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The photochemistry of uranyl: spin selectivity and magnetic effects

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ABSTRACT. The very large range of photochemical reactions of uranyl conforms to certain general principles; and these are summarised, correlated, and from them the main types of photochemical reactions are classified. It is shown that the primary fundamental photoreactions of uranyl are selective with respect to electron spin and are therefore magnetosensitive. In these reactions there are found to be magnetic effects, including the most important—a magnetic isotope effect which is accompanied by the separation of uranium isotopes (magnetic ^{235}U and nonmagnetic ^{238}U).

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I. Introduction

Uranium is famous for its ^{235}U isotope, whose natural content is about 0.72%; and on increasing its content by a factor of only 2–3, nuclear fuel is obtained.[1] Salts of the uranyl ion UO_2^{2+}, in which uranium is in a hexavalent state, are common compounds of uranium. The main "non-nuclear" application of uranium compounds is related to the utilisation of the photochemical properties of these salts, which absorb ultraviolet and visible light and have a green luminescence.

Both the luminescence of uranium and its photochemistry have been studied for over fifty years[2] and a large amount of information has been obtained (see a monograph[3] and four reviews[2,4–6]). However a number of questions that are fundamental to the photochemistry and photophysics of uranyl remain:

—whether the large range of photochemical reactions of uranyl conforms to certain general principles, what are these principles (if, of course, they exist); is it possible to predict the photochemical behaviour of uranyl;

—which photochemical reactions of uranyl are primary and which are secondary, which of the photoreduction reactions of uranyl—through electron transfer or through hydrogen atom transfer—predominates; in which reactions is the UO_2 atomic shell of uranyl preserved and in which is it destroyed;

—what is the nature of the spin of the excited state of the uranyl ion UO_2^{2+}; is it singlet or triplet or is it altogether impossible to assign a definite spin multiplicity to this state (such a view has in all seriousness been expressed);

—what are the magnetic properties of the uranoyl ion UO_2^+, formed in the fundamental reaction of excited uranyl; what are the geminate reactions of this ion; are they magnetosensitive, and does the magnetic moment of the uranium nucleus have an effect on the spin behaviour of radical pairs involving the paramagnetic uranoyl ion UO_2^+?

The present article discusses the answers to these questions. The answers to some of them are clearer, while to others they are less certain.

II. Photochemistry of uranyl salts

1. Photoreduction of uranyl salts

The photoexcited uranyl ion participates in processes that are typical for many electronically excited molecules, namely, luminescence and radiationless deactivation. The decrease in intensity of luminescence and the reduction in lifetime of the excited state in the presence of many chemical reagents is regarded as an indication of "chemical" or "physical" quenching of excited uranyl. In its ground state uranyl is a weak electron acceptor (E^0 = 0.06 V relative to a standard hydrogen electrode); on excitation of the uranyl ion its electron affinity increases substantially (E^0 = 2.6–2.7 V).[4–6] In terms of its oxidising properties photoexcited uranyl is similar to molecular fluorine.[7] Therefore the main photochemical reaction of the uranyl ion is removal of a hydrogen atom (or electron) from the donor SH_2:

$$(UO_2^{2+})^* + SH_2 \rightarrow UO_2^+ + SH^\cdot + H^+. \quad (1)$$

This reaction is similar to the reaction of aromatic ketones or quinones excited to the n,π^* state.[4] For them the following general rule is typical: there is an increase in the rate constant with an increase in donor properties and a decrease in ionisation potential (or redox potential) of the donor and a decrease in energy of dissociation of the bond undergoing attack.[2,8–14]

Molecules of solvent (including water) can, in particular, act as a hydrogen donor.[9,15] The reaction of $(UO_2^{2+})^*$ with water

$$(UO_2^{2+})^* + H_2O \rightarrow UO_2^+ + OH^\cdot + H^+ \quad (1a)$$

occurs with a rate constant of $k \cong 10^2$ litre mol^{-1} s^{-1}.[9] Recently it was possible to record the spin adducts of the hydroxyl radical on photoexcitation of uranyl nitrate in water in the presence of a spin trap, providing additional evidence for reaction (1*a*).[15] The lifetime

of luminescence of uranyl in aqueous solution is of the order of several microseconds, so that the quantum yield of reaction (1*a*) is of the order of several percent.[16]

Added quantities of chemical compounds to solutions of uranyl salts also quench $(UO_2^{2+})^*$ in a "physical" manner—without the formation of chemical products:

$$(UO_2^{2+})^* + SH_2 \rightarrow UO_2^{2+} + SH_2. \qquad (2)$$

In the discussion of "reaction" (2) arguments have been more or less developed concerning the formation of exciplexes $[(UO_2^{2+})^*...SH_2]$ [5,10,13,18–20] and complexes in the ground state $UO_2^{2+}...SH_2$.[21] In particular, in the presence of aromatic compounds the formation of π-complexes has been postulated.[10,13,19]

The quantum yields of the reaction products of (1) vary over a wide range—from zero to unity—depending on the nature of SH_2, the solvent, and other conditions.[16–18,22,23]

Uranyl has luminescence in the region 490–650 nm; the absorption spectrum of $(UO_2^{2+})^*$, which was first recorded by Allen et al.,[24] has an absorption maximum at λ = 580 nm.[2,25,26] The kinetics of reactions (1) and (2) can be studied from luminescence quenching (during steady-state or pulsed excitation) or from the kinetics of luminescence decay of $(UO_2^{2+})^*$. A large number of studies have been devoted to the luminescence quenching of uranyl by different organic compounds, metal ions, halide ions, etc. In these experiments either the rate constants of quenching $k_q = k_1$ and k_2 or the Stern–Volmer constants K_{SV} have been determined. In the luminescence quenching the general principle noted above was found: k_q and k_{SV} are higher, the greater the electron-donating properties of the quencher (see, for example the studies of Sandhu et al;[8,10] a summary of k_q values is given by Hoffman et al.[27]).

2. Dualism in the reactivity of photoexcited uranyl

A very large number of organic and inorganic compounds,[2–6,28–33] alcohols,[13,20,33,34–40] organic acids,[24,36,38,41–48] amines,[25] amides,[28] cellulose,[28] phenols,[25,49] benzhydrol,[48] hydroquinone,[50] and others[8,10,14,36,51–58] participate in photooxidation with uranyl salts. The results of detailed EPR studies of the reaction products of (1) involving a very wide range of chemical compounds in the solid state and at low temperatures have been reported by Kemp et al.[28,29] We will not present the results of these detailed studies but will merely discuss the general properties of the reactions of excited uranyl.

Two principal mechanisms of the reactions of the electronically excited uranyl ion can be stated. On the uranium atom in the uranyl ion there are five coordination sites[59] to which ligands add (five water molecules in the complex $[UO_2(H_2O)_5]^{2+}$, two carboxyl anions and one water molecule in the complex $[UO_2(RCOO)_2.H_2O]$, two acetylacetone anions and one tetrahydrofuran molecule in $[UO_2(acac)_2.THF]$, etc.). All of the ligands lie in a single equatorial plane; the O–U–O axis is perpendicular to this plane and the "yl" oxygen atoms are situated at the poles. Hence a dualism is possible in the reactivity of the ion; electronically excited uranyl reacts either on the "equator", involving the uranium atom and the ligands, or on the "pole", involving the oxygen atoms. The first reactions occur intramolecularly, as a rule, and the second reactions are intermolecular. Furthermore, electron transfer from a ligand to the central atom is characteristic of the first reactions (U^{6+} is converted to U^{5+} as a result of this intramolecular transfer), while for the second reactions, hydrogen atom transfer to an "yl" oxygen is a typical feature. A typical example of the first reaction is the photodecarboxylation of salts of carboxylic acids, an example of the second is the photoreduction of uranyl in alcohols. In far from every case has it been possible to distinguish these two routes. Thus, generation of the ·OH radical on photolysis of uranyl salts in water [reaction (1*a*)] can occur by both routes—either by electron transfer from an equatorial ligand and the subsequent deprotonation of $H_2O^{\ddagger}$ or by an intermolecular reaction involving hydrogen atom transfer from a water molecule to an "yl" oxygen of uranyl. The dualism in the reactivity of excited uranyl is particularly clear when it is possible to establish competition between the two reaction routes. For example, in pure methanol the photolysis of UO_2^{2+} generates $CH_3O^{\cdot}$, while during photolysis in water–methanol mixtures (2:1 by volume) when the equatorial plane of UO_2^{2+} is occupied by water molecules, photoreduction occurs on the "polar" oxygen of uranyl to form the radical $\dot{C}H_2OH$.[34] It is clear that in the first case reaction mainly occurs on the "equator" through electron transfer and subsequent deprotonation while in the second case intermolecular photoreduction of uranyl on the "pole" occurs preferentially.

