

Kinetic Study of the Fast Step of the Alkaline Hydrolysis of *p*-Chloranil Using Stopped Flow Technique

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ABSTRACT: The alkaline hydrolysis of *p*-chloranil or 2,3,5,6-tetrachloro-1,4-benzoquinone ($C_6Cl_4O_2$, Q) was studied, using stopped flow spectrophotometry and Electron Spin Resonance techniques (E.S.R.). In the present study it was shown for the first time, that a free radical is produced chemically and that it can account for the propagation of the reaction. It was found that in alkaline conditions chloranil in a "Michael" fashion undergoes 1,2 addition being hydrolyzed and in turn produces a chloranil free radical ($Q\cdot$). The hydrolysis then proceeds via a number of intermediates yielded by this radical and a number of different products is formed. The formation of these products, both quantitatively and qualitatively has a strong dependence on the concentration of the OH^- species and chloranil. The various possible routes of the hydrolysis are studied either spectrophotometrically or by E.S.R. Two different intermediates are observed absorbing at 426 nm and at 540 nm, respectively. Each species was formed and destroyed within 10 s to 30 min depending on the exact conditions. The reaction rate constants for the formation and the decay of the intermediates was estimated using the Guggenheim method. At both wavelengths the rate constants seem to have a complex relation to the concentration of the anion. © 1997 John Wiley & Sons, Inc. *Int J Chem Kinet* **29**: 385–391, 1997.

INTRODUCTION

According to the literature [1–5] *p*-Chloranil or 2,3,5,6-tetrachloro-1,4-benzoquinone ($C_6Cl_4O_2$, Q), in alkaline conditions yields chloranilic acid or 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone ($C_6Cl_2O_4H_2$). The exact mechanism of the process is not clearly understood. It has been suggested that in excess of alkali the reaction proceeds via two steps. In the first step *p*-chloranil undergoes nucleophilic

substitution, losing one chloride ion, and producing monohydroxy chloranilic acid or 2,3,5-trichloro-6-hydroxy-1,4 benzoquinone ($C_6Cl_3O_3H$) and subsequently in the second step another chlorine ion is lost to get eventually chloranilic acid. In this work there is no concluding evidence of chloranilic acid being produced within the time scales measured, and at 25°C. There is experimental evidence that the reaction proceeds through a different mechanism, than previously suggested, involving more reactive intermediates.

The presence of intermediates, other than the corresponding acids, has been suggested in the literature

although their identity has not been revealed. Slifkin [1] has indicated that the reaction proceeds through a "transit state" that could not be identified, while Bishop [2] could not account for a compound formed when *p*-chloranil was dissolved in cold KOH.

p-chloranil is a very good electron acceptor that can draw electrons forming free radicals [6]. Rich literature exists [6–9] on the formation of free radicals, using laser "flush photolysis," by benzoquinones that under appropriate conditions produce the benzoquinone free radical in the single, triplet, the neutral, and the anionic form.

In order to monitor this reaction the stopped-flow technique was chosen. According to this method two solutions flow separately and are mixed at the reaction vessel, where the flow is abruptly interrupted. At the point of interruption the reaction between the two solutions is monitored spectrophotometrically. All reagents were made in a 1:1 dioxane to water mixture.

EXPERIMENTAL

All chemicals were of analytical grade obtained either from Sigma or from Merck. The stopped-flow was the model "The bio sequential SX17MV" made by Applied Photophysics Ltd, England and the E.S.R. was "VARIAN E-109 Spectrometer." Working solutions of *p*-chloranil in dioxane were made up at equal volumes with water. The resulting solution was introduced into one of the syringes of the instrument. In the other syringe was a solution containing an alkaline solution made up of 1/1 by volume with dioxane. So both syringes contained solutions of the same mixture of solvents (v/v water to dioxane). Spectra were obtained approximately 1 min after mixing unless otherwise stated. Temperature was controlled at 25°C.

