In a broader sense, it is clear that STM can provide key insight into understanding the atomic level properties of other interesting and important low-dimensional materials. For example: (1) new and fascinating electronic properties of graphite intercalation compounds have recently been elucidated by us[43] and other groups;[44] (2) additionally, STM is providing essential data on the structural and electronic properties of high-temperature copper oxide superconductors and how these properties evolve locally upon metal and oxygen doping.[9,45,46] These and other studies will undoubtedly lead to significant advances in our understanding of these materials in the future.

We acknowledge our co-workers whose efforts are referenced in this account and the Air Force Office of Scientific Research, National Science Foundation, David and Lucile Packard Foundation, A. P. Sloan Foundation, and Camile and Henry Dreyfus Foundation for financial support.

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Magnetic and Spin Effects in Photoreduction of Uranyl Salts

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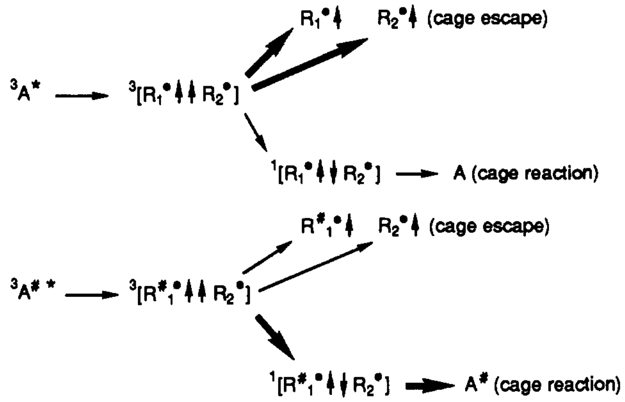
A remarkable feature of spin-selective chemical reactions is their magnetic sensitivity. This sensitivity arises from magnetic interactions of electrons and nuclei with an external magnetic field and also from electron–nuclear hyperfine interactions. From an energy standpoint these magnetic interactions are negligible, but they nevertheless influence the overall chemistry by reorienting electron spins and removing spin prohibition in a spin-selective reaction. Spin prohibition means that not all spin states are reactive; only reactions in which electron spin is conserved are allowed. Magnetic interactions can remove the spin prohibition and thereby strongly influence the rate and efficiency of certain chemical reactions. Well-established magnetic effects include chemically induced dynamic nuclear and electron polarizations (CIDNP and CIDEP), magnetic field effects (MFE; an external magnetic field influences reaction rates), and magnetic isotope effects (MIE).[1] The MIE is the most interesting because it reflects the reaction-rate dependence of paramagnetic particles on the spin and magnetic moments of their nuclei.[2] This rate dependence provides a basis for separation of magnetic and nonmagnetic isotopes in chemical reactions, and it has been observed for isotopes of carbon,[3] oxygen,[4] silicon,[5] and sulfur.[6,7]

The following reaction scheme has been found successful for analysis of most isotope separation processes.[2] Reagent A/A$^\#$ containing magnetic (A$^\#$) and nonmagnetic isotopes (A) is photoexcited and then reacts in the triplet state (^{3}A*; Scheme I). A triplet radical pair (RP) is formed ^{3}[R$_1^\bullet$,R$_2^\bullet$]. The RP can

Scheme I[a]



[a] Square brackets denote the solvent cage.

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Scheme II

$$ {}^3[R_1^\bullet, R_2^\bullet] \xleftrightarrow{\text{HFC}} {}^1[R_1^\bullet, R_2^\bullet] \quad \text{ISC spin dependent} $$

$$ {}^3[R_1^\bullet, R_2^\bullet] \xleftrightarrow{\text{SOC}} {}^1[R_1^\bullet, R_2^\bullet] \quad \text{ISC spin dependent} $$

dissociate, and the individual radicals can react in the solvent bulk to form R_1H and R_2H or other compounds. Reaction of "cage" combination or disproportionation between the two radicals in a triplet RP is prohibited. Thus, the RP can react to form cage products after intersystem crossing to a singlet state. Under the proper conditions triplet–singlet evolution of a geminate radical pair occurs as determined mainly by the electron–nuclear hyperfine coupling interaction (HFC mechanism[1]). This interaction is stronger (and thus the rate is faster) in the presence of magnetic isotopes. Thus, the cage product(s) are isotopically enriched, and the cage escape products are depleted isotopically.[2]

It would be useful to exploit this effect in reactions of uranium compounds where one of the isotopes, ^{238}U, is nonmagnetic while another, ^{235}U, is magnetic (nuclear spin $I = {}^7/_2$, magnetic moment $\mu_I = -0.31\mu_N$). The potential practical application is obvious: even a 2- or 3-fold increase in the ^{235}U isotope content of natural uranium (0.72%) would greatly increase its value as a nuclear fuel.