The photooxidation of lactic acid occurs by different mechanisms at different pH values: at pH > 3.5 it is accompanied by decarboxylation and the formation of acetaldehyde:[41]

$$UO_2^{2+} + CH_3CH(OH)COOH \xrightarrow{h\nu} U^{4+} + CH_3CHO. \qquad (1)$$

at pH 0 dehydrogenation occurs without decarboxylation and a keto acid (pyruvic acid) is formed:

$$UO_2^{2+} + CH_3CH(OH)COOH \xrightarrow{h\nu} U^{4+} + CH_3C(O)COOH. \qquad (2)$$

In the first case lactic acid is present in the form of lactate anion $CH_3CH(OH)COO^-$ and reacts in the coordination sphere (on the "equator") by electron transfer and decarboxylation followed by conversion of $CH_3\dot{C}HOH$ to acetaldehyde.

At low pH values in aqueous solution lactic acid is predominantly in the molecular form and photoreduction occurs on the pole to form the radical $CH_3\dot{C}(OH)COOH$, which is then converted to the keto acid.

On photoreduction of alcohols an isotope effect occurs. In the pairs of systems CH_3OH-CD_3OH and CH_3OD-CD_3OD the isotope effect has a normal sign of $k_1(CH)/k_1(CD)$ = 2.4–2.9.[41] In the pairs CH_3OH-CH_3OD and CD_3OH-CD_3OD the isotope effect is very small (0.98 and 0.85) and has the reverse sign.[41] It is clear that the reaction of excited uranyl on the C–H bonds occurs on the "pole" as an intermolecular hydrogen atom transfer while the reaction on the O–H bonds occurs as an intramolecular electron transfer ("equatorial" reaction).

Thus, the dualism in the reactivity of photoexcited uranyl is determined by the competition of reactions along two pathways—on the equatorial plane of the ion and on a "polar" oxygen atom. These routes have a different sensitivity to the reaction conditions and this phenomenon is the reason for the very considerable variability in the chemical behaviour of uranyl.

In certain cases when the formation of U(IV) and new chemical products is recorded using conventional steady-state methods but the formation of primary products of one-electron oxidation or removal of a hydrogen atom is not detected, two-electron oxidation or oxygen atom transfer processes are postulated.[8,10,51,52,60] For

example, according to Sandhu et al.,[60] the oxidation of dialkyl sulphides occurs according to the following reaction:

$$(UO_2^{2+})^* + R_2S \rightarrow U^{4+} + R_2SO. \quad (3)$$

It has been proposed that the same reaction involving oxygen atom transfer [reaction (3)] occurs by reaction of $(UO_2^{2+})^*$ with triphenylphosphine, triphenylarsine, triphenylbismuth, and certain other compounds. However, in the oxidation of dicyclohexyl sulphide in dry acetone the cationic species UO_2^+ are formed,[17] while in the oxidation of a number of other disulphides, radical cations are formed.[18] Addition of dilute hydrochloric acid to a solution of dicyclohexyl sulphide in acetone is accompanied by the formation of U(IV), but only in secondary reactions:

$$UO_2^{2+} + R_2S \overset{h\nu}{\rightleftharpoons} [UO_2^{2+} \ldots R_2S]^* \quad (3a)$$

$$[UO_2^+ \ldots R_2S^+] \xrightarrow{H_2O,\ H^+} UO^{2+} + R_2SO\,. \quad (3b)$$

There is a high probability that all of the remaining reactions of type (3) occur via a one-electron transfer to form UO_2^+ [reaction (1)].

The photoreduction of uranyl nitrate with tri-n-butyl phosphate is accompanied by the formation of nitrite and nitrous acid, which oxidise U(IV). The combination of primary and secondary reactions leads to the results having poor reproducibility and a strong dependence of the yield of U(IV) on temperature, wavelength of exciting light, etc.[23] Moreover, the photolysis of uranyl nitrate can lead to formation of the pair $[UO_2^+, NO_3]$ and nitrite can be formed directly by photoexcitation of nitrate.[23,61]

Uranoyl is an intermediate in the photolysis of a number of uranyl compounds in the solid state.[62,63]

Above, there has mainly been a discussion of the photoexcitation of uranyl in water or other homogeneous solvents. The luminescence of uranyl and its photochemical reactions in heterogeneous and microheterogeneous solutions have also been investigated.[25,64–67] The photochemistry of uranyl adsorbed on colloidal silicon, zeolites, and alumina has been studied in relation to the possible photocatalytic effect of such systems.[65,66] Moreover, it is well known that in heterogeneous media (including micelles) conditions are favourable for the display of different magnetic effects in spin-selective reactions,[68–71] and this circumstance has stimulated additional interest in such studies. However, in principle, the photochemistry of uranyl in heterogeneous systems repeats the normal "homogeneous" chemistry.

3. The radical pair uranoyl–free radical

The primary product of excited uranyl with a donor is the radical pair (RP) $[UO_2^+, \dot{S}H]$, which either dissociates or its partners react together (forward or reverse electron transfer or disproportionation):

$$[UO_2^+, \dot{S}H] \begin{cases} \xrightarrow{k_4} UO_2^+ + \dot{S}H, & (4) \\ \xrightarrow{k_5} UO_2^{2+} + SH_2, & (5) \\ \xrightarrow{k_6} U^{4+} + S. & (6) \end{cases}$$

From a knowledge of the redox potentials of the pairs $E^0(UO_2^{2+}/UO_2^+) = 0.06$ V and $E^0(UO_2^+/U^{4+}) = 0.55$ V relative to a standard hydrogen electrode,[2–6] it can be predicted that oxidising radicals (with a potential $E^0 > 0.06$ V) will regenerate the initial reagents, while the strong oxidising agent—uranoyl—will oxidise many radicals to tetravalent uranium compounds. It is necessary to bear in mind that the values of the redox potentials are significantly dependent on the pH of the solution and the reagents.

Little is known about the cage reactions of the uranoyl ion and therefore different ideas have been put forward. There is definite interest in recording them directly. The cage reactions (4)–(6) are exhibited during laser photolysis, in particular in the photooxidation of the leuco base of a thionine dye (SH_2) sensitised with uranyl nitrate. The conversion of SH_2 to $\dot{S}H$ and S is accompanied by marked spectroscopic changes.[26] In the first instant after a flash the excited state $(UO_2^{2+})^*$ is formed, the "physical" (2) and "chemical" (1) destruction of which lasts 800 ns (Fig. 1). By this time $\dot{S}H$ has accumulated and, what is significant, S is formed in appreciable concentration (Fig. 1). Thus, these direct results demonstrate the occurrence of a successive two-stage oxidation of SH_2 by photoexcited uranyl with primary formation of the uranoyl ion. The quantity of $\dot{S}H$ oxidised in the cage comprises about 5% of the quantity of $\dot{S}H$ formed in bulk [reaction (4)].[26]

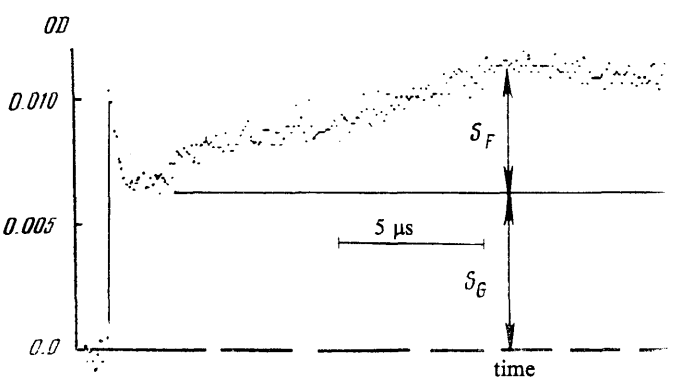


Figure 1. Changes in the optical density *OD* of aqueous solutions of uranyl nitrate in the presence of leucothionine which occur during laser photolysis with $\lambda = 600$ nm.[26] Here S_G is the optical density due to S formed in the cage; S_F is the optical density of S formed in extracage reactions.

