CONCLUSIONS

1. The kinetics of the alkaline hydrolysis of $Me_2P(S)OC_6H_4X$ -p and $MeC(O)OC_6H_4X$ -p in mixtures of water with different THF content at 25°C were studied spectrophotometrically.

2. A change in the character of the joint influence of substituent X and the medium on transition from mixtures containing 0-50% of THF to mixtures containing 60-80% of THF has been discovered.

3. A linear dependence of $\rho(II)$ on $\rho(I)$ has been shown in mixtures of water with ethanol, dioxane, acetonitrile, and THF, indicating the similarity of specific mechanisms of the alkaline hydrolysis of phosphinates and acetates in these media.

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CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION AND THE MECHANISM FOR THE PHOTOLYSIS OF SOME DIALKYL AND ARYL ALKYL KETONES

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The photolysis of carbonyl compounds and, especially, of ketones has been studied extensively with the aim of finding efficient photoinitiators for chain reactions of industrial importance [1]. Interest in the photochemistry of ketones has increased with the discovery of the magnetic isotope effect and the new principle of isotope enrichment in chemical reactions [2, 3].

In the present work, results are given for a study of chemically induced dynamic nuclear polarization (CIDNP) and the mechanism of the photochemical reactions of the following ketones: methyl n-propyl ketone $CH_3COCH_2CH_2CH_3$ (I), methyl benzyl ketone $PhCH_2COCH_3$ (II), and adamantyl ketone $CH_3COC_{10}H_{15}$ (III).

<u>The Photolysis of Ketone (I)</u>. CIDNP of the starting ketone molecules and the products arises in the photolysis of (I) (Figs. 1 and 2). The assignment of the lines and CIDNP signs are given in Table 1. The CIDNP of ketone (I) indicates the cleavage of the α -bond (Norrish type-I cleavage) along with intramolecular photoreduction which is characteristic for carbonyl compounds with hydrogen atoms in the γ -position. The biradical formed in the intramolecular photoreduction undergoes two types of transformation (scheme I [4]): Norrish type-II cleavage with the formation of an olefin and the enol form of the ketone (pathway A), and cyclization to give cyclobutanol (pathway B). These products, namely, a cyclic alcohol, ethylene, and acetone (the enol transformation product) were identified by NMR spectroscopy. However, CIDNP was not found, probably as a consequence of strong exchange interaction of the electrons in the biradical which suppresses the triplet—singlet conversion at the given magnetic field (H \approx 21 T). In principle CIDNP in the biradical conversion products may be seen in magnetic fields when g β H \sim 2J. Since J in the given biradical is large, this condition is satisfied only at very high H.

In the case of α -cleavage of the excited ketone (I), a radical pair (RP) is formed which undergoes two types of transformations within the solvent cage: recombination with regeneration of the starting ketone, and disproportionation with the formation of propylene and acetaldehyde. CIDNP is observed specifically in these three products. The positive polarization of the aldehyde proton in CH₃CHO and the negative polarization of the α - and γ -hydrogen atoms

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Fig. 1. PMR spectra of ketone (I): a) initial spectrum and b) spectrum during photolysis. Signals for the product nuclei: 1) CH₃CHO; 2) CH₃--CH=CH₂; 3) CH₃--CH=CH₂; 4) CH₂=CH₂; 5) not identified; 6) CH₃COCOCH₃; 7) C₄H₆(OH)CH₃; *) CD₃C; and **) the H₂O signal which is broadened and shifted upfield during the photolysis.

of the propyl group indicate the formation of AcH due to the transfer of a β -hydrogen atom of the propyl group to the acyl group. The CH₃CO and CH₂CO protons of the regenerated ketone are negatively polarized while the CH₃CH₂ protons are not polarized since the coupling constant for the methyl protons in the propyl group is negligibly small.

Alternation of the signs of the polarization of the carbon atoms of the propyl group of ketone (I) is clearly seen in the ¹³C CIDNP spectra (Fig. 2 and Table 1) which indicates alternation of the signs of the coupling constants on the ¹³C nuclei in the n-propyl group.

