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PHOTOCHEMISTRY OF KETONES IN MICELLAR SOLUTION: STRUCTURAL AND VISCOSITY EFFECTS ON CARBON-13 ISOTOPIC ENRICHMENT.

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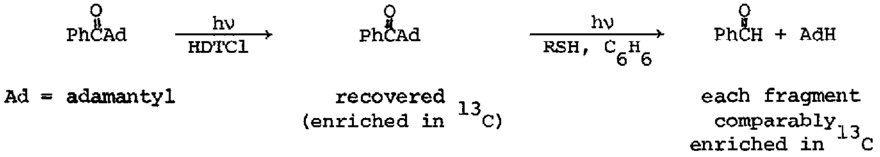
A study of the ^{13}C enrichment of ketones in micellar solution as a function of structure and viscosity is presented.

The photolysis of micellar solutions of dibenzyl ketone (DBK) results in the ^{13}C enrichment of DBK that is recovered after partial photolysis.[1] We report studies of the effects of varying ketone structure and micelle structure on the ^{13}C enrichment in micellar solutions. In addition, we report the influence of solvent viscosity on the efficiency of ^{13}C enrichment.

The proposed mechanism[1] leading to ^{13}C enrichment of DBK in micellar systems is shown in Scheme I. The key step in the sorting of ^{12}C from the ^{13}C in DBK occurs in the competition between hyperfine induced triplet to singlet intersystem crossing and "escape" of the radical pair via exit from the micelle or decarbonylation. A DBK molecule that goes through the recombination cycle becomes enriched in ^{13}C because ^{13}C-containing radicals undergo hyperfine induced intersystem crossing faster than radicals that do not contain ^{13}C ($^{13}k_{TS} > {}^{12}k_{TS}$). The role of the micelle is to enhance reencounters of radical pairs after the triplet-singlet conversion has occurred.

Further support for the hyperfine mechanism is found in the observation that phenyl benzyl ketone (PBK) and phenyl adamantyl ketone (PAK) both are enriched in ^{13}C after partial photolysis in micelle solutions (Table 1). The degree of ^{13}C enrichment is most conveniently expressed in terms of Bernstein's single stage enrichment factor, α, as a function of per cent conversion.[2]

The magnetic properties[3] of the PAK radical pairs allow for interesting speculation: 1-adamantyl radicals possess a rather large ^{13}C hyperfine coupling at the 1-carbon atom (137G), as do benzoyl radicals at the carbonyl-carbon atom (128G). We expect, therefore, that each "piece" of the PAK radical pair will be comparably enriched in ^{13}C. In order to test this prediction PAK was photolyzed to 90% conversion in HDTCl solution. The remaining PAK was extracted with CH_2Cl_2 and isolated by preparative vpc. The purified, enriched PAK was then dissolved in benzene containing n-BuSH and was photolyzed to ∿ 90% destruction.[4] From vpc analysis, benzaldehyde and adamantane were formed quantitatively. Analysis of the benzaldehyde and adamantane by gc-ms showed that each molecule was comparably enriched (eq. 1). Assuming selective enrichment at the CO carbon of benzaldehyde and the 1-carbon of adamantane, the former was enriched ∿ 160% in ^{13}C and the latter was enriched ∿ 180% in ^{13}C. The ^{13}C enriched PAK from which these two molecules arose had been found to be ∿ 200% enriched in ^{13}C, assuming selective enrichment in the two carbons mentioned above.



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}Ad} \xrightarrow[\text{HDTCl}]{h\nu} \mathrm{Ph\overset{O}{\overset{\|}{C}}Ad} \xrightarrow[\text{RSH, } C_6H_6]{h\nu} \mathrm{Ph\overset{O}{\overset{\|}{C}}H + AdH} \qquad (1)$$

Ad = adamantyl

recovered (enriched in ^{13}C)

each fragment comparably enriched in ^{13}C

The proposed role of micelles in the ^{13}C enrichment of ketones, that of imposing a "reduced dimensionality" on the radical pairs, should be a general characteristic of micelles.[5] In order to test for this generality, DBK was photolyzed to partial conversion in a series of different micellar solutions. The results are shown in Table II. Although the degree of ^{13}C enrichment in each micellar solution is quantitatively slightly different, the qualitative result is unambiguous: ^{13}C enrichment is considerably enhanced in micellar solution compared to that in homogeneous fluid solution (e.g., benzene).

Solvent viscosity should also influence the ^{13}C enrichment in the photolysis of ketones. By increasing the solvent viscosity, and hence slowing down the rate of escape from the solvent cage, the two partners of the radical pair are held in a "solvent cage" for a longer period of time. Thus the chance of reencounter of radical pairs after the triplet-singlet conversion has occurred is increased, and the sorting of ^{13}C from ^{12}C becomes more efficient.[6] Since the interior of a micelle is considerably more viscous than a fluid solution such as benzene[7] the question arises - is viscosity the cause of enhanced ^{13}C enrichment in micelles? To answer this question, DBK and PAK were photolyzed in solvents of varying viscosity. The ^{13}C enrichments in the remaining ketones were measured by gc-ms, and the results were compared to those for photolysis in HDTCl (see Table III). As predicted from the above discussion in both DBK and PAK photolyses the ^{13}C enrichments were slightly enhanced by increasing solvent viscosity. But since the estimated viscosity[7] of the interior of HDTCl micelles (30-40 cP) is well within the range of viscosities studied, and since the ^{13}C enrichments in HDTCl solution are drastically greater than any in fluid solution, we conclude that viscosity plays only a minor role in the ^{13}C enrichment of ketones in micellar solution.

