

Laser photoemission generation and electrochemical study of methyl radicals as secondary products of OH radicals capture by dimethyl sulfoxide molecules

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Abstract Electrode reactions of intermediates formed during capture of OH radicals by dimethylsulfoxide molecules were studied by laser photoemission in aqueous buffer solutions and pH range from acidic to basic. The results were compared with those obtained previously for electrochemical behaviour of methyl radicals generated via photoemission from CH₃Cl. The essential similarity was found for parameters of irreversible one-electron transfer from/to these intermediates, i.e. the potentials $E_{1/2}$ on time-resolved voltammograms and rate constants at $E = E_{1/2}$. Hence, both active particles were concluded to be equivalent and corresponded to methyl radical. The primary product of OH radicals capture by DMSO molecules, i.e. adduct (CH₃)₂SO(OH), was spontaneously decomposed to form ·CH₃ with time as low as $<2 \times 10^{-5}$ s. A simultaneous increase of the reduction wave height was observed at pH transition from low basic to low acidic and at illumination times T_m of an electrode with UV light if $T_m \geq 90$ –300 ms. The increase exceeded considerably the one-electron reduction level. These features were presumably caused by the rather slow formation of organomercury intermediates

as interaction products of the components of the system with a mercury electrode.

Keywords Laser photoemission · DMSO · Methyl radical · Organomercury intermediates

Introduction

The use of optical effects and methods in electrochemical praxis [1–10], e.g., electrochemiluminescence [1–3], photo-modulated voltammetry [4, 5] or photoemission [6–9], allows the investigation of reactivity as well as kinetic and thermodynamic characteristics of many intermediates, including those that cannot be created by methods of traditional electrochemistry. Intermediates of electrochemically non-active organic solvents including dimethyl sulfoxide (DMSO) belong to them as well. DMSO is one of the most widespread solvents in electrochemistry [11, 12] due to its universality, high permittivity, chemical and electrochemical stability, low toxicity and other valuable advantages.

However, even being a rather poor acceptor of solvated (hydrated) electron e_s^- (e_{aq}^-) with respect to other common organic solvents like acetonitrile, dimethyl formamide, propylene carbonate, etc. [13], the rate constant of the electron capture in the case of DMSO is nevertheless of many orders higher than that of water [13]. Such solvents may thus compete for the electron capture with another acceptor added into a solution. Therefore, its concentration has to be relatively high (especially in pure nonaqueous solvents) to prevent the electron capture by a solvent in processes like photoemission/photoinjection (see, e.g., [14,

This article is dedicated to the 70th birthday of Fritz Pragst.

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15]). The reaction products of these solvents with an electron (e_s^-) as well as their electrochemical properties are often unknown [13].

Besides the electron capture (reduction), other reactions of solvents with highly reactive radicals are possible. The topic of this study is the reaction of DMSO with $\cdot\text{OH}$ radical which is a strong oxidant.

The reaction of C–S bond rupture at OH radical attack on sulphoxides was first reported by R. Norman et al. in 1964 [16] who evidenced the formation of $\cdot\text{CH}_3$ radical in the system aqueous $\text{DMSO-Ti}^{\text{III}}-\text{H}_2\text{O}_2$ by ESR technique. The formation of a primary transient OH adduct $\text{R}_2\text{SO}\cdot(\text{OH})$ as a very short-lived intermediate has been suggested, but no direct proofs of its existence was presented so far. An exception is the study [17] where a signal on EPR spectra recorded in photochemical system aqueous $\text{DMSO-H}_2\text{O}_2$ by time-resolved EPR techniques within 100–300 ns was tentatively attributed to this radical. K.-D. Asmus et al. have demonstrated [18] the unimolecular decay of $(\text{CH}_3)_2\text{SO}\cdot(\text{OH})$ adduct to $\cdot\text{CH}_3$ and methanesulfinic acid with half-time up to 100 ns. Alkyl radical depletion in this reaction is typical for dialkyl sulfoxides [18].