The kinetics of the geminate recombination (5) of the pair $[UO_2^+ . (C_6H_5)_2NH^{+\cdot}]$ obtained by pulsed laser photoexcitation of uranyl nitrate in the presence of diphenylamine in reverse micelles of sodium di(2-ethylhexyl)sulphosuccinate (Aerosol OT) (AOT) have been recorded.[25] In this case uranyl nitrate occurs in aqueous solution inside the micelles. The destruction of the RP is given by a first-order kinetic equation with a constant $k_q = k_4 + k_5$ and depends on the ratio $[H_2O]/[AOT]$, namely, on the size of the micelles. The cage effect in all of the experiments was approximately 0.9.[25] Such experiments are for the time being scarce in number, but they make it possible to record directly both the kinetics of geminate recombination and the magnitude of the cage effects.

There are many indications that excited uranyl has a triplet state, and when it undergoes photoreduction in a triplet RP is formed (see later).

III. Reactivity of the uranoyl ion

There is no doubt that the primary photoprocess—transfer of a hydrogen atom or electron to the uranyl ion [reaction (1)]—occurs with retention of the monolithic shell of UO_2 (see Section II.2). Destruction of this shell occurs in secondary, mainly dark, reactions, about whose mechanism little is known for certain. Amongst these is disproportionation of uranoyl ions

$$UO_2^+ + UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O, \quad (7)$$

with regeneration of uranyl and the readily hydrolysed ion of oxygen-free tetravalent uranium. Despite its outward simplicity, the mechanism of reaction (7) is quite complex and has not been completely elucidated.[72] The reaction is significantly accelerated with a decrease in pH, occurs more rapidly in heavy water than in normal water, and is accelerated in the presence of fluoride ions.[72,73] Kinetic schemes that involve the formation of the dimer of UO_2^+ in protonated form UO_2H^{2+} represent the experimental data to the most adequate degree. In the region of pH 2–3 the UO_2^+ cation is relatively stable; in more acidic media the approximate relationship $k_7[H^+]^{-1} \cong 5.0 \times 10^2$ litre^{-2}mol^{-2}s^{-1} (water, 293 K, ionic strength 2.5) is valid.[72]

Another reaction involving destruction of the shell is the exchange of oxygen atoms between uranyl and water molecules. It was known some time ago (see for example, Okuyama et al.[74]) that the dark exchange which is extremely slow ($\sim 10^4$ h) in acid solution is markedly accelerated (by many orders) on irradiation with light in the absorption band of uranyl. It was proposed that exchange occurs in the electronically excited state of the uranyl ion,[74] but doubts about this mechanism arose straight away since no correlation was found between the rate of exchange and the lifetime of the excited (luminescent) state. In strongly acid solutions the rate of exchange decreased substantially, although the lifetime of the excited state increased.[75]

This phenomenon was noted in a series of outstanding studies by Suglobov et al.[16,22,55,58,76,77] on the kinetics and mechanism of photostimulated oxygen exchange between uranyl and water. The kinetic features of the exchange reaction were reliably established: 1) isotopic exchange ($^{16}O-{}^{18}O$) between uranyl oxygen and water is only induced by light that is photochemically active towards UO_2^{2+}; 2) the quantum yield of exchange (the number of fundamental exchange reactions per photochemically active quantum) is considerably greater than unity and amounts to tens or even hundreds in water (depending on the pH), and in the presence of ethanol reaches 3500; this indicates that the exchange reaction is a chain process; 3) the quantum yield has a linear dependence on the concentration of the initial uranyl; 4) it is inversely proportional to the square root of the light intensity; 5) the quantum yield decreases sharply in the presence of small quantities of added persulphate, whose ions do not quench the luminescence of UO_2^{2+} but oxidise uranoyl ions:

$$UO_2^+ + S_2O_8^{2-} \rightarrow UO_2^{2+} + SO_4^{\cdot} + SO_4^{2-}. \quad (8)$$

All these features clearly demonstrate that the uranoyl ion UO_2^+ (or its protonated form), in which the triatomic shell becomes unstable, is responsible for oxygen exchange:

$$U^{18}O_2^+ + H_3^{16}O^+ \rightleftarrows U^{18}O_2H^{2+} + H_2^{16}O, \quad (9)$$

$$U^{18}O_2H^{2+} + H_3^{16}O^+ \rightleftarrows U^{16}O_2H^{2+} + H_3^{18}O^+. \quad (10)$$

Let us adopt the following kinetic scheme of exchange

$$[UO_2^{2+}]^* + H_2O \xrightarrow{W_i} UO_2^+ + OH^{\cdot} \quad (1a)$$

(The photochemical generation of the uranoyl ion occurs with rate W_i);

$$UO_2^+ + UO_2^{2+} \rightleftarrows UO_2^{2+} + UO_2^+ \quad (11)$$

the reaction of electron recharging (electron exchange) ensures the propagation of the kinetic chain of oxygen exchange:

$$UO_2^+ + UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O \quad (7)$$

(disproportionation, destruction of the uranoyl ion, termination of the kinetic chain).

The scheme assumes a rapid oxygen-isotope exchange of each UO_2^+ ion with water (its mechanism has so far not been discussed), propagation of the chain through electron recharging between the isotopically exchanged UO_2^+ and "native" $UO_2^{2+}$and termination of the kinetic chain through disproportionation of uranoyl ions.

The rate W_i of generating UO_2^+ is equal to φI, where φ is the quantum yield of generation of UO_2^+, I is the intensity (number) of quanta absorbed. The quantum yield of oxygen exchange can be given in the form

$$\Phi = W_i\nu/I = \varphi\nu, \quad (12)$$

where ν is the length of the kinetic chain. The lifetime of an individual uranoyl ion $\tau^* = \{k_{11}[UO_2^+]\}^{-1}$, while the lifetime of the kinetic chain $\tau = \{k_7[UO_2^+]\}^{-1}$, where the steady-state concentration of $[UO_2^+] = (W_i/k_7)^{1/2}$. Hence we can readily obtain the length of the kinetic chain

$$\nu = \tau/\tau^* = \frac{k_{11}[UO_2^+]}{(k_7W_i)^{1/2}} = \frac{k_{11}[UO_2^+]}{(k_7\varphi I)^{1/2}} \quad (13)$$

and the quantum yield

$$\Phi = \frac{W_i}{I} = \frac{\varphi^{1/2}k_{11}[UO_2^+]}{k_7^{1/2}I^{1/2}} \quad (14)$$

The dependences of Φ on $[UO_2^+]$ and I as predicted by Eqn. (14) are consistent with experiment and quantitative determinations of Φ (with the current uncertainty in the constant k_{11}) are in reasonable agreement with the experimental values of Φ.[16]

In solutions of uranyl in perchloric acid ($[HClO_4] = 0.1$ M), $\Phi = 43$, while under the same conditions but in the presence of ammonium persulphate, which suppresses the chain process through reaction (8), $\Phi^* = 0.08$.[16] Since in this case $\nu = 1$, it is easy to determine that the length of the kinetic chain of oxygen exchange of uranoyl in water is equal to $\nu = \Phi/\Phi^* = 540$.

The physical meaning of the dependence of Φ on I is also clear. The greater the intensity of light, the higher the steady-state concentration of UO_2^+ ions, and hence, the rate of quadratic chain termination, and the lower the yield of oxygen exchange.

It is clear that the limiting quantum yield ($\Phi = \varphi\nu$) when $\varphi = 1$ is equal to the length of the kinetic chain of oxygen exchange $\Phi = 540$. However, in aqueous ethanol solutions Φ increases with an increase in concentration of ethanol and reaches a maximum value of $\Phi = 3500$.[16] This considerably exceeds the expected value of 540 and would appear to indicate that in aqueous ethanol solutions an increase in φ to unity is insufficient and that it is necessary also to

assume that the rate constants k_7 and k_{11} vary (relative to purely aqueous solutions of uranyl) in Eqns. (13) and (14).

