MAGNETIC ISOTOPE EFFECT AND ISOTOPE SEPARATION IN THE PHOTOLYSIS OF DIBENZYL KETONE: DEPENDENCE ON VISCOSITY AND THE ELECTRON – NUCLEAR INTERACTION

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The magnetic (nuclear spin) isotope effect leads to a redistribution of the isotopes in the products from chemical radical reactions. The efficiency of this redistribution is characterized by the quantity [1, 2]

$$\alpha=\frac{1}{v}\frac{dR}{dt}\Big/\frac{1}{v^*}\frac{dR^*}{dt} \tag{1}$$

where v and v* are the rates of formation of radicals (radical pairs) differing in isotopic composition, and dR/dt and dR*/dt are the rates of formation (consumption) of the products, respectively.

If the kinetic regime of the reaction satisfies steady-state conditions, then (dR/dt)/v is simply the fraction of radicals (or radical pairs) generated which form the product being considered. If the corresponding fractions are equal, then $\alpha = 1$ and no redistribution of the isotopes at all takes place. The value of α is determined principally by three factors, viz., the viscosity of the solvent in which the reaction is being carried out, the magnitude of the electron–nuclear hyperfine interactions (hfi constants) in the radicals, and the rate of the chemical reactions of the radicals.

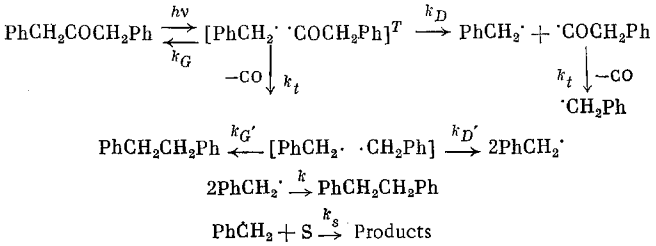
In this investigation we have studied the dependence of the efficiency in the redistribution of the magnetic isotopes on the viscosity of the solvent, taking the photolysis of dibenzyl ketone (DBK) as the example.

EXPERIMENTAL

DBK ($2\cdot10^{-2}$ M) was photolyzed in a thermostatted quartz cuvette by light from a DRSh-1000 (280 nm) Hg lamp at 1 ∓ 0.5°C in glycerol–tert-butanol mixtures (1:4, 2:3, 1:1 and 7:3, respectively). The conversion of DBK was determined by GLC on a Tsvet-104 chromatograph (column 1 m × 3 mm, stationary phase OV-1 on Super Inerton, internal standard benzophenone). Isotopic analysis was conducted mass spectrometrically by the method described in [3]. Analytical-grade glycerol was used without further purification, and tert-butanol was purified by well-known procedures. The photolytic products were separated by thin-layer chromatography and high-performance liquid column chromatography.

DISCUSSION OF RESULTS

The photochemical reactions of DBK [4-6] can be represented by the scheme



$$PhCH_2COCH_2Ph \underset{k_G}{\overset{h\nu}{\rightleftarrows}} [PhCH_2^{\cdot}\ {}^{\cdot}COCH_2Ph]^T \xrightarrow{k_D} PhCH_2^{\cdot} + {}^{\cdot}COCH_2Ph$$

$$[PhCH_2^{\cdot}\ {}^{\cdot}COCH_2Ph]^T \xrightarrow[k_t]{-CO} [PhCH_2^{\cdot}\ {}^{\cdot}CH_2Ph]; \qquad {}^{\cdot}COCH_2Ph \xrightarrow[k_t]{-CO} {}^{\cdot}CH_2Ph$$

$$PhCH_2CH_2Ph \xleftarrow{k_G'} [PhCH_2^{\cdot}\ {}^{\cdot}CH_2Ph] \xrightarrow{k_D'} 2PhCH_2^{\cdot}$$

$$2PhCH_2^{\cdot} \xrightarrow{k} PhCH_2CH_2Ph$$

$$Ph\dot{C}H_2 + S \xrightarrow{k_s} \text{Products}$$

In the photodissociation of DBK a primary triplet geminal radical pair (RP) is formed, which either recombines to form the original DBK or is consumed in forming acyl and benzyl free radicals, or is transformed into a secondary geminal RP of benzyl radicals, due to the dissociation of an acyl radical. The benzyl radicals do not disproportionate but form dibenzyl (DB) on recombination. Since the rate constant for the decarbonylation

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of acyl radicals is low ($k_t \simeq 2 \cdot 10^8$ sec^{-1} [5]), in the absence of active radical scavengers even in such a low-activity solvent as glycerol the scavenging of these radicals can be neglected, this being more true for geminal RP [7]. On the other hand, the scavenging of benzyl radicals cannot be neglected because the yield of DB lies within the range 45-60%, increasing to some extent with the content of tert-butanol. The effective scavenging of these radicals is certainly connected with a small constant for diffusion encounters (under our conditions $2k_{diff} \simeq 10^6$ liters/mole·sec).