RESULTS AND DISCUSSION

The spectrum of *p*-chloranil in dioxane shows no peaks as seen in Figure 1(a). Upon addition of NaOH, two new peaks appear, Figure 1(b). Both these peaks show the same decay with respect to time while a further peak is formed later at 332 nm. Under specific conditions (low NaOH concentration) another peak is formed at 362 nm. Attempts were made to study the spectra in the UV region. However, it soon became

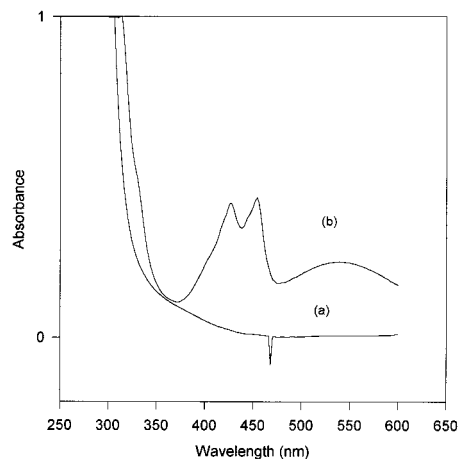


Figure 1 Spectrum of 1.25×10^{-4} M *p*-chloranil (a) and after treatment with 1.25×10^{-2} M NaOH (b).

apparent that all reactants, products, and intermediates absorb in that region, and so distinguishing between the different absorption bands would be very difficult. Thus, all efforts were concentrated in the visible area of the spectrum. Another important observation made was that small changes in the reactant concentration resulted in significant changes in the reaction pattern, that could not be explained by experimental error. This is in accordance with the literature [7]. Figure 2 illustrates this observation where variations on the concentration of NaOH result in significant differences in the form of the spectra. This lead us to believe that the intermediates formed (very

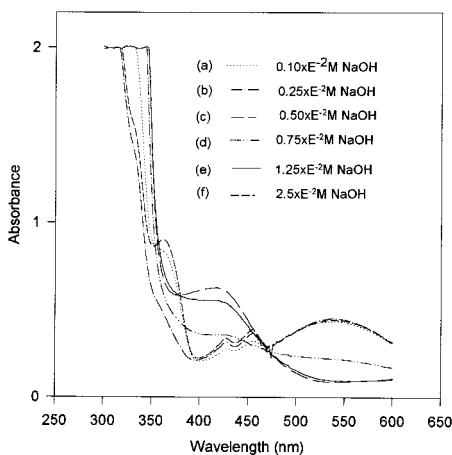


Figure 2 Spectra of 1.25×10^{-4} M *p*-chloranil after treatment with six successive solutions of different NaOH concentration.

rapidly) have a complex dependence on the concentration of the reactants.

KINETIC STUDY

The kinetic behavior of the species resulting in the two peaks (Fig. 1), is shown in Figures 3(a) and 3(b). Under different experimental conditions similarly shaped curves were obtained. If the reaction was a simple hydrolysis then the two peaks at 426 nm and 540 nm would be attributed to intermediates (e.g., the monohydroxy acid) and the peak at 332 nm to the final product (chloranilic acid). According to the literature these peaks (with the exception of the peak at 332 nm, which was identified in the literature as chloranilic acid) correspond either to photochemically produced radicals [13] or to complexes of the acid [15]. Since the formation of a chloranilic acid complex was unlikely we tested the hypothesis that free radicals were present, produced chemically.

The same experimental procedure was followed but substituting NaOH with KOH and Na₂CO₃. In the case of KOH the experimental observations were similar to those of NaOH except that the rate of decomposition of the peak at 426 nm was reduced, while the formation of that peak accelerated. That led us to believe that there is some process of stabilization involving the cation Na⁺ or K⁺. In the case of the carbonate group the intermediate was much more stable and the behavior of the system was reminiscent of that observed at low concentrations of NaOH

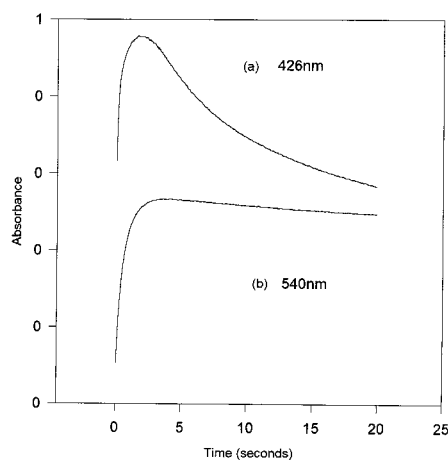


Figure 3 Kinetic curve of the production and decay of the intermediate at 426 nm (a) and 540 nm (b). Initial concentrations: *p*-chloranil 1.25×10^{-4} M and NaOH 1.25×10^{-2} M.

which was expected since the alkaline strength of the group is much smaller.