On addition of metal salts to the solutions being studied in perchloric acid there is a change in Φ.[58] The introduction of ions that reduce $(UO_2^{2+})^*$ (Fe^{2+}, Ce^{3+}, Mn^{2+}) leads to an increase in Φ, whereas the introduction of ions that oxidise UO_2^+ (Fe^{3+}, Ag^+) leads to a decrease in Φ.[58]

The most unclear stage in this mechanism is the actual reaction of oxygen exchange in the UO_2^+ ion, namely, destruction of the UO_2 shell. The rate of exchange is strongly dependent on the pH of solution. For example, when $[UO_2^{2+}] = 0.1$ M, with an increase in acidity from 0.01 to 0.4 $HClO_4$ the quantum yield increases from 10 to a maximum value of 80, and then with a further increase in $HClO_4$ concentration it decreases to $\Phi = 1$ at 12 M $HClO_4$. In solutions with pH $\leqslant$ 0.4 both of the oxygen atoms of uranoyl are exchanged (two-oxygen exchange) and the quantum yield of this exchange $\Phi_2 \approx [H^+]^2$.[16] When pH > 1.5 the exchange involves one oxygen, i.e. each oxygen atom is exchanged independently and the quantum yield of exchange $\Phi_1 \approx [H^+]$.[16] It is clear that singly or doubly protonated forms of the uranoyl ion participate in exchange (the reaction occurs on a single oxygen atom [Eqn. (10)] or on both simultaneously) and that exchange is catalysed by hydroxonium ions. Reasonable and plausible chemical schemes of catalytic exchange can be put forward,[77] but they should be treated with caution. Direct methods are needed (with a time resolution of the order of picoseconds) for detecting the intermediate species and their dynamics.

As was mentioned above, in the photoreactions of uranyl with Ph_3P, Ph_3As, R_2S, and R_2SO, transfer of an oxygen atom occurs.[8,10,51,52,60] In this case phosphite is converted to phosphate, sulphide to sulphoxide, sulphoxide to sulphone, and the Ph_3As group to Ph_3AsO. The quantum yield of these reactions is low and equals 0.01–0.05. Photooxidation of sulphoxide to sulphone with uranyl is a thermally activated reaction and required an energy of activation of about 25 kJ mol^{-1},[52] which is unusual for photoreactions. It must be assumed from these characteristics that transfer of oxygen in these reactions is a secondary reaction that occurs with the involvement of the resulting uranoyl ion UO_2^+. In certain cases there is direct evidence for this mechanism (see above).

There is no doubt that destruction of the shell also occurs in $^{235}U-^{238}U$ isotope exchange[54]

$$^{235}UO_2^{2+} + {}^{238}U^{4+} \rightleftarrows {}^{238}UO_2^{2+} + {}^{235}U^{4+} . \qquad (15)$$

For a solution of uranyl in hydrochloric acid (8.0 M), $k_{15} = 7.17 \times 10^{-4}$ litre mol^{-1} min^{-1}.[54] Reaction occurs via the formation of uranoyl and is markedly accelerated by visible and UV light.[54] In the absence of other donors uranyl is photoreduced by U(IV) to form a superequilibrium concentration of UO_2^+.[50,54]

The mechanism of reaction (11), in which electron exchange and hence isotope exchange occur is debatable. The reaction occurs either by one-electron transfer, as according to Eqn. (11),[78] or via a stage involving the formation of a complex[16]

$$UO_2^+ + UO_2^{2+} \rightleftarrows UO_2^+ \ldots UO_2^{2+}, \qquad (16)$$

$$UO_2^+ \ldots UO_2^{2+} \rightarrow UO_2^{2+} + UO_2^+. \qquad (17)$$

The values of the rate constants have been determined: $k_{11} = 1-10$ litre mol^{-1} s^{-1};[78] $k_{16} = 16-30$ litre mol^{-1} s^{-1},[16,72] $k_{17} = (1.0 \pm 0.1) \times 10^3$ s^{-1}.[16]

Of the other reactions of uranoyl we should mention the formation of a binuclear complex [reaction (16)] which stabilises uranoyl.[72,79] It is assumed that formation of the complex between uranoyl and the radical resulting from photooxidation of a donor also stabilises UO_2^+.[17,80]

In the photoreduction of (8-crown-6)uranyl perchlorate in acetonitrile, a U(V) compound is obtained which has the formula UO(18-crown-6)$(ClO_4)_3$.[81] It is relatively stable and does not disproportionate, being shielded by the macrocyclic ligand.[81]

The UO_2^+ formed in the primary photochemical reaction, in addition to disproportionation and isotope exchange, participates in reactions with the initial SH_2

$$UO_2^+ + SH_2 \rightarrow U^{4+} + SH_2^{\cdot} \qquad (18)$$

and with the corresponding radical $SH^{\cdot}$ ($SH^{\cdot}$)

$$UO_2^+ + SH^{\cdot} \rightarrow \text{products}. \qquad (19)$$

The latter reaction is rapid,[82–84] and it is frequently geminate. The routes of reactions of the type (18) and (19) can be predicted from the one-electron redox potentials of the reactants.[26,57,58,84]

It was shown by Sergeeva et al.[50] that UO_2^+ oxidises ethanol, ascorbic acid, and hydroquinone. It is very probable that it is reaction (18) involving ethanol that is responsible for the excess value of the quantum yield of U(IV) of 0.5 in the photoreduction of uranyl in aqueous solution containing a high concentration of ethanol rather than the transfer of two electrons as was proposed by Suglobov et al.[22]

Values of k_{19} ranging from 10^4 to 10^9 litre mol^{-1} s^{-1} have been obtained for a number of organic and inorganic radicals acting as partners of uranoyl.[50,82,84]

We should note in conclusion that the whole range of photochemical reactions for the reduction of uranyl is reduced to two key processes—oxidation of the substrate in the inner sphere by one-electron transfer (reaction on the "equator", reaction of the U atom) and removal of a hydrogen atom on the "pole" (reaction of an O atom). These reactions of photoexcited uranyl are primary and are accompanied by retention of the triatomic shell of UO_2. Break-up of this shell occurs in secondary reactions of the further reduction of U(V) to U(IV), occurring both inside the cage and in extracage reactions. Of the latter the most characteristic is disproportionation of U(V) [reaction (7)], which results in the formation of the final photoreduction product of uranyl—uranium(IV).

IV. Spin and magnetic properties of excited uranyl and the uranoyl ion

1. The lowest excited state of uranyl

The question of the spin state of the reacting excited ion of uranyl is of fundamental significance—it determines the spin selectivity of the reactions and the scale of the magnetic effects. A solution to the problem of the nature of the spin state of $(UO_2^{2+})^*$ can be provided by quantum-chemical calculations, an analysis of the lifetimes of luminescence, experiments on energy transfer, and research into magnetic and spin effects in the photochemical reactions of uranyl.

The absorption of uranyl in the visible region is mainly due to transitions from the highest occupied molecular orbital located primarily on the oxygen atoms to the 5*f* orbitals of uranium.[85–92]

These transitions are symmetry-forbidden and have low intensity (extinction coefficient $\varepsilon \cong 10-50$ litre mol^{-1} cm^{-1}). The substantial spin-orbit coupling (SOC) in the uranium atom (it is thought that in the uranium atom the SOC constant is in the region of $\zeta = 1740-2000$ cm^{-1})[87] places in doubt the possibility of assigning a definite spin state to $(UO_2^{2+})^*$. The authors of two studies[93,94] believe that singlet and triplet are so highly mixed and indistinguishable that there is no point in raising the question of the spin state of excited uranyl. However, such a conclusion is scarcely constructive. Thus, detailed calculations[85] indicate that both schemes (interelectron repulsion of the terms greater than the spin-orbit coupling between the terms and *vice versa*) represent the excited states of the uranyl ion, with the first scheme representing them even better. Attempts to determine experimentally the nature of the excited states of the uranyl ion in liquid solution during energy transfer experiments involving organic molecules and molecular oxygen proved unsuccessful.[95,96] The luminescence of uranyl is hardly excited at all by other donors, and there is hardly any evidence of energy transfer from photoexcited uranyl salts (energy of the lowest level $E = 20500$ cm^{-1})[4,96,97] to typical acceptors of triplet energy. In particular, molecular oxygen even at a pressure of 2×10^6 Pa does not quence the luminescence of uranyl.[96] Similar results led Sergeeva et al.[95] to assume that the excited state of the uranyl ion is singlet. However, the low efficiency of energy transfer from $(UO_2^{2+})^*$ to acceptors is a weak argument for such a conclusion, since it may be related to shielding of excitation to the 5*f* orbitals by the outer filled orbitals and the orbitals of the oxygen atoms.[96] Such a cause of inertness in energy transfer is not new, it is known for complex compounds with localised excited states.[2] Claudel et al.[63] have also proposed (without careful reasoning) that the reactive state of $(UO_2^{2+})^*$ in the solid state is singlet.