The variation in the isotopic composition in DBK and DB is chiefly associated with the variation in the isotope content in the CO and CH_2 groups. It is therefore meaningful to consider the kinetics of the isotopic enrichment of six types of DBK molecules having the fragments

$$\begin{array}{ll} CH_2COCH_2\ (c_1) & \overset{*}{C}H_2COCH_2(c_2) \\ CH_2\overset{*}{C}OCH_2\ (c_3) & \overset{*}{C}H_2\overset{*}{C}OCH_2(c_4) \\ \overset{*}{C}H_2CO\overset{*}{C}H_2\ (c_5) & \overset{*}{C}H_2\overset{*}{C}O\overset{*}{C}H_2(c_6) \end{array} \tag{2}$$

The asterisk signifies the presence of the isotope ^{13}C, and the concentrations of the corresponding molecules are indicated in parentheses (molecules whose CH_2COCH_2 fragment contains ^{13}C will be called magnetic). From these six types of molecules eight types of radical pairs may be formed (the probabilities of the geminal recombination of these pairs are indicated in parentheses)

$$\begin{array}{ll} CH_2CO^{\cdot\cdot}CH_2\ (\tilde{p}_1) & \overset{*}{C}H_2CO^{\cdot\cdot}CH_2\ (\tilde{p}_2) \\ CH_2\overset{*}{C}O^{\cdot\cdot}CH_2(\tilde{p}_3) & CH_2CO^{\cdot\cdot}\overset{*}{C}H_2\ (\tilde{p}_4) \\ \overset{*}{C}H_2C\overset{*}{O}^{\cdot\cdot}CH_2\ (\tilde{p}_5) & \overset{*}{C}H_2CO^{\cdot\cdot}\overset{*}{C}H_2\ (\tilde{p}_6) \\ CH_2\overset{*}{C}O^{\cdot\cdot}\overset{*}{C}H_2\ (\tilde{p}_7) & \overset{*}{C}H_2\overset{*}{C}O^{\cdot\cdot}\overset{*}{C}H_2\ (\tilde{p}_8) \end{array}$$

The contribution to the total isotopic composition of molecules having two or three ^{13}C isotopes in the fragments listed can, of course, be neglected in the case of DBK having a natural ^{13}C content ($\simeq 1.1\%$). However, it is appropriate to take account of these pairs from the point of view of a kinetic analysis of the problem and, what is far more important, it provides the possibility of discussing the dependence of the isotope separation efficiency (α) on the effective hfi constant in a RP.

Since only processes in geminal RP are important for the kinetics of DBK consumption, then for each of the six types of molecules we have

$$dc_i/dt = -v_i\,(1 - p_i) \tag{3}$$

$$v_i = \chi c_i$$

where

$$p_1 = \tilde{p}_1;\ p_2 = (\tilde{p}_2 + \tilde{p}_4)/2;\ p_3 = \tilde{p}_3$$

$$p_4 = (\tilde{p}_5 + \tilde{p}_7)/2;\ \ p_5 = \tilde{p}_6;\ p_6 = \tilde{p}_8$$

$$\chi = \int\limits_{\lambda\,280\,\text{nm}}^{\infty} \varphi I_0 \varepsilon \frac{1 - \exp\left\{\left(\varepsilon \sum\limits_{i=1}^{6} c_i + \varepsilon_s c_s\right) l\right\}}{\left(\varepsilon \sum\limits_{i=1}^{6} c_i + \varepsilon_s c_s\right) l}\, d\lambda \tag{4}$$

ε being the extinction coefficients of DBK in the region $\lambda \geq 280$ nm (we consider that ε is independent of the isotopic composition of the molecule); $\varepsilon_s c_s$ takes account of the shielding due to the formation of secondary products; l is the optical length; φ is the quantum yield for pair formation, identical for all types of molecules; I_0 is the spectral density of the incident light.

