^{1}H Chemically Induced Dynamic Nuclear Polarization in the Photodecomposition of Uranyl Carboxylates

Stanislav V. Rykov,[*,a] **Igor V. Khudyakov,**[*,a] **Eugeniy D. Skakovsky,**[a] **Hugh D. Burrows,**[*,b] **Sebastião J. Formosinho**[b] **and Maria da Graça M. Miguel**[b]
[a] *Institute of Chemical Physics, Academy of Sciences of the USSR, 117977 Moscow, USSR*
[b] *Departamento de Química, Universidade de Coimbra, 3049 Coimbra, Portugal*

Chemically induced dynamic nuclear polarization (^{1}H CIDNP) has been observed during photolysis of uranyl salts of pivalic, propionic, and acetic acids in D_2O solution, [$^2H_6$]acetone, [$^2H_4$]methanol, or in some other solvent. The multiplet polarization of isobutene and isobutane protons has been found under photolysis of deoxygenated pivalate solution. The polarized compounds are formed in the triplet pairs of *tert*-butyl free radicals. ^{1}H Emission of the *tert*-butylperoxyl group and emission of ^{1}H from isobutene have been recorded under photolysis of air-saturated pivalate solutions. The CIDNP of butane protons stays as a multiplet. Such changes in the presence of air/oxygen have arisen apparently because of the formation of *tert*-butylperoxyl free radical and its reaction with *tert*-butyl radical products, *i.e.* hydroperoxide (peroxide) and isobutene. Isobutene probably forms a complex with molecular oxygen which has a very short proton relaxation time.

During the photolysis of uranyl pivalate in the presence of *p*-benzoquinone (5×10^{-2}–0.1 mol dm^{-3}) we have not observed any CIDNP, whereas under *p*-benzoquinone concentrations of 10^{-3}–10^{-2} mol dm^{-3} the CIDNP from both hydroquinone and *p*-benzoquinone has been followed.

Photolysis of uranyl propionate has led to CIDNP from butane protons. An emission from methyl group protons of a compound with an ethylperoxyl fragment in the presence of air/oxygen has been observed. The same polarization picture has arisen under interaction of photoexcited uranyl with propionic acid.

During the photolysis of uranyl acetate at relatively low concentrations (10^{-2} mol dm^{-3}) a CIDNP very similar to that registered for uranyl propionate was recorded. The ethyl fragment is probably obtained in reactions for two methyl radicals formed from acetate with the parent uranyl acetate, namely hydrogen-atom abstraction and addition reactions.

The photooxidation of carboxylic acids by uranyl compounds has been known for nearly 200 years[1] but whilst these reactions have been extensively studied and reviewed[2–4] we are still far from a detailed understanding of the mechanisms of these processes. The normal reaction involves decarboxylation of the acid, and may proceed *via* so-called 'normal' or 'sensitized' photooxidations.[5] Photooxidations with uranyl ion normally involve electron or hydrogen-atom transfers,[3] producing free radicals. These intermediates have been detected by EPR spectroscopy during photooxidation of carboxylic acids by uranyl ion in solution,[6] and in glasses at low temperature;[5] with the hydroxy-acid benzilic acid, the diphenylketyl radical has been observed during flash photolysis.[7] However, although these processes presumably also involve reduction of UO_2^{2+} to uranium(V), for many simple carboxylic acids the quantum yields of reduced uranium species are generally small,[8–10] indicating that most intermediate U^V species must be reoxidized in a subsequent step.

CIDNP is a powerful tool for studying photooxidized free radical reactions, and has been applied to the photoreaction of certain uranyl salts to study the elementary steps of these processes and to obtain a deeper insight into the mechanism of these photooxidations.[11,12] In solution, uranyl ion frequently forms strong complexes with organic carboxylates.[13] The present work is devoted to the ^{1}H CIDNP study of photodecomposition of uranyl carboxylates, and of the photooxidation of propionic acid sensitized by uranyl nitrate.

Experimental

Details of the CIDNP method used have been described elsewhere.[11,12] In addition to the Bruker HX-90 ER NMR spectrometer employed in these earlier studies, we have used Varian XL-100, Tesler BS-487 and Bruker MSL-300 instruments.

