

Studies of Radiation-Induced Reactions of 2,5-Dichlorohydroquinone in Aqueous Solutions

I. Reactions in the Absence of Oxygen

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ABSTRACT. The radiolysis of 2,5-dichlorohydroquinone (H_2QCl_2) at different pHs leads to no change in the system. The addition of some alcohols leads only to a small removal of H_2QCl_2 . This was taken to indicate an efficient back reaction. The saturation of H_2QCl_2 with N_2O leads to the formation of 2,5-dichlorobenzoquinone (QCl_2). Its yield is dependent on dose and it increases with pH being a maximum in the pH range 2.1-2.8. A satisfactory agreement is obtained between $G(QCl_2)_{calc.}$ and $G(QCl_2)_{meas.}$ upto pH ~ 2.1 . At higher pH, the low yields were taken to indicate a back reaction involving N_2O^- and the semiquinone radical ($H\dot{Q}Cl_2$). In the presence of H_2O_2 , QCl_2 is also produced. Its yield is dependent on radiation dose, $[H^+]$, $[H_2O_2]$ and $[H_2QCl_2]$. This system has indicated that, in addition to the oxidation of H_2QCl_2 by OH, perhydroxyl radical (HO_2) can also oxidize H_2QCl_2 and possibly $H\dot{Q}Cl_2$. Whatever the reaction mechanism may be, it is concluded that H_2QCl_2 has a strong resistance to radiation damage.

The pulse and γ -radiolysis of *p*-hydroquinone (H_2Q) and the γ -radiolysis of *p*-benzoquinone (Q) have been thoroughly investigated both in deaerated and oxygenated solutions [Al-Suhybani and Hughes 1985]. It was found that the radiation chemistry of H_2Q was relatively better understood in the presence of O_2 , while for Q the opposite is the case. H_2QCl_2 was chosen to examine the effect of a substituent on the radiation induced oxidation of H_2Q and also to examine in more detail the claim of others [Bielski and Becker 1960] that the radiation chemistry of this system is simple, *i.e.* $G(QCl_2) = \frac{1}{2}G_{OH}$. This claim has been discounted by the work of Fellows and Hughes [1973]. The work of these authors was, however, very limited and H_2O_2 was not determined accurately. It was hoped therefore to be able to present a more detailed reaction mechanism for the radiation-induced reactions of H_2QCl_2 .

Experimental

Deaerated solutions were irradiated with 0.66 MeV γ -rays from a 90 Ci ^{137}Cs source at $20 \pm 2^\circ\text{C}$ at dose rates $0.38\text{--}1.85 \times 10^{19}$ eVL min^{-1} . The experimental arrangements have already been described [Fellows and Hughes 1972]. H_2QCl_2 was an Eastman product and was recrystallized twice from hot dilute H_2SO_4 . QCl_2 was also an Eastman product and was recrystallized twice from hot aqueous ethanol. These two products were determined spectrophotometrically using a Unicam SP 500. The maximum for H_2QCl_2 is at 298 nm and its extinction coefficient (ϵ) was determined as $4.56 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. For QCl_2 , the corresponding values were 272 nm and $1.99 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. The optical densities of the irradiated samples were corrected for the change in $[\text{H}_2\text{QCl}_2]$. H_2O_2 was determined using the horseradish peroxidase method (HRP) [Yamazaki and Piette 1965, Elliott 1932, Yamazaki *et al.* 1960].

The pH of the solutions was varied by changing the concentration of H_2SO_4 . pH values were calculated for the higher $[\text{H}_2\text{SO}_4]$ but were measured using a glass electrode for the lower concentrations.

