

PHOTOLYSIS OF DIBENZYL KETONE IN MICELLAR SOLUTION. CORRELATION OF ISOTOPIC ENRICHMENT FACTORS WITH PHOTOCHEMICAL EFFICIENCY PARAMETERS

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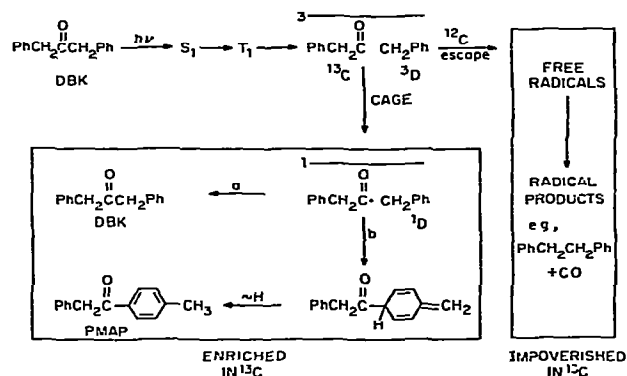
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A quantitative correlation is established between isotopic enrichment parameters (derived experimentally from measurements of isotopic enrichment as a function of conversion) and photochemical efficiencies (derived experimentally from measurement of the disappearance of starting ketone or appearance of products) for the photochemistry of dibenzyl ketone in micellar solution.

1. Introduction

The photolysis of dibenzyl ketone in micellar solutions [1] is consistent with the pathways represented in scheme 1. The occurrence of electron-nuclear hyperfine coupling (hfc) in the radical pairs serves as a mechanism for separation of magnetic isotopes from non-magnetic isotopes [2]. In particular, triplet radical pairs (3D) possessing ^{13}C nuclei may undergo rapid hfc induced intersystem crossing (isc) to singlet radical pairs (1D). The latter then undergo cage recombination reactions to form phenyl-*p*-methylacetophenone (PMAP, pathway b in scheme 1, minor) or regenerate dibenzyl ketone (DBK, pathway a in scheme 1, major). Since ^{12}C nuclei are non-magnetic, such carbon nuclei cannot induce $^3D \rightarrow ^1D$ intersystem crossing via hfc. As a result, radical pairs containing ^{13}C nuclei are expected to form cage products faster than those containing ^{12}C nuclei (at the corresponding position), and the cage products (DBK and PMAP) are enriched in ^{13}C relative to starting material (e.g., with natural abundance ^{13}C). The large hfc constant for the carbonyl carbon in a ^{13}C containing phenacetyl radical causes the enrichment to be particularly efficient at this position.

The ^{13}C enrichment in DBK is expected and found



Scheme 1

[1] to depend on the extent of conversion, since each photochemical cycle delivers the ^{13}C enriched DBK back to a "pool" of (less enriched) DBK. On the other hand, if PMAP is formed in a single photochemical reaction sequence, then the ^{13}C enrichment found in PMAP should be less sensitive to the extent of conversion, and should already be high and nearly constant at low conversions (where ^{13}C enrichment in DBK is still negligible). According to Bernstein [3], isotopic enrichment in first order reactions may be characterized by a parameter, α , which is independent of the extent of conversion:

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$$\log S_f = [(\alpha - 1)/\alpha] \{ \log [(1 - F_0^*)/(1 - F_f^*)] - \log(1 - f) \}, \quad (1)$$

where F_0^* and F_f^* are the molar fractions of ^{13}C in the starting ketone before reaction and after the fraction f of starting ketone has been converted respectively, and S_f is given by

$$S_f = \frac{{}^{13}\text{C}_f / {}^{12}\text{C}_f}{{}^{13}\text{C}_0 / {}^{12}\text{C}_0}. \quad (2)$$

In eq. (2), ${}^{13}\text{C}_f / {}^{12}\text{C}_f$ is the ratio of concentrations of ^{13}C and ^{12}C in the ketone after a fractional conversion of an amount f , and ${}^{13}\text{C}_0 / {}^{12}\text{C}_0$ is the corresponding ratio in the starting ketone. We show here, that under the conditions of scheme 1 α may be connected to an important photochemical parameter, the quantum yield Φ . The correspondence between α and Φ allows a simple experimental check of the reaction mechanism postulated in scheme 1 and the theoretical basis for the derivation of α .

