Kinetics and Mechanism of The Addition of Triphenylphosphoniocyclopenta-dienide to Tetrachloro-p-benzoquinone

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The kinetics and mechanism of the reaction of triphenylphosphoniocyclopentadienide **1** with tetra-chloro-p-benzoquinone (chloranil **2a**) to yield 2,3,5-trichloro-6-(3-triphenylphosphoranylidene-cyclopenta-1,4-dienyl)-p-benzoquinone **3** in dichloromethane solution are reported. The rate limiting step was found to be electrophilic attack of tetrachloro-p-benzoquinone on the aromatic cyclopentadiene ring of the ylide. A thermochemical study of the system showed a small enthalpy and a large negative entropy of activation in agreement with the existence of a highly polar betaine as an intermediate in the reaction. The proposed mechanism involves bimolecular transfer of a proton to a molecule of ylide. No evidence was found either for the formation of a π-complex or for acid catalysis of the reaction.

It is well known from the work of Ramirez and Levy that triphenylphosphoniocyclopentadienide **1** exhibits unusual

1

2a X = Cl
b X = Br
c X = I

3

4
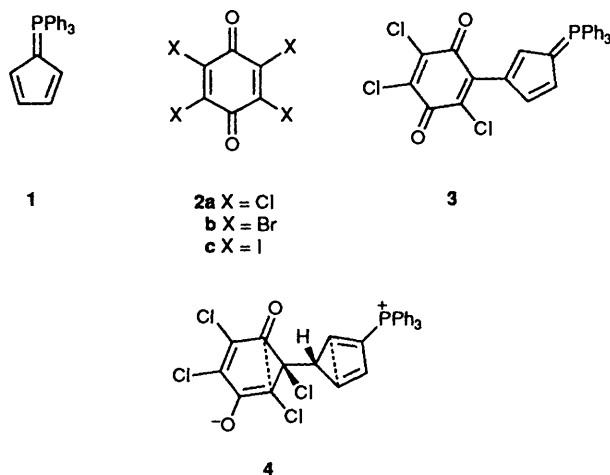
stability and reactivity.[1] Thus, **1** does not take part in the Wittig reaction[1,2] nor does it yield Diels–Alder products by reaction with dienophiles.[3] Instead reaction of the ylide with powerful dienophiles such as acetylene dicarboxylates or tetracyano-ethylene yields exclusively Michaelis addition products at position 2 of the cyclopentadiene ring,[4] which illustrates the strongly aromatic character of the delocalised carbanion. The aromaticity has been confirmed by crystallographic analysis of the structure and by electron density calculations on the cyclopentadiene ring.[5] Quantum chemistry calculations also support this conclusion.[4,6] The ylide undergoes aromatic substitution reactions with strongly electron-deficient com-pounds (e.g., diazonium salts) and thus coloured azo-derivatives of the ylide are known.[7–9] The kinetics and mechanism of nucleophilic addition of the ylide to substituted cyanovinyl-benzenes in polar organic media have also been studied.[10–13] The general mechanism of addition involves a π-intermediate which evolves to give a polar betaine. The betaine is protonated by proton-transfer species present in the reaction medium, or it proceeds to product via an intramolecular proton transfer; these reactions are catalysed by acids.

The ylide also reacts with other molecules possessing electron-

deficient double bonds, such as p-benzoquinones, to give coloured products which were originally attributed to charge transfer complexes.[14–16] Interactions between the ylide and tetrachloro-p-benzoquinone (chloranil), which exhibits a strong electron-withdrawing capacity,[17,18] are reported in this paper.

Reaction mixtures of dichloromethane solutions of chlor-anil[19–21] and ylide develop a deep blue colour very rapidly at room temperature. The absorbance spectrum shows a broad band located between 500 and 850 nm (ε_{max} ca. 9180 dm^3 mol^{-1} cm^{-1}, λ_{max} = 690 nm, T = 298 K). The band was originally attributed to a charge transfer complex, but its anomalous behaviour showed that it was best assigned to a σ-bonded compound which was subsequently isolated and character-ized.[22] Compound **3** is a new class of zwitterionic dye which may be of interest as a result of its potential value as an organic conductor and/or semiconductor.[23,24] This paper deals with the kinetics of the electrophilic addition of chloranil to ylide to yield **3** in aprotic media.

Experimental

Materials.—Triphenylphosphoniocyclopentadienide **1** was prepared by a modification[10] of the method reported by Ramirez.[1] For kinetic runs further purification was carried out by recrystallization three times from ethanol[10] followed by a recrystallization from toluene.[5] The quality of the purified product was checked by IR and ^{1}H and ^{31}P NMR spectro-scopy.[1,10]

Tetrachloro-p-benzoquinone **2** was supplied by Fluka Chemie AG. The commercial product was recrystallized twice from acetone and then sublimed as previously reported[19] to give bright yellow crystals, m.p. = 290 °C. The quality of the purified product was checked by IR spectroscopy.

Dichloromethane (IR grade) was used as supplied by Panreac. The solvent was dried by adding NaOH (25 g dm^{-3}) and stirring the mixture for 10 min at room temperature. The solvent was then decanted and distilled twice from calcium hydride. Only freshly distilled dichloromethane was used for kinetic runs.

