

Pulse Radiolysis of Deaerated Hydroquinone Solutions

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Summary: The pulse radiolysis of deaerated hydroquinone, (H_2Q), solutions has been investigated. It has been shown that OH adds to H_2Q to form the trihydroxycyclohexadienyl radical (H_2Q-OH) to H_2Q to form the trihydroxycyclohexadienyl radical (H_2Q-OH) with $k = 5.25 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$. This radical decays by first order kinetics giving the semiquinone radical (HQ). This reaction is catalysed by H^+ . The spectrum of HQ, and its extinction coefficient were obtained. The decay of HQ is second order and $k = 1.2 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$. It is concluded that HQ disappears mainly through reaction with H_2Q-H .

Introduction

It is well known that the radiolysis of water yields mainly hydroxyl radicals (OH) and the hydrated electron (e^-_{aq}); the latter is converted to a hydrogen atom in the presence of acid. These radicals can react, for example, with added organic solutes. Thus Wilson and Patel [1,2] have investigated the formation of different semiquinone radicals which resulted from the reaction of radiolytic species (e.g. e^-_{aq} , H and OH) with the quinones. Similar work has been reported by Adams and Michael [3] who were able to identify the spectra of HQ, Q and the H_2Q-OH adduct. This adduct was reported to decay unimolecularly by the elimination of water to give HQ. The reaction is catalysed by H. On the other hand, H has been shown to react with H_2Q to form an adduct

with a rate coefficient of $1.3 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$ [4]. The absorption of this adduct and its extinction coefficient have been determined. Some aromatics have been shown to react with H to give adducts which have similar absorptions and extinction coefficients to those formed by the reaction of OH with these compounds [5,6]. Here we report work on the pulse radiolysis of H_2Q solutions where attention is paid to the effect of pH and dose rate. These results help to explain work on the γ -radiolysis of this system to be published later.

Experimental

The present work was carried out at the Patterson Laboratories, Christie Hospital and Holt Radium Institute

* It will be convenient to use the symbols $H_2Q, Q, Q, HQ, Q, H_2Q-OH$ and H_2Q-H to indicate: hydroquinone, quinone, semiquinone radicals, semiquinone radical anion, OH adduct with H_2Q and H adduct with H_2Q respectively.

Manchester. A Vickers 12 MeV Linear accelerator was used to produce short pulses of electrons from 5 ns to 5 μ s. The transient species were detected by optical methods. The amount of absorbed energy was determined by the oxidation of 10^{-3} M ferrocyanide in neutral, O_2 , saturated solutions.

The ferricyanide produced was measured spectrophotometrically at 420 nm where its extinction coefficient was taken to be $10^3 M^{-1} cm^{-1}$. In calculating dose, $G_{OH} = G[Fe(CN)_6] = 2.75$ in neutral solutions was assumed. As an example, the dose per 20 ns pulse = $7.45 \times 10^{19} eV L^{-1}$. The reproducibility was good provided that all experimental conditions were kept the same. The general pulse radiolysis technique and methods of handling solutions have been described elsewhere [7].

Materials

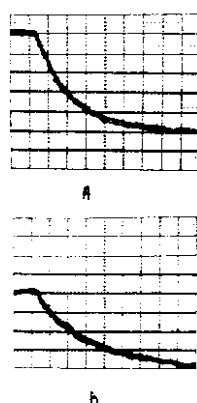
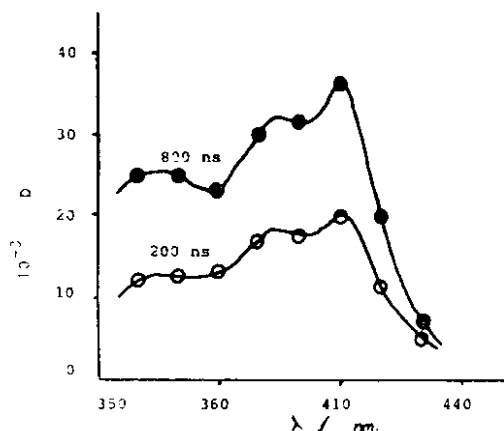
In all experiments, triply distilled water was used. H_2SO_4 was 95-98% BDH and hydroquinone was an Eastman product and both were analar grade.

