

PULSE RADIOLYSIS STUDY OF 2-MERCAPTO-BENZOTHAZOLE--A CORROSION INHIBITOR

H.S. MAHAL, T. MUKHERJEE* and J.P. MITTAL

Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received 14 October 1996; accepted 2 April 1997

Abstract--Pulse radiolysis of 2-Mercaptobenzothiazole (2-MBT) has been undertaken in aqueous solution. The semi-oxidized species formed at pH 4.5 due to the reaction of OH^\bullet , $\text{Br}_2^{\bullet-}$ and N_3^\bullet and at pH 10.5 with OH^\bullet yielded a spectrum with $\lambda_{\text{max}} = 348$ and 595 nm. These semi-oxidized species were able to oxidize phenothiazine drugs ($E^\circ \approx 0.8$ V). Reducing species such as e_{aq}^- , $\text{CO}_2^{\bullet-}$ and H^\bullet atoms react with 2-MBT resulting in the formation of a transient having $\lambda_{\text{max}} = 350$ nm and reducing in nature. Kinetic and spectroscopic data of interest are reported.

INTRODUCTION

Use of inhibitors in minimizing corrosion of metals has attracted a lot of interest [1-3]. The use of certain heterocyclic compounds as corrosion inhibitors is well known [4-6]. Although the mechanism of action of such inhibitors is far from being understood surface adsorption properties seem to be most widely accepted for explaining their mode of action [7].

Several types of organic inhibitors have been tested and some of these compounds have found use in the chemical formulations developed for decontamination of nuclear power plants [8-10]. During their exposure to highly radioactive environment, there are likely to undergo degradation, resulting in loss of the inhibitor [9,11]. It is therefore of interest to study the radiation chemistry of these compounds.

Studies on the transients formed during one-electron oxidation and reduction reactions of benzotriazole [12] and 2-mercaptobenzimidazole [13] in aqueous solutions have been reported earlier. The semi-oxidized and semi-reduced species of benzotriazole were shown to form intramolecular three-electron bonded species. However, during pulse radiolysis studies of 2-mercaptothiazoline [14] we have no evidence to show the formation of intramolecular three electron bonded species. Gamma radiolysis of 2-mercaptobenzothiazole (2-MBT), another corrosion inhibitor and an analogue of 2-mercaptothiazoline has been studied by Jayson *et al.* [8].

These authors have identified some of the products of radiolysis and shown that the decomposition of this inhibitor was negligible in the post-irradiated samples under oxygen-free conditions and at near neutral pH. However, the basic reaction mechanism is still not well understood.

In the present paper we have attempted to study the formation and characteristics of some of the intermediate species formed by the reactions of various oxidizing (OH^\bullet , N_3^\bullet , $\text{Br}_2^{\bullet-}$) and reducing (e_{aq}^- , H^\bullet , $\text{CO}_2^{\bullet-}$) species in aqueous media using pulse radiolysis technique. Results show the formation of resonance stabilized structures on reaction with various one-electron oxidants as observed during studies with 2-MT [14].

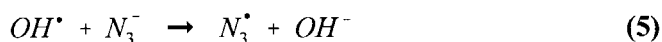
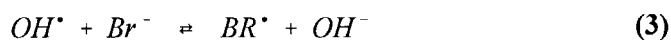
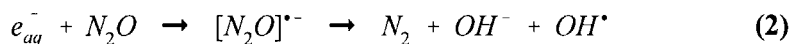
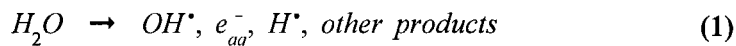
EXPERIMENTAL

2-Mercaptobenzothiazole was obtained from Fluka. All other chemicals were of AnalaR grade or equivalent. Pulse radiolysis experiments were undertaken with a 7 MeV linear electron accelerator (Forward Industries, formerly Ray Technologies, UK.) delivering 50 ns pulses. Details of the pulse radiolysis set-up has been given elsewhere [15]. A dose rate of ~ 12 Gy/pulse was used as determined by KSCN dosimetry, $G\epsilon = 21,520 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per 100 eV at 500 nm [16]. All solutions were prepared in phosphate buffer just before experimentation using water from Barnstead Nanopure water filtering assembly, having a sp. conductivity of $< 0.1 \mu\text{S cm}^{-1}$. pH was adjusted using either dilute HClO_4 or NaOH . IOLAR grade N_2 or N_2O gases (Indian Oxygen Ltd.) were used to purge the samples prior to pulsing. A Hitachi 330 spectrophotometer was used to obtain the ground state absorption spectra of 2-MBT.

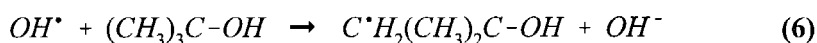
Cyclic voltammetric experiments were performed using model 173 controlled potential polarograph along with model 175 universal programmer and a recorder (Princeton Instruments Co. NJ.), coupled to a three electrode system consisting of a dropping mercury electrode, a standard Ag/AgCl reference electrode and a platinum counter electrode. Measurement of the voltammogram was performed at 25°C in N_2 -saturated solution containing 0.2 mol dm^{-3} KCl , $5 \times 10^{-4} \text{ mol dm}^{-3}$ 2-MBT, $1 \times 10^{-3} \text{ mol dm}^{-3}$ phosphate buffer, adjusted to a pH 4.1 ± 0.1 by adding dilute acid. The scan rate was 100 mV s^{-1} .

Pulse radiolysis of water results in the generation of OH^\bullet , e_{aq}^- and H^\bullet (reaction 1). In N_2O -saturated aqueous solutions the OH^\bullet radicals formed directly as well as due to scavenging of e_{aq}^- by N_2O , result in an overall yield of OH^\bullet radicals to be $\sim 90\%$ of the total radicals formed. Generations of various other inorganic one-electron oxidants ($\text{Br}_2^{\bullet-}$, N_3^\bullet) was achieved by pulsing the above solutions in the additional presence of $5 \times 10^{-2} \text{ mol dm}^{-3}$ of bromide or azide ions. Reactions 2-5

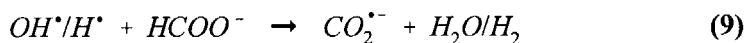
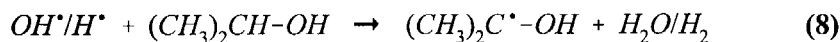
predominate.



Radiolysis of N_2 -bubbled aqueous solution containing 1 mol dm^{-3} *t*-butanol under neutral and acidic conditions results in the formation of e_{aq}^- and H^\bullet radicals respectively due to scavenging of the OH^\bullet radical by *t*-butanol. Reactions 1, 6 and 7 predominate.