Absorbance Measurements.—Absorbance vs. time curves were recorded with a spectrophotometer (Kontron, Uvikon 930) attached to a fast mixer unit (Hitech, SAF-11) and a
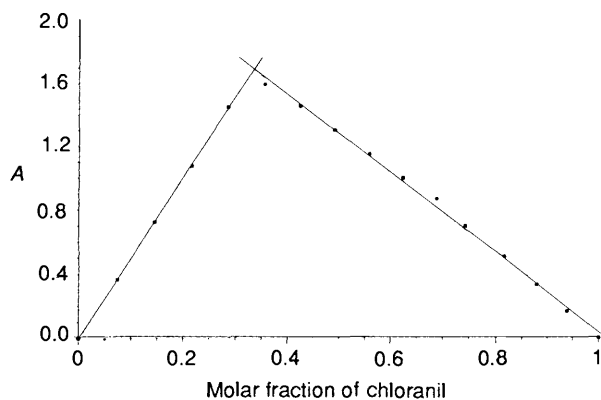
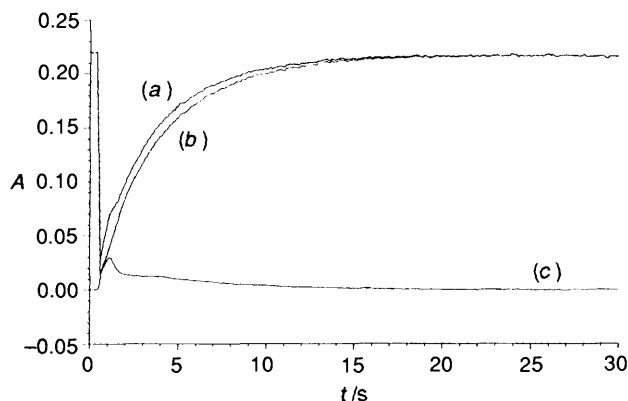**Fig. 1** Job plot for the chloranil–ylide system at 298 K in CH_2Cl_2

Fig. 2 Absorbance vs. time curves (a, uncorrected) and (b, corrected) and base line (c) obtained at 690 nm from a reaction mixture containing 2.0×10^{-5} mol dm^{-3} chloranil and 5.0×10^{-4} mol dm^{-3} ylide at 273 K with CH_2Cl_2 as solvent
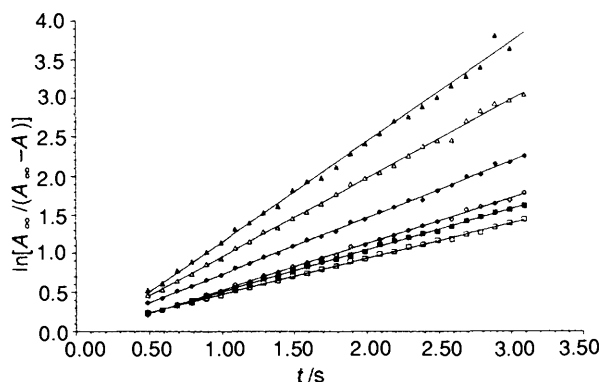

Fig. 3 Typical plots from eqn. (1) at 690 nm and 298 K in CH_2Cl_2 $[CA]_0 = 2.0 \times 10^{-5}$ mol dm^{-3}; $[Y]_0 = 4 \times 10^{-4}$ (□), 4.5 × 10^{-4} (■), 5.0 × 10^{-4} (◇), 6.0 × 10^{-4} (◆), 8.0 × 10^{-4} (△) and 1 × 10^{-3} (▲)

temperature-regulated cell holder. Circulating water maintained a constant holder temperature to an accuracy of ± 0.1 °C. The temperature was monitored with a thermocouple attached to a stopped flow quartz cell of 1 cm path length. Nitrogen flow was maintained during measurements to avoid water condensation on the walls of the cells at low temperatures.

The wavelength chosen for the kinetic measurements was 690 nm at which the final product has the maximum absorbance values and ylide and chloranil do not absorb. Beer's law was obeyed by the product at this wavelength giving a molar absorption coefficient of 9180 $\pm$ 50 dm^3 mol^{-1} cm^{-1} at 25 °C in CH_2Cl_2.

Equilibrium Experiments.—In order to determine the

stoichiometry of the reaction, the absorbance of reaction mixtures containing 5.5×10^{-3} mol dm^{-3} of $[CA]_0 + [Y]_0$ was measured. The Job plot obtained is shown in Fig. 1. In a second experiment the ^{1}H NMR spectrum of a reaction mixture containing 2.63×10^{-3} mol dm^{-3} ylide and 1.20×10^{-3} mol dm^{-3} chloranil at 297 K in CD_2Cl_2 was recorded. The spectrum showed three multiplets between 6.10 and 7.30 ppm centred at 6.35, 7.10 and 7.20 ppm, assigned [22] to the cyclopentadiene protons of compound 3. A broad band was also observed at 3.62 ppm assigned to a CH_2 group of the protonated cyclopentadiene ring of compound 1. When a drop of triethylamine was added to the reaction mixture the resultant spectrum showed the above mentioned multiplets and an additional one centred at 6.20 ppm assigned [25] to the cyclopentadiene ring of compound 1. The band centred at 3.62 ppm was removed by the addition of the base.

In a third experiment five mixtures containing the same excess of ylide and variable amounts of choranil were extracted with distilled water and the aqueous phase was then titrated against sodium hydroxide.

Kinetic Experiments.—Stock solutions (2×10^{-3} mol dm^{-3}) of ylide and chloranil were prepared and the chloranil solution was stored in darkness.

In order to determine the order of reaction, stock solutions of chloranil and ylide were diluted to 0.4, 0.6, 0.8 and 1.0×10^{-4} mol dm^{-3} and to 0.2, 0.4, 0.8, 1.2 and 1.6×10^{-3} mol dm^{-3} respectively. Reaction mixtures were prepared by mixing equal volumes of each solution of chloranil with each solution of ylide. The absorbance vs. time curves at 25 °C were monitored every 0.1 s over a period of 30 s when more than 99.5% conversion was achieved. Rates at each concentration were measured five times.

In a second experiment a 4×10^{-5} mol dm^{-3} solution of chloranil was prepared. The stock solution of ylide was diluted from 1.0×10^{-3} to 1.0×10^{-4} mol dm^{-3} (six different excess concentrations of ylide). The absorbance curves of reaction mixtures obtained by mixing equal volumes of the chloranil solution with each of the ylide solutions were again monitored every 0.1 s for 30 s. The experiment was repeated at 0.3, 4.5, 9.9, 15.0, 20.1, 25.1, 30.1 and 35.1 °C. Each curve was recorded either five or six times.

A base line curve was measured for each of the absorbance vs. time curves. A straight line possessing a zero slope and intercept was expected, the solvent being transparent at 690 nm. However, a signal was recorded whose origin is probably the physical process of mixing. The signal was temperature dependent, the maximum correction being equal to 0.03 at 0.3 °C. The signal was not observed when water, ethanol, acetone or ethanol–water mixtures were used.

