Kinetics and Mechanism of the Addition of Triphenylphosphonio-cyclopentadienide to Tetrahalo-*p*-benzoquinones. Part 2. Reaction with Bromanil and Iodanil

Rosa Valero,*[,a] Francisco Pérez Plá,[a] Juan Palou,[a] C. Dennis Hall[b] and Peter Speers[b]

[a] *Departamento de Química Física, Universidad de Valencia, Spain*

[b] *Department of Chemistry, King's College, London, Strand, London, WC2R 2LS, UK*

The reaction of tetrahalo-*p*-benzoquinones with triphenylphosphoniocyclopentadienide yields 6-(tri-phenylphosphonio-3′-cyclopentadienyl)-2,3,5-trihalocyclohexa-2,5-diene-1,4-dione (**4a–d**), a new class of zwitterionic dyes containing phosphorus. The rate-limiting step has been found to be the addition of the ylide to the quinone through a highly polar betaine intermediate. The elimination of hydrogen halide from the betaine, is of the E_2 or E_1cB type for the bromanil system and of the E_1 type for iodanil. SCF–AM1 calculations suggest that the E_1cB path is energetically favoured relative to the E_1 elimination path.

The conventional chemistry of haloquinones is characterized by the formation of charge transfer complexes (CT) and nucleophilic substitution of the halides of the quinone nucleus. The stabilities of CT complexes depend upon the difference in ionization potential between the electron donors and the haloquinones. There are examples of complete electron transfer in which the halosemiquinone radical anion (HSQ) is formed, as occurs in the dispersion of alkaline metals (Na, K) in organic solutions of chloranil (**1b**) and bromanil (**1c**), from which an ionic solid having the composition $(M^+HSQ)^{2-5}$ can be isolated. In contrast, the formation of weak charge transfer complexes occurs with electron donors of high ionization potential. This is the case with 1:1 complexes between phenyl-carbamates and chloranil, which, depending on the substitution of the benzene nucleus, possess formation constants between 0.8 and 2.0 at room temperature.[6] Intermediate cases are exemplified by the formation of CT complexes between 2,7-bis(methyl-thio)-1,6-dithiapyrene (TMTDTPY) and fluoranil (**1a**), chlor-anil and bromanil in dichloromethane. These complexes can be isolated in crystalline polymorphic phases where the extent of charge donation is *ca.* 30% as revealed by X-ray crystallography. It has also been demonstrated that complexes between TMTDTPY and fluoranil have semiconductor properties, while the adducts with chloranil and fluoranil show metallic conductivity.[7,8]

The second type of reaction is represented by the hydrolysis of chloranil in alkaline media to form chloranilic acid.[9,10] Also included in this type is the reaction of aliphatic amines with haloquinones.[11–15] In excess of primary and secondary amines, chloranil reacts to form disubstitution products, while tertiary amines form CT complexes in which the tetrachlorosemi-quinone radical anion has been detected. Some authors[11,12] have indicated that the initial phase of these reactions takes place through radical intermediates, implying the previous formation of CT complexes. The mechanism proposed for the reaction with aromatic amines involves the consecutive formation of π-complexes and σ-complexes.[16]

The ylide **2a** contains a delocalized cyclopentadiene ring whose reactivity[17,18] is typical of non-benzenoid aromatic systems. The tetrahalo-*p*-benzoquinones and ylide solutions in dichloromethane give rise in a matter of seconds to an intense blue colour, λ_{max} 690–700 nm. The ^{1}H NMR spectra from the reaction mixtures reveal the formation of a new σ-bonded compound and not the formation of a CT complex. In the case of chloranil, the product was isolated and character-ized as **4b**.[19] The reaction between ylide and chloranil involves the

rate-determining addition of the ylide to the quinone to form a polar intermediate without the intervention of π-complexes.[1] The overall reactivity is similar to that found for other strong electron acceptors such as cyanovinylbenzenes[20–23] or tetra-cyanoethylene.[18]

In this work the mechanistic results obtained for the reaction between bromanil (**1c**) and iodanil (**1d**) and the ylide (**2a, b**) are reported. At the same time, the role of σ-intermediates in the reactions of tetrahalo-*p*-benzoquinones with the ylide are explained.

Experimental

Materials.—Triphenylphosphoniocyclopentadienide (**2a**) was prepared by a modification[20] of the method reported by Ramirez.[17] For kinetic runs further purification was carried out by re-crystallizing the ylide from ethanol[20] (× 3) and toluene.[24] The quality of the purified product was checked by recording the IR spectrum[17,20] and the ^{31}P NMR spectrum ($\delta = 13.6$).[19]

2,3,4,5-Tetradeuteriotriphenylphosphoniocyclopentadienide (**2b**) was prepared from **2a** by H–D exchange in deuterioacetic acid–deuterium oxide medium.[20] The level of deuteriation as assessed by ^{1}H NMR was 85%.

Chloranil was supplied by Fluka Chemie AG and the commercial product was recrystallized from acetone (× 2) and then sublimed as previously reported[14] to give lustrous yellow crystals, m.p. 290 °C.

Bromanil (ex-Hopkin and Williams) was recrystallized from acetone (× 2) to give lustrous yellow crystals, m.p. 296 °C.

Iodanil was prepared by the method of Jackson and Bolton[25] and was recrystallized (× 2) from glacial acetic acid to give dark purple needles, m.p. (sealed tube) 279–281 °C, lit. 282 °C.

Dichloromethane of IR grade (Panreac) was dried by adding 25 g dm^{-3} of NaOH and stirring the mixture for ten minutes at room temperature. The solvent was decanted and distilled (× 2) from calcium hydride.

Absorbance Measurements.—Absorbance *vs.* time curves were recorded with a spectrophotometer (Kontron, Uvikon 930) attached to a fast mixer unit (Hitech, SFA-11) and a temperature regulated cell holder. The temperature of the cells was maintained constant to an accuracy of ±0.1 °C by circulating water. The temperature was monitored with a thermocouple attached to a stopped flow quartz cell of 1 cm pathlength. Nitrogen flow across the face of the cells was

1a X = F
1b X = Cl
1c X = Br
1d X = I

2a X = H
2b X = D

3a X = F
3b X = Cl
3c X = Br
3d X = I

4a X = F
4b X = Cl
4c X = Br
4d X = I
(Product P)

5a X = F
5b X = Cl
5c X = Br
5d X = I
σ-complex

6a X = F
6b X = Cl
6c X = Br
6d X = I
E₁ intermediate

7a X = F
7b X = Cl
7c X = Br
7d X = I
E₁cB intermediate

$$Q + Y \xrightleftharpoons[k_2]{k_1} \sigma \xrightarrow{k_3} (\sigma H^+, X^-)$$