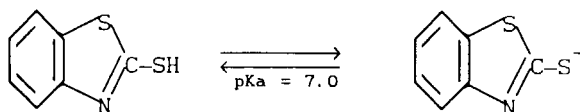
Other reducing radicals (acetone ketyl radical and $CO_2^{\bullet -}$ radical) were generated according to reactions 8 and 9 in N_2O -saturated solutions.



RESULTS AND DISCUSSION

UV-Visible Absorption Spectra and pK_a Values

The UV-vis. absorption spectra of 2-MBT showed absorption bands at 205, 235 and 315 nm and the pK_a value of 7.0 was determined by plotting change in absorbance as a function of pH.



Reactivity of OH^\bullet Radicals with 2-MBT

Reaction of OH^\bullet radicals with 2-MBT ($pK_a = 7.0$) were studied in aqueous solutions at pH 5 and 10.5. Time-resolved transient absorption spectra obtained on pulse radiolysis of a N_2O -saturated 5×10^{-4} mol dm^{-3} solution of 2-MBT (Figures 1 and 2) showed two strong absorption bands with $\lambda_{max} = 348$ and 595 nm. Their respective extinction coefficients at the above two pHs are given in Table 1. A third weak band with $\lambda_{max} = 391$ nm was also observed. These spectra are uncorrected for any

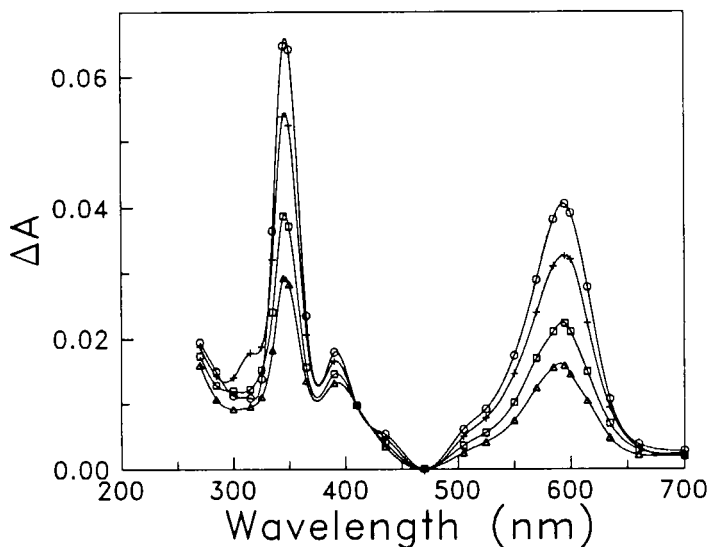


Figure 1. Time resolved absorption spectra of the transient species formed by the OH^\bullet radical reaction with (5×10^{-4} mol dm^{-3}) 2-MBT in N_2O -saturated aqueous solution, pH 5.0 at (○) 1 μs , (+) 5 μs , (□) 15 μs , and (-) 30 μs after the electron pulse. (Dose ~ 12 Gy/pulse).

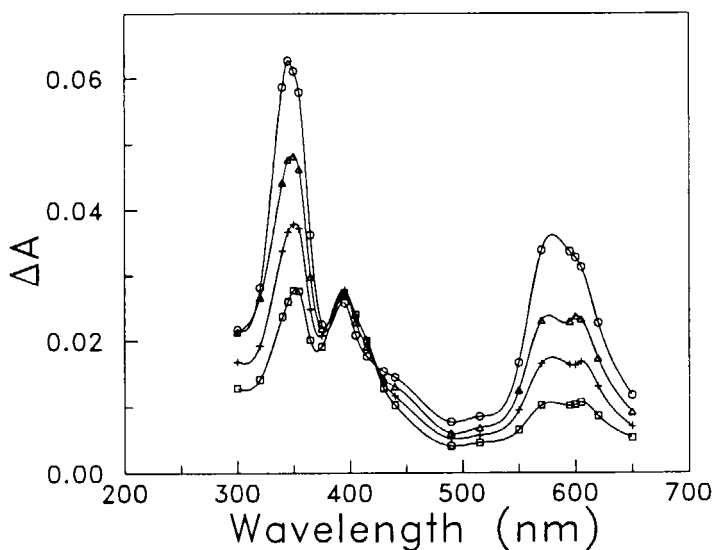


Figure 2. Time resolved absorption spectra of the transient species formed by the OH^\bullet radical reaction with $(5 \times 10^{-4} \text{ mol dm}^{-3})$ 2-MBT in N_2O -saturated aqueous solution, pH 10.5 at (O) 1 μs , (Δ) 10 μs , (+) 15 μs , and (\square) 30 μs , after the electron pulse. (Dose $\sim 12 \text{ Gy/pulse}$).

Table 1

Spectral and kinetic properties of the transients formed in aqueous solutions in the reaction of various one-electron oxidants with 2-MBT at different pHs.

Reactions	pH	λ_{max} (nm)	$\epsilon_{\lambda_{\text{max}}} \pm 200$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$k \times 10^{-9}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$2k \times 10^{-9}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
$\text{OH}^\bullet + 2\text{-MBT}$	5	348	8,350	14.5	9.0
$\text{OH}^\bullet + 2\text{-MBT}$	5	595	5,230	14.5	9.0
$\text{OH}^\bullet + 2\text{-MBT}$	10.5	348	8,050	18.0	9.6
$\text{OH}^\bullet + 2\text{-MBT}$	10.5	585	4,350	17.3	-
$\text{Br}_2^{\bullet-} + 2\text{-MBT}$	5	348	9,900	a	a
$\text{Br}_2^{\bullet-} + 2\text{-MBT}$	5	595	7,150	10.0	7.6
$\text{N}_3^{\bullet} + 2\text{-MBT}$	5	348	8,100	7.5	5.0
$\text{N}_3^{\bullet} + 2\text{-MBT}$	5	595	5,400	7.5	5.0

a: Could not be determined as $\text{Br}_2^{\bullet-}$ has a strong absorption at this wavelength.

contribution in absorption from either the parent molecule or from a H-adduct formed by the reaction of H^\bullet atom with 2-MBT. Figures 1 and 2 show that the absorption decreased with time without the formation of any new band. It was

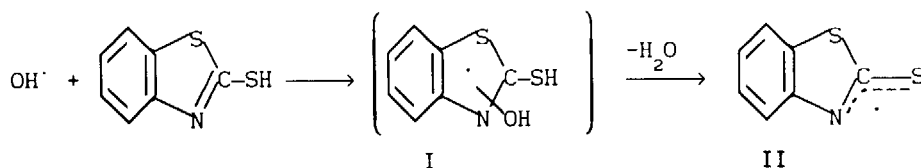
concluded that the transient decayed to form some stable product. Also, the spectral characteristics at both the pHs remained essentially identical except that, there was a slight reduction in the absorption at 595 nm for 2-MBT solutions at pH 10.5.