However, the idea of the triplet nature of $(UO_2^{2+})^*$, first put forward by McGlynn and Smith,[104] has been accepted by the majority of research workers (see, for example, several studies).[48,54,61,76,98–103] Moreover, there is experimental evidence for it, obtained in magnetic circular dichroism at low temperature for uranyl compounds.[98] A number of indications suggest a triplet as the excited reacting state of uranyl. First of all the lifetime of the excited state (2–10 μs in water[2] and 440 μs (!) for a colloidal solution of uranyl bonded to silicon[65]) is too great to belong to a singlet—especially when the presence of the uranium atom with strong spin-orbit interaction (~2000 cm^{-1}) is taken into account. It is true that it still does not follow from this fact directly that this luminescent state is reactive or responsible for the reaction of excited uranyl.

There is other also indirect evidence resulting from the reaction characteristics of excited uranyl. This relates in particular to photoreduction reactions on the "pole", namely, reactions on "yl" oxygen (see Section II.2). As was mentioned above, these are almost identical to reactions of triplet benzophenone: the same H/D isotope effects and reactions on the C–H bonds of alcohols, the same order of increase in quantum yields of photoreduction in the series methanol < ethanol < isopropanol (0.15, 0.31, and 0.34 respectively)[4] and the same absolute values of the rate constants k_1 of photoreduction (about 10^6 litre mol^{-1} s^{-1}). Even in its ground state UO_2^{2+} is similar to benzophenone. For example, it is an acceptor of a hydroxy hydrogen atom (see below), removing it from the radicals $(C_6H_5)_2COH$, CH_3COH, and $CH_3C(OH)COOH$. None of this evidence can be regarded as reliable confirmation; the latter only developed out of magnetic spin effects in reactions of uranyl (see Section V).

2. Magnetic and other physical properties of the uranoyl ion

The uranoyl ion is a primary product of the photoreduction of uranyl salts; it is also obtained by electrochemical or chemical reduction of uranyl.[105] the reducing agents can be free radicals such as $(CH_3)_2COH$, $CO_2^{\cdot-}$, etc.[44,47,106] Uranoyl is a labile species whose lifetime is mainly dictated by the disproportionation reaction

$$UO_2^+ + UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O. \qquad (7)$$

Its rate constant depends on the pH of the aqueous solution, the solvent, and the composition of the solution, so it is possible to find the conditions under which it achieves a high (up to 10^{-2} M) steady-state concentration of uranoyl[17,51,53,78–81,105,107] (for more detail, see Section III).

The absorption spectrum of uranoyl extends into the visible and infrared regions. The positions of the absorption maxima and values of the extinction coefficients of uranyl are given in several studies.[17,51,53,78,80,103,107–113]

The absorption spectra of UO_2^+ are sensitive to the solvent and depend on the nature and concentration of SH_2 and the concentration of UO_2^{2+}, and these dependences result from the complexation of UO_2^+. The absorption spectra of UO_2^+ are mainly used for identification of this intermediate compound. From the existing data it is possible to distinguish U(V) from U(IV) and U(VI) in the absorption spectra with complete confidence.[17,51,53]

The uranoyl ion has the electron shell [Rn]$5f^1$ and is a free radical. Its EPR spectrum has been recorded at low temperature (77 and 153 K) during electrochemical and photochemical reduction of $UO_2(dmf)_5(ClO_4)_2$ in *N,N*-dimethylformamide (dmf) and also $UO_2(dmso)_5(NO_3)_2$ and $UO_2(tep)_2(NO_3)_2$ in dimethyl sulphoxide (dmso) and triethyl phosphate (tep) respectively, which enter into the coordination sphere of uranyl.[110,114] Miyake et al.[110,114] consider that there are two types of spectra comprising isolated lines with the parameters $g_\perp = 2.5$, $g_\parallel \approx 0$, line width 150 mT, symmetrical line (spectrum of the first type) and $g_\perp = 1.97$, $g_\parallel \approx 1.3$, line width 10 mT, asymmetric line (spectrum of the second type). An average value of the *g* factor of $\bar{g} = 1.7$ corresponds to both type of spectrum. Spectra of the first type are obtained by photo- or electro-chemical reduction of perchlorates, and in these the perchlorate anion always remains outside the first coordination sphere and the equatorial plane is occupied by molecules of the organic solvent,[114] while spectra of the second type are obtained by photoreduction of nitrates. In this case the nitrate anion is situated in the equatorial plane of the complexes and remains in it during photoreduction, giving rise to the asymmetry of the EPR spectrum. This interpretation of the spectra is very much in doubt. Firstly, the EPR line ascribed to UO_2^+ is always asymmetric (even in the case of uranyl perchlorate); secondly, the theoretical interpretation of the spectrum is complex and ambiguous and requires a number of doubtful assumptions and approximations concerning the strength and symmetry of the crystal field and the spin-orbit coupling in the UO_2^+ ion. It is all the more difficult to correlate the theoretical and experimental EPR spectra.

It may also be doubtful that the isotropic *g* factor of UO_2^+ has a value close to 1.7, although the fact that it is less than the *g* factor of a free electron (2.0023) has been confirmed with complete reliability.[115–117] It was shown in these three studies[115–117] that the uranoyl ion has a considerable effect on the magnetic resonance parameters of organic radicals that are complexed with it.[28,115–117] Thus, in complexes of UO_2^{2+} with a phenanthrenequinone radical anion PQ^- and neutral radical

HPQ$^{\cdot}$, the g factors and electron relaxation times T_1 differ considerably from the g-factor and T_1 of free $PQ^{\cdot-}$ and HPQ$^{\cdot}$: $T_1(PQ^{\cdot-}) = 4-10$ μs, $T_1([UO_2PQ]^{+}) = 0.8$ μs, the g factors for $PQ^{\cdot-}$, $[UO_2PQ]^{+}$ and UO_2HPQ^{2+} are 2.0045, 1.9940, and 1.9945 respectively.[116] The presence of the uranium atom with its spin-orbit interaction opens up an additional route for paramagnetic relaxation and reduces the electron relaxation times of the complexes. In complexes of substituted *o*-benzo-semiquinones with uranoyl T_1 is even less (<0.2 μs).[117] The decrease in the g factor of the complexes results from the delocalisation of the spin from the organic anion to uranoyl. This means that the g factor of uranoyl is less than the g factor of a free electron.

Evidence for this assertion is provided by the EPR spectrum of the radical pair $^3[UO_2^+, NO_3]$ which is formed by photolysis of a monocrystal of the triethyl phosphate complex of uranyl nitrate $UO_2(NO_3)_2.2OP(OC_2H_5)_3$.[61] The angular dependence of the spectrum is dictated by the anisotropy of the g factor (its primary values lie within the region of 1.996 to 1.871). Even the largest of the components of the g factor is less than 2.0023. The additional interaction between the electrons in the pair has an angular dependence, with its maximum value amounting to 87 mT. This corresponds to a distance of 2.8 Å between the electrons, and it is approximately equal to the distance between the partners in the pair. In itself the observation of the EPR spectrum of a radical pair at the low temperatures used (less than 10 K) is an indication of a triplet precursor of the excited ion $(UO_2^{2+})^*$. However, strictly speaking the sign of the exchange interaction J and hence the spin state of the pair cannot be deduced from the EPR spectrum. Moreover, Giacometti et al.[61] did not estimate the value of J either, although this is possible by comparing the value of a_N—the ^{14}N hyperfine interaction in NO_3. If $J \gg a_N$, the ^{14}N hyperfine splitting in the pair must be $\frac{1}{2}a_N$ in the individual NO_3 radical; if $J \ll a_N$, a_N in the pair must coincide with a_N for the free NO_3 radical.

It is of course necessary to have reliable information about the g factor and hyperfine electron-nuclear interactions on the ^{235}U nucleus in the uranoyl ion. Further efforts are needed to obtain the EPR spectra of this ion in an oriented state—in monocrystals, in liquid crystal systems or by photolysis with polarised light, i.e. under conditions of photoselection with respect to orientation.