Analysis of the Kinetic Curves

In order to describe the curves shown on Figure 3 the Guggenheim method was applied [10,11]. This is a method for estimating the rate constant of a first-order reaction when the absorbance at infinite time is not known. According to this method a plot of $\ln(A_t - A_{t+\tau})$ vs. t , where τ is an arbitrary time constant, yields a straight line of slope equal to the rate of the reaction (k_{obs1}). Tables I and II show the rates obtained by this method. Equation (1) is true for two consecutive first-order reactions [10–12].

All k 's refer to k observed:

$$T_{\text{max}} = \ln(k_2/k_1)/(k_2 - k_1) \quad (1)$$

Since the rate of the second reaction is much slower than that of the first $k_1 \gg k_2$ then eq. (1) becomes:

$$\begin{aligned} T_{\text{max}} &\cong \ln(k_2/k_1)/(-k_1) \implies \\ k_1 \times T_{\text{max}} &\cong -\ln(k_2/k_1) \implies \\ k_2/k_1 &\cong e^{-k_1 T_{\text{max}}} \implies \\ k_2 &\cong k_1 e^{-k_1 T_{\text{max}}} \quad (2) \end{aligned}$$

Therefore, from eq. (2) the values of k_2 can be calculated knowing k_1 and T_{max} .

The complexity of the reaction is obvious from Tables I and II. However, by studying the Guggenheim method it can be seen that the rate constant of all the reactions decreases with increasing OH⁻ concentration. Also it can be seen that at both wavelengths the rate constant remains unchanged with respect to *p*-chloranil concentration when KOH was used. The values for the decay of the intermediate differ from those given in the literature [13,17] probably because the conditions are not identical. Taking into account the spreading of these values this should only be expected.

E.S.R. STUDY

Proof for the presence of the free radical was obtained from the E.S.R. studies. A solution containing 1×10^{-3} *p*-chloranil in dioxane and 0.05 M NaOH was introduced into the instrument and within 1 min

Table I Calculations of K_{obs} Values by Guggenheim's Method using KOH as the Anion Donor

$\text{KOH} \times \text{E}^{-2}$ M	$\text{Chl} \times \text{E}^{-4}$ M	426 nm			540 nm		
		$T_{\text{max}},$ s	$k_{\text{obs1}},$ s^{-1}	$k_{\text{obs2}},$ s^{-1}	$T_{\text{max}},$ s	$k_{\text{obs1}},$ s^{-1}	$k_{\text{obs2}},$ s^{-1}
1.25	0.5	0.7	6.9	5.5×10^{-2}	1.6	4.1	5.8×10^{-3}
1.25	1.25	0.7	6.9	5.5×10^{-2}	1.7	4.5	2.1×10^{-3}
1.25	2.5	0.6	6.9	1.1×10^{-1}	1.7	4.5	2.1×10^{-3}
1.25	5.0	0.6	6.9	1.1×10^{-1}	1.5	4.4	6.0×10^{-3}
0.25	0.5	3.2*	14.0	4.9×10^{-19}	0.7	9.2	1.5×10^{-2}
0.62	0.5	3.2*	12.1	1.8×10^{-16}	0.8	9.2	5.8×10^{-3}
2.5	0.5	1.2	8.9	2.0×10^{-4}	1.7	4.5	2.1×10^{-3}

*At these values it was very difficult to read T_{max} since k_{obs2} was very small.

the spectrum obtained. g -values were measured with reference to diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$). The g -value for the radical produced in solution was calculated as 2.0059. This value is very close to both the neutral radical of the semibenzoquinone ($g = 2.0055$) [13] and to the anionic radical ($g = 2.0057$) [16]. From this information it cannot be concluded which radical form was produced since g -values from different laboratories are difficult to compare [13,14]. However, this radical is charged since when produced with KOH instead of NaOH its kinetic behavior was altered.