An analysis of the decay rates for the transient absorption at 348 and 595 nm, showed that the species decayed by second order kinetics at both the wavelengths with ($2k = 9 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$).

The formation rate constants for the OH^\bullet radical reaction with 2-MBT at pH 5 were determined by following the build-up kinetics at 348 and 595 nm for solute concentrations in the range $0.5\text{--}5 \times 10^{-5} \text{ mol dm}^{-3}$ and were seen to be identical, with $k = 1.45 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ whereas at pH 10.5 $k_{(\text{OH}^\bullet + 2\text{MBT})} = 1.8 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Since the extent of reduction in the optical density values at 348 and 595 nm as seen from the time resolved spectra is the same and the decay rates at both the above wavelengths are also the same, it can be concluded that the absorption at the two wavelengths is due to the same species. Similar observation has been made in the case of 2-mercaptobenzimidazole [13] which bears structural resemblance to 2-MBT. These authors have reported the formation of two transient absorption bands with $\lambda_{\text{max}} = 330$ and 590 nm, which is fairly close to that observed in the present study.

The most probable reaction mechanism for the OH^\bullet radical reaction with 2-MBT could be due to either (i) H-atom abstraction from -SH group or (ii) due to OH^\bullet addition at the double bond site in 2-MBT followed by elimination of water to give the resonance-stabilized radical (II) having an unpaired electron which remains delocalized over the S-C-N region of the radical (II). Since abstraction reactions are generally slow $k \leq 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ the first possibility is ruled out. Hence, the reaction takes place according to Scheme 1 below.



Scheme 1

Reactivity of $\text{Br}_2^{\bullet-}$ with 2-MBT

Time-resolved transient absorption spectra obtained by the reaction of $\text{Br}_2^{\bullet-}$ with 2-MBT on pulse-irradiating an N_2O -saturated solution containing $5 \times 10^{-4} \text{ mol dm}^{-3}$ of 2-MBT and $2 \times 10^{-2} \text{ mol dm}^{-3}$ potassium bromide at a solution pH = 5 showed two main absorption bands with $\lambda_{\text{max}} = 348$ and 595 nm with a small shoulder at ~ 391

nm (Figure 3). Since both OH^\bullet and to a lesser extent $\text{Br}_2^{\bullet-}$ are known to undergo additional reactions with the substrate molecules having double bonds, it is likely that the small band with $\lambda_{\text{max}} \sim 391$ nm as observed during OH^\bullet and $\text{Br}_2^{\bullet-}$ radical reactions with 2-MBT is due to the formation of an adduct with 2-MBT. The presence of a small shoulder at 391 nm (Figure 3) indicates that the formation of $\text{Br}_2^{\bullet-}$ radical adduct occurs to a lesser extent than that seen during the reaction of OH^\bullet radicals with 2-MBT.

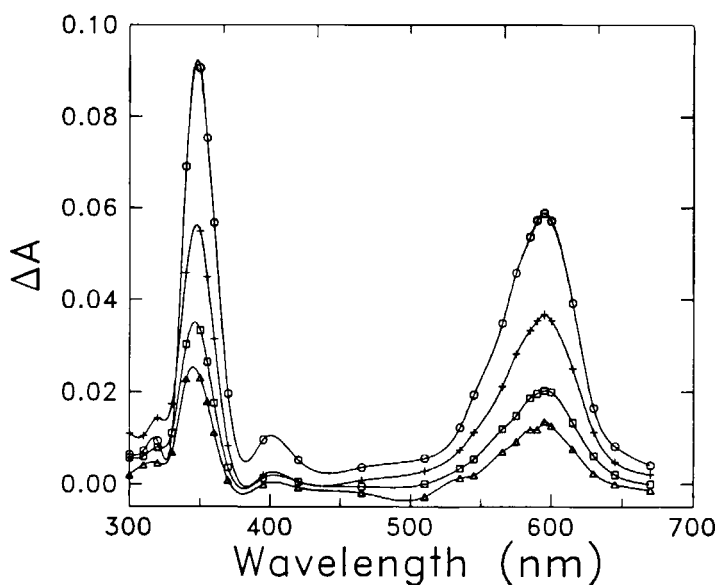


Figure 3. Time resolved absorption spectra of the transient species formed by the reaction of $\text{Br}_2^{\bullet-}$ radicals with 2-MBT, pH 5 measured at (O) 1 μs , (+) 15 μs , (\square) 70 μs , and (-) 120 μs , after the electron pulse. Matrix: N_2O -saturated aqueous solution, containing (5×10^{-4} mol dm^{-3}) 2-MBT and (5×10^{-2} mol dm^{-3}) KBr. (Dose ~ 12 Gy/pulse).

In the case of reaction of the azide radicals, (N_3^\bullet selectively undergoes only electron transfer reactions with solutes) with 2-MBT, no absorbance was seen at ~ 391 nm. The same Figure 3 also shows that there is a proportional reduction in the absorbance with time at these wavelengths without the formation of any new species, indicating that only one transient is formed by $\text{Br}_2^{\bullet-}$ radical reaction. These observations are quite similar to the one seen during OH^\bullet radical reaction with 2-MBT.

Since, $\text{Br}_2^{\bullet-}$ has a very strong absorbance at ~ 350 nm, the value of 'k' was determined only at 595 nm while determining the rate constant for $\text{Br}_2^{\bullet-}$ radical

reaction with 2-MBT and was found to be $k = 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 3.2). The transient decayed by second order kinetics with $2k = 7.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Reactivity of Azide Radicals with 2-MBT

Figure 4 shows the time-resolved transient spectra obtained by the reaction of N_3^\bullet radicals with 2-MBT on pulse irradiating a N_2O -saturated aqueous solution of 2-MBT ($5 \times 10^{-4} \text{ mol dm}^{-3}$) containing $2 \times 10^{-2} \text{ mol dm}^{-3}$ of sodium azide at pH 5. Two absorption bands with $\lambda_{\text{max}} = 348 \text{ nm}$ and 595 nm [$\epsilon_{348\text{nm}} = 8,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{595\text{nm}} = 5,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$] were observed in the case of OH^\bullet radical reaction with 2-MBT. It was also seen that the optical density of the species formed at these

