetic field, the recombination efficiency of the radical pair formed by α-cleavage is suppressed in micelles relative to δ-hydrogen abstraction and cyclization of the 1,5-biradical. In homogeneous solvents, aqueous solutions of cyclodextrin complexes or solid cyclodextrin complexes, there is no significant magnetic field effect on the product ratios. These results are interpreted in terms of a mechanism in which δ-hydrogen abstraction occurs from the singlet state of the ketone and type I α-cleavage occurs from the triplet state of the ketone, and by conformational factors which favor or disfavor the relative competition between the δ-hydrogen abstraction and α-cleavage.

1. Introduction

Molecular organization plays a vital role in many complex biochemical processes [1], and photochemical investigations of guest molecules adsorbed in various microheterogeneous systems which mimic biological functions have been an extremely active area of recent research [2–5]. Photoreactions, such as the common γ-hydrogen-atom abstraction of ketones, have been employed as probes of microheterogeneous systems [2–4]. Although less common, examples of δ-hydrogen abstraction of photoexcited ketones in homogeneous solutions and in the solid state have been reported [6, 7]. In this paper, we report the effects of environment and an applied magnetic field on the product distribution of the photolysis of *o*-methyl dibenzyl ketone [5] (*o*-MeDBK, Scheme 1).

This reaction was selected because it exhibits clean competition between δ-hydrogen abstraction (step a) and type I cleavage (step c) and because the eventual product

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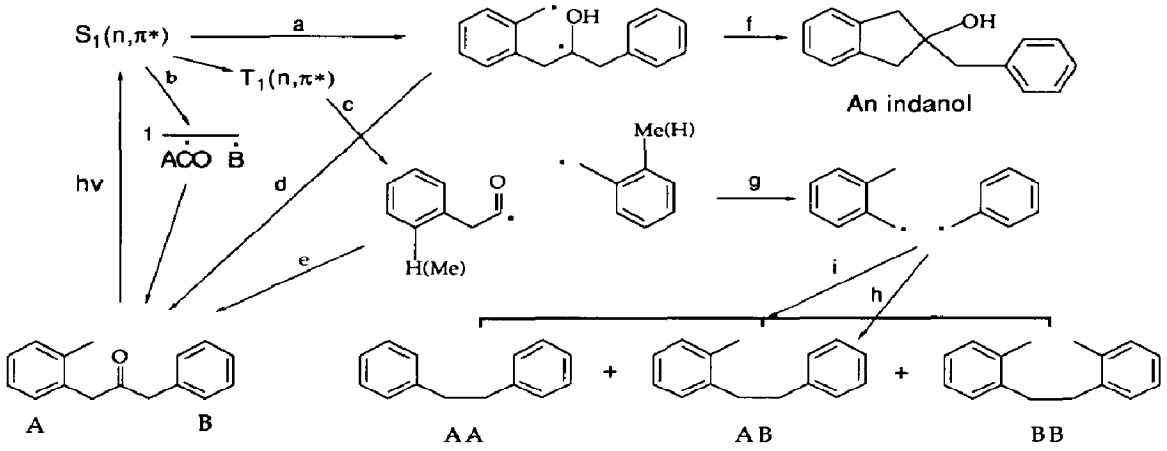

Scheme 1. Paradigm for the photolysis of *o*-MeDBK. The relevant pathways are as follows: (1) δ-hydrogen abstraction from the singlet state (a) and Type I from the triplet state (c); (2) intersystem crossing rate limiting return of the geminate primary pair to the starting ketone (e) and decarbonylation (g); (3) reverse hydrogen abstraction and cyclization to the indanol (f); (4) coupling of geminate decarbonylated pairs (h) and coupling of escaped free radicals (i); (4) recombination of the radical pair generated from the singlet state (b) and recyclization of the biradical (d).