Argon was from B.O.C. All these materials were used without further purification.

Results and Discussion

Fig. 1 shows the absorption spectra produced in 5×10^{-4} M H_2O in 1 M H_2SO_4 Ar saturated solutions taken 200 and 800 ns after 20 ns pulse. Similar spectra are produced in 10^{-2} M H_2Q in 1 M H_2SO_4 , though the rate of formation is ~ 13 times faster. Fig. 2 shows the spectra produced under similar conditions (10^{-2} M H_2Q), but at longer time scales, i.e. after the decay has started. The kinetics of formation is dependent, to some extent, upon the wavelength. Thus it can be seen from inspection of the oscillograms, that the half-life at 410 nm (10^{-2} M H_2Q) is ~ 18 ns and at 360 nm is ~ 28 ns.

When the acid concentration is lowered, $< 10^{-2}$ M, the shape of the spectra becomes time dependent.



Inset:-

Oscilloscope trace of absorption at
(a) 410 nm
(b) 360 nm
Horizontal : 220ns/div
Vertical : 1.8/div.

Fig. 1: Absorption spectra produced in 5×10^{-4} M H_2O in 1M H_2SO_4 , Ar saturated
Pulse length = 10 ns.

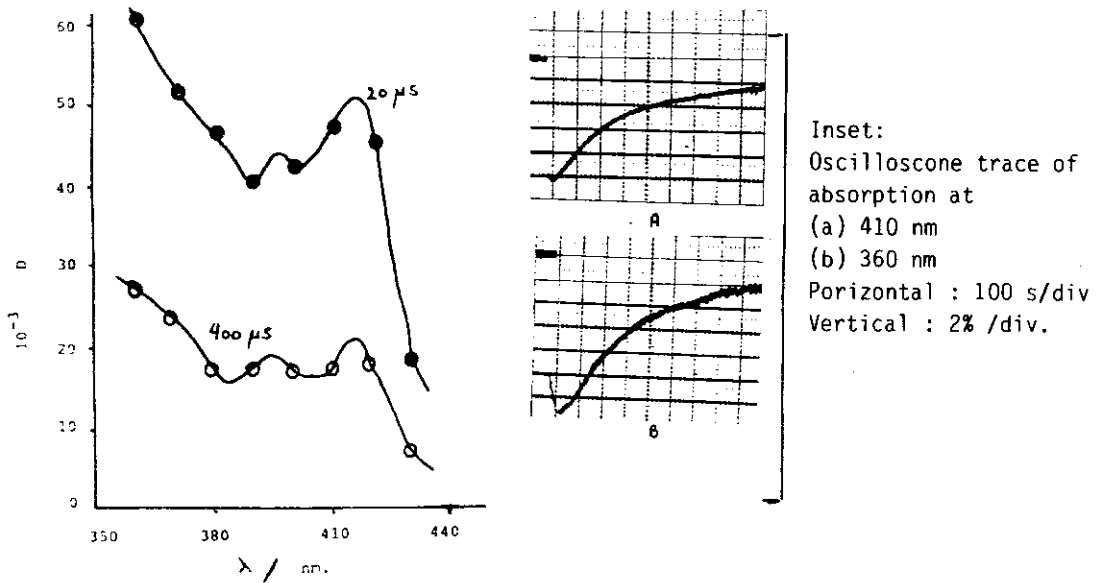


Fig.2: Absorption spectra produced in 10^{-2} M H_2Q in 1 M H_2SO_4 , Ar saturated.
pulse length = 20 ns

Thus, while initially the peak at 410 nm is small compared with that at 360 nm, it builds up with time. Moreover, it was found that the lower the acid concentration, the longer is the time needed to form the spectrum. Fig. 3 shows the spectrum taken 2 15 s after a 20 ns pulse in 10^{-2} M H_2Q containing 3×10^{-4} M H_2SO_4 , Ar saturated solution. It was found that the kinetics at 360 nm is too fast to be followed while it was possible to follow the kinetics at 410 nm. This is in contrast to the situation in 1 M H_2SO_4 where the rate of formation at 360 nm is about half that at 410 nm. These observations indicate that the spectrum at 360 nm is not due to a single species.