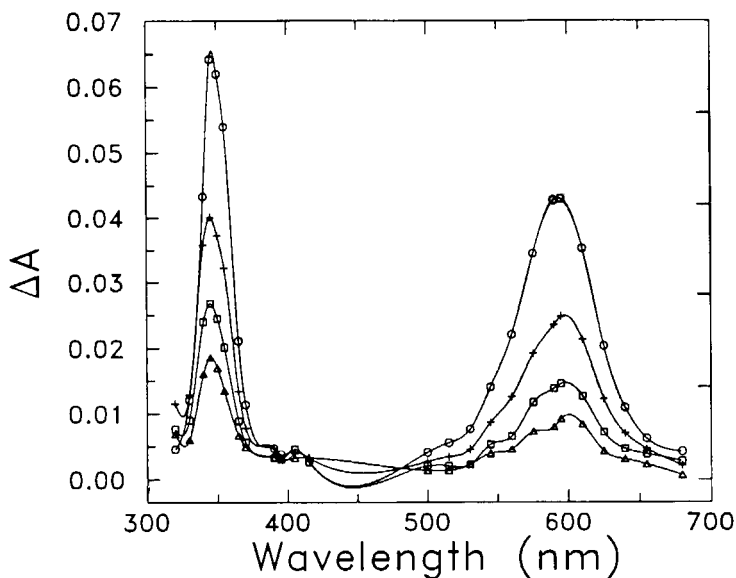
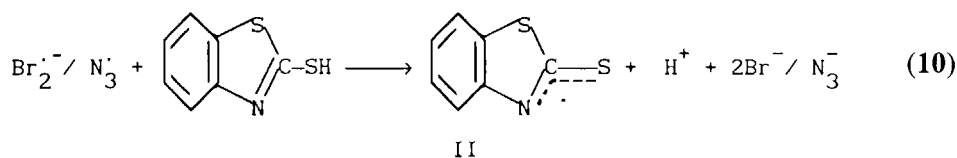


Figure 4. Time resolved absorption spectra of the transient species formed by the reaction of N_3^\bullet radicals with 2-MBT, pH 5 measured at (O) 10 μs , (+) 35 μs , (\square) 70 μs , and (-) 120 μs , after the electron pulse. Matrix: N_2O -saturated aqueous solution, containing ($5 \times 10^{-4} \text{ mol dm}^{-3}$) 2-MBT and ($5 \times 10^{-2} \text{ mol dm}^{-3}$) NaN_3 . (Dose $\sim 12 \text{ Gy/pulse}$).

two wavelengths reduced with time to the same extent without the formation of any new species. These observations are in line with the results obtained from OH^\bullet and Br_2^\bullet radical reactions with the inhibitors. Thus, the transient formed in the reaction of various oxidizing radicals with 2-MBT is the same (Eq. (10)).



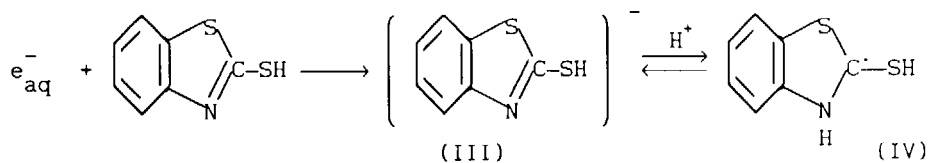
The transient species formed as mentioned above, decayed by second order kinetics with $2k \approx 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at both the wavelengths with the formation of species of the type R_2S_2 . This species has also been observed by Jayson *et al.* [8].

The reaction rate constant of the azide radical with 2-MBT were determined by following the build-up kinetics at 348 and 595 nm at various solute concentrations. The value of 'k' was identical ($k = 7.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

Table 1 gives the salient details on the kinetic and spectroscopic data of interest evolved during the reaction of one-electron oxidation of 2-MBT with some oxidizing radicals ($\text{Br}_2^{\cdot-}$, OH^{\cdot} , N_3^{\cdot}).

Reactivity of the Reducing Radicals with 2-MBT

Reactivity of e_{aq}^- Time-resolved transient absorption spectrum of the semi-reduced species derived on pulsing N_2 -bubbled aqueous solution of ($1 \times 10^{-3} \text{ mol dm}^{-3}$) 2-MBT containing *t*-butanol at pH 5 is shown in Figure 5. The spectrum is uncorrected for any contribution in absorption due to the H-adduct formation which also absorbs at the same wavelength as shown later. At pH 10.5 the spectrum was similar to that obtained at pH 5. The appearance of λ_{max} at 350 nm as a consequence of e_{aq}^- reaction with 2-MBT at pH 5 and 10.5 is due to the formation of an e_{aq}^- adduct with the substrate (Scheme 2).



Scheme 2

At lower pHs, it is likely that the electron adduct (III) formed undergoes fast protonation to form a neutral radical (IV) which is responsible for the observed

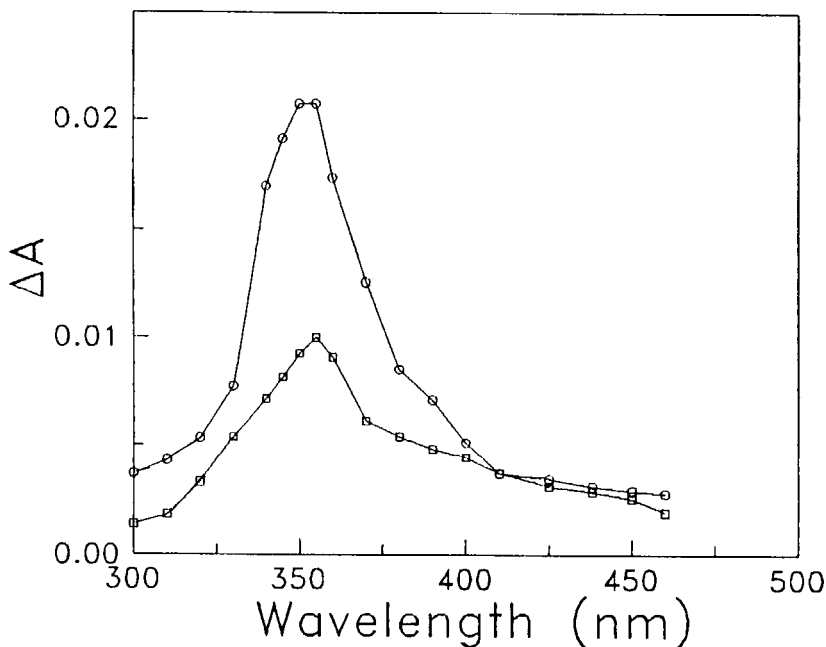


Figure 5. Time resolved absorption spectra of the semi-reduced species formed due to reaction of e_{aq}^- with 2-MBT on pulse radiolysis of aqueous solution containing ($1 \times 10^{-3} \text{ mol dm}^{-3}$) 2-MBT, 0.5 mol dm^{-3} *t*-butanol N_2 -bubbled, pH 5.0 at (O) 3 μs , and (□) 35 μs after electron pulse. (Dose $\sim 12 \text{ Gy/pulse}$).

absorption at 350 nm. This is supported by the fact that in the case of H-atom reaction with 2-MBT a transient absorption occurs at the same wavelength as that seen during the electron reaction.