Commercially available carboxylic acids and uranyl salts were purified according to standard procedures. Uranyl pivalate and propionate were prepared by dissolution of uranyl nitrate in solutions of the corresponding acids, followed by evaporation and recrystallization. The formation of uranyl carboxylates was confirmed by NMR analysis. *p*-Benzoquinone (BQ) was recrystallized from aq. ethanol.

The commercially available solvents [$^2H_6$]dimethyl sulphoxide ([$^2H_6$]DMSO), D_2O, [$^2H_6$]acetone, CD_3OD, [$^2H_6$]benzene, $CDCl_3$ and carbon tetrachloride were used without further purification. (For brevity, we shall not indicate that the solvents are deuteriated.) Concentrations of uranyl salts in solution were between 10^{-3} and 0.1 mol dm^{-3}. Deoxygenation of solutions was performed with prolonged argon bubbling. All experiments were carried out at room temperature.

Results and Discussion

Uranyl Pivalate.—We have observed CIDNP from the reaction products of the photolysis of deoxygenated $(Bu^tCO_2)_2UO_2$ solution in water–acetone binary mixture, or in methanol, benzene, or acetone. Although we have been unable to find literature data on the photodecomposition products of uranyl pivalate, it is known[14] that pivalic acid quenches excited uranyl ion, and if it is assumed that the dominant reaction is oxidative decarboxylation, the products are likely to be similar to those for photocatalytic decarboxylation of this acid by the

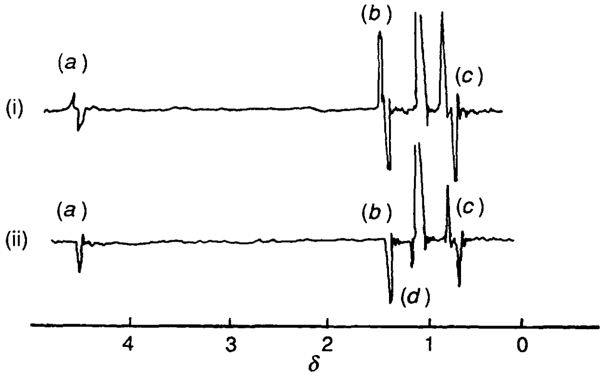


Fig. 1 ^1H NMR spectrum of uranyl pivalate in benzene during irradiation of: (i) deoxygenated solution; (ii) air-saturated solution. Peaks (*a*) and (*b*) correspond to isobutene, (*c*) to isobutane and/or *tert*-butyl radical decomposition products, and (*d*) to Bu^tOOR.

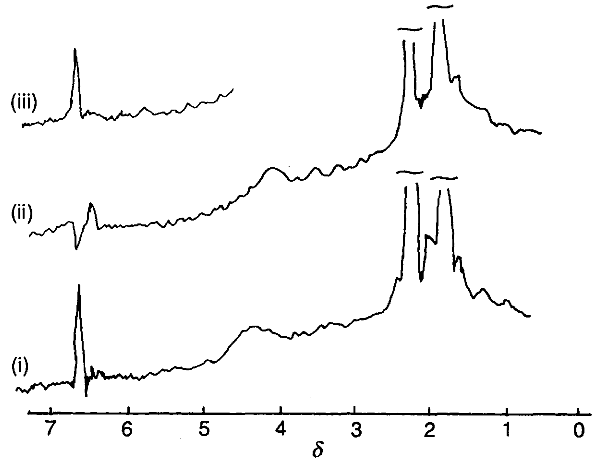


Fig. 2 ^1H NMR spectrum of uranyl pivalate in acetone in the presence of benzoquinone (5×10^{-3} mol dm^{-3}): (i) before irradiation; (ii) during irradiation; (iii) after irradiation. The peak at δ 6.7 is due to benzoquinone.

closely related catalyst TiO_2, namely isobutane, isobutene, CO_2, and H_2.[15,16] The reaction products observed by CIDNP on photolysis of uranyl pivalate are isobutane and isobutene, which show multiplet absorption/emission (A/E) polarization (Fig. 1). The polarization observed may be formed either in geminate triplet pairs or in random pairs of *tert*-butyl free radicals. On introduction of effective free-radical scavengers, such as ionole (2,6-di-*tert*-butyl-4-methylphenol) or carbon tetrachloride, into the reagent solution there was no effect on either the polarization or the intensity of polarized NMR signals. This indicates that the yield of geminate triplet radical pairs (RPs) dominates in the polarization, and that only relatively few radicals leave the cage. It is possible to suggest the following reaction scheme (Scheme 1).