The shape of the spectrum at longer times is similar to that attributed to HQ produced by radiation induced oxidation of H_2Q and the reduction of Q [1,2]. The maximum is reported to

lie at 415 nm and there is another smaller peak at 390–400 nm. The fact that Q has its peak at 430 nm [1,2] and the pK of its formation is 4 makes its contribution negligible in the acid range 3×10^{-4} 1 M H_2SO_4 . Similarly, H_2Q-OH has its maximum at <320 nm [3] and therefore, any possible contribution from it will be negligible.

The hydrogen atom reacts with H_2Q to form an adduct, H_2Q-H with k 1.3×10^9 $M^{-1} s^{-1}$ [5] and H is expected, therefore, to be scavenged by H_2Q under the experimental conditions. The H_2Q-H adduct is reported to have an absorption maximum at 360 nm with an extinction coefficient of $3000 M^{-1} cm^{-1}$. This adduct absorbs weakly at 400 nm and its decay is slow.

Assuming that the only absorbing species at 410 nm is HQ, which seems justified from the above considera-

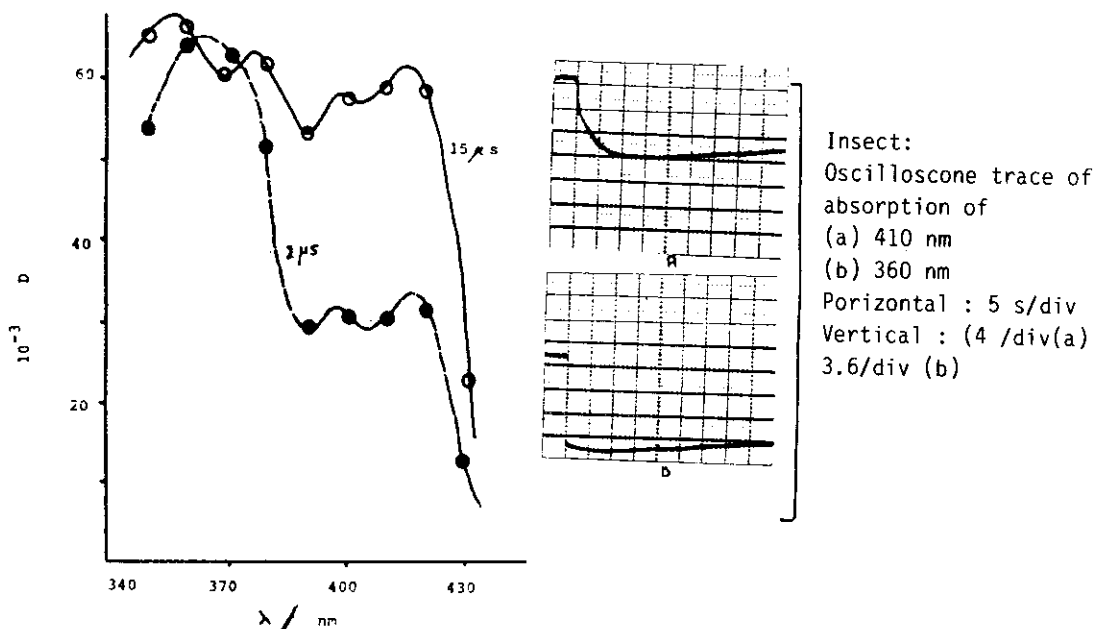


Fig.3: Absorption spectra in $10^{-2} M H_2Q/3 \times 10^{-4} M H_2SO_4$, Ar saturated pulse length = 20 ns

tions, then can be determined from known dose. It is assumed that HQ arises only from the reaction of OH with H_2Q and that $G_{OH} = 2.9$ in acid solution.

The extinction coefficient was determined taking D_{max} in Ar saturated solutions at different $[H^+]$. At 410 nm the value of D_{max} determined as outlined above is $5.1 \pm 0.8 \times 10^{-3} M^{-1} cm^{-1}$. This is to be compared with 4.3×10^3 and 5.5×10^3 (at 415 nm) $M^{-1} cm^{-1}$ found by others [1-3].