Since there was a marked change in the extinction coefficient values at pH 5 and at 10.5 (see Table 2) it indicates the existence of a pK_a of the e_{aq}^- radical adduct of 2-MBT. Figure 6 shows a plot of change in absorbance with pH on a N_2 -bubbled aqueous solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ 2-MBT and 0.5 mol dm^{-3} *t*-butanol. The pK_a for the equilibrium reaction shown in Scheme 2 was estimated to be 5.

The e_{aq}^- reaction rate constant with 2-MBT at pH 5 was determined by following the pseudo-first order decay rate of e_{aq}^- at 720 nm for varying concentrations of 2-MBT ($0.5 - 5 \times 10^{-5} \text{ mol dm}^{-3}$). By plotting the pseudo-first order rate constant values against [2-MBT], the value of the bimolecular rate constant was obtained ($k = \sim 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). These values are in good agreement with the bimolecular rate constant as determined from the formation traces of the semi-reduced species at 350 nm (Table 2). At pH 10.5, 2-MBT is

Table 2

Absorption maxima, extinction coefficients, formation and decay rates of the transients formed by the reactions of various one-electron reductants with 2-MBT.

Reactions	pH	λ_{\max} (nm)	$\epsilon_{\lambda_{\max}} \pm 200$ ($\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	$k \times 10^{-9}$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	$k_{(s^{*-}+s)}$
$e_{\text{aq}}^- + 2\text{-MBT}$	5	350	4,950	20.0 20.0 ^a	8.8×10^7
$e_{\text{aq}}^- + 2\text{-MBT}$	10.5	350	6,020	3.0 ^a	2.0×10^7
$\text{H}^\bullet + 2\text{-MBT}$	1.5	350	4,600	11.0	6.9×10^7
$\text{H}^\bullet + 2\text{-MBT}$	1.5	420	-	2.8	-
$\text{CO}_2^{\bullet-} + 2\text{-MBT}$	5.0	350	570	-	-

^aValue of 'k' determined at 720 nm by following the decay of e_{aq}^- where, $s = 2\text{-MBT}$.

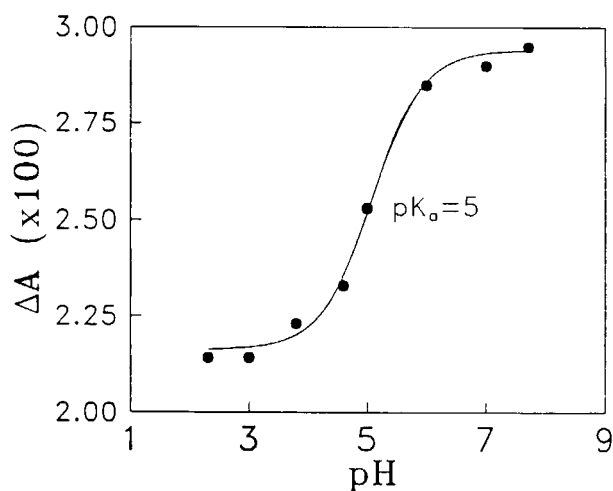
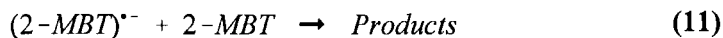


Figure 6. A sigmoidal curve showing pH dependence of absorbance of the transient formed in aqueous buffered solutions at 350 nm in the reduction of 2-MBT yielding a $\text{pK} = 5.0 \pm 0.1$.

present as an anion hence the rate constant is lower by almost an order of magnitude.

The transient formed at 350 nm decayed predominantly by first order and was also dependent on [2-MBT]. From this dependence the bimolecular rate constant was determined to be $8.8 \times 10^6 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ (reaction 11).



Hydrated electrons react with aliphatic amino thiols yielding carbon-centred radicals and H_2S [17,18]. However, in the present investigation, by adding DTNB reagent [19] no H_2S was detected spectrophotometrically in gamma-irradiated, N_2 -bubbled samples of 2-MBT, suggesting a different reaction path.

The semi-reduced species of 2-MBT formed in the aqueous solution at pH 5.5 were in turn able to reduce methyl viologen (MV^{2+}) [$E^\circ = -0.45 \text{ V}$] [20] with a rate constant of $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It can thus be concluded that the $E'_{5.5}$ of (2-MBT)/(2-MBT) $^{\bullet-}$ is $< -0.45 \text{ V}$ vs NHE.

Cyclic voltammogram of $5 \times 10^{-4} \text{ mol dm}^{-3}$ solution of 2-MBT at pH 4.1 was recorded by using a voltage sweep rate of 100 mV s^{-1} and scanning through a potential range of -0.5 to -1.5 V . The voltammogram is presented in Figure 7. Two cathodic peaks, $E_{\text{pc}}^1 = -1.26 \text{ V}$ and $E_{\text{pc}}^2 = -1.4 \text{ V}$ were obtained during the forward sweep. No peak was observed during the reverse sweep.

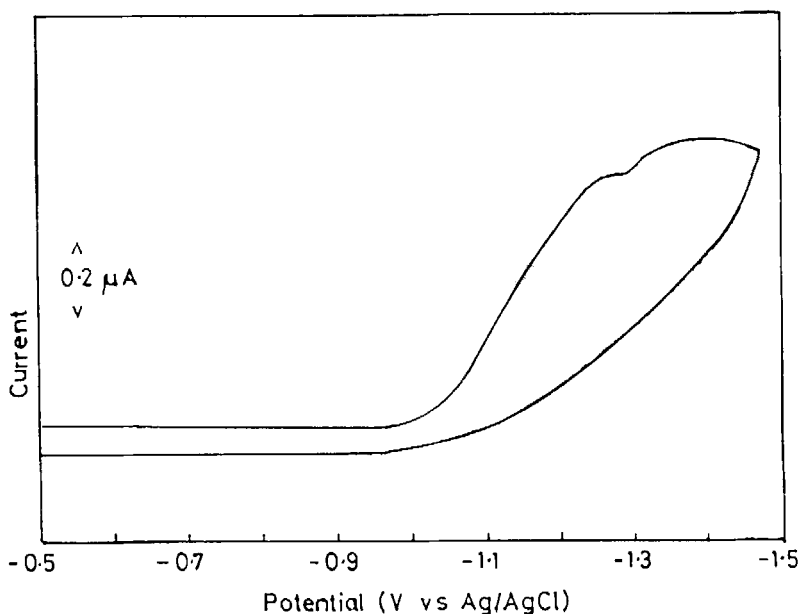


Figure 7. Cyclic voltammogram of a $5 \times 10^{-4} \text{ mol dm}^{-3}$ solution of 2-MBT containing 0.5 mol dm^{-3} *t*-butanol in deaerated phosphate buffer ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at pH 4.1. Scan rate = 100 mV/s .

