

Kinetic Isotope Effect for Hydrogen Abstraction by $\bullet\text{OH}$ Radicals from Normal and Carbon-Deuterated Ethyl Alcohol and Methylamine in Aqueous Solutions[†]

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Selective H/D kinetic isotope effects (KIEs) have been determined for the various routes by which $\bullet\text{OH}$ radicals react with ethanol ($\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CD}_3\text{CD}_2\text{OH}$) and methylamine (CH_3NH_2 and CD_3NH_2) in H_2O solutions. The KIEs have been evaluated from overall rate constants and the yields in which the individual primary radicals were generated in the $\bullet\text{OH}$ reaction with these compounds. The analytical method applied for the yield determinations was redox titration with suitable scavengers, namely, methyl viologen and $\text{Fe}(\text{CN})_6^{3-}$ for the reducing radicals ($\text{CH}_3\text{C}\bullet\text{HOH}/\text{CD}_3\text{C}\bullet\text{DOH}$ and $\text{C}\bullet\text{H}_2\text{NH}_2/\text{C}\bullet\text{D}_2\text{NH}_2$) and I^- and hydroquinone for the oxidizing radicals ($\text{CH}_3\text{CH}_2\text{O}\bullet/\text{CD}_3\text{CD}_2\text{O}\bullet$ and $\text{N}\bullet\text{HCH}_3/\text{N}\bullet\text{HCD}_3$). The numerical results obtained also include, besides yields relative to total available $\bullet\text{OH}$, absolute rate constants for most of these scavenging reactions. For the alcohol, the major process (almost 90%) is H/D abstraction from the C_α bond with $\text{KIE} = 1.96$. For methylamine, abstraction from C_α H/D occurs with only 37% (H) and 26% (D) but at a similar $\text{KIE} = 1.86$. The remainder, denoting the major process in this case, accounts for the formation of aminyl radicals. The secondary KIEs for N–H cleavage, and O–H cleavage in the case of the alcohol, are close to unity, reflecting the expected negligible influence of C–H/D substitution in the attached alkyl groups. Abstraction of β -C-attached H/D in ethanol shows, also in qualitative agreement with expectation, a larger $\text{KIE} = 3.4$ than that for α -C H/D. An interestingly high $\text{KIE} \approx 50$ was obtained for the 1,2 hydrogen shift that converts the $\text{CH}_3\text{CH}_2\text{O}\bullet$ and $\text{CD}_3\text{CD}_2\text{O}\bullet$ oxyl radicals into the corresponding α -hydroxyethyl radicals $\text{CH}_3\text{C}\bullet\text{HOH}$ and $\text{CD}_3\text{C}\bullet\text{DOH}$. All of the results are discussed in light of existing literature data on relevant H/D isotope effects, the influence of solvent relative to gas phase, the selectivity of the $\bullet\text{OH}$ attack, and other mechanistic considerations. Specifically, the mechanism by which the $\bullet\text{OH}$ reacts with the amine seems likely to involve a transient, caged aminium/hydroxide ion pair.

Introduction

Hydroxyl radicals ($\bullet\text{OH}$) are formed as short-lived intermediates in several different processes. These include radiolysis and photolysis and Fenton and Fenton-like reactions as well as reactions of NO_x species. The hydroxyl radicals are thus produced in atmospheric and in metabolic processes in living organisms. $\bullet\text{OH}$ is one of the most aggressive oxidative species known and is implicated in oxidative damage in living cells. Its reactions with organic substrates typically occur by addition, H-atom abstraction, or electron transfer (ET). The large HO–H bond-dissociation enthalpy of water ensures that H abstraction is generally exothermic. Thus, activation energies for H-abstraction reactions are low, and the rates are relatively rapid. In terms of ET, the small size of $\bullet\text{OH}$ means that its reorganization energy is expected to be large, and this process is therefore likely to compete only with H abstraction in cases where the difference in reduction potentials is appreciable. However, the reduction potential is also quite high ($E^\circ(\bullet\text{OH}/\text{OH}^-) = 1.9 \text{ V}^1$),

and there is now substantial evidence that ET competes with H abstraction in substrates with parent ion reduction potentials $\leq 1.5 \text{ V}$. Nitrogen-containing compounds (NR), which have $E^\circ(^+\text{NR}/\text{NR})$ values below this, are typical cases where this may occur, trimethylamine being a case in point.²

One of the problems relating to the elucidation of mechanisms of reactions of $\bullet\text{OH}$ is that the H abstraction and ET processes are often difficult to differentiate. This arises from the fact that electron transfer can be followed by the rapid loss of a proton from the one-electron-oxidized substrate, thus giving the same product as H-atom abstraction.² Such a mechanistic problem prevailed, for example, in the oxidation of simple amino acids in their anionic form where several different radical products have been observed as result of the $\bullet\text{OH}$ reaction (e.g., a total of six in the case of alanine).^{3–5}

To distinguish between the various routes and mechanisms by which these radicals were formed in the amino acid system, time-resolved esr and redox titrations have successfully been applied.^{5–7} These pulse radiolysis studies, supported by some laser flash photolysis, revealed the concurrent action of the $\bullet\text{OH}$ radical as a hydrogen-abstracting agent as well as an electrophile interacting with the lone electron pair at the amino acid's nitrogen. Although much of the overall mechanism could be disclosed, some of the mechanistic details remained obscured

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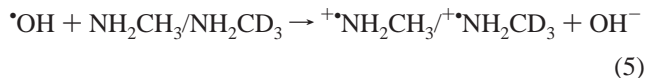
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and called for additional support through, for example, H/D isotope effect studies. However, it became quite clear during the early stages of such investigations that the complexity of the amino acid system would still leave certain ambiguities. For quantitative assignments and interpretations, it seemed mandatory to first obtain reliable and unambiguous data from even simpler systems.

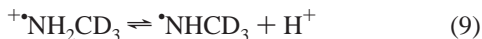
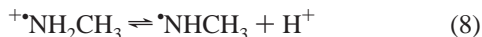
In view of all of this, we therefore decided to conduct a series of experiments on H/D isotope effects concerning the reaction of •OH with simple alcohols and amines. The reactions in focus are eqs 1 and 2 for ethyl alcohol and 3 and 4 for methylamine:



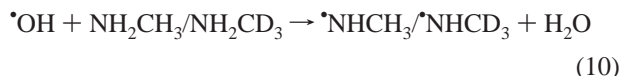
For ethyl alcohol, such reactions can proceed only via the hydrogen atom abstraction mechanism, and the alternative electron/proton-transfer mechanism can be excluded. In contrast, for methylamine, both mechanisms are possible: (i) a direct hydrogen abstraction as indicated by reactions 3 and 4 and (ii) an electron transfer from nitrogen leading to the N-centered aminium radical cation, reaction 5, followed by a rapid loss of H^+/D^+ from the neighboring carbon atom, reaction 6 or 7.



The latter mechanism gains in likelihood in view of the relatively low reduction potential of the general couple (${}^+\text{NH}_2\text{—R}/\text{NH}_2\text{—R}$), $E^\circ \approx 1.3 \text{ V}$.⁸ It also should be recognized in this context that the aminium cation is formed together with a strong base, OH^- . Effective deprotonation should thus already be facilitated within the initial solvent cage. Deprotonation of an aminium radical cation with the loss of a proton from $\text{C}_\alpha\text{—H}$ has been shown to occur in the case of ${}^+\text{N}(\text{CH}_3)_3$ ² (and it also occurs in the oxidative C—H activation of certain hydrocarbons⁹). However, the proton loss is expected to occur more readily from the acidic N—H position and to result in the respective aminyl radicals, reactions 8 and 9.



The same aminyl radicals may, however, also be produced by direct H-atom abstraction, reaction 10.



Both the C-centered $\bullet\text{CH}_2\text{NH}_2$ and N-centered $\bullet\text{NHCH}_3$ radicals have, in fact, been proposed as products of the reaction of hydroxyl radicals with CH_3NH_2 in basic aqueous solution¹⁰ without, however, a quantitative determination of their yields.

