Free-Radical Species from Methyl Vinyl Ketone in Aqueous Solution: A Pulse Radiolysis Study

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FREE-RADICAL SPECIES FROM METHYL VINYL KETONE IN AQUEOUS SOLUTION: A PULSE RADIOLYSIS STUDY

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ABSTRACT

Transient species (T_1 and T_2), formed respectively by the reactions of hydrated electrons and hydroxyl radicals with methyl vinyl ketone monomer in aqueous solution, were characterized by their spectra, redox behavior, and decay kinetics. These were found to have λ_{max} at 290 and 310 nm with low extinction coefficient values of 94 and 70 m^2/mol, respectively. Rate constants for the reactions of methyl vinyl ketone with e_{aq}^- and $^{\cdot}$OH were found to be 3.2×10^9 and 7×10^8 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}, respectively. The first propagation step for species T_2 was found to be much faster ($k_{p1} \approx 1.5 \times 10^6$ dm$^3 \cdot$mol$^{-1} \cdot$s^{-1} than that for species T_1 ($k_{p1} \approx 7.0 \times 10^5$ dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}). Both were found to be reducing in nature, and the rate constants for the reduction of thionine and safranine with these species were determined. The most probable structures of these species are suggested.

INTRODUCTION

Conventional polymerization of methyl vinyl ketone is well known. Attempts to understand the mechanism of polymerization started with studies of photochemical polymerization of neat methyl vinyl ketone and acetone-sensitized polymerization in the vapor state [1]. Aqueous polymerization of methyl vinyl ketone was studied by Miller [2] and Kawada [3]. Detailed studies of radiation-induced polymerization were

carried out by Tabata [4] and Fujii [5] to find R_p, activation energy, dose rate exponent, and effect of solvents and inhibitors. These studies showed that methyl vinyl ketone polymerizes by a free-radical mechanism. On the other hand, anionic polymerization of methyl vinyl ketone [6, 7] with initiation by organometallic catalysts (such as $CaEt_4Zn$, $PhMgBr \cdot OEt_2$, Et_3Al, etc.) is also known.

From the results of steady-state polymerization, only average propagation rate constant can be obtained, whereas a fast time-resolved technique, such as pulse radiolysis, is required to determine the rate constants [8–13] for the individual propagation steps (i.e., k_{p1}, k_{p2}, etc.). In the present study, likely initial processes (i.e., initiation and first propagation step) for the radiation polymerization of methyl vinyl ketone in aqueous medium have been investigated by the technique of pulse radiolysis.

EXPERIMENTAL

G.R. grade methyl vinyl ketone from Koch-Light Laboratories Ltd. was further purified by vacuum distillation and dried with $CaCl_2$ before use. Fluka puriss grade thionine was further purified by repeated extraction with chloroform, and safranine was recrystallized from triply distilled water and extracted with chloroform. Gases used for purging the solutions were Iolar grade from Indian Oxygen Ltd. All other chemicals used were of G.R. grade.

Solutions were prepared in triply distilled water and were buffered to different pH by using H_2SO_4, Na_2HPO_4, KH_2PO_4, $Na_2B_4O_7 \cdot 10H_2O$, and $NaOH$ in suitable combinations, and the total ionic strength was kept at about 0.08 mol/dm^3 with Na_2SO_4. For the study of OH radical reaction, nitrous oxide gas was used for converting hydrated electrons to OH radicals. For studying hydrated electron reactions, t-butanol was used as the OH radical scavenger, and the solutions were saturated with oxygen-free nitrogen gas at 1 atm.

Full details of the pulse radiolysis set-up are given elsewhere [14]. For recording the spectra, 2 μs pulses of 7 MeV electrons were employed, typical doses being 1.17×10^5 J/m^3, but for kinetic studies and extinction coefficient determination 25 ns pulses with typical doses of 2.40×10^4 J/m^3 were used. Aerated KSCN solution (0.05 mol/dm^3) was used for measuring the electron pulse dose. The $(CNS)_2{}^-$ species having $(G.\varepsilon) = 2.23 \times 10^{-4}$ m^2/J [15], formed by oxidation of CNS^- by OH radicals, was monitored at 500 nm.

