# Interaction of Excited Dioxouranium(VI) Ion with Amino-acids: a Laser Flash Photolysis, Quantum Yield and ESR Investigation

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## Abstract

The luminescence of uranyl ion in aqueous perchloric acid is rather weakly quenched on addition of simple amino-acids, and photoredox quantum yields measured as $\phi$[U(IV)] are low (<0.2), but prolonged photolysis of frozen samples both in $H_2O$ and $D_2O$ at 77 K leads to the production of substrate-derived radicals identified by ESR, indicating decarboxylation as the principal pathway of photodecomposition.

The presence of sulphur atoms in amino-acids leads to: (i) much more efficient quenching (ii) lower photoredox quantum yields and (iii) the production of sulphur-centred radicals.

## Introduction

Amino-acids are not easily oxidised by transition-metal oxidants, and their interaction generally leads to complex formation. However these complexes are photo-labile even at 77 K and intermediate radicals have been identified following photolysis when the central metal is Ce(IV) [1], $[Fe(CN)_6]^{3-}$ [2], Fe(III) [3–5], Co(III) [6] and Pb(IV) [7]. Photo-generated hydrogen atoms abstract from C–H bonds of amino-acids in acidic glasses at 77 K [8]. Flash photolysis of Cu(II) complexes of various amino-acids leads to Cu(II)–alkyl intermediates [9–11]. While many reports exist of the interaction of $[UO_2^{2+}]^*$ with carboxylic acids and hydroxy-acids [12], few studies have been carried out on amino-acids [13]. In this paper we detail kinetic results obtained by laser flash photolysis, indicating the level of reactivity, quantum yields of U(IV), indicating the degree of charge-separation from the initial radical-pair configuration, and ESR data referring to the nature of the primary ligand-derived radical. We note particularly the profound effects of introducing a sulphur atom into the amino-acid.

## Experimental

Laser flash photolysis experiments were carried out with an Applied Photophysics Model K-347 system using 50 ns pulses of 347 nm radiation (*ca.* 100 mJ) as described before [14].

ESR experiments were performed at 77 K with a Bruker Model ER-200 tt spectrometer as described previously [13].

Samples were prepared by dissolving the amino-acid in a solution of uranyl perchlorate in aqueous $HClO_4$. Where heavy water was used as a solvent, the final isotopic composition was at least 99.8% $^2H$. Samples were frozen to 77 K prior to photolysis for 1–4 h using a 100 W Xe/Hg point-source, the output of which was filtered through pyrex and a UG-5 filter, *i.e.* $\lambda_{irr}$ = 330–410 nm. Quantum yield measurements were also performed as reported previously [14].

## Results

### *Laser Flash Photolysis*

The lifetime of $[UO_2^{2+}]^*$ determined at its emission maximum of 508 nm in acidic solution was systematically reduced on addition of the various amino-acids. Pseudo-first-order rate constants ($k_1$) were determined at ten concentrations of each quencher to give the second-order quenching rate constants, $k_2$, exemplified in Fig. 1 and collated in Table I.

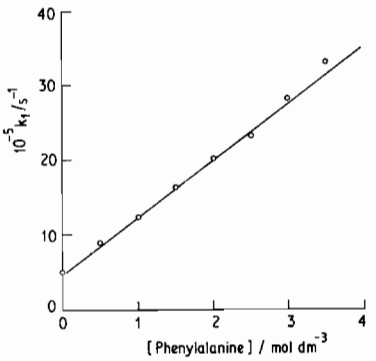


Fig. 1. Quenching of excited uranyl ion by L-phenylalanine. $[UO_2(NO_3)_2]$ = 0.20 mol dm$^{-3}$, $[HClO_4]$ = 0.20 mol dm$^{-3}$, $T$ = 293 ± 1 K.