What factors can cause the HFC mechanism to be ineffective? In general, with increased nuclear charge the spin–orbit coupling (SOC) of an element increases.[8] SOC originates from the interaction of electronic spin and orbital angular momenta. Spin and orbital movements of an electron become strongly interconnected in a heavy atom, in a radical containing a heavy atom, or in a contact RP containing a heavy-atom radical. The manifestation of heavy-atom-induced SOC is well-known in photochemistry. For example, the quantum yield of the triplet-state population in the photoexciited molecule increases after introduction of heavy atoms (Cl, Br, I) into its structure.[8] The reason is that SOC partially removes the prohibition for transition between states of different multiplicity, such as an excited singlet state and a triplet state. In the case of triplet–singlet evolution of the RP, our main interest, SOC competes with HFC and creates non-isotope-dependent "leakage" in intersystem crossing[7b,9] (Scheme II).

The search for MIE on uranium involves the following three problems: (1) identification of reactions of uranium compounds which involve the participation of paramagnetic transients; (2) elucidation of spin-selective stages in reactions of these transients and determination of the starting spin multiplicity of the stages; (3) quantitative analysis of the isotope distribution in the reaction products.

The present paper summarizes our initial results in a search for spin-selective reactions of uranium compounds. We provide evidence for spin selectivity due to MIE acting on uranium nuclei in some reactions.

Photochemistry of Uranyl Salts. The most promising reactions of uranium compounds among those we have tested are the photoreactions of uranyl salts in water and organic solvents. The uranyl ion [U(VI)] in water exists as the hydrate $[UO_2(H_2O)_5]^{2+}$, where five water molecules are arranged in the equatorial plane.[10,11a] Uranyl is an active complex forming agent: in the presence of amines, amides, ketones, carboxylic acids, a number of mineral acids, and numerous other compounds, a water ligand may be substituted by other ligands. In organic solvents, uranyl salts often attack the solvent to form complexes.

The photochemistry of uranyl salts has been studied extensively,[11] and two basic mechanisms of electronically excited uranyl ion reactions have emerged. The first, an inner-sphere mechanism, involves the reaction of the central atom, U(VI), with equatorial ligands. The rate-determining step of these reactions is often the inner-sphere electron transfer to the central atom resulting in carboxylic acid decarboxylation, formation of alkoxyl radicals from alcohols, and other events.[12–16] The second, a charge-transfer hydrogen abstraction mechanism, is the reduction with the participation of the polar oxygen atom of uranyl. These reactions proceed as a bimolecular reaction between $UO_2^{2+}*$ and the substrate SH_2.[11–16]

$$ {=}U{=}O^{2+}* + SH_2 \rightarrow {=}U{=}O^+ + SH^\bullet + H^+ \quad (1) $$

Reaction 1 is similar in many respects to the photoreduction reactions of triplet benzophenone and other carbonyl compounds in the n,π* state via electron (or hydrogen atom) transfer:[11c]

$$ {>}C{=}O^*_T + SH_2 \rightarrow {>}C{-}O^{\bullet-} + SH^\bullet + H^+ \quad (2) $$

There is also evidence suggesting competition between the two mechanisms in uranyl photoreduction. For example, uranyl perchlorate photosensitized oxidation of lactic acid, $CH_3CHOHCOOH$, leads to two organic products: acetaldehyde (formed after acid decarboxylation) and pyruvic acid, $CH_3COCOOH$.[15] The relative quantum yields of the two reactions depend strongly upon the pH of the aqueous solution. At pH ≥3.5 only acetaldehyde is formed, while at pH 0 only pyruvic acid is formed.[15] In the first case, the reaction occurs in the equatorial plane with the coordinated lactic acid. In the second case, photoreduction of the polar oxygen is predominant. It has been demonstrated that the quantum yields of the products strongly correlate with the uranyl–lactate complex concentration in a pH-dependent solution. Convincing evidence for

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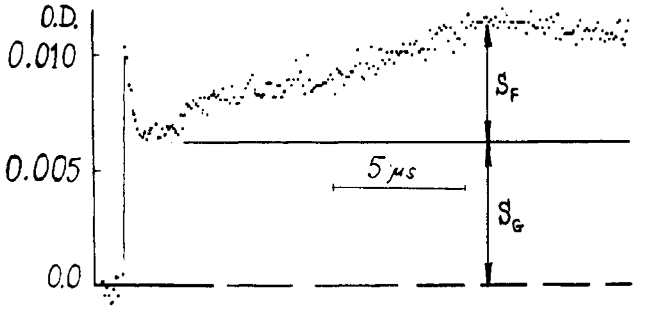


Figure 1. Variations of optical density (OD) at λ 600 nm caused by the formation and decay of $UO_2^{2+}*$ and thionine, S. Data was obtained by laser photolysis of an aqueous solution of uranyl nitrate in the presence of leucothionine. Here S_G is the OD of S formed in a cage and S_F is the OD of S formed in a solvent bulk due to $SH^\bullet$ disproportionation.[17]

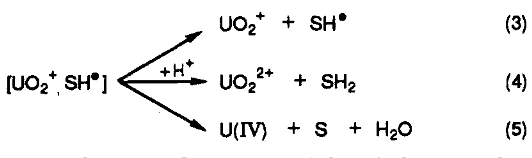
the photooxidation mechanism has been obtained.[15]

