

A FLASH PHOTOLYSIS STUDY OF PHOTOCHEMICAL REACTIONS OF URANYL IONS

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Summary

A study of photochemical reactions of uranyl ions in aqueous acid solutions was carried out by means of flash photolysis. Short-lived absorption ($\sim 10^{-4}$ s) was observed on flash excitation of uranyl ion in solution and was assigned to singlet-singlet transitions. In the presence of certain organic substances a new transient absorption was detected due to production of U^V intermediate. Deactivation pathways of excited ion (UO_2^{2+})* and decay kinetics of U^V were studied. Values of rate constants for some elementary processes were determined.

Introduction

The photochemistry of the uranyl ion UO_2^{2+} remains a very important field for many reasons. Whilst the stable products of photochemical reactions of the uranyl ion in solution have been studied exhaustively [1 - 4], our understanding of the primary processes involved was far from satisfactory. Assignment of the electronic states involved in the photochemistry of uranyl ions was rather more controversial. The absorption spectrum of U^V intermediate was not detected so its role in redox reactions was the subject of numerous speculations. True mechanism of the photochemical reaction of the uranyl ion can be readily established using a flash photolysis method.

In this paper we present results of the study of the primary processes involved and of the pathways leading to stable products of the photochemistry of the uranyl ion in aqueous acid solutions.

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Experimental

Absorption spectra and decay kinetics of the short-lived intermediates produced on flash excitation of the uranyl ion solutions (10^{-4} – 10^{-1} M) were measured by means of a flash photolysis apparatus described elsewhere [5]. Fluorescence decay of the uranyl ion was recorded with the same apparatus while the monitoring light beam had been switched off. The time duration of the flash was 10^{-5} s for 1000 J of energy dissipated (the value used in most runs). Quartz cell ($l = 20$ cm) and glass filters (in the wavelength region 400 - 560 nm) were used.

Some experiments were carried out in the presence of O_2 and certain quenchers of fluorescence [aliphatic alcohols, aliphatic acids, amino compounds and oxycompounds of benzene and naphthalene, U^{IV} , chrysoidine (10^{-3} – 10^{-2} M)], added in aqueous solutions of $HClO_4$, H_3PO_4 , H_2SO_4 . The quenchers used were spectroscopically pure. The absorption spectra of the uranyl ions were measured before and after the flash by means of a Shimadzu MPS-50L spectrophotometer. All measurements were carried out at room temperature.

Results and Discussions

Flash excitation of the uranyl ion in plain aqueous acid solutions gives rise to short-lived changes in absorption in the visible and near i.r. region. Figure 1 shows the absorption spectrum obtained [6, 7]. These short-lived changes in absorption were confirmed recently by Creatorex *et al.* [8].

Flash excitation of the uranyl ion also leads to emission [6, 7] with a spectrum similar to the fluorescence spectrum of the uranyl ion.

To explain the relationship between the emission and short-lived absorption of $(UO_2^{2+})^*$ and to determine the nature of levels responsible for both processes a comparative study of the decay kinetics of both short-lived absorption (at $\lambda = 590$ nm) and emission (at $\lambda = 520$ nm) of the uranyl ions was carried out in 1 M H_3PO_4 with and without various quenchers.

It was revealed that the $(UO_2^{2+})^*$ decay follows first-order kinetics and the rate constants of the excited uranyl ion deactivation coincide (Table 1).

The latter fact means that the emission and transient absorption occur from the same excited level of the uranyl ion.

The lowest excited level of the uranyl ion is a singlet one. It follows from this that the life-times of the excited uranyl ions measured in de-aerated and air-saturated solutions are equal. Also typical $T-T$ absorption for such acceptors as anthracene α -sulphonic acid ($T = 14,930$ cm^{-1}), rhodamine 6G ($T = 14,600$ cm^{-1}) and 3,3'-diethylthiocarbocyanine ($T = 13,710$ cm^{-1}) was absent in the experiments on $T-T$ energy transfer from excited uranyl ion ($\nu = 20,500$ cm^{-1}).