Data Treatment.—The absorbance vs. time curves were corrected by substracting the base line measured at each temperature. A typical absorbance vs. time curve and its base line are shown in Fig. 2, where a shoulder is seen on the uncorrected curve. Pseudo-first order rate coefficients were overestimated if no base line correction was made.

Eqn. (1) was applied to the absorbance vs. time data while it was obeyed. In fact when concentration of ylide was not in a great excess over concentration of chloranil, as in the first and second rows of Table 2, a curve was obtained whose initial slope was taken as k. For the results in Table 1 in which the ylide:chloranil ratio was 40 or more eqn. (1) was obeyed until at least 95% completion.

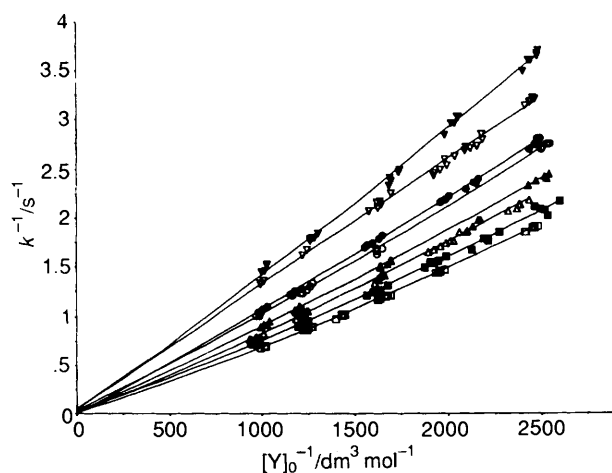$$\ln\left(\frac{A_\infty}{A_\infty - A}\right) = k(\tau - \delta) \tag{1}$$

Fig. 4 Plots of $1/k$ vs. $1/[Y]_0$ over a range of temperatures with CH_2Cl_2 as solvent. $T/K = 273.3$ (▼), 277.6 (▽), 283.1 (●), 288.2 (○), 293.2 (▲), 298.2 (△), 303.2 (■) and 308.1 (□).
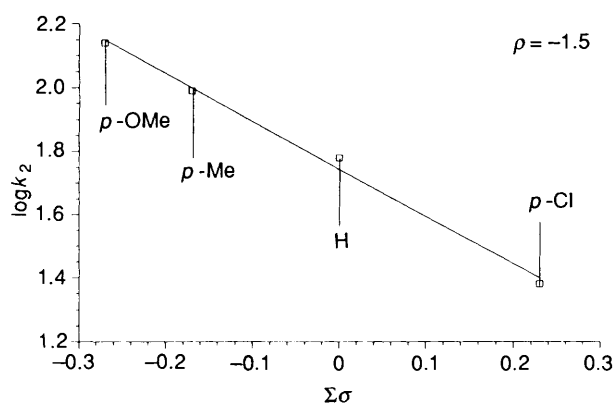
Fig. 5 Hammett plot of pseudo-second-order rate coefficients for the $(X-C_6H_4)Ph_2P=C_5H_4$ ($X = p$-Cl, H, p-Me, p-OMe) system at 303 K in toluene

In eqn. (1) k is the pseudo-first order rate coefficient, τ is the spectrophotometer measured time and δ the delay time between the true reaction time and the measured time, since measured time includes shut down and mixing time. Linearized corrected curves using eqn. (1) are shown in Fig. 3.

As a result of the randomness of the shut down time, each curve possesses a different origin time. Therefore, corrected curves cannot be averaged and must be treated separately. This is the reason why Table 1 gives 30–36 data points per experiment. Furthermore, we have observed that the injection volume ratio of reactants is a random quantity. Consequently, the ylide concentration must be estimated as described in the Appendix.

As will be described later, k vs. $[Y]_0([Y]_0 = $ initial concentration of ylide) curves were fitted using the weighted least-squares method [26] to empirical eqns. (2) and (3), and statistically more significant results were obtained using eqn. (3).

$$\frac{1}{k} = a_0 + a_1\frac{1}{[Y]_0}$$ (2)

$$\frac{1}{k} = a_1\frac{1}{[Y]_0} + a_2\left(\frac{1}{[Y]_0}\right)^2 \equiv \frac{[Y]_0}{k} = a_1 + a_2\frac{1}{[Y]_0}$$ (3)

It is noticeable as a consequence of the injection process that the fractional error obtained in k measurements is similar to that obtained in $[Y]_0$ measurements. Therefore, we prefer to use $1/k$ as dependent variable rather than $[Y]_0/k$ since the

fractional error in $([Y]_0/k)$ is equal to $1.4 \times$ fractional error in $(1/k)$.

Results and Discussion

Stoichiometry.—The Job plot shown in Fig. 1 exhibits a maximum at the molar ratio 1:2 (choranil:ylide). This indicates that two moles of ylide are needed to form one mole of compound **3**. Since only one molecule of ylide is found to be incorporated in the final product [22] the second one must play an important role in the reaction, and in all probability the second molecule reacts with an intermediate as a base.

The ^1H NMR spectrum of a reaction mixture containing a 1:2 mole ratio of chloranil:ylide, and the spectrum of the same reaction mixture to which a drop of triethylamine had been added, have been described previously. The final product signals were unaltered by addition of base but a new signal centred at 6.20 ppm appeared due to regeneration of the ylide. This reaction is clearly a proton transfer to the amine. The integrated signal ratio of the hydrogens of the cyclopentadiene ring of the final product and those of the ylide was unity. This agrees with the hypothesis that one molecule of ylide is used to form the final product and the other remains in solution as its hydrochloride salt. Thus ^1H and ^{31}P NMR spectra support the hypothesis that a proton is transferred to a second molecule of ylide from a reaction intermediate. Finally, the second molecule of ylide remains as the hydrochloride salt since the ^1H NMR spectra of reaction mixtures exhibit a broad band belonging to a CH_2 group centred at 3.62 ppm, which is removed by addition of base, consistent with the existence of a rapid intramolecular proton exchange. On the other hand, when reaction mixtures are extracted with pure water they yield an acidic aqueous phase whose titration curves indicate the presence of a weak acid. In fact, two inflexion points are observed; one of them associated with free HCl and the other associated with the hydrochloride salt. The addition of $AgNO_3$ to the aqueous phase gave a precipitate of AgCl. The measured extraction coefficient of the hydrochloride with water was 0.6 at 25 °C.