Another example is uranyl photolysis in aqueous methanolic solutions. The uranyl photolysis in pure methanol leads to formation of alkoxyl free radicals $CH_3O^\bullet$, whereas the photolysis in water–methanol (2:1 v/v) with the equatorial plane filled mainly with water molecules results in photoreduction on the oxygen atoms and formation of hydroxymethyl radicals $^\bullet CH_2OH$.[16] Moreover, isotope effects in these two reactions have different signs: in the first reaction with CH_3OH and CH_3OD the ratio is $k_1(OH)/k_1(OD) = 0.8–1.0$, whereas in the second reaction with CH_3OD and CD_3OD, $k_1(CH)/k_1(CD) = 2.4–2.9$.[12] This and many similar observations[11c] testify to the fact that equatorial uranyl reactions include preferably inner-sphere electron transfer whereas polar reactions predominantly exhibit the features of intermolecular photoreduction.

Pairs Consisting of the Uranoyl and Another Free Radical. An intermediate product of the elementary reaction 1 between an excited uranyl ion and a donor is the radical pair (RP) which includes a uranium(V) compound, uranoyl:

$$UO_2^{2+}* + SH_2 \rightarrow [UO_2^+,SH^\bullet] + H^+ \qquad (1')$$

The reactivity of the pair determines the products (eqs 3–5) of the reaction: it either dissociates or participates in forward or back electron transfer (or disproportionation):



$$[UO_2^+,SH^\bullet] \rightarrow UO_2^+ + SH^\bullet \qquad (3)$$
$$[UO_2^+,SH^\bullet] \xrightarrow{+H^+} UO_2^{2+} + SH_2 \qquad (4)$$
$$[UO_2^+,SH^\bullet] \rightarrow U(IV) + S + H_2O \qquad (5)$$

Bearing in mind the redox potentials of the couples $E°(UO_2^{2+}/UO_2^+) = 0.06$ and $E°(UO_2^+/U^{4+}) = 0.55$ V (vs NHE),[11] one can expect radical–oxidant pairs to regenerate the starting reagents whereas the strong oxidant uranoyl is supposed to oxidize many radicals with the formation of uranium(IV) compounds. Certainly the redox potentials strongly depend upon the pH of the solution and upon the state of complexing of the reagents. In this section and in the next sections we will discuss reaction 5, which is often ignored when the mechanistic photochemistry of uranyl compounds is considered.

Reactions 1–5 have been studied by the nanosecond laser photolysis technique with the aim of observing cage processes.[17] The thionine leuco dye has been chosen as SH_2. The oxidation of leucothionine by photoexcited uranyl into $SH^\bullet$ and S is accompanied by dramatic spectral changes, which facilitates the study of the reaction with optical techniques.[17] The laser flash produces the excited $UO_2^{2+}*$ with the pulse. "Physical" and "chemical" quenching of this species (reaction 1) lasts ~800 ns (Figure 1). As the radical $SH^\bullet$ is accumulating it is important to note that S is being formed in considerable concentration (Figure 1). Thus, this result confirms the occurrence of a consecutive two-state SH_2 oxidation by photoexcited uranyl (reactions 1 and 5). The amount of $SH^\bullet$ oxidized in a cage (reaction 5) is ca. 5% of the amount of $SH^\bullet$ that escapes the cage (reaction 3).[17] These experiments allow direct observation and measurement of cage reaction kinetics as well as the cage-effect values.[17,18]

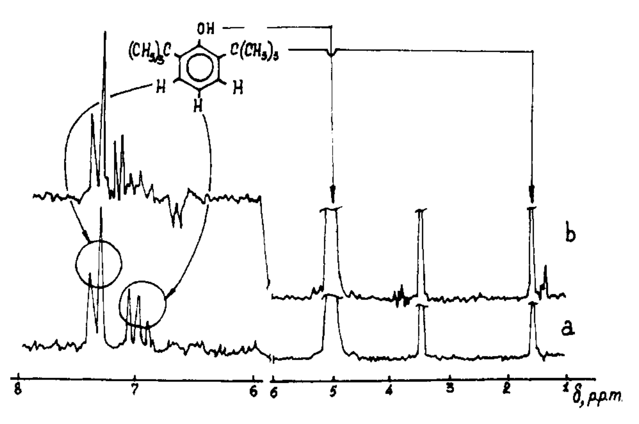


Figure 2. ^1H NMR spectrum of 2,6-di-*tert*-butylphenol and uranyl nitrate in methanol-d_4 (a) before and (b) during irradiation. The $UO_2(NO_3)_2$ absorbed the light.[20]

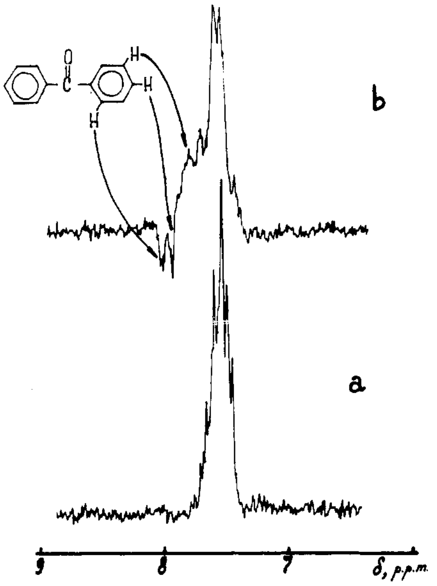


Figure 3. ^1H NMR spectrum of acidified methanol-d_4 solution with benzilic acid and uranyl nitrate (a) before and (b) during irradiation. The $UO_2(NO_3)_2$ absorbed the light.[21a] Reprinted with permission from ref 21a. Copyright 1989 Elsevier Science Publishers.