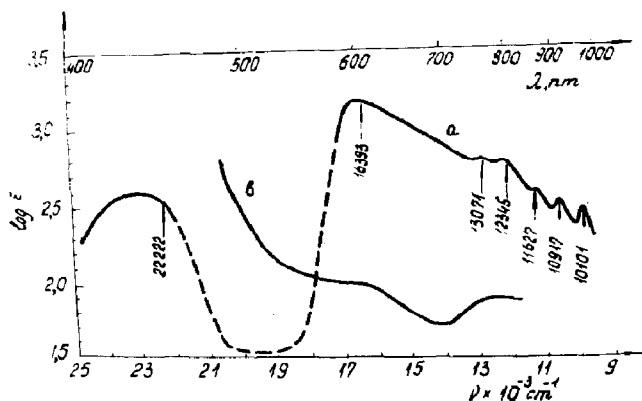


Fig. 1. Spectra of transient absorption of (a) $(U^{VI})^*$ and (b) U^V in $1 M H_3PO_4$. Arrows indicate the calculated position of the maxima.

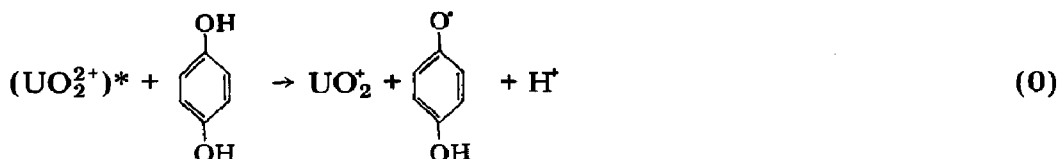
TABLE 1

Rate constants for the quenching of the excited uranyl ion in $1 M H_3PO_4$

Quencher	Emission measurements, $k_q (M^{-1} s^{-1})$	Absorption measurements, $k_q (M^{-1} s^{-1})$
without quencher	$(6.1 \pm 1.8) \times 10^3$ *	$(6.0 \pm 1.8) \times 10^3$ *
ethanol	$(1.5 \pm 0.4) \times 10^9$	$(1.4 \pm 0.5) \times 10^9$
hydroquinone	$(1.0 \pm 0.3) \times 10^9$	$(1.0 \pm 0.3) \times 10^9$
KI	$(8.1 \pm 2.4) \times 10^8$	$(7.8 \pm 2.3) \times 10^8$
U^{IV}	$(6.4 \pm 2.0) \times 10^7$	$(6.8 \pm 2.0) \times 10^7$

The value of the rate constant for the deactivation (K_1) of UO_2^ .

The values of extinction coefficients for $(UO_2^{2+})^*$ were calculated at surplus of hydroquinone ($10^{-2} M$) using the stoichiometry of the reaction (0) and high energy of excitation (1000 J)



The large values of extinction coefficients $(UO_2^{2+})^*$ ($2.5 \times 10^3 \text{ cm}^{-1} M^{-1}$ l in $1 M H_3PO_4$; $7.0 \times 10^2 \text{ cm}^{-1} M^{-1}$ l in $1 M H_2SO_4$ at $\lambda = 590 \text{ nm}$) indicate on the allowed character of transition. Therefore observed changes in absorption (Fig. 1) are the result of transitions between the first excited singlet level of the uranyl ion (S_1^*) and the higher levels (S_n^*).

The existence of a few absorption bands ($S_1^* \rightarrow S_n^*$) for uranyl ion in visible and near infra-red range confirms the existence of a few excited states of the uranyl ion.

The maxima of absorption bands (shown in Fig. 1 with arrows) were calculated using uranyl ion transition energies [9] between different electronic states and proved to be in a good agreement with experimental data.

Thus, the obtained singlet-singlet absorption spectrum of the excited uranyl ion may also be further evidence of the existence of a few excited states of the uranyl ion [10, 11].