The ¹H and ¹³C CIDNP signs unequivocally indicate that the primary RP is formed in the triplet state and the photolysis occurs through the triplet state of the ketone. The radicals which avoid recombination in the primary RP depart into the bulk and participate in diffusional encounters, forming F-pairs, and give the same products as in the pairs with the same polarization sign. In the presence of RSH radical acceptors, this reaction pathway is suppressed and, thus, the CIDNP intensity of the products drops (Table 1).

The CH₃CO radicals which escape into the bulk give biacetyl with a polarization sign opposite to that of the cage products. In the presence of a radical trap, biacetyl is not formed as expected.

Since the nuclear polarization of the aldehyde and starting ketone is produced in the same radical pair, the ratio of the integral intensities of the CIDNP signals of these products permits us to evaluate the ratio of the probabilities for recombination and disproportionation in the pair by using the following equation [5]:

$$I_{\text{ald}} / I_{\text{ket}} = \left(\frac{\alpha_{\text{dispr}}}{\alpha_{\text{rec}}}\right) \left(\frac{T_{1 \text{ ald}}}{T_{1 \text{ ket}}}\right)$$



Fig. 2. ¹³C NMR spectra of ketone (I): a) initial spectrum; b) spectrum during photolysis.

| | | | CNP | sign ^b |
|--|--------------|----------|---------------------|-------------------|
| Product | Nucleus | ó, ppm | with- out RSH | with RSH |
| CH COCH CH CH | | 0.04 | | |
| CH3COCH2CH2CH3 | | 0,94 | - | |
| | H_3CH_2 | 1,60 | A | A' < A |
| | CH₃CO | 2,12 | E | $E' \ll E$ |
| | CĤ₂CO | 2,47 | E | E' < E |
| | ĈH₃CH₂ | 13,52 | A | - |
| | CH₃CH₂ | 17,55 | Ε | - |
| | CH₂CO | 45,50 | A | |
| | ĈH₃CO | 29,50 | Ε | - |
| | Ĉo | 209,2 | Ε | - |
| CH3CHO | CHO | 9,76 | A | $A' {<} A$ |
| $CH_{3}CH = CH_{2}$ | $C\hat{H}_2$ | ~ 5 | Ε | |
| | CĤ | ~6 | A | · _ |
| CH ₃ COCOCH ₃ | CĤ̃₃ | 2,31 | Α | None |
| (CH ₃) ₂ CO | CH̃₃ | 2,15 | None | » |
| $\mathrm{C_4H_6}\left(\mathrm{OH}\right)\mathrm{CH_3}$ | CĤ₃ | 1,33 | » | » |
| $CH_2 = CH_2$ | CH̃₂ | 5,47 | » | » |

TABLE 1. Assignment of Lines in the NMR Spectra and CIDNP signs in the Photolysis of Ketone $(I)^a$

^aThe asterisks indicate nuclei whose chemical shifts are given in the next column. ^bA' and A indicate enhanced absorption while E' and E indicate emission in the NMR spectra. The prime signs relate to CIDNP in the presence of RSH

radical trap.

where I is the CIDNP signal intensity, T_1 is the nuclear relaxation time in the aldehyde and ketone molecules, and α is the probability of the formation of these molecules in a pair, i.e., the probability of the disproportionation and recombination reactions.

The measured relaxation times of the acetyl and methyl protons of the initial ketone have the following values: $T_{1ald} = 32$ sec and $T_{1ket} = 14$ sec. Since the integral intensities per proton are related as $I_{ald}/I_{ket} = 3/4$, we find that $\alpha_{dispr}/\alpha_{rec} = 0.3$. The ratio of the intensities of the methyl group protons for acetone and 1-methylcyclobutanol indicates