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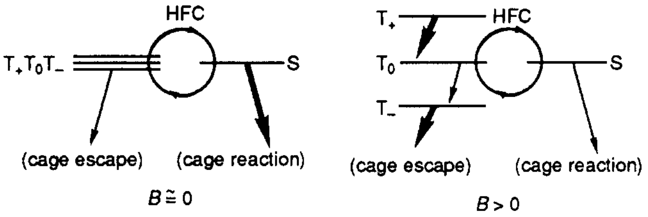
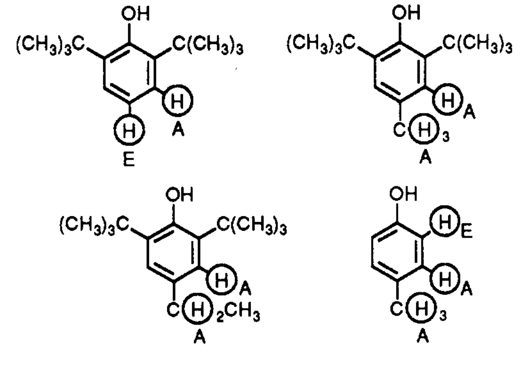
Scheme III



Neither the spin multiplicity of the RP[19] nor that of reacting uranyl is known. We have focused on the study of the spin selectivity of uranyl reactions and of the excited ion spin state through CIDNP, MFE, and MIE.

CIDNP. ^{1}H CIDNP has been observed in uranyl nitrate photoreduction reactions 1 by a series of alkyl-substituted phenols, benzilic acid, and benzhydrol[20,21a] (Figures 2 and 3). The polarization signs of various phenols are shown below (A, enhanced absorption; E, emission):[20]

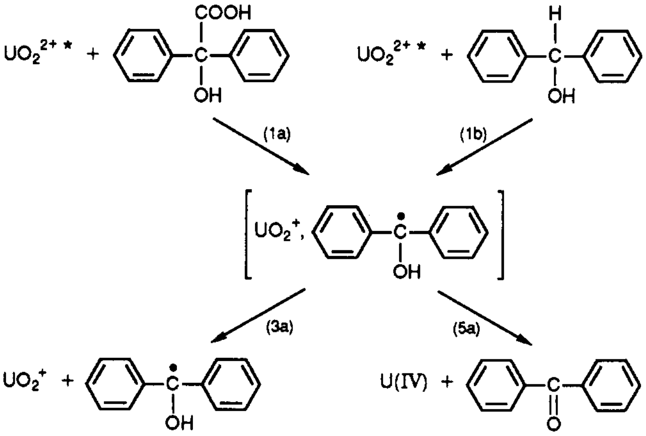


Polarization of aroxyl radical recombination products formed in the solvent bulk has also been observed. The photooxidation of phenols includes elementary steps 1′, 3, and 4. Aroxyl radicals are poor electron donors and good acceptors, so that reaction 3, leading to formation of polarized phenols, proceeds in the cage.

Observing CIDNP in such reactions with participation of a heavy-atom-centered radical is not trivial. However, its observation demonstrates, without specific knowledge of the RP multiplicity, that the reaction is spin selective and that a definite spin multiplicity exists for RP. Hence, one can expect magnetosensitivity of reactions and magnetoselectivity of radicals.

The observed ^{1}H CIDNP of phenols in their reaction with UO_2^{2+}* reproduces precisely the polarization of the same phenols formed in the reaction with triplet benzophenone.[20,22] This is suggestive evidence that uranyl reacts in the triplet state and produces a RP with definite triplet character.

The benzophenone ketyl free radical is formed as an intermediate during the photooxidation of benzhydrol and benzilic acid. This radical, in contrast to aroxyls which are poor donors, is oxidized to the ketone in the cage:



The benzophenone formed through reaction 5a appears to be polarized[21a] (Figure 3). The polarization signs of phenols and benzophenone are characterized according to theory: the RP is in the triplet state, the polarized product is formed by cage reaction, and the g factor of uranoyl ion is approximately 1.7.[23] (The organic radical g factors are close to 2.00.)

Thus CIDNP data suggest that the dominant contribution to the reactive state of photoexcited uranyl is the triplet[20,21] and that spin multiplicity is conserved for the chemical transformation of uranyl into the RP.