As mentioned above in the presence of organic and inorganic quenchers the emission and short-lived absorption were not detected. This may be the result of the effective deactivating processes for the excited uranyl ion.

Numerous studies [1, 4, 12 - 19] imply the possibility of two different mechanisms for the decay of the excited uranyl ion. One mechanism is generally related to the energy transfer from the excited uranyl ion to quencher molecules [12 - 19]. The other one is related to either α -hydrogen atom abstraction or to electron transfer [1 - 4].

Recently [3, 4] the following mechanism for the quenching of the excited uranyl ion by Q was assumed (scheme 1):



However, the authors [3, 4] could not detect intermediates in the photoreactions of $(U^{VI})^*$.

Recently [6] we have observed the production of a U^V intermediate on flash excitation of uranyl ion in the presence of certain electron donors (hydroquinone *etc.*). In this study we have carried out detailed measurements of the kinetics of production and decay of U^V species.

In the presence of the electron donors (10^{-3} – 10^{-2} M) absorption of $(U^{VI})^*$ disappeared and new absorptions were observed in the visible range owing to formation of U^V (Fig. 1) as well as cation radicals of quenchers and U^{IV} [20, 21]. The absorption spectra of U^V , cation radicals and radicals of the organic compounds measured in this study coincide well with those previously published [22 - 27].

Values of extinction coefficients for U^V were determined using the method described above. The kinetic analysis of the decay of short-lived absorption carried out with and without quenchers revealed that the deactivation of $(U^{VI})^*$ occurs as a result of the intramolecular electron transfer or hydrogen abstraction (the first group of quencher molecules: methanol, ethanol, isopropanol, t-butanol, aniline, diphenylamine, β -naphthylamine, phenol, β -naphthol, hydroquinone, ascorbic acid, formic acid, oxalic acid) as well as the intramolecular energy transfer (the second group of quencher molecules: U^{IV} , chrysoidine).

When the level of the excited state of the uranyl ion to be quenched is positioned in the range of 51 - 59 kcal/mol and is much lower than the lowest excited state of the quenchers (the first group of quencher molecules),

the intramolecular electron transfer or hydrogen abstraction occurs.

The energy transfer from the excited uranyl ion to quencher molecules is a highly endothermic process; and efficient transfer in such a highly endothermic process would not occur [28 - 30].

The intramolecular energy transfer was observed to occur from the excited uranyl ion to U^{IV} and chrysoidine (the second group of quencher molecules). Also the intramolecular electron transfer was observed to occur from the excited uranyl ion to the second group of quencher molecules. Pronounced properties of the acceptor-uranyl ion, increase in electron affinity of that on excitation and decrease in potential ionization of donor-quenchers at the expense of the hydrogen-bond production in the external coordinated sphere of uranyl ions favour the ability of electron transfer [11, 31, 32].

The values of extinction coefficients for U^{VI} and U^V were used to determine the rate constants for "physical" (2) and "chemical" (3) deactivation pathways of excited uranyl ion.

From the above kinetic scheme 1 one can write the following equations:

$$-\frac{d[(U^{VI})^*]}{dt} = \{k_1 + (k_2 + k_3)[Q]\} [(U^{VI})^*] \quad (5)$$

$$\frac{d[U^V]}{dt} = k_3 [Q] [(U^{VI})^*] \quad (6)$$

It is easy to see that the rate of the production of U^V has to be much higher than that for the decay of U^V . The last requirement is fulfilled by experience.

Dividing eqn. (5) by eqn. (6), one can obtain the following expression:

$$\frac{[(U^{VI})^*]_0}{[U^V]_{\max}} = \frac{k_2 + k_3}{k_3} + \frac{k_1}{k_3} \cdot \frac{1}{[Q]} \quad (7)$$

where $[(U^{VI})^*]_0$ is the concentration of $(U^{VI})^*$ without quenchers, $[U^V]_{\max}$ is the maximum concentration of U^V measured at $t = 5 \times 10^{-5}$ s after the flash.

