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## **PULSE RADIOLYSIS STUDY OF INITIATION, DIMERIZATION, AND PROPAGATION STEPS OF 3,3-DIMETHYLACRYLIC ACID IN AQUEOUS MEDIUM**

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### **ABSTRACT**

Rates of initiation, dimerization, and first propagation steps originating from the hydrated electron and hydroxyl radical reactions with 3,3-dimethylacrylic acid monomer have been investigated using the technique of pulse radiolysis. The initiation step for the protonated monomer is found to be faster than that of the deprotonated form. The dimerization step is about two orders of magnitude faster than the first propagation step. Radical species are more reactive than the corresponding radical-anionic species, and the  $\beta$ -protonated electron adduct to the monomer is found to propagate faster than other electron adduct species. The different transient species have been characterized by their absorption spectra,  $\lambda_{\max}$ , extinction coefficient,  $pK$ , and redox behavior. Based on these observations, the most probable structures are suggested.

### **INTRODUCTION**

Steady-state propagation step rate constants for vinyl monomers have been investigated by various workers in the past; however, not much has been reported about the rate constants of the individual propagation

steps [1-5]. In the present study the likely initial processes (i.e., initiation, first propagation, and dimerization step) induced by both hydrated electron and hydroxyl radical in the radiation polymerization of 3,3-dimethylacrylic acid in aqueous medium have been investigated by the technique of pulse radiolysis in an attempt to understand the mechanism of polymerization. Pulse radiolysis investigations of electron adducts of acrylic acid and its derivatives have been reported by Hayon et al. [6, 7] and other workers [8]. ESR techniques [9, 10] and pulsed conductance measurements [11] were also utilized for characterizing electron adduct species of acrylic acid derivatives.

## EXPERIMENTAL

3,3-Dimethylacrylic acid from Sisco Research Laboratories was recrystallized from petroleum ether before use. Fluka puriss grade thionine was used after purification by repeated extraction with chloroform. Gases used for purging the solutions were Iolar grade from Indian Oxygen. All other chemicals used were GR grade.

Solutions were prepared in triply distilled water and were buffered to different pH's by using  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and  $\text{NaOH}$  in suitable combinations, and the total ionic strength was kept at about  $0.09 \text{ mol/dm}^3$  by using  $\text{Na}_2\text{SO}_4$ . For the study of OH radical reaction, nitrous oxide gas was used for converting hydrated electrons to OH radicals. In the study of the reaction of hydrated electrons, *t*-butanol was used as an OH radical scavenger and the solutions were saturated with oxygen-free nitrogen gas at 1 atm.

Full details of the pulse radiolysis setup are given elsewhere [12]. For recording the transient absorption spectra,  $2 \mu\text{s}$  pulses of 7 MeV electrons were employed, typical doses being  $1.1 \times 10^5 \text{ J/m}^3$ , but for extinction coefficient determinations, 25 and 500 ns pulses (with each dose in the range of about  $1.2 \times 10^4$  to  $6.0 \times 10^4 \text{ J/m}^3$ ) were used. The pseudo-first-order kinetics behavior (such as the first propagation step) of different transient species was studied at a lower dose ( $1.2 \times 10^4 \text{ J/m}^3$ ) and a higher monomer concentration. In the case of second-order kinetics (such as the dimerization step), a higher dose ( $\sim 1 \times 10^5 \text{ J/m}^3$ ) and a lower monomer concentration were used to reduce interference from unwanted competing reactions to less than  $\sim 10\%$ . An aerated KSCN solution ( $0.05 \text{ mol/dm}^3$ ) was used for measuring the electron pulse dose. For this purpose the  $(\text{CNS})_2^-$  species having  $G\epsilon = 2.23 \times 10^{-4} \text{ m}^2/\text{J}$

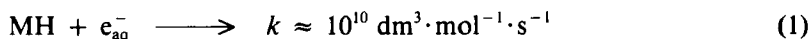
[13], formed due to oxidation of  $\text{CNS}^-$  by OH radical, was monitored at 500 nm.