RESULTS AND DISCUSSIONS

In the pulse radiolysis of dilute aqueous monomer solutions, the primary species of water radiolysis (i.e., e_{aq}^-, $\cdot OH$, can react with monomer (initiation step) to form free-radical species, which can subsequently propagate polymerization if exper-

imental conditions are suitable. Generally, the propagation rate constants of free-radical polymerizations have been found to decrease up to the fourth or fifth step and, thereafter, to attain a constant average value, as inferred from steady-state polymerization studies. Kinetic studies and characterization of the transients formed by the reactions of e_{aq}^- and OH radicals with methyl vinyl ketone were carried out in the present work.

I. Reaction of Hydrated Electron with Methyl Vinyl Ketone

The transient absorption spectrum observed on pulse radiolysis of N_2-saturated solution containing 5×10^{-3} mol/dm^3 methyl vinyl ketone and 0.8 mol/dm^3 t-butanol at pH 5.8 is shown in Fig. 1. This transient species was found to have λ_{max} at 290 nm with extinction coefficient of 94 m^2/mol. No change in the transient spectrum was
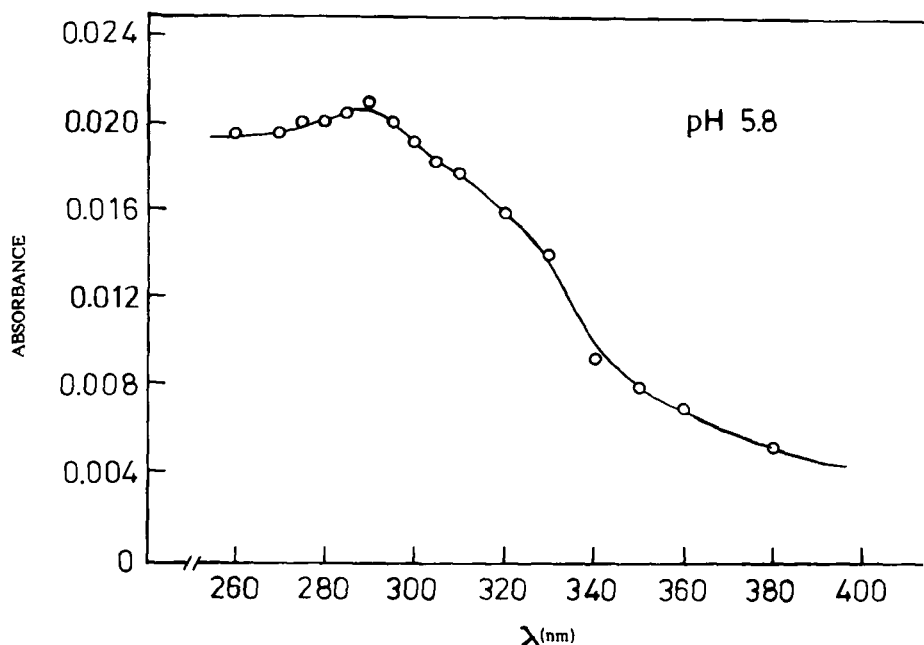

FIG. 1. Absorption spectrum of the transient species formed by the reaction of hydrated electron with methyl vinyl ketone.

observed in the pH range 3.5 to 11.0. Studies could not be carried out below pH 3.5 and above pH 11.0 because, at low pH, hydrated electrons are preferentially converted to H atoms by reaction with H_3O^+ ions, and in highly alkaline solutions the monomer was found to undergo a slow, irreversible change.