Equation (7) implies that the plot of $[(U^{VI})^*]_0/[U^V]_{\max}$ vs. $1/[Q]$ represents the linear dependence. The obtained dependence was found to be linear for all quenchers used (e.g. Fig. 2). From the kinetic measurements and the linear dependence (7) values of the rate constants for the "physical" and "chemical" deactivation processes of the excited uranyl ion were calculated and are given in Table 2.

From Table 2 one can see that the competition between "physical" and "chemical" processes of deactivation of excited uranyl ions greatly depends upon the nature of the quenchers.

In particular as an example of the predomination of "physical" deactivation of excited uranyl ions can be used the absence of absorption

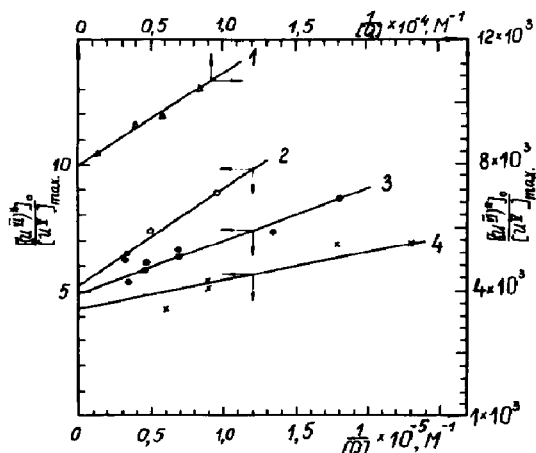


Fig. 2. Plot of $[(U^{VI})^*]_0/[U^V]_{max}$ vs. $1/[Q]$ in mixture of 1 M H_3PO_4 and alcohols: 1, t-butanol; 2, methanol; 3, ethanol; 4, isopropanol.

TABLE 2

Rate constants for the "physical" (k_2) and "chemical" (k_3) quenching of the excited uranyl ion

Quencher	$k_2 (M^{-1} s^{-1})$	$k_3 (M^{-1} s^{-1})$	Ionization potential (eV)
methanol	5.7×10^8	1.4×10^8	10.9
ethanol	1.1×10^9	2.8×10^8	10.5
isopropanol	1.8×10^9	5.5×10^8	10.2
t-butanol	8.0×10^7	$<10^4$	9.7
benzene	1.6×10^9	$<10^4$	9.2
aniline*	8.0×10^8	7.2×10^7	8.0
diphenylamine*	$<10^4$	1.1×10^9	7.4
β -naphthylamine*	4.5×10^8	1.9×10^8	7.5
phenol	1.1×10^8	5.9×10^7	8.5
β -naphthol	$<10^4$	9.9×10^7	7.7
hydroquinone	8.5×10^8	1.5×10^8	8.0
ascorbic acid	1.3×10^8	5.2×10^7	8.0
formic acid	1.1×10^6	7.0×10^4	11.1
oxalic acid	1.4×10^5	2.4×10^4	10.5
U^{IV}	$<10^4$	1.0×10^8	—
chrysoidine	9.0×10^8	3.2×10^9	—

* Amines react in protonation form because the photoreduction of U^{VI} was carried out in acid media.

spectrum of the cation radical of benzene and U^V on flash excitation of acid uranyl solutions in the presence of benzene and t-butanol.

From Table 2 one can see that the values of rate constants of "physical" and "chemical" deactivation of excited uranyl ions depend not only upon groups applied as quenchers, but upon their nature at the limits of one group. For example, one can see the dependence of values of rate constants of "chemical" deactivation upon the molecular structure of alcohols (namely upon the mobility of α -hydrogen atom).

The highest value of the rate constant of "chemical" deactivation of excited uranyl ion is given by isopropanol, which has the most mobile α -hydrogen atom. The smallest value of the rate constant of "chemical" deactivation of excited uranyl ion is given by t-butanol, which has no α -hydrogen atom at all. The same dependence remains in the study [2 - 4] of quenching of fluorescence of uranyl solutions by aliphatic alcohols.