The signs of the multiplet effect (A/E) of polarized products show, in accordance with Kaptein's rules,[17] that the polarization is formed in triplet RPs. This conclusion is in agreement with earlier results[11,12] that the photoreactivity of uranyl salts involves a 'nominal' triplet state. The adjective 'nominal' is used although spin is probably not a good quantum number for uranyl[18] owing to high spin–orbit coupling;[19] the reactivity indicates that the lowest excited state has largely triplet character.

The creation of polarization in the latter RP means that RP-1 [as well as all other conceivable RPs formed from $Bu^tCO_2\cdot$ and $UO_2(Bu^tCO_2)\cdot$ radicals] has a very short lifetime ($t < 10^{-10}$ s) because of extremely fast decarboxylation of *tert*-butylacyloxyl free radicals. We have not followed CIDNP from the *tert*-butyl radical recombination product hexamethylethane. This is not surprising because a net polarization cannot be created in pairs of identical radicals and a multiplet polarization cannot be observed from this compound, which shows only a single line in the NMR spectrum.

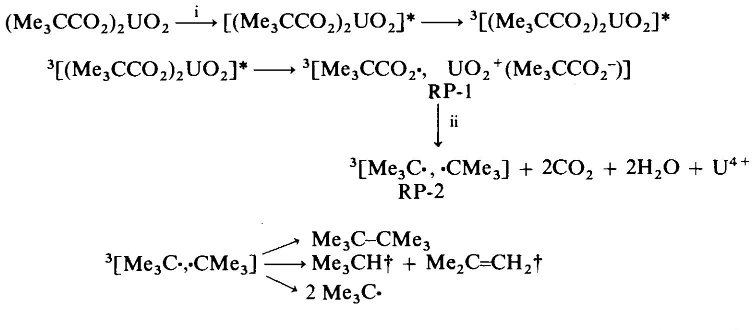
The polarization picture changes drastically in the presence of air (or oxygen) (Fig. 1). The multiplet CIDNP from isobutane is retained in the spectrum, while CIDNP from isobutene becomes negative. One can observe, simultaneously, net emission from ^1H of the *tert*-butylperoxyl group of the Bu^tCO_2R compound at δ 1.18 (Fig. 1). Oxygen consumption takes place as the photolysis occurs under relatively high initial salt concentration, and the net polarization of isobutene indicated above transforms from E, first into E + A/E polarization, then, after a certain time, into the multiplet A/E polarization, as observed in deoxygenated solutions.

In the presence of relatively high oxygen concentrations, *tert*-butyl radicals from the pertinent RP may react with this compound. The same reaction, leading to formation of the peroxyl radical, occurs in the bulk solvent with radicals that have left the cage (see Scheme 2).

CIDNP from isobutene protons is expected to be the sum of both net (E) and multiplet (A/E) polarizations. However, under relatively high oxygen concentration we have observed only net emissive polarization (Fig. 1). The NMR signal of isobutene is absent, probably because of formation of short-lived complexes of this compound with molecular oxygen.

No NMR ^1H signal of the OOH group of *tert*-butyl hydroperoxide was seen, probably owing to formation of complexes between hydroperoxide and uranyl and/or an exchange process with traces of any acid.

Irradiation of pivalate–uranyl in acetone in the presence of BQ in the concentration range of 5×10^{-2}–0.1 mol dm^{-3} led to quenching of the photoexcited salt and no photolysis. In the presence of low BQ concentrations (10^{-3}–10^{-2} mol dm^{-3}) we observed emission from BQ protons and enhanced absorption of aromatic protons of the hydroquinone formed (Fig. 2). Apparently, in the presence of high concentrations of BQ, a static quenching of the photoexcited salt occurs, and in the



$$(Me_3CCO_2)_2UO_2 \xrightarrow{\text{i}} [(Me_3CCO_2)_2UO_2]^* \longrightarrow {}^3[(Me_3CCO_2)_2UO_2]^*$$