If it is assumed that the production of HQ is by a First order process, i.e.

then $X \xrightarrow{\quad} HQ$

$$\text{the } -\frac{d[X]}{dt} = d[HQ]/dt = k_{obs}[X]$$

This integrates to:

$$-\ln \frac{[X]}{[X]_0} = k_{obs} t$$

where $[X]_0$ is the concentration of X at $t = 0$. It is assumed that the absorption at 410 nm is due only to HQ. Then, if the absorptions at times t and ∞ are D_t and D_∞ respectively.

$$D_\infty \propto [X]_0 \text{ and } D_t \propto [X]_0 - [X]$$

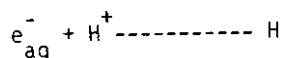
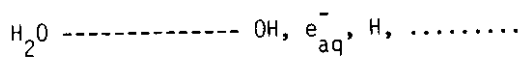
$$\text{i.e. } \ln \frac{D_\infty - D_t}{D_\infty} = k_{obs} t$$

The a plot of $\ln [D_\infty - D_t]$ versus t should be linear and the slope of the graph is given by $-k_{obs}$.

The rate coefficients for the formation of HQ are tabulated in Table 1. A typical example of a first order plot

is shown in Fig.4. As can be seen from Table 1. there is little effect of dose rate, as would be expected for a first order reaction.

In the radiolysis of acidic deaerated water, the following reactions will occur:



Both H and OH will react with H_2Q to form adducts which in case of HQ, is the trihydroxycyclohexadienyl radical.

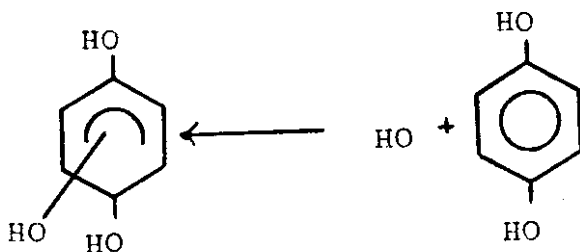


Table-1: Formation rate coefficients of HQ (decay of $\text{H}_2\text{Q-OH}$) in the pulse radiolysis of $10^{-2}\text{M H}_2\text{Q/H}_2\text{SO}_4$ solutions, under Ar ($\lambda = 410\text{ nm}$).

$[\text{H}^+]$ M	Pulse length ns	$10^{-6}k_{\text{obs}}$ s^{-1}	Remarks
1.0	20	49.5	
1.0	20	2.74	$5 \times 10^{-4}\text{ M H}_2\text{Q}$
2.61×10^{-2}	20	10.7	
2.61×10^{-2}	50	12.3	
1.45×10^{-2}	20	5.62	
1.45×10^{-2}	50	6.81	
5.07×10^{-3}	20	2.24	
5.07×10^{-3}	10	2.08	
1.86×10^{-3}	20	0.82	
1.86×10^{-3}	50	0.99	
5.85×10^{-4}	20	0.31	
5.85×10^{-4}	10	0.26	
$1.0 \times 10^{-4} (\text{HCl})$	20	0.074	$5 \times 10^{-4}\text{ H}_2\text{Q}, \lambda = 400\text{ nm}$