| | | · | CIDNP sign | |
|---|--|-------------------------------------|------------------|-----------------|
| Product | Nucleus | δ, ppm | without RSH | with RSH |
| CH-COCH-Ph | * CH2 | 2.05 | E | F' < F |
| | CH_3 Ph (H) | $^{2,00}_{\sim 7}$ | E A | E' < E $A' < A$ |
| | ĈH₃ | 29,30 | Ε | - |
| | $\begin{array}{c} { m \widetilde{C}H_2} \\ { m PhC^1} \\ { m C^{2,6}} \\ { m C^{3,5}} \end{array}$ | 50,50 135,80 130,27 129,04 | A E A E | |
| | C" | 127,30 | A | - |
| | CO * | 206,52 | .E | |
| CH ₅ CHO | CHO | 9,62 | A | - |
| | CHO | 197,94 | A | - |
| CH:COCOCH3 | CH ₃ | 2,30 | A | - |
| $\rm PhCH_2CH_2Ph$ | $C\hat{H}_{2}$ | 2,86 | A | - |
| PhCH ₂ COCH ₂ COCH ₃ | COCĤ₂CO | 3,12 | Ε | None |
| PhCH ₂ C(OH) = CH ₂ | PhCH₂ | 3,40 | A | » |
| | \tilde{CH}_2 | 4,86 | E | » |
| thCH: | [*] С (ОН) СН ₃ | $142,56 \\ 2,20$ | A A | » .» |

TABLE 2. Assignment of Lines in the NMR Spectra and CIDNP Signs in the Photolysis of Ketone (II)

that about 70% of initial ketone reacts by pathway A and about 30% reacts by photocyclizaton pathway B.

The contribution of the radical pathway (Norrish type-1) was evaluated relative to the ratio of the integral intensities of the spectra of the starting ketone and the products of its photolysis. The decrease in the total integral intensity of the spectrum of the initial ketone is equal to the total integral intensity of the spectrum of the products of the biradical pathways to within $\pm 2\%$. This implies that the contribution of the radical pathway relative to all the pathways for the photodecomposition of (I) is not more than 2%. However, the CIDNP in the α -cleavage products clearly indicates the existence of this pathway for the photodecomposition.

Photolysis of Ketone (II). In contrast to (I), the photolysis of ketone (II) proceeds only by a Norrish type-I reaction. CIDNP of the starting ketone and its photoconversion products is also seen in this case (Figs. 3 and 4). The assignment of lines in the ¹³C and ¹H NMR spectra and the CIDNP signs are given in Table 2.

The primary step in the photolysis of ketone (II) is α -cleavage with the formation of a radical pair which retains the spin multiplicity of the triplet-excited molecular precursor (Scheme 2). In this radical pair, $g_{PhCH_2} = 2.0025$ and $g_{CH_3CO} = 2.0007$. The coupling constants of the methyl and methylene protons are opposite in sign.

Scheme 2 O PhCH₂CCH₃ $\xrightarrow{h\nu}$ [PhCH₂COCH₃]^T· ^F \rightarrow PhCH₂COCH₃ [2PhCH₂]^F \rightarrow PhCH₂CH₂Ph PhCH₂ + CH₃COCH₂Ph \rightarrow PhCH₃ + CH₂COCH₂Ph [2CH₃CO]^F \rightarrow CH₃COCOCH₃ CH₃CO + CH₃COCH₂Ph \rightarrow CH₃CHO + CH₂COCH₂Ph Secondary Reactions

 $CH_{3}\dot{CO} + PhC\dot{H}_{2}C\dot{H}_{2}Ph \rightarrow CH_{3}C\dot{HO} + PhCH_{2}\dot{C}HPh$ $[CH_{3}\dot{CO} \dot{C}H_{2}COCH_{2}Ph]^{F} \rightarrow CH_{3}COC\dot{H}_{2}COCH_{2}Ph$



Fig. 3. PMR spectra of ketone (II): a) initial spectrum; b) during photolysis; c) during photolysis in the presence of 0.001 M RSH. The signals for the product nuclei: 1) $CH_3COCOCH_3$; 2) $PhCH_2$. CH_2Ph ; 3) $PhCH_2COCH_2COCH_3$; 4) $PhCH_2C(OH)=CH_2$; 5) $PhCH_2C(OH)=CH_2$, 6) CH_3CHO ; *) CD_3CN .



Fig. 4. ¹³C NMR spectra of ketone (II): a) initial spectrum; b) spectrum during photolysis; *) CD₃CN.