## RESULTS AND DISCUSSIONS

In the pulse radiolysis of dilute aqueous monomer solutions, the primary species from water radiolysis (i.e., hydrated electron, hydroxyl radical, and hydrogen atom) play an important role. Initiating species are produced by the reactions of these primary species with the monomer, and these resultant species subsequently propagate polymerization with different rates depending upon their structure and experimental conditions. Kinetic studies and characterization of the transient species formed by the reactions of hydrated electrons and hydroxyl radicals with the monomer 3,3-dimethylacrylic acid were carried out in the present work.

### Reaction of Hydrated Electron with 3,3-Dimethylacrylic Acid

The transient absorption spectra observed on pulse radiolysis of  $\text{N}_2$ -saturated aqueous solution containing  $1.1 \times 10^{-3} \text{ mol/dm}^3$  3,3-dimethylacrylic acid and  $0.4 \text{ mol/dm}^3$  *t*-butanol at three different pH's (i.e., 3.7, 9.2, and 12) are shown in Fig. 1. The transient spectrum at pH 3.7 was found to have  $\lambda_{\text{max}}$  at 260 nm with an extinction coefficient of  $\sim 410 \text{ m}^2/\text{mol}$  calculated by taking into consideration the competing reaction of an  $\text{e}_{\text{aq}}^-$  with a proton. The rate constant for the reaction of  $\text{e}_{\text{aq}}^-$  with the acidic form of the monomer 3,3-dimethylacrylic acid (MH) was determined from the pseudofirst-order formation kinetics of the transient at 260 nm with respect to the monomer concentration.



The spectrum at pH 9.2 was found to have  $\lambda_{\text{max}}$  at 270 nm with an extinction coefficient value of  $404 \text{ m}^2/\text{mol}$ . Formation kinetics of this transient species was also found to be pseudofirst order with respect to the monomer concentration, and the rate constant for the reaction of  $\text{e}_{\text{aq}}^-$  with the conjugate-base form of the monomer ( $\text{M}^-$ ) was determined (see Reaction 2); this value is in agreement with that obtained ( $6.4 \times 10^8 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) by decay kinetics of the hydrated electron at 700 nm in the presence of the monomer.

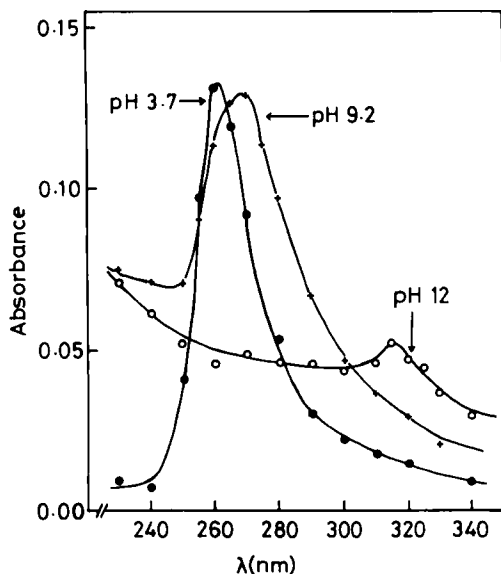
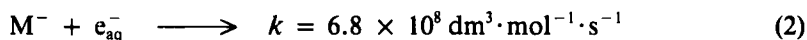


FIG. 1. Transient absorption spectra produced by the reaction of  $e_{aq}^-$  with  $1.1 \times 10^{-3}$  mol/dm<sup>3</sup> 3,3-dimethylacrylic acid at three different pH's in 0.4 mol/dm<sup>3</sup> aqueous *t*-butanol under 1 atm of N<sub>2</sub>. Dose:  $\sim 1.1 \times 10^5$  J/m<sup>3</sup> per pulse.



The transient species formed at pH 12 was found to have  $\lambda_{\text{max}}$  at 315 nm with a relatively lower extinction coefficient value of  $\sim 141$  m<sup>2</sup>/mol. Thus the rate constant for the reaction of the conjugate-acid form of the monomer with  $e_{aq}^-$  is much higher than that of the conjugate-base form. The transient species formed by the reaction of  $e_{aq}^-$  with the monomer showed a  $pK_a$  of 7.6 as determined by measuring changes in absorbance at 270 nm with pH (Fig. 2). A significant change in absorbance was also observed at higher pH's, which may or may not be due to a change in  $pK_a$ . The ground state  $pK_a$  of the monomer was found to be 5.1.