$$(\sigma H^+, X^-) + Y \xrightarrow{k_4} P + (YH^+, X^-)$$

$$(YH^+, X^-) \xrightleftharpoons[k_6]{k_5} Y + HX$$

E₁ mechanism

$$Q + Y \xrightleftharpoons[k_2]{k_1} \sigma$$

$$\sigma + Y \xrightarrow{k_7} (\sigma^-, YH^+)$$

$$(\sigma^-, YH^+) \xrightarrow{k_8} P + (YH^+, X^-)$$

$$(YH^+, X^-) \xrightleftharpoons[k_6]{k_5} Y + HX$$

E₁cB mechanism

$$Q + Y \xrightleftharpoons[k_2]{k_1} \sigma$$

$$\sigma + Y \xrightarrow{k_9} P + (YH^+, X^-)$$

$$(YH^+, X^-) \xrightleftharpoons[k_6]{k_5} Y + HX$$

E₂ mechanism
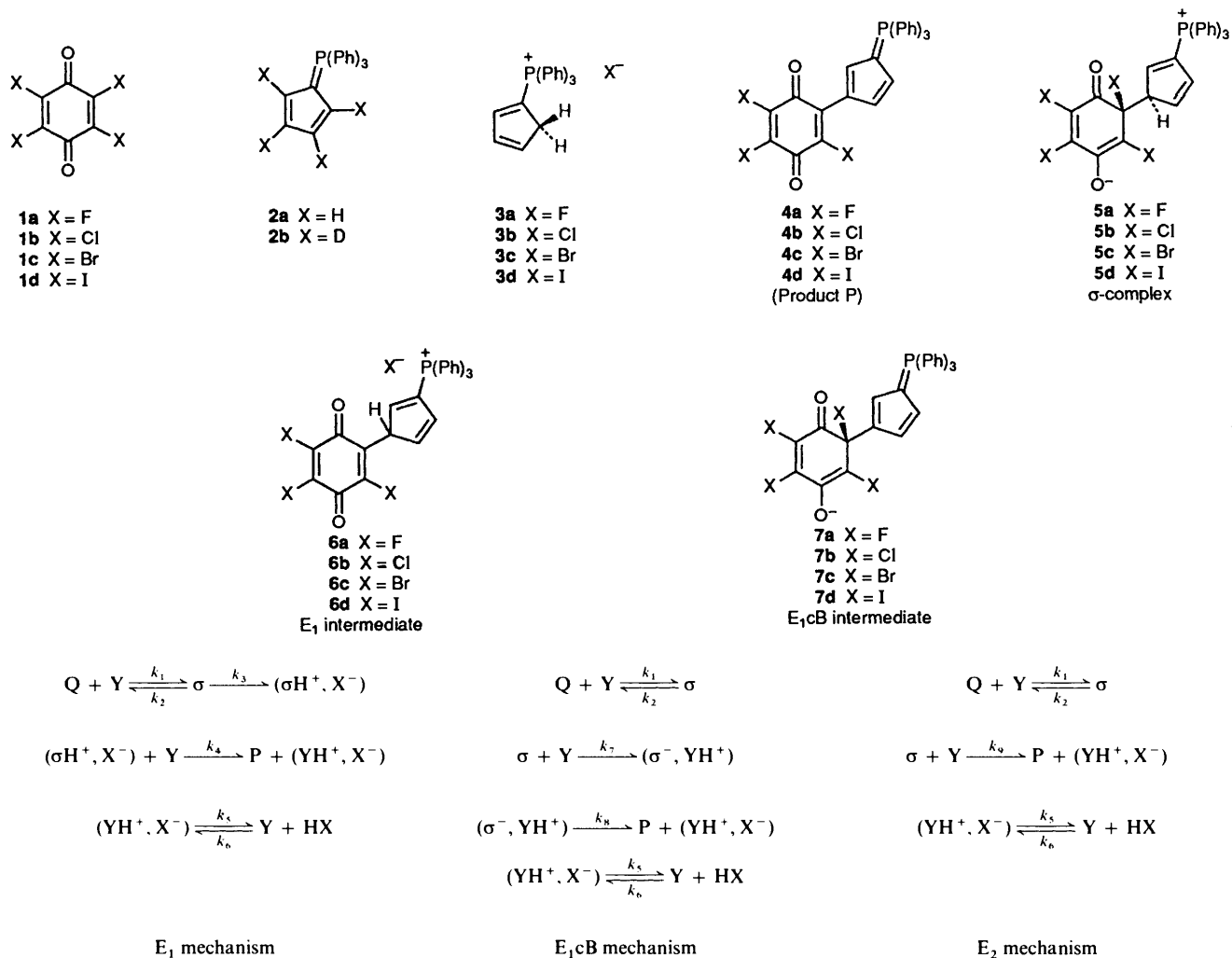
Scheme 1

Table 1 Elemental analysis, mass spectral and visible spectroscopy data on **4b–d**

	Cl	Br	I
C (found)	65.0	51.85	43.25
C (required)	64.45	52.03	42.97
H (found)	3.55	3.1	2.65
H (required)	3.39	2.70	2.24
P (found)	5.3	4.6	4.0
P (required)	5.48	4.63	3.83
X (found)	19.85	33.9	46.95
X (required)	19.41	33.26	47.01
M⁺	537	669	811
λ_max/nm	694	693	694
ε/dm⁻³ mol⁻¹ cm⁻¹	7736	8536	9002

maintained during measurements to avoid water condensation on the wall of the cells at low temperatures.

Product Characterization.—The products (**4b–d**) of the reactions of **2a** with **1b–d** were isolated by flash chromatography on 60 H silica (CH₂Cl₂ as eluent) and characterized by mass spectrometry/elemental analysis, see Table 1, and by ³¹P, ¹H and ¹³C NMR spectroscopy, see Table 2.

Stoichiometry Measurements.—In order to determine the stoichiometry of the reaction, the ¹H NMR spectrum (Bruker 200 MHz) of a reaction mixture of 1.42 × 10⁻³ mol dm⁻³ in bromanil and 3.46 × 10⁻³ mol dm⁻³ in ylide, using CD₂Cl₂ as a solvent, was recorded at 300 K. The spectrum of the same reaction mixture containing a drop of triethylamine was also recorded. This experiment was repeated using iodanil (1.71 × 10⁻³ mol dm⁻³) and ylide (2.4 × 10⁻³ mol dm⁻³) in CD₂Cl₂. The spectrum of the reaction mixture of bromanil and ylide between 6.0 and 7.4 ppm showed a multiplet at 6.33 ppm and two multiplets which were very close together at 7.05 ppm whose intensity was double that of the previous one. These signals were attributed to the cyclopentadiene protons of the product **4c**. In addition, two weak broad signals centred at 6.87 and 7.28 ppm were attributed to the cp H of **3c** and a broad band centred at 3.62 ppm was attributed to the methylene group of **3c**. After the addition of amine the signals at 6.87, 7.28 and 3.62 ppm disappeared but the signals originating from the product **4c** were maintained at the same intensity and two symmetrical quintuplets centred at 6.2 ppm appeared which were assigned to the cp hydrogens of **2a**.²⁶,²⁷ Similarly the spectrum of the product from the iodanil–ylide mixture consisted of three multiplets centred at 6.31, 6.97 and 7.10 ppm integrating for one proton each and attributed to the cp hydrogens of **4d**. After the addition of amine the signals centred at 6.97 and 7.10 ppm maintained their intensity and two quintuplets due to **2a** appeared. Unlike the previous case, the quintuplets were not symmetrical, the one centred at 6.23