Concerning either mechanistic possibility, H/D isotope effects should provide further insight. Although we are not aware of any study on the effect of the deuteration of aliphatic amines, overall or total rate constants for abstractions from all possible sites are available for the reactions of hydroxyl radicals with $\text{CH}_3\text{CH}_2\text{OH}$ ¹¹ and $\text{CD}_3\text{CD}_2\text{OH}$.¹² However, just taking the ratio of these two rate constants would not be sufficient for the present purposes because they include reactions 11 and 12, which take place simultaneously with reaction 1.¹³ A very similar situation can be expected for the deuterated molecule, reactions 13 and 14, but again, no determination of individual products has been reported.



In addition to an experimental determination of absolute rate constants and yields, we will briefly discuss some attempts to put our results, particularly those referring to isotope effects, into a theory-based perspective.

Finally, the results presented here for simple primary alcohol and amine molecules could also be of relevance for the elucidation of processes in biological or other organic systems. For example, the H/D isotope effect has recently been applied in an attempt to identify hydroxyl radical-like species within the metal-binding site of a protein.¹⁴

Experimental Section

All investigations have been conducted with aqueous solutions with water purified by the Serv-A-Pure Co. system. Absolute ethyl alcohol (200 proof, Aaper Alcohol and Chemical Company), $\text{CD}_3\text{CD}_2\text{OD}$ (Aldrich, anhydrous, 99+ atom % D), methylamine (Aldrich, 40 wt % solution in water), methylamine-*d*₅ deuteriochloride (Aldrich, 98+ atom % D), and other chemicals (Aldrich, Fluka) were used as received from the vendors.

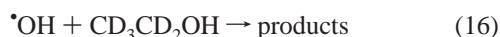
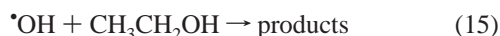
Pulse radiolysis was performed with an 8-MeV Titan Beta model TBS-8/16-1S LINAC at the Notre Dame Radiation Laboratory with pulses of 2.5-ns duration and doses per pulse in the range of 2–10 Gy. A description of the pulse radiolysis setup, data collection, and processing can be found elsewhere.¹⁵ All solutions were freshly prepared before each experiment. Solutions containing deuterated compounds were always used within a period of 4 h after preparation of the solution. This ensured that there was no exchange of carbon-bound D atoms with H atoms from water. Oxygen- and nitrogen-bound deuterium, however, suffered fast H/D exchange (i.e., $\text{CD}_3\text{CD}_2\text{OD}$ and $\text{CD}_3\text{ND}_2\cdot\text{DCl}$ were present as $\text{CD}_3\text{CD}_2\text{OH}$ and a mixture of $\text{CD}_3\text{NH}_2/\text{CD}_3\text{NH}_3^+$ at the pH ranges applied in this study). Solutions were generally deaerated (N_2) and saturated with N_2O . Under these conditions, approximately 90% of all primary species available for reaction with solutes were •OH radicals. The remaining ~10% are H^\bullet atoms, and for their yield, a value of $G(\text{H}^\bullet) = 0.06 \mu\text{mol J}^{-1}$ was used throughout the study, independent of the solute concentrations.¹⁶ The yield of scavengable hydroxyl radicals, $G(\bullet\text{OH})$, was calculated by taking into account the total scavenging capacity in each solution (concentration multiplied by rate constant for all substrates reacting with hydroxyl radicals) according to a generally applicable formula.¹⁷ The total concentration of •OH radicals

per pulse applied in our present investigation of N₂O-saturated systems amounts to about 1–6 μM. Dosimetry was performed with thiocyanate solutions as described earlier.¹⁸ All experiments have been conducted at room temperature.

The accuracy of radiation chemical experiments is generally considered to be about ±10%. This also applies to our present set of data. Error limits given for the specific numerical values refer only to the standard deviation of the mean of a series of single measurements taken (usually three for each individual system/concentration).

Results and Discussion

Overall Reaction Rate Constants. Because none of the radicals involved in the reactions studied (i.e., hydroxyl or radicals derived from ethyl alcohol or methylamine) shows any significant optical absorption in the range suitable for accurate direct measurements of their kinetics, the rate constants were determined using the competition kinetics method. The reference reactant was the ferrocyanide ion, Fe(CN)₆⁴⁻, which is oxidized by •OH radicals with a rate constant of $k_{17} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.¹¹



Ethyl Alcohol. The yields of Fe(CN)₆³⁻ generated via reaction 17 in neutral, N₂O-saturated aqueous solution containing 1 mM Fe(CN)₆⁴⁻ were determined by measuring its optical absorption at 420 nm in the absence (OD₀) and in the presence (OD) of various amounts of normal or deuterated ethyl alcohol (1–13 mM). Absorption intensities were measured only during the few first microseconds after the pulse to allow all of the primary reactions (i.e., 15 or 16 and 17) to be completed while still avoiding possible second-order back reduction of Fe(CN)₆³⁻ via the simultaneously formed α-hydroxyalkyl radicals. The possible error caused by the latter reaction was also kept to a minimum because of the relatively low dose per pulse (ca. 3 Gy).

The overall rate constants $k_{15} = (2.40 \pm 0.06) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{16} = (1.24 \pm 0.03) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the •OH reactions with CH₃CH₂OH and CD₃CD₂OH, respectively, have been calculated from the slopes of the straight lines obtained by plotting $([\text{OD}_0]/[\text{OD}])_{\text{corr}}$ versus $[\text{alcohol}]/[\text{Fe(CN)}_6^{4-}]$ according to expression I.

$$\left(\frac{[\text{OD}_0]}{[\text{OD}]}\right)_{\text{corr}} = 1 + \frac{k_{15,16}}{k_{17}} \left(\frac{[\text{alcohol}]}{[\text{Fe(CN)}_6^{4-}]}\right) \quad (\text{I})$$

where $([\text{OD}_0]/[\text{OD}])_{\text{corr}} = ([\text{OD}_0]/[\text{OD}])_{\text{measured}} \times (G(\bullet\text{OH})_{\text{alcohol}}/G(\bullet\text{OH})_0)$. $G(\bullet\text{OH})_0$ is the calculated yield of scavengable hydroxyl radicals for the solution containing only 1 mM Fe(CN)₆⁴⁻, and $G(\bullet\text{OH})_{\text{alcohol}}$ refers to solutions containing, in addition, various concentrations of ethyl alcohol.

The corresponding plots are shown in Figure 1, and the rate constants are listed in the second column of Table 2. The correction of the measured $[\text{OD}_0]/[\text{OD}]$ ratios was necessary because the yield of hydroxyl radicals available for reactions is not constant but increases with the total scavenger capacity of substrates (alcohol plus Fe(CN)₆⁴⁻) in the solution.^{16,17} For the first calculation of the respective $G(\bullet\text{OH})$ available for reaction in each solution, the originally reported rate constants¹¹ of k_{15}

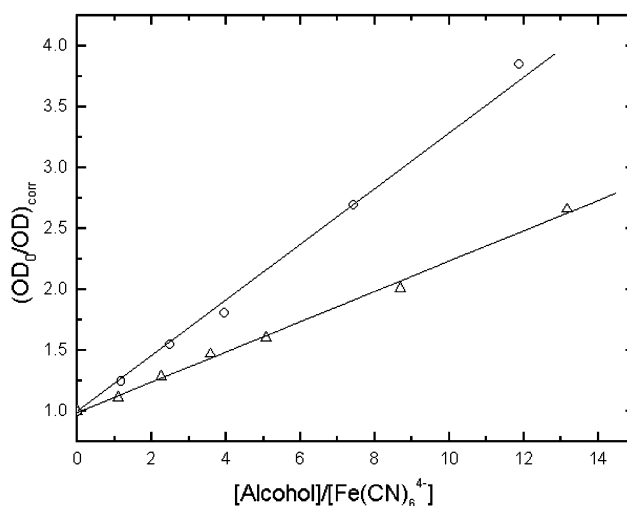


Figure 1. Ratio of optical densities at 420 nm in the absence (OD₀) and presence of ethyl alcohols (OD) versus the reacting substrates concentration ratio obtained in pulse-irradiated, N₂O-saturated aqueous solutions containing 1 mM Fe(CN)₆⁴⁻ and various amounts of CH₃CH₂OH (○) or CD₃CD₂OH (△). Dose per pulse: 3 Gy. Experimentally obtained values are corrected for the amount of scavengable hydroxyl radicals for each solution. (For details, see text.)