The one-electron reduction potential of 2-MBT was also determined using methyl viologen (MV^{2+}) as a standard. Determination of $E'_{(2\text{MBT}/2\text{MBT}^{\bullet-})}$ is possible from the equilibrium reaction 12 by employing the following relation (Equation (13)).



$$E^1_{(2\text{MBT}/2\text{MBT}^{\bullet-})} = E^1_{(2\text{MV}^{2+}/2\text{MV}^{\bullet+})} - 59 \log K \quad (13)$$

Monitoring of $\text{MV}^{\bullet+}$ radical absorption at 610 nm was carried out by employing single pulses of dose rate ~ 6 Gy to N_2 -bubbled solutions of 2-MBT ($0.5 - 1 \times 10^{-3}$ mol dm^{-3}), 0.5 mol dm^{-3} *t*-butanol and ($0.3 - 2.5 \times 10^{-5}$ mol dm^{-3}) MV^{2+} at various $[2\text{-MBT}]:[\text{MV}^{2+}]$ concentration ratios. The electron transfer was virtually complete in all cases. A limiting value of $E^1 < -600$ mV vs NHE could be estimated.

Reactivity of H^\bullet Atoms with 2-MBT

On pulse radiolysis of N_2 -bubbled solutions containing 1 mol dm^{-3} *t*-butanol and 1×10^{-3} mol dm^{-3} of 2-MBT at pH 1.5, a transient absorption was observed having a λ_{max} at 350 nm with $\epsilon_{350\text{nm}} = 4,600 \pm 200$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ (Figure 8). This absorption

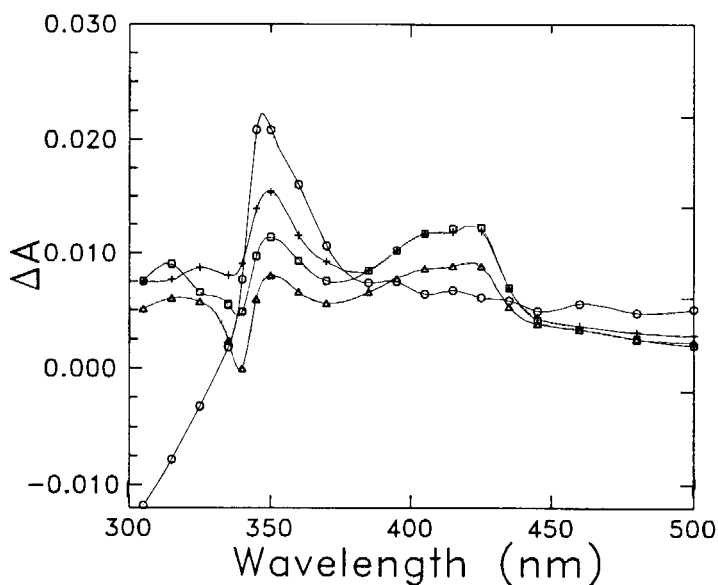
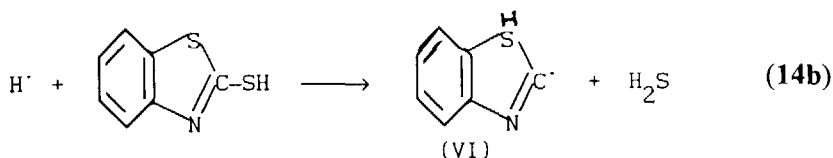
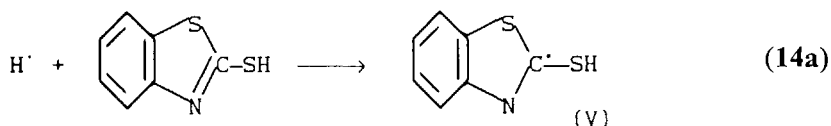


Figure 8. Time resolved absorption spectra of the H-adduct of 2-MBT on pulse irradiating an N_2 -bubbled aqueous solution of (1×10^{-3} mol dm^{-3}) 2-MBT, 1 mol dm^{-3} *t*-butanol, pH ~ 1.5 at (O) $2 \mu\text{s}$, (+) $4 \mu\text{s}$, (□) $6 \mu\text{s}$, and (Δ) $9 \mu\text{s}$ after the electron pulse. (Dose ~ 12 Gy/pulse).

is attributed to the formation of an H-adduct of 2-MBT. The transient displayed a concentration dependent first order decay kinetics and the bimolecular rate constant was calculated to be $6.9 \times 10^7 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. As the spectral characteristics and the decay rates are the same as those observed for the transient formed by the reaction of e^-_{aq} with 2-MBT, it is reasonable to conclude that the transient species formed have a similar structure.

Because of the electrophilic nature of H^\bullet atoms, the most likely site for the H^\bullet atom addition will be the polarized $\text{C}=\text{N}$ double bond giving rise to a transient having an absorption at 350 nm, with the electron remaining delocalized in the aromatic π -electron system (reaction 3.14a). For the determination of yields of H_2S , aqueous gamma-irradiated samples of 2-MBT containing *t*-butanol at pH 1.5 were first neutralized. To this known amounts of DTNB reagent was added and the absorbance determined at 412 nm. $G(\text{H}_2\text{S})$ was found to be ~ 1.5 . Hence, there is a possibility that as in the case of aliphatic thiols, the H^\bullet atom could also be partially reacting at the $\text{C}-\text{SH}$ site to form a carbon-centered radical (VI) (reaction 3.14b).