Table 2 NMR data for **4b-d** in CD_2Cl_2 at -30 °C

¹H NMR				¹³C NMR				³¹P NMR
δ	No. of H atoms	Assignment	J/Hz	δ	Dept	Assignment	J/Hz	δ[a]
X = Cl								
7.6 (mult.)	15	2"-6"		181.1	0	C-1	0	15.04
7.05 (sext.)	1	5'	J_P 4.9; $J_{4'}$ 4.7; $J_{2'}$ 2.1	172.7	0	C-4	0	
6.94 (sext.)	1	2'	J_P 6.3; $J_{4'}$ 2.1	143.0	0	C-2	0	
6.36 (quint.)	1	4'	J_P 2.5	141.2	0	C-3	0	
				140.3	0	C-5	0	
				135.7	+	C-4'	0	
				135.7	+	C-2", C-6"	10.0	
				133.1	+	C-2'	15.8	
				131.5	+	C-3", C-5"	12.5	
				124.7	0	C-1"	90.6	
				124.0	0	C-6	0	
				124.0	0	C-3'	20.3	
				123.7	+	C-5'	13.6	
				121.4	+	C-4'	13.6	
				95.4	0	C-1'	110.0	
X = Br								
7.6 (mult.)	15	2"-6"		178.5	0	C-1	0	15.04
7.05 (sext.)	1	5'	J_P 4.8; $J_{4'}$ 4.7; $J_{2'}$ 2.4	170.6	0	C-4	0	
6.94 (dxt.)	1	2'	J_P 6.6; $J_{4'}$ 2.1	142.5	0	C-2	0	
6.36 (quint.)	1	4'	J_P 2.1	139.2	0	C-3	0	
				136.5	0	C-5	0	
				133.7	+	C-4'	0	
				133.65	+	C-2", C-6"	10.4	
				130.8	+	C-2'	15.7	
				129.4	+	C-3", C-5"	12.5	
				123.4	0	C-3'	19.5	
				122.7	0	C-1"	90.9	
				121.7	+	C-5'	13.7	
				118.9	+	C-4'	13.8	
				114.5	0	C-6	0	
				92.8	0	C-1'	109.9	
X = I								
7.7 (mult.)	15	2"-6"		177.9	0	C-1	0	15.02
7.08 (dxt.)	1	5'	J_P 5.0; $J_{4'}$ 4.7; $J_{2'}$ 2.1	172.6	0	C-4	0	
6.99 (sext.)	1	2'	J_P 4.6; $J_{4'}$ 2.1	147.95	0	C-2	0	
6.37 (quint.)	1	4'	J_P 2.0	147.9	0	C-3	0	
				147.8	0	C-5	0	
				133.7	+	C-4"	0	
				133.6	+	C-2", C-6"	10.3	
				133.6	+	C-2'	15.3	
				130.6	0	C-6	0	
				129.4	+	C-3", C-5"	12.4	
				125.7	0	C-3'	19.1	
				122.8	0	C-1"	90.9	
				121.4	+	C-5'	14.1	
				118.2	+	C-4'	13.8	
				91.7	0	C-1'	109.8	

[a] δ_P for ylide, 13.6.
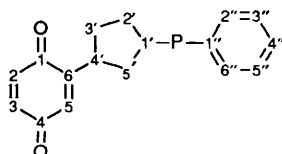
having double the intensity of the one centred at 6.15, since the former overlapped with the signal of **4d** at 6.31.

Data Treatment.—The absorbance *vs.* time curves were corrected by subtracting the base line.[1] Curves from experiments carried out with an excess of ylide fit eqn. (1). Good regression

lines (r > 0.99) up to 95% degree of conversion were obtained and the resulting values of k are given in Tables 3 and 4.

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

In eqn. (1), A_{∞} is the absorbance measured at infinite time, k

Table 3 First-order rate constants for the bromanil–ylide system in dichloromethane solution. $[Y]_0$ in 10^{-4} mol dm^{-3}.