At low dose and high monomer concentration ( $0.53 \times 10^{-3}$  to  $1.6 \times 10^{-3}$  mol/dm<sup>3</sup>) at pH 3.7, the decay of the product species at 260 nm was found to be pseudofirst order with respect to the monomer concentration, whereas at a higher dose condition and at a monomer concentration of  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup>, the decay followed second-order kinetics. These two decays are suggestive of an initial propagation step

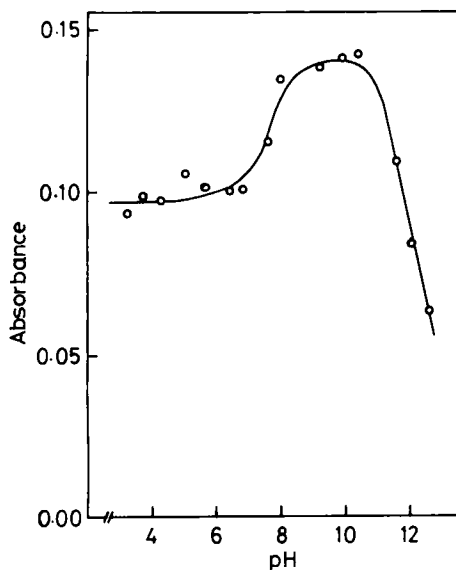
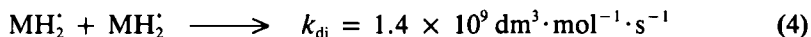
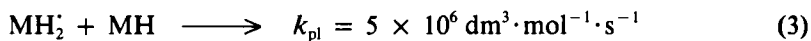
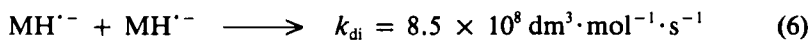
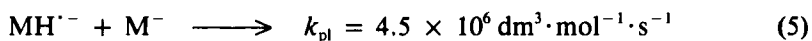


FIG. 2. Change in absorbance of pH for the transient species produced by the reaction of  $e_{aq}^-$  with  $1.1 \times 10^{-3} \text{ mol/dm}^3$  3,3-dimethylacrylic acid and in  $0.4 \text{ mol/dm}^3$  aqueous *t*-butanol at 270 nm under 1 atm of  $N_2$ . Dose:  $\sim 1.1 \times 10^5 \text{ J/m}^3$  per pulse.

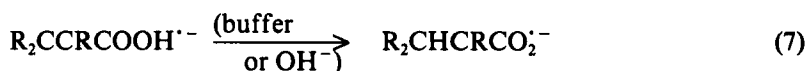
(Reaction 3) and a dimerization step (Reaction 4) of the protonated electron adduct species ( $MH_2^-$ ).



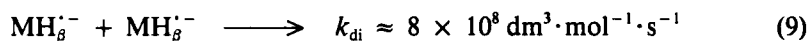
At pH 9.2 the decay of the product species at 270 nm was also found to follow pseudofirst-order kinetics with respect to the monomer concentration at low dose and high monomer concentration and second-order kinetics at high dose and low monomer concentration condition, as in the case of  $MH_2^-$  species. Thus these two decays are assigned to the first propagation step (Reaction 5) and dimerization step (Reaction 6) of protonated electron adduct species ( $MH^{\cdot-}$ ) as given below.



At pH 12, the decay of the resultant transient at 315 nm also showed pseudofirst-order and second-order kinetic behavior under two different dose and monomer concentration conditions as shown above. It is well known that in alkaline conditions the electron adducts (with a single negative charge) of acrylic acid and its derivatives isomerize into the corresponding  $\beta$ -protonated isomer:



This reaction is much faster than deprotonation [7]. Thus the two decay kinetics mentioned above (at pH 12) can be assigned to the first propagation step (Reaction 8) and dimerization step (Reaction 9) of the  $\beta$ -protonated electron adduct species ( $\text{MH}_\beta^{\cdot-}$ ):