Using the definition (1) for each type of molecule we obtain from (3)

$$\alpha_{G_i} = \left(\frac{1}{v_1}\frac{dc_1}{dt}\right) \Big/ \left(\frac{1}{v_i}\frac{dc_i}{dt}\right) = \frac{1 - p_1}{1 - p_i} \tag{5}$$

The subscript G signifies that only geminal recombination processes are taken into account. Since the p_i values are independent of time, then Eq. (5) is readily integrated and we obtain

$$\ln\,(1 - f_1) = \alpha_{G_i} \ln\,(1 - f_i) \tag{6}$$

where $(1 - f_1)$ represents the conversion of nonmagnetic DBK molecules, and $(1 - f_i)$ represents the conversion of magnetic (i.e., containing ^{13}C) DBK molecules.

Let r_1 be the probability that a carbon nucleus in the CO position in the DBK molecule is magnetic (^{13}C), and r_2 be the corresponding probability for the CH_2 position. Then the concentrations c_i can be expressed through the overall concentration c

$$c_i = a_i c \tag{7a}$$

where a_i is the probability of a particular one of the isotopic configurations for the CH_2COCH_2 fragment listed above being in the DBK molecule

$$\begin{aligned} a_1 &= (1 - r_1)(1 - r_2)^2 & a_4 &= 2\,(1 - r_2) r_2 r_1 \\ a_2 &= 2\,(1 - r_1)(1 - r_2)\, r_2 & a_5 &= (1 - r_1)\, r_2^2 \\ a_3 &= (1 - r_2)^2\, r_1 & a_6 &= r_1 r_2^2 \end{aligned} \tag{7b}$$

Using the expressions (7) we obtain a connection between the experimentally measured conversion

$$1 - f_e = \Big(\sum_{i=1}^{6} c_i\Big) \Big/ \Big(\sum_{i=1}^{6} c_{i0}\Big)$$

and the conversion with respect to a given type of isotopic molecules $(1 - f_i)$

$$1 - f_i = (1 - f_e)\, a_i / a_{i0} \tag{8}$$

where a_{i0} relate to the initial state ($a_{i0} = a_i$ for $f_i = 0$).

Subsequently we assume in the calculations that in the initial state $r_1 = r_2 = r_0$, i.e., the initial content of the isotope is the same for any position in the DBK molecule, while for the phenyl rings it does not vary during photolysis.

The changes in the isotopic composition in the DB molecules are associated exclusively with a change in the ^{13}C content in the CH_2 groups. DB is formed on recombination of secondary RP and in diffusion pairs. The contribution of the diffusion RP to the efficiency of redistribution of the isotopes can be neglected [2]. We can show that in this case the competition between the scavenging of benzyl radicals liberated into the bulk and their recombination does not lead to an additional redistribution of the isotopes. Based on the scheme for the photochemical reactions of DBK we can write to a steady-state approximation

$$(d\mathrm{CH}_2/dt)_\mathrm{R} = A\varphi_\mathrm{R}$$
$$(d\overset{*}{\mathrm{C}}\mathrm{H}_2/dt)_\mathrm{R} = B\varphi_\mathrm{R}^*$$

$(d\mathrm{CH}_2/dt)_\mathrm{R}$ and $(d\overset{*}{\mathrm{C}}\mathrm{H}_2/dt)_\mathrm{R}$ being the rates of accumulation of the CH_2 and $\overset{*}{\mathrm{C}}\mathrm{H}_2$ groups in the DB molecules as a result of the recombination of random RP; A and B are the rates of formation of the magnetic and nonmagnetic free benzyl radicals; φ_R and φ_R^* are the fractions of recombining radicals, and $1 - \varphi_\mathrm{R}$ and $1 - \varphi_\mathrm{R}^*$ are the fractions of scavenged radicals. Here

$$\varphi_\mathrm{R} = \varphi_\mathrm{R}^* = 4k\,(A + B)/[k_s + \sqrt{k_s^2 + 4k\,(A + B)}]^2$$

Then

$$\alpha_\mathrm{R} = \left(\frac{1}{A}\frac{d\,\mathrm{CH}_2}{dt}\right) \Big/ \left(\frac{1}{B}\frac{d\,\overset{*}{\mathrm{C}}\mathrm{H}_2}{dt}\right) = \frac{\varphi_\mathrm{R}}{\varphi_\mathrm{R}^*} = 1$$

We note that this result is valid only under steady-state conditions.