distribution depends on both the competing recombination of the primary geminate radical pair, produced by Type I cleavage, to the starting ketone and conformational factors which either favor or inhibit δ-hydrogen abstraction. In addition, the cage effect of the secondary radical pair resulting from decarbonylation (step g) provides an independent probe of the competing processes in the microenvironment (radical combination and escape from the environmental cage). Finally, magnetic field effects can be employed to probe the competition available to the radical pair at both the primary and secondary stages; for example, from Scheme 1 the return of the primary radical pair (step e) to regenerate the starting ketone is dependent on the magnetic field, so that the yield of products from the secondary pair will also be dependent on the magnetic field; however, the competing pathway to indanol (step a then f) is not expected to be dependent on the magnetic field. Therefore, the ratio of the secondary coupling products (AA, AB and BB) to indanol will be dependent on the magnetic field, as will the magnitude of the secondary cage effect. In contrast, the unimolecular deactivation pathways available to the biradical produced by δ-hydrogen abstraction are expected to be independent of the "cage" aspects of the microenvironment and of the application of moderate magnetic fields (approximately 1000 G), because of the strong exchange interactions in the 1,5-biradical, which cause the singlet and triplet states of the biradical to be split by an energy much larger than that provided by a moderate externally applied field.

2. Experimental details

2.1. Materials

o-MeDBK was prepared and purified by the method described for *p*-MeDBK [8] by replacing *p*-methylbenzyl chloride with *o*-methylbenzyl chloride. Solvents, surfactants and cyclodextrins (CDs) were commercially available and used as received. Deionized water was used throughout.

2.2. Formation of inclusion complexes of o-MeDBK with CDs

To a saturated CD aqueous solution [9] (*e.g.* 92.5 mg of β-CD in 5 ml of water (0.081 mM) or 232 mg of γ-CD in 1 ml of water (0.179 mM)), 19.2 mg (0.086 mM) or 42 mg (0.188 mM) of *o*-MeDBK were added. The mixtures were stirred magnetically at room temperature overnight and the inclusion complexes were obtained as white precipitates. The precipitates were filtered and washed with cold water, and then with a small amount of ether to remove the uncomplexed DBK and CD. The precipitate was then dried in vacuum at 50 °C overnight.

2.3. Identification of products

A benzene solution of 200 mg of *o*-MeDBK was degassed in a quartz cell and irradiated through a potassium chromate filter solution with a 450 W mercury lamp. The products of photolysis were separated by column chromatography (silica gel, 5% ether in hexane) and identified by nuclear magnetic resonance (NMR) spectroscopy and by comparison with an authentic sample prepared by the reaction of benzyl magnesium chloride with 2-indanone in anhydrous ether followed by hydrolysis. NMR δ (200 MHz, tetramethylsilane (TMS)): diphenylethane; 2.92 (s, 4H), 7.1–7.4 (m, 10H); *o*-methyl-diphenylethane; 2.32 (s, 3H), 2.89 (s, 4H), 7.1–7.4 (m, 9H); *o,o'*-dimethyl-diphenylethane; 2.30 (s, 6H), 2.86 (s, 4H), 7.1–7.4 (m, 8H); 2-benzyl-2-indanol; 1.78 (s, broad, 1H), 2.86 (d, 2H), 3.05 (s, 2H), 3.18 (d, 2H), 7.1–7.4 (m, 9H).

2.4. Photolysis and analysis of products

The concentration of *o*-MeDBK employed for photolysis in benzene, ethanol and surfactant aqueous solutions was 1 mM. After irradiation the products were extracted with ether. For α-CD, a 1:1 (mol) aqueous solution with *o*-MeDBK was used, whereas for β- or γ-CD, saturated solutions of solid inclusion complex with *o*-MeDBK were employed. For these solutions, the reaction products were extracted three times with ether. Solid complexes were degassed in a quartz cell. During the photolysis, the samples were tumbled continuously to encourage uniform photolysis. After the photolysis, the complex was dissolved in water and extracted with ether. Products were analyzed by a gas chromatograph (Varian model 3700) with a SE-30 capillary column. The conversion of the ketone was controlled to be of order of 50%.