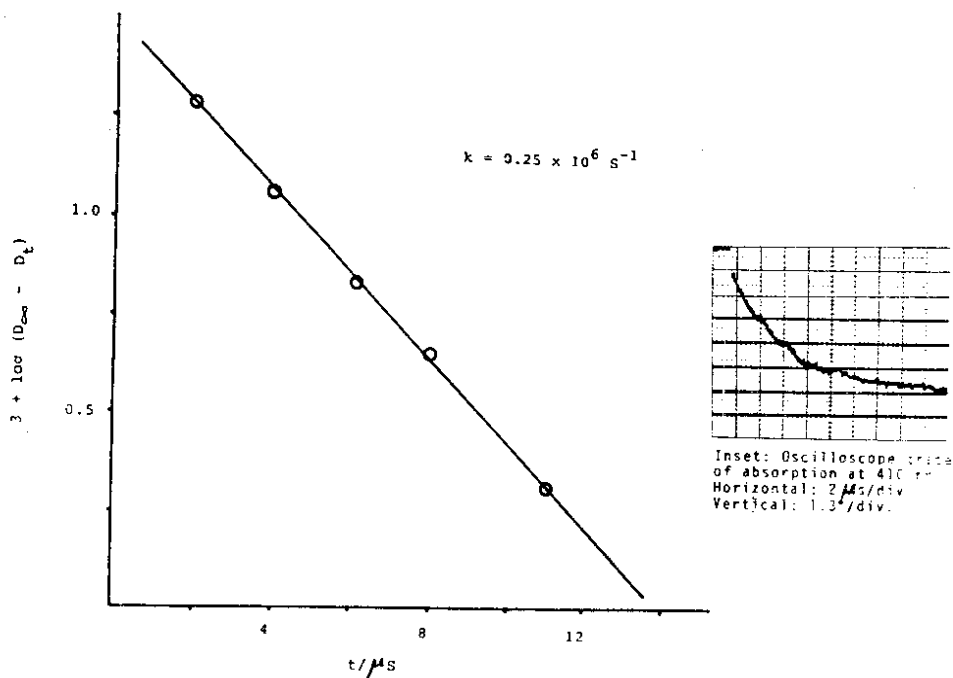
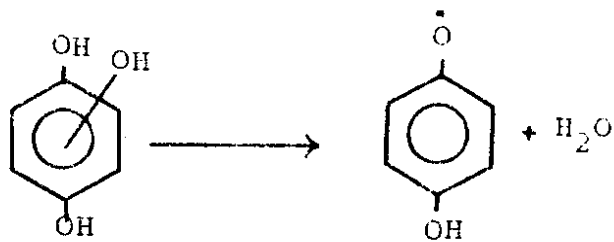


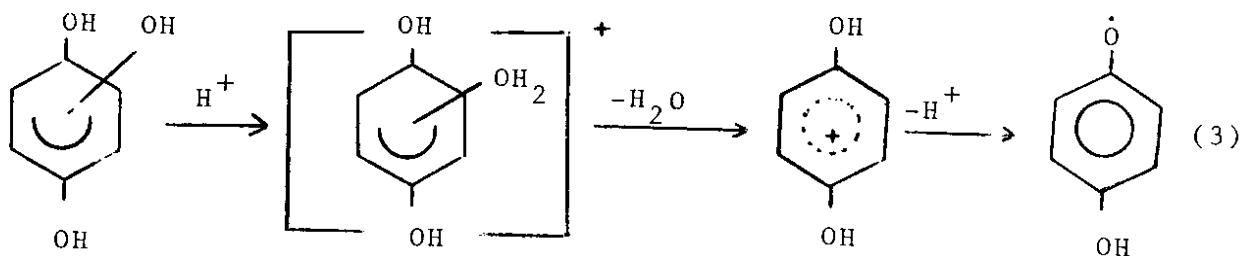
Fig.4: Typical 1st order plot for the formation of H_2Q in $10^{-2} \text{ M H}_2\text{Q} / 5.86 \times 10^{-4} \text{ M H}^+$, Ar saturated. pulse length = 10 ns.

This radical will undergo spontaneous decomposition with the elimination of H_2O and this process is catalysed by H^+ .

The fact that the dehydration is



(2)



catalysed by H^+ is shown by the dependence of k_{obs} for the formation of HQ on $[\text{H}^+]$ as can be seen in Table 1. Plotting k_{obs} versus $[\text{H}^+]$ gives a straight line at low $[\text{H}^+]$ as can be seen in Fig.5. If, however, $\log k_{\text{obs}}$ is plotted against pH, a titration-type curve is obtained as can be seen in Fig.6. Clearly there are ranges at which k_{obs} is pH independent (low and high pH) and at intermediate pH, k_{obs} is pH dependent