From the values of the extinction coefficient and the yield of H_2S it seems that the H^\bullet atoms react with 2-MBT by two pathways. This can be explained by considering that, out of the total $G_{(\text{H}^\bullet)} = 3.6$ available for reacting with 2-MBT, nearly 41% reacts with the substrate so as to yield H_2S , the remaining H^\bullet atoms [$G_{(\text{H}^\bullet)} = 2.1$], reacting in a manner to give species (V). Now, taking the value of $\epsilon_{350\text{nm}} = 4,950 \pm 200 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ from the reaction of e^-_{aq} with 2-MBT at pH 5 to calculate the extinction coefficient of the species (V) formed as a consequence of H^\bullet atom reaction with 2-MBT one arrives at a value of $3,150 \pm 200 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$. This value is lower than the reported value of $4,600 \pm 200 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ (assuming $G_{(\text{H}^\bullet)} = 3.6$ at pH = 1.5). This suggests that the species produced at pH 1.5 is not only the protonated form of the H-adduct but there also exists another species with λ_{max} in the vicinity of 350 nm having an extinction coefficient lower than the species (V).

The overall rate constant of the H^\bullet atom reaction, calculated from the pseudo-first order rates versus [2-MBT], $k \approx 9.5 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Reactivity of the Secondary Reducing Radicals with 2-MBT

Reduction of 2-MBT was also studied with more specific one-electron reductants such as $\text{CO}_2^{\bullet-}$ [$E^\circ = -1.9 \text{ V}$] [21]. It was observed that the semi-reduced species of 2-MBT (reaction 15) formed on reduction by $\text{CO}_2^{\bullet-}$ (pH = 5.5) absorbed at 350 nm and $\epsilon_{350\text{nm}} = 570 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. The spectrum is identical to that of the semi-reduced species formed by the reaction of e^-_{aq} with 2-MBT, but the yield seems to be quite low i.e., reduction of 2-MBT with $\text{CO}_2^{\bullet-}$ is only partial.



From this data it can be inferred that it is difficult to reduce this inhibitor with $\text{CO}_2^{\bullet-}$. Also, a lower limit of $E^1 > -1.9 \text{ V}$ versus NHE could be given for this couple. Thus $-0.6 \text{ V} > E^1_{(2\text{MBT}/2\text{MBT}^{\bullet-})} > -1.9 \text{ V}$ versus NHE at 25 °C could be given. This was further confirmed from cyclic voltammetric data.

Reactions of Semi-oxidized Radicals of 2-MBT with Some Phenothiazine Drugs [P]

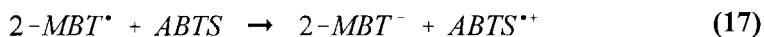
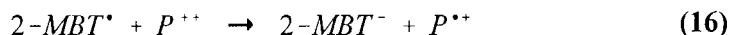
It is well known that thiyl radicals (RS^\bullet) act as pro-oxidants and are known to bring about oxidation of lipids [22] and ascorbic acid [24] as well as of many phenothiazine drugs [23-25] and other oxidizable solute such as 2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonate) ABTS.

We have earlier shown pulse radiolytically that the oxidation of these drugs with 2-MT $^\bullet$ radicals [14] proceeds at a much faster rate than that seen with the aminothiols.

2-MBT radicals were conveniently generated pulse radiolytically in N_2O -saturated aqueous media by the reaction of 2-MBT ($5 \times 10^{-4} \text{ mol dm}^{-3}$) with OH^\bullet radicals at pH 5.5, in the additional presence of either phenothiazine drugs ($0.7 - 5 \times 10^{-5} \text{ mol dm}^{-3}$) such as promethazine (PMZ), chlorpromazine (CPZ), prochlorperazine (PPZ), trimeprazine tartrate (TMZ), a transient absorption was observed around 520 to 525 nm. A similar absorption is observed when these phenothiazine drugs react with OH^\bullet , $\text{Br}_2^{\bullet-}$ radicals resulting in the formation of the phenothiazine radical cation and having an intense absorption at $\sim 525 \text{ nm}$ [26,27]. One can therefore by analogy say that the 525 nm absorption observed during the

reaction of 2-MBT[•] radical with phenothiazine drugs is due to electron transfer reaction with the formation of radical cation of these drugs (reaction 16).

Similarly, on pulsing an N₂O-saturated solution containing 2-MBT (5 x 10⁻⁴ mol dm⁻³) in the presence of ABTS (0.2 - 2 x 10⁻⁵ mol dm⁻³) a strong absorption with λ_{max} at 415 nm was observed which was attributed to the formation of ABTS^{•+} (reaction 17).



The ease with which 2-MBT[•] radicals were able to oxidize phenothiazine drugs having one-electron reduction potential around 0.8 V suggests that its reduction potential must be > 0.8 V.

The formation rates were pseudo-first order and dependent on [ABTS] or [P], from which the bimolecular rate constants were calculated (Table 3.6). Based

Table 3

Rate constants for the formation of semi-oxidized species of phenothiazines and ABTS due to 2-MBT radical reaction in N₂O-saturated aqueous solution at pH 5.5.

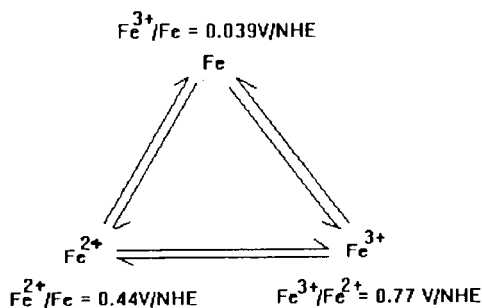
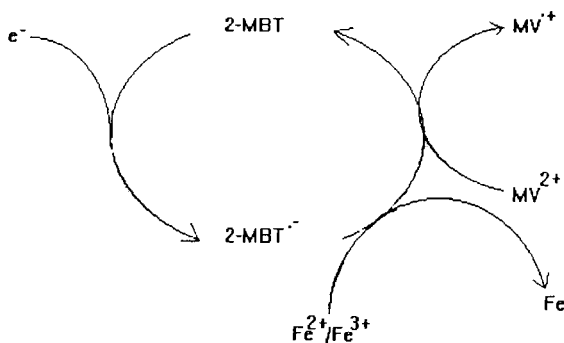
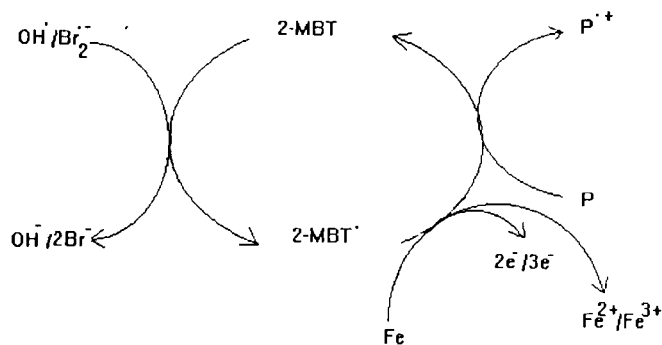
Reaction	λ (nm)	k x 10 ⁻⁹ (dm ³ mol ⁻¹ s ⁻¹)
2-MBT [•] + PMZ	520	5.2
2-MBT [•] + CPZ	525	3.7
2-MBT [•] + PPZ	525	1.9
2-MBT [•] + TMZ	520	9.0
2-MBT [•] + ABTS	415	12.5

on these high rate constant values it can be said that the reaction of 2-MBT[•] radicals with various phenothiazines and ABTS proceeds via electron transfer and not by H-abstraction. The above Table also shows that the present rate constant values are higher by an order of magnitude compared to the rate constants obtained by the reaction of aliphatic thiyl radicals with various phenothiazines and ABTS.