TABLE 1: Relative Yield of Radicals Formed in Reactions with •OH

compound	radical (α-C)	<i>G</i> _{rel}	radical (β-C)	<i>G</i> _{rel}	radical (O/N)	<i>G</i> _{rel}
CH ₃ CH ₂ OH	CH ₃ •CHOH	0.89	•CH ₂ CH ₂ OH	0.07	CH ₃ CH ₂ •	0.04
CD ₃ CD ₂ OH	CD ₃ •CDOH	0.88	•CD ₂ CD ₂ OH	0.04	CD ₃ CD ₂ •	0.08
CH ₃ NH ₂	•CH ₂ NH ₂	0.37			•NHCH ₃	0.63
CD ₃ NH ₂	•CD ₂ NH ₂	0.26			•NHCD ₃	0.74

TABLE 2: Total and Partial Rate Constants for the Attack of •OH on Specific Atoms and Kinetic Isotope Effects for H/D Abstraction^a

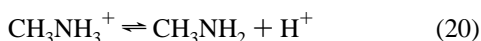
	<i>k</i> _{total}	<i>k</i> _{α-C}	<i>k</i> _{β-C}	<i>k</i> _{O/N}
CH ₃ CH ₂ OH	2.40	2.14	0.17	0.10
CD ₃ CD ₂ OH	1.24	1.09	0.05	0.10
	<i>k</i> _H / <i>k</i> _D = 1.93	<i>k</i> _H / <i>k</i> _D = 1.96	<i>k</i> _H / <i>k</i> _D = 3.4	<i>k</i> _H / <i>k</i> _D = 1.0
CH ₃ NH ₂	3.60	1.33		2.27
CD ₃ NH ₂	2.75	0.715		2.04
	<i>k</i> _H / <i>k</i> _D = 1.31	<i>k</i> _H / <i>k</i> _D = 1.86		<i>k</i> _H / <i>k</i> _D = 1.11

^a Units: 10⁹ M⁻¹ s⁻¹.

= $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{16} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ have been used. Applying the somewhat higher rate constant k_{15} obtained in the present study did not lead to any significant change. It is further noted that for the range of scavenger concentrations applied in this study the corrections remained small (i.e., the rate constants obtained with the corrected values were only 5–7% higher than those from uncorrected data).

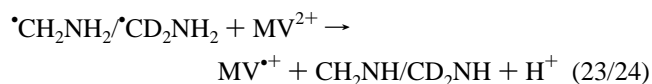
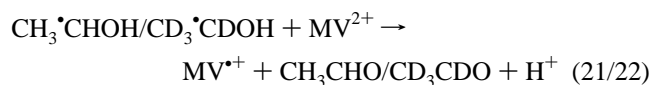
For CD₃CD₂OH, the overall rate constant obtained in this work is identical to that published earlier.¹² The agreement is not as good for the fully hydrogenated CH₃CH₂OH. In fact, the rate constant for reaction 15 has been measured repeatedly by different research groups with reported values between $(1.6\text{--}2.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the recommended value being $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ An inspection of conditions and procedures in the original publications revealed that probably no corrections had been made for the change of $G(\bullet\text{OH})$ at different scavengers concentrations. Such corrections would, however, result in up to 10% higher rate constants, which would bring the earlier reported values of k_{15} very close to the value determined in this study.

Methylamine. Basically, the same procedure as described above was applied for the evaluation of the corresponding overall rate constants k_{18} and k_{19} for the reaction of $\bullet\text{OH}$ with normal and deuterated methylamines. Experiments were, however, performed at pH 10.8–11.0. This pH range was selected to push equilibrium 20 as much as possible to the right-hand side while still not allowing appreciable dissociation of the $\bullet\text{OH}$ radicals ($\text{p}K_{\text{a}}(\bullet\text{OH}) = 11.9$). Also, only the actual concentrations of unprotonated amine, as calculated from the amine's $\text{p}K_{\text{a}}$ and the pH of the solution, were used for the determination of the rate constants. (For both the normal and C-deuterated methylamine, a $\text{p}K_{\text{a}}$ of 10.65 was employed.) The reaction of hydroxyl radicals with protonated amine, CH_3NH_3^+ , can be neglected at these high pH values. Because of its low rate constant ($k = 3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$),¹⁹ this reaction contributes less than 1% to the overall rate. The same was assumed to apply to the deuterated amine cation, CD_3NH_3^+ , for which a rate constant with $\bullet\text{OH}$ radicals has neither been reported in the literature nor determined in this work.



Actual measurements were conducted in N_2O -saturated solutions containing 0.5 mM $\text{Fe}(\text{CN})_6^{4-}$ and various concentration of CH_3NH_2 (0.2–1.3 mM) or CD_3NH_2 (0.4–3.5 mM). The respective rate constants were determined from plots similar to the ones shown in Figure 1 and were calculated to be $k_{18} = (3.6 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{19} = (2.75 \pm 0.06) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. They are also listed in the second column of Table 2. Only the value for k_{18} can be compared with previously reported data that range from $(1.8\text{--}5.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{10,20}

Yields and Individual Rate Constants. The yields of the individual radicals produced in the overall oxidations of the alcohols and amines (reactions 1–14) were determined by the same selective redox titration that was applied in related previous studies of ours on the $\bullet\text{OH}$ -induced oxidation of aliphatic amino acids.^{3,5} Thus, the strong reducing character of all C-centered α -hydroxy and α -amino radicals allowed their convenient titration with methyl viologen (MV^{2+} , $E_0 = -0.45 \text{ V}$ for the $\text{MV}^{2+}/\text{MV}^{\bullet+}$ couple),¹ as stoichiometrically outlined in the general reactions 20–24. Yields were quantitatively determined by measurements of the optical absorption of $\text{MV}^{\bullet+}$ at 600 nm and using $\epsilon_{600} = 12\,820 \text{ M}^{-1} \text{ cm}^{-1}$.³ Rate constants were evaluated from the formation kinetics of $\text{MV}^{\bullet+}$ at varying MV^{2+} concentrations. Whenever possible, the latter were kept at $\leq 0.5 \text{ mM}$ to avoid the direct reduction of MV^{2+} by hydrated electrons. (For respective rate constants, see ref 11.)



The less-reducing β -hydroxyalkyl radicals generated in reactions 11 and 13 (i.e., $\bullet\text{CH}_2\text{CH}_2\text{OH}$ and $\bullet\text{CD}_2\text{CD}_2\text{OH}$) cannot be quantified via a corresponding reaction with MV^{2+} . Their oxidation affords a more potent redox partner such as $\text{Fe}(\text{CN})_6^{3-}$. However, these reactions are very slow, hampering an unambiguous quantitative determination. We therefore did not embark

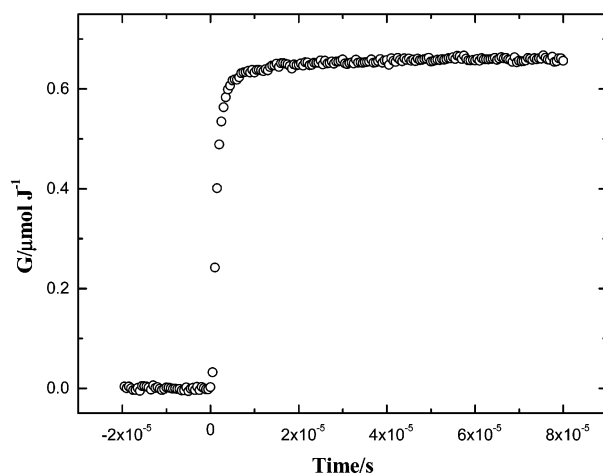
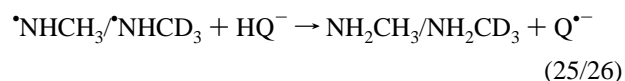


Figure 2. Formation of $\text{MV}^{\bullet+}$ as a function of time measured at 600 nm in a pulse-irradiated N_2O -saturated aqueous solution containing 0.1 M $\text{CD}_3\text{CD}_2\text{OH}$ and 0.5 mM MV^{2+} . Optical absorption intensity is expressed as the yield of $\text{MV}^{\bullet+}$ ($G/\mu\text{mol J}^{-1}$). Dose per pulse: 1.4 Gy.