From Table 2 one can also see that the rate constants of "chemical" deactivation are determined by the potential value of ionization of quencher molecules.

We were unable to determine the general law for quenching upon the used molecules for values of k_2 in Table 2, characterizing the process of inducing internal conversion, which do not result in the formation of U^V , \dot{Q}^+ , Q ["physical" deactivation of $(U^{VI})^*$]. It is necessary to point out, that the "physical" deactivation for $(U^{VI})^*$ is the general process for many photochemical reactions, limiting quantum yield [33]. For this a large dependence of this process upon the dipole moment of medium is assumed.

Assuming that "physical" and "chemical" deactivation of $(U^{VI})^*$ occur via the uranyl exciplex ($[U^{VI}\dots Q]^*$) eqns. (11) and (12) can be derived according to (scheme 2) [3, 4]:



with

$$k_2 = \frac{k_8 \cdot k_9}{(k'_8 + k_9 + k_{10})} \quad (11)$$

and

$$k_3 = \frac{k_8 \cdot k_{10}}{(k'_8 + k_9 + k_{10})} \quad (12)$$

From eqns. (11) and (12) and assuming $k_8 = k_{diff.} = 7.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, $(k'_8 + k_9 + k_{10})^{-1} = \tau_{exciplex} \leq 10^{-6} \text{ s}$, one can estimate $k_9 \geq 7 \times 10^4 \text{ s}^{-1}$, $k_{10} \geq 2 \times 10^4 \text{ s}^{-1}$, $k'_8 \leq 9 \times 10^5 \text{ s}^{-1}$, $K = \frac{k_8}{k'_8} \geq 8 \times 10^3 \text{ M}^{-1}$ for aqueous acid solutions of the uranyl ion with methanol.

To establish the role of the surrounding medium in the "physical" and "chemical" pathways of $(U^{VI})^*$ decay kinetic measurements were

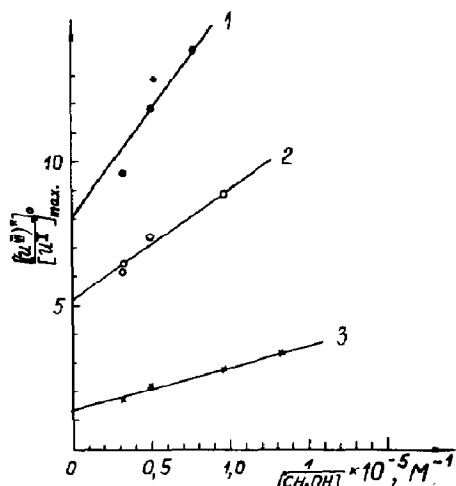


Fig. 3. Plot of $[(U^{VI})^*]_0/[U^V]_{\max}$ vs. $1/[CH_3OH]$ in different acids: 1, 1 M H_3PO_4 ; 2, 1 M H_2SO_4 ; 3, 1 M $HClO_4$.

TABLE 3

Rate constants for the deactivation (k_1) and the "physical" (k_2) and "chemical" (k_3) quenching of the excited uranyl ion by methanol.

Acid	k_1 (s^{-1})	k_2 ($M^{-1} s^{-1}$)	k_3 ($M^{-1} s^{-1}$)	$(k_2 + k_3)$ ($M^{-1} s^{-1}$)	Viscosity (cP)
1 M H_3PO_4	5.9×10^3	5.7×10^8	1.4×10^8	7.1×10^8	0.0105
1 M H_2SO_4	1.5×10^4	1.3×10^9	1.9×10^8	1.5×10^9	0.0089
1 M $HClO_4$	6.0×10^4	1.5×10^9	3.8×10^9	5.3×10^9	0.0082

carried out in mixtures of methanol with different acids (1 M $HClO_4$, 1 M H_2SO_4 , 1 M H_3PO_4).