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TABLE I. Quenching of $[UO_2^{2+}]^*$ by Amino-acids and Aminopolycarboxylates[a]

| Amino-acid | $k_2$ ($mol^{-1}$ $dm^3$ $s^{-1}$) |
|---|---|
| Glycine | enhancement |
| DL-alanine | enhancement |
| β-alanine | enhancement |
| Serine | $(1.92 \pm 0.42) \times 10^6$ |
| DL-valine | $(1.13 \pm 0.29) \times 10^6$ |
| DL-leucine | $(5.71 \pm 0.25) \times 10^6$ |
| Threonine | $(4.29 \pm 0.22) \times 10^6$ |
| D-asparagine | $(2.45 \pm 0.31) \times 10^6$ |
| L-glutamine | $(2.48 \pm 0.21) \times 10^6$ |
| Isoleucine | $(4.78 \pm 0.22) \times 10^6$ |
| Histidine | $(1.78 \pm 0.08) \times 10^8$ |
| Tyrosine | $(1.66 \pm 0.10) \times 10^9$ |
| L-tryptophan | $(2.97 \pm 0.09) \times 10^9$ |
| L-phenylalanine | $(7.92 \pm 0.16) \times 10^8$ |
| DL-methionine | $(1.28 \pm 0.06) \times 10^9$ |
| L-cystine | $(5.67 \pm 0.01) \times 10^8$ |
| Cysteine | $(7.48 \pm 0.04) \times 10^8$ |
| CDTA | $(6.15 \pm 0.51) \times 10^8$ |
| EDTA | $(4.77 \pm 0.49) \times 10^8$ |

[a] $[UO_2^{2+}] = 0.2$ mol $dm^{-3}$, $[HClO_4] = 0.2$ mol $dm^{-3}$; medium water.

*Quantum Yield Measurements*

These were determined in the form of appearance of U(IV) at 648 nm and are exemplified in Fig. 2 and collated in Table II.

*ESR Spectra*

These are given in terms of the individual amino-acids below, and are exemplified in Fig. 3, and are collated in Table III.

*β-Alanine*

A six-line spectrum was obtained in $H_2O$ medium with $a(H)_{av} = 23.0$ G (10 G = 1 mT) and $g = 2.0031$. The same spectrum was produced in $D_2O$, indicating that no coupling occurs to the N–H(D) protons.

We attribute the spectrum to the radical $^{\bullet}CH_2$-$CH_2NH_3^+$ in which both α-protons and one β-proton show $a(H) = 23$ G, while the other β-proton shows $a(H) = 46$ G, corresponding to a 'locked' conformation facilitating hyperconjugation with the semi-occupied orbital at C(1) [16] as in $CH_3CH_2CH_2^{\bullet}$ [17] and other radicals of structure $XCH_2CH_2^{\bullet}$.

*Glycine*

While a six-line spectrum of approximately binomial distribution was obtained in $H_2O$ with $a(H)_{av} = 30.0$ G and $g = 2.00243$, this was reduced to a 1:2:1 triplet in $D_2O$ with $a(H)_{av} = 23.5$ G. The radicals responsible are, respectively, $^{\bullet}CH_2NH_3^+$ and $^{\bullet}CH_2ND_3^+$, in agreement with earlier findings [1, 2, 18].

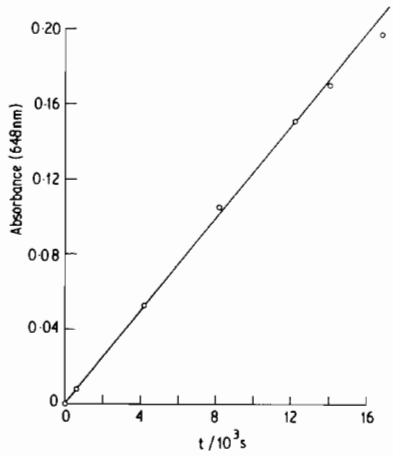


Fig. 2. Development of absorbance of U(IV) at 648 nm during 401 nm photolysis of EDTA ($4.75 \times 10^{-3}$ mol $dm^{-3}$) and uranyl ion (as nitrate, 0.08 mol $dm^{-3}$) in aqueous $HClO_4$ (0.20 mol $dm^{-3}$). $T = 293 \pm 1$ K.