3. Results

The photolysis of *o*-MeDBK in both homogenous (benzene and ethanol) and heterogeneous (micelles and CDs) systems (Scheme 1) results in δ-hydrogen abstraction to yield an indanol and α-cleavage [5] (step c) followed by decarbonylation (step g) to yield the diphenylethanes AA, AB and BB. Presumably, the recombination of the primary radical pair to the starting material (step e), which is not detected directly in these experiments, also occurs. Triplet quenching experiments show that the α-cleavage process occurs mainly from the triplet state. However, the δ-hydrogen abstraction (path a, Scheme 1) occurs mainly from the singlet state [10]. The chemical yields of the products were determined by gas chromatography, and the percentage of the secondary cage effect (% CE) was evaluated according to eqn. (1) by determining the relative yields of the three diphenylethanes shown in Scheme 1 [8]

$$\% \text{ CE} = \frac{\text{AB} - (\text{AA} + \text{BB})}{\text{AB} + (\text{AA} + \text{BB})} \times 100 \qquad (1)$$

The results are summarized in Table 1.

TABLE 1

Secondary cage effect and yield of indanol on photolysis of *o*-MeDBK in homogeneous and heterogeneous systems[a]

System	0 G		2000 G		μ	ϕ
	CE (%)	Indanol (%)	CE (%)	Indanol (%)		
Benzene	0.6±0.2	6.2±0.3	0.7±0.3	6.2±0.9	0	0
Ethanol	1.4±1.0	8.7±0.3	0.1±0.2	8.6±0.4	0	0
TX-100	37.0±2.0	12.0±1.0	16.5±0.5	11.5±1.0	55	4
SDS	39.2±1.0	22.1±2.0	21.6±2.0	17.4±2.0	56	21
CTAB	56.6±3.0	14.5±1.0	29.5±2.0	11.2±1.0	48	23
α-CD(aq)[b]	1.5±1.0	19.5±1.0	2.5±1.0	18.8±1.0	0	4
β-CD(aq)[c]	3.0±1.0	25.6±3.0	4.1±0.9	22.6±3.0	0	12
β-CD(s)[d]	95.0±2.0	10.9±1.0	95.0±2.0	10.3±1.0	0	6
γ-CD(aq)[c]	0±2.0	17.2±2.0	2.7±2.0	16.2±3.0	0	6
γ-CD(s)[d]	91.0±2.0	7.2±1.0	90.1±2.0	7.1±1.0	0	0

[a][SDS] = 70 mM; [TX] = 70 mM; [CTAB] = 15 mM.
[b][CD]/[ketone] = 1:1 (mol).
[c]Saturated aqueous solution of 1:1 solid inclusion complex.
[d]1:1 solid inclusion complex.
SDS, sodium dodecylsulfate; CTAB, cetyltrimethylammonium bromide; TX-100, Triton X-100.

The homogeneous systems (benzene and ethanol) serve as "benchmark" non-polar and polar "open" environments for comparison with heterogeneous systems. In homogeneous solutions the general results are as follows: (1) the cage effects for diphenylethanes are close to 0%; (2) the yield of indanol is approximately 7%; (3) there is no magnetic field effect on the cage effect or the yield of indanol (*i.e.* there is no magnetic field effect on any of the observables).

For the evaluation of the influence of the magnetic field on the cage effect and the yield of indanol, we introduce two product distribution parameters, μ and ϕ. The parameter μ is defined as the percentage reduction of the cage effect in the presence of a magnetic field of 2 kG relative to that observed in the earth's field, and ϕ is defined as the percentage decrease in the yield of indanol in the presence of a magnetic field of 2 kG relative to that observed in the earth's field.

For each of the micellar systems, it is observed that, relative to homogeneous systems, the cage effect is significant (% CE ≈ 37%–57%) and the yield of indanol increases significantly (approximately 200%–300%). In addition, for each of the micellar systems there is a significant magnetic field effect (earth's field *vs.* 2 kG) on the product ratios: the cage effects decrease dramatically at 2 kG (μ values approximately 50% of those at the earth's field) and the yield of indanol decreases modestly (ϕ values approximately 20%–30% of those at the earth's field) for the ionic micelles. Although μ is significant for non-ionic micelles (approximately 50%), the value of ϕ is close to the experimental error (approximately 4%).