2. Correlation of α and quantum yields

For small ^{13}C contents and small values of α , eq. (1) can be approximated by

$$\log S_f \approx -[(\alpha - 1)/\alpha] \log(1 - f). \quad (3)$$

When eq. (3) is applicable, α is readily attained from a plot of $\log S_f$ versus $\log(1 - f)$. A typical plot is shown in fig. 1, for which the total ^{13}C enrichment in DBK recovered after partial photolysis is monitored as a function of conversion f .

A general definition of α refers to the ratio of disappearance of ^{12}C containing DBK (^{12}C ketone) relative to ^{13}C containing DBK (^{13}C ketone):

$$\alpha = \frac{\text{rate of disappearance of } ^{12}\text{C ketone}}{\text{rate of disappearance of } ^{13}\text{C ketone}}. \quad (4)$$

Under conditions of equal absorption, the ratio of disappearance of ^{12}C ketone to ^{13}C ketone is given by ${}^{12}\Phi / {}^{13}\Phi$, the ratio of quantum yields of disappearance for ^{12}C ketone and ^{13}C ketone. This correlation,

$$\alpha = {}^{12}\Phi / {}^{13}\Phi, \quad (5)$$

has been verified experimentally [4]. Insertion of eq. (5) into eq. (3) yields:

$$\log S_f \approx [({}^{12}\Phi - {}^{13}\Phi) / {}^{12}\Phi] \log(1 - f). \quad (6)$$

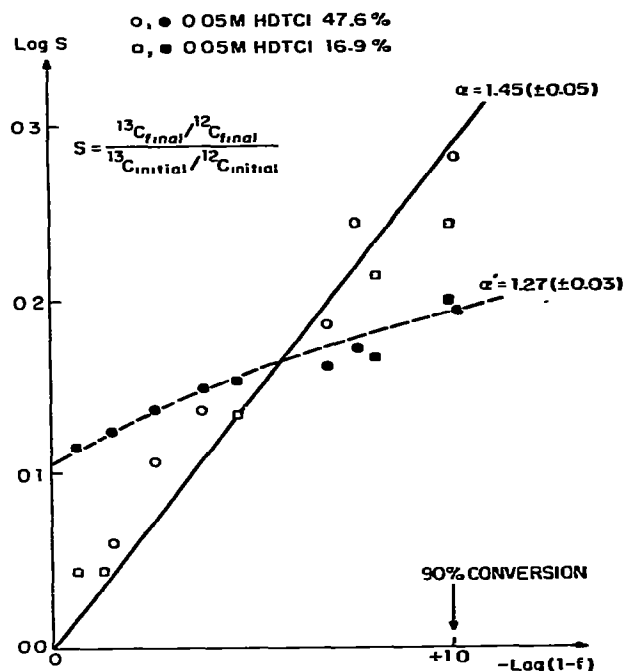
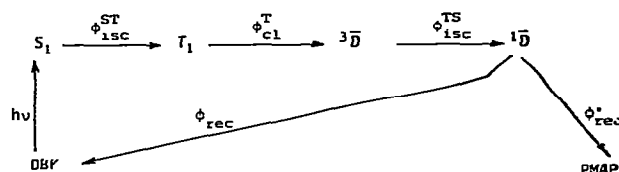


Fig. 1. ^{13}C content of recovered DBK and of PMAP from the photolysis of DBK in aqueous 0.05 M HDTCl solution. Plot of the separation factor, S , versus fraction, f , of reacted DBK. The equation $\log S = -\alpha^{-1}(\alpha - 1) \log(1 - f)$ is used to determine α for DBK (experimental points: \circ, \square). The enrichment factor α' for PMAP can be obtained from extrapolation of the experimental points (\bullet, \blacksquare) to zero conversion. Initial ^{13}C content in the carbonyl of DBK. $\square, \blacksquare = 16.9\%$, $\circ, \bullet = 47.6\%$.