To study $\cdot\text{OH}$ interaction with DMSO, various ways of OH radical generation were used [16–23], i.e. radiolysis of aqueous systems, the Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) or the reaction of hydrogen peroxide with other ions of transition metals (e.g., Ti^{3+} , Cr^{2+} , Cu^+ , etc.), Haber–Weiss reaction ($\text{O}^{2-} + \text{H}_2\text{O}_2$), UV laser (flash) photolysis, treatment of a solution with oxidase or peroxidase, catalase and other enzymes, etc. A comparative study of reaction of DMSO with OH radicals generated by radiolysis and the Fenton's reagent was performed in [22]. Not only was the mechanism of the reaction established to be similar but also the yield of products was found to be practically the same. It was also demonstrated that this reaction could have synthetic potentialities [23]. As far as the rate of the reaction of DMSO with OH radicals occurred to be sufficiently high [13], this solvent was proposed to be used as a perspective radioprotector and anti-inflammatory agent for living organisms (see, e.g., [20, 24]).

Since the development of simple and rapid methods of OH radical detection including those in biological systems is still relevant, there is a possibility to use this reaction in voltammetric analysis [25] among other methods for an indirect electrochemical determination of $\cdot\text{OH}$ [26–28].

Methyl radical itself is formed not only by DMSO reaction with OH radical but also with other active species, namely, radical anions $\text{CO}_3^{\cdot-}$ [21], $\text{SO}_4^{\cdot-}$ [16, 21] or $\text{HO}_2\cdot$ radicals [21] although they have somewhat less pronounced redox properties than $\cdot\text{OH}$ [29]. However, according to the opinion of authors [21], it is not desirable to apply DMSO in biological objects as a probe for quantitative and selective indirect detection of OH radicals (via generation of $\cdot\text{CH}_3$) because the HCO_3^- ions that are also able to

participate in $\cdot\text{OH}$ generation are always present in such systems. The voltammetric [26, 27] or electrochemical impedance [28] detection of OH radicals by their reaction with self-assembled monolayers of alkylthiols on gold electrodes is much more suitable for biological systems.

In the presence of O_2 , formaldehyde is formed as a main product of the following reaction sequence. DMSO interacts with $\cdot\text{OH}$, giving rise to the $\text{CH}_3\cdot$ radicals. They react with O_2 to produce $\text{CH}_3\text{OO}\cdot$ radicals [21], which decay rapidly, and the end-products of their transformations are CH_3OH and CH_2O [21]. All these allowed to call into doubt [21] many statements on non-toxicity of DMSO for living organisms. The voltammetric detection of OH radicals in such cases is carried out on the wave height of formaldehyde reduction [25].

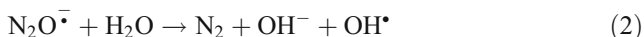
Electrode reactions of $\cdot\text{CH}_3$ were studied previously [19, 30–32]. The radical was generated by the reaction of methane with $\cdot\text{OH}$ at a pressure of 50 atm, and products of pulse radiolysis were investigated by polarography [30]. That radical was obtained also via photoemission capture of e_{aq}^- by methyl chloride [31, 32] and studied by photoemission methods.

One more route of $\cdot\text{CH}_3$ generation is reaction of $\text{SO}_4^{\cdot-}$ radical anion with OAc^- , *t*-BuOH or DMSO, and differential polarograms of products of the reaction were recorded [19]. For unambiguous electrochemical identification of $\cdot\text{CH}_3$ as a product of DMSO reaction with OH radical, it is necessary to study both the reduction and oxidation of this intermediate. The polarographic measurements in [19] have been made, however, only within the range from -1.0 to -1.5 V that was far behind the potentials of $\cdot\text{CH}_3$ oxidation [30, 32]. Thus, the complex information on the electrochemical properties of this system was absent. Therefore, respective measurements for the system $\text{DMSO} + \cdot\text{OH}$ within a broad range of experimental conditions (electrode potential, pH, etc.) and determination of the characteristics of electron transfer have to be carried out.

Experimental

A three-electrode cell of quartz was used for laser photoemission experiments. The working electrode was a stationary hanging mercury drop of the Kemula type (see, e.g., [9]). The auxiliary electrode was a Pt foil with a large surface area. All the potentials were referred to a saturated calomel electrode. The range of DMSO concentrations was from 0.03 to 1.3 M. The experiments proceeded in buffer solutions in the pH range 2.4–13.2 with addition of 0.1 M Na_2SO_4 or 0.5–1 M KCl. The measurements in more acidic solutions were rather difficult due to the competitive capture of e_{aq}^- by H_3O^+ [6, 7]. All the solutions were prepared from triply distilled water. DMSO was purified by

a standard procedure like in [9] that included double-distillation under reduced pressure. Dissolved oxygen was removed from aqueous DMSO solutions in photoelectrochemical cell by long-term bubbling with Ar. After that, the solution was saturated with N₂O/Ar mixture where N₂O concentration was either 0.008 or 0.015 M. N₂O was a source of OH radicals generated via the next reaction sequence:



where the rate constant k_a of e_s^- capture by N₂O molecule was equal to $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [6]. N₂O and Ar were used without further purification.