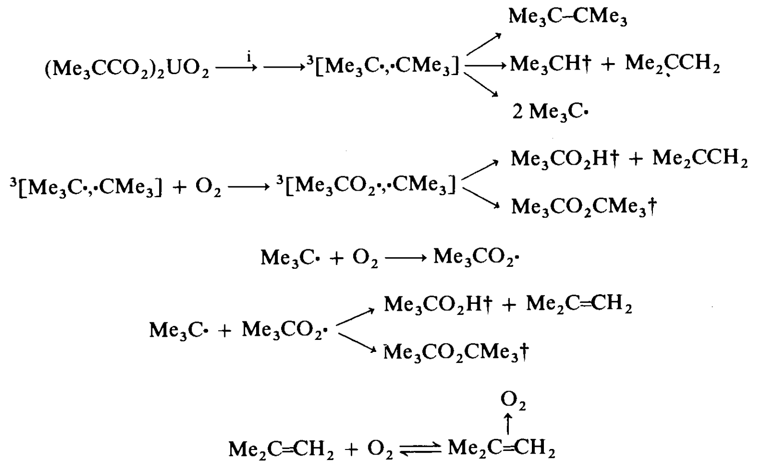
$${}^3[(Me_3CCO_2)_2UO_2]^* \longrightarrow \underset{\text{RP-1}}{{}^3[Me_3CCO_2\cdot,\ UO_2{}^+(Me_3CCO_2{}^-)]}$$

$$\Big\downarrow \text{ii}$$

$$\underset{\text{RP-2}}{{}^3[Me_3C\cdot,\ \cdot CMe_3]} + 2CO_2 + 2H_2O + U^{4+}$$

$${}^3[Me_3C\cdot,\cdot CMe_3] \longrightarrow \begin{cases} Me_3C{-}CMe_3 \\ Me_3CH\dagger + Me_2C{=}CH_2\dagger \\ 2\,Me_3C\cdot \end{cases}$$

Scheme 1 *Reagents and conditions:* i, *hν*; ii, $4H^+$. The sign † here and later indicates formation of a product showing CIDNP.



$$(Me_3CCO_2)_2UO_2 \xrightarrow{i} \longrightarrow {}^3[Me_3C\cdot,\cdot CMe_3] \longrightarrow \begin{cases} Me_3C\text{–}CMe_3 \\ Me_3CH\dagger + Me_2CCH_2 \\ 2\,Me_3C\cdot \end{cases}$$

$${}^3[Me_3C\cdot,\cdot CMe_3] + O_2 \longrightarrow {}^3[Me_3CO_2\cdot,\cdot CMe_3] \longrightarrow \begin{cases} Me_3CO_2H\dagger + Me_2CCH_2 \\ Me_3CO_2CMe_3\dagger \end{cases}$$

$$Me_3C\cdot + O_2 \longrightarrow Me_3CO_2\cdot$$

$$Me_3C\cdot + Me_3CO_2\cdot \longrightarrow \begin{cases} Me_3CO_2H\dagger + Me_2C{=}CH_2 \\ Me_3CO_2CMe_3\dagger \end{cases}$$

$$Me_2C{=}CH_2 + O_2 \rightleftharpoons \overset{O_2\uparrow}{Me_2C{=}CH_2}$$

Scheme 2 *Conditions:* i, *hv*

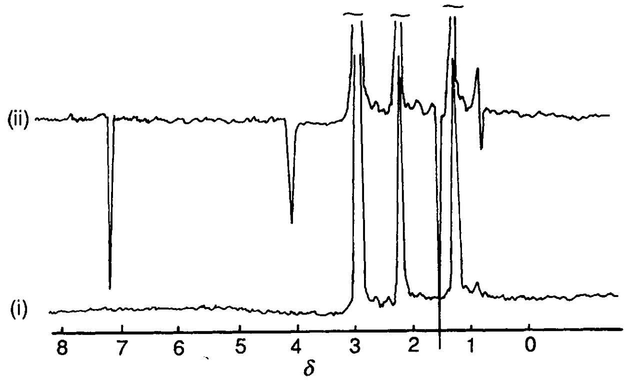
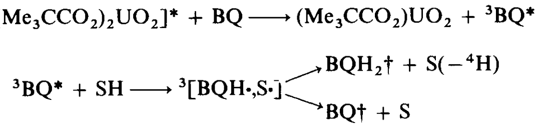