The transient absorbance buildup at 290 nm (pH 5.8) was found to be pseudo-first-order with respect to the monomer concentration, from which the rate constant for the reaction between monomer and e_{aq}^- was determined to be 3.2 $\times$ 10^9 dm^3·mol^{-1}·s^{-1}. Within the limits of experimental error, this value agreed with that estimated by directly following the decay of the e_{aq}^- signal at 720 nm in the presence of methyl vinyl ketone (2.5 $\times$ 10^9 dm^3·mol^{-1}·s^{-1}).

The decay of this transient species (T_1) at 290 nm was found to be pseudo-first-order with respect to the monomer concentration and to lead to another species (T_1') with a much lower extinction coefficient at 290 nm ($\sim$20 m^2/mol), as shown in a typical oscilloscope trace (Fig. 2). This can be interpreted as the first propagation step. Figure 3 shows the linear plot of the observed pseudo-first-order rate constant (k_ϕ) versus concentration of the monomer. The rate constant (k_{p1}) for the first propagation step was estimated to be 7 $\times$ 10^5 dm^3·mol^{-1}·s^{-1} from the slope of this plot.
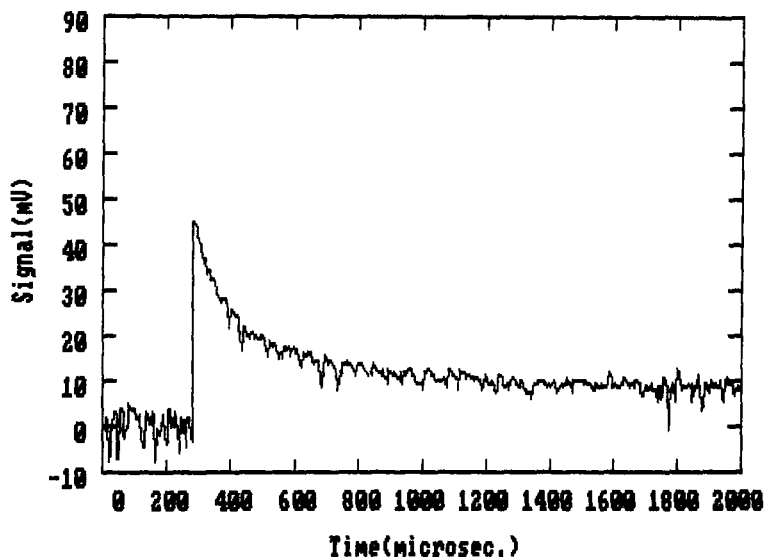

FIG. 2. A typical trace of the transient formed by the reaction of hydrated electron with the monomer at 290 nm.
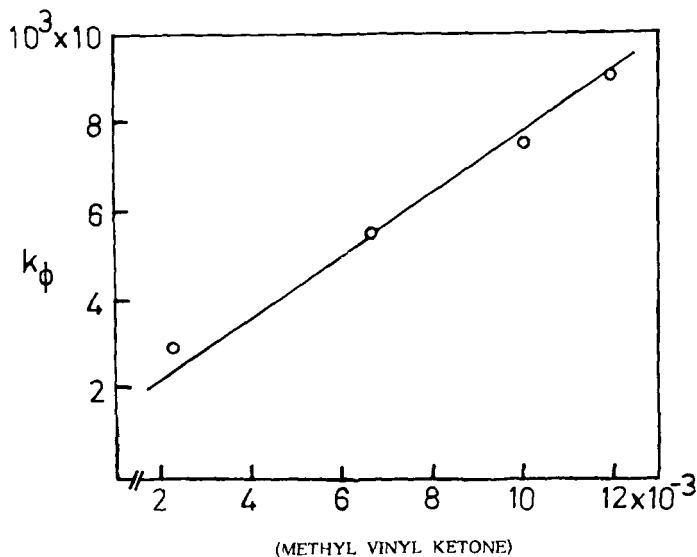
FIG. 3. Pseudo-first-order rate constant (k_ϕ) for the decay of the transient species T_1 formed by the reaction of hydrated electron with the monomer as a function of the concentration of the monomer.