Laser photoemission method [6] improved in [8, 9] was used in the measurements of photocurrent J within potentiostatic conditions (the registration of time-resolved voltammograms (TRV) at modulated laser illumination). A photoelectrochemical cell was maintained in a potentiostatic regime with the aid of a specially elaborated high-speed low-current potentiostat. The potential of an electrode E was automatically switched within limits as assigned by an operator. A photocurrent signal from a current–voltage converter was amplified by a preliminary amplifier and supplied on input of a D/A transformer of a computer.

The value of J was obtained by a numerical Fourier transform of a signal from a photoelectrochemical cell illuminated with a modulated light with the period $T_m = 1.0 - 10^{-3} \text{ s}$. Here, T_m is the main operation parameter in TRV's registration like, e.g., scan rate in voltammetry or current density in chronopotentiometry.

Pulse and continuous lasers were used as UV-light irradiation sources. They were nitrogen pulse laser LGI-505 (Russia) (wavelength $\lambda = 337 \text{ nm}$) with a repetition frequency of pulse light of 1 kHz, pulse duration of 8 ns and an average power of $\sim 0.1 \text{ W}$, and continuous He–Cd laser GKKL-8UM (I) (Russia) ($\lambda = 325 \text{ nm}$, an average power of $\sim 0.01 \text{ W}$).

To improve a signal/noise relation, signal registered without illumination was subtracted automatically from the signal accumulated during the electrode illumination. That was the way on how to obtain the dependence of the photocurrent on electrode potential (J, E dependence) for the acceptors investigated. Then, in order to exclude a dependence of the quantum yield of photoemission on the electrode potential, it was normalized to a J_0, E dependence in a solution containing N₂O, which is an “ideal acceptor”. The electroreduction of the products of the reaction of N₂O with e_{aq}^- (OH radicals, cf. Eqs. 1 and 2) occurs at highly positive potentials (the standard potential of OH radical is +2.56 V SCE [29]). Hence, the value of

J_0 is proportional to the quantum yield of photoemission over the whole range of the working potential. Thus, it could respect in some degree to a depolarizer reduction within the regime of limiting diffusion current in traditional electrochemistry. A normalized $J/J_0, E$ dependence has the shape of a wave for a radical under study and its height reflects the number of transmitted electrons and therefore does not depend on T_m in a general case. The position of the half-wave potential $E_{1/2}$ in the axis of potential E is defined by the relation between the rate constants W_R/W_{Ox} of reduction/oxidation of adsorbed intermediates R^*_{ads} and a period T_m of the modulation of the recording signal. The accuracy of the determination of $E_{1/2}$ for TRV was equal to $\pm 0.01 \text{ V}$.

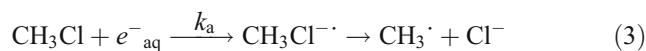
This approach allows the determination of absolute values of oxidation and reduction rate constants of intermediates (W_{Ox} and W_{red} , respectively) and the creation of the experimental Tafel plots ($\lg W, E$ dependencies). The transition from $E_{1/2}, T_m$ dependencies to W, E dependencies is based on the coincidence of the $E_{1/2}$ value and the potential where $W = KT_m^{-1}$ ($K = 5.31$ for one-electron irreversible reduction and 10.88 for one-electron irreversible oxidation of R^*_{ads}) [8, 9]. A detailed mathematical description could be found elsewhere [7].

In order to expand the effective range of the measured rate constants W_R/W_{Ox} , a package of applied programs was developed for the automatic determination of values of $E_{1/2}$ and transfer coefficients for electrooxidation β and electroreduction α at higher harmonics of a factual frequency of modulation of illumination of a pulse laser. It provided for the measurement of values of W_R/W_{Ox} in the interval 5.0 to $5.0 \times 10^4 \text{ s}^{-1}$. The transfer coefficients were also derived from Tafel plots and TRV's slope for oxidation and reduction of intermediates [6–8].