Dependence of Pseudo-first-order Coefficients on the Initial Concentrations of Ylide and Choranil.—The results of the *first* experiment (see Experimental section) are given in Table 2. The variation of the rate coefficients is close to zero along a row of the table, but they increase down a column. This fact eliminates the possibility of any catalysis of the reaction by chloranil.

The results of the *second* kinetic experiment are given in Table 1. A plot of $1/k$ vs. $1/[Y]_0$ is shown in Fig. 4 and all the plots show a slight curvature. If the data are forced to fit in a straight line [eqn. (2)] a significant negative intercept is obtained, but the data are well fitted to eqn. (3).

Reaction Mechanism.—The reaction passes through three important processes involving (i) formation of a new C–C bond, (ii) a C–H bond rupture and (iii) a C–Cl bond rupture. In previous work,[22] we demonstrated that the rate of the reaction of tetrahalogeno-p-benzoquinones with ylide decreases in the order F > Cl ~ Br > I. The energy of dissociation of a C–X bond (X = F, Cl, Br, I) decreases in the same order, and hence, rupture of the C–X bond cannot be the rate determining step.

The effect on the reaction rate of substitution of cyclopentadiene ring hydrogens by deuterium is given in Table 3. If proton transfer from the cyclopentadiene ring was the rate determining step a large $k_H:k_D$ ratio would be expected. However, a ratio close to 1 is observed indicating that C–H rupture does not control the reaction rate. The $k_H:k_D$ ratio is also unity with toluene as solvent. Therefore, the rate limiting step must be the formation of a new C–C bond between chloranil and ylide. This agrees with the fact that the reaction
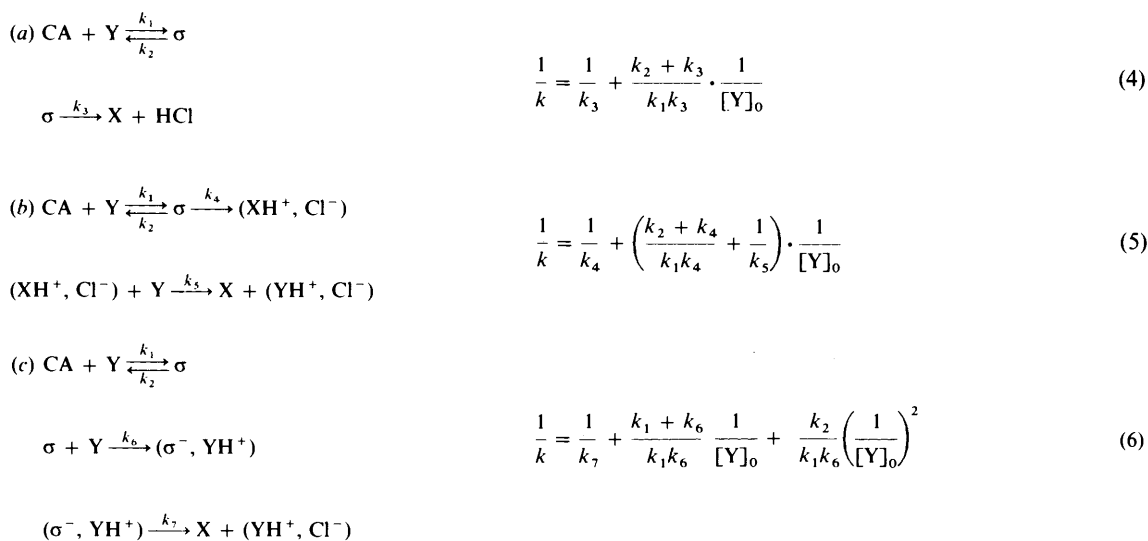
Table 1 Pseudo-first-order rate coefficients for the reaction of chloranil with ylide[a]