TABLE II. Quantum Yields for U(IV) Appearance[a]

| Compound | $\phi(U^{IV})$ |
|---|---|
| Glycine | <0.017 |
| DL-alanine | 0.094 |
| β-alanine | <0.005 |
| Serine | 0.084 |
| DL-valine | 0.145 |
| DL-leucine | 0.120 |
| Threonine | 0.191 |
| D-asparagine | 0.0182 |
| L-glutamine | 0.128 |
| Isoleucine | 0.143 |
| Histidine | <0.005 |
| Tyrosine | <0.005 |
| L-tryptophan | <0.005 |
| L-phenylalanine | <0.005 |
| CDTA | 0.191 |
| EDTA | 0.194 |
| $MeN(CO_2H)_2$ | 0.020 |
| DL-methionine | 0.017 |
| L-cystine | 0.0019 |
| Cysteine | 0.007 |

[a] $[UO_2^{2+}] = 0.08$ mol $dm^{-3}$, $[HClO_4] = 0.2$ mol $dm^{-3}$ medium water.

*Valine*

While in $H_2O$ a broad, poorly-resolved spectrum was obtained, in $D_2O$ this simplified to a 1:2:1 triplet with $a(H) = 24$ G, $g = 2.0028$ which is assigned to $Me_2\dot{C}HCHND_3^+$ in agreement with Poupko *et al.* [2].

*α-Alanine*

An intense, complex spectrum is produced in $H_2O$ while in $D_2O$ this reduces to a five-line spectrum in a binomial intensity distribution with $a(H)_{av} =$