T/K 309.0±0.1		303.3±0.1		298.3±0.1		293.3±0.1		287.9±0.1		282.9±0.1		278.1±0.1		273.8±0.1	
k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$
0.562±0.010	4.27±0.12	0.491±0.003	4.06±0.05	0.406±0.010	4.50±0.10	0.438±0.003	4.25±0.07	0.353±0.008	4.41±0.10	0.335±0.004	4.20±0.05	0.302±0.004	4.10±0.08	0.276±0.006	4.19±0.06
0.550±0.009	4.22±0.12	0.482±0.003	4.00±0.05	0.405±0.010	4.28±0.09	0.433±0.003	4.25±0.07	0.364±0.008	4.21±0.10	0.326±0.006	4.06±0.05	0.290±0.004	4.13±0.08	0.269±0.017	4.12±0.06
0.523±0.006	4.02±0.12	0.525±0.002	4.21±0.05	0.391±0.009	4.13±0.10	0.431±0.002	4.27±0.07	0.376±0.007	4.29±0.10	0.335±0.004	4.14±0.05	0.294±0.005	4.11±0.08	0.263±0.016	4.11±0.06
0.561±0.009	4.28±0.12	0.500±0.003	4.13±0.05	0.392±0.006	4.22±0.09	0.438±0.003	4.30±0.07	0.368±0.007	4.19±0.10	0.335±0.004	4.10±0.05	0.293±0.004	4.05±0.08	0.266±0.014	4.11±0.06
0.552±0.008	4.16±0.12	0.500±0.003	4.14±0.05	0.373±0.005	4.06±0.10	0.442±0.003	4.36±0.07	0.369±0.005	4.24±0.10	0.330±0.004	4.08±0.05	0.295±0.005	4.10±0.08	0.262±0.016	4.08±0.06
0.675±0.012	5.21±0.15	0.597±0.004	4.95±0.06	0.537±0.005	5.23±0.12	0.524±0.012	5.33±0.09	0.458±0.004	5.41±0.11	0.427±0.007	5.16±0.07	0.380±0.007	5.15±0.10	0.337±0.008	5.10±0.08
0.642±0.013	5.10±0.15	0.608±0.005	4.98±0.06	0.530±0.006	5.19±0.12	0.560±0.008	5.37±0.09	0.447±0.008	5.31±0.12	0.419±0.005	5.02±0.07	0.364±0.005	5.03±0.11	0.340±0.007	5.10±0.08
0.636±0.013	5.07±0.15	0.615±0.006	5.04±0.06	0.522±0.006	5.17±0.12	0.516±0.011	5.23±0.09	0.446±0.007	5.30±0.11	0.423±0.006	5.14±0.07	0.368±0.005	5.08±0.10	0.334±0.009	5.01±0.08
0.663±0.020	5.29±0.15	0.597±0.003	4.99±0.06	0.557±0.004	5.34±0.12	0.520±0.011	5.35±0.09	0.448±0.007	5.36±0.11	0.425±0.006	5.13±0.07	0.379±0.006	5.19±0.10	0.334±0.008	5.00±0.08
0.836±0.000	5.34±0.15	0.605±0.003	5.03±0.06	0.537±0.005	5.26±0.12	0.528±0.011	5.26±0.09	0.461±0.005	5.42±0.12	0.416±0.007	5.11±0.07	0.366±0.006	5.12±0.10	0.329±0.007	5.10±0.08
0.884±0.025	7.27±0.20	0.724±0.006	5.96±0.07	0.672±0.005	6.20±0.14	0.618±0.014	6.28±0.11	0.526±0.006	6.44±0.14	0.498±0.007	6.16±0.08	0.458±0.009	6.33±0.12	0.423±0.007	6.23±0.09
0.895±0.035	7.48±0.20	0.702±0.007	5.92±0.07	0.644±0.007	6.16±0.15	0.636±0.016	6.39±0.11	0.537±0.008	6.42±0.14	0.503±0.005	6.15±0.08	0.463±0.010	6.26±0.12	0.415±0.008	6.16±0.10
0.877±0.035	7.51±0.20	0.721±0.007	5.96±0.07	0.651±0.006	6.15±0.15	0.627±0.013	6.24±0.11	0.523±0.008	6.35±0.14	0.507±0.006	6.18±0.08	0.442±0.009	6.08±0.13	0.411±0.009	6.22±0.10
0.954±0.038	7.76±0.19	0.709±0.007	5.93±0.07	0.695±0.008	6.15±0.15	0.628±0.018	6.32±0.11	0.541±0.008	6.52±0.14	0.502±0.006	6.13±0.08	0.457±0.008	6.27±0.12	0.435±0.010	6.26±0.09
0.950±0.020	7.51±0.20	0.706±0.006	5.95±0.07	0.666±0.007	6.27±0.14	0.630±0.020	6.44±0.11	0.539±0.005	6.50±0.14	0.507±0.006	6.15±0.08	0.467±0.007	6.48±0.12	0.417±0.007	6.26±0.09
0.769±0.033	6.44±0.17	0.835±0.008	6.90±0.09	0.771±0.008	7.26±0.16	0.763±0.016	7.31±0.13	0.620±0.013	7.25±0.16	0.564±0.009	7.13±0.09	0.530±0.010	7.43±0.14	0.480±0.012	7.28±0.11
0.865±0.014	6.47±0.17	0.856±0.008	6.99±0.08	0.768±0.011	7.28±0.16	0.742±0.018	7.36±0.13	0.630±0.013	7.27±0.15	0.578±0.008	7.17±0.09	0.515±0.011	7.28±0.14	0.472±0.012	7.24±0.11
0.859±0.017	6.62±0.17	0.849±0.007	7.00±0.09	0.750±0.011	7.23±0.16	0.776±0.017	7.48±0.12	0.646±0.016	7.29±0.16	0.579±0.008	7.14±0.09	0.507±0.010	7.10±0.15	0.485±0.015	7.32±0.11
0.809±0.021	6.18±0.18	0.866±0.007	7.04±0.09	0.782±0.021	7.70±0.16	0.770±0.014	7.40±0.13	0.651±0.014	7.34±0.15	0.560±0.009	7.17±0.09	0.512±0.011	7.19±0.14	0.449±0.013	7.07±0.11
0.838±0.016	6.29±0.18	0.878±0.006	6.99±0.08	0.739±0.012	7.06±0.17	0.768±0.015	7.36±0.13	0.652±0.015	7.31±0.15			0.519±0.010	7.26±0.14	0.481±0.013	7.22±0.11
1.015±0.039	8.36±0.23	0.997±0.010	8.07±0.09	0.849±0.010	7.86±0.20	0.814±0.021	8.36±0.14	0.709±0.013	8.31±0.16	0.666±0.010	8.10±0.10	0.606±0.010	8.15±0.17	0.562±0.010	8.19±0.13
1.061±0.021	8.22±0.23	0.970±0.011	8.01±0.09	0.878±0.015	8.32±0.19	0.842±0.017	8.26±0.15	0.726±0.021	7.99±0.10	0.669±0.009	7.99±0.10	0.612±0.011	8.21±0.17	0.589±0.017	8.41±0.13
1.097±0.038	8.75±0.22	0.960±0.009	7.83±0.09	0.875±0.014	8.18±0.19	0.841±0.017	8.33±0.15	0.741±0.023	8.08±0.10	0.679±0.009	8.08±0.10	0.617±0.010	8.10±0.17	0.557±0.015	8.11±0.13
1.056±0.037	8.47±0.23	0.984±0.010	8.02±0.09	0.851±0.011	7.88±0.20	0.833±0.021	8.18±0.15	0.733±0.025	8.12±0.10	0.673±0.011	8.12±0.10	0.612±0.011	8.32±0.17	0.562±0.014	8.11±0.13
1.058±0.037	8.60±0.22	0.981±0.011	7.94±0.09	0.872±0.017	8.27±0.19	0.835±0.019	8.20±0.15	0.761±0.020	8.00±0.10	0.667±0.011	8.00±0.10	0.612±0.010	8.17±0.17	0.567±0.020	8.01±0.13
1.320±0.039	10.34±0.27	1.226±0.010	9.85±0.11	1.133±0.025	10.52±0.23	1.152±0.025	10.52±0.17	0.928±0.015	10.09±0.17	0.815±0.017	10.03±0.11	0.742±0.019	9.91±0.20	0.661±0.012	10.08±0.15
1.296±0.021	10.41±0.26	1.240±0.011	9.82±0.11	1.070±0.036	10.51±0.23	1.179±0.026	10.46±0.18	0.933±0.021	10.03±0.17	0.822±0.021	9.99±0.11	0.738±0.017	9.79±0.20	0.646±0.012	10.08±0.15
1.281±0.038	9.98±0.28	1.227±0.009	9.76±0.11	1.100±0.030	10.51±0.23	1.158±0.027	10.34±0.18	0.978±0.015	10.34±0.18	0.819±0.016	9.94±0.12	0.749±0.016	9.94±0.20	0.656±0.015	10.13±0.15
1.351±0.037	10.22±0.27	1.241±0.010	9.82±0.11	1.078±0.034	10.49±0.23	1.185±0.019	10.41±0.17	0.940±0.014	10.41±0.17	0.825±0.020	9.92±0.11	0.765±0.014	10.13±0.20	0.657±0.013	9.90±0.15
1.366±0.037	10.46±0.26			1.104±0.025	10.39±0.23	1.149±0.033	10.32±0.18		9.96±0.17	0.840±0.012	9.92±0.11	0.767±0.016	9.92±0.20	0.647±0.013	9.77±0.15

Table 4 First-order rate constants for the iodanil–ylide system in dichloromethane solution. $[Y]_0$ in 10^{-4} mol dm^{-3}.