This expression demonstrates how the overall enrichment at any conversion, f , depends upon the quantum yields for disappearance of starting ketone.



Scheme 2

Based on a simplified mechanism shown in scheme 2, a testable correlation between the efficiency of intersystem crossing of the radical pair, Φ_{isc}^{TS} , and the measurable quantum yields (or enrichment parameter α) is predicted:

$$^{12}\Phi = ^{12}\phi_{isc}^{ST} ^{12}\phi_{cl}^T (1 - ^{12}\phi_{isc}^{TS} ^{12}\phi_{rec}), \quad (7a)$$

$$^{13}\Phi = ^{13}\phi_{isc}^{ST} ^{13}\phi_{cl}^T (1 - ^{13}\phi_{isc}^{TS} ^{13}\phi_{rec}). \quad (7b)$$

The low experimental ^{13}C enrichment in DBK when photolysis is conducted in various (protic or aprotic) solutions not containing micelles ($\alpha \lesssim 1.05$) [1,5] justifies the assumption that isotope effects on ϕ_{isc}^{ST} and ϕ_{cl}^T are negligible. Similarly we approximate $^{12}\phi_{rec}$ and $^{13}\phi_{rec}$ by the common value ϕ_{rec} neglecting the influence of a (small) ^{13}C kinetic mass isotope effect on this efficiency via an effect on the competing decarbonylation of $^3\bar{\text{D}}$. With these assumptions substitution of $\phi_{isc}^{TS} \phi_{cl}^T$ by ϕ_{cl} then leads to:

$$^{12}\Phi = \phi_{cl} (1 - ^{12}\phi_{isc}^{TS} \phi_{rec}), \quad (8a)$$

$$^{13}\Phi = \phi_{cl} (1 - ^{13}\phi_{isc}^{TS} \phi_{rec}). \quad (8b)$$

Eqs. (8a) and (8b) demonstrate that the disappearance quantum yields approach the efficiency ϕ_{cl} of generating radical pairs, whenever the efficiency of radical recombinations, ϕ_{rec} , is small. This limit is observed for photolysis of DBK in homogeneous solutions [6]. Similarly, the enrichment parameter α should approach unity under these circumstances, as is found [4].

3. Correlation of α' and quantum yields

The observation of PMAP as a reaction product and the determination of its ^{13}C content allow the correlation of a second isotopic enrichment parameter α' with the experimental quantum yield values. In analogy to eq. (4)

$$\alpha' = \frac{\text{rate of appearance of } ^{13}\text{C PMAP}}{\text{rate of appearance of } ^{12}\text{C PMAP}} = \frac{^{13}\Phi_{\text{PMAP}}}{^{12}\Phi_{\text{PMAP}}} \quad (9)$$

and correspondingly from scheme 2 and the assumptions analogous to those used to derive eqs. (8a) and (8b)

$$^{13}\Phi_{\text{PMAP}} = \phi_{cl} ^{13}\phi_{isc}^{TS} \phi'_{rec}, \quad (10a)$$

$$^{12}\Phi_{\text{PMAP}} = \phi_{cl} ^{12}\phi_{isc}^{TS} \phi'_{rec}, \quad (10b)$$

where a common radical pair path is assumed for the cyclic regeneration of DBK and the formation of PMAP.