Results and Discussion

The irradiation of $0.8\text{--}5 \times 10^{-4}$ M H_2QCl_2 at different pH resulted in no change in the system. At high pH this behaviour is similar to that observed in the H_2Q system [Al-Suhybani and Hughes 1985] but at low pH the two hydroquinones differ considerably *viz*:

$$G(-\text{H}_2\text{Q}) \sim 3 \text{ and } G(-\text{H}_2\text{QCl}_2) = 0 \text{ at } \text{pH} = 0$$

As can be seen in table 1, the addition of some alcohols leads to some removal of H_2QCl_2 . Clearly $G(-\text{H}_2\text{QCl}_2)$ depends on the alcohol and its concentration but in any case, it is quite low and may not be of significance. The following reactions may explain these observations:

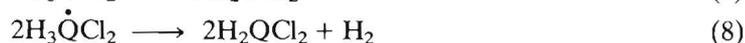
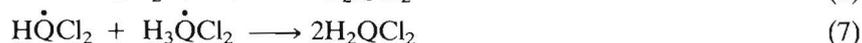


Table 1. $G(-H_2QCl_2)$ in the radiolysis of $5 \times 10^{-4} M H_2QCl_2$ in deaerated solutions.

$[H_2SO_4]$ M	solute	$[solute]$ M	$G(-H_2QCl_2)$
1	—	—	0
5×10^{-4}	—	—	0
1	propan-2-ol	0.1	0
1	propan-2-ol	0.001	0.21
1	ethanol	0.1	0.5
1	ethanol	0.01	0.9
0.5	methanol	0.1	1.2
1	t-butanol	0.012	0.9
1	t-butanol	0.2	1.2
1	t-butanol	1	0.6
1	Sod. Chloride	0.1	0.1

Reaction (4) is more probable than reaction (6), since it was reported that the rate coefficient of reaction (4) in the case of H_2Q is $1.3 \times 10^9 M^{-1} s^{-1}$ [Micic and Nenadovic 1976]. Because of the electron withdrawing effect of Cl, H_2QCl_2 would probably have a higher rate coefficient than H_2Q .

Table 1 shows the effect of the addition of some alcohols and NaCl on the disappearance of H_2QCl_2 . This disappearance is much less than that observed for H_2Q . This result may indicate that the product of reaction (4) may disappear in reaction(s) other than (7 & 8), such as:



Since there is not much information which can help to explain the reaction mechanism, then the addition of an e_{aq}^- and H scavengers may help to clarify the situation. N_2O and H_2O_2 are such scavengers which not only react with the reducing species but also convert them to oxidizing species.

The saturation of $5 \times 10^{-4} M H_2QCl_2$ with N_2O leads to the formation of QCl_2 . Its yield is very sensitive to dose and a typical plot is shown in Fig. 1. All the reported G values are the initial values as obtained from the initial slopes. The effect of pH on $G(QCl_2)$ is shown in table 2. The behaviour of this system is similar to that observed in the radiolysis of H_2Q [Al-Suhybani and Hughes 1985]. Table 3 shows the effect of $[H_2QCl_2]$ at pH = 2.6.

In the presence of N_2O , the following reactions will occur, in addition to those occurring in its absence:

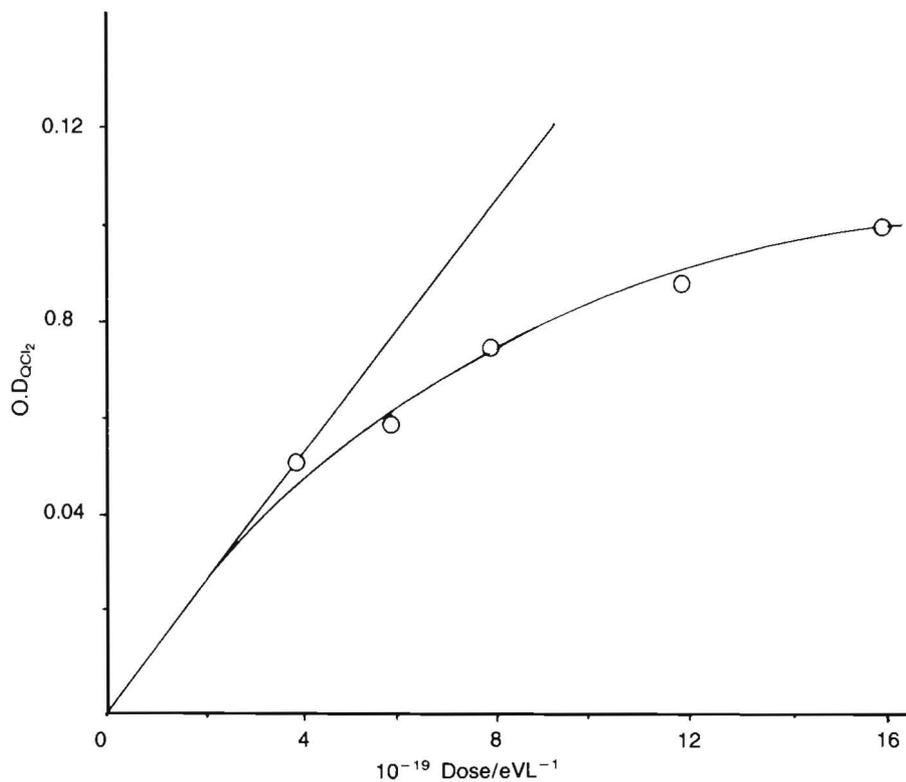
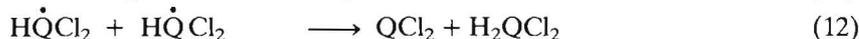
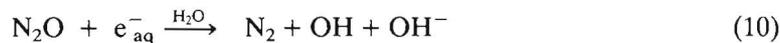