Fig. 3 ^1H NMR spectrum of uranyl pivalate in a binary mixture of DMSO–carbon tetrachloride: (i) before irradiation; (ii) during irradiation. The peak at δ 7.2 is due to $CHCl_3$. Other peaks are as in Fig. 1.

presence of low BQ concentrations energy transfer from the photoexcited salt to BQ takes place (Scheme 3).



$${}^3[(Me_3CCO_2)_2UO_2]^* + BQ \longrightarrow (Me_3CCO_2)UO_2 + {}^3BQ^*$$

$${}^3BQ^* + SH \longrightarrow {}^3[BQH\cdot,S\cdot] \longrightarrow \begin{cases} BQH_2\dagger + S(-{}^4H) \\ BQ\dagger + S \end{cases}$$

Scheme 3

The correlation of triplet energy levels of uranyl and BQ favours this energy transfer (235 and 210 kJ mol,$^{-1}$ respectively). Energy transfer from uranyl ion usually occurs with low efficiency.[20] However, the high sensitivity of this method enables one to register CIDNP from the reaction products of triplet photoexcited BQ.

Carbon tetrachloride showed behaviour similar to that of BQ. Under photolysis of uranyl pivalate in the presence of small quantities of carbon tetrachloride in acetone (or any other solvent) an enhanced absorption from *tert*-butyl chloride protons and emissions from 1,1,1-trichloro-2,2-dimethylpropane and chloroform protons were observed (Fig. 3). As is well known, it is very convenient to register chloroform polarization because of the presence of a single line in the NMR spectrum of this compound and its long relaxation time.

When carbon tetrachloride was used as solvent, the photolysis occurred with high quantum yield (~ 0.8); however, in the NMR spectrum, only a weak emission of chloroform protons was observed. It is probable that pivalate is present in the form of complexes with the solvent, and the portion of molecules which is decomposed to give kinetically free radicals is low.

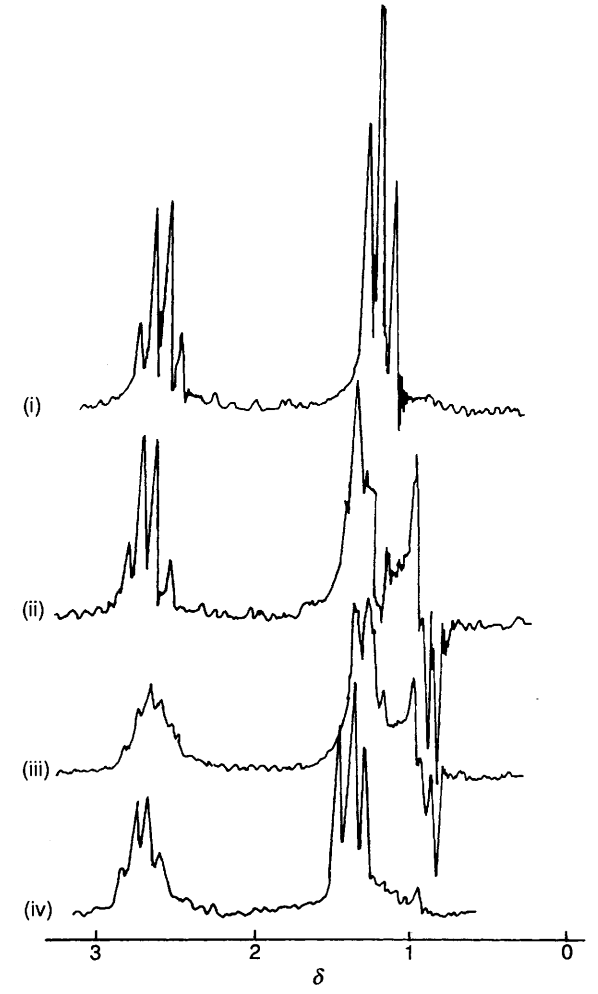


Fig. 4 ^1H NMR spectrum of uranyl propionate in water: (i) before irradiation; (ii), (iii) during irradiation; (iv) after irradiation. Peaks at δ 0.7–1.1 observed during photolysis are due to alkyl radical combination products. Note broadening of $-CH_2-$ (2.5–2.9) and $-Me$ (1.2–1.5) peaks of propionic acid during photolysis.