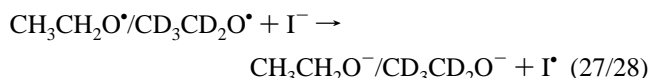
on such titrations but identified their yields simply as the difference between the total $\bullet\text{OH}/\text{H}^{\bullet}$ yield and the sum of the radicals that were quantitatively accessible via redox titration.

For yields and rate constants of the oxidizing radicals, two different reactions were applied. The titration of the aminyl radicals was performed using hydroquinone ($E_0 = 0.023 \text{ V}$ for the $\text{Q}^{\bullet-}/\text{Q}^{2-}$ couple)²¹ (eq 25/26).^{3–5}



The analysis was based on the formation kinetics and yields of the semiquinone radical anion, $\text{Q}^{\bullet-}$ ($\lambda_{\text{max}} = 427 \text{ nm}$, $\epsilon = 7200 \text{ M}^{-1} \text{ cm}^{-1}$). Actual measurements were performed at pH 11, where the hydroquinone exists in all three possible protonation states, H_2Q , HQ^- , and Q^{2-} , in the ratio of 6:72:23, respectively. Rate constants determined this way, therefore, represent a weighted value for this composition.

The alkoxyl radicals were analyzed by applying iodide as a selective scavenger.¹³ In this case, the overall reaction sequence (eqs 27/28 and 29) leads to the formation of the optically detectable $\text{I}_2^{\bullet-}$ radical anion ($\lambda_{\text{max}} = 380 \text{ nm}$; $\epsilon_{380} = 9400 \text{ M}^{-1} \text{ cm}^{-1}$).²²

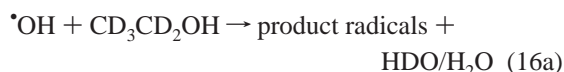


The actual results obtained concerning all of the radicals of interest are presented and discussed in the following sections under the headlines of their respective molecular precursors.

C-Deuterated Ethyl Alcohol. Figure 2 shows a typical trace obtained at 600 nm in pulse-irradiated N_2O -saturated solution containing, in this case, 0.11 M $\text{CD}_3\text{CD}_2\text{OH}$ and 0.5 mM MV^{2+} . The signal intensity due to the optical absorption of $\text{MV}^{\bullet+}$ has been normalized for the dose and the $\text{MV}^{\bullet+}$ molar extinction coefficient. This allows one to display the optical signal directly in terms of an absolute yield, $G(\text{MV}^{\bullet+})/\mu\text{mol J}^{-1}$, as a function of time. Two kinetically distinguishable processes can be realized: the majority of the $\text{MV}^{\bullet+}$ formation has been completed within a few microseconds, and an additional generation occurs on a longer time scale ($\sim 50 \mu\text{s}$). The combined total yield amounts to $G(\text{MV}^{\bullet+}) = (0.682 \pm 0.010)$

$\mu\text{mol J}^{-1}$. It did not change (within indicated error limit) when the MV^{2+} concentration was lowered to 0.1 or 0.3 mM. Under the experimental conditions, the only radicals available for reaction with $\text{CD}_3\text{CD}_2\text{OH}$ were $\bullet\text{OH}$ and H^\bullet (conversion of e_{aq}^- to $\bullet\text{OH}$ via reaction with N_2O occurs with $t_{1/2} \approx 3$ ns). The absolute yield of scavengable $\bullet\text{OH}$ radicals for this alcohol concentration was calculated to $0.647 \mu\text{mol J}^{-1}$.¹⁷ For H^\bullet atoms, $G = 0.06 \mu\text{mol J}^{-1}$ was taken.

Hydrogen atoms are less reactive than $\bullet\text{OH}$ radicals and thus most likely more selective. Accordingly, they should preferentially undergo a H/D abstraction reaction from the most labile α -C position in the alcohol, reaction 30, producing $\text{CD}_3\bullet\text{CDOH}$ as the major radical. An abstraction from the β position will presumably be negligible considering that the rate constant of this reaction is as low as $k_{30} = 2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.²³ (See ref 44.) The overall reaction of the $\bullet\text{OH}$ radical (eq 16a), however, occurs almost 3 orders of magnitude faster ($k_{16} = 1.24 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, see also Table 2).



The total yield of $\text{MV}^{\bullet+}$ (i.e., the yield of MV^{2+} reducing radicals) due to the reactions of $\bullet\text{OH}$ radicals alone with $\text{CD}_3\text{CD}_2\text{OH}$ accordingly amounts to

$$G(\text{MV}^{\bullet+})_{\text{OH}} = G(\text{MV}^{\bullet+})_{\text{total}} - G(\text{H}^\bullet) = 0.68 - 0.06 = 0.62 \mu\text{mol J}^{-1}$$

or in relative units

$$G(\text{MV}^{\bullet+})_{\text{OH, relative}} = \frac{G(\text{MV}^{\bullet+})_{\text{OH}}}{G(\bullet\text{OH})} = \frac{0.62}{0.647} = 0.96.$$

In other words, 96% of the hydroxyl radicals reacting with $\text{CD}_3\text{CD}_2\text{OH}$ end up as radicals capable of reducing MV^{2+} . The remainder of 4% (i.e., of radicals that are not able to reduce MV^{2+}) is ascribed to the formation of β -hydroxy-C-centered radicals $\bullet\text{CD}_2\text{CD}_2\text{OH}$ formed by reaction 13. (See ref 45.)

The reducing species are considered to be $\text{CD}_3\bullet\text{CDOH}$ radicals. Not all of them are, however, the immediate result of a D-atom abstraction by the $\bullet\text{OH}$ radicals at C_α (eq 2), as becomes apparent upon inspection and analysis of the formation kinetics of $\text{MV}^{\bullet+}$ displayed in Figure 2. Two processes are evident. The first is complete in $\sim 1\text{--}2 \mu\text{s}$ whereas the second slower process has a first-order growth rate of $(1.1 \pm 0.1) \times 10^5 \text{ s}^{-1}$. Only the fast process was dependent on $[\text{MV}^{2+}]$ in a way that is characteristic for a pseudo-first-order reaction. Thus, only this fast process can be assigned to the $\text{CD}_3\bullet\text{CDOH}$ radicals resulting from reaction 2 and their subsequent reaction with MV^{2+} (eq 20). The total yield of this contribution (i.e., the yield of directly generated $\text{CD}_3\bullet\text{CDOH}$ radicals) corresponds to $G = 0.573 \mu\text{mol J}^{-1}$ or, on a relative scale, to 88% of the $\bullet\text{OH}$ radicals. An analysis of the $\text{MV}^{\bullet+}$ formation kinetics in solutions of varying MV^{2+} concentration (0.1–0.5 mM) gave a bimolecular rate constant of $k_{22} = (2.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This and other rate constants for radical-induced titration reactions are listed in Table 3.

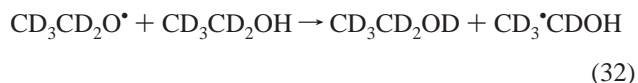
The minor but clearly distinguishable slower process in Figure 2 is associated with $\text{CD}_3\bullet\text{CDOH}$ radicals formed via a different, additional route. It is important to recognize its exponential but completely $[\text{MV}^{2+}]$ -independent kinetics. The assumed mech-

TABLE 3: Rate Constants for the Various Redox Titration and Rearrangement Reactions

reaction	rate constant
$\text{CH}_3\text{C}^\bullet\text{HOH} + \text{MV}^{2+} \rightarrow \text{MV}^{\bullet+} + \dots$	$(2.1 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\text{CD}_3\text{C}^\bullet\text{DOH} + \text{MV}^{2+} \rightarrow \text{MV}^{\bullet+} + \dots$	$(2.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\bullet\text{CH}_2\text{NH}_2 + \text{MV}^{2+} \rightarrow \text{MV}^{\bullet+} + \dots$	$(3.6 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\bullet\text{CD}_2\text{NH}_2 + \text{MV}^{2+} \rightarrow \text{MV}^{\bullet+} + \dots$	$3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{CH}_2\text{O}^\bullet + \text{I}^- \rightarrow \text{I}^\bullet + \dots$	$4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1a}$
$\text{CH}_3\text{N}^\bullet\text{H} + \text{HQ}^- \rightarrow \text{Q}^{\bullet-} + \dots$	$(1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
$\text{CH}_3\text{CH}_2\text{O}^\bullet \rightarrow \text{CH}_3\text{C}^\bullet\text{HOH}$	$(5 \pm 2) \times 10^6 \text{ s}^{-1}$
$\text{CD}_3\text{CD}_2\text{O}^\bullet \rightarrow \text{CD}_3\text{C}^\bullet\text{DOD}$	$(1.1 \pm 0.1) \times 10^5 \text{ s}^{-1}$
$\text{CD}_3\text{CD}_2\text{O}^\bullet + \text{CD}_3\text{CD}_2\text{OH} \rightarrow \text{CD}_3\text{CD}_2\text{OD} + \text{CD}_3\text{C}^\bullet\text{DOH}$	$2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1a}$