Results and discussion

Two well-resolved one-electron waves were observed on TRV's of intermediates formed during the capture of OH radicals by DMSO molecules (Figs. 1 and 2) within the whole pH range studied. These waves were of approximately equal height that did not depend on T_m and pH $\sim (6.5 - 13.2)$ (Fig. 1) with a slight decrease in more acidic solutions. The $E_{1/2}$ of the first wave was within ~ -0.30 to -0.56 V , and the $E_{1/2}$ of the second one was within ~ -1.3 to -1.7 V , respectively, depending on the irradiation time of an electrode with UV light T_m .

Note that the TRV's for such intermediates were practically coinciding with those recorded by us previously [32] (dotted lines on Fig. 1) within a similar pH range (3.4–12.1) and T_m $1.1 - 10^{-2} \text{ s}$ for methyl radical generated by the reaction:



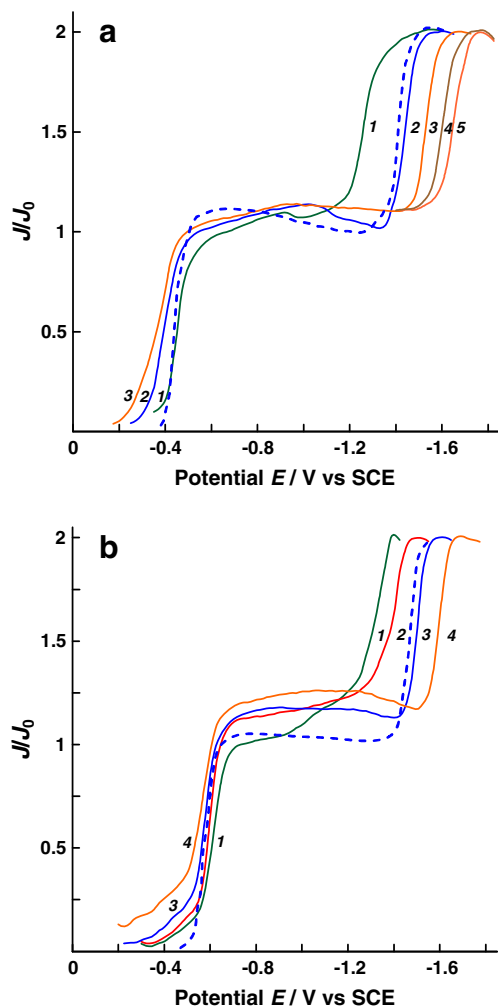


Fig. 1 **a** Time-resolved voltammograms of solutions containing 0.07 M DMSO and 0.008 M N_2O . Dependence on the irradiation time at low basic pH. Britton–Walford buffer +0.1 M Na_2SO_4 , pH 9.1. The irradiation times of an electrode with UV light, T_m , ms: 1—1000, 2—30, 3—3.5, 4—0.91, 5—0.3. Dashed line, data of [32] (saturated solution of CH_3Cl , phosphate buffer +0.5 M KCl, pH 6.86, $T_m=30$ ms). **b** Time-resolved voltammograms of solutions containing 1 M DMSO and 0.008 M N_2O . Dependence on the irradiation time at a higher concentration of DMSO and strongly basic pH. Basic buffer +0.1 M Na_2SO_4 , pH 13.2. The irradiation times of an electrode with UV light, T_m , ms: 1—1000, 2—290, 3—29, 4—2.9. Dashed line, data of [32] (saturated solution of CH_3Cl , Britton–Walford buffer +0.5 M KCl, pH 11.5, $T_m=30$ ms)

where $k_a=1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [13] and the dissociation of the formed radical anion occurred extremely fast and almost barrierless [33].

According to [32], the first wave corresponds to a one-electron irreversible oxidation of $\cdot CH_3$:



and the second one to its irreversible reduction:

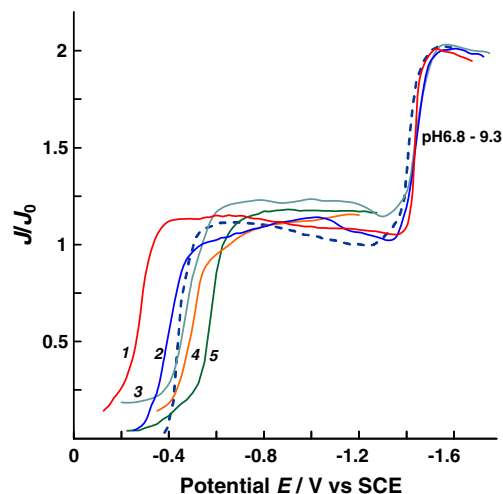
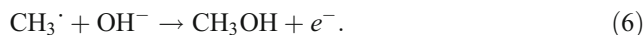