Fig. 1. Dependence of $O.D_{OCl_2}$ on dose in the radiolysis of $5 \times 10^{-4}M$ H_2QCl_2 at pH 2.30 saturated with N_2O .

Table 2. $G(QCl_2)$ in the radiolysis of $5 \times 10^{-4}M$ H_2QCl_2 in the presence of N_2O at different PH.

pH	$G(QCl_2)_{\text{meas.}}$	$G(QCl_2)_{\text{calc.}}$
1.18	0.40	~ 0
1.41	0.38	0.23
1.64	0.67	0.48
1.79	0.94	0.84
2.06	1.42	1.29
2.30	1.21	1.64
2.60	1.25	2.40
2.83	1.25	—
3.29	0.95	—
4.30	0.74	—



Reaction (11) is slow [Abar and Neta 1967] and could be neglected. The increase in $G(\text{QCl}_2)$ with increasing pH is expected since reaction (10) will compete effectively with reaction (2) upon increasing pH. Assuming that reactions (4 & 7) are taking place, then $G(\text{QCl}_2)$ would be given by the following expression:

$$G(\text{QCl}_2) = \frac{1}{2} [G_{\text{OH}}] + G_{e_{\text{aq}}^-} \frac{k_{10}[\text{N}_2\text{O}]}{k_2[\text{H}^+] + k_{10}[\text{N}_2\text{O}]} - G(\text{H}_3\dot{\text{Q}}\text{Cl}_2) \quad (13)$$

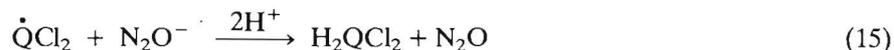
Here $\text{H}_3\dot{\text{Q}}\text{Cl}_2$ is the product of reaction (4) and its yield is given by:

$$G(\text{H}_3\dot{\text{Q}}\text{Cl}_2) = G_{e_{\text{aq}}^-} \frac{k_2[\text{H}^+]}{k_2[\text{H}^+] + k_{10}[\text{N}_2\text{O}]} + G_{\text{H}} \quad (14)$$

Table 3. $G(\text{QCl}_2)$ in the radiolysis of H_2QCl_2 in the presence of N_2O at pH 2.6.

$10^4[\text{H}_2\text{QCl}_2]$ M	$G(\text{QCl}_2)$
1.0	1.28
2.5	1.25
5.0	1.25
10.0	0.81

As can be seen in table 2, upto pH ~ 2.1 there is a fair agreement between measured and calculated $G(\text{QCl}_2)$. At high pH, $G(\text{QCl}_2)_{\text{calc}} \geq G(\text{QCl}_2)_{\text{meas}}$ and the difference gets bigger at high pH. This indicates that at low pH, reaction (7) is occurring. At high pH, N_2O will react with most of the e_{aq}^- and the low yield of QCl_2 indicates another efficient back reaction. A possible reaction is:



This reaction is pH dependent so that the yield of QCl_2 would be pH dependent. The fact that $G(\text{QCl}_2)$ is independent of $[\text{H}_2\text{QCl}_2]$ in the range $10^{-4} - 5 \times 10^{-4} \text{M}$ would indicate that the intermediate N_2O^- is not reacting with H_2QCl_2 .