Decay of T_1' is not apparent from the oscilloscope trace shown in Fig. 2. It was, however, found to decay very slowly, indicating that the second propagation step is much slower than the first. The rate constant for this and subsequent steps could not be reliably evaluated.

II. Reaction of Hydroxyl Radicals with Methyl Vinyl Ketone

The transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated solution containing 4×10^{-3} mol/dm^3 methyl vinyl ketone at pH 5.8 is shown in Fig. 4. The transient (T_2) responsible for this spectrum was found to have λ_{max} at 310 nm with an extinction coefficient of 70 m^2/mol at pH 5.8. No pK was observed in the pH range of 3.5 to 11.0 for this transient.

The rate constant for the reaction between monomer and hydroxyl radical was determined by the competition kinetics method with KSCN as standard solute by monitoring the $(CNS)_2^{\cdot-}$ species formed at 500 nm (pH 6.8), and was found to be 8.5×10^8 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}. This value was confirmed by directly following the formation kinetics of the transient (T_2) at 310 nm, the value so obtained being 7×10^8 dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}.
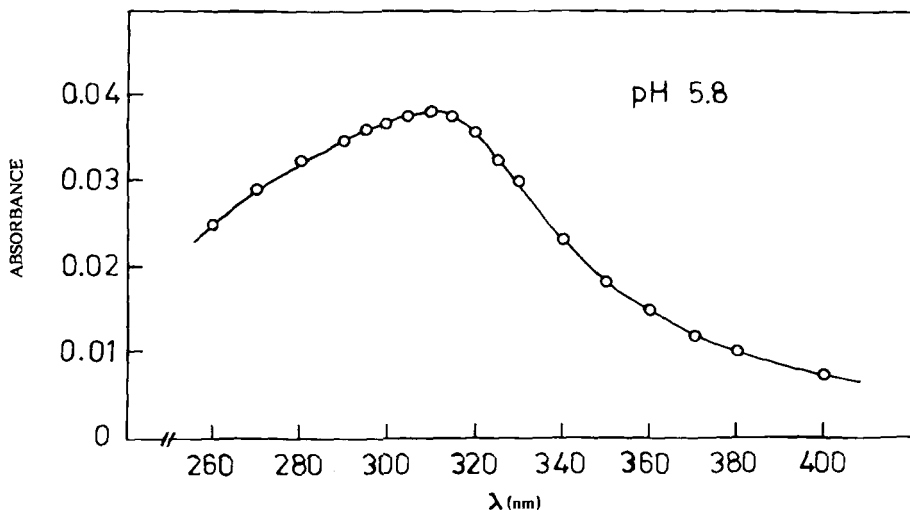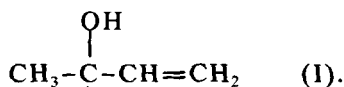
FIG. 4. Absorption spectrum of the transient species formed by the reaction of hydroxyl radical with methyl vinyl ketone.

A typical oscilloscope trace of the transient signal at 310 nm is shown in Fig. 5. The decay of the transient (T_2) at this wavelength was found to be pseudo-first-order with respect to the monomer concentration. From the slope of the plot of the pseudo-first-order rate constant versus monomer concentration, the rate constant for the first propagation step (k_{p1}) was calculated to be 1.5×10^6 $dm^3 \cdot mol^{-1} \cdot s^{-1}$. As in the case of T_1, species T_2 was found to decay to a relatively slow decaying species (T_2'), having a low extinction coefficient of ~24 m^2/mol at 310 nm.