The recombination of radicals with such magnetic parameters should lead to negative CIDNP for the protons of both groups of the regenerated ketone, as observed experimentally. The conversion products of the radicals which escape the RP cage (dibenzyl and biacetyl) have a negative polarization sing. In the presence of radical traps, the CIDNP of the starting ketone drops, which indicates triplet multiplicity of the primary RP.

A β -diketone whose methylene protons (COCH₂CO) are negatively polarized was identified among the products of the secondary reactions. The CIDNP signs imply that this product is formed in the diffusional pairs of radicals CH₃CO and PhCH₂COCH₂. The polarization of the ¹H and ¹³C aldehyde fragment indicates that the aldehyde is a product of the conversion of radicals which escape recombination or disproportionation in the cage. In the latter case, the carbonyl carbon should be negatively polarized. However, the ¹³C and ¹H CIDNP of the CHO group was found to be positive. This is a result of the transfer of a hydrogen atom upon the encounter of the acetyl radical with some molecule carrying the same polarization sign (most likely, with a dibenzyl molecule). During photolysis, the PMR spectra also showed signals with enhanced absorption (A) at 3.40 ppm and emission (E) at 4.86 ppm, while the ¹³C NMR spec-

| Product | Nucleus | ð, ppm | CNP sign without RSH |
|--------------|---------------------|--------|----------------------------|
| | | | |
| CH3COAd | $Ad: CH_2$ | 1,79 | A |
| | CH₂ | 1,83 | A |
| | CH | 1,87 | A |
| | CH₃ | 2,10 | E |
| | Ad : C ¹ | 45,5 | A |
| | LC [*] | 37,2 | |
| | IC' | 22,7 | |
| | | 35,5 | Ľ |
| | CH₃ | 27,3 | E |
| | ČΟ | 212,3 | E |
| CH3COCOCH3 | CH ₃ | 2,30 | A |
| | ČH₃ | 27,2 | A |
| CH₃CHO | CHO | 9,76 | A |
| CH3COCH2COAd | CH3 | 2,24 | E |
| | ČH₃ | 27,6 | E |
| | CH_2 | 3,70 ª | |
| | CH ₃ CO | 195,9 | E |
| | AdCO | 185,4 | Ε |
| | 1 | | ł |

TABLE 3. Assignment of Lines in the NMR Spectrum and CIDNP Signs in the Photolysis of Ketone (III)

^aNot shown in Fig. 5.

^bThis assignment is not unequivocal and the signal may belong to the biacetyl CO.

tra showed enhanced absorption at 142.56 ppm. The appearance of these signals may be attributed to the existence of the polarized enol of phenylacetone. The CIDNP signs indicate that these molecules are formed in the recombination of a triplet radical pair, in which the signs of the coupling constants of the CH_2 and $=CH_2$ protons are negative and $g_{CH_2}=COH > gPhCH$. Such a radical pair arises in the α -cleavage of the triplet-excited enol of phenylacetone.

Thus, the photolysis of ketone (II) proceeds through a Norrish type-I mechanism with the predominance of recombination in the radical pair and with regeneration of the starting ketone.

Photolysis of Ketone (III). CIDNP was also found in the ¹H and ¹³C NMR spectra during the photolysis of (III). The ¹H and ¹³C NMR chemical shifts as well as the CIDNP signs are given in Table 3. The spectra are given in Figs. 5 and 6.

The polarization of the starting ketone and the appearance of such products resulting from cage escape as CH₃CHO and biacetyl (Scheme 3) indicate that homolytic cleavage of the

Scheme 3

 $\begin{array}{c} 0 \\ \text{AdCCH}_3 \xrightarrow{h\nu} (\text{AdCOCH}_3)^* \\ \uparrow & 0 \\ \text{[Ad} & \text{CCH}_3]^T, F \longrightarrow \begin{array}{c} [2\text{CH}_3\text{CO}]^F \rightarrow \text{CH}_3\text{COCOCH}_3 \\ \longrightarrow & \text{CH}_3\text{CO} + \text{CH}_3\text{COAd} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{COAd} \\ \longrightarrow & \text{Ad} + \text{CH}_3\text{COAd} \rightarrow \text{AdH} + \text{CH}_2\text{COAd} \end{array}$