T/K	308.3±0.1		303.2±0.1		298.3±0.1		293.3±0.1		287.2±0.1		282.7±0.1		277.7±0.1	
	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$	k/s^{-1}	$[Y]_0$
	0.111±0.002	4.24±0.09	0.095±0.002	4.21±0.09	0.089±0.006	4.39±0.08	0.074±0.002	4.25±0.09	0.068±0.007	4.47±0.13	0.064±0.002	4.42±0.13	0.058±0.002	4.49±0.20
	0.113±0.002	4.26±0.09	0.098±0.002	4.28±0.08	0.085±0.005	4.21±0.09	0.074±0.002	4.24±0.09	0.067±0.007	4.40±0.13	0.063±0.002	4.33±0.14	0.057±0.002	4.48±0.20
	0.108±0.002	4.13±0.09	0.097±0.002	4.24±0.09	0.086±0.006	4.22±0.09	0.074±0.002	4.26±0.09	0.067±0.007	4.42±0.13	0.063±0.001	4.36±0.14	0.057±0.002	4.41±0.20
	0.110±0.002	4.18±0.09	0.094±0.001	4.14±0.09	0.086±0.006	4.20±0.09	0.072±0.002	4.19±0.09	0.069±0.008	4.51±0.13	0.062±0.005	4.32±0.14	0.057±0.002	4.48±0.20
	0.111±0.002	4.16±0.09	0.094±0.002	4.15±0.09	0.087±0.005	4.30±0.08	0.075±0.002	4.29±0.09	0.067±0.008	4.34±0.13	0.062±0.002	4.34±0.14	0.057±0.002	4.46±0.20
	0.142±0.003	5.43±0.11	0.114±0.002	5.10±0.11	0.104±0.002	5.18±0.11	0.088±0.002	5.12±0.12	0.082±0.002	5.48±0.17	0.077±0.002	5.31±0.17	0.067±0.002	6.16±0.33
	0.139±0.003	5.32±0.11	0.116±0.002	5.15±0.11	0.104±0.002	5.15±0.11	0.087±0.002	5.08±0.12	0.083±0.002	5.50±0.17	0.073±0.003	5.11±0.18	0.068±0.003	6.17±0.33
	0.141±0.003	5.32±0.11	0.114±0.002	5.07±0.11	0.104±0.002	5.14±0.11	0.090±0.002	5.21±0.11	0.080±0.002	5.33±0.18	0.076±0.002	5.33±0.17	0.067±0.003	6.17±0.33
	0.130±0.002	5.04±0.12	0.115±0.002	5.09±0.11	0.106±0.002	5.24±0.11	0.089±0.002	5.16±0.12	0.082±0.002	5.42±0.17	0.074±0.002	5.17±0.18	0.068±0.003	6.21±0.32
	0.136±0.002	5.18±0.11	0.119±0.002	5.30±0.11	0.106±0.005	5.21±0.11	0.088±0.002	5.11±0.11	0.081±0.002	5.37±0.18	0.075±0.003	5.26±0.18	0.066±0.002	6.21±0.32
	0.164±0.004	6.31±0.13	0.136±0.003	6.00±0.13	0.121±0.003	6.14±0.13	0.103±0.003	6.13±0.14	0.097±0.003	6.53±0.21	0.088±0.002	6.31±0.21	0.086±0.004	7.07±0.40
	0.162±0.003	6.21±0.14	0.136±0.003	6.10±0.13	0.122±0.003	6.20±0.13	0.106±0.003	6.28±0.13	0.095±0.002	6.45±0.21	0.086±0.003	6.24±0.21	0.083±0.004	6.91±0.40
	0.161±0.003	6.19±0.14	0.134±0.003	5.97±0.13	0.122±0.003	6.20±0.13	0.103±0.002	6.15±0.14	0.098±0.002	6.56±0.20	0.089±0.003	6.32±0.21	0.085±0.005	7.07±0.40
	0.164±0.004	6.32±0.13	0.137±0.003	6.13±0.12	0.122±0.003	6.15±0.13	0.105±0.003	6.31±0.13	0.094±0.002	6.38±0.21	0.087±0.003	6.21±0.21	0.085±0.004	7.14±0.39
	0.159±0.004	6.13±0.14	0.138±0.003	6.17±0.12	0.124±0.003	6.27±0.13	0.106±0.003	6.25±0.14	0.097±0.002	6.56±0.21	0.086±0.003	6.15±0.22	0.086±0.004	7.21±0.39
	0.185±0.004	7.12±0.16	0.156±0.004	7.02±0.12	0.141±0.003	7.32±0.15	0.115±0.003	7.21±0.16	0.107±0.003	7.33±0.25	0.097±0.003	7.06±0.25	0.094±0.003	7.90±0.45
	0.179±0.003	6.90±0.16	0.152±0.004	6.93±0.15	0.138±0.003	7.22±0.15	0.118±0.003	7.23±0.16	0.106±0.002	7.34±0.25	0.097±0.003	7.09±0.25	0.093±0.004	7.85±0.46
	0.186±0.004	7.14±0.16	0.157±0.004	7.10±0.15	0.139±0.003	7.24±0.15	0.121±0.003	7.22±0.16	0.107±0.003	7.37±0.25	0.098±0.004	7.15±0.25	0.090±0.004	7.65±0.47
	0.186±0.004	7.14±0.16	0.158±0.004	7.10±0.15	0.137±0.003	7.10±0.15	0.116±0.004	7.39±0.16	0.107±0.003	7.38±0.25	0.097±0.003	7.07±0.25	0.090±0.004	7.67±0.47
	0.187±0.004	7.25±0.15	0.158±0.004	7.10±0.15	0.137±0.003	7.11±0.15	0.117±0.003	7.37±0.16	0.109±0.003	7.63±0.24	0.097±0.003	7.04±0.25	0.092±0.003	7.92±0.45
	0.210±0.005	8.32±0.18	0.175±0.005	8.12±0.17	0.160±0.003	8.42±0.17	0.141±0.003	8.32±0.18	0.119±0.003	8.25±0.29	0.114±0.004	8.16±0.29	0.111±0.003	9.48±0.56
	0.213±0.004	8.34±0.18	0.174±0.005	8.05±0.17	0.163±0.003	8.32±0.17	0.141±0.004	8.34±0.18	0.120±0.003	8.39±0.29	0.111±0.004	8.07±0.29	0.112±0.004	9.67±0.55
	0.212±0.004	8.33±0.18	0.174±0.005	8.03±0.17	0.159±0.004	8.40±0.17	0.140±0.004	8.40±0.17	0.124±0.004	8.59±0.28	0.108±0.004	7.82±0.30	0.111±0.004	9.55±0.56
	0.213±0.006	8.45±0.18	0.174±0.005	8.02±0.17	0.161±0.003	8.55±0.17	0.144±0.004	8.53±0.17	0.123±0.004	8.51±0.28	0.111±0.003	8.02±0.29	0.108±0.004	9.44±0.57
	0.200±0.005	7.90±0.19	0.172±0.005	7.95±0.17	0.163±0.003	8.59±0.17	0.143±0.004	8.50±0.17	0.119±0.002	8.18±0.29	0.112±0.004	8.01±0.29	0.110±0.003	9.53±0.56
	0.260±0.005	9.99±0.21	0.221±0.006	9.95±0.19	0.193±0.004	9.98±0.20	0.171±0.005	10.10±0.21	0.150±0.004	10.41±0.33	0.135±0.004	9.62±0.35		
	0.269±0.004	10.29±0.21	0.214±0.005	9.62±0.20	0.189±0.004	9.98±0.20	0.165±0.005	9.84±0.22	0.142±0.004	9.97±0.35	0.133±0.004	9.65±0.35		
	0.261±0.004	9.98±0.21	0.218±0.006	9.82±0.20	0.190±0.004	10.03±0.20	0.163±0.005	9.74±0.22	0.143±0.004	10.04±0.35	0.133±0.004	9.70±0.35		
	0.269±0.006	10.16±0.21	0.218±0.006	9.83±0.19	0.185±0.004	9.68±0.20	0.163±0.005	10.08±0.21	0.142±0.003	10.00±0.35	0.132±0.004	9.78±0.35		
	0.269±0.005	10.17±0.21	0.217±0.005	9.74±0.20	0.190±0.005	9.97±0.20	0.164±0.005	9.75±0.22	0.144±0.004	10.18±0.34	0.132±0.004	9.83±0.35		

Table 5 Dependence of second-order rate coefficients $(dm^3\ mol^{-1}\ s^{-1})$ on isotopic substitution in CH_2Cl_2 at 298 K

System	k_H	k_D	k_H/k_D
Bromanil	1024 ± 25	1480 ± 30	0.69
Iodanil	216 ± 13	198 ± 10	1.09
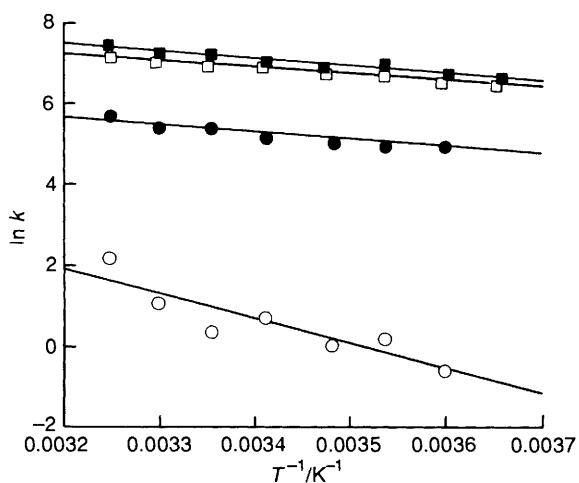
Fig. 1 Arrhenius plots for quinone–ylide systems in CH_2Cl_2 solution. (■) In k_1 chloranil. (□) In k_1 bromanil. (●) In k_1 iodanil. (○) In k_3 iodanil.

the first-order rate coefficient, τ the time measured by the spectrophotometer and δ a correction due to the fact that τ includes the mixing and discharge time.[1]