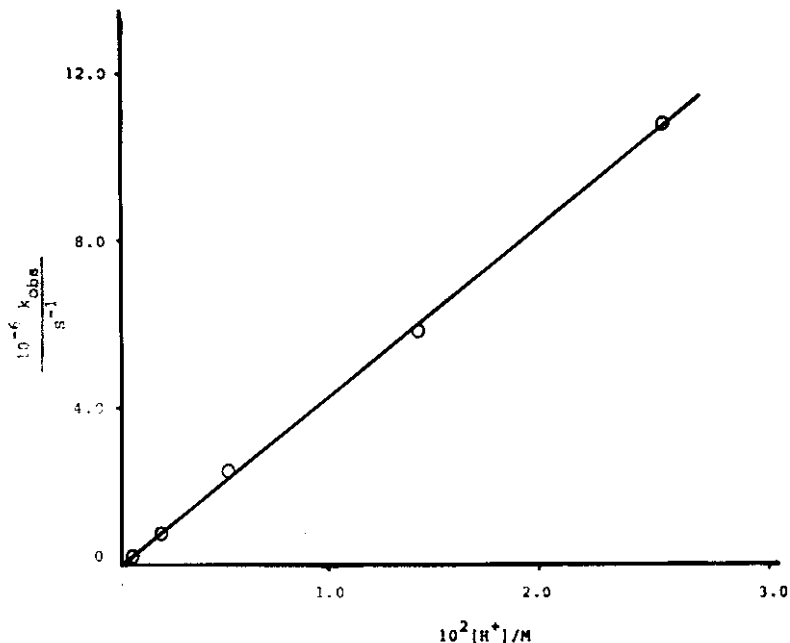


Fig. 5: Plot of k_{obs} against $[H^+]$ in the radiolysis of $10^{-2} M$ H_2Q in H_2SO_4 solution, Ar saturated. pulse length = 20 ns.

From the reactions (1,2,3) above,

$$\frac{-d[H_2Q-OH]}{dt} = k_{obs} [H_2Q - OH] \quad (4a)$$

$$= k_2 [H_2Q-OH] + k_3 [H^+] [H_2Q-OH] \quad (4b)$$

i.e $k_{obs} = k_2 + k_3 [H^+] \quad (5)$

From Fig. (5), $k_2 \sim 5 \times 10^4 s^{-1}$

and $k_3 \sim 4.1 \times 10^8 M^{-1} s^{-1}$

At high $[H^+]$, the elimination of water will be very rapid. Under these conditions, then, the rate determining step for the appearance of HQ is reaction (1) i.e.,

$$k_{obs} = k_1 [H_2Q]$$

The data of Table 1 for $[H_2Q] = 10^{-2}$ and $5 \times 10^{-4} M$ lead to values of $k_1 = 5 \times 10^9$ and $5.5 \times 10^9 M^{-1} S^{-1}$ respectively.

The semiquinone radical is believed to disproportionate according to:



If this is the case, then:

$$\frac{-d [HQ]}{dt} = k [HQ]^2$$

$$\text{and } \frac{1}{D} - \frac{1}{D_0} = \frac{kt}{\epsilon l}$$

where D and D_0 are the optical densities at times t and 0 , respectively, ϵ is the extinction coefficient of HQ at 410 and l is the light path. Thus a plot of $\frac{1}{D}$ against time should be linear

and gradient of the graph is given by $k/\epsilon l$.

A typical second order plot is shown in Fig.7 and the data are summarized in table 2. The rate coefficients are independent of $[H^+]$ in the range 5.83