308.2 K		303.2 K		298.2 K		293.2 K	
[Y]	k	[Y]	k	[Y]	k	[Y]	k
4.05 ± 0.06	0.525 ± 0.003	4.06 ± 0.11	0.473 ± 0.004	4.18 ± 0.10	0.469 ± 0.003	0.97 ± 0.03	0.095 ± 0.001
4.13 ± 0.05	0.539 ± 0.003	3.97 ± 0.11	0.480 ± 0.005	4.10 ± 0.10	0.458 ± 0.004	0.99 ± 0.03	0.099 ± 0.001
4.14 ± 0.05	0.539 ± 0.003	4.01 ± 0.11	0.479 ± 0.004	4.20 ± 0.10	0.468 ± 0.004	0.96 ± 0.03	0.096 ± 0.002
4.08 ± 0.05	0.528 ± 0.003	3.94 ± 0.11	0.494 ± 0.004	4.19 ± 0.10	0.468 ± 0.004	1.00 ± 0.03	0.099 ± 0.002
4.03 ± 0.06	0.522 ± 0.003	3.84 ± 0.11	0.461 ± 0.004	4.31 ± 0.10	0.484 ± 0.004	1.00 ± 0.03	0.099 ± 0.002
4.05 ± 0.05	0.527 ± 0.003	4.52 ± 0.12	0.559 ± 0.006	4.22 ± 0.10	0.480 ± 0.004	1.96 ± 0.06	0.188 ± 0.003
5.11 ± 0.07	0.690 ± 0.004	4.51 ± 0.12	0.567 ± 0.004	4.75 ± 0.11	0.536 ± 0.004	1.96 ± 0.06	0.194 ± 0.002
5.12 ± 0.07	0.686 ± 0.004	4.39 ± 0.13	0.540 ± 0.005	4.85 ± 0.11	0.539 ± 0.005	2.02 ± 0.05	0.188 ± 0.002
5.04 ± 0.07	0.679 ± 0.004	4.56 ± 0.12	0.560 ± 0.005	4.62 ± 0.12	0.506 ± 0.005	1.97 ± 0.06	0.201 ± 0.003
5.17 ± 0.07	0.697 ± 0.005	4.71 ± 0.12	0.597 ± 0.004	4.69 ± 0.12	0.525 ± 0.006	1.93 ± 0.06	0.185 ± 0.002
5.13 ± 0.07	0.696 ± 0.005	5.13 ± 0.13	0.641 ± 0.006	4.60 ± 0.12	0.507 ± 0.005	4.11 ± 0.11	0.429 ± 0.005
6.16 ± 0.08	0.860 ± 0.008	5.02 ± 0.14	0.623 ± 0.007	4.77 ± 0.11	0.539 ± 0.004	4.05 ± 0.11	0.421 ± 0.004
6.12 ± 0.08	0.855 ± 0.009	5.33 ± 0.13	0.673 ± 0.008	5.28 ± 0.12	0.608 ± 0.005	3.93 ± 0.11	0.411 ± 0.003
6.14 ± 0.08	0.838 ± 0.006	5.19 ± 0.13	0.649 ± 0.006	5.10 ± 0.13	0.586 ± 0.006	3.95 ± 0.11	0.417 ± 0.004
6.00 ± 0.08	0.832 ± 0.008	5.24 ± 0.13	0.646 ± 0.006	5.03 ± 0.13	0.573 ± 0.006	3.97 ± 0.11	0.413 ± 0.004
5.97 ± 0.08	0.824 ± 0.007	6.25 ± 0.16	0.806 ± 0.010	5.20 ± 0.12	0.597 ± 0.006	5.97 ± 0.16	0.657 ± 0.006
5.91 ± 0.08	0.824 ± 0.008	6.13 ± 0.16	0.793 ± 0.011	4.96 ± 0.13	0.566 ± 0.005	6.13 ± 0.16	0.666 ± 0.009
6.92 ± 0.09	0.985 ± 0.011	6.40 ± 0.16	0.828 ± 0.014	4.92 ± 0.13	0.568 ± 0.004	6.11 ± 0.16	0.670 ± 0.008
6.99 ± 0.09	0.991 ± 0.008	6.19 ± 0.16	0.805 ± 0.009	6.25 ± 0.15	0.748 ± 0.008	5.90 ± 0.17	0.641 ± 0.006
7.02 ± 0.09	0.998 ± 0.058	5.98 ± 0.17	0.764 ± 0.009	6.04 ± 0.15	0.707 ± 0.007	5.92 ± 0.16	0.643 ± 0.009
7.00 ± 0.09	0.984 ± 0.007	8.21 ± 0.21	1.091 ± 0.015	6.07 ± 0.15	0.709 ± 0.006	8.45 ± 0.20	0.958 ± 0.015
7.15 ± 0.09	1.027 ± 0.014	8.02 ± 0.22	1.050 ± 0.011	6.12 ± 0.15	0.716 ± 0.007	8.21 ± 0.21	0.927 ± 0.013
6.92 ± 0.09	0.988 ± 0.011	8.06 ± 0.22	1.059 ± 0.016	6.17 ± 0.15	0.725 ± 0.006	8.27 ± 0.21	0.921 ± 0.011
8.11 ± 0.11	1.163 ± 0.020	8.23 ± 0.21	1.068 ± 0.017	6.14 ± 0.15	0.730 ± 0.009	8.33 ± 0.21	0.910 ± 0.014
8.16 ± 0.11	1.161 ± 0.020	8.14 ± 0.22	1.030 ± 0.015	8.19 ± 0.21	0.984 ± 0.011	8.49 ± 0.20	0.937 ± 0.020
7.85 ± 0.11	1.123 ± 0.017	8.39 ± 0.04	1.117 ± 0.013	8.14 ± 0.21	0.973 ± 0.012	9.90 ± 0.27	1.095 ± 0.022
8.02 ± 0.11	1.139 ± 0.021	10.64 ± 0.26	1.387 ± 0.027	8.31 ± 0.20	0.985 ± 0.010	10.07 ± 0.27	1.114 ± 0.029
8.06 ± 0.11	1.163 ± 0.016	10.31 ± 0.37	1.369 ± 0.029	8.02 ± 0.21	0.947 ± 0.014	9.60 ± 0.28	1.054 ± 0.019
7.91 ± 0.13	1.125 ± 0.016	10.44 ± 0.26	1.371 ± 0.032	8.04 ± 0.21	0.952 ± 0.013	9.72 ± 0.28	1.086 ± 0.016
9.86 ± 0.13	1.438 ± 0.025	10.53 ± 0.26	1.403 ± 0.020	8.45 ± 0.04	1.025 ± 0.012	10.10 ± 0.27	1.115 ± 0.016
10.07 ± 0.13	1.479 ± 0.027	10.16 ± 0.27	1.328 ± 0.023	10.71 ± 0.24	1.306 ± 0.039		
9.82 ± 0.13	1.450 ± 0.024			10.14 ± 0.25	1.289 ± 0.013		
9.86 ± 0.13	1.443 ± 0.023			10.32 ± 0.25	1.264 ± 0.018		
9.80 ± 0.13	1.453 ± 0.025			9.92 ± 0.25	1.212 ± 0.019		
				10.68 ± 0.24	1.322 ± 0.016		
				10.56 ± 0.05	1.290 ± 0.017		

[a] Rate coefficient in s^{-1}, ylide concentrations in 10^{-4} mol dm^{-3}.