CIDNP from reaction products of uranyl nitrate with pivalic acid has not been found.

Uranyl Propionate.—During photolysis of uranyl propionate in water, acetone, or methanol, mainly multiplet polarization was observed, with a certain yield of net emissive polarization (Fig. 4). The CIDNP has been proposed to be produced from

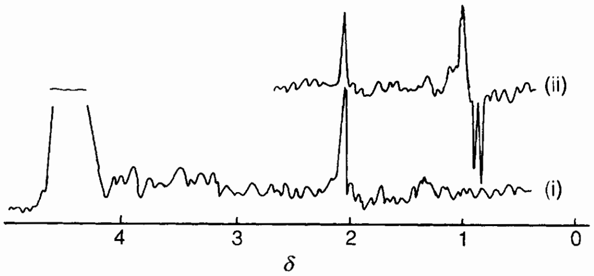


Fig. 5 ^1H NMR spectrum of uranyl acetate in water: (i) before irradiation; (ii) during irradiation. Peaks at δ 0.7–1.2 are due to primary and secondary combination products of alkyl radicals.

$$\underbrace{Me{-}CH_2}_{E + A/E}{-}\underbrace{CH_2{-}Me}_{A + A/E}\dagger$$

the recombination product of ethyl radicals, *i.e.* butane. It must be assumed that the multiplet polarization has been formed by 'secondary' geminate pairs of ethyl radicals whereas the net polarization has arisen from 'primary' triplet geminate with RPs uranium(v) and ethylacyloxyl free radical or, alternatively, that polarization has occurred in the parent uranyl according to a triplet mechanism (Scheme 4).

$$^3[(EtCO_2)_2UO_2]^* \longrightarrow {}^3[EtCO_2\cdot,UO_2{}^+(EtCO_2{}^-)]$$

$$\Big\downarrow \text{i}$$

$$^3[Et\cdot,\cdot Et] + 2CO_2 + 2H_2O + U^{4+}$$

$$^3[Et\cdot,\cdot Et] \begin{cases} \nearrow C_4H_{10}\dagger \\ \searrow C_2H_6 + CH_2{=}CH_2 \end{cases}$$

Scheme 4 *Reagent:* i, 4H$^+$

The main products observed on steady-state photolysis of propionic acid in the presence of uranyl chloride are carbon dioxide and ethane.[8] No CIDNP has been observed from ethane and ethylene protons because a multiplet polarization of singlet lines is impossible (see above), but net polarization yield is low. It should also be mentioned that, in contrast to the case of *tert*-butyl radicals, the disproportionation rate constant for ethyl radicals is significantly less than the recombination rate constant.[20] It is known, too, that under direct photolysis or thermolysis of propionyl peroxide in carbon tetrachloride one can follow CIDNP from butane (E/A) and from ethyl chloride (A/E), while no polarized signals are observed from ethane or ethylene.[21]

In the presence of air (or oxygen) a strong emission of the methyl group protons of the ethylperoxyl fragment $MeCH_2$-OOR has been observed [R = Et, $UO_2(O_2CEt)$]. The NMR signal of the methyl group is practically coincidental with the signal of the same group of uranyl propionate and thus creates a deceptive picture of a strong net emissive polarization for uranyl propionate. An NMR signal from the methylene group of the ethylperoxyl fragment has not been observed because it is buried by the absorption of the water protons.

Propionic Acid and Uranyl Nitrate.—Under photoexcitation of uranyl nitrate in the presence of propionic acid (10^{-2}–0.1 mol dm^{-3}) in water, methanol, or their binary mixtures, the same polarization picture was observed as under photolysis of uranyl propionate (Fig. 4). Introduction of radical scavengers (thiols, ionole) led to diminution of polarization coefficients. This confirms that polarization occurs mainly in random radical pairs. A certain fraction of the propionic acid is in the form of uranyl propionate. The photodecomposition of the latter compound leads to the yield of net polarization as given in Scheme 5.