These results will serve a useful purpose of not only throwing light on the reactivity of the semi-oxidized species of these inhibitors but will also reflect on their ability to influence oxidation of base metals during their application as chemical inhibitors in decontamination.

Compounds of the type R_2S , RSH , RS^- are soft Lewis bases and they can get adsorbed on the metal surface by virtue of electron donor properties of S-atoms and thus prevent corrosion. Yet, during their application in radiolytic environment one has to give due consideration to the possible formation of semi-oxidized species since their reduction potential may be sufficiently high to promote corrosion of iron whose various redox couples are $[E^\circ (Fe^{2+}/Fe) = +0.44 \text{ V}]$; $[E^\circ (Fe^{3+}/Fe) = +0.035 \text{ V}]$ and $[E^\circ (Fe^{3+}/Fe^{2+}) = +0.77 \text{ V}]$. Thus by maintaining reducing conditions one may be able to minimize corrosion.

The scheme below shows various oxidation reduction cycles.



CONCLUSIONS

- (i) Results show that the nature of the transient species formed during the oxidation of 2-MBT with specific one-electron oxidants is essentially the same as that formed during the reaction of the OH^\bullet radical with the inhibitors.
- (ii) Weaker oxidants such as Br_2^\bullet and N_3^\bullet show lower reactivity with the inhibitors in comparison to OH^\bullet radicals.
- (iii) The semi-reduced species formed as a result of reaction of e^-_{aq} and CO_2^\bullet with the inhibitors appear to be the same, as seen from the similarity in their absorption maxima.
- (iv) The semi-reduced species formed by hydrated electron reaction with the inhibitors were in turn able to reduce methyl viologen by electron transfer reaction, indicating that these are strong reductants.

REFERENCES

1. G. TrabANELLI. In: *Corrosion Mechanisms*, F. Mansfield (Ed.), Marcel Dekker Inc., New York, 1987, p. 119.
2. N. Hackerman and E.S. Snavelly. In: *Fundamentals of Inhibitors, NACE Basic Corrosion Course*, 1970, p. 9-1.
3. G. TrabANELLI, *Fundamentals and General Aspects of Inhibition Science*, Corrosion /89, Paper 133, Houston TX: NACE, 1989.
4. A. Frignani, C. Monticelli, G. Brunoro, and M. Zucchini, *Br. Corros. J.* **28**, 37 (1988).
5. I. Singh, A.K. Lehri, V.A. Altekar, *Proc. 5th Intl. Cong. on Metallic Corr.*, NACE, Tokyo, Japan, 1972, p. 570.
6. G. TrabANELLI, F. Zucchi, G. Gullini, and V. Cararsiti, *Proc. 4th Intl. Cong. on Metallic Corros.*, N.E. Hammer (Ed.), NACE Houston, Texas, 1972, p. 602.
7. I.L. Rosenfield, *Corrosion* **37**, 371 (1981).
8. K.H. Wiedeman, *Werkst. Korros.* **39**, 332, (1988).
9. G.J.C. Nash, *Proc. Intl. Conf. organized by British Nuclear Energy Society*, Bournemouth, 24-27 October, 1997, p. 377.
10. J. Severa and J. Bar, *Handbook of Radioactive Contamination and Decontamination*, Elsevier, Amsterdam, New York, 1991, p. 213.
11. G.G. Jayson, P. McAteer, and A. Wood, *Proc. Intl. Conf. organized by British Nuclear Energy Society*, Bournemouth, 14-17 October, 1981, p. 409.
12. D.B. Naik and P.N. Morthy, *Radiat. Phys. Chem.* **42**, 652 (1995).
13. G.R. Dey, D.B. Naik, K. Kishore, and P.N. Moorthy, *Res. Chem. Intermed.* **21**, 47 (1995).
14. H.S. Mahal, T. Mukherjee, and J.P. Mittall, communicated *J. Chem. Soc., Perkin Trans. 2*.
15. T. Mukherjee. In: *Atomic, Molecular and Cluster Physics*, S.A. Ahmed (Ed.), Narosa, 1996, p. 299-311.
16. E.M. Fielden. In: *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, J.H. Baxendale and F. Busi (Eds.), D. Reidel Pub. Co., Dordrecht, 1984, p. 59.
17. M.Z. Hoffman and E. Hayon, *J. Phys. Chem.* **77**, 990 (1973).

18. C.L. Greenstock, C. Banerjee, and G.W. Ruddock. In: *Proc. Fourth Tihany Symp. on Radiat. Chem.*, P. Hedvig and R. Schiller (Eds.), Akad Kiado, Budapest, Hungary, 1977, p. 871-879.
19. G.L. Ellman, *Arch. Biochem. Biophys.* **82**, 70 (1959).
20. A.J. Swallow. In: *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, J.H. Baxendale and F. Busi (Eds.), D. Reidel Pub. Co., Dordrecht, 1984, p. 297.
21. J. Butler and A. Henglein, *Radiat. Phys. Chem.* **15**, 603 (1980).
22. C. Schoneich and K.D. Asmus, *Radiat. Environ. Biophys.* **29**, 263 (1990).
23. H.S. Mahal and M. Lal, *Can. J. Chem.* **68**, 1376 (1990).
24. L.G. Forni, J. Monig, V.O. Mora-Arellano, and R.L. Willson, *J. Chem. Soc., Perkin Trans. 2* **961** (1983).
25. P. O'Neil and M. Tamba, *J. Chem. Soc., Perkin Trans. 2* **1681** (1991).
26. A.K. Davies, E.J. Land, S. Navaratnam, B.J. Parsons, and G.O. Phillips, *J. Chem. Soc., Faraday Trans. 1* **75**, 22 (1979).
27. D. Bahnemann, K.D. Asmus, and R.L. Willson, *J. Chem. Soc., Perkin Trans. 2* **1661** (1983).