The results are shown in Table 3 and Fig. 3. Figure 3 implies that the plot of $[(U^{VI})^*]_0/[U^V]_{\max}$ vs. $1/[CH_3OH]$ represents the linear dependence (7).

Consequently, the nature of the anions (ClO_4^- , SO_4^{2-} , PO_4^{3-}) has no important bearing upon the mechanism of the photoreactions of the uranyl ion.

Comparing values of the rate constants for "physical" and "chemical" pathways of deactivation of $(U^{VI})^*$ in the different acids (Table 3) it was revealed that the life-times of the excited uranyl ion strongly decrease but the values of k_2 and k_3 increase from H_3PO_4 to $HClO_4$. The upper limit of these rate constants is the diffusion controlled rate constant.

Observed phenomena may be explained by the decrease of the viscosity of H_3PO_4 in comparison with that of H_2SO_4 and $HClO_4$ and as well as by the decrease of ability to complex formation of uranyl ion with anions [1].

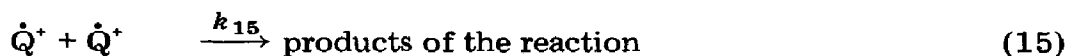
There are two different mechanisms of photochemical reduction of uranyl ion by organic substances. One of them is attributed to the transfer of two electrons for one act [34].

In the other, the authors [2 - 4] assume that U^V is one of the intermediates produced in the photochemical reduction of U^{VI} by organic substances. A disproportionation reaction of U^V is the main reaction for the production of U^{IV} . However, the production of U^V was not observed by Matsushima and Sakuraba [2 - 4].

As noted above, we have detected a U^V intermediate.

So far it has been possible to follow the decay kinetics of U^V and to establish its role in the photochemical production of U^{IV} .

Assuming that the formation of U^{IV} occurs through the following elementary steps:



kinetic measurements for the decay of U^V ($\lambda_{obs} = 590$ nm) and the production of U^{IV} ($\lambda = 656$ nm) on flashing the solutions of U^{VI} in the presence of ethanol, ascorbic acid and hydroquinone as reductants, were carried out.

The formation of U^{IV} was observed [35] only on the photochemical reduction of the uranyl ion in the presence of ethanol and ascorbic acid.

From eqns. (4), (13) and (14), the following equations can be written for the decay of the U^V and the production of the U^{IV} :

$$-\frac{d[U^V]}{dt} = 2k_4[U^V]^2 + k_{13}[U^V][Q] + k_{14}[U^V][\dot{Q}^+] \quad (16)$$

$$\frac{d[U^{IV}]}{dt} = k_4[U^V]^2 + k_{13}[U^V][\dot{Q}^+] \quad (17)$$

The values of rate constants k_4 and k_{13} (Table 4) were found using the data of Fig. 5. From eqn. (16) and assuming that $[Q] \gg [U^V]$ and of U^V and U^{IV} respectively. The values of k_{14} obtained are given in Table 4.

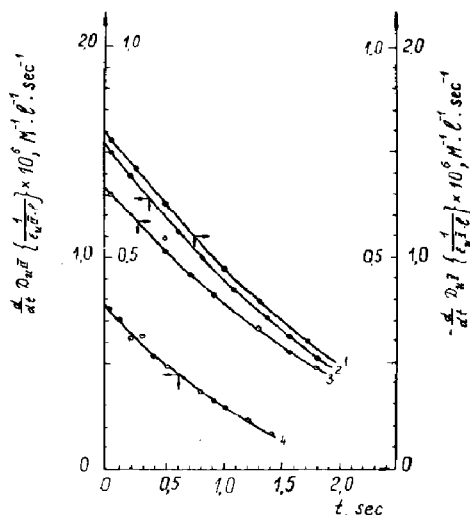


Fig. 4. Kinetics of the decay of U^V (curves 1, 3) and the production of U^{IV} (curves 2, 4) in photoreduction of the uranyl ion by ascorbic acid (\circ) and ethanol (\bullet) in 1 M H_2SO_4 . Internal scale of the ordinate axis is for ethanol; external scale of the ordinate axis is for ascorbic acid.