In aqueous solutions of CDs, the cage effect is close to 0% and there is little or no magnetic field effect on the product ratios, *i.e.* the results are similar to those obtained in homogeneous solution. However, in the presence of each of the CDs, the yield of indanol is considerably greater (approximately 200%–400%) than in homogeneous

solution (approximately 6%–8%). For the solid complexes of β-CD and γ-CD with *o*-MeDBK, the cage effect is very high (%CE ≈ 90%–95%), but there is no magnetic field effect on the product ratios (μ and ϕ are close to the experimental error). The yield of indanol is similar to that found in homogeneous solution (approximately 7%–11%).

4. Discussion

4.1. The working mechanism for the photochemistry of o-MeDBK

Table 1 shows that both the cage effect and the relative yield of indanol during the photolysis of *o*-MeDBK in micelles are significantly higher than those observed in homogeneous solutions, with SDS providing the highest yield of indanol among the three micellar systems. In addition, for each of the micellar systems, the percentage cage effect decreases dramatically and comparably on application of a magnetic field (μ = 48%–56%), but the relative yield of indanol is only slightly affected by the application of an external field. In contrast, in homogeneous solutions and CD–*o*-MeDBK (with the possible exception of β-CD) complex solutions, the percentage cage effect is close to zero and the yields of indanol are not affected by the external magnetic field (μ and ϕ approximately equal to zero). However, for all CD solutions the yield of indanol is higher than for aqueous solutions. Finally, in solid CD complexes, the percentage cage effect is very high, but the change in the yields of indanol and the magnetic effects are negligible, as in homogeneous solution.

We seek to explain these results in terms of the mechanism of photolysis of *o*-MeDBK shown in Scheme 1, with the additional consideration of conformational factors influencing δ-hydrogen abstraction, which are imposed on *o*-MeDBK when it is adsorbed in microheterogeneous systems. First, however, we briefly review some of the quantitative aspects of the mechanism of Scheme 1.

Given the known rate constants for α-cleavage of dialkyl ketones, which cleave much more slowly from the singlet state than from the triplet state [11, 12], it is expected that this process will occur only in the triplet and not in the singlet state of *o*-MeDBK. (It should be noted, however, that there is some controversy concerning the contribution of singlet and triplet α-cleavage in the photolysis of dibenzyl ketone [12].) Furthermore, it is expected that α-cleavage of the triplet state will be too rapid for competition by δ-hydrogen abstraction. For example, the rate constant for δ-hydrogen abstraction [6] in α-*o*-tolyl-acetophenone is approximately 2×10^8 s^{-1} and the rate constant for α-cleavage [7] of the triplet state of DBK is approximately 10^{10} s^{-1}. However, given the known rate constants for intramolecular hydrogen abstraction of dialkyl ketones [11], which abstract γ-hydrogens much more rapidly in the singlet state than in the triplet state, and the relatively slow rate of intersystem crossing of dialkyl ketones, δ-hydrogen abstraction may be expected to occur, *a priori*, from the singlet state of *o*-MeDBK, with a rate constant of approximately 10^9 s^{-1}. Indeed, quenching of the photolysis of *o*-MeDBK with 1,3-cyclohexadiene, a selective triplet quencher, demonstrates [10] that the diphenylethane products resulting from α-cleavage are strongly quenched, but indanol formation is only slightly affected by the triplet quencher under comparable conditions. This conclusion is consistent with the observation of a small solvent effect on the yield of indanol [13] since a singlet biradical, with its inherently short lifetime, is expected to be less sensitive to solvent effects than a triplet biradical. (We thank a referee for pointing out the unusual nature of the observation of indanol formation, which led us to probe the mechanism of this reaction in more

detail.) Thus, we conclude, provisionally, that the δ-hydrogen abstraction (step a) in Scheme 1 occurs from the singlet state of *o*-MeDBK, and that the α-cleavage (step b) in Scheme 1 occurs mainly from the triplet state of *o*-MeDBK. We now employ this working mechanism to interpret our results.