For the recombination of secondary geminal RP in which additional redistribution of isotopes is possible we can write

$$(d\mathrm{CH}_2/dt)_{G'} = 2v_1'p_1' + v_2'p_2'$$
$$(d\overset{*}{\mathrm{C}}\mathrm{H}_2/dt)_{G'} = v_2'p_2' + 2v_3'p_3'$$

where $(d\mathrm{CH}_2/dt)_{G'}$ and $(d\overset{*}{\mathrm{C}}\mathrm{H}_2/dt)_{G'}$ are the rates of accumulation of the CH_2 and $\overset{*}{\mathrm{C}}\mathrm{H}_2$ groups in the DB molecules due to recombination of the secondary geminal RP; v_1', v_2', and v_3' are respectively the rates of formation of $[\mathrm{CH}_2{\cdot}\mathrm{CH}_2]$, $[\mathrm{CH}_2{\cdot\cdot}\overset{*}{\mathrm{C}}\mathrm{H}_2]$, and $[\overset{*}{\mathrm{C}}\mathrm{H}_2{\cdot\cdot}\overset{*}{\mathrm{C}}\mathrm{H}_2]$, these being secondary geminal pairs; p_1', p_2', and p_3' are the probabilities of their recombination. Then, neglecting the contribution from the $v_2'p_2'$ term to $(d\mathrm{CH}_2/dt)_\mathrm{G}$ and of $2v_3'p_3'$ to $(d\overset{*}{\mathrm{C}}\mathrm{H}_2/dt)_\mathrm{G}$, i.e., with an accuracy to 10^{-2}, we obtain

TABLE 1. Values of α_{G_i} for the Photolysis of Dibenzyl Ketone*

t-BuOH : $C_3H_5(OH)_3$	$\alpha_{G_2} \pm 0{,}01$	$\alpha_{G_3} \pm 0{,}02$	$\alpha_{G_4} \pm 0{,}03$	$\alpha_{G_5} \pm 0{,}02$	$\alpha_{G_1} \pm 0{,}04$
1 : 4	1,07	1,13	1,22	1,14	1,32
2 : 5	1,09	1,19	1,31	1,19	1,47
1 : 1	1,08	1,24	1,37	1,18	1,53
7 : 3	1,07	1,17	1,27	1,15	1,38

* The values of α_{G_i} are obtained by averaging three to four measurements for different conversions.

$$\alpha_G' = \left[\frac{1}{2v_1'}\left(\frac{d\,CH_2}{dt}\right)_G'\right] \Big/ \left[\frac{1}{v_2'}\left(\frac{d\,\overset{*}{C}H_2}{dt}\right)_G'\right] = \frac{p_1'}{p_2'}$$

The secondary geminal pairs retain the multiplet nature of the primary pairs, $p_2' > p_1'$; consequently, $\alpha_G' < 1$ (for products being reformed this signifies enrichment).

Thus, the recombination of secondary geminal pairs should lead to an additional redistribution of the isotopes in the direction of an enrichment of ^{13}C in DB. However, there are a number of reasons why this additional redistribution may not affect the ^{13}C content effectively in the CH_2 groups in DB. First, only some of the primary RP are converted into secondary RP; second, not all the radicals liberated into the bulk are scavenged and their recombination compensates the change in the ^{13}C content in the DB molecules formed in the geminal pairs. (In the absence of scavenging, where $k_S = 0$, this compensation is total.) Third, and this is most important in our view, the initial spin state of the secondary RP cannot be considered as a purely triplet state. In fact, the rate constant for the singlet–triplet transitions in the RP k_{ST} is proportional to the effective hfi constant A_{eff}. For primary RP $k_{ST} \simeq 5 \cdot 10^8$ sec^{-1}, and $k_t \simeq 2 \cdot 10^8$ sec^{-1}. This means that at the moment a primary geminal pair is converted to a secondary pair it may alter its multiplet nature or lose the spin correlation in general. These considerations lead to the conclusion that isotopes are also not redistributed in secondary geminal pairs.