It can be concluded from the above results that in the case of different forms of the hydrated electron adduct of the monomer, the dimerization step, which is equivalent to the termination step, is about two orders of magnitude faster than the first propagation step. Rate constants for the first propagation step of  $\text{MH}_2^{\cdot-}$  and  $\text{MH}^{\cdot-}$  are comparable but the  $\beta$ -protonated electron adduct ( $\text{MH}_\beta^{\cdot-}$ ) propagates much faster. Dimerization of radical species ( $\text{MH}_2^{\cdot-}$ ) is much faster than that of anionic species  $\text{MH}^{\cdot-}$  and  $\text{MH}_\beta^{\cdot-}$ , which can be explained on the basis of the electronic structure of these transient species.

### Reaction of Hydroxyl Radical with 3,3-Dimethylacrylic Acid

The transient absorption spectra observed on pulse radiolysis of  $\text{N}_2\text{O}$  saturated aqueous ( $1.5 \times 10^{-2} \text{ mol/dm}^3$ ) monomer solutions at three different pH's (i.e., 3.7, 9.2, and 12) are shown in Fig. 3. The transient spectrum at pH 3.7 was found to have  $\lambda_{\text{max}}$  at 270 nm with an extinction coefficient of  $164 \text{ m}^2/\text{mol}$ . From the formation kinetics (pseudofirst order with respect to the monomer concentration) of the transient species at  $\lambda_{\text{max}}$ , the rate constant for the reaction of OH radical with the conjugated-acid form of 3,3-dimethylacrylic acid (MH) was determined.

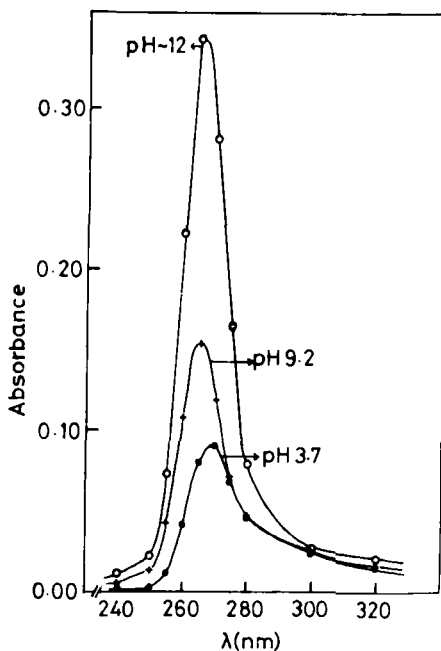
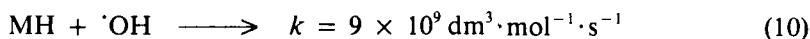


FIG. 3. Transient absorption spectra produced by the reaction of OH radical with  $1.5 \times 10^{-3}$  mol/dm<sup>3</sup> 3,3-dimethylacrylic acid at three different pH's in aqueous medium under 1 atm of N<sub>2</sub>O. Dose:  $\sim 1.1 \times 10^5$  J/m<sup>3</sup> per pulse.

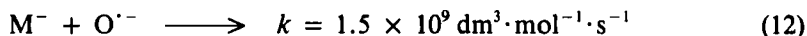


The spectra at both pH 9.2 and 12 were found to have  $\lambda_{\text{max}}$  at 265 nm with extinction coefficient values of 281 and 598 m<sup>2</sup>/mol, respectively. Formation kinetics of the transient species at pH 9.2 at 265 nm was also found to be pseudofirst order with respect to the monomer concentration, and the rate constant for the reaction of OH radical with the conjugate-base form of the monomer (M<sup>-</sup>) was determined as given below in Reaction (11). This value compares well with that obtained by competition kinetics ( $6.0 \times 10^9$  dm<sup>3</sup>·mol<sup>-1</sup>·s<sup>-1</sup>) using KSCN as standard solute and monitoring the (CNS)<sub>2</sub><sup>-</sup> species formed at 500 nm.



The pseudofirst-order formation kinetics of the transient species at pH 12 at 265 nm gave a rate constant for the reaction of M<sup>-</sup> with O<sup>·-</sup>:





Thus the initiation reaction of the conjugate-acid form of the monomer with OH radical is faster than that of the conjugate-base form, and initiation by  $O^{\cdot-}$  is much slower.