^a Estimate.

anism includes, as the first step, the formation of alkoxy radicals $\text{CD}_3\text{CD}_2\text{O}^\bullet$ (eq 14). These are oxidizing species and therefore not reactive toward MV^{2+} . But they are known to undergo an intramolecular 1,2 hydrogen shift readily (possibly solvent-assisted), thereby being transformed into the MV^{2+} -reducing $\text{CD}_3\bullet\text{CDOD}$ radicals (eq 31). The same result would be achieved by a second-order hydrogen-abstraction reaction from the parent molecule (eq 32).¹⁶ (In the H_2O solvent, both of the $-\text{OD}$ functional groups formed in eqs 31 and 32 will, of course, undergo fast D \rightarrow H exchange.)



The overall first-order rate constant of $(1.1 \pm 0.1) \times 10^5 \text{ s}^{-1}$ noted above for the slow process therefore corresponds to $(k_{31} + k_{32}[\text{CD}_3\text{CD}_2\text{OH}])$. We did not make an attempt to evaluate the individual values for k_{31} and k_{32} by an extra set of experiments at different $\text{CD}_3\text{CD}_2\text{OH}$ concentrations. In view of some published rate constants for similar reactions, namely, $2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{CH}_3\text{O}^\bullet + \text{CH}_3\text{OH} \rightarrow \bullet\text{CH}_2\text{OH} + \text{CH}_3\text{OH}$ ²⁶ and $1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for $(\text{CH}_3)_3\text{CO}^\bullet + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\bullet\text{CHOH} + (\text{CH}_3)_3\text{COH}$,²⁷ the estimated contribution of $k_{32}[\text{CD}_3\text{CD}_2\text{OH}]$ amounts to $\sim 2 \times 10^4 \text{ s}^{-1}$, leaving reaction 31 as the clearly dominating process. In any case, the rate-determining step for the slow MV^{2+} reduction is attributable to the conversion of $\text{CD}_3\text{CD}_2\text{O}^\bullet$ to $\text{CD}_3\bullet\text{CDOD}$, irrespective of the actual mechanism.

A quantitative evaluation of the overall small yield of the slow process was achieved with solutions containing an MV^{2+} concentration of 2 mM, which allows a clear and unambiguous distinction of the two processes. The absolute yield of the slow part reflecting the yield of $\text{CD}_3\text{CD}_2\text{O}^\bullet$ radicals amounted to $(0.049 \pm 0.006) \mu\text{mol J}^{-1}$. In units relative to $G(\bullet\text{OH})$, this corresponds to $G(\text{CD}_3\text{CD}_2\text{O}^\bullet)_{\text{relative}} = (0.08 \pm 0.01)$. In other words, about 8% of all $\bullet\text{OH}$ radicals end up as alkoxy radicals. (The presence of 2 mM MV^{2+} lowers $G(\bullet\text{OH})$ by up to ca. 5% because of its competition with N_2O for e_{aq}^- . This was taken in account although it did not significantly influence the final result.)

Normal Ethyl Alcohol. In a pulse-irradiated N_2O -saturated solution containing 0.1 M $\text{CH}_3\text{CH}_2\text{OH}$ and 0.1–0.4 mM MV^{2+} , the formation of $\text{MV}^{\bullet+}$ (traced at 600 nm) occurred by just one exponential process, the rate of which was proportional to the MV^{2+} concentration. For this alcohol, the separation of $\text{CH}_3\bullet\text{CHOH}$ from the $\text{CH}_3\text{CH}_2\text{O}^\bullet$ radical, similar to the procedure described above for $\text{CD}_3\text{CD}_2\text{OH}/\text{MV}^{2+}$ system, is not

possible because of the presumably much faster intramolecular transformation of $\text{CH}_3\text{CH}_2\text{O}^\bullet$ to $\text{CH}_3^\bullet\text{CHOH}$ (eq 33). By comparison with some related literature data²⁸ and the value we derive below from our own experiments, this is indeed the case.



The bimolecular rate constant for the reduction of MV^{2+} by $\text{CH}_3^\bullet\text{CHOH}$ has been measured to be $k_{21} = (2.1 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. ($[\text{MV}^{2+}]$ in these experiments was varied from 0.1 to 0.5 mM). This rate constant is somewhat lower than the previously published early pulse radiolysis value of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,²⁹ which by comparison with several published values in the range of $(2.1\text{--}3.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ³⁰ for the corresponding reaction of the even better reductant $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$ seems too high. We therefore attribute the higher accuracy to our present value of k_{21} .

The total yield of $\text{MV}^{\bullet+}$ was determined to be $G(\text{MV}^{\bullet+})_{\text{total}} = (0.684 \pm 0.004) \mu\text{mol J}^{-1}$. From calculations similar to those for the $\text{CD}_3\text{CD}_2\text{OH}$ system, the yield due to the reactions of only •OH radicals with $\text{CH}_3\text{CH}_2\text{OH}$ is equal to

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH}} = G(\text{MV}^{\bullet+})_{\text{total}} - G(\text{H}^\bullet) = 0.684 - 0.06 = 0.624 \mu\text{mol J}^{-1}$$

or in relative units

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH}, \text{relative}} = \frac{G(\text{MV}^{\bullet+})_{\bullet\text{OH}}}{G(\bullet\text{OH})} = \frac{0.624}{0.67} = 0.93$$

(i.e., 93% of all hydroxyl radicals reacting with $\text{CH}_3\text{CH}_2\text{OH}$ produce $\text{CH}_3^\bullet\text{CHOH}$ (partially via $\text{CH}_3\text{CH}_2\text{O}^\bullet$ radicals)). The remainder of 7% is due to the formation of β -hydroxy-C-centered radicals $\bullet\text{CH}_2\text{CH}_2\text{OH}$ formed in reaction 11.

The fraction of •OH radicals leading to $\text{CH}_3\text{CH}_2\text{O}^\bullet$ radicals was determined by measuring the absolute yield of $\text{I}_2^{\bullet-}$ in N_2O -saturated, neutral aqueous solutions containing 0.86 M $\text{CH}_3\text{CH}_2\text{OH}$ and iodide in the range of 3.3 to 10 mM. Upon pulse irradiation, $\text{I}_2^{\bullet-}$ was formed in increasing yield as $[\text{I}^-]$ was increased, and values of $G = 0.035$ up to $0.070 \mu\text{mol J}^{-1}$ were measured within the employed iodide concentration range. These values had to be corrected, however, for the small (but, in the correlation with the total yield of $\text{I}_2^{\bullet-}$ measured, still significant) amount of $\text{I}_2^{\bullet-}$ formed directly in the reaction of iodide with •OH radicals. The corrective terms were calculated from the known alcohol and iodide concentrations in each system and the respective rate constants for the •OH reactions. The thus-corrected $G(\text{I}_2^{\bullet-})_{\text{oxyl}}$ values were then related to the total yield of •OH radicals (i.e., $G_{\text{rel}} = G(\text{I}_2^{\bullet-})_{\text{oxyl}}/G(\bullet\text{OH})$) and plotted according to

$$\frac{1}{G_{\text{rel}}} = \frac{1}{G^0(\text{I}_2^{\bullet-})_{\text{oxyl}, \text{relative}}} \left(1 + \frac{k}{k_{27}} \left(\frac{1}{[\text{I}^-]} \right) \right)$$

as $1/G_{\text{rel}}$ versus the reciprocal iodide concentration in Figure 3. From the intercept (i.e., at infinite iodide concentration), $G^0(\text{I}_2^{\bullet-})_{\text{oxyl}, \text{relative}} = G_{\text{rel}}(\text{CH}_3\text{CH}_2\text{O}^\bullet) = 0.043 \pm 0.005$ has been obtained. This means that about 4% of all •OH radicals lead initially to the formation of $\text{CH}_3\text{CH}_2\text{O}^\bullet$ radicals (reaction 12). Accordingly, the relative yield of $\text{CH}_3^\bullet\text{CHOH}$ radicals produced via reaction 1 amounts to $G(\text{CH}_3^\bullet\text{CHOH})_{\bullet\text{OH}, \text{relative}} = G(\text{MV}^{\bullet+})_{\bullet\text{OH}, \text{relative}} - G(\text{I}_2^{\bullet-})_{\text{oxyl}, \text{relative}} = 0.93 - 0.04 = 0.89$ (i.e., 89% of the •OH radicals directly yield the α -hydroxyethyl radical).