$$^3[UO_2{}^+,EtCO_2\cdot] + H^+ \longrightarrow UO_2{}^{2+} + C_2H_6 + CO_2 \qquad (1)$$

$$^*UO_2{}^{2+} + EtCO_2H \longrightarrow {}^3[UO_2{}^+,EtCO_2\cdot] + H^+$$

$$^3[UO_2{}^+,EtCO_2\cdot] \longrightarrow UO_2{}^+ + Et\cdot + CO_2$$

$$UO_2(NO_3)_2 + 2EtCO_2H \rightleftharpoons (EtCO_2)_2UO_2 + 2HNO_3$$

$$Et\cdot + Et\cdot \begin{cases} \nearrow C_4H_{10}\dagger \\ \searrow C_2H_6 + CH_2{=}CH_2 \end{cases}$$

$$(EtCO_2)_2UO_2 \xrightarrow{\text{i}} {}^3[Et\cdot,Et\cdot] \begin{cases} \nearrow C_4H_{10}\dagger \\ \searrow C_2H_6 + CH_2{=}CH_2 \end{cases}$$

Scheme 5 *Conditions:* i, *hν*

Addition of nitric acid led to the disappearance of CIDNP. The reason for this lies, presumably, in an acceleration, in the presence of acid, of reaction (1) which leads to sensitized photooxidation of the propionic acid and to the formation of the main acid decomposition product, ethane.[2] Under such conditions the fraction of radicals that leaves the cage decreases, and the CIDNP is not observed.

It is known that at low temperatures 1-carboxyethyl radical is formed under propionic acid photooxidation [reaction (2)].[5,6]

$$^*UO_2{}^{2+} + EtCO_2H \longrightarrow UO_2{}^+ + Me\cdot CHCO_2H + H^+ \quad (2)$$

It is natural to assume that, at room temperature, the formation of two radicals, 1-carboxyethyl and ethyl, is most probable. Recombination of these two radicals leads to formation of 2-methylbutyric acid [reaction (3)]. However, we have not

$$Me\cdot CHCO_2H + Et\cdot \longrightarrow EtCH(Me)CO_2H \qquad (3)$$

observed CIDNP from protons of this acid, nor have we observed polarized ^1H signals from the methylene group. This may be due to the acid forming short lived, short relaxation time complexes with uranyl.

Uranyl Acetate.—The main products reported for steady-state photolysis of $UO_2{}^{2+}$ in the presence of acetic acid are methane and CO_2.[8] Photolysis of uranyl acetate leads to a polarization picture very similar to that observed during photolysis of propionate (Fig. 5). That means that methyl radicals are somehow transformed into ethyl radicals. A possible route involves a methyl radical abstracting a hydrogen atom from the acetoxyl group to give $H_2\dot{C}CO_2H$, with the subsequent addition of a second methyl radical to this dehydrogenated product (Scheme 6).

$$UO_2(OAc)_2 \xrightarrow{\text{i}} 2\,Me\cdot + 2CO_2 + 2H_2O + UO_2^{2+}$$

$$Me\cdot + UO_2(OAc)_2 \longrightarrow CH_4 + UO_2(OAc)(O_2C\dot{C}H_2)$$

$$Me\cdot + UO_2(OAc)(O_2C\dot{C}H_2) \longrightarrow UO_2(OAc)(O_2CEt)$$

$$UO_2(OAc)(O_2CEt) \xrightarrow{\text{ii}} {}^3[Me\cdot,Et\cdot] \begin{cases} \nearrow C_3H_8\dagger \\ \searrow CH_4 + C_2H_4 \end{cases}$$

Scheme 6 *Reagents and conditions:* i, *hν*, 4 H$^+$; ii, *hν*

Both $\cdot CH_3$ and $\dot{C}H_2CO_2H$ have been observed by EPR spectroscopy on photolysis of uranyl perchlorate, and acetic acid in low-temperature glasses.[5] We have not observed any CIDNP during photolysis of uranyl nitrate in the presence of acetic acid. There may be many reasons for the absence of CIDNP in this case and in the case of pivalic acid. One reason, in particular, may be the relatively slow formation of RPs (low rate of 'pumping').