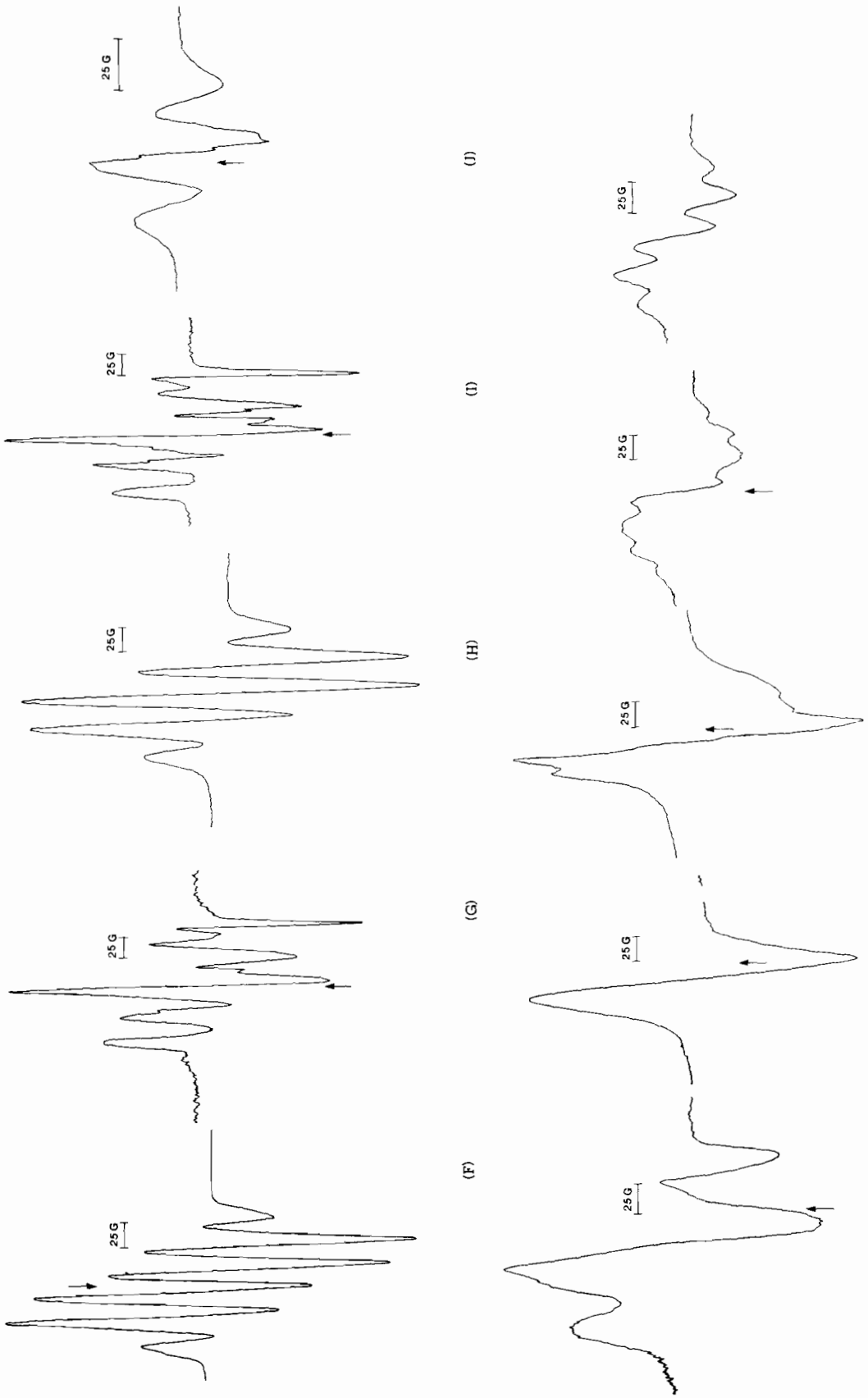


Fig. 3. ESR spectra produced at 77 K on photolysis (λ = 330–410 nm) of samples of amino-acids in aqueous $HClO_4$ media containing uranyl perchlorate. Arrow refers to DPPH standard: (a) β-alanine/$D_2O$; (b) α-alanine/$H_2O$; (c) α-alanine/$D_2O$; (d) glycine/$D_2O$; (e) glycine/$H_2O$; (f) valine/$H_2O$; (g) methionine/$H_2O$; (h) cysteine/$H_2O$; (i) glutamine/$H_2O$; (j) glutamine/$D_2O$.

TABLE III. Summary of ESR Data Relating to Radicals Produced at 77 K by Interaction of Amino-acids with Excited Uranyl Ion

| Substrate | Medium | ESR spectrum | Assignment |
|---|---|---|---|
| $CH_2(NH_3^+)CO_2^-$ | $H_2O$ | 6 lines, 5H<br>$a$ = 30 G | $^{\bullet}CH_2NH_3^+$ |
| | $D_2O$ | 3 lines, 2H<br>$a$ = 23.5 G | $^{\bullet}CH_2ND_3^+$ |
| $H_3\overset{+}{N}CH_2CH_2CO_2^-$ | $H_2O$ | 6 lines, 4H<br>$a(H)_\alpha$ = 23 G<br>$a(H)_\beta$ = 46 G | $\dot{C}H_2CH_2\overset{+}{N}H_3$ |
| | $D_2O$ | 6 lines, 4H | $\dot{C}H_2CH_2\overset{+}{N}D_3$ |
| $Me_2CHCH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | broad, poorly, resolved | $Me_2CH\dot{C}H\overset{+}{N}H_3$ |
| | $D_2O$ | 3 lines, 2H<br>$a$(H) = 24 G | $Me_2CH\dot{C}H\overset{+}{N}D_3$ |
| $^-O_2CCH_2CH_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | 6 lines<br>$a(H)_{av}$ = 23 G | $\dot{C}H_2CH_2CH(\overset{+}{N}H_3)(CO_2^-)$ |
| | $D_2O$ | 6 lines | $\dot{C}H_2CH_2CH(\overset{+}{N}D_3)(CO_2^-)$ |
| $^-O_2CCH_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | 5 lines<br>$a(H)_{av}$ = 22 G | $\dot{C}H_2CH(\overset{+}{N}H_3)(CO_2^-)$ |
| $NH_2COCH_2CH_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | 7 lines, 6H<br>$a$(2H) = 26 G<br>$a$(1H) = 52 G | $NH_2COCH_2CH_2\dot{C}H\overset{+}{N}H_3$ |
| | $D_2O$ | 5 lines | $NH_2COCH_2CH_2\dot{C}H\overset{+}{N}D_3$ |
| $NH_2COCH_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | 7 lines, 6H | $NH_2COCH_2\dot{C}H\overset{+}{N}H_3$ |
| | $D_2O$ | 3 lines<br>$a$(2H) = 26 G | $NH_2COCH_2\dot{C}H\overset{+}{N}D_3$ |
| $HOCH_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $D_2O$ | 3 lines<br>$a$(2H) = 23 G | $DOCH_2\dot{C}H\overset{+}{N}D_3$ |
| $Me-S-(CH_2)_2CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | intense singlet<br>$\Delta H_{pp}$ = 33 G | S-centred species |
| $HS-CH_2-CH(\overset{+}{N}H_3)(CO_2^-)$ | $H_2O$ | singlet $\Delta H_{pp}$ = 32.5 G | |
| $[SCH_2CH(\overset{+}{N}H_3)(CO_2^-)]_2$ | $H_2O$ | singlet $\Delta H_{pp}$ = 28 G | |