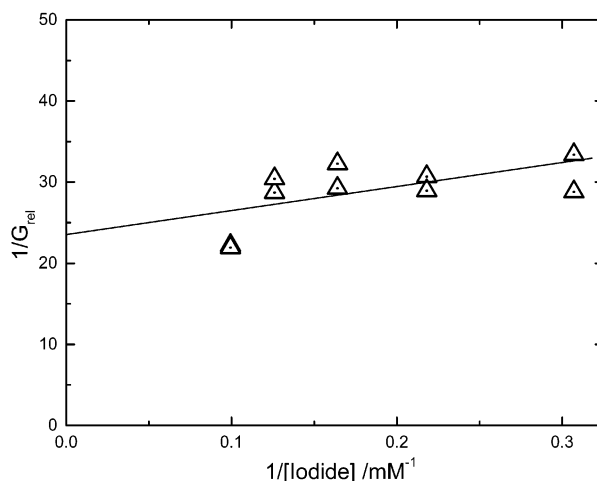
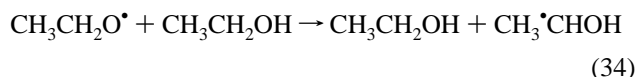


Figure 3. Plot of reciprocal relative yield of $\text{I}_2^{\bullet-}$ ($1/G_{\text{rel}}$ formed only in the reaction with $\text{CH}_3\text{CH}_2\text{O}^\bullet$; for details, see text) versus reciprocal iodide concentration as measured at 380 nm. Pulse-irradiated, N_2O -saturated, neutral aqueous solution contained iodide and 0.86 M $\text{CH}_3\text{CH}_2\text{OH}$.

From the slope of this reciprocal plot (slope = intercept $\times k/k_{27}$), it is possible to estimate the overall rate constant k for those $\text{CH}_3\text{CH}_2\text{O}^\bullet$ radical reactions that compete with the iodide oxidation. Taking $k_{27} \approx 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the latter (i.e., a value similar to the reported one for the oxidation of iodide by $\text{CH}_3\text{O}^\bullet$ radicals, see above), we calculate $k \approx (5 \pm 2) \times 10^6 \text{ s}^{-1}$. This is very close to $8 \times 10^6 \text{ s}^{-1}$ reported for the 1,2 H-atom shift of alkoxy radicals²⁸ such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^\bullet$, and accordingly, we assign this rate constant essentially to reaction 33. There may be a small contribution by the second-order process (eq 34) that, on the basis of known rate constants for similar reactions,^{26,27} may not exceed 10%.



Finally, it seems appropriate at this point to comment on some earlier data¹³ on the relative yields of abstraction in light of the present results. The relative yield of oxyl radicals $\text{CH}_3\text{CH}_2\text{O}^\bullet$ had been found to be 2.5% (i.e., practically identical to our present finding). The 84.3% yield reported in this earlier study for initially generated reducing $\text{CH}_3^\bullet\text{CHOH}$ radicals is, however, slightly lower than our present value of 89%. Accordingly, the relative yield of the redox inert $\bullet\text{CH}_2\text{CH}_2\text{OH}$ (calculated as a difference) is higher in this earlier report (13.2 vs 7%). Possible reasons for the slight discrepancy in the $\text{CH}_3^\bullet\text{CHOH}$ yield may be the higher accuracy of the pulse radiolysis system employed in our present study. Furthermore, no mathematical dependence of scavengable •OH yields as a function of scavenger concentration had been established at that time. Also, the possible contributions of H•-atom reactions with the alcohol and the scavenger used for titrating reducing species (tetranitromethane) were not fully recognized. Given all of the possible uncertainties, there is no point in reevaluating the old system because the two important values (i.e., the relative yields of oxyl and α -hydroxyethyl radicals) are not very different. Nevertheless, we recommend the data from our present study for further applications.

Methylamine. The yields of reducing, C-centered α -amino-methyl radicals in N_2O -saturated solutions containing 0.5 mM MV^{2+} and 0.12 M normal methylamine, pH 10.8, or 0.05 M deuterated methylamine, pH 10.9, were again determined by measuring the yields of produced $\text{MV}^{\bullet+}$ at 600 nm. The values

obtained were 0.308 and 0.227 $\mu\text{mol J}^{-1}$, respectively. As in the case of normal ethanol, the formation of $\text{MV}^{\bullet+}$ occurred via an exponential $[\text{MV}^{2+}]$ -dependent process. The measured yields include the 0.06 $\mu\text{mol J}^{-1}$ contribution by H atoms, which were considered to react exclusively with neutral methylamine molecules and to yield only the reducing α -aminomethyl radicals. The yields of scavengable hydroxyl radicals in each of the above solutions were calculated to be $G(\bullet\text{OH})_{\text{total}} = 0.67$ and 0.63 $\mu\text{mol J}^{-1}$, respectively. Thus, the reaction of $\bullet\text{OH}$ radicals with CH_3NH_2 leads to the formation of $\bullet\text{CH}_2\text{NH}_2$ radicals with a yield of

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH}} = G(\text{MV}^{\bullet+})_{\text{total}} - G(\text{H}^{\bullet}) = 0.308 - 0.06 = 0.248 \mu\text{mol J}^{-1}$$

or, expressed in relative units,

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH, relative}} = \frac{G(\text{MV}^{\bullet+})_{\bullet\text{OH}}}{G(\bullet\text{OH})} = \frac{0.248}{0.67} = 0.37$$

Accordingly, 37% of all $\bullet\text{OH}$ radicals yield $\bullet\text{CH}_2\text{NH}_2$ radicals whereas the remainder of 63% is assigned to the formation of oxidizing $\bullet\text{NHCH}_3$ radicals. For the system with CD_3NH_2 , the numerical values are

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH}} = G(\text{MV}^{\bullet+})_{\text{total}} - G(\text{H}^{\bullet}) = 0.227 - 0.06 = 0.167 \mu\text{mol J}^{-1}$$

or, expressed in relative units,

$$G(\text{MV}^{\bullet+})_{\bullet\text{OH, relative}} = \frac{G(\text{MV}^{\bullet+})_{\bullet\text{OH}}}{G(\bullet\text{OH})} = \frac{0.167}{0.63} = 0.26$$

In this case, 26% of all $\bullet\text{OH}$ radicals generate $\bullet\text{CD}_2\text{NH}_2$, and the remainder of 74% is assigned to the formation of oxidizing $\bullet\text{NHCD}_3$ radicals.

The respective rate constants for the MV^{2+} reduction by $\bullet\text{CH}_2\text{NH}_2$ have been measured to be $k_{23} = (3.6 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The same number was also obtained for the corresponding reaction of $\bullet\text{CD}_2\text{NH}_2$, though only from a single-point measurement. Our present measurement nicely confirms our previous $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ value for the reduction of MV^{2+} by $\bullet\text{CHRNH}_2$ radicals that were formed as the result of an oxidative decarboxylation of glycine anions (at pH 10.6)⁵ or methionine.³¹

The formation of the oxidizing N-centered radicals was additionally proven and quantitatively measured for solutions containing CH_3NH_2 . The $\bullet\text{NHCH}_3$ radicals generated in this system were titrated by using hydroquinone as a scavenger following the procedure that was successfully applied for the quantification of similar $\bullet\text{NH-R}$ radicals formed in the $\bullet\text{OH}$ -induced oxidation of amino acid anions.³ Actual pulse-radiolysis measurements were performed with N_2O -saturated, pH 11.0 solutions containing 0.12 M methylamine and hydroquinone in the concentration range of 0.2–1.2 mM. The relevant reaction



has already been introduced in an earlier section (and discussed with respect to the hydroquinone's pK values).