The question of the hyperfine coupling (HFC) on the magnetic nucleus of ^{235}U is very important. It is known that in UF_5 radical located in crystal lattices of halides of alkali or alkaline earth metals, the isotropic HFC is 5 mT on average. For UO_2^+ the hyperfine coupling is quite unknown and new measurements of EPR spectra of this ion with an enriched content of magnetic isotope are needed.

The paramagnetism of UO_2^+ is also detected in NMR spectra. This was first demonstrated by Pershin et al.[39] On irradiation of uranyl nitrate in ethanol, paramagnetic shifts and broadening of the NMR lines of ethanol appeared on the recording unit of the NMR spectrometer. The kinetics of the shifts and broadening on turning the light on and off clearly corresponded to the kinetics of the photochemical formation and dark destruction of the paramagnetic UO_2^+ ion. This indicates that the shifts and broadening of the NMR lines of the solvent occur when these molecules enter into the coordination sphere of the UO_2^+ ion and by a rapid exchange of the coordinated molecules with free ones.

The patterns of shifts and broadening are distinctive. The NMR line of the protons of the CH_3 group is hardly shifted and is not broadened, the line due to CH_2 is broadened and shifted downfield, but the hydroxyl protons of ethanol undergo the most broadening and a shift upfield. These are all indications that the paramagnetic shifts are due to contact hyperfine coupling of the unpaired electron with the nuclei of the ligand and that the ligand adds to the UO_2^+ ion via its hydroxyl group and through it spin density from the UO_2^+ ion is partially transferred to the ligand.[39]

Paramagnetic shifts and broadening of the NMR lines of the solvent were also observed in the photolysis of UO_2^{2+} in dimethyl sulphoxide.[80] The resonance lines due to the methyl groups in the ^1H and ^{13}C NMR spectra were shifted upfield (the magnitude of the shift was proportional to the concentration of paramagnetic UO_2^+ ions). In this case also the shifts and broadening occur on introduction of a solvent molecule into the coordination sphere of the UO_2^+ ion, but they are induced by a pseudocontact interaction (the same sign of the ^1H and ^{13}C shifts indicates this). In other words, in complexes of UO_2^+ with DMSO spin density is not transferred to the ligand (in contrast to complexes of UO_2^+ with ethanol). It is difficult to identify clearly the reason for these differences, but it is most likely that ethanol adds as a ligand to an oxygen atom of UO_2^+ on the pole while DMSO enters the plane of the coordination sphere on the equator.

V. Spin-selective reactions of uranoyl and magnetic effects

Let us return again to the question of the spin state of the excited uranyl ion. It was previously argued that this state has a given multiplicity, namely, a triplet. Since the spin is retained in fundamental reactions, the spin state of the excited ion is converted unchanged into the primary photoreduction product of uranyl—a radical pair—and therefore manifests itself in the spin selectivity of the photochemical reactions of uranyl.

A feature of spin-selective chemical reactions is their magneto-sensitivity, i.e. the sensitivity to the magnetic interactions of electrons and nuclei with an external magnetic field and to electron-nuclear hyperfine coupling. Energetically the magnetic interactions are small, but they are unique in the sense that it is only they that can change electron spins and remove the spin restriction in the spin-selective reaction. The spin restriction means that not all spin states can react, i.e. there are states that are reaction-forbidden.

The notable phenomena related to spin restriction are chemical polarisation of nuclei and electrons (CPN and CPE), the magnetic field effect (MFE), and magnetic isotope effect (MIE).[68–71] The most interesting of these is the MIE, namely, the dependence of the rate of reaction of paramagnetic species on the spin and magnetic moment of their nuclei.[70] It leads to a separation of magnetic and nonmagnetic isotopes in chemical reactions. A magnetic isotope effect has been detected for carbon, oxygen, silicon, and sulphur.[70,119,120] It would be tempting to find this effect also for reactions involving uranium compounds, in which one of the isotopes—^{238}U—is nonmagnetic, while the other—^{235}U—is magnetic (nuclear spin $I = {}^7/_2$, magnetic moment $\mu_I = -0.36\ \mu_N$).[121]

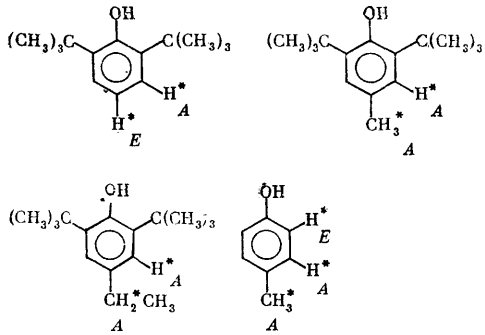
Research into the MIE in uranium aims to reach the solution to three problems: 1) to find reactions of uranium compounds involving paramagnetic intermediates; 2) to find the spin-selective stages in the reactions of these species and to establish the initial spin multiplicity in these stages; 3) to study the distribution of isotopes in the products of these reactions.

A solution to the first problem is evident. It is clear that photoreduction reactions of uranyl give radical pairs with the paramagnetic UO_2^+ ion and that these reactions are most suitable for

solving the subsequent two problems. We shall discuss below the methods for solving them through magneto-spin effects.

1. Chemical polarisation of nuclei in photoreduction reactions of uranyl salts

Chemical polarisation of ^1H nuclei has been observed in the photoreduction of uranyl nitrate with a number of alkyl-substituted phenols, benzilic acid, and benzhydrol (Figs. 2 and 3).[48,102] The polarisation indicators are shown below on the diagram (A = enhanced absorption E = emission):[102]



Polarisation of the extracage products of the recombination of the resulting phenoxyl radicals has also been detected. The reaction involves the fundamental stages (22), (23), and (24) (see section V.3). Phenoxyl radicals are poor electron donors and good acceptors, so the spin-selective reaction (24), resulting in the formation of a phenol with polarised nuclei takes place in the cage.

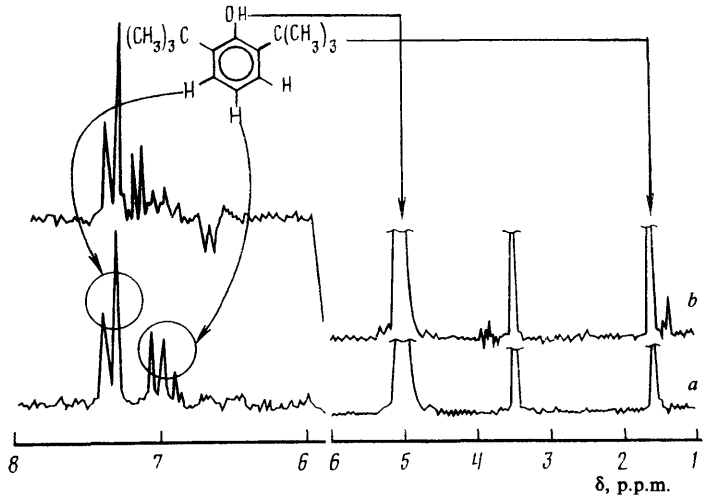


Figure 2. PMR spectrum of a solution of 2,6-di-t-butylphenol and uranyl nitrate in methanol-d_4 before (a) and during (b) irradiation of solution.

The fact that CPN occurs is not insignificant. It demonstrates the spin selectivity of the reaction and determines the spin multiplicity of the RP, from which the magnetosensitivity of the reactions and magnetoselectivity of the radicals is to be expected.

Chemical polarisation of the protons of the phenols accurately reproduces the polarisation in reactions of the same phenols with triplet benzophenone,[102] and this provides a firm (but not conclusive) basis for the assertion that uranyl reacts in a triplet state and generates a triplet RP.

The ketyl radical of benzophenone is formed as an intermediate on oxidation of benzhydrol and benzilic acid.[48] This radical, on the other hand, is a good donor[44,47] and oxidation of ketyl to ketone occurs in the cage (see scheme below).