28 G, $g$ = 2.0024. The radical responsible is considered to be $Me\dot{C}HNH_3^+$ ($Me\dot{C}HND_3^+$ in $D_2O$) in agreement with Poupko *et al.* [2].

*Glutamic acid*

A six-line spectrum was found in both $H_2O$ and $D_2O$. In $H_2O$ the spectrum has $a(H)_{av}$ = 23 G and $g$ = 2.0026, and we assign it to the radical $\dot{C}H_2CH_2$-$CH(NH_3^+)CO_2^-$.

*Aspartic acid*

A five-line spectrum was found in $H_2O$ with $a(H)_{av}$ = 22 G, $g$ = 2.0026 which is assigned to $\dot{C}H_2$-$CH(\overset{+}{N}H_3)(CO_2^-)$.

*Glutamine*

A symmetrical weakly-resolved seven-line spectrum was produced in $H_2O$ with $a(H)_{av}$ = 26 G and $g$ = 2.00265 which, in $D_2O$, yielded only five lines. The latter species corresponds to $NH_2COCH_2CH_2$-$\dot{C}HND_3^+$ with $a$(2H) = 26 G, $a$(1H) = 52 G.

*Asparagine*

A poorly-resolved seven-line spectrum in $H_2O$ was reduced in $D_2O$ to a basic broad triplet exhibiting some further structure, with $a$(2H) = 26.0 G, for which the most probable candidate species is $NH_2$-$COCH_2\dot{C}HND_3^+$.

*Serine*

A complex spectrum in $H_2O$ became a basic triplet in $D_2O$ with $a$(2H) = 23.0 G and $g$ = 2.0056, similar to that given by asparagine, and the most reasonable assignment is to the analogous radical, *i.e.* to $HOCH_2$-$\dot{C}HND_3^+$.

*Methionine*

An intense singlet was formed in $H_2O$ with $g$ = 2.0125 and $\Delta H_{pp}$ = 33 G.

*Cysteine*

A singlet featuring some sub-structure was formed in $H_2O$ with $g$ = 2.0105 and $\Delta H_{pp}$ = 32.5 G.

*Cystine*

A singlet with some sub-structure was observed in $H_2O$ with $g = 2.0056$ and $\Delta H_{pp} = 28$ G.

## Discussion

We have noted before [13] the general inertness of glycine towards $[UO_2^{2+}]^*$ despite the highly oxidising character of the latter species, with an estimated reduction potential of +2.60 V [19]. This obviously extends to molecules of the general structure $RCH(NH_3^+)CO_2^-$ (R = alkyl), and only when significant additional functional groups are present does the second-order quenching rate constant exceed $4 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$. The fast rates of quenching with amino-acids bearing aromatic rings is associated with fast, reversible exciplex formation between the $\pi$-system and the excited U(VI) species, as established for a series of substituted benzenes [20] and benzoic acids and alkenes [21]. Support for this view is indicated by the immeasurably small quantum yields for U(IV) formation with this particular group of amino-acids (Table II).