Fig. 2 Time-resolved voltammograms of solutions containing DMSO and 0.008 M N_2O at different pH values and $T_m=30$ ms. Buffer solutions with addition of 0.1 M Na_2SO_4 or 0.5 M KCl. DMSO concentration: 0.07 M (pH 9.1), 0.1 M (pH 7.4), 0.5 M (pH 9.3), 1 M (pH 9.5 and 13.2). N_2O concentration: 0.008 M (curves 1, 2, 5), 0.016 M (curves 3, 4), pH: 1—7.4, 2—9.1, 3—9.3, 4—9.5, 5—13.2. Dashed line – data of [32] (saturated solution of CH_3Cl , phosphate buffer +0.5 M KCl, pH 6.86)

There was a sufficiently broad area between the waves where photocurrents relation J/J_0 was close to 1. Sometimes some distortions (minimizations) on TRV's were observed at the foot of the reduction wave if DMSO concentration was no less than 0.1–0.5 M and $pH \leq 9-10$ (Figs. 1 and 2). Such distortions were observed also in [32] and supposed to be associated with adsorption phenomena at $CH_3\cdot$ reduction.

Note that although the potential of the reduction wave does not depend on pH like in [19, 30–32], it is valid for oxidation in neutral and low acidic solutions only. The oxidation wave is shifted to more negative values in basic solutions as it is evident from the comparison of TRV's in Fig. 2 recorded at the same T_m (30 ms). According to [30], this may imply to occur in the next process in basic solutions instead of Reaction (4):

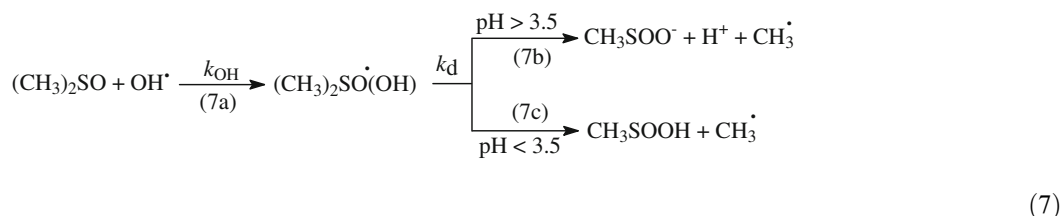


The reduction wave height increases both with pH changing from low basic to low acidic values and with T_m . This effect took place only for a rather long modulation time $T_m \geq 100-300$ ms and at a DMSO concentration of more than 0.05–0.1 M. The half-wave potential of this wave is getting more positive at these conditions than that predicted from the Tafel plot for the reduction of $\cdot CH_3$. The height of the wave considerably exceeded the one-electron level, too (curves 1, 1'–3, 3' of

Fig. 3). It is especially evident from the comparison of curves 1, 1'–3, 3' and curve 4 from Fig. 3 since the last one corresponds to a one-electron reduction level like all the reduction waves in Figs. 1 and 2. The reduction wave is split into two within the narrow pH range ~6.8–9.1 and $T_m=30\text{--}900\text{ ms}$ (curves 1 and 2, inset in Fig. 3). The transfer coefficient α can increase here until ~0.65–0.90 (cf. curves 3 and 4, inset in Fig. 3) which is similar to values presented in [31] for the reduction of $\cdot\text{CH}_3$ in 1 M KCl ($\alpha\sim 1$). Probably, all are caused by the rather slow formation of organomercury intermediates resulting from the interaction of the system components with a mercury electrode. Such phenomena were often observed as

processes accompanying adsorption or electrode reactions of organic chalcogenides on mercury [34–36], especially in acidic media and in the presence of halide ions [36]. Organometallic derivatives are able to create a near-electrode condensed phase due to their low solubility in aqueous media [34, 35, 37]. Similar effects were observed previously by photoemission at electroreduction of acetone (in acidic medium) or isopropyl bromide on a lead electrode (see [36, 38]). We did not study these processes in detail.