The existence of large spin–orbit coupliing (SOC)[11,24] in the uranyl ion caused by the heavy uranium atom lessens the appropriate assignment of a definite spin label to UO_2^{2+}*. (For the 5f uranium orbital, the SOC constant $\zeta \cong 2000$ cm^{-1},[25] which is much higher than the SOC constant for "light" atoms (such as oxygen or carbon), for which $\zeta \cong 100$ cm^{-1}.[2]) Detailed calculations,[26] however, show that, despite significant SOC, uranyl excited states are better described with the assumption that electrostatic repulsion is greater than the SOC rather than with the opposite assumption. Most researchers share the view that UO_2^{2+}* is triplet in nature.[27,28] This view is supported by experimental evidence obtained by using magnetic circular dichroism.[29]

We have mentioned the uranoyl magnetic resonance parameters deduced from CIDNP above. Unfortunately, there are scarce data from ESR spectra of this radical.[23,30] The uranoyl g factor is highly anisotropic with an average value of 1.7. Depending on the experimental conditions, two pairs of g-factor components

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(19) The ESR spectrum of the RP consisting of UO_2^+ and $NO_3^\bullet$ radicals has been recorded at very low temperatures (4.2–10 K) (Giacometti, G.; Agostini, G.; Gennary, G.; Corvaja, C. *J. Chem. Soc., Chem. Commun.* **1981**, 1019). The fact that an ESR spectrum of RP exists is an indication that the RP and its precursor UO_2^{2+}* are in the triplet state. However the conclusion on a sign of exchange interaction in the RP is not available from the presented ESR spectra.

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for this linear radical have been obtained: (1) $g_\perp = 2.5$, $g_\parallel = 0$; (2) $g_\perp = 1.97$, $g_\parallel = 1.3$.[23] The ESR spectrum of $^{235}UO_2^+$ is unknown, although it has been suggested that the uranium nucleus hyperfine coupling constant should be $a_U \cong 2$ mT.[31] Experimental data from the ESR spectra of $^{235}U^{5+}$ in alkali halide crystals doped with uranium-235 oxides lead to an average value $a_U \cong 5$ mT.[32]

Magnetic Field Effects. It is known that photochemical reactions proceeding via triplet RP formation exhibit significant external MFE.[1] The application of a moderate external magnetic field increases the efficiency of radical exit from the triplet RP (and decreases the cage effect) due to retardation of S–T evolution according to a HFC mechanism (see Scheme III).

It has been stated above that uranyl photoreduction is associated with the formation of a triplet (or nominal triplet) RP. One may expect the uranyl photoreduction reaction to demonstrate MFE. A MFE observed in the free-radical polymerization of *N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride (RH^+Cl^-) photoinitiated by uranyl diacetate is unequivocal evidence of the triplet multiplicity of reacting $UO_2^{2+}*$ and of the formation of a triplet RP.[33]

The initiation stage of this reaction is postulated as the following:[33]

$$UO_2^{2+}* + RH^+ \rightarrow$$

$$UO_2^+ + H^+ + R^+ \text{ (reactive form of monomer)} \qquad (1c)$$

$$R^{\bullet+} + RH^+ \rightarrow R(RH)^{2+} \text{ (propagating monomer)} \qquad (6)$$

The polymerization rate (v) under conditions at low conversion[34] ($q < 15\%$) is well described by the familiar equation[2a,33]

$$v = w_i^{1/2} k_p k_t^{-1/2} [RH^+Cl^-] \qquad (7)$$

where w_i is the initiation rate, k_p is the propagation rate constant, and k_t is the termination rate constant.

The effect of an applied magnetic field on the rate of polymerization is clearly seen in Figure 4: application of an external field ($B = 0.17$ T) causes an increase in the rate of polymerization by 10–40%. This effect is reproduced independently of when the field is switched on or off (Figure 4). When polymerization accelerates in the field, the molecular mass of the polymer decreases. Both these results clearly establish that the spin-selective stage is the initiation (1c), i.e., the primary RP consists of UO_2^+ and a free radical of the monomer. The primary pair is a triplet. Only in triplet pairs does a magnetic field depress conversion into singlet pairs, and causes an increase both in the number of radicals escaping the cage and in the initiation. This is because it is only for triplets that the magnetic field depresses conversion into the singlet state and increases radical exit into the solvent bulk thereby increasing w_i (Scheme III). The reduction of the polymer molecular mass occurs as a result of this acceleration of initiation. The accumulation of uranium(IV) formed both in a solvent cage and in bulk takes place during the polymerization reaction. The yield of U(IV) decreases in the field.[33]

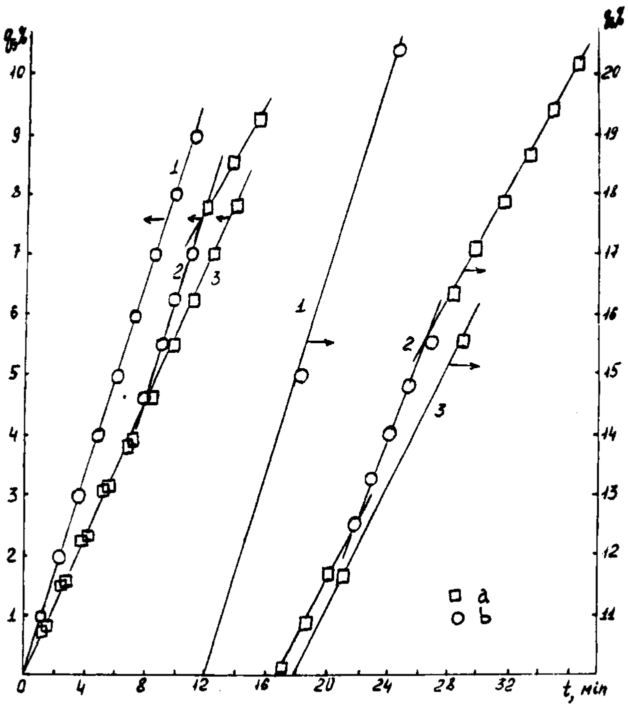
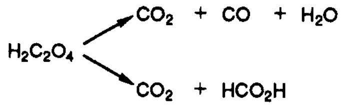