One final interesting fact is that, in many cases, one observes blurring of the NMR signal of the initial uranyl salt and a decrease in its net intensity. This effect is very pronounced in the cases of uranyl pivalate and uranyl propionate (see, for example, Fig. 4). Similar changes had been observed earlier during photolysis of lead and mercury pivalates.[22] The observed effects may apparently be explained by the weak emissive CIDNP of the initial salt produced according to the triplet mechanism (variant of optical polarization). Another possible explanation consists of the exchange reaction (4) which leads to dephasing of

$$(\mathrm{RCO_2})_2\mathrm{UO_2}^* + (\mathrm{RCO_2})_2\mathrm{UO_2} \rightleftharpoons (\mathrm{RCO_2})_2\mathrm{UO_2} + (\mathrm{RCO_2})_2\mathrm{UO_2}^* \quad (4)$$

a part of the magnetization vector in the xy plane in this process. The latter phenomenon manifests itself as if it were an emissive polarization.

Conclusions

The present work is devoted to CIDNP spectra observed during the photolysis of uranyl carboxylates and during photooxidation of carboxylic acids sensitized by uranyl nitrate. In the cases of uranyl pivalate and uranyl propionate the CIDNP is formed in secondary geminate triplet pairs. Polarization signs are in accord with those expected on the basis of Kaptein's rules,[17] assuming formation of triplet pairs in the photolysis. The present data confirm our earlier conclusions[11,12] about reactivity of the triplet excited state of uranyl salts.

The photolysis of uranyl pivalates and propionates in the presence of air (or oxygen) leads to formation of peroxides or hydroperoxides. ^{1}H NMR signals of the latter compounds demonstrate CIDNP.

In the case of uranyl acetate, polarization occurs in triplet RPs (ethyl radical, methyl radical) which are obtained in the photolysis of this salt under interaction with primary methyl radicals.

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References

1 A. Buchkolz, *Ann. Chim. Phys.*, 1805, **56**, 142.
2 E. Rabinowitch and R. L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon, Oxford, 1964.
3 H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.
4 H. D. Burrows, S. J. Formosinho, F. Pinto Coelho, M. G. M. Miguel and M. E. D. G. Azenha, *Mem. Acad. Ciências Lisboa*, 1989, **30**, 33.
5 D. Greatorex, R. J. Hill, T. J. Kemp and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 2059.
6 D. Greatorex, R. J. Hill, T. J. Kemp and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 216.
7 H. D. Burrows, D. Greatorex and T. J. Kemp, *J. Am. Chem. Soc.*, 1971, **93**, 2539.
8 G. E. Heckler, A. E. Taylor, C. Jensen, D. Percival, R. Jensen and P. Fung, *J. Phys. Chem.*, 1963, **67**, 1.
9 L. J. Heidt, G. W. Tregay and F. A. Middleton, Jr, *J. Phys. Chem.*, 1970, **74**, 1876.
10 M. Ahmad, A. Cox, T. J. Kemp and (in part) Q. Sultana, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1867.
11 A. Z. Yankelevitch, I. V. Khudyakov and A. L. Buchachenko, *Khim. Fiz.*, 1988, **7**, 734.
12 A. L. Buchachenko, I. V. Khudyakov, E. S. Klimtchuk, L. A. Margulis and A. Z. Yankelevitch, *J. Photochem. Photobiol., A: Chemistry*, 1989, **46**, 281.
13 H. Gusten, in Gmelin '*Handbook of Inorganic Chemistry-Uranium*, Springer-Verlag, Berlin, 8th edn., 1983, suppl. vol. A6, ch. 3.
14 S. S. Sandhu, M. S. Sidhu and R. J. Singh, *J. Photochem. Photobiol., A: Chemistry*, 1988, **42**, 251.
15 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 5985.
16 M. Bideau, B. Claudel, L. Faure and M. Rachimoellah, *J. Photochem.*, 1987, **39**, 107.
17 R. Kaptein, J. Hollander, D. Antheunis and L. Ooserhoff, *Chem. Commun.*, 1970, 1687.
18 C. K. Jorgensen and R. Reisfeld, *Chem. Phys. Lett.*, 1975, **35**, 441.
19 R. G. Denning, J. R. Snellgrove and D. R. Woodwark, *Mol. Phys.*, 1979, **37**, 1109.
20 A. R. Darmanyan and I. V. Khudyakov, *Photochem. Photobiol.*, 1990, **57**, 293.
21 *Landolt-Bornstein Data and Functional Relationships: Science and Technology, New Series, Group: Atomic and Molecular Physics*, ed. H. Fischer, Springer-Verlag, Berlin, 1984, p. 13.
22 E. D. Skakovsky and S. V. Rykov, unpublished results.

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