The data obtained from the E.S.R. study, together with the proximity of the visible spectrum, compared to that of the laser-flash photolysis experiments [6,7,15,16], made us believe that this intermediate is the same free radical as that produced by the laser experiments. The wavelengths where the radicals showed maximum absorbance almost coincided with those of the chemical production of the free radical.

The free radicals produced by KOH and NaOH

had similar g -values of 2.00585 and 2.00578, respectively. The proximity of these values leads to the conclusion that it is the same free radical present in all these systems. The decay of the radical as studied by E.S.R. is shown on Figure 4, which shows consecutive spectra obtained every 0.3 min. Using the infinite time method k_{obs} was found to be 0.005 s^{-1} . This value was comparable to the k_{obs} values found from the Guggenheim method for the intermediate decaying at 426 nm, thus providing further evidence that the free radical is absorbed at this wavelength.

In order to study further the formation of this radical a stopped-flow/E.S.R. instrumental arrangement would be necessary.

MECHANISM

A mechanism can be drawn for the alkaline hydrolysis of chloranil involving three steps:

Table II Calculations of K_{obs} Values by Guggenheim's Method using NaOH as the Anion Donor

$\text{NaOH} \times \text{E}^{-2}$ M	$\text{Chl} \times \text{E}^{-4}$ M	426 nm			540 nm		
		$T_{\text{max}},$ s	$k_{\text{obs1}},$ s^{-1}	$k_{\text{obs2}},$ s^{-1}	$T_{\text{max}},$ s	$k_{\text{obs1}},$ s^{-1}	$k_{\text{obs2}},$ s^{-1}
0.1	5.0	1.6	13.3	7.6×10^{-9}	0.4	7.3	3.9×10^{-1}
0.25	5.0	2.7	4.6	1.9×10^{-5}	1.2	9.1	1.6×10^{-4}
0.5	5.0	6.0*	4.4	1.5×10^{-11}	1.6	7.7	3.4×10^{-5}
0.62	5.0	5.1*	7.6	1.1×10^{-16}	1.9	4.2	1.4×10^{-3}
1.25	5.0	1.8	6.3	7.5×10^{-5}	2.2	2.4	1.2×10^{-2}
2.5	5.0	0.9	7.3	1.0×10^{-2}	1.5	2.3	7.3×10^{-2}
5.0	5.0	0.6	7.3	9.1×10^{-2}	1.3	2.3	1.2×10^{-1}

*At these values it was very difficult to read T_{max} since k_{obs2} was very small.