The transient species formed by the reaction of OH radical with the monomer showed a  $pK_a$  value of 6.3 as determined by measuring absorbance changes as a function of pH at 265 nm (Fig. 4). There is an enormous change in absorbance in the pH region between 11 to 12.5, which may be attributed to the fact that  $O^{\cdot-}$  is the reacting species instead of the OH radical at lower pH. Since, except for difference in extinction

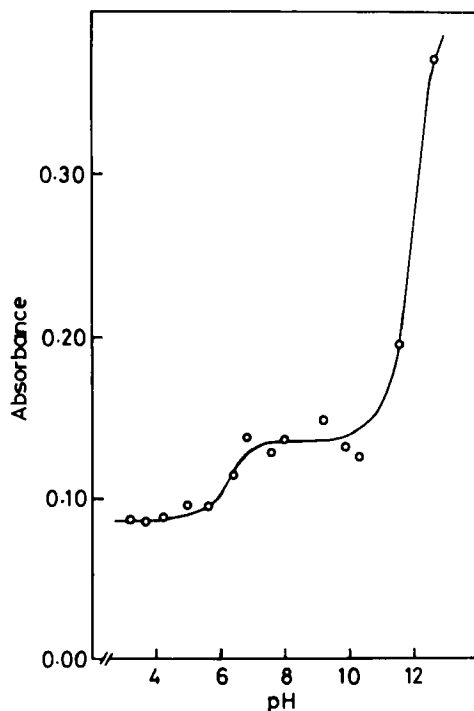
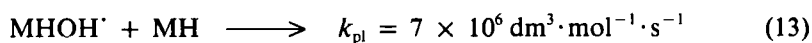


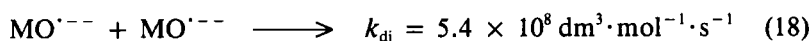
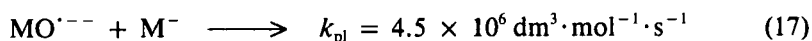
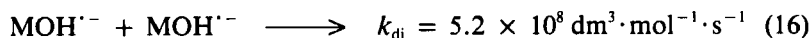
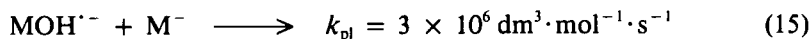
FIG. 4. Change in absorbance with pH for the transient species produced by the reaction of OH radical with  $1.5 \times 10^{-3} \text{ mol/dm}^3$  3,3-dimethylacrylic acid in aqueous medium at 265 nm under 1 atm of  $N_2O$ . Dose:  $\sim 1.1 \times 10^5 \text{ J/m}^3$  per pulse.

coefficient, the spectral characteristics of the two transient species at pH 12 and 9.2 are similar, they are expected to have a similar structure.

At pH 3.7 the decay of the resultant species at 270 nm was found to be pseudofirst-order with respect to the monomer concentration at low dose and high monomer concentration ( $0.5 \times 10^{-3}$  to  $1.5 \times 10^{-3}$  mol/dm<sup>3</sup>). On the other hand, at the higher dose and lower monomer concentration ( $\sim 0.8 \times 10^{-4}$  mol/dm<sup>3</sup>) conditions, the decay followed second-order kinetics. These observations are suggestive of a first propagation step (Reaction 13) and a dimerization step (Reaction 14) of the OH radical adduct species (MHOH<sup>•</sup>) of protonated monomer.



At pH 9.2 and 12, the decay of the product species at 265 nm was also found to follow pseudofirst-order kinetics with respect to the monomer concentration at the low dose and high monomer concentration ( $1.5 \times 10^{-3}$  to  $4.5 \times 10^{-3}$  mol/dm<sup>3</sup>) condition, and second-order kinetics at the high dose and low concentration ( $\sim 2.0 \times 10^{-4}$  mol/dm<sup>3</sup>) as discussed above. Thus these decays are assigned to the first propagation steps (Reactions 15 and 17) and dimerization steps (Reactions 16 and 18) of monoprotonated species (MOH<sup>•-</sup>) and species (MO<sup>•--</sup>) formed by the reaction of O<sup>•-</sup>:

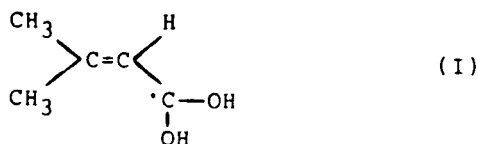


Here also for different forms of the OH radical adduct of 3,3-dimethylacrylic acid, the dimerization step is about two orders of magnitude faster than the first propagation step. The rate constant for the first propagation step of MHOH<sup>•</sup> species is higher than that of MOH<sup>•-</sup> and MO<sup>•--</sup> species. Reaction of a radical species with neutral monomer (protonated form) is expected to be faster than reaction of a radical-anionic or -dianionic species with the anionic form of the monomer. The

dimerization step of  $\text{MHOH}^\cdot$  is also faster than that of the other two species, i.e.,  $\text{MOH}^{\cdot-}$  and  $\text{M}^{\cdot-}$ , which may be explained on the basis of the combined influence of ionic strength and electronic structure of these transient species.

### Probable Structures of the Transient Species

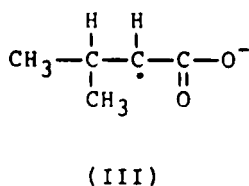
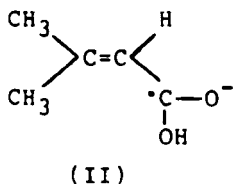
Most probable site of attack by  $e_{\text{aq}}^-$  is the carbonyl group of the monomer [14], resulting in the following structure for the protonated electron adduct ( $\text{MH}_2^\cdot$ ) of 3,3-dimethylacrylic acid.



Pulse radiolysis of an  $\text{N}_2$ -purged aqueous solution containing  $5.0 \times 10^{-3}$  mol/dm<sup>3</sup> of the monomer,  $\sim 10^{-5}$  mol/dm<sup>3</sup> of reducible dye thionine, and  $\sim 1.0$  mol/dm<sup>3</sup> *t*-butanol at pH 6 was carried out in order to determine whether the  $\text{MH}_2^\cdot$  species is capable of acting as a reducing agent. The conditions chosen were such that almost all the  $e_{\text{aq}}^-$  produced by the pulse reacted with the monomer and not with the dye molecules; the resultant transient ( $\text{MH}_2^\cdot$ ) should react with thionine almost exclusively. Formation of the reduced dye was monitored at 770 nm, and it was found that the transient ( $\text{MH}_2^\cdot$ ) is capable of reducing thionine ( $\text{TH}^+$ ):

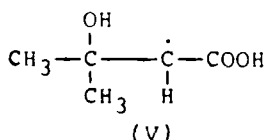
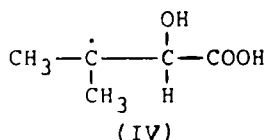


Hence, Structure (I) may be most probably assigned to the  $\text{MH}_2^\cdot$  species, since this is similar to the radical derived by the  $\alpha$ -hydrogen abstraction from alcohols, which are known to be reducing in nature [15], the only difference being the presence of two hydroxyl groups in place of one. The structures of the protonated electron adduct ( $\text{MH}^{\cdot-}$ ) may be written as Structure (II) or the  $\beta$ -protonated isomer ( $\text{MH}_\beta^{\cdot-}$ ):

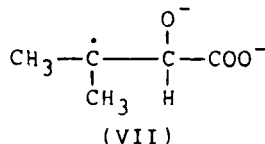
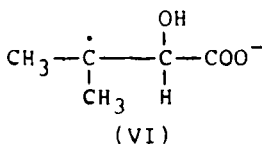


The most probable reaction of OH radical with the monomer is addi-

tion to the C—C double bond. The two possible structures that can be assigned to the OH radical adduct species (MHOH') are



It was found that, under our experimental conditions, e.g., N<sub>2</sub>O-saturated 1.0 × 10<sup>-3</sup> mol/dm<sup>3</sup> monomer aqueous solution containing 3.0 × 10<sup>-5</sup> mol/dm<sup>3</sup> thionine at pH 7.6, where the reaction of the OH radical with the monomer and the reaction of the resulting adduct species (MOH'⁻) with thionine are favored over other competing reactions, the transient species (MOH'⁻) cannot reduce thionine. Both of the above structures seem to be less reducing in nature, but very little can be inferred from this information regarding the structure of the transient species. Since tertiary carbon-centered radicals are known to be more stable than secondary carbon-centered radicals, and the attack of an OH radical at the α-carbon atom is sterically favored, Structure (IV) is more probable than Structure (V) for the species (MHOH'). The corresponding structures of the adduct species (MOH'⁻) and unprotonated species (MO''⁻) can be expressed as Structures (VI) and (VII), respectively.



