

**THE DYNAMICS OF THE PHOTODECARBONYLATION OF DIBENZYLKETONE
IN A MICELLAR DETERGENT SOLUTION: EFFECT OF TEMPERATURE
ON THE ABSOLUTE QUANTUM YIELDS AND ON ^{13}C ENRICHMENT**

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An investigation is reported of the influence of temperature on the quantum efficiencies and ^{13}C enrichment efficiency of photolysis of dibenzylketone in micellar solution.

1. Introduction

The photodecarbonylation of dibenzylketone (DBK) in solution is accompanied by enrichment of ^{13}C in the starting material. This effect, originally found for photolysis of DBK in homogeneous solution [1] is enhanced by more than an order of magnitude in micellar detergent solution [2] and has been ascribed to result from a hyperfine coupling induced intersystem crossing in the radical pair generated by α -cleavage of the ketone, as a manifestation of a magnetic isotope effect [3]. Our explanation for the dramatically increased magnetic isotope effect in the micellar system is the action of micelles as "super cages", wherein radical pairs recombine efficiently. Further experimental support for this postulate has been provided by measurements of disappearance quantum yields for DBK ($\Phi_{\text{-DBK}}$) in homogeneous and micellar solutions at room temperature [4]. In benzene solution DBK is photolyzed with a quantum yield of nearly unity ($\Phi_{\text{-DBK}}^{\text{benzene}} \approx 0.84$), whereas a strongly decreased quantum yield is found in a 0.05 M aqueous solution of hexadecyltrimethylammonium chloride (HDTCl), in agreement with a

high recombination efficiency of radical pairs within the micelles ($\Phi_{\text{-DBK}}^{\text{HDTCl}} \approx 0.3$). Moreover, a recombination path for the primary radical pair, absent in homogeneous solution, resulted in the isolation of an isomeric ketone, 1-phenyl-*p*-methyl-acetophenone (PMAP). The latter material was also found to possess a substantial ^{13}C enrichment in the ketone carbonyl. This observation allows us to investigate the crucial stage of the phenacetylbenzyl radical pair from a second independent side [5].

For the photodecarbonylation of DBK in micellar detergent solutions, all the data supported the notion of a "reactive escape" [6] by decarbonylation instead of the ordinarily encountered "diffusive escape" of the spin correlated radical pair which is generally the life limiting factor of the pair in homogeneous solution. The rate of the escape reaction (the loss of carbon monoxide from the phenacetyl radical) is expected to be of crucial importance for the ^{13}C enrichment as well as most other kinetic parameters of the photoreaction. A study of the effect of temperature on the photodecarbonylation of DBK in aqueous 0.05 M HDTCl was undertaken in order to investigate the kinetics of CO-loss from the primary radical pair,

and to derive numerical values for several crucial efficiency parameters of the photoreaction.

2. ^{13}C enrichment studies: mass spectrometric analysis

Samples taken from a stock solution of 0.005 M DBK (containing 16.9% ^{13}C labelled carbonyl) in 0.05 M HDTCl were placed in quartz tubes, deoxygenated and thermostatted to the desired temperature. Photolysis with a medium pressure Hanovia Hg lamp to various conversions (in the range of 30–90%) resulted in reaction mixtures, from which the organic materials were recovered by extraction. Subsequently, these samples were subjected to VPC and VPC–MS analysis, and the total ^{13}C enrichment S for DBK and S' for PMAP were determined. The corresponding single step enrichment factors α and α' were then calculated[‡], and are plotted as a function of temperature in fig. 1.

[‡] The derivation of the correlation between the enrichment factors, α and α' and observed enrichment values and quantum yields is given in ref. [5], on the basis of a kinetic treatment of reactions with first-order kinetics by Bernstein [7].