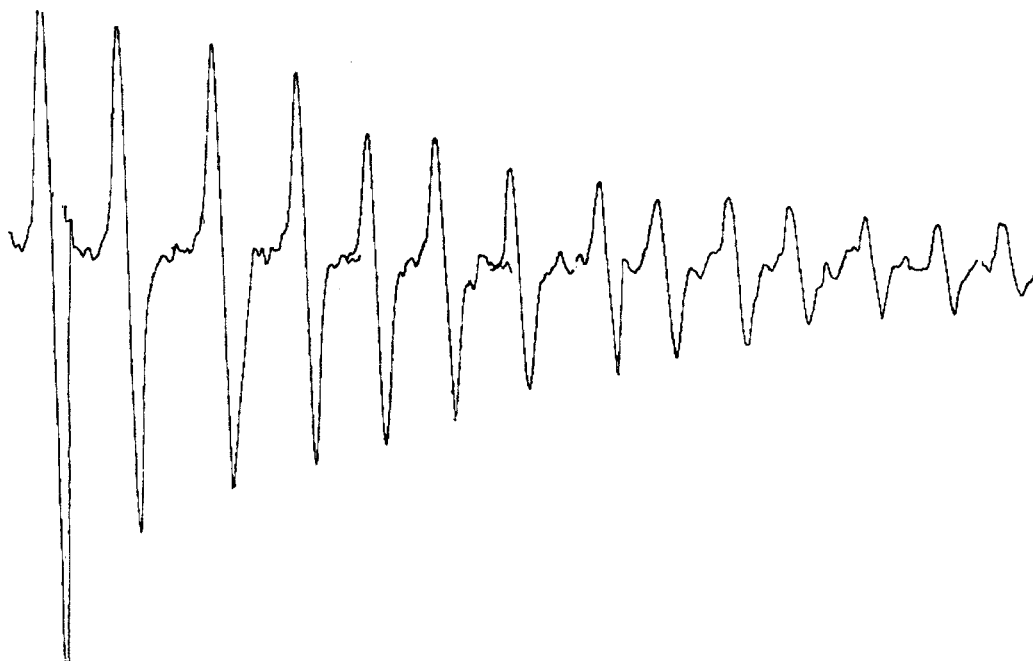


Figure 4 Decay of the intermediate as observed by the E.S.R. Initial concentrations: *p*-chloranil 1.25×10^{-4} M and NaOH 1.25×10^{-2} M.

Step 1

The first step is the alkaline hydrolysis of chloranil in a "Michael" fashion, i.e., 1,2 addition (Fig. 5). The anion (I) produced reacts with another chloranil molecule yielding neutral radical (II) and a radical anion (III). The neutral radical has a very short life time and probably does not take any further part in the reaction. The radical anion was observed in the spectrophotometric experiments giving rise to the double peak at 426 and 454 nm and in the E.S.R. spectrum with a *g*-value of 2.00585. This radical can exist in the three resonance forms shown in Figure 6 (IV, V, VI).

Step 2

When chloranil is in abundance then either self disproportionation, yielding compound (VII), or self substitution (compounds VIII and IX) can occur.

Step 3

When the OH^- is in excess then the reaction proceeds as shown in Figure 7. The OH^- attacks radical VI and produces the two resonance forms noted, X and XI. Form X reacts with another chloranil molecule yielding monohydroxy acid (XII) and the origi-

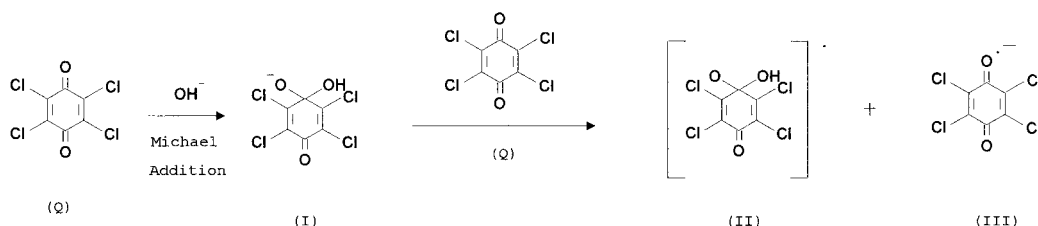


Figure 5 Suggestive mechanism of the first step of the alkaline hydrolysis of *p*-chloranil.

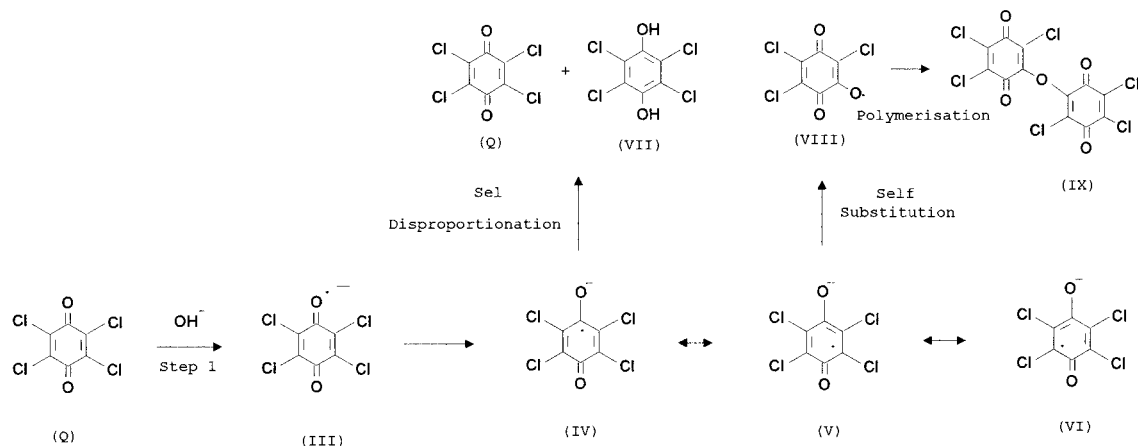


Figure 6 Suggestive mechanism of the second step of the alkaline hydrolysis of *p*-chloranil.

nal radical anion (III). Form XI is attacked by another OH^- molecule producing compound XIII, which, in turn with another chloranil molecule, can yield chloranilic acid (XIV) and the original radical anion III.