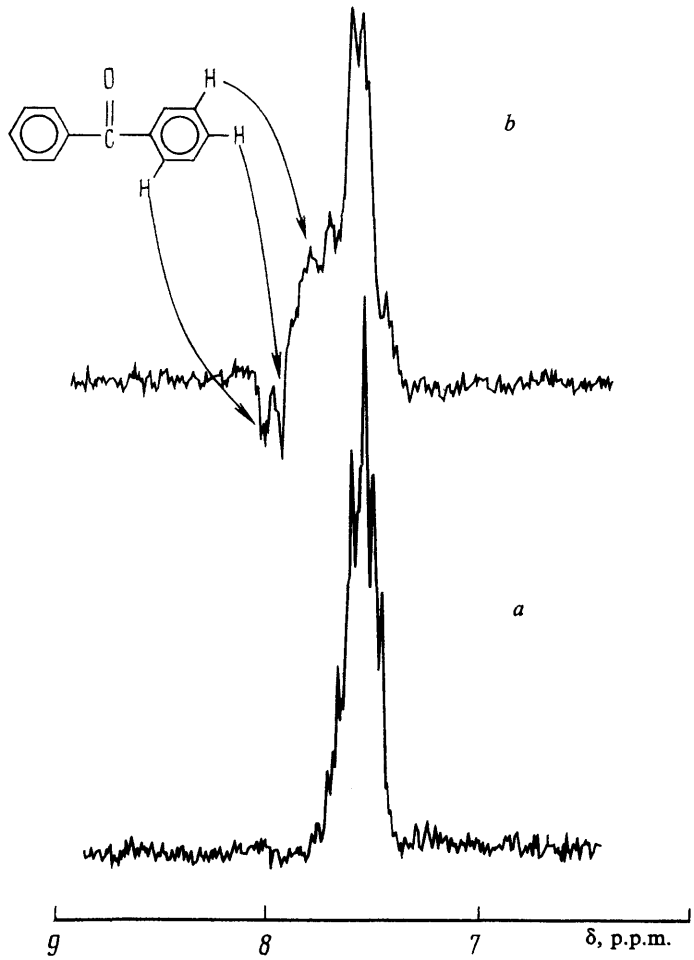
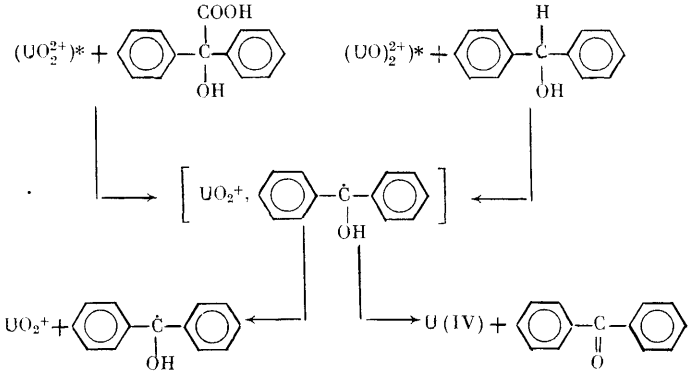


Figure 3. PMR spectrum of a solution of benzilic acid and uranyl nitrate in methanol-d_4 before (a) and during (b) irradiation of solution.[48]

The resulting benzophenone proves to be polarised (Fig. 3). The polarisation signs of the phenols and benzophenone are in agreement with the theoretical values on the basis of the following assumptions:

1) the RP is triplet; 2) the cage product is polarised; and 3) the g factor of uranoyl UO_2^+ is less than the g factor of phenoxyl (ketyl). The latter assumption was substantiated to a sufficient degree of reliability in section IV.1. Thus, the CPN data indicate that the predominant contribution to the reactive form of uranyl is provided by its triplet state, which is preserved during its chemical conversion to an RP.



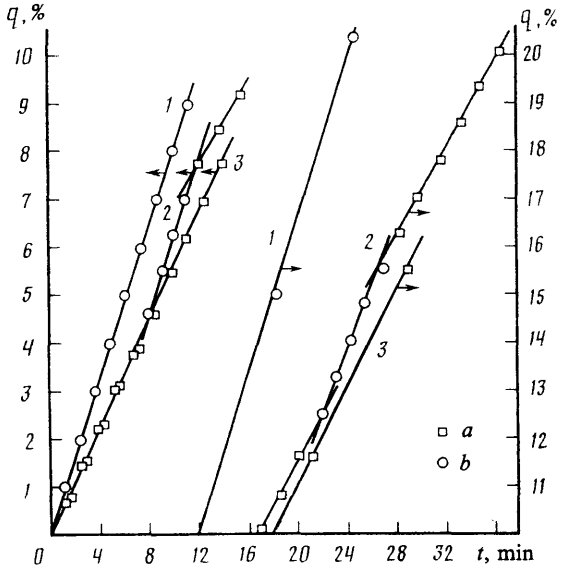


Figure 4. Dependence of conversion (q) on time in the polymerisation of *N,N,N,N*-dimethyldiallylammonium chloride in the earth's field (a) and in an external magnetic field (b):[101] *1*, polymerisation in the magnetic field; *2*, polymerisation with alternate installation and removal of the magnet; *3*, polymerisation in the earth's field.

2. Effect of an external magnetic field

Photochemical reactions that occur via the formation of triplet radical pairs are known to demonstrate significant magnetic field effects (MFE).[1,68–71] It may be expected that the spin-selective photochemical reactions of uranoyl will also be sensitive to an external magnetic field. A clear indication of the triplet multiplicity of the reacting photoexcited uranyl and the subsequent RP is the MFE in the photopolymerisation of *N,N,N,N*-dimethyldiallylammonium chloride photoinitiated with uranyl acetate.[101] The effect is clearly visible in Fig. 4. An external magnetic field (B = 0.17 T) causes a 10–40% acceleration of polymerisation. This result is reproducible regardless of when the field is applied or disconnected. At the same time as an increase in the rate of polymerisation, the molecular weight of the resulting polymer decreases in the field. Both of these results clearly suggest that: 1) initiation is the spin-selective stage, i.e. the UO_2^+ ion and the monomer molecule radical are partners of the primary RP; 2) this primary pair is a triplet, since only under this condition does the magnetic field suppress its conversion to a singlet, which increases the yield of radicals and the efficiency of initiation resulting in an acceleration of polymerisation and a decrease in the kinetic length of the polymerisation chain (or the molecular weight of the polymer). During the reaction there is an accumulation of U(IV) formed in both cage and extracage reactions: the yield of U(IV) decreases in the field.[101] The photodecomposition of uranyl oxalate (or oxalic acid in the presence of uranyl nitrate and a mineral acid) is of considerable interest. This reaction forms the basis of the uranyl oxalate actinometer. By titrating oxalic acid it is possible to determine its decomposition on photolysis with great accuracy. The reaction mainly involves the uranyl-sensitised oxidation of oxalic acid:[3,28,38,45]

$$H_2C_2O_4 \longrightarrow \begin{cases} \longrightarrow CO_2 + CO + H_2O\,, \\ \longrightarrow CO_2 + HCO_2H\,. \end{cases} \qquad (20)$$

Moreover, there is no doubt that an RP involving $CO_2^{\cdot-}$ and UO_2^+ is formed in this reaction. The EPR spectrum of the $CO_2^{\cdot-}$ radical anion in this system was recorded at low temperature.[28] A radical anion released from the cage recombines and oxalic acid (after protonation) is regenerated. An external magnetic field could affect the outflow of radicals from the cage and the rate of consumption of oxalate ions on photolysis, but no effect from a magnetic field on the rate of this reaction involving uranyl containing 10% ^{235}U was found (within the limits of an experimental error of ~2%).[15] A previously unexplained phenomenon was also reported: the strong oxidising agent uranoyl oxidises the strong reducing agent $CO_2^{\cdot-}$ in the cage with low efficiency:[28]

$$^3[UO_2^+,\ CO_2^{\cdot-}] \rightarrow U^{4+} + CO_2. \qquad (21)$$

The reason for this phenomenon and the absence of an MFE in uranyl oxalate reactions would appear to have a common origin. For reaction (21) to occur it is necessary for the triplet pair to evolve into a singlet, which is made difficult because of the lack of hyperfine coupling between the two radical partners, and therefore the RP $[UO_2^+, CO_2^{\cdot-}]$ mainly participates in other reactions.[28]

Within the limits of experimental error (2–5%) no MFE was detected by Khudyakov et al.[25,26] in the outflow of free radicals from the solvent cage during pulsed photooxidation of a number of donors in homogeneous and micellar solutions of uranyl salts containing a natural percentage of magnetic isotope.