It is interesting to note that δ-hydrogen abstraction does not occur to a measurable extent in the photolysis of α-*o*-tolyl acetone [14]. According to the mechanism outlined so far, this is perhaps surprising considering that α(*o*-tolyl)-acetophenones undergo δ-hydrogen-atom abstraction [13] with a rate constant of about 10^8 s^{-1}, and given the expected higher reactivity of dialkyl ketone singlets [11] towards hydrogen abstraction and the fact that the rate of intersystem crossing of dialkyl ketones is relatively slow and of the order of 10^9 s^{-1}. However, this result is understandable if there is a ground state steric preference for a conformer which places the methyl groups distal from the carbonyl function. Indeed, the inspection of molecular models suggests that, for *o*-MeDBK, a preference exists, relative to α-*o*-tolyl acetone, for conformations which place the methyl group of the *o*-tolyl moiety close to the carbonyl group in an excellent position for δ-hydrogen abstraction. This conformational difference provides an explanation for the observation of δ-hydrogen abstraction from the singlet state of *o*-MeDBK and its absence in the photolysis of α-*o*-tolyl acetone, and also suggests that the competition between δ-hydrogen abstraction and intersystem crossing (which is rate limiting for α-cleavage in the triplet state) will be sensitive to conformational factors. Therefore, we are prepared to modify our working mechanism to include the effect of conformational factors on the product distributions.

4.2. Product distributions in the photolysis of o-MeDBK in various environments

The adsorption of *o*-MeDBK onto the surface and/or into the core of a micellar aggregate creates a "supercage" environment for the primary (phenylacetyl–benzyl pair, created in step c) and secondary (benzyl–benzyl pair, created in step g) geminate triplet radical pairs resulting from photoexcitation and type I cleavage of the ketone. Cage recombination (after intersystem crossing) of the former pair regenerates *o*-MeDBK (step e), whereas geminate cage recombination of the latter pair forms only AB (step h). The primary geminate triplet pair is formed in competition with δ-hydrogen abstraction (step a) from the singlet ketone to give a singlet 1,5-biradical, which cyclizes efficiently. However, the diphenylethane products monitored result from the competition between intersystem crossing of the primary triplet pair and regeneration of the starting ketone (step e) and irreversible decarbonylation of the primary triplet pair (step g). Since the yield of indanol in ethanol and aqueous micellar or CD environments should parallel closely the irreversible formation of the singlet 1,5-biradical resulting from δ-hydrogen abstraction, the yield of diphenylethanes relative to indanol should, in turn, represent the competition between type I cleavage (corrected for recombination of the primary radical pair to the starting ketone, step e) and δ-hydrogen abstraction from the ketone singlet. The "correction" factor will depend on the efficiency with which the supercage environment encourages the return of the primary geminate radical pair to the starting ketone and is expected to be dependent on the magnetic field, since it involves an intersystem crossing in a triplet radical pair. The encouragement of the primary pairs to return to the starting ketone has been shown to parallel the encouragement of the secondary pairs to undergo cage combination [15].

As defined above, the influence of the magnetic field on the cage effect is expressed by the parameter, μ. From a wide range of previous experiments it is expected that the primary and secondary triplet radical pairs will be subjected to significant magnetic field effects if a competition between radical pair reaction and hyperfine-induced

intersystem crossing exists. Furthermore, it is expected that singlet 1,5-biradicals will not be subject to magnetic field effects on their competing reaction pathways, because of the significant exchange interactions, which will tend to quench hyperfine-induced intersystem crossing and magnetic field effects, and the short lifetime of the singlet biradicals.

From the above considerations, the probability of recombination of the primary pair (step e) should increase as the percentage cage effect increases (*e.g.* CTAB > SDS > TX-100). Thus, in the simplest case, we expect that the relative yield of indanol to diphenylethanes will increase as the cage effect increases, *i.e.* more returns of the primary radical pair to the starting ketone will decrease the number of primary pairs that decarbonylate. This will lead to fewer benzyl–benzyl radical pairs and, in turn, should lead to a higher yield of indanol relative to diphenylethanes. However, this is not observed since, although the SDS system yields a comparable cage effect to the TX-100 system, it also gives a much higher yield of indanol. Thus we conclude that factors in addition to those considered so far are involved and we must take into account, as anticipated above, the influence of conformational variation on the observed product ratios.