Table 1 (continued)

288.2 K

[Y]	k
1.03 ± 0.02	0.082 ± 0.002
1.03 ± 0.02	0.084 ± 0.001
1.00 ± 0.02	0.078 ± 0.002
1.05 ± 0.02	0.086 ± 0.002
1.00 ± 0.02	0.079 ± 0.004
1.96 ± 0.04	0.173 ± 0.002
1.99 ± 0.04	0.178 ± 0.002
1.94 ± 0.04	0.171 ± 0.002
2.01 ± 0.04	0.176 ± 0.002
2.05 ± 0.04	0.182 ± 0.002
4.00 ± 0.09	0.371 ± 0.002
3.99 ± 0.08	0.369 ± 0.003
3.94 ± 0.08	0.364 ± 0.003
3.92 ± 0.08	0.364 ± 0.004
3.95 ± 0.08	0.365 ± 0.003
6.19 ± 0.12	0.601 ± 0.007
6.07 ± 0.13	0.594 ± 0.006
6.07 ± 0.12	0.636 ± 0.006
6.18 ± 0.12	0.615 ± 0.007
6.18 ± 0.12	0.594 ± 0.006
8.14 ± 0.16	0.757 ± 0.011
7.86 ± 0.17	0.752 ± 0.012
8.20 ± 0.16	0.813 ± 0.012
8.30 ± 0.16	0.812 ± 0.011
7.93 ± 0.17	0.768 ± 0.009
10.16 ± 0.20	0.973 ± 0.023
10.33 ± 0.20	0.992 ± 0.002
10.00 ± 0.21	0.950 ± 0.017
10.12 ± 0.21	0.991 ± 0.014
10.21 ± 0.20	0.967 ± 0.024

283.1 K

[Y]	k
4.01 ± 0.10	0.357 ± 0.002
4.04 ± 0.10	0.357 ± 0.002
4.03 ± 0.10	0.362 ± 0.002
4.10 ± 0.09	0.372 ± 0.003
4.06 ± 0.09	0.364 ± 0.003
4.05 ± 0.10	0.365 ± 0.002
4.77 ± 0.10	0.436 ± 0.005
4.67 ± 0.11	0.424 ± 0.004
4.62 ± 0.11	0.418 ± 0.004
4.62 ± 0.11	0.418 ± 0.004
4.65 ± 0.11	0.425 ± 0.004
5.04 ± 0.12	0.460 ± 0.005
5.10 ± 0.12	0.463 ± 0.004
4.98 ± 0.12	0.449 ± 0.004
5.03 ± 0.12	0.455 ± 0.004
5.09 ± 0.12	0.462 ± 0.004
6.07 ± 0.14	0.548 ± 0.007
6.41 ± 0.14	0.583 ± 0.008
6.29 ± 0.14	0.576 ± 0.008
6.28 ± 0.14	0.577 ± 0.007
6.46 ± 0.14	0.590 ± 0.007
6.15 ± 0.14	0.559 ± 0.006
8.52 ± 0.19	0.798 ± 0.015
8.59 ± 0.18	0.825 ± 0.010
8.67 ± 0.18	0.819 ± 0.020
8.27 ± 0.19	0.783 ± 0.012
8.58 ± 0.18	0.849 ± 0.009
8.60 ± 0.04	0.819 ± 0.019
9.94 ± 0.24	0.935 ± 0.012
9.73 ± 0.24	0.914 ± 0.016
10.21 ± 0.23	1.017 ± 0.013
10.29 ± 0.23	1.007 ± 0.019
10.16 ± 0.23	0.998 ± 0.012
10.28 ± 0.05	1.029 ± 0.019

277.6 L

[Y]	k
4.10 ± 0.09	0.314 ± 0.003
4.07 ± 0.09	0.311 ± 0.003
4.11 ± 0.24	0.315 ± 0.003
4.15 ± 0.09	0.319 ± 0.003
4.05 ± 0.09	0.312 ± 0.003
4.58 ± 0.10	0.358 ± 0.004
4.64 ± 0.10	0.367 ± 0.004
4.71 ± 0.10	0.370 ± 0.005
4.59 ± 0.10	0.351 ± 0.003
4.78 ± 0.10	0.373 ± 0.005
4.77 ± 0.10	0.369 ± 0.005
5.18 ± 0.11	0.408 ± 0.005
4.90 ± 0.11	0.381 ± 0.004
5.04 ± 0.11	0.386 ± 0.005
5.11 ± 0.11	0.402 ± 0.005
5.02 ± 0.11	0.395 ± 0.004
5.20 ± 0.11	0.412 ± 0.006
6.19 ± 0.13	0.464 ± 0.008
6.16 ± 0.13	0.476 ± 0.007
5.90 ± 0.14	0.444 ± 0.007
6.12 ± 0.13	0.461 ± 0.007
6.09 ± 0.13	0.467 ± 0.006
6.36 ± 0.13	0.484 ± 0.008
7.93 ± 0.19	0.617 ± 0.013
7.95 ± 0.18	0.625 ± 0.012
8.05 ± 0.18	0.598 ± 0.014
8.23 ± 0.17	0.618 ± 0.013
8.44 ± 0.17	0.674 ± 0.012
8.50 ± 0.04	0.667 ± 0.015
10.10 ± 0.22	0.759 ± 0.024
10.07 ± 0.22	0.750 ± 0.015
9.82 ± 0.23	0.705 ± 0.019
10.11 ± 0.22	0.750 ± 0.020

273.2 K

[Y]	k
4.04 ± 0.08	0.274 ± 0.003
4.03 ± 0.08	0.270 ± 0.003
4.10 ± 0.08	0.278 ± 0.003
4.04 ± 0.08	0.273 ± 0.003
4.11 ± 0.07	0.277 ± 0.003
4.17 ± 0.07	0.286 ± 0.003
4.21 ± 0.08	0.297 ± 0.003
4.31 ± 0.08	0.307 ± 0.005
4.14 ± 0.08	0.302 ± 0.003
4.38 ± 0.08	0.325 ± 0.004
4.15 ± 0.08	0.299 ± 0.006
4.26 ± 0.08	0.314 ± 0.003
5.04 ± 0.09	0.353 ± 0.004
4.96 ± 0.09	0.338 ± 0.004
4.90 ± 0.09	0.338 ± 0.004
4.86 ± 0.10	0.332 ± 0.004
4.87 ± 0.09	0.330 ± 0.003
4.86 ± 0.10	0.330 ± 0.004
5.92 ± 0.11	0.421 ± 0.006
5.93 ± 0.11	0.415 ± 0.007
5.75 ± 0.12	0.403 ± 0.006
5.76 ± 0.12	0.405 ± 0.006
6.15 ± 0.11	0.401 ± 0.005
5.95 ± 0.11	0.429 ± 0.006
7.80 ± 0.15	0.555 ± 0.008
7.67 ± 0.15	0.542 ± 0.008
7.94 ± 0.15	0.568 ± 0.014
7.88 ± 0.15	0.556 ± 0.010
7.80 ± 0.15	0.536 ± 0.010
7.94 ± 0.04	0.561 ± 0.009
9.99 ± 0.18	0.689 ± 0.013
9.75 ± 0.19	0.661 ± 0.012
10.10 ± 0.18	0.743 ± 0.019
9.69 ± 0.19	0.701 ± 0.015
9.91 ± 0.22	0.737 ± 0.024
9.73 ± 0.19	0.653 ± 0.017