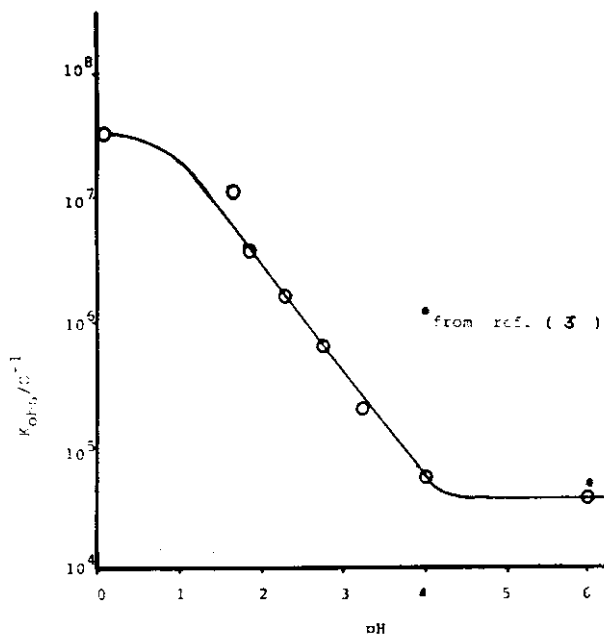


Fig.6: Plot of long k_{obs} against pH in the pulse radiolysis of 10^{-2} M H_2Q in Ar saturated.

Table-2: Decay rate coefficients of HQ in the pulse radiolysis of 10^{-2} M H_2SO_4 solution, Ar saturated.

$[H^+]/M$	Pulse length/ns	$10^{-9}/M^{-1}s^{-1}$	Remarks
1.00	100	1.7	=410 nm
1.00	20	1.25	""
5.83×10^{-2}	20	1.03	""
5.83×10^{-2}	100	1.20	=400 nm
10^{-4}	20	0.69	""
10^{-4}	20	0.63	"", N_2O
10^{-4}	10	0.68	"", N_2O

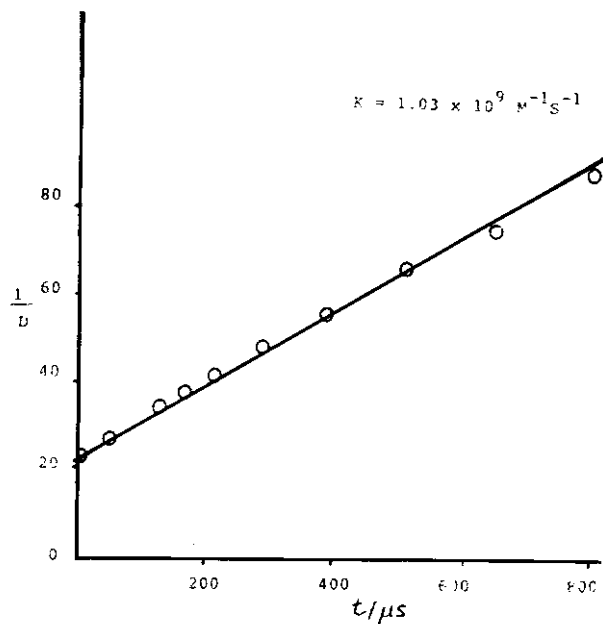
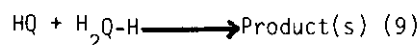
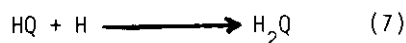


Fig.7: Typical 2nd order plot for the decay of HQ in 10^{-2} M $H_2O/0.05$ M H_2SO_4 . Ar saturated. Pulse length = 20 ns.

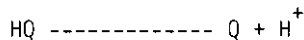
$\times 10^{-21}$ M and dose rate within five fold change as can be seen in Table 2. In 10^{-4} M H^+ , Ar saturated solution the rate coefficients are ~ half those at high $[H^+]$ and again there is little dose rate effect.

In Ar saturated solutions, HQ may disappear by reaction with H or H_2Q-H , in addition to reaction (6).



Reaction (9) is the most likely one since, as will be reported later, the γ -radiolysis results show that in deaerated solutions, H_2Q disappears while only small amounts of Q (~ 10%, of H_2Q disappeared) are produced.

Therefore one may exclude reactions (7,8). In addition, these two reactions might be excluded on the grounds that H will be scavenged effectively by H_2Q . That second order kinetics are still observed for the disappearance of HQ arises then from the fact that HQ and H_2Q-H are produced in approximately equal concentrations. The decrease in the rate coefficient at $10^{-4}M H^+$ is expected since for HQ the equilibrium.



has a pK of 4 [1-3] and, therefore, a considerable amount of the ionized form will be presented and will react with a different rate from the HQ, since it has been well established that Q is more stable than HQ due to the loss of the symmetry in the latter [9]. A similar observation has been made by others [3].

Acknowledgement

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