## CONCLUSIONS

Rate constants of the different initiation, first propagation, and dimerization steps are summarized in Table 1. Rate constants for the initiation reactions by e<sub>aq</sub><sup>-</sup> and OH radicals with protonated 3,3-dimethylacrylic acid monomer in aqueous solution are much higher than those of the corresponding deprotonated form. The dimerization step is about two orders of magnitude faster than the first propagation step, and the dimerization step of radical species is faster than that of corresponding anionic species resulting from the reaction of e<sub>aq</sub><sup>-</sup> and OH radical with the monomer. The first propagation step of the β-protonated electron

TABLE 1. Rate Constants of the Initial Processes of 3,3-Dimethylacrylic Acid in Aqueous Medium, Induced by Hydrated Electron and Hydroxyl Radical<sup>a</sup>

Initiation step ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )	First propagation step ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )	Dimerization step ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
$k < \text{MH} > \approx 10^{10}$	$k_{\text{pi}} < \text{MH}_2 > = 5 \times 10^6$	$k_{\text{di}} < \text{MH}_2 > = 1.4 \times 10^9$
$k < \text{M}^- > = 6.8 \times 10^8$	$k_{\text{pi}} < \text{MH}^{\cdot -} > = 4.5 \times 10^6$	$k_{\text{di}} < \text{MH}^{\cdot -} > = 8.5 \times 10^8$
	$k_{\text{pi}} < \text{MH}_\beta^{\cdot -} > \approx 1 \times 10^7$	$k_{\text{di}} < \text{MH}_\beta^{\cdot -} > \approx 8 \times 10^8$
<u>For Reactions Induced by <math>e_{\text{aq}}^-</math></u>		
	<u>For Reactions Induced by <math>\text{OH}^\cdot</math></u>	
$k < \text{MH} > = 9 \times 10^9$	$k_{\text{pi}} < \text{MHOH}^\cdot > = 7 \times 10^6$	$k_{\text{di}} < \text{MOH}^\cdot > = 1.1 \times 10^9$
$k < \text{M}^- > = 5.7 \times 10^9$	$k_{\text{pi}} < \text{MOH}^{\cdot -} > = 3 \times 10^6$	$k_{\text{di}} < \text{MOH}^{\cdot -} > = 5.2 \times 10^8$
	$k_{\text{pi}} < \text{MO}^{\cdot - -} > = 4.5 \times 10^6$	$k_{\text{di}} < \text{MO}^{\cdot - -} > = 5.4 \times 10^8$

<sup>a</sup>Where MH is the conjugate-acid form of the monomer,  $\text{M}^-$  is the conjugate-base form,  $\text{MH}_2$  is the protonated electron adduct,  $\text{MH}^{\cdot -}$  is the conjugate-base form of  $\text{MH}_2$ ,  $\text{MH}_\beta^{\cdot -}$  is the  $\beta$ -protonated electron adduct,  $\text{MHOH}^\cdot$  is the OH radical adduct,  $\text{MOH}^{\cdot -}$  is the monoprotonated form, and  $\text{MO}^{\cdot - -}$  is the deprotonated form.

adducts is faster than other electron adduct species, and the rate constant for the first propagation step of radical species is faster than that of other OH radical adduct species (i.e., anionic species). All these observations are correlated with structure, electronic nature of different transient species, and influence of ionic strength. The most probable site of attack by  $e_{aq}^-$  is the carbonyl group of the monomer, resulting in a carbon-centered radical species capable of reducing thionine. On the other hand, OH radical addition of the C—C double bond of the monomer results in a tertiary radical.

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