III. Reducing Nature of the Radicals and Their Probable Structures

The two possible sites of attack in methyl vinyl ketone by e_{aq}^- are (i) the C–C double bond and (ii) the carbonyl group, of which the latter seems to be more probable on the following grounds. If e_{aq}^- attacks at the carbonyl group of the monomer, the structure which can be assigned to the transient T_1 (in its protonated form) is

$$CH_3-\underset{\displaystyle |}{\overset{\displaystyle OH}{C}}-CH=CH_2 \qquad (I).$$
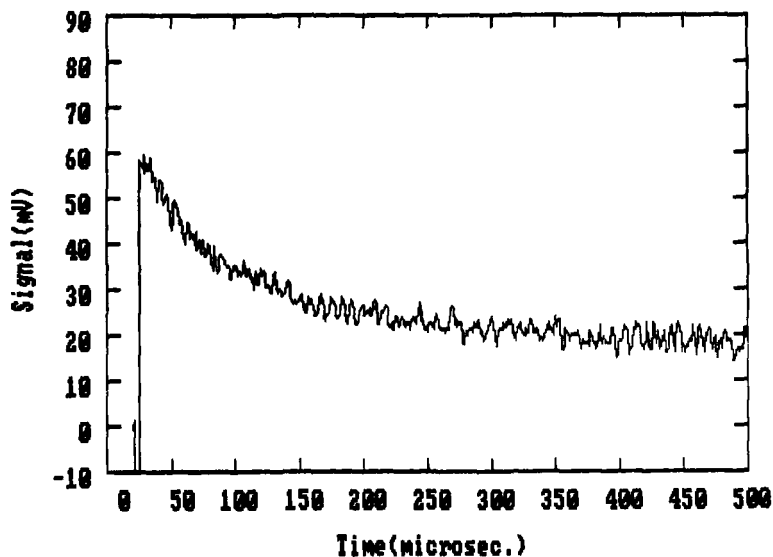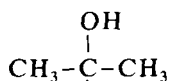
FIG. 5. A typical trace of the transient species formed by the reaction of hydroxyl radical with the monomer at 310 nm.

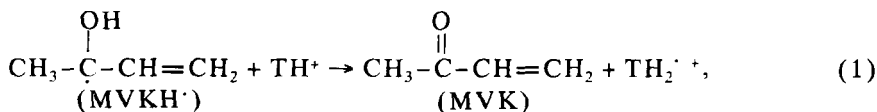This is similar to protonated ketyl radicals such as

$$\begin{array}{c} OH \\ | \\ CH_3-C-CH_3 \end{array}$$

derived by α-hydrogen abstraction from alcohols, which are known to be highly reducing in nature [16]. Pulse radiolysis of N_2-purged aqueous solution containing 6 mmol/dm³ methyl vinyl ketone, 50 µmol/dm³ of reducible dye thionine (TH⁺) or safranine (SF), and 0.8 mol/dm³ t-butanol at pH 6.8 was carried out to find out whether species T_1 is reducing in nature. For this purpose, formation of the reduced species from the above dyes was monitored at 770 nm for thionine and at 650 nm for safranine. The conditions chosen above were such that almost all the e_{aq}^- produced by the pulse reacted with methyl vinyl ketone and not with the dye molecules, and the resultant transient (T_1) could react with thionine or safranine almost exclusively. Since the transient (T_1) is capable of reducing both thionine and safranine, it may be
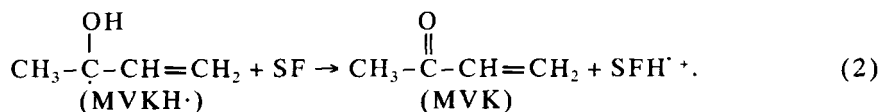
concluded that it has Structure (I), i.e., e_{aq}^- attacks methyl vinyl ketone at the carbonyl group.