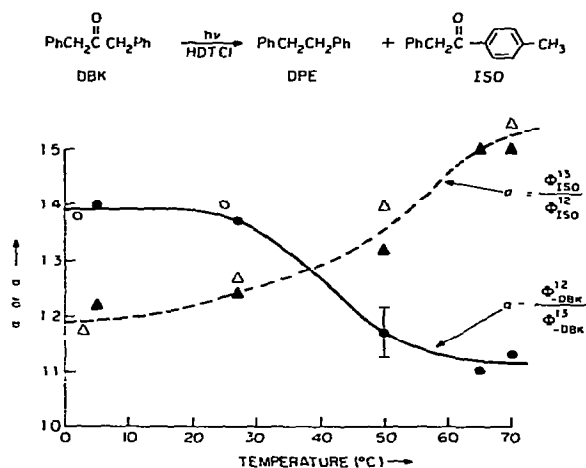


Fig. 1. Photolysis of ^{13}C -labelled dibenzylketone (0.005 M) in 0.05 M aqueous solution of hexadecyltrimethylammonium chloride (HDTCl) at various temperatures: single stage enrichment factors for starting material, α , and for the isomeric ketones, α' , as determined using ^{13}C -enrichment studies (full circles and triangles) and using quantum yield values (open circles and triangles).

3. ^{13}C enrichment studies: quantum yield measurements

The absolute disappearance quantum yields $\Phi_{\text{-DBK}}$ for DBK were determined for natural abundance DBK ($= \Phi_{\text{-DBK}}^{12}$) as well as for labelled DBK containing 90% ^{13}C in the carbonyl (^{13}C -DBK) for photolysis in Ar saturated aqueous 0.05 M solution of HDTCl, thermostatted to 27°C and 70°C. Relative quantum yields were also determined at various temperatures ranging from 5°C to 70°C (table 1)^{*}. The disappearance quantum yield for 100% ^{13}C -labelled DBK ($\Phi_{\text{-DBK}}^{13}$) was then extrapolated from these data. In the same set of measurements, the appearance quantum Φ_{ISO}^{12} and Φ_{ISO}^{13} for natural abundance PMAP and ^{13}C labelled PMAP were obtained.

4. Correlation between quantum yields and enrichment factors

As noted before [4,5], a quantitative correlation exists between the enrichment factors α and the DBK disappearance quantum yields

$$\alpha = \Phi_{\text{-DBK}}^{12} / \Phi_{\text{-DBK}}^{13} \quad (1a)$$

Similarly [5], the disappearance quantum yields for PMAP correlate with the enrichment factor α' ,

$$\alpha' = \Phi_{\text{ISO}}^{13} / \Phi_{\text{ISO}}^{12} \quad (1b)$$

The results presented here demonstrate a strong temperature dependence of α and α' (with opposite trends) as well as the validity of eqs. (1a) and (1b) at the temperatures where the Φ were measured.

5. Derivation of efficiency values

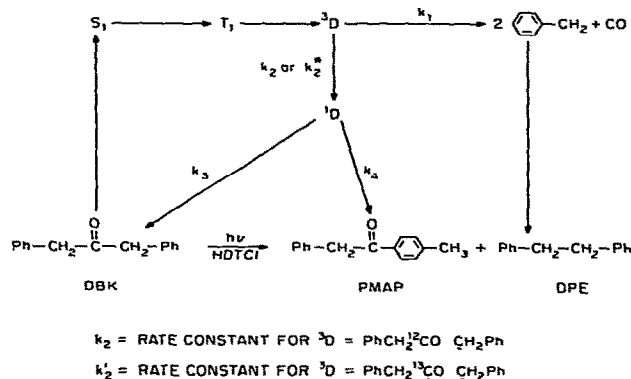
Based on the mechanism represented in scheme I, the efficiencies of the various steps may be extracted

^{*} The quantum yield measurements were performed in a thermostatted "merry-go-round" system, with a valerophenone/*t*-butanol ($\Phi = 1.0$, see ref. [8]) standard, light of 313 nm from a medium pressure Hanovia Hg lamp was selected using a K_2CrO_4 (5%) solution and a Corning 7-54 filter, 0.05 M dibenzyl ketones in 0.05 M aqueous, deoxygenated HDTCl were photolyzed to typically 10–20% conversion.