While the kinetic quenching rates of $[UO_2^{2+}]^*$ by $RCH(NH_3^+)CO_2^-$ are very low for R = H, Me, $Me_2$-CH, $Me_2CHCH_2$, MeEtCH (Table I), the quantum yields for U(IV) production are nearly, or exceed, 0.1 where R is a branched alkyl group (valine, leucine, isoleucine). One must note here that the value of $\phi$[U(IV)] as measured refers to all secondary processes leading to U(IV) after the initial primary photochemical act, eqn. (1). These will include not

$$Me_2CHCH(NH_3^+)CO_2^- + [U(VI)]^* \longrightarrow Me_2C\dot{C}H(NH_3^+) + UO_2^+ + CO_2 \quad (1)$$

$$Me_2C\dot{C}H(NH_3^+) + UO_2^{2+} \longrightarrow Me_2\overset{+}{C}HCH(NH_2) + H^+ + UO_2^+ \quad (2)$$

$$2UO_2^+ \longrightarrow UO_2^{2+} + U(IV) \quad (3)$$

$$Me_2\overset{+}{C}HCH(NH_2) + 2H_2O \longrightarrow Me_2CHCH(OH)(NH_2) + H_3O^+ \quad (4)$$

$$Me_2CHCH(OH)(NH_2) \longrightarrow Me_2CHCH{=}O + NH_3 \quad (5)$$

only fast reduction of a second molecule of uranyl ion by the alkyl radical, eqn. (2), followed by the disproportionation, eqn. (3), but subsequent attack on $[UO_2^{2+}]^*$ by the reactive aldehyde generated in eqn. (5): the ready photoreduction of U(VI) by simple aldehydes is established [22]. The amino-acids containing hydroxyalkyl groups such as serine and threonine give sizeable values for $\phi$[U(IV)], in accord with the well-known reactivity of alkanols towards $[UO_2^{2+}]^*$ [23]. Values of just under 0.2 are given by the polyaminocarboxylic acids, EDTA and CDTA, and these show a $10^2$-fold increase over the simple amino-acids in their rate of quenching of $[UO_2^{2+}]^*$: however, this reactivity must originate largely either in physical quenching processes, or in chemical quenching not leading to correspondingly large yields of separated radical-pairs.

A similar basic situation must exist for the three sulphur-containing amino-acids: these display second-order kinetic quenching rate constants of between $5.67 \times 10^8$ and $1.29 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, *i.e.* rather similar to those reported for simple thioethers and other sulphur compounds [15] while, as with these simple compounds, the quantum yield of the redox process is very small.

Thus while the rate of interaction between $[UO_2^{2+}]^*$ and the thio-compounds is $>10^2$-fold faster than for the simple amino-acids, the yield of redox products is *ca.* 10-fold lower.

Evidently the step $k_{30a}$ operates in the Weller-type scheme [24] eqn. (6), with high efficiency in these systems:

$$R_2S + [UO_2^{2+}]^* \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [R_2S{\cdot}UO_2^{2+}]^* \qquad [R_2S{\cdot}UO_2^{2+}]^* \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [R_2S^{+\bullet}{\cdot}UO_2^+] \quad (6)$$

$[R_2S^{+\bullet}{\cdot}UO_2^+]$ $\swarrow^{k_{30a}}$ $\searrow^{k_{30b}}$

$R_2S + UO_2^{2+}$ (back-ET) $\qquad$ $R_2S^{+\bullet} + UO_2^+$ (diffusion apart)

The production of sulphur-centred, rather than carbon-centred radicals from the thio compounds is strongly suggested by the line-shapes and $g$-tensors of the ESR spectra of the irradiated systems (Table III), [15, 25]. Although in some respects $[UO_2^{2+}]^*$ behaves like $[O{=}U^V{-}\dot{O}]$, *i.e.* a radical with its SOMO centred on an oxygen atom, such as HO$^\bullet$, t-BuO$^\bullet$ and triplet benzophenone, $Ph_2\dot{C}{-}O^\bullet$, in its interaction with amino-acids it behaves uniquely. Thus while triplet benzophenone, like $[UO_2^{2+}]^*$ reacts very slowly with glycine at pH 7, and rapidly with EDTA, histidine, tryptophan tyrosine, and methionine [26], the yields of redox species determined by flash photolysis are generally much higher for triplet benzophenone than for the excited uranyl ion, *i.e.* in eqn. (5), $k_{30b} \geqslant k_{30a}$ for $^3Ph_2CO$.

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