Figure 4. Dependence of the conversion (q) during polymerization of *N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride on reaction time: (1) polymerization in the field; (2) polymerization under establishment and removal of the permanent magnet; (3) polymerization in the Earth's field; (a) reaction proceeds in the Earth's field; (b) reaction proceeds in the magnetic field. It is clear that the polymerization rate, i.e., slope of section of line, increases under application of the field, and thus MFE displays itself.[33]

So, two of the problems formulated above are solved: spin-selective reactions of uranium compounds have been found, and the spin multiplicity of the intermediate RP has been determined. Before we tackle the third problem, i.e., MIE on uranium nuclei, we shall present the data of another investigation of the MFE on rates of photoreactions of uranyl salts. Some modest success has also been found here.

There is considerable interest in the uranyl oxalate photodecomposition (or photodecomposition of oxalic acid in the presence of uranyl nitrate and a mineral acid) in connection with the present topic, vide infra. This reaction is the basis of the classic uranyl oxalate actinometer:[11b] oxalic acid titration enables one to determine with high accuracy its consumption during photolysis. The reaction proceeds mainly as a sensitized oxidation with the regeneration of uranyl:[11b,13]



$$H_2C_2O_4 \begin{cases} \rightarrow CO_2 + CO + H_2O \\ \rightarrow CO_2 + HCO_2H \end{cases} \qquad (8)$$

There is no doubt about the formation of the RP which includes $CO_2^{\bullet-}$. The ESR spectrum of the radical has been recorded at low temperature.[13] The radical anion which exits from the cage recombines to form oxalic acid. The external magnetic field might affect escape of the radicals from the cage and the rate of oxalic acid consumption during photolysis. However, in the reaction of uranyl nitrate where the ^{235}U isotope content is 10% we have not observed any MFE on the reaction rate ($B = 0.1$–0.2 T, experimental error ~2%).[35] The

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(31) Evance, G. T.; Lawler, R. G. *Mol. Phys.* **1975**, *30*, 1085.

(32) (a) Ursu, I. *Rezonanta Magnetica in Compusi cu Uranium*; Academiei: Romania, 1979; Chapter 4. (b) Lupei, V.; Lupei, A.; Georgesku, S.; Ursu, I. *J. Phys. C: Solid State Phys.* **1976**, *9*, 2619.

(33) Golubkova, N. A.; Khudyakov, I. V.; Topchiev, D. A.; Buchachenko, A. L. *Dokl. Akad. Nauk SSSR* **1988**, *300*, 147.

(34) The conversion $q = ([RH^+Cl^-]_0 - [RH^+Cl^-])/[RH^+Cl^-]_0$, where $[RH^+Cl^-]_0$ is the initial and $[RH^+Cl^-]$ is the current monomer concentration.

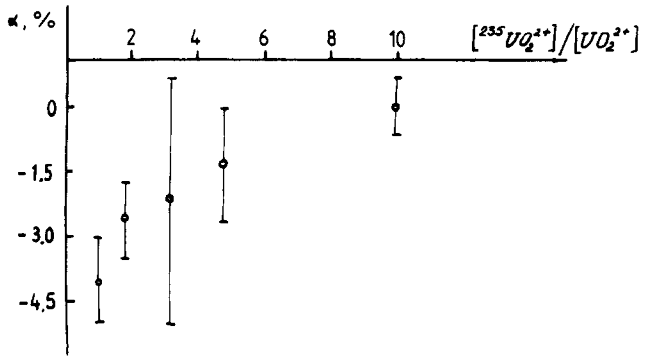


Figure 5. Dependence of the MFE α (relative change of the exit of *p*-hydroxyphenoxyl radicals from the cage under an external magnetic field of $B = 0.19$ T) upon the content of ^{235}U isotope. Data were obtained by flash photolysis of uranyl nitrate and hydroquinone in glycerol solution at 285 K. Radical yields in solvent bulk decrease under application of the field; this is the MFE manifestation.[36]

reason for this fact apparently lies in the negligible value of the effective HFC of the RP [$CO_2^{\bullet-}$, UO_2^+]. There is no HFC between electrons and nuclei nor are the magnetosensitive transitions (according to the HFC mechanism in the absence of ^{13}C and ^{235}U) in the given RP. These considerations make clear that the strong oxidant uranoyl oxidizes the strong reducing agent $CO_2^{\bullet-}$ with low efficiency:[13]

$$^3[UO_2^+,CO_2^{\bullet-}] \rightarrow U(IV) + CO_2 \qquad (5b)$$

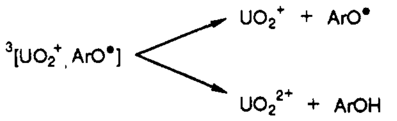
The reason seems to be clear: for the occurrence of reaction 5b the evolution of a triplet RP into a singlet is necessary. The evolution is prohibited in the absence of the hyperfine or other relaxation mechanism. The RP under consideration participates mainly in other elementary reactions leading to products of reaction 8.[13]