Secondary Reactions

 $CH_{3}\dot{C}O + A\dot{d}COC\dot{H}_{3} \rightarrow CH_{3}C\dot{H}O + A\dot{d}COCH_{3}$ $[CH_{3}\dot{C}O\dot{C}H_{2}COAd]^{F} \rightarrow CH_{3}COC\dot{H}_{2}COAd$



Fig. 5. PMR spectra for ketone (III): a) initial spectrum; b) spectrum during photolysis. Signals for product nuclei: 1) CH₃COCOCH₃; 2) CH₃COCH₂COAd; 3) CH₃CHO; *) CD₃CN.

 α -bond of the excited ketone molecule (Norrish type-I) occurs in the photolysis of (III). The recombination of the pairs formed leads to regeneration of the starting ketone with polarized nuclei (see Table 3). The CIDNP signs at the ¹H and ¹³C nuclei indicate recombination in the triplet radical pair.

The difference in the g-factors in the primary radical pair and the signs of the coupling constants in the CH₂CO radical are positive, which leads to negative polarization of all the nuclei of the acetyl fragment of the regenerated ketone. All the ¹³C nuclei (except for C¹) are negatively polarized. This finding implies that the spin density on the carbon nuclei in the σ -radical alternates only from C¹ to C² and then spreads out as in an aliphatic chain. All the adamantyl protons of the initial ketone are positively polarized. Hence, $a_{\rm Ad}^{\rm H} > 0$.

Upon escaping recombination in the primary pair, the acetyl radicals recombine in a diffusion pair. The integral positive CIDNP of the biacetyl methyl protons support this conclusion. The negatively polarized β -diketone is formed as a result of the encounter of acetyl and the secondary \dot{CH}_2 COAd radical.

We assume that, as in the case of ketone (II), the positive polarization of the aldehyde proton results from its origin in the transfer of a polarized hydrogen atom upon the encounter of an acetyl radical with a polarized molecule of regenerated ketone (III) and not from disproportionation in the primary radical pair. Thus, photolysis of ketone (III) occurs in the Norrish type-I process in the triplet state without disproportionation in the radical pairs.

EXPERIMENTAL

The solutions of ketones which were purified by fractional distillation and recrystallization were prepared in CD_3CN (0.05 M for ¹H CIDNP) and in $CH_3CN + CD_3CN$ (0.1 M for ¹³C CIDNP) and photolyzed using a DRSh-500 high-pressure mercury lamp at 270-320 nm.



Fig. 6. ¹³C NMR spectra of ketone (III): a) initial spectrum; b) spectrum during photolysis.

The dithiol (HSCH₂-CHOH)₂ was used as the free-radical trap at $10^{-3}-10^{-2}$ M. The photolysis was carried out in the probe of an NMR spectrometer modified for photochemical reactions in quartz ampuls. The spectra were recorded on a Bruker HX-90-EP spectrometer using the Fourier transform technique. All the samples were deoxygenated using a stream of dry argon. The measurements were carried out at ~20°C. The relaxation times T₁ were measured relative to the kinetics for the restoration of the equilibrium intensity of the signal after its saturation in the continuous spectrometer operation mode.

CONCLUSIONS

1. ¹H and ¹³C NMR spectroscopy was used to study the photoconversion of methyl n-propyl ketone, methyl benzyl ketone, and methyl adamantyl ketone. The ¹³C and ¹H CIDNP signs indicated that the polarization arises upon the cleavage of excited ketones in the triplet state.

2. The competition of the radical photodecomposition (Norrish type-I) and "biradical" photodecomposition was studied in the photolysis of methyl n-propyl ketone. The ratio of the probabilities of the two radical pathways (recombination and disproportionation) is 3:1, while the ratio of the two biradical pathways (photocyclization and Norrish type-II decomposition) is 3:7.

3. A mechanism was established for the steps in the conversions of the radicals and radical pairs arising in the photolysis of the ketones studied.

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