The formation of the reduced species of thionine (at 770 nm) was found to be pseudo-first-order with respect to thionine concentration, and the rate constant for the reaction between the transient (T_1) and thionine (TH^+),
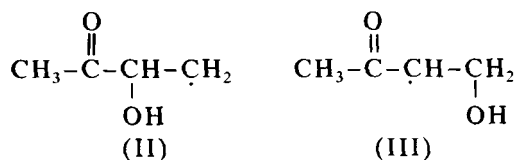
$$\begin{array}{cc} \underset{|}{\overset{\displaystyle OH}{\underset{|}{}}} & \overset{\displaystyle O}{\underset{}{\|}} \\ CH_3-\underset{\cdot}{C}-CH{=}CH_2 + TH^+ \rightarrow CH_3-C-CH{=}CH_2 + TH_2^{\cdot\,+}, \\ (MVKH^\cdot) & (MVK) \end{array} \qquad (1)$$

was evaluated to be 3.2×10^9 dm$^3\cdot$mol$^{-1}\cdot$s^{-1}.

Similarly formation kinetics of reduced species of safranine (at 650 nm), which was also found to be pseudo-first-order with respect to safranine (SF) concentration, led to a value of 1.6×10^9 dm$^3\cdot$mol$^{-1}\cdot$s^{-1} for the rate constant of the corresponding reaction

$$\begin{array}{cc} \underset{|}{\overset{\displaystyle OH}{\underset{|}{}}} & \overset{\displaystyle O}{\underset{}{\|}} \\ CH_3-\underset{\cdot}{C}-CH{=}CH_2 + SF \rightarrow CH_3-C-CH{=}CH_2 + SFH^{\cdot\,+}. \\ (MVKH\cdot) & (MVK) \end{array} \qquad (2)$$

From the correlation between the electron-transfer rate constant and one-electron reduction potentials ($E°$) of the radicals [14] and our experimental rate constant for the MVKH· radical, a rough estimate of $E°$ for this radical was obtained as −0.1 V vs NHE.

The most probable reaction of the OH radical with methyl vinyl ketone is addition to its C–C double bond. The two possible structures that can be assigned to the transient (T_2) are

$$\begin{array}{cc} \overset{\displaystyle O}{\|} & \overset{\displaystyle O}{\|} \\ CH_3-C-\underset{|}{CH}-\underset{\cdot}{CH_2} & CH_3-C-\underset{\cdot}{CH}-\underset{|}{CH_2} \\ OH & OH \\ (II) & (III) \end{array}$$

It was also found that, under our experimental conditions (N$_2$O-saturated solution containing 4 mmol/dm^3 methyl vinyl ketone and 10 μmol/dm^3 thionine at pH 6.8), where reaction of ·OH with methyl vinyl ketone and reaction of the resulting transient T_2 with thionine are favored over the other competing reactions, the transient T_2 can

reduce thionine, although not as efficiently as T_1. Of Structures II and III, the former is similar to the radical

$$
\begin{array}{c}
\overset{\displaystyle \cdot\text{CH}_2}{\underset{\displaystyle \text{CH}_3}{\text{CH}_3-\text{C}-\text{OH}}}
\end{array}
$$
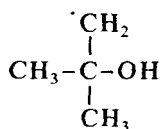
derived by hydrogen abstraction from t-butanol. This radical is a very poor reducant [16]. In view of the fact that T_2 is reducing in nature, Structure II may be ruled out and III may be inferred to be more acceptable.

The formation kinetics of the reduced species of thionine (at 770 nm) was found to be pseudo-first-order with respect to the thionine concentration, and the rate constant for the reaction between T_2 and thionine was estimated to be $7 \times 10^9 \mathrm{dm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$.

CONCLUSIONS

Rate constants for the initiation reactions by hydrated electrons and OH radicals with methyl vinyl ketone in aqueous solution are high ($\sim 10^9 \mathrm{~dm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$). The first propagation step rate constants for the resultant radical species are of the order of $10^6 \mathrm{dm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$, while the subsequent ones are much lower. The most probable site of attack by e_{aq}^- is the carbonyl group of the monomer, resulting in a ketyl type of radical species capable of reducing both thionine and safranine, as expected. On the other hand, the OH radical adds onto the C–C double bond of the monomer, resulting in a secondary radical, which is also reducing in nature.

ACKNOWLEDGMENTS

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