The points $1/k_{obs}$ vs. $1/[Y]_0$ (where $[Y]_0$ is the initial concentration of ylide) obtained in the experiments carried out in excess of ylide were fitted to eqn. (2) using the weighted least squares method.[28] The $[Y]_0$ values were obtained using the procedure described previously[1] and the results are shown in Tables 3 and 4.

$$\frac{1}{k_{obs}} = a_0 + a_1 \frac{1}{[Y]_0} + a_2 \frac{1}{[Y]_0^2} \tag{2}$$

Results and Discussion

Stoichiometry.—The ^1H NMR spectra of the reaction mixtures are similar to those described for chloranil, in an earlier report.[1] The integration of the spectra indicates that for each mole of the product formed, two moles of ylide are consumed as deduced from the integration of the signals from the products **4c–d** and from the signal due to ylide cyclopentadiene hydrogens after adding amine. One mole of the ylide forms part of the product **4b–d** and the other remains as **3c–d**, with the appearance of band at 3.62 ppm corresponding to the formation of a methylene group by protonation of the cyclopentadiene ring. The broad nature of the bands attributed to **3c,d** indicates a rapid exchange of the proton between the cyclopentadiene carbons. The addition of amine causes the transfer of the protons from ylide to amine causing the hydrochloride signals at 6.2 and 3.62 ppm to disappear.

Reaction Mechanism.—The overall mechanism involves nucleophilic addition of **2** to the quinones **1a–d** to form an intermediate σ-complex **5a–d** followed by elimination of hydrogen halide to form the products, P, (**4a–d**). The rate-limiting step in this mechanistic scheme is the nucleophilic addition of **2** to **1a–d** as evidenced by the element effect[20] $(X = F \gg X = Cl \sim X = Br > X = I)$ analogous to the classical sequence established for nucleophilic substitution in activated aryl halides[29] and by the isotope effects observed with **1b–d** and **2b**

which in each case showed $k_H/k_D < 1$ (Table 5). The latter results show that the loss of a proton from the intermediates **5b–d** is not involved in the rate-limiting process. The question then arises as to whether the data will allow one to define the mechanism for the elimination of hydrogen halide from **5a–d**. The three possible mechanisms are E_1, E_2 and E_1cB (see Scheme) and since the reactions are monitored by the appearance of the products **4b–d**, the equations corresponding to these mechanisms (as derived from the steady state approximation and mass balance) are eqns. (3)–(5) respectively.

$$\frac{1}{k_{obs}} = \frac{1}{k_3} + \left(\frac{k_2 + k_3}{k_1 k_3} + \frac{1}{k_4}\right)\frac{1}{[Y]_0} \tag{3}$$

$$a_0 = \frac{1}{k_3}; \quad a_1 = \frac{k_2 + k_3}{k_1 k_3} + \frac{1}{k_4} \approx \frac{1}{k_1}; \quad a_2 = 0$$

$$\frac{1}{k_{obs}} = \frac{1}{k_8} + \frac{k_1 + k_7}{k_1 k_7}\frac{1}{[Y]_0} + \frac{k_2}{k_1 k_7}\frac{1}{[Y]_0^2} \tag{4}$$

$$a_0 = \frac{1}{k_8} \approx 0; \quad a_1 = \frac{k_1 + k_7}{k_1 k_7} \approx \frac{1}{k_1}; \quad a_2 = \frac{k_2}{k_1 k_7}$$

$$\frac{1}{k_{obs}} = \frac{k_1 + k_9}{k_1 k_9}\frac{1}{[Y]_0} + \frac{k_2}{k_1 k_9}\frac{1}{[Y]_0^2} \tag{5}$$

$$a_0 = 0; \quad a_1 = \frac{k_1 + k_9}{k_1 k_9} \approx \frac{1}{k_1}; \quad a_2 = \frac{k_2}{k_1 k_9}$$

The E_1 mechanism. The value deduced for $1/k_{obs}$ is shown in eqn. (3). A plot of $1/k_{obs}$ vs. $1/[Y]_0$ would produce a straight line of slope a_1 and intercept a_0. If k_4 is large, as expected for a proton transfer, then $a_1 = (k_2 + k_3)/k_1 k_3$, and if $k_3 \gg k_2$, then $a_1 = 1/k_1$. The value of the intercept is $a_0 = 1/k_3$ and hence a value of k_3 for the elimination of the halide may be derived.

The most likely reaction to conform to this mechanism is where $X = I$ (iodanil) and analysis of the data (Table 6) for this reaction seems to support this view. The plots of k_{obs} vs. $[Y]_0$ although linear $(r = 1.00)$ all gave positive intercepts. The correlation coefficients of the plots of $1/k_{obs}$ vs. $1/[Y]_0$ were all also *ca.* 1.00 and all again gave positive intercepts. Plots of ln $(1/a_1)$ vs. $1/T$ and ln $(1/a_0)$ vs. $1/T$ gave E_a values of 15 kJ mol^{-1} $(r = 0.9_z)$ and 44 kJ mol^{-1} $(r = 0.93)$ respectively (Table 7, Fig. 1). Thus the E_1 mechanism seems likely for iodanil and this is consistent with the leaving group ability of the iodide ion. The plots of k_{obs} vs. $[Y]_0$ or $1/k_{obs}$ vs. $1/[Y]_0$ for chloranil (CA) and bromanil (BA) also gave excellent linear correlations but *negative* intercepts at almost every temperature. Thus these quinones do not appear to conform to the E_1 mechanism since k_3 for $X = Br$ or Cl would both be expected to be less than for $X = I$ which would make the intercepts for $X = Br$ or Cl in an E_1 mechanism larger than that for $X = I$. The alternative mechanisms are E_2 or E_1cB and these are analysed below.

The E_2 mechanism. The value deduced for $1/k_{obs}$ is shown in eqn. (5). The quadratic fit of $1/k_{obs}$ vs. $1/[Y]_0$ would pass

$$\frac{[Y]_0}{k_{obs}} = \frac{k_1 + k_9}{k_1 k_9} + \frac{k_2}{k_1 k_9}\frac{1}{[Y]_0} \tag{6}$$

through the origin and a plot of $[Y]_0/k_{obs}$ vs. $1/[Y]_0$ would lead to a linear plot in which, if $k_9 \gg k_1$, the intercept, $a_0 = 1/k_1$ and the slope $a_1 = k_2/k_1 k_9$ [eqn. (6)].

The E_1cB mechanism. The value deduced for $1/k_{obs}$ is shown in eqn. (4). Clearly, if k_8 is very large the E_1cB mechanism would approximate to the E_2 mechanism but if $1/k_8$ is significant, the

Table 6 Experimental a_0 and a_1 parameters obtained from eqn. (3) in CH_2Cl_2

Bromanil system			Iodanil system		
T/K	a_0/s	$1/a_1 \approx k_1/dm^3 \, mol^{-1} \, s^{-1}$	T/K	$1/a_0 \approx k_3/s^{-1}$ [a]	$1/a_1 \approx k_1/dm^3 \, mol^{-1} \, s^{-1}$
273.9 ± 0.1	−0.05 ± 0.03	650 ± 10			
278.1	−0.09 ± 0.02	697 ± 7	277.8 ± 0.1	0.56 ± 0.03	142 ± 14
282.9	−0.04 + 0.02	800 ± 9	282.8	1.1 ± 0.1	152 ± 12
287.9	0.00 ± 0.04	860 ± 20	287.2	1.1 ± 0.1	163 ± 9
293.4	0.01 ± 0.03	1000 ± 15	293.4	1.9 ± 0.3	180 ± 20
298.4	−0.03 ± 0.03	1025 ± 25	298.1	1.4 ± 0.1	216 ± 13
303.4	−0.06 ± 0.01	1160 ± 10	303.2	3.0 ± 0.4	234 ± 10
308.0	0.09 ± 0.04	1280 ± 40	308.0	8 ± 2	270 ± 15

[a] E_1 mechanism.