TABLE 4

Rate constants for the decay U^V on photoreduction of U^{VI} in 1 M H_2SO_4

Reductant	$k_4 (M^{-1} s^{-1})$	$k_{13} (M^{-1} s^{-1})$	$k_{14} (M^{-1} s^{-1})$	Ionization potential (eV)
ethanol	0.6×10^6	16	1.5×10^4	10.5
ascorbic acid	1.3×10^6	85	1.2×10^6	8.0
hydroquinone	— *	— *	5.0×10^8	8.0

*The value of rate constants was not determined.

$k_{14} [\dot{Q}^+][U^V] \ll 2k_4[U^V]^2 + k_{13}[U^V][Q]$ one can obtain the equation:

$$\frac{d}{dt} \ln \frac{D_{OU^V}}{D_{UV}} = k_{13}[Q] + \frac{2k_4}{\epsilon_{UV} \cdot l} \cdot D_{UV} \quad (18)$$

The production of U^{IV} was not observed on photochemical reduction by hydroquinone. Only the formation of semiquinone radicals was detected (reactions (13), (14) and (15)).

In this case, the value of k_{14} was determined from:

$$-\frac{d[\dot{Q}^+]}{dt} = k_{14}[\dot{Q}^+][U^V] + k_{15}[\dot{Q}^+]^2 \quad (19)$$

where $[\dot{Q}^+]$ is the semiquinone radical.

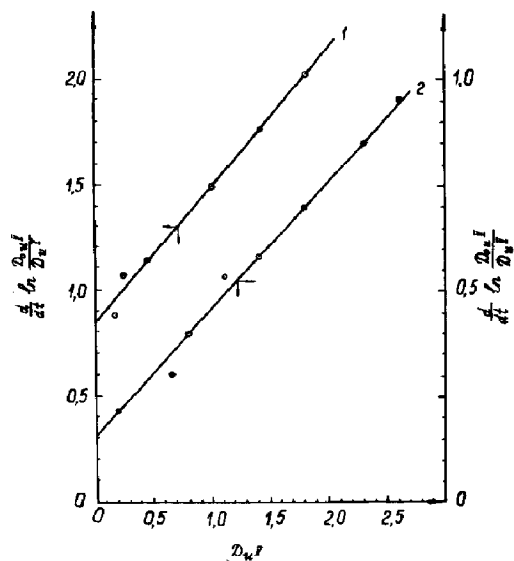


Fig. 5. Plot of $d/dt \ln D_{OU^{VI}}/D_{U^{VI}}$ vs. D_{U^I} in photoreduction of the uranyl ions by ascorbic acid (1) and ethanol (2).

From data of Table 4 it follows that depending upon the nature of organic additive used as a reductant of U^{VI} the photoreduction proceeds according to different mechanisms and with differing efficiency.

In particular the reaction does not proceed to completion with hydroquinone as a reductant because U^V formed at the first step is then oxidized with semiquinone radical again to initial U^{VI} . As a result of this we were unable to determine the values of k_4 and k_{13} in this case.

Conclusions

Thus the application of the flash photolysis method for the study of photochemical reactions of the UO_2^{2+} made it possible:

- (1) to establish the singlet nature of the lowest excited state of the uranyl ion responsible for the photochemical reaction of UO_2^{2+} ;
- (2) for the first time to measure the absorption $S_1^* \rightarrow S_n^*$ spectrum of $(UO_2^{2+})^*$ quantitatively;
- (3) for the first time to measure the absorption spectrum of U^V quantitatively and to study the elementary steps of the decay of U^V ;
- (4) to show that the decay of $(UO_2^{2+})^*$ in aqueous acid solutions occurs either through "physical" quenching or "chemical" quenching and to calculate the rate constants of these processes.

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