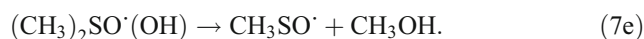
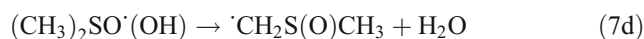
The interaction of OH radicals with DMSO molecules can lead not only to the formation of methyl radicals. According to [18], its mechanism could be described by the following general scheme:



where k_{OH} is within $5.8\text{--}7\times 10^9\text{ M}^{-1}\text{s}^{-1}$ [13] and for β -fragmentation reaction (Eq. 7b) or (Eq. 7c) $k_d=1.5\times 10^7\text{ s}^{-1}$ [18].

According to ab initio calculations [39], the fast subsequent decay of $(\text{CH}_3)_2\text{SO}\cdot(\text{OH})$ adduct into $\text{CH}_3\text{S}(\text{O})\text{OH} + \text{CH}_3\cdot$ in the gas phase has an energy barrier on -29.8 kJ/mol

lower than DMSO + OH interaction although the exothermic formation of one or two products is possible:



Methylsulfinic methyl radical (dimethyl) $\cdot\text{CH}_2\text{S}(\text{O})\text{CH}_3$ has been identified in solution as one of secondary product (Eqs. 7a–7e) reactions [17] with low yield [17, 40] (ca. 5% [40]). It was demonstrated that the route (Eq. 7d) is less favourable in the gas phase compared to the routes (Eqs. 7b and 7c) [39]. Such radicals are usually formed in specific conditions, for example, upon addition of small amounts of sodium methylate [41].

As to the Eq. 7e route, it is the least likely at atmospheric temperatures [39] and no CH_3OH was experimentally detected in deaerated solutions [20]. It can be formed in photochemical conditions only in a system DMSO–hydrogen peroxide as a result of secondary reactions (direct interaction of $\text{CH}_3\cdot$ radical with H_2O_2 [17]). No other waves except $\cdot\text{CH}_3$ reduction or oxidation were observed on TRV's. It means that the content of intermediates other than $\cdot\text{CH}_3$ is between 0% and 5%.

Together with Reactions 7b and 7c, the acid-catalysed ionization of $(\text{CH}_3)_2\text{S}\cdot(\text{OH})$ is also possible at $\text{pH} \ll 6$ [42]:

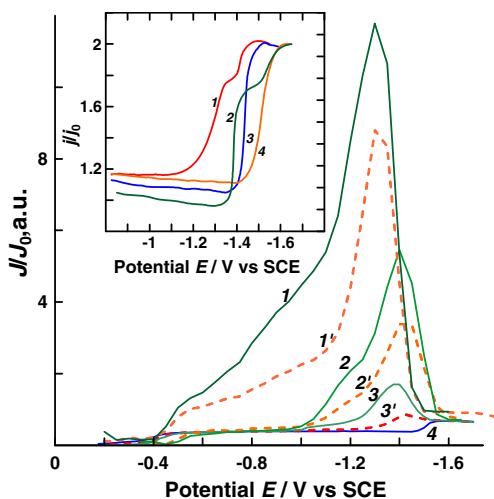
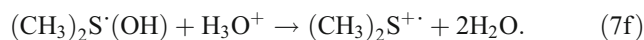


Fig. 3 Time-resolved voltammograms of solutions containing 1 M DMSO and 0.008 or 0.016 M N_2O recorded at various pH and $T_m=900$ (2) or 1000 ms (1, 3) (solid lines) and 300 ms (dashed lines). 1, 1'—0.5 M KCl, 0.016 M N_2O ; 2, 2'—pH 9.5, 0.016 M N_2O ; 3, 3'—pH 10, 0.008 M N_2O ; 4—one-electron level of reduction. $T_m=30\text{ ms}$, pH 10, 0.008 M N_2O . Inset, reduction waves in neutral solutions containing DMSO and 0.008 M N_2O . DMSO concentration: 0.1 M, pH 7.39 (curves 1, 3, 4), 0.033 M, pH 6.67 (curve 2). $T_m=300\text{ ms}$ (curve 1), 30 ms (curves 2, 3), and 3.5 ms (curve 4)

The radical $(\text{CH}_3)_2\text{S}(\text{OH})$ can be tentatively formed as a product of H atom addition generated via the competitive capture of e_{aq}^- by H_3O^+ in sufficiently acidic DMSO solutions (see above). These processes can definitely decrease the concentration of $\text{CH}_3\cdot$ formed in Reactions 7b and 7c and, consequently, diminish the wave height. Such phenomenon certainly cannot be observed if the radicals were generated via Eq. 3 [32].