Triplet–singlet transitions in the pair $[UO_2^+, SH^{\cdot}]$ can be induced not only by hyperfine electron-nuclear coupling. Thus, in the photoreduction of uranyl nitrate with hydroquinone and *p*-methoxyphenol at 285–293 K in a viscous solvent, a negative MFE for the outflow of aromatic radicals into the bulk of the solvent was

found.[122] The reason for the negative MFE may be either a triplet mechanism (if the magnetosensitive stage is the action of the magnetic field on mixing of the triplet levels of the exciplex) or a Δg mechanism in the RP.[68] The large difference between the g factors of an organic radical and uranoyl may lead to measurable MFE effects through a Δg mechanism even in a moderate field.[122]

An increase in the content of ^{235}U isotope in the salt from 0.7 to $\approx$10% leads to a build-up of a positive MFE.[122] In fact, increasing the content of magnetic isotope leads to an increase in the content of $[^{235}UO_2^+, SH^{\cdot}]$ pairs, which have more effective HFC constants in both partners than $[^{238}UO_2^+, SH^{\cdot}]$ pairs. With a 10% content of ^{235}U isotope, the effect of the opposite sign is approximately balanced and the magnitude of the MFE is within the limits of experimental error.[122]

Strictly speaking, from the results discussed it is not possible to make any definite quantitative conclusions about the magnetic interactions in an RP involving uranoyl, but the characteristics of the dependence of the MFE on the isotopic composition of uranyl provides a basis for the expectation that HFC with the ^{235}U nucleus contributes to the spin dynamics of the pair, and hence a magnetic isotope effect can be anticipated.

3. Magnetic isotope effect

The photoreduction of uranyl with phenols, as demonstrated above, is a spin-selective reaction; and therefore, in addition to an MFE, an effect from the internal magnetic field of the ^{235}U nucleus, namely, an MIE, can be expected in these reactions. A magnetic isotope effect was detected in the photoreduction of uranyl nitrate with *p*-methoxyphenol (PhOH) in heavy water in the presence of ammonium fluoride.[49] In this system the following fundamental stages occur:

$$(UO_2^{2+})^* + PhOH \rightarrow {}^3[UO_2^+, PhO^{\cdot}] + H^+, \quad (22)$$

$$^3[UO_2^+, PhO^{\cdot}] \longrightarrow UO_2^+ + PhO^{\cdot}, \quad (23)$$

$$^3[UO_2^+, PhO^{\cdot}] \longrightarrow UO_2^{2+} + PhOH, \quad (24)$$

$$UO_2^+ + UO_2^+ + 4HF \rightarrow UO_2^{2+} + UF_4 + 2H_2O. \quad (25)$$

The *p*-methoxyphenoxyl radical formed in the reaction has relatively small HFC constants from the *ortho*-protons and it may be assumed that the a_U constant in $^{235}UO_2^+$, even if it is not that large, will contribute to the effective HFC constant of the radical pair. With conversions of uranyl of less than 20%, Khudyakov et al.[49] detected the depletion of ^{235}U isotope in the precipitate of UF_4. In the initial uranyl nitrate the ratio of $^{238}U:^{235}U$ was 8.93 $\pm$ 0.01, while in the UF_4 reaction product this ratio occurred within the limits 8.970 $\pm$ 0.005 to 8.945 $\pm$ 0.008.[49] This corresponds to an enrichment of the initial unreacted uranyl with ^{235}U isotope and agrees in sign with that expected theoretically: a triplet pair with "magnetic" ^{235}U nuclei should undergo reductive reaction (24) more rapidly, and then the ^{235}U nuclei will separate into regenerated uranyl. The magnitude of the effect is small (apparently, the electron-nuclear interaction in the ^{235}U ion is small in reality), but it exceeds the experimental error of isotopic analysis.

The coefficient of isotope separation determined by us was α = 1.02. This value is small, but significantly exceeds the value of the classical isotope effect, determined, for example, as $(238/235)^{1/4}$ = 1.006. The reaction was conducted in pulsed mode so as to increase the contribution of disproportionation of uranyl [reaction (25)] and to decrease the contribution of the exchange reaction between uranyl and uranoyl [reaction (11)], which is accompanied by a loss of the effect (see Section III).

In the patent literature there are two reports on the separation of uranium isotopes based on the MIE. In one patent[123] the separation of isotopes by photoreduction of uranyl acetate in water or water containing "complexing" components (fluoride, carbonate, oxalate, etc.) is reported. Judging from the description, it appears that the authors[123] started from general conclusions rather than the experimental data.

According to another patent,[124] separation of the isotopes occurs by photopolymerisation of uranyl acrylate in a strong magnetic field in a solution of ethanol. The precipitate is enriched with ^{235}U isotope up to a 50% level. The content of this isotope in the initial nitrate is not reported. It was not possible[15] to reproduce the results of this patent.

Independently and at the same time as the study of Khudyakov et al.[49] a reliable MIE in uranium was detected in the decomposition of uranyl oxalate.[125] On photolysis of acid solutions containing 10% ^{235}U, enrichment of the precipitate—uranium(IV) oxalate—and depletion of the initial uranium(VI) occur.[125] For example, with 18% conversion of uranyl having a ratio of $^{238}U:^{235}U$ = 10:1, it becomes depleted in magnetic isotope (this ratio becomes equal to 10.2:1). For U(IV) this ratio is 9.4:1, the fundamental coefficient of isotope separation being α = 1.08.[125] It is logical that the product of the cage reaction—uranium(IV)—should be enriched. Cage reaction (21) occurs more rapidly for uranoyl containing magnetic isotope (see above).[125] The "destructive" isotopic exchange (11) in extracage reactions is apparently inhibited because uranyl is present as a complex with oxalate. The degree of enrichment decreases with an increase in conversion.[125] The results of this study were subsequently reproduced by Klimchuk.[15]

VI. Conclusion

Certain general principles are in evidence amongst the very large range of photochemical reactions of uranyl.

Firstly, the primary reactions almost always occur with transfer of an electron or hydrogen atom from the partner to uranyl to form the UO_2^+ radical ion.

Secondly, in these reactions the UO_2 shell is preserved, destruction of which occurs in secondary reactions (disproportionation of uranoyl ions, exchange of oxygen atoms, etc.).

Thirdly, the majority of the reactions can be differentiated according to a single important criterion—whether the reaction occurs in the equatorial plane of the uranyl ion (i.e. involving equatorial ligands) or whether it takes place on the "pole" (i.e. involving the oxygen atoms of uranyl). The first reactions take place preferentially as electron transfer, the second occur as a hydrogen atom transfer from the reagent to an "yl" oxygen atom (these latter are almost identical in many respects to the reactions of triplet benzophenone). It is true that the question of transfer of an electron or hydrogen atom, as always, is unclear and the preference for a given route remains uncertain in many cases.

Fourthly, the excited reacting uranyl ion can be confidently assigned a given spin state, namely—triplet. A number of indirect findings (the lifetimes, radiospectroscopy of radical pairs, chemical properties) as well as direct evidence [magneto-spin (CPN) and magneto-field effects] attest in favour of this assertion. Thus,

reactions of excited uranyl are spin-selective and hence magnetosensitive.

In this respect the magnetic properties of the uranoyl ion UO_2^+ become important, and in this case there is considerable uncertainty and much needs to be done to measure the *g* factor and hyperfine coupling in this ion in molecularly oriented systems.

The contribution of the magnetic moment of the ^{235}U nucleus and hyperfine coupling to the spin dynamics of pairs involving a uranoyl radical is of particular interest. The separation of uranium isotopes in spin-selective reactions of uranium compounds based on an MIE over a period of fifteen years has proved to be a vital problem.[71,126] It must be assumed that the presence of a heavy uranium atom and the danger of spin-orbit coupling has deterred researchers of the MIE. However, the scale of the MIE does not vary very much throughout the series of elements for which it was detected (^{13}C, ^{17}O, ^{29}Si, ^{33}S), although the spin-orbit coupling constant in this series increases by a factor of more than ten—from $\zeta = 28$ cm^{-1} (for carbon) to $\zeta = 382$ cm^{-1} (for sulphur).[119,120] This means that the role of spin-orbit coupling in spin dynamics has been exaggerated. At the present time the MIE and separation of uranium isotopes based on it have been detected in two reactions—the photoreduction of uranyl with a substituted phenol and the uranyl-sensitised photodecomposition of oxalic acid. This is, of course, an outstanding result, and it will stimulate interest in heavy multielectron atoms and a measurement of the magnetic resonance parameters of the $^{235}UO_2^+$ ion involving its hyperfine coupling with the ^{235}U nucleus.

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