(a) $CA + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sigma$

$\sigma \overset{k_3}{\longrightarrow} X + HCl$

(b) $CA + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sigma \overset{k_4}{\longrightarrow} (XH^+, Cl^-)$

$(XH^+, Cl^-) + Y \overset{k_5}{\longrightarrow} X + (YH^+, Cl^-)$

(c) $CA + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sigma$

$\sigma + Y \overset{k_6}{\longrightarrow} (\sigma^-, YH^+)$

$(\sigma^-, YH^+) \overset{k_7}{\longrightarrow} X + (YH^+, Cl^-)$

$$\frac{1}{k} = \frac{1}{k_3} + \frac{k_2 + k_3}{k_1 k_3} \cdot \frac{1}{[Y]_0} \tag{4}$$

$$\frac{1}{k} = \frac{1}{k_4} + \left(\frac{k_2 + k_4}{k_1 k_4} + \frac{1}{k_5}\right) \cdot \frac{1}{[Y]_0} \tag{5}$$

$$\frac{1}{k} = \frac{1}{k_7} + \frac{k_1 + k_6}{k_1 k_6} \frac{1}{[Y]_0} + \frac{k_2}{k_1 k_6}\left(\frac{1}{[Y]_0}\right)^2 \tag{6}$$

Scheme 1 CA, chloranil; Y, ylide; σ, reaction intermediate; X, final product

Table 2 Variation of rate constants (s^{-1}) with initial concentration of reactants for the chloranil–ylide system at 298 K in CH_2Cl_2

$[Y]_0/10^{-4}$ mol dm^{-3}	$[CA]/10^{-5}$ mol dm^{-3}			
	2.1	3.1	4.2	5.2
1.01	0.124	0.131	0.148	0.140
	±0.002	±0.001	±0.002	±0.003
2.13	0.242	0.242	0.248	0.239
	±0.001	±0.001	±0.003	±0.004
4.06	0.517	0.484	0.497	0.477
	±0.003	±0.004	±0.005	±0.004
6.09	0.805	0.754	0.791	0.793
	±0.007	±0.006	±0.008	±0.008
8.12	1.128	1.048	1.136	1.060
	±0.012	±0.011	±0.010	±0.013
10.10	1.362	1.38	1.34	1.34
	±0.025	±0.03	±0.03	±0.04

Table 3 Deuterium isotope effect for reaction of chloranil with ylide at 303 K

Solvent	$k_H{}^a$	$k_D{}^a$	k_H/k_D
Dichloromethane	1440 ± 100	1600 ± 300	0.9
Toluene	61 ± 6	60 ± 8	1.0

^{a} In dm^3 mol^{-1} s^{-1}.

rate increases with the electronegativity (electron-withdrawing capacity) of the halogen. The Hammett plot derived from the $(XC_6H_4)Ph_2P=C_5H_4$ (X = p-Cl, p-Me, p-OMe) system in toluene (Fig. 5) exhibits a negative slope indicating that the reaction rate is enhanced by electron-donating substituents on the ylide. This supports the contention that the mechanism involves nucleophilic attack by the ylide on the quinone via a σ-complex intermediate. Three mechanisms which agree with the experimental data are shown in Scheme 1. The corresponding relationships between k and $[Y]_0$ in the presence of an excess of ylide, which assume the stationary state for all the intermediates and take into account the mass balance, are also shown [eqns. (4)–(6)].

The first mechanism implies formation of an intermediate which proceeds to products in one step, possibly the synchronous removal of HCl via a four-centre transition state.[3] The

second mechanism indicates that addition to the tetrachloro-p-benzoquinone is followed by two fast steps. A chloride anion is lost in the first of these steps, to yield a second intermediate (XH^+) which transfers a proton to a molecule of ylide. Mechanism (b) is analogous to the mechanism governing nucleophilic substitution in activated aryl halides.[27] Finally, the third mechanism is similar to (b) but removal of the proton and elimination of halide occur in a synchronous fashion (E2) or non-synchronous (ElcB-type) mechanism with ylide acting as a base.

A theoretical linear relationship is found between $1/k$ and $1/[Y]_0$ for mechanisms (a) and (b). Eqns. (4) and (5) indicate that the intercepts should be greater than zero. Since k_3 and k_4 are associated with fast unimolecular steps their maximum value should range between 10 and 100 s^{-1} and hence an intercept ranging from 0.1 to 0.01 s should be observed. However, a negative intercept $(ca. -0.1)$ is obtained when data are fitted to a straight-line. It seems likely therefore, that the reaction is not well described by mechanisms (a) or (b). Furthermore, there is some theoretical[28] evidence that concerted or synchronous reactions such as (a) are not energetically favoured but take place in two or more steps.

Mechanism (c) explains within experimental error the relationship found between k and $[Y]_0$. The curves exhibit a slight concavity as can be seen in Fig. 4. Thus, they are better fitted when a quadratic term is added to the linear term. Equations arising from mechanism (c) give this quadratic term because of the bimolecular evolution of the intermediate σ complex.