The formation of the semiquinone radicals was followed at the maximum of their optical absorbance at 427 nm. A typical time-resolved trace is shown as the upper inset in Figure 4 for a total H_2Q concentration of 0.42 mM. It is noted, as a common

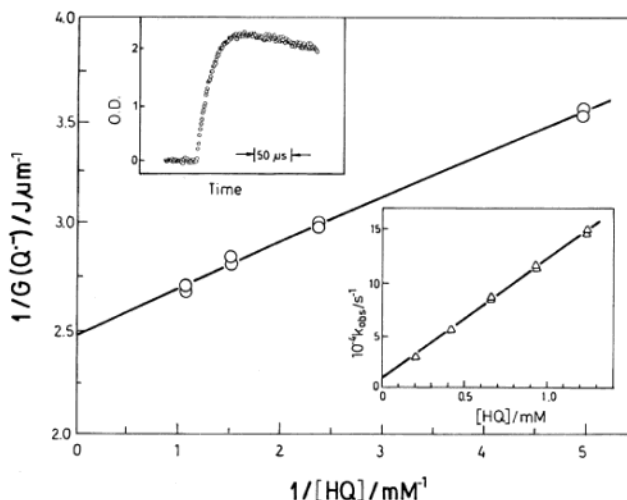


Figure 4. Plot of reciprocal semiquinone yield expressed as $1/G(\text{Q}^{\bullet-})$ versus $[\text{H}_2\text{Q}]^{-1}$ measured at 427 nm in pulse-irradiated, N_2O -saturated aqueous solution at pH 11.0 containing hydroquinone and 0.12 M methylamine. Upper inset: absorption (arbitrary units) versus the time trace at 427 nm obtained in the same solution containing 0.42 mM hydroquinone. Lower inset: plot of k_{obs} for semiquinone formation versus $[\text{H}_2\text{Q}]$ in the same solutions as in the main plot.

feature for all employed H_2Q concentrations, that the signals were not stable after the growth period. They always showed some second-order decay that, tentatively, we assign to the back reduction of the semiquinone radical by the methylamine-derived, reductive radicals produced simultaneously. The pseudo-first-order rate constants for the semiquinone formation were, therefore, obtained by fitting the experimental data to an expression with a sequential growth and decay. Results are shown in the bottom inset of Figure 4 as k_{obs} versus hydroquinone concentration. From the slope of the obtained straight line, a rate constant of $(1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was calculated and assigned to reaction 25. This rate constant seems to be characteristic for the oxidation of hydroquinone at pH 11.0 by alkylaminyl radicals, in general, because it is very similar to the values reported previously for aminyl radicals derived from alanine and glycine (1.1×10^8 and $0.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively).^{3,4}

The yield of semiquinone radicals, calculated from the measured maximum absorbances by using the known molar extinction coefficient of $7200 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Q}^{\bullet-}$ and applying corrections for the slight decay, increased with the concentration of hydroquinone. This indicates the occurrence of additional reactions of $\bullet\text{NHCH}_3$ radicals in competition with reaction 25. To analyze for this, the reciprocal $\text{Q}^{\bullet-}$ yield has been plotted versus the reciprocal hydroquinone concentration in Figure 4. From the intercept of the straight line, $G(\text{Q}^{\bullet-}) = 0.404 \mu\text{mol J}^{-1}$ is obtained at infinite hydroquinone concentration. In units relative to the yield of scavengable $\bullet\text{OH}$ radicals (calculated to be 0.675 $\mu\text{mol J}^{-1}$ in the investigated solution), it is $G(\text{Q}^{\bullet-})_{\text{relative}} = G(\bullet\text{NHCH}_3)_{\text{relative}} = 0.404/0.675 = 0.60$. This is very close to the value of 0.63 deduced from the results presented above using methyl viologen as a scavenger for the reducing radicals. Such a good fit also confirms that the procedures applied in this study for yield determinations are meaningful and correct.

Finally, it might be interesting to stress the relatively high stability of both aminyl radicals, $\bullet\text{NHCH}_3$ and $\bullet\text{NHCD}_3$. Under the experimental conditions used in this study, it seems that they decay only by second-order radical–radical reactions as indicated by the slight disappearance of $\text{MV}^{\bullet+}$ on the time scale of $\sim 200 \mu\text{s}$. In particular, it seems that neither the first-order nor the second-order transformation into C-centered radicals,

reactions 35 and 36, plays any significant role on this time scale.



This parallels correspondingly low reactivities, with respect to these processes, of aminyl radicals derived from amino acids (e.g., glycine, $\bullet\text{NH}-\text{CH}_2-\text{CO}_2^-$).^{3,4} (Such radicals decay, however, also by additional intramolecular homolytic C–C bond rupture liberating $\bullet\text{CO}_2^-$, a reaction not possible, of course, for the methylamine-derived radicals.)

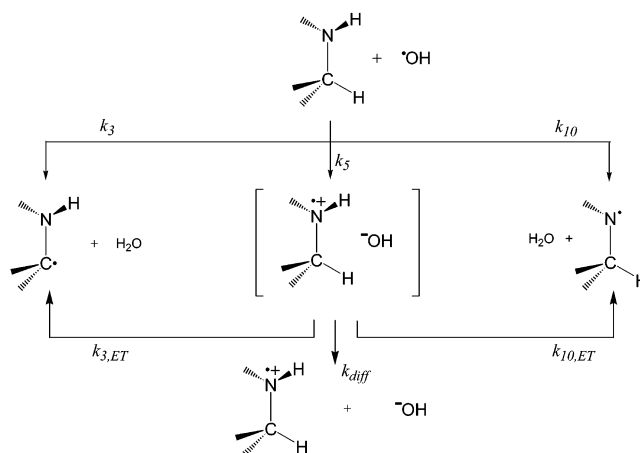
Table 2 summarizes the overall rate constants (k_{total}) for the reactions of $\bullet\text{OH}$ radicals with $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CD}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{-NH}_2$, and CD_3NH_2 . Also displayed are the partial rate constants for the formation of all radicals detected as products. These rate constants were obtained by multiplying k_{total} by the relative yields of the respective radicals listed in Table 1. Rate constants for the various redox titration and rearrangement reactions, which were measured and are new, are summarized in Table 3.

Kinetic Isotope Effects. The kinetic isotope effects (KIEs or values of $k_{\text{H}}/k_{\text{D}}$) for the $\bullet\text{OH}$ reactions have been given in Table 2 for the total and for each of the partial rate constants. KIEs for total rates of reaction with $\bullet\text{OH}$ are not available from the literature for CH_3NH_2 , and those derived for ethanol from the earlier solution data give values of 1.3 to 1.8 depending on which result is used for k_{15} . The earlier gas-phase value of 2.6³² is more precise, and it could be significant that the present solution result of 1.93 (Table 2) lies below it. This may be an indication that the barrier heights of the present reactions are lowered in solution because of polar transition states³³ or the fact that tunneling is reduced.³⁴ An elucidation of these points requires high-level theoretical calculations. Further discussion is centered on KIEs of the individual or partial reactions, the weighted sums of which make up the total KIEs.

As is to be expected,³⁵ the highest isotope effect applies to the abstraction of a primary hydrogen atom from an unsubstituted alkyl group ("unsubstituted" meaning connected only to an alkyl group or to hydrogen). In our study, this applies to the terminal methyl group in ethanol for which KIE = 3.4 has been found. This value can be compared to 4.6 for the H/D KIE in ethane in the gas phase.³⁶ Again, the solution result is smaller. However, a relatively high error limit must be allowed in the present result because of the low relative yields of the β -hydroxy radicals, which are the basis for the calculation of the $k_{\beta-\text{C}}$ rate constants. For secondary hydrogens in unsubstituted methylene groups, a recent review³⁵ lists KIE = 2.6 both in the gas phase and in solution. This is to be compared with 1.96 in Table 2 for the H/D abstraction from the C_α position in ethanol (yielding the α -hydroxyalkyl radical). Here, the yields, rate constants, and consequently the KIE could be determined at high accuracy, and the difference from the pure aliphatic system must be taken as real. A plausible rationale is the C–H/C–D bond-weakening effect exerted by the α -positioned hydroxy group³⁷ in combination with the reported³⁵ and generally accepted fact that the KIEs decrease with decreasing bond-dissociation energies.