In the presence of H_2O_2 , the measured product was QCl_2 and its yield was found to depend on dose and on $[\text{H}^+]$, $[\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{QCl}_2]$ as can be seen in tables 4-6 respectively. It was not possible to reduce $[\text{H}^+]$ further because it was observed that a thermal reaction between H_2O_2 and H_2QCl_2 becomes appreciable at lower $[\text{H}^+]$.

Table 4. $G(\text{QCl}_2)$ in the radiolysis of $5 \times 10^{-4} \text{M}$ H_2QCl_2 and $7.4 \times 10^{-2} \text{M}$ H_2O_2 in H_2SO_4 , deaerated solutions.

$\frac{[\text{H}_2\text{SO}_4]}{\text{M}}$	$G(\text{QCl}_2)$
0.005	1.34
0.01	1.20
0.02	1.42
0.05	1.56
0.1	1.96
0.25	2.00
1.0	2.03

In the presence of H_2O_2 , the following reactions will occur:



$k_{18} \geq k_{17} \geq k_{16}$ [Anbar and Neta 1967] so that only at high $[\text{H}_2\text{O}_2]$ will radiolytic species be converted to HO_2 . At the concentrations used in this work, both OH and HO_2 will be present in concentrations depending on $[\text{H}^+]$, $[\text{H}_2\text{O}_2]$ and $[\text{H}_2\text{QCl}_2]$. A precise quantitative analysis is not possible due to the absence of any information concerning reactions 3 & 4 and also to the impossibility of determining $G(\text{H}_2\text{O}_2)$. It is, however, possible to give a qualitative description of this system.

Assuming that reaction (18) is slow in comparison with reaction (2) in 1M H_2SO_4 , then H_3QCl_2 will remove an equal amount of HQCl_2 , but HO_2 will react according to:



Table 5. $G(\text{QCl}_2)$ as a function of $[\text{H}_2\text{O}_2]$ in the radiolysis of $5 \times 10^{-4} \text{M}$ H_2QCl_2 in 1M H_2SO_4 , deaerated solutions.

$10^2[\text{H}_2\text{O}_2]$ M	$G(\text{QCl}_2)$ meas.	$G(\text{QCl}_2)$ calc.	$\Delta G(\text{QCl}_2)$
0	0	—	—
0.20	0.18	0.64	0.46
0.30	0.22	0.96	0.74
0.45	0.54	1.32	0.78
0.70	1.15	1.72	0.57
1.10	1.38	2.11	0.73
1.20	1.30	2.15	0.85
1.90	1.38	2.51	1.13
2.40	1.89	2.63	0.74
3.70	1.94	2.83	0.89
11.0	2.16	3.12	0.96
15.0	2.59	3.16	0.57
24.0	2.59	3.27	0.68
33.0	2.68	3.27	0.59

$G(\text{HO}_2)$ and $G(\text{H}_3\dot{\text{QCl}}_2)$ are calculated from the following expressions:

$$G(\text{HO}_2) = [G_{\text{OH}} \frac{k_{16}[\text{H}_2\text{O}_2]}{k_3[\text{H}_2\text{QCl}_2] + k_{16}[\text{H}_2\text{O}_2]} + G(\text{H}) \frac{k_{17}[\text{H}_2\text{O}_2]}{k_4[\text{H}_2\text{QCl}_2] + k_{17}[\text{H}_2\text{O}_2]}] \times \frac{k_{16}[\text{H}_2\text{O}_2]}{k_3[\text{H}_2\text{QCl}_2] + k_{16}[\text{H}_2\text{O}_2]} \quad (20)$$

$$G(\text{H}_3\dot{\text{QCl}}_2) = G(\text{H}) \frac{k_4[\text{H}_2\text{QCl}_2]}{k_4[\text{H}_2\text{QCl}_2] + k_{17}[\text{H}_2\text{O}_2]} \quad (21)$$

QCl_2 is, then, produced according to reaction (12). In other words, $\text{H}\dot{\text{QCl}}_2$ will be produced by reactions 3 and/or 19 and according to the above assumptions, its yield will be given by:

$$G(\text{H}\dot{\text{QCl}}_2) = \frac{1}{2} [G(\text{Radicals}) - 2G(\text{H}_3\dot{\text{QCl}}_2)]$$

In the above calculations the values of the rate coefficients of reactions 16, 17 and 18 were taken as: 1.2×10^7 , 1.6×10^8 and $1.2 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ respectively (Anbar and Neta 1967).