Table 7 Parameters of activation for the bromanil and iodanil–ylide systems

System	$E_a/kJ \, mol^{-1}$	$\Delta H^{\ddagger}/kJ \, mol^{-1}$	$\Delta S^{\ddagger}/J \, mol^{-1} \, K^{-1}$	$\Delta G^{\ddagger}/kJ \, mol^{-1}$
k_1 Bromanil [a]	13.8 ± 0.5	11.6 ± 0.5	−148 ± 2	52 ± 1
k_1 Bromanil [b]	37	35	−81	59
k_1 Iodanil [a]	15.0 ± 1.1	12.6 ± 1.1	−158 ± 3	60 ± 2
k_1 Iodanil [b]	42	39	−78	62
k_3 Iodanil [a]	44 ± 10	42 ± 10	−97 ± 35	71 ± 16

[a] In CH_2Cl_2. [b] In toluene.

quadratic fit of $1/k_{obs}$ vs. $1/[Y]_0$ would give a positive intercept. In addition, plots of $1/k_{obs}$ vs. $1/[Y]_0$ or $[Y]_0/k_{obs}$ vs. $1/[Y]_0$ would not be linear.

We have already argued that the reaction with chloranil (**1b**) probably belongs to the E_1cB category.[1] Analysis of the data for bromanil in Table 6 reveals that quadratic fits of the plots of $1/k_{obs}$ vs. $1/[Y]_0$ over the whole temperature range give intercepts of −0.1 ± 0.5. Thus within experimental error the plots effectively pass through the origin. Furthermore, plots of $[Y]_0/k_{obs}$ vs. $1/[Y]_0$, although affording poor linearity, give intercepts ($a_0 = 1/k_1$) which give an E_a value of 14 kJ mol⁻¹, in excellent agreement with the value derived from the simple plots of k_{obs} vs. $[Y]_0$ at each temperature. Thus the bromanil reaction appears to be best represented by an E_2 elimination of hydrogen bromide from the σ-complex. We may in fact be observing the whole range of elimination mechanisms from E_1 to E_1cB as the halogen varies from I to F. Further studies on fluoranil and the details of the deuterium isotope effects for each halogen are in hand in an attempt to verify this hypothesis.

The activation parameters established for k_1 (bromanil and iodanil) are precisely those one would expect for a rate-limiting addition of a neutral nucleophile (the ylide) to a neutral electrophile (the quinone). The Arrhenius activation energy is low (i.e. the sensitivity of the reaction to temperature changes is low) but the entropy of activation shows a high negative value consistent with a high degree of order developing between the ground state and the transition state. As expected, the $\Delta S^{\ddagger}$ values are less negative in toluene than in dichloromethane indicating a less polar, less ordered transition state in the former solvent. Thus in toluene enthalpy factors are dominant whereas in dichloromethane the entropy factors are most important.

Quantum Mechanical Calculations.—For the purpose of clarifying the role which the σ intermediates play in the reaction mechanism, a set of quantum mechanical calculations was carried out, using the AM1 method,[30] implemented in the MOPAC program.[31] The enthalpies of formation of the compounds listed in Table 8 were calculated. Based on these heats the enthalpies of the reactions were calculated (see Table

9). The direct and inverse activation barriers for the addition of the tetrahalo-*p*-benzoquinones to ylide were estimated. The methodology used for the calculations was the following: The ylide and the tetrahalo-*p*-benzoquinone were completely optimized. In calculations of other structures in which the ylide fragment appears, the internal structures of the phenyl groups were not optimized, allowing only for variations in their relative position. The minimum was obtained when the gradient was smaller or the same as the required 0.2 kJ Å⁻¹. However, slightly higher gradients (0.4 kJ Å⁻¹) were obtained in the same structures containing iodine atoms. The activation barriers were determined by elongation of the C–C bond, which connects the ylide and quinone fragments in the structures **5a–d**, from its equilibrium value to $r = 3$ Å, the point at which the energy of the supermolecule was similar to that obtained from the total of the fragments individually. The maximum was obtained by interpolation of the curve ΔH_f vs. r. An overestimation of the atomic charges on the phosphorus atom was observed with respect to the values calculated for **2a**, which gave good agreement between the calculated and the experimental structure as measured by X-ray diffraction.[26]

From Table 8 one may conclude that the heat of formation of the σ-complexes **5a–d** is slightly higher (15–30 kJ mol⁻¹) than the heat of formation of the reactants **1a–d** and **2** individually. Consequently, the formation of a σ-type complex is a likely reaction path since a highly polar intermediate is formed with minimum expenditure of energy, which leads, in successive steps, to formation of the products. A low ΔH_f is expected in CH_2Cl_2, since the polarity of the σ-complexes is greater than that of the reactants.

In Table 10 the direct, E_1, and inverse, E_{-1}, enthalpies of activation are given for the addition of ylide to quinone. These quantities are clearly overestimated because the AM1 calculations do not take into account the interactions with the solvent. The dipole moments estimated for the TS are intermediate between those calculated for the σ-complexes and the reactants, and are very similar for all systems studied. As a consequence, we expect the stabilization due to solvent effects to be very similar in the four systems. The E_1 values follow the same trend as the experimental ones. The E_{-1} values are always smaller than the forward ones, these facts being in agreement with the reversibility of the first step. The increase in E_{-1}, in going from chloranil to bromanil, is in qualitative agreement with a decrease in k_2.

In Table 9, six elementary steps which may take place in the system are shown. Step 2 is a global transfer of a HX molecule from the σ-complex to an ylide molecule. It is observed that this transfer becomes less favourable along the series Cl–Br–I. The high enthalpies of reaction for the bromanil and iodanil systems suggest that the transfer should take place in more than one step. Steps 3 and 4 show the E_1cB and E_1 decomposition of the σ-intermediate respectively. Charged products are formed from charged intermediates (σ-complexes) and therefore solvation

Table 8 AM1 enthalpies of formation and dipole moments for reactants, products and intermediates of the reactions

Compound		$\Delta H_f/\text{kJ mol}^{-1}$	μ/D	Compound		$\Delta H_f/\text{kJ mol}^{-1}$	μ/D
$C_6O_2F_4$	1a	−795.6	0.0	$C_{29}H_{19}O_2F_3P^+$	6a	648.3	—
$C_6O_2Cl_4$	1b	−161.9	0.0	$C_{29}H_{19}O_2Cl_3P^+$	6b	837.6	—
$C_6O_2Br_4$	1c	47.4	0.0	$C_{29}H_{19}O_2PBr_3^+$	6c	994.0	—
$C_6O_2I_4$	1d	232.9	0.0	$C_{29}H_{19}O_2PI_3^+$	6d	1140.2	—
$C_{23}H_{19}P$	2	424.9	8.1 (7.0[a])	$C_{29}H_{18}O_2F_4P^-$	7a	−571.6	—
$C_{23}H_{20}FP$	3a	341.9	1.4	$C_{29}H_{18}O_2Cl_4P^-$	7b	55.6	—
$C_{23}H_{20}ClP$	3b	433.7	7.4	$C_{29}H_{18}O_2PBr_4^-$	7c	243.0	—
$C_{23}H_{20}PBr$	3c	549.3	8.0	$C_{29}H_{18}O_2PI_4^-$	7d	431.6	—
$C_{23}H_{20}PI$	3d	654.0	8.3				
$C_{23}H_{20}P^+$	3e	900.2	—				
$C_{29}H_{18}O_2F_3P$	4a	−217.1	13.7	HF	—	−310.9	1.7
$C_{29}H_{18}O_2Cl_3P$	4b	278.8	12.6	HCl	—	−103.0	1.4
$C_{29}H_{18}O_2PBr_3$	4c	430.6	12.7	HBr	—	−43.9	1.4
$C_{29}H_{18}O_2PI_3$	4d	581.7	12.8	HI	—	33.2	1.3
$C_{29}H_{19}O_2F_4P$	5a	−337.0	20.4	F^-	—	14.4	—
$C_{29}H_{19}O_2Cl_4P$	5b	291.2	19.3	Cl^-	—	−157.6	—
$C_{29}H_{19}O_2PBr_4$	5c	486.5	19.1	Br^-	—	−85.5	—
$C_{29}H_{19}O_2PI_4$	5d	678.2	19.2	I^-	—	9.3	—