Experiment confirms this conclusion. In fact, if the redistribution were effective, then for very high conversions of DBK, where the contribution of the CH_2 groups in DBK to the total isotopic composition of the CH_2 groups in DB and DBK can be neglected, dibenzyl should be enriched. However, even for 96% conversion of DBK in the tert-butanol–glycerol (1:1) system, DB is depleted in ^{13}C in the CH_2 group compared with the initial ^{13}C content in the CH_2 group of DBK, this depletion being 0.2%.

Thus, it can be stated that ^{13}C is redistributed among the CH_2 groups in DB and DBK in primary geminal pairs, and since the formation of DB does not lead to additional redistribution of the isotopes, the total isotopic composition of the CH_2 groups in DB and DBK should remain unchanged. Hence follows the isotopic balance equation

$$[\overset{*}{C}H_2]/[CH_2] = \left(\sum_i{}^{*} c_{i0} f_i\right) \Big/ \left(\sum_i c_{i0} f_i\right) = r_2'/(1 - r_2') \tag{9}$$

where $r_2'/(1 - r_2')$ is the ^{13}C content in the DB molecules, and the asterisk indicates summation with respect to those types of DBK molecules which contain ^{13}C in a CH_2 group of the CH_2COCH_2 fragment.

Using Eqs. (8) and (7b) we obtain

$$r_2'/(1 - r_2') = \left[\sum_i{}^{*} a_{i0} - (1 - f_e) \sum_i{}^{*} a_{i0}\right] \Big/ \left[\sum_i a_{i0} - (1 - f_e) \sum_i a_i\right] =$$
$$= [r_0 - (1 - f_e)\, r_2]/[1 - r_0 - (1 - f_e)(1 - r_2)]$$

Hence

$$r_0 = r_2' f_e + (1 - f_e)\, r_2 \tag{10}$$

Thus, the scheme for calculations of α_{G_i} appears to be as follows. The experimentally determined value of $\delta = {}^{13}C/{}^{12}C$ is connected with the average ^{13}C content in the molecule $\langle r \rangle$ by the relationship

$$\langle r \rangle = \delta/(1 + \delta) \tag{11}$$

Since the ^{13}C content in the phenyl rings of the molecules does not vary during photolysis, then for the DB molecules the condition

$$14 \langle r \rangle_{\mathrm{DB}} = 12 r_0 + 2 r_2' \tag{12}$$

is satisfied. From the experimentally measured values of r_0 and $\langle r \rangle_{\mathrm{DB}}$ we obtain the value of r_2'. For DBK molecules the isotopic balance is satisfied by the condition

$$15 \langle r \rangle_{\mathrm{DBK}} = 12 r_0 + 2 r_2 + r_1$$

where $\langle r \rangle_{\mathrm{DBK}}$ is measured experimentally. Now we find the value of $1 - f_i$ from Eq. (7b) and (8) and the experimentally measured conversion $1 - f_e$, and then the values of α_{Gi} from Eq. (6) (Table 1).

Although a theoretical analysis of α_{Gi} will be given in a subsequent paper, two conclusions should be drawn here:

1) The effective hfi constants in the RP considered vary in the sequence $A_{6\mathrm{eff}} > A_{4\mathrm{eff}} > A_{3\mathrm{eff}} > A_{5\mathrm{eff}} > A_{2\mathrm{eff}}$. It is seen from the table that values of α_{Gi} also vary in precisely the same sequence. Thus, the first conclusion from the theoretical analysis in [1, 2], viz., that the efficiency of isotope separation is higher, the greater the difference between the effective electron–nuclear interactions in magnetic and nonmagnetic RP, has been confirmed experimentally.

2. The viscosity of the solvent decreases monotonically with an increase in tert-butanol content, but the values of α_{Gi} pass through a maximum for all pairs. Thus, the second postulate of the theory, viz., that optimal values of the viscosity of a medium exist where the isotope separation is most efficient, has been confirmed experimentally.

CONCLUSIONS

1. The variations in the ^{13}C content in molecules of dibenzyl ketone (DBK) on photolysis and in molecules of dibenzyl (a photolytic product of DBK) have been measured.

2. The efficiency of isotope separation is higher, the greater the difference between the effective electron–nuclear interactions in magnetic and nonmagnetic RP. Isotope separation takes place most efficiently at a specific optimal viscosity of the solvent in which the reaction is being carried out.

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