Spin evolution according to the HFC mechanism certainly is not the unique mechanism of S–T evolution in a pair [UO_2^+,S$^\bullet$]. A negative MFE ($-\alpha$ = 3–10%) on the yield of aromatic free radicals into solvent bulk has been detected under uranyl photoreduction by hydroquinone and *p*-methoxyphenol in a viscous solvent[36] (Figure 5).

The probable cause of the negative MFE is the Δg mechanism.[37] The increase of the ^{235}U isotope content in the salt from 0.7 to 10% leads to the opposite-sign effect. In fact, the "magnetic" isotope content increase leads to a greater number of [$^{235}UO_2^+$,SH$^\bullet$] pairs having larger HFC constants than those of [$^{238}UO_2^+$,SH$^\bullet$]. The opposite-sign effects approximately compensate each other when the ^{235}U content is ~10% resulting in $|\alpha| < 2\%$ (Figure 5). Strictly speaking, so far it is impossible to draw any definite quantitative estimates of the magnetic interactions in the RP involving uranoyl, but the dependence of the MFE on the isotope content in uranyl (Figure 5) is a good reason to state that the HFC with a ^{235}U nucleus contributes measurably to the spin dynamics of the RP.

Magnetic Isotope Effects. It has been shown above (CIDNP, MFE) that uranyl photoreduction by phenols is a spin-selective reaction; therefore one may expect that the internal magnetic field of a $^{235}UO_2^{2+}$ nucleus will influence the reaction rate, i.e., MIE. A MIE has been found in the photoreduction of uranyl nitrate by *p*-methoxyphenol (ArOH) in deuterium oxide containing ammonium fluoride.[38] The process mainly consists of the following elementary reactions:

$$UO_2^{2+} + ArOH \rightarrow {}^3[UO_2^+, ArO^\bullet] + H^+ \qquad (1d)$$



$$^3[UO_2^+, ArO^\bullet] \rightarrow UO_2^+ + ArO^\bullet \qquad (3b)$$

$$^3[UO_2^+, ArO^\bullet] \rightarrow UO_2^{2+} + ArOH \qquad (4a)$$

$$UO_2^+ + UO_2^+ + 4HF \rightarrow UO_2^{2+} + UF_4\downarrow + 2H_2O \qquad (9)$$

The *p*-methoxyphenoxyl radical ArO$^\bullet$ formed in reaction 1d has comparatively small ortho-proton HFC constants, and it is probable that the a_U of $^{235}UO_2^+$, even though it is not large, will make a considerable contribution to the RP effective HFC constant. The depletion of the precipitated UF_4 by the ^{235}U isotope has been found under uranyl conversions less than 20%.[38] In the starting uranyl nitrate, the $^{238}U/^{235}U$ ratio (*R*) was $R = 8.93 \pm 0.01$ while in the reaction product UF_4 it was within the range (8.970 ± 0.005)–(8.945 ± 0.008).[38] This observation corresponds to the enrichment of the ^{235}U isotope of the nonreacted uranyl; the sign of MIE is as expected. The triplet pairs with the "magnetic" ^{235}U nuclei undergo faster triplet–singlet evolution and carry ^{235}U nuclei into regenerated uranyl after redox reaction 4 takes place. The MIE value is low (it may be concluded that the efficiency of electron–nuclear interaction in $^{235}UO_2^+$ is apparently small), but it exceeds the isotope analysis error.

We have estimated the single stage separation factor as $A = 1.02$; this is a small value, but it considerably exceeds the classical isotope effect value (one estimate being $A = (238/235)^{1/2} = 1.006$). The process has been initiated by a large number of flash irradiations in order to increase the contribution of the uranoyl disproportionation (reaction 9) rate into uranoyl reaction rates and possibly to decrease the uranyl–uranoyl electron exchange (reaction 10) resulting in the loss of the effect:[28,39]

$$^{235}UO_2^+ + {}^{238}UO_2^{2+} \rightleftarrows {}^{235}UO_2^{2+} + {}^{238}UO_2^+ \qquad (10)$$

(It is probable that reaction 10 proceeds via formation of the $UO_2^+\cdots UO_2^{2+}$ complex.[28,40])

Steady-state photolysis of an aqueous solution of sodium dodecyl sulfate micelles containing 2,6-diphenyl-4-stearoxyphenol and uranyl perchlorate with the same starting *R* has led to marked depletion of U(IV) ($R = 9.075 \pm 0.005$) and enrichment of nonreacted U(VI) ($R = 8.90 \pm 0.01$).[41] The uranyl conversion was 15%.[41]

There are two claims for the MIE-based uranium isotope separation in patent literature.[42,43] The patent[42]

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(35) Khudyakov, I. V., et al., 1990, unpublished results.