This mechanism considers the various possible steps of the alkaline hydrolysis of *p*-chloranil when a free radical is formed. Other possibilities exist when no radical is present mainly the 1,4 addition yielding chloranilic acid. However, under the conditions stud-

ied this was not the case due to the reactivity of the radicals.

The scheme shown could be summarized as follows:

Step 1 (1,2 addition)

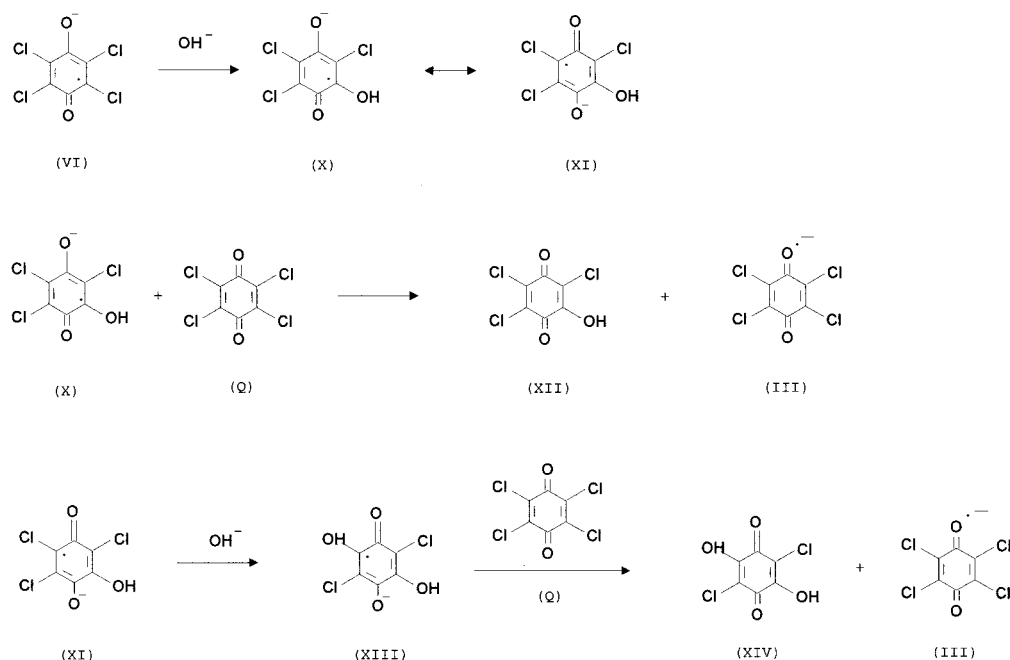
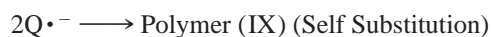
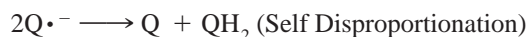
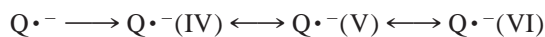
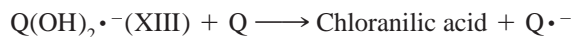
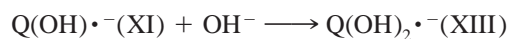
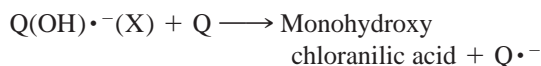
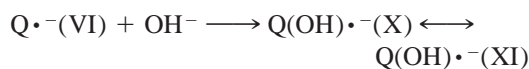


Figure 7 Suggestive mechanism of the third step of the alkaline hydrolysis of *p*-chloranil.

Step 2



Step 3



No conclusive experimental evidence can be provided for all the different steps shown in this mechanism. However, this scheme can explain the complex dependence of the rate of the reaction to the concentration of the reactants and the complicated appearance of Tables I and II.

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