We suggest that that abnormally high yield of indanol in SDS may result from conformational factors which favor the formation of a 1,5-biradical (we assume that cyclization of this biradical is not significantly environmentally dependent because of the small solvent dependence of the yield of indanol, Table 1). It has been reported that the intramolecular reactivity in acyclic triplet ketones is governed by conformational factors [5, 16]. The efficiency of the hydrogen abstraction reaction depends on the probability that, during its lifetime, the excited triplet can reach a conformation which brings the hydrogen within abstraction distance to the carbonyl oxygen [13, 14]. The 1,5-biradical thus formed can adopt a syn (methyl close to carbonyl) or anti geometry, of which only the syn form can cyclize to give the cyclic alcohol. Isotropic solvents, and more so protic solvents, disfavor the syn conformation of the starting ketone [17]. As the extent of geminate phenylacetyl–benzyl radical pair recombination increases (step e), the yield of indanol increases, because fewer secondary pairs (step g) are formed.

The values of the magnetic field parameter μ for the three micellar systems are comparable, suggesting that the competition between micellar escape and magnetic-field-dependent intersystem crossing is similar in the three systems.

The percentage of indanol produced from solutions of CD complexes is much larger than that produced from homogeneous alcohol solution. The values of the parameters ϕ and μ are close to zero, a result similar to that found in homogeneous solutions. We suggest that in the triplet CD complex, a fast diffusional separation of the primary radical pair occurs (as in homogeneous solutions) after type I cleavage, leading to a negligible cage effect and magnetic field effect. These results are consistent with the postulate that aqueous CD solutions behave in a similar manner to homogeneous solvents with respect to the competitions available to the radical pair. However, we propose that conformational differences in the positioning of the *o*-methyl-substituted ring occur on binding to the CD, and this binding favors the conformer which places the abstractable hydrogen on the same side of the molecule as the carbonyl function, thereby enhancing δ-hydrogen abstraction relative to type I cleavage. This postulate is consistent with the interpretation proposed above to explain the failure of *o*-tolyl acetone to undergo δ-hydrogen abstraction to any measurable extent [13, 14]. Both β- and γ-CD can host one phenyl ring or both phenyl rings of DBK [17]. However, in the case of *o*-MeDBK–CD complexes, the methyl group may prevent its connecting

phenyl group from being included in the CD (α-, β-CD) cavity, or prevent the inclusion of both phenyl rings into the same CD cavity. It is also possible that inclusion is weak (γ-CD), so that recombination takes place only between the radicals which diffuse into the aqueous phase. As a result, a statistical mixture of the coupling products AA, AB and BB (1:2:1) is obtained and the percentage cage effect is zero.

For the solid CD complexes, the high cage effect and lack of a magnetic field effect argue for the absence of a competitive pathway for diffusional escape of the primary or secondary radical pairs. This result is consistent with recent reports of the photolysis of related ketones in solid CD complexes [18, 19]. The yields of indanol in the complexes are comparable with those observed in homogeneous solution, so that the results provide no evidence for a strong conformational change of *o*-MeDBK in the solid complex. It is interesting to note that rearranged isomers of the starting ketones are only formed in trace amounts, which shows that the primary pair does not undergo rotational motion leading to rearrangement in competition with decarbonylation. The absence of a magnetic field effect on the product ratios indicates either the absence of competition between the reaction pathways available to the triplet radical pair intermediates and intersystem crossing or a suppression of the magnetic field dependence of intersystem crossing due to a large exchange effect on the included radical pair.

5. Conclusions

The product distributions in the photolysis of *o*-MeDBK are controlled by both cage and conformational factors provided by the environments in which the photolyses are conducted. The cage effect increases the ratios of recombination of both the primary and secondary radical pairs and thus increases the percentage yield of indanol. Conformational factors favor (in micelles and aqueous CD complexes) or disfavor (in solid CD complexes) the δ-hydrogen abstraction and cyclization of the 1,5-biradicals. An external magnetic field suppresses cage recombination, but not the cyclization of the 1,5-biradical, when intersystem crossing in the secondary triplet pair is suppressed by the magnetic field.

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