The Tafel plots for the reduction of $\cdot\text{CH}_3$ are given in Fig. 4. The dotted line is the corresponding dependence for $\cdot\text{CH}_3$ reduction taken from [32]. From the comparison of Figs. 2 and 4, one can conclude that the reduction rate of $\cdot\text{CH}_3$ radical practically does not depend on pH within the range from 3.4 to 13.2. A small shift to a more negative potential of ca. 0.05–0.07 V is only observed in basic solutions at pH \sim 10–13. The absence of such dependence, especially in acidic solutions, confirms a direct electron transfer from electrode to methyl radical. There is no appreciable dependence of the reduction rate neither on the nature and concentration of a background electrolyte (0.1–1 M KCl, Na_2SO_4) nor on the composition of a buffer. The Tafel plots for the reduction of “both” types of $\cdot\text{CH}_3$ radicals, i.e. generated either from CH_3Cl [32] or from DMSO (this study), as well as their transfer coefficients α (0.49 and 0.51 (\pm 0.05), respectively) are sufficiently close.

The values of $E_{1/2}$ for the one-electron reduction of methyl radical reported by other authors were as follows: -1.43 V (1 M KCl, photoemission) [31], -1.42 V (pH 3–11.5, buffer solutions of 0.3 M Na_2SO_4 with addition of HClO_4 , H_2SO_4

or NaOH, polarography of products of pulse radiolysis) [30] and -1.33 V (buffer solutions of 0.06 M KH_2PO_4 –0.01 M $\text{Na}_2\text{B}_4\text{O}_7$, pH 5.8–9.0, differential polarography; the potential scan rate was 0.25 V/s) [19]. One can see that all these values fall into the potential range of the Tafel plot in Fig. 4 derived in this study, ca. -1.25 to -1.70 V. However, there are problems to compare these potentials obtained by various methods [7]. The main reason is that, in the mentioned investigations [19, 30, 31], no attempts were made to determine the rate constants of $\cdot\text{CH}_3$ reduction at the respective potentials.

Some authors [19] claim, however, that the process of $\cdot\text{CH}_3$ reduction is reversible, which is in disagreement with the present study as well as with [32]. According to [6, 9], the irreversibility of alkyl radicals reduction including $\cdot\text{CH}_3$ is caused first of all by the very low stability of respective carbanions in protic media, even in spite of a sufficiently high barrier of protonation of alkyl carbanions (ca. 150–200 kJ mol^{-1}) [6]. The standard potential E^0 of $\cdot\text{CH}_3/\text{CH}_3^-$ redox couple was estimated to be -1.01 ± 0.16 V [6] (calculated from the Tafel plot for $\cdot\text{CH}_3$ reduction [32] and the thermodynamic cycle: $\text{CH}_4(\text{g}) \rightarrow \text{CH}_4(\text{aq}) \rightarrow \text{CH}_3^-(\text{aq}) \rightarrow \cdot\text{CH}_3(\text{aq}) \rightarrow \cdot\text{CH}_3(\text{g})$) [6, 7], and -1.19 ± 0.15 V [43] (obtained by a method of indirect reduction, namely, competition between coupling and reduction of radicals by radical anions [44]). Thus, the difference between E^0 and $E_{1/2}$ for $\cdot\text{CH}_3$ reduction can reach 0.3–0.7 V. This difference should be attributed to an overvoltage caused by the slow $\cdot\text{CH}_3$ reduction (Eq. 5).

The W_{ox} , E dependencies for oxidation of the radical within pH range from low acidic to strongly basic are also presented on the Fig. 4. In distinction from the reduction, the oxidation rate of $\cdot\text{CH}_3$ depends on pH in basic solutions but such dependence practically does not take place in neutral and low acidic media. The respective shift of $E_{1/2}$ from neutral to strongly basic solutions (i.e. from pH 7.1–7.5 to 13.2) consists of ca. 0.25–0.3 V that is in qualitative agreement with the data of [30] where $E_{1/2}$ values changed from ca. -0.18 to -0.22 V (pH 4–6) to ca. -0.42 V (pH 11.5). The transfer coefficient β for oxidation occurred to be too high and apparently did not correspond to a simple electron transfer. Together with available dependence of $\cdot\text{CH}_3$ oxidation rate on pH, it could represent an influence of a certain chemical stage on the electrode process (for example, an antecedent formation of a metastable complex of an intermediate with a proton acceptor [45]).