The KIE (=1.86) for the H/D abstraction from the methyl group in methylamine can be explained in a similar manner by the influence of the amino group. Indeed, the fact that it is slightly lower than that for the abstraction of the secondary hydrogen in ethanol conforms to the difference in the BDEs for the $\text{C}_{\alpha-\text{H}}$ bonds in ethanol (397 kJ mol^{-1})³⁷ and methylamine (393 kJ mol^{-1}).³⁸ However, the barrier heights in both of these systems are low enough that tunneling may be very important, and detailed conclusions will require a careful theoretical analysis.

SCHEME 1



An important aspect of the present work is a comparison of the partitioning of $\bullet\text{OH}$ attack on the aliphatic groups versus the OH or NH_2 components in the ethanol and methylamine molecules, respectively. As pointed out earlier, ET to $\bullet\text{OH}$ (reaction 5) is feasible in the case of methylamine, and the C-centered radicals may be formed subsequently by proton loss (reactions 6 or 7). This is particularly evident when one considers that the initial product of reaction 5 is a closely spaced $[\text{HO} \cdots \text{N}^+\text{H}_2\text{CH}_3 / \text{N}^+\text{H}_2\text{CD}_3]$ ion pair as shown in Scheme 1. Proton transfer to the strong base HO^- may occur before outward diffusion, which takes several picoseconds (rate k_{diff}).⁷ The overall process via this route that includes reaction 5 followed by reaction 6 has been denoted as $k_{3,\text{ET}}$ in Scheme 1 to indicate its alternative character to the direct abstraction route (reaction 3). (For the deuterated system, the reference reactions are 4 and 7 instead of 3 and 6.) In any case, if that were the dominant mode of reaction of $\bullet\text{OH}$, then deuteration of the C center should have a negligible (or minimal) effect on the value of k_{total} . This is because any possible reduction in the yield of C-centered radicals due to the KIE for the overall electron-transfer route (and expressing itself in $k_{3,\text{ET-H}}$ and $k_{3,\text{ET-D}}$ for the hydrogenated and deuterated systems, respectively) should be made up by a compensating increase in aminium deprotonation. Instead, what is seen in Table 2 is a very significant reduction in k_{total} (KIE = 1.31) coupled with a small reduction (rather than increase) in k_{N} (KIE = 1.11). In fact, apart from the latter effect, the behavior for methylamine very closely parallels that of ethanol, for which ET to $\bullet\text{OH}$ is expected to be negligible;⁴⁶ viz., in both systems, deuteration causes a very significant reduction in $k_{\alpha-\text{C}}$ and a very small or negligible effect on $k_{\text{O/N}}$. One may therefore conclude that in ethanol and methylamine the C-centered radicals are formed by H-abstraction reactions (i.e., via reaction 3) with no significant contributions from reactions 5 and 6 or 7 ($k_{3,\text{ET}}$ route in Scheme 1) and their counterparts in ethanol. The discussion in the preceding section, showing that the present $k_{\alpha-\text{C}}$ KIEs can be rationalized on the basis of literature values for known abstraction reactions in related systems, is in accord with this.

Because the rapid proton exchange between the N–D bonds in the original CD_3ND_2 and the solvent H_2O precludes any primary isotope effect in the attack of $\bullet\text{OH}$ on the amino group, the present study gives no information on the relative roles of reaction 5 followed by reaction 8 or 9 ($k_{10,\text{ET}}$ route in Scheme 1) as opposed to reaction 10. However, one remarkable aspect of the present data is the approximately 20-fold-higher (reducing to 10-fold higher on a per H atom available basis) rate constant for H abstraction from N–H compared to that for O–H in our investigated systems (compare k_{N} and k_{O} in Table 2). If direct

H abstraction is involved, then the deciding parameter would be the difference in BDEs (423 kJ mol⁻¹ for MeNH–H³⁸ versus 437 kJ mol⁻¹ for EtO–H⁴⁰), which would affect the barrier heights. However, ET is also a factor that could enhance the rate for MeNH₂. The KIE for *k*_O in Table 2 is 1.0. The KIE of 1.11 for *k*_N is close to, if not within, the experimental error limits. However, a secondary KIE of this magnitude might arise in ET (reaction 5) or in an H abstraction (reaction 10).

All of the rate constants discussed above find their reflection in the various yields of radicals and products. Accordingly, there is no point in entering into a similarly detailed analysis of yields with basically the same arguments again. However, the rate constant data in Table 3 are worth a comment. The first four are for ETs from radicals to MV²⁺. For the first two, the radicals are CH₃C•HOH and CD₃C•DOH, and for the second two, •CH₂–NH₂ and •CD₂NH₂. Since D is a slightly better electron-density-releasing substituent than H,⁴¹ the overall electron density at oxygen or nitrogen should be higher in the deuterated radicals, and one might expect faster ET from those species. The rate for CD₃C•DOH is marginally larger than for CH₃C•HOH, but overall, the results show that the effect is small or negligible.

Two other comments concern the intramolecular conversion of the ethoxyl radicals to their respective α-hydroxyethyl radicals (eqs 31 and 33). Our experiments reveal a KIE of about 50 (see first-order rate constants in Table 3). Although our rate constant for the 1,2 H-atom shift of CH₃CH₂O•, reaction 33, was similar to that of the CH₃CH₂CH₂O• alkoxyl radical from reference 28, we were unable to find KIEs for the 1,2 H shift of CH₃CH₂O• or similar alkyl alkoxyl radicals. Thus, our presently measured value appears to be the first of this kind. The very high KIE is an indication that tunneling probably plays a significant role indeed in the solvent-assisted mechanism proposed earlier for this process.^{28,42} It has, in fact, been noted in a recent publication⁴³ that “some of the largest deuterium isotope effects that have been reported involve unimolecular H-atom shift in radicals.” Other than this 1,2 H-atom shift, the intermolecular hydrogen transfer (eqs 32 and 34) shows a probably very normal KIE (actual numbers related to literature values^{26,27} vary from 1.5 to 6.1 but must allow very high error limits).

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- Methyl viologen is quoted to react with hydrogen atoms at pH 1 with *k* = 6 × 10⁸ M⁻¹ s⁻¹, forming a product that does not absorb at 600 nm.²⁴ This would mean that, under the conditions of our experiment, H• radicals would also be partially scavenged by methyl viologen (ca. 25, 40, and 55% for solutions containing 0.11 M CD₃CD₂OH and 0.1, 0.3, and 0.5 mM MV²⁺, respectively). H• radicals are produced only at low yield in N₂O-saturated aqueous solutions at pH > 3 (ca. only 10% of G(•OH)). Considering the very low error limit for the analysis of MV^{•+}, the decrease in total G(MV^{•+}) caused by this reaction should, nevertheless, be clearly detectable. Because this was not the case and the yield of reduced MV²⁺ stayed constant at all [MV²⁺] employed, we concluded that in the system under investigation all H• radicals reacted exclusively with CD₃CD₂OH.
- Possible conversion of the less-reducing •CD₂CD₂OH into strongly reducing CD₃CDOH radicals via the reaction •CD₂CD₂OH + CD₃CD₂OH → CD₃CDOH + CD₃CD₂OH is very slow (*k* = 16 M⁻¹ s⁻¹ for normal ethyl alcohol²⁵) and does not occur on the ~200-μs time scale of this experiment.
- Pearson³⁹ estimated *E*^o(MeOH^{•+}/MeOH) = 2.75 V, and *E*^o(EtOH^{•+}/EtOH) will be about 0.3 V less. With *E*^o(•OH/OH⁻) = 1.90 V,¹ ET from EtOH to •OH will be about 0.5 V endergonic, about the same as for nitrate or sulfate ion oxidation by •OH.