(36) Klimtchuk, E. S.; Khudyakov, I. V.; Serebrennikov, Y. A. *Zh. Fiz. Khim.* **1990**, *64*, 2833.

(37) Larmor frequencies of two radicals precessing in a magnetic field are different due to differences in their *g* factors. This results in the periodic formation of T_0 and S states of the RP. This mechanism of S–T evolution is called the Δg mechanism.[1] Usually this mechanism manifests itself when $B > \sim 1$ T for a pair of organic radicals with $\Delta g \cong 10^{-3}$ in nonviscous solvents.[1a] Contrary to the HFC mechanism, the Δg mechanism leads to a negative MFE on the radicals escaping from a cage.

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(41) Buchachenko, A. L.; Khudyakov, I. V.; Klimtchuk, E. S.; Golubkova, N. A., 1990, unpublished results.

Acc. Chem. Res. **1991**, *24*, 183–190

claims that the isotope separation is present in the uranyl acetate photoreduction either in water or in water containing complex-forming additives (fluoride, carbonate, oxalate, and others). As seen from the patent description, the authors[42] were guided by "general considerations" rather than by experimental data.

According to ref 43, the isotope separation occurs during the photopolymerization of uranyl acrylate in ethanol solution in a strong permanent magnetic field. The precipitated polymer contains the enriched uranium; the content of the ^{235}U isotope may be up to 50%.[43] The content of this isotope in the starting uranyl acrylate has not been reported. We have not been able to reproduce the data in ref 43.[35]

A reproducible MIE on uranium has been found in the reaction of uranyl oxalate decomposition[44] (simultaneously with our study[38] and independently of it). Both the enrichment of the precipitated uranium(IV) oxalate containing ^{235}U and the depletion of the starting uranyl have taken place during the photolysis of acidic solutions of uranyl oxalate having 10% ^{235}U content. Logically, it is the cage reaction product uranium(IV) that has been enriched:[44] reaction 5b between uranoyl and $CO_2^{\bullet -}$ proceeds faster in the case of uranoyl containing the ^{235}U magnetic isotope. The "spoiling" isotope exchange (reaction 10) in solvent bulk is probably retarded due to the presence of uranyl in the form of an oxalate complex. The extent of isotope separation decreases with the reaction conversion.[44] The data of ref 44 have been reproduced.[35]

Conclusions and Perspectives. In a series of elements for which a MIE has been found (^{13}C, ^{17}O, ^{29}Si, ^{33}S)[3–6] the SOC constant increases from $\zeta = 28$ cm^{-1} (for carbon) to 382 cm^{-1} (for sulfur), more than 1 order of magnitude.[2] The MIE scale, however, does not change much in the series.

The separation of uranium isotopes based on the MIE has been a challenging problem during the past 15 years.[31,45] One can suggest that the existence of a uranium heavy atom and overestimation of the SOC role a priori led researchers be pessimistic about success in demonstration of a measurable MIE for uranium systems. A MIE has been determined quite recently in two uranyl photosensitized reactions: the oxidation of phenols and the decomposition of oxalic acid.[38,44] It is to be hoped that the data obtained on the MIE involving heavy isotopes will stimulate progress in the development of RP theory, which accounts for significant SOC and new channels of singlet–triplet evolution.

The uranoyl radical differs considerably from radicals centered on carbon and other elements, for which the MIE was previously discovered, with its magnetic resonance parameters. For better understanding of the MIE, a detailed study of the ESR spectrum and magnetic resonance characteristics of $^{235}UO_2^+$ is required.

It is difficult at present to speculate on the practical exploitation of the uranium enrichment method based on the MIE without examination of pertinent technological and commercial aspects. In favor of the MIE method we shall mention that the coefficient *A* obtained in this method seems to be higher than the *A* found in widely used gas diffusion and ultracentrifuge methods.[46] Additionally, uranyl photoreactions can be initiated by solar light. It is probable that in the future, if one employs viscous liquids or micellar solutions, a more significant isotopic separation than that presented above will be found. This improvement may allow the practical use of MIE. In the present paper we have tried to show that to obtain MIE, one should be able to govern the reaction and its physics and chemistry and to provide conditions of spin, molecular, and chemical dynamics favorable for MIE.

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Registry No. UO_2, 16637-16-4; ^{235}U, 15117-96-1.

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Mapping the Path of a Growing Ribonucleic Acid Molecule

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The proteins and nucleic acids responsible for the orderly functioning of biological cells are linear polymers. They are synthesized processively (without stopping) by elaborate assemblies of macromolecules. The synthesis of ribonucleic acid begins with a ribonucleotide monomer whose ribose 3′-OH is phosphorylated by another nucleotide; this process is repeated thousands of times to produce a finished RNA molecule. The sequence of nucleotide bases in the RNA is determined by the pairing of each successive incoming nucleotide to a complementary nucleotide in a DNA molecule that serves as a template. Only those bases that pair with the template (e.g., uracil with adenine,

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