Table 1
Kinetic parameters for the photolysis of dibenzylketone in 0.05 M HDTCI a)

Compound	Temperature (°C)	$\Phi_{\text{-DBK}}$	Φ_{ISO}	Φ_{Cl}	$\Phi_{\text{-CO}}$ b)	Φ_{R} c)	τ	k_1 d) (10^7 s^{-1})	k_2 e) (10^7 s^{-1})	α f)	α' f)
DBK	27	0.30	0.060	0.64	0.38	0.85	1.7	5.4	8.8	1.38	1.24
^{13}C -DBK	27	0.22	0.074	0.64	0.23	0.85	3.3		18		
DBK	70	0.75	0.034	0.89	0.81	0.80	0.23	27	6.3	1.13	1.50
^{13}C -DBK	70	0.67	0.051	0.89	0.70	0.81	0.43		12		

a) Symbols, see text. b) Assuming $\Phi_{\text{-CO}} + \Phi_{\text{ISC}} = 1$. c) Assuming $\Phi_{\text{R}} + \Phi_{\text{IR}} = 1$.
d) Calculated via $k_2 = \Phi_{\text{ISC}}(k_2 + k_1)$. e) Calculated using values recommended in ref. [9].
f) Calculated from the quantum yields



from experimental measurements of the quantum yields for loss of DBK and for formation of ISO-DBK under the following assumptions. (1) no significant escape of the radicals composing ${}^3\text{D}$ and ${}^1\text{D}$ from micelles occurs, (2) the rate constants k_1 for decarbonylation and α -cleavage are not subject to a significant isotope effect and (3) the partitioning of ${}^1\text{D}$ to DBK and ISO-DBK is not subject to a significant isotope effect. Assumption (1) is justified because Cu^{2+} scavenging does not influence the quantum yield for loss of DBK [4]. Assumptions (2) and (3) are justified because $^{12}\text{C}/^{13}\text{C}$ mass isotope effects are generally of the order of a few per cent of the observed effects and because magnetic isotope effects on the cleavages and combinations are unprecedented. More direct experimental support of assumptions (2) and (3) are presently being sought.

From scheme 1, with assumptions (1), (2) and (3)

the experimental quantum yields for loss of DBK and for formation of ISO-DBK are given by:

$$\Phi_{\text{-DBK}}^{12} = \Phi_{\text{Cl}}(\Phi_{\text{-CO}} + \Phi_{\text{ISC}}\Phi_{\text{IR}}), \quad (2)$$

$$\Phi_{\text{-DBK}}^{13} = \Phi_{\text{Cl}}(\Phi_{\text{-CO}} + \Phi'_{\text{ISC}}\Phi_{\text{IR}}), \quad (3)$$

$$\Phi_{\text{ISO}}^{12} = \Phi_{\text{Cl}}(\Phi_{\text{ISC}}\Phi_{\text{IR}}), \quad (4)$$

$$\Phi_{\text{ISO}}^{13} = \Phi_{\text{Cl}}(\Phi'_{\text{ISC}}\Phi_{\text{IR}}). \quad (5)$$

In eqs. (2)–(5), Φ_{Cl} is the quantum yield for cleavage of electronically excited DBK into a triplet $\text{PhCH}_2\dot{\text{C}}\text{O}\dot{\text{C}}\text{H}_2\text{Ph}$ radical pair ${}^3\text{D}$; rate constants with primes refer to steps involving radical pairs possessing ^{13}C at the carbonyl carbon atom which are expected to be subject to a substantial magnetic isotope effect; Φ_{ISC} is the state efficiency for intersystem crossing of ${}^3\text{D}$ to ${}^1\text{D}$, Φ'_{ISC} is the state efficiency for intersystem crossing of ${}^3\text{D}'$ to ${}^1\text{D}$; and Φ_{IR} and Φ_{R} are state efficiencies for recombination of ${}^1\text{D}$ to form ISO-DBK and DBK, respectively, $\Phi_{\text{-CO}}$ is the state efficiency for decarbonylation of ${}^3\text{D}$.

From the definitions of α and α' eqs. (2) and (3) may be alternatively expressed as

$$\Phi_{\text{-DBK}}^{12} = \Phi_{\text{Cl}}(\alpha\alpha' - \alpha)/(\alpha\alpha' - 1), \quad (6)$$

$$\Phi_{\text{-DBK}}^{13} = \Phi_{\text{Cl}}(\alpha' - 1)/(\alpha\alpha' - 1). \quad (7)$$

Since $\Phi_{\text{-DBK}}$, Φ_{ISO} , α and α' are experimentally measurable quantities, eqs. (6) and (7) allow access to the quantum yield and state efficiency in eqs. (2)–(5).