Finally, a low yield (∿1-5%) of an isomer of DBK was observed when micellar solutions of DBK were irradiated through quartz rather than through Pyrex. This isomer was shown to be 4-methylphenyl benzyl ketone (PMAP, Scheme I). If this compound is produced by cage recombination, it should be enriched in ^{13}C. GC-MS analysis showed that the PMAP was indeed enriched in

^{13}C. Assuming the enrichment occurs selectively at the carbonyl carbon, enrichment corresponding to $\alpha = 1.3$ was found. The ^{13}C enrichment in PMAP is related to, but does not appear to directly parallel, the ^{13}C enrichment in DBK. Mechanistic and kinetic implications of the MPBK enrichment are under investigation.

Work is currently in progress to further clarify the effects of magnetic isotopes and magnetic fields on the ^{13}C enrichment of ketones by photolysis in micellar solution.

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(4) The procedure is an adaptation of that described previously by: H.G. Heine, W. Hartmann, D.R. Kory, J.G. Magyar, C.E. Hoyle, J.K. McVey and F.D. Lewis, J. Org. Chem., 39, 691 (1974).

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Scheme 1.

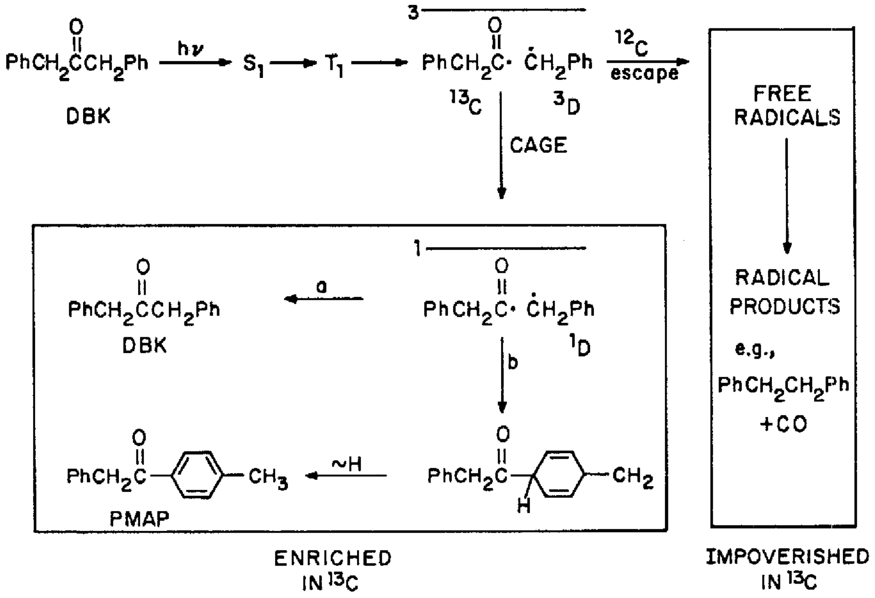

Table 1. ^{13}C Enrichment of Ketones by Photolysis in Micellar Solutions.[a]

Ketone	% Conversion	% Enrichment	α
DBK	95	200[b]	1.7[b]
PBK	90	140[b]	1.6[b]
PAK	95	220[c]	1.8[c]

[a] 0.005 M ketone, 0.05 M HDTCl, N_2 degassed, photolyzed through Pyrex with a Hanovia medium pressure lamp.

[b] Calculated assuming all ^{13}C enrichment occurred in one carbon.

[c] Calculated assuming ^{13}C enrichment distributed over two carbons.

Table 2. ^{13}C Enrichment of DBK by Photolysis in Various Micellar Solutions.[a]

Micellar Solution	Detergent Structure	α
HDTCl	$CH_3(CH_2)_{15}N(CH_3)_3Cl$	1.68
DDTCl	$CH_3(CH_2)_{11}N(CH_3)_3Cl$	1.66
HDTBr	$CH_3(CH_2)_{15}N(CH_3)_3Br$	1.41
SDS	$CH_3(CH_2)_{11}OSO_3Na$	1.47
benzene	C_6H_6	1.04

[a] 0.005 M DBK, 0.05 M detergent, N_2 degassed, photolyzed through Pyrex with a Hanovia medium pressure Hg lamp.

Table 3. Effect of Solvent Viscosity on the ^{13}C Enrichment of DBK and PAK by Photolysis.[a]

Ketone	Solvent	Viscosity (cp) (at 25°C)	α
DBK	benzene	0.6	1.04
	n-dodecane	1.35	1.05
	cyclohexanol	60	1.08
	HDTCl[b]	30-40	1.68
PAK	cyclohexane	0.9	1.02
	n-dodecane	1.35	1.06
	cyclohexanol	60	1.17
	HDTCl[b]	30-40	1.75

[a] 0.005 M ketone, N_2 degassed, photolyzed through Pyrex with a Hanovia medium pressure Hg lamp.

[b] 0.05 M HDTCl.

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