If mechanism (c) is assumed, we may define two empirical coefficients a_1 and a_2 as given in eqns. (7) and (8).

$$a_1 = \frac{k_1 + k_6}{k_1 k_6} \approx \frac{1}{k_1} \tag{7}$$

$$a_2 = \frac{k_2}{k_1 k_6} \tag{8}$$

Since the first step is rate limiting it is reasonable to assume $k_6 \gg k_1$. As a consequence, $1/a_1$ will behave approximately as k_1. A plot of $-\ln a_1$ vs. $1/T$ should be a straight line as observed. The values of k_1 and a_2 at each temperature are given in Table 4. Parameter a_2 cannot be obtained as accurately since the

Table 4 Temperature dependence of k_1 and a_2 for the chloranil–ylide system in CH_2Cl_2

T/K	$k_1/dm^3\ mol^{-1}\ s^{-1}$	$a_2/10^{-8}\ dm^6\ mol^{-2}\ s$
273.4	729 $\pm$ 1	4.1 $\pm$ 1.0
277.6	802 $\pm$ 1	0.0 $\pm$ 0.3
283.0	976 $\pm$ 8	3.7 $\pm$ 0.4
288.1	998 $\pm$ 7	2.6 $\pm$ 0.2
293.2	1151 $\pm$ 13	3.2 $\pm$ 0.3
298.2	1310 $\pm$ 14	5.7 $\pm$ 0.4
303.2	1421 $\pm$ 19	4.8 $\pm$ 0.5
308.2	1615 $\pm$ 8	6.2 $\pm$ 0.2

Table 5 Activation parameters for the chloranil–ylide system

Solvent	E_a/kJ mol^{-1}	$\Delta H^{\ddagger,a}/kJ$ mol^{-1}	$\Delta S^{\ddagger,a}/J$ $mol^{-1}\ K^{-1}$	$\Delta G^{\ddagger,a}/kJ$ mol^{-1}
Dichloromethane	16.1 $\pm$ 0.4	13.6 $\pm$ 0.4	-140 ± 1	55.3 $\pm$ 0.7
Toluene	32	30	-95	58

a At 298 K.

concavity of the curves is too small and the parameter does not show a clear variation with temperature. If a value not greater than $10\ s^{-1}$ for k_2 is assumed however, the order of magnitude of k_6 obtained from eqn. (8) is close to $10^5\ dm^3\ mol^{-1}\ s^{-1}$ in dichloromethane solution. Furthermore, $1/k_7$ must be close to zero since k_7 is related to a proton transfer process.

Activation parameters for the reaction in dichloromethane and toluene are given in Table 5. The analysis of the Gibb's free energy of activation indicates that the reaction proceeds faster in dichloromethane solution. The large negative activation entropy is consistent with the existence of a polar activated complex possessing a large charge separation. This complex should exhibit a structure similar to the betaine **4** proposed as an intermediate, in which no significant H–C or Cl–C rupture had occurred. The small activation enthalpy indicates a large interaction between the activated complex and the polar solvent (CH_2Cl_2). The thermochemical data for the reaction in toluene reinforce this hypothesis since the increase of the activation enthalpy and a decrease of the negative activation entropy indicate the expected smaller interaction of the transition state with the less polar solvent. It appears that the solvent change causes a compensating effect on the height of the activation barrier since chloranil is strongly solvated in toluene and the ylide is strongly solvated in dichloromethane, as the solubilities of these reactants in both solvents indicate.

An alternative to betaine as a reaction intermediate would be a π-complex, and a new visible band should be observed in this case. The analysis of the visible spectra of reaction mixtures recorded over 10 s every 0.1 s at room temperature, using a diode array spectrophotometer (Hewlett Packard, HP98155A), did not reveal any rapidly changing visible band. The π-complex would not be as polar as the betaine and hence would be far less affected on changing the solvent. On the other hand, the betaine would not absorb, since its structure is similar to a molecule of protonated product **3**, which is transparent at 690 nm but exhibits a broad weak band centred at 430 nm. In fact solutions of **3** change abruptly from blue to yellow after addition of an organic acid (formic, acetic).

Conclusion

The activation parameters are similar to those found for electrophilic attack of cyanovinylbenzenes on ylides. However, the present reaction is not acid-catalysed and π-complexes, if

formed, do not play an important role in the mechanism of reaction. The reaction is rationalised as an electrophilic attack of the tetrachloro-*p*-benzoquinone on the aromatic cyclopentadiene ring of the ylide *via* a σ-complex analogous to electrophilic aromatic substitutions taking place through Wheland intermediates.

Acknowledgements

Appendix

Determination of the Initial Value of Concentration of Ylide.— The initial concentration of ylide can be determined if the chloranil:ylide volume ratio injected into the flow cell is known.

Let us assume a stopped-flow cell whose volume is V. The actual volume of each reactant solution injected is x of chloranil and $V - x$ of ylide. The initial concentration of chloranil ($[CA]_i$) in the cell can be determined since the final absorbance (A_∞) can be measured easily, and from the mass balance the final concentration of compound **3** is equal to the initial concentration of chloranil. The relationship between $[CA]_i$ and A_∞ is given in eqn. (9) where the subscript '0' refers to conditions in the syringe before the injection and subscript 'i' refers to conditions in the stopped-flow cell after the injection.

$$[CA]_i = [CA]_0 \frac{x}{V} = [CA]_0 \alpha = \frac{A_\infty}{\varepsilon} \qquad (9)$$

Likewise, the concentration of ylide in the stopped-flow cell can be determined using eqn. (10).

$$[Y]_i = [Y]_0\left(1 - \frac{x}{V}\right) = [Y]_0(1 - \alpha) \qquad (10)$$

Eliminating α between eqns. (9) and (10) a relationship between the initial concentration of ylide in the cell and the measured quantities is obtained [eqn. (11)]. The concentration of ylide in the syringe is calculated from Beer's law.

$$[Y]_i = [Y]_0\left(1 - \frac{A_\infty}{\varepsilon[CA]_0}\right) = [Y]_0\left(1 - \frac{A_\infty}{2\bar{A}_\infty}\right) \qquad (11)$$

The averaged final absorbance of all injections carried out from the same stock solution of chloranil (30–36 data) appears in the denominator of the last equation. This quantity was used assuming that the average injected concentration was half of the concentration after the injection. This condition is formalized in eqn. (12).

$$\varepsilon[CA]_0 = 2\bar{A}_\infty \qquad (12)$$

This method avoids using the molar absorption coefficient, and hence increases the accuracy of the results. The initial concentrations of ylide in the stopped-flow cell for each of the experiments are given in Table 1.

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