First, the value of Φ_{Cl} may be evaluated directly

from eqs (6) and (7) from measurement of Φ_{-DBK}^{12} , Φ_{-DBK}^{13} , α and α' . The values of Φ_{Cl} obtained thereby are listed in table 1. Under the assumption that triplet radical pairs (3D) undergo only intersystem crossing to 1D or decarbonylate (i.e., $\Phi_{-CO} + \Phi_{ISC} = 1$), the values of the state efficiencies Φ_{-CO} and Φ_{ISC} may be evaluated. Finally, from the quantum yield for formation of ISO-DBK and the value of Φ_{Cl} , the state efficiencies Φ_R and Φ_{IR} may be evaluated.

6. Discussion

From the experimentally determined absolute quantum yield values and ^{13}C enrichment factors for the photolysis of partially labelled DBK in 0.05 M HDTCl solution, a strong temperature dependence is apparent. Upon raising the temperature, the enrichment factor α decreases while the disappearance quantum yield Φ_{-DBK} increases sharply. Inspection of table 1 shows the main factor responsible for an increased Φ_{-DBK} to be the greatly diminished efficiency of recombination of the photogenerated radical pair, represented by an increase of the decarbonylation efficiency, Φ_{-CO} (a slight influence by an increase of Φ_{Cl} with temperature probably adds to the overall effects). Indeed, the two reaction channels available for the phenacetylbenzyl radical pair 3D decarbonylation and recombination, are populated with strongly different efficiencies depending upon the photolysis temperature for DBK, at 27°C, 38% of the reacting molecules follow the decarbonylation path, contrasting with 81% at 70°C, etc. (table 1).

The decreased efficiency for radical pair recombination manifests itself also in a strongly decreased chemical yield of the product of the second recombination, PMAP, at elevated temperature. However, there seems to be no significant effect of the temperature on the partitioning of the two recombination paths, i.e., Φ_R and Φ_{IR} do not depend on temperature. Projected from the quantum yield measurements, the relative yield of PMAP (20% at 27°C for DBK) decreases by a factor of ca. 5 upon raising the temperature to 70°C. A similar decrease is also noted in the preparative scale experiments.

Quite in contrast, however, to the effect of temperature on α , the ^{13}C enrichment determined in

PMAP and expressed by the single stage enrichment factor α' shows the opposite dependence on temperature. Indeed, *the enrichment efficiency increases with increasing temperature*. A rationale for this effect can be found by considering the time scales for hfc induced intersystem crossings and the decarbonylation reaction.

For the purpose of comparison, it is convenient to look at the corresponding efficiency ratios $\zeta = \Phi_{ISC}/\Phi_{-CO} = k_2/k_1$ (assuming that ISC is the rate limiting step preceding the radical pair recombination), listed in table 1. If $^{13}C/^{12}C$ mass isotope effects on k_1 is assumed to be unimportant, $\zeta(^{13}C-DBK)/\zeta(DBK) = k'_2/k_2 \approx 2$, i.e., the ratio of the ISC rate constants for the two isotopomeric radical pairs thus obtained does not depend significantly on the temperature. Finally, using the estimated rate constants for decarbonylation [9] listed in table 1, also the absolute values of the ISC rates k_2 and k'_2 for DBK and $^{13}C-DBK$ do not show a strong temperature dependence. An order of magnitude estimate of the hfc induced ISC frequency, k_{ISC} , can be independently obtained based on the measured hfc constants, using the equation [10]

$$k_{ISC} \approx 3 \times 10^6 a I s^{-1} G^{-1}, \quad (8)$$

where a is the coupling constant in gauss with the nucleus of spin I . Using only the most relevant nuclei (benzyl protons and carbonyl ^{13}CO in the primary radical pairs derived from DBK and $^{13}C-DBK$), a rough estimate yields $k_{ISC}^{12} \approx 4 \times 10^7 s^{-1}$ and $k_{ISC}^{13} \approx 2 \times 10^8 s^{-1}$ for DBK and $^{13}C-DBK$ derived radical pairs, respectively. These values should be compared to the data in table 1. We feel that, considering the approximate nature of the rate values, the agreement between the two sets of numbers is acceptable. Indeed, the lack of a strong temperature dependence on the ISC-rates, as indicated in table 1, supports the mechanistic picture of a hfc induced ISC, as it should depend only indirectly on temperature modulated processes (i.e., molecular motions). *The estimated value obtained for the ratio of ISC rate constants on the basis of the experimental rate data, $k'_2/k_2 \approx 2$, can be taken as the direct measure of the kinetic isotope effect due to the ^{13}C -spin.*

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