Table 6. $G(\text{QCl}_2)$ as a function of $[\text{H}_2\text{QCl}_2]$ in the radiolysis of 0.15 M H_2SO_4 deaerated solutions.

$\frac{10^4[\text{H}_2\text{QCl}_2]}{\text{M}}$	$G(\text{QCl}_2)$
0	0
0.5	0.84
1.0	1.44
2.0	1.79
2.8	2.30
3.5	2.59
5.0	2.59
7.0	2.77
9.0	2.77
11.5	2.77
14.0	2.82
17.0	2.77
20	2.77

In addition, the above calculations assumed that reactions 6 and 9 were ignored and that reaction 12 is slow in comparison to reaction 7. These assumptions could be taken to account for the differences between the observed and calculated $G(\text{QCl}_2)$. As can be seen in table 5, $G(\text{QCl}_2)_{\text{calc}}$ increases with increasing $[\text{H}_2\text{O}_2]$ and becomes constant at $\sim 0.15\text{M}$ H_2O_2 . This behaviour is similar to that found experimentally, though the absolute values are higher. It is worth mentioning that $\Delta G(\text{QCl}_2) = G(\text{QCl}_2)_{\text{calc}} - G(\text{QCl}_2)_{\text{meas}}$ is roughly constant as can be seen in table 5. This difference may also be attributed to the uncertainty in the values of the rate coefficients of some of the reactions involved.

At constant $[\text{H}_2\text{O}_2]$, $G(\text{QCl}_2)$ increases with increasing $[\text{H}_2\text{QCl}_2]$ and becomes constant at $2.5 \times 10^{-4}\text{M}$ H_2QCl_2 , as can be seen in table 6. If the reaction mechanism outlined above is assumed to be the most likely pathway for the formation of QCl_2 , then decreasing $[\text{H}_2\text{QCl}_2]$ should have an effect on $G(\text{QCl}_2)$ similar to that produced by increasing $[\text{H}_2\text{O}_2]$, *i.e.* $G(\text{QCl}_2)$ should be higher at low $[\text{H}_2\text{QCl}_2]$ and *vice-versa*. As table 6 shows, this is not the case. This need not represent a contradiction with the result obtained above, since at low $[\text{H}_2\text{QCl}_2]$, other complications would arise from, for example the reaction:



which would proceed in competition with reaction (19). For example, at 0.15M H_2O_2 and 10^{-4}M H_2QCl_2 , $G(\text{OH})$ would be ≈ 0.8 , $G(\text{HO}_2) \approx 5.7$ and $G(\text{H}_3\text{QCl}_2)$

$\approx \text{O}$. This would indicate that reaction (22) is the most favourable reaction by which all the HO_2 disappears under these conditions. It can be also concluded that since $\text{G}(\text{QCl}_2) \approx 2 \text{G}(\text{OH})$, reaction (19) is more probable than the reaction:



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دراسات إشعاعية على مركب ٢ و ٥ - ثنائي كلوروهيدروكينون في المحاليل المائية

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المملكة المتحدة

إن تشعيع المركب ٢ و ٥ - ثنائي كلوروهيدروكينون عند قيم مختلفة للرقم الهيدروجيني لا ينتج عنه أي تغيير في المركب كما أن إضافة NaCl وبعض الكحولات يؤدي إلى اختفاء كمية ضئيلة من المركب الهيدروكينوني وهذا يدل على وجود تفاعل عكسي نشط . أما عند إضافة H_2O_2, N_2O فإنه يلاحظ تكون ٢ و ٥ - ثنائي كلوروهيدروكينون . وقيمة G لهذا الناتج تعتمد على الجرعة الإشعاعية والرقم الهيدروجيني . . . الخ . وقد اقترحت ميكانيكية للتفاعل تأخذ بعين الاعتبار الملاحظات التجريبية . وقد استنتج أن هذا الهيدروكينون مقاوم للتلف الإشعاعي .