Thus, within the assumptions and approximations of scheme 2 and of the preceding paragraph, α' equals directly the ratio of intersystem crossing efficiencies of

^{13}C and ^{12}C containing radical pairs.

$$\alpha' = ^{13}\phi_{isc}^{TS} / ^{12}\phi_{isc}^{TS}. \quad (11)$$

From eqs. (5) and (11) α' can be correlated with the disappearance quantum yields of DBK:

$$\alpha' = (\phi_{cl} - ^{13}\Phi) / (\phi_{cl} - ^{12}\Phi), \quad (12)$$

so that

$$^{12}\Phi = \phi_{cl} (\alpha \alpha' - \alpha) / (\alpha \alpha' - 1), \quad (13)$$

$$^{13}\Phi = \phi_{cl} (\alpha' - 1) / (\alpha \alpha' - 1). \quad (14)$$

4. Comparison of theory with experimental results

Values of α' and α were obtained experimentally from measurements of ^{13}C enrichment in DBK and in PMAP [7]. The major point of ^{13}C enrichment is the carbonyl carbon in both cases. For the photolysis of DBK in 0.05 M hexadecyltrimethyl ammonium chloride at 25°C a value of $\alpha' \approx 1.27$ and $\alpha \approx 1.45$ were determined. Both α and α' were strongly reduced, when the photolysis was conducted in the presence of a strong laboratory magnetic field (table 1). Thus a magnetic isotope effect is operating. Indeed, at 100 kG the values of α and α' are nearly 1.0, the value expected for the complete absence of a $^{13}\text{C}/^{12}\text{C}$ isotope effect of any type. This result provides strong experimental support for the assumption, that mass isotope effects contribute negligibly to the observed enrichments. From eq. (11), the value of α' of 1.27 represents the ratio of efficiencies of intersystem crossing of triplet radical pairs possessing ^{13}C and ^{12}C at the carbonyl carbon respectively.

From eqs. (13) and (14) a quantitative correlation

Table 1
Photolysis of DBK (10^{-3} M) in 0.05 M hexadecyltrimethylammonium chloride in water at 25°C a)

	Applied magnetic field		
	$H = 0$	$H = 14.5$ kG	$H = 100$ kG
α	1.45	1.15	1.02
α'	1.27	1.08	1.03

a) Precision in measurement of α and α' is better than $\pm 5\%$ in all cases

between α and α' is expected. Based on α and α' , the disappearance quantum yields $^{12}\Phi$ and $^{13}\Phi$ for DBK (in 0.05 M hexadecyltrimethyl ammonium chloride at 25°C) can be calculated to be $^{12}\Phi \approx 0.45 \phi_{cl}$ and $^{13}\Phi \approx 0.30 \phi_{cl}$. In other words, in the micelles used, after formation of the triplet radical pair, slightly more than 50% of the pairs possessing a ^{12}C at the carbonyl carbon are calculated to regenerate DBK, but about 70% of pairs possessing a ^{13}C at the carbonyl.

Correlation with the experimentally determined [4] quantum yields $^{12}\Phi \approx 0.24$ and $^{13}\Phi \approx 0.17$ require a low efficiency for formation of the radical pairs, $\phi_{cl} \approx 0.6$. Such a value for ϕ_{cl} is somewhat lower than in homogeneous (aprotic) solution (e.g. benzene $^{12}\Phi \approx 0.7-0.8$ [4,6]). This conclusion is consistent with a lower rate of cleavage of T_1 in the micellar environment as a result of a greater π, π^* character induced by the polar environment [8] near the micelle surface at which the ketone is expected to reside [9]. Alternatively, if enriched DBK and PMAP are formed via (totally or partially) different pathways, eqs. (11) or (13) and (14) begin to become inaccurate. Such a difference could arise via partial formation of radical pairs via S_1 or possibly because of non-identical time domains for the lives of the radical pairs responsible for recombination to form DBK or PMAP.

5. Conclusion

The isotopic enrichment due to a magnetic isotope effect supplies additional information concerning a photochemical reaction involving radical pairs. The correlation of the isotopic enrichment parameters with photochemical quantum yields provides a means to estimate photochemical parameters on the basis of enrichment measurements (and vice versa) as well as an independent check of the postulated reaction mechanism.

For the photolysis of DBK in micellar detergent solution, a low efficiency for radical formation is indicated.

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