The Tafel plots for reduction are straight lines within a sufficiently broad range of measured W_{R} . It means that the electrode process corresponds to a simple one-electron transfer that is not complicated with chemical steps. No deviations are present on the respective plot for $\cdot\text{CH}_3$ reduction generated from DMSO until $W_{\text{R}} = W_{\text{max}} \sim 5 \times 10^5 \text{ s}^{-1}$. Hence, the lifetime of $(\text{CH}_3)_2\text{SO}(\text{OH})$ adduct is $<1/W_{\text{max}}$, i.e. it is $<2 \times 10^{-5}$ s.

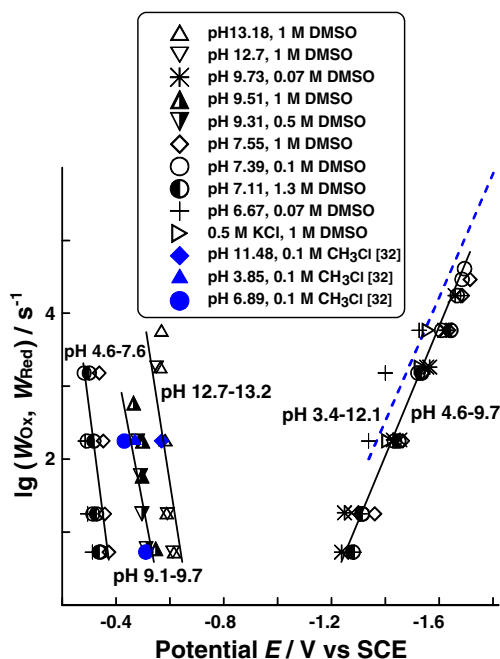


Fig. 4 Tafel plots for $\cdot\text{CH}_3$ oxidation rate constants W_{ox} (left side) and reduction rate constants W_{red} (right side). The dashed line and filled symbols are data of [32]

Conclusions

Electrode reactions of intermediates formed during the capture of OH radicals by dimethylsulfoxide molecules according to the known reaction scheme (Eq. 7) were studied by laser photoemission. The results of the present study were compared with those from [32] where $\cdot\text{CH}_3$ radicals were generated via photoemission from CH_3Cl . It was concluded that the same radical was formed in the reaction of OH radicals with DMSO molecules. According to the scheme (Eq. 7), it should be considered as one of the secondary decay products of short-lived intermediate $(\text{CH}_3)_2\text{SO}\cdot(\text{OH})$ which lifetime was found to be $<2 \times 10^{-5}$ s. The similarity was revealed for electrochemical characteristics of one-electron irreversible reduction and oxidation of $\cdot\text{CH}_3$ radicals generated by the above mentioned different ways (potentials $E_{1/2}$ of time-resolved voltammograms and rate constants of their electrode reactions).

Several possible routes of formation of various intermediates in the reaction of OH radicals with DMSO were considered but no signals other than $\cdot\text{CH}_3$ reduction or oxidation were detected. However, the increase of the reduction wave height both with pH changing from basic to acidic values and with T_m was observed. This effect took place only at rather long illumination time $T_m \geq 100\text{--}300$ ms and at a DMSO concentration higher than 0.05–0.1 M. The reduction wave height considerably exceeded the one-electron level under these conditions. Its half-wave potential was shifted more positively than that predicted from the Tafel plot for the reduction of $\cdot\text{CH}_3$. All these phenomena are most probably caused by the rather slow formation of organomercury intermediates resulting from the interaction of the components of the system with a mercury electrode.

The reduction rate of $\cdot\text{CH}_3$ did not depend on pH and corresponded to a simple one-electron transfer. On the other hand, the rate of $\cdot\text{CH}_3$ oxidation has been found to depend on pH in basic media, which indicated a possible participation of OH^- in the process. The presented data are in a good agreement with those available in literature, where $\cdot\text{CH}_3$ was generated by alternative ways. The findings described represent an electrochemical evidence of the formation of methyl radicals as a result of the capture of OH radicals by DMSO molecules.

Hence, DMSO should not be used as a solvent in electrochemical investigations of systems where active oxidants like OH radicals or other highly reactive agents of similar properties are present, unless generation of methyl radicals is needed.

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