[a] In benzene at 298 K.[17]

Table 9 AM1 Enthalpies (kJ mol⁻¹) of reaction for elementary steps[a]

Step	Fluoranil	Chloranil	Bromanil	Iodanil
(1) $Q + Y = \sigma$	33.6	28.3	14.1	20.5
(2) $\sigma + Y = X + (YH^+, X^-)$	37.0	−3.8	68.4	132.6
(3) $\sigma + Y = \sigma^- + YH^+$	240.8	239.7	231.8	228.7
(4) $\sigma = \sigma H^+ + X^-$	999.7	460.9	422.1	452.7
(5) $(YH^+, X^-) = Y + HX$	−228.3	−111.9	−168.4	−195.9
(6) $Q + Y = X + HX$	−157.3	−87.4	−85.6	−42.9

[a] Q = tetrahalo-p-benzoquinone; Y = ylide; YH^+ = 3e; X = 4a–c; σ = 5a–d; σH^+ = 6a–c; σ^- = 7a–c; X^- = F^-, Cl^-, Br^-, I^-; HX = hydrogen halide.

Table 10 AM1-estimated energy of activation and dipole moments of TS for ylide–quinone step

X	$E_1/\text{kJ mol}^{-1}$	$E_{-1}/\text{kJ mol}^{-1}$	$r/\text{Å}$	μ/D
F	72.8	39.2	2.1	12.6
Cl	87.1	58.7	2.1	12.1
Br	80.2	66.0	2.1	11.8
I	86.6	66.1	2.1	12.2

factors can make the value of the heat of formation vary substantially. For this reason the heats of formation are far too high. The E_1cB path is always favoured energetically over the E_1 path. The enthalpy of step 3 (E_1cB type) decreases in the F to I series, indicating that the acidity of the σ-complexes increases in that order. The decrease in the enthalpy of step 4 suggests that the E_1 type mechanism is increasingly feasible when going from fluoranil to iodanil.

The calculation indicates that the deprotonation of ylide is an extremely exothermic process and therefore the ylide is a weak base (pK_a = 4.69 in ethanol–water mixture).[32] Reaction 6 indicates that the global process is exothermic.

Conclusions

The experimental activation parameters indicate that the reactivities of bromanil and iodanil with 2 are similar to that with chloranil. In an initial stage, quinone and ylide form a polar σ-complex 5a–d, whose energy is similar to the sum of the energies of quinone and ylide individually. After this step, three reaction paths are possible. In the first one, of E_1cB type, a

proton is transferred from the σ-complex, forming an anion which rapidly expells a halide anion. This is the case for chloranil where the C–halogen bond energy is high. An alternative path is the E_1 type elimination of the halide to form an acidic cation which rapidly transfers a proton. This happens with iodanil in which the energy of the C–halogen bond is lower. The energy of the C–halogen bond in bromanil induces an intermediate situation. Experimental data suggest that bromanil reacts through an E_2 type mechanism.

Acknowledgements

References

1 F. Pérez Plà, J. Palou, R. Valero, C. D. Hall and P. Speers, J. Chem. Soc., Perkin Trans. 2, 1991, 1925.
2 A. Giraldo, L. Morelli and C. Pecille, Chem. Phys. Lett., 1973, 22, 553.
3 M. Konno, H. Kobayashi, F. Marumo and Y. Saito, Bull. Chem. Soc. Jpn., 1973, 46, 1987.
4 S. Hiroma and H. Kuroda, Bull. Chem. Soc. Jpn., 1973, 46, 3645.
5 S. Hiroma and H. Kuroda, Bull. Chem. Soc. Jpn., 1974, 47, 3014.
6 J. Veselovská, H. Remko, J. Cizmarik, L. Removka and D. Novosedliková, Z. Phys. Chem., 1987, 268, 1003.
7 K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inocuchi, A. Kawamoto and J. Tanaka, J. Am. Chem. Soc., 1987, 109, 6970.
8 K. Imaeda, T. Enoki, T. Mori, H. Inocuchi, M. Sasaki, K. Nakasuji and I. Murata, Bull. Chem. Soc. Jpn., 1989, 62, 372.

9 M. A. Slifkin, R. A. Sumner and J. G. Heathcote, *Spectrochimica Acta, Part A*, 1967, **2**, 1751.

10 M. A. Slifkin, B. M. Smith and R. H. Walmsley, *Spectrochimica Acta, Part A*, 1969, **25**, 1479.

11 T. Yamakoa and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2971.

12 R. Foster, *Recueil.*, 1964, **83**, 711.

13 A. Codoñer, I. Monzó, J. Palou and R. Valero, *Anales de Quimica*, 1987, **84**, 319.

14 A. Codoñer, I. Monzó, J. Palou and R. Valero, *J. Chem. Soc., Perkin Trans. 2*, 1988, 221.

15 I. Monzó, J. Palou, J. Roca and R. Valero, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1995.

16 T. Nogomi, K. Yoshihara, H. Hosoya and S. Nagakura, *J. Phys. Chem.*, 1969, **73** 2670.

17 F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, 1957, **79**, 67.

18 K. Iwata, S. Yonena and Z. Yoshida, *J. Am. Chem. Soc.*, 1971, **93**, 6745.

19 C. D. Hall, P. Speers, R. Valero, F. Pérez Plá and D. B. Denney, *Phosphorus, Sulfur and Silicon*, 1989, **45**, 249.

20 E. Lord, M. P. Naan and C. D. Hall, *J. Chem. Soc. B*, 1970, 1401.

21 E. Lord, M. P. Naan and C. D. Hall, *J. Chem. Soc. B*, 1971, 213.

22 E. Lord, M. P. Naan and C. D. Hall, *J. Chem. Soc. B*, 1971, 220.

23 C. W. Rigby, E. Lord, M. P. Naan and C. D. Hall, *J. Chem. Soc. B*, 1971, 1192.

24 H. L. Ammon, G. L. Wheeler and P. H. Watts, Jr., *J. Am. Chem. Soc.*, 1973, **95**, 6158.

25 C. L. Jackson and E. K. Bolton, *J. Am. Chem. Soc.*, 1914, **36**, 301.

26 W. B. Smith, W. H. Watson and S. Chiranjeevi, *J. Am. Chem. Soc.*, 1967, **89**, 1438.

27 R. M. G. Roberts, *Tetrahedron*, 1980, **36**, 3295.

28 D. M. Himmelblau, *Process Analysis by Statistical Methods*, Wiley, New York, 1970.

29 J. F. Bunnett, E. W. Garbisch and K. M. Pruitt, *J. Am. Chem. Soc.*, 1957, **79**, 385.

30 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

31 F. J. Sailer, *QCPE Bull.*, 1990, **10**, program number 455.

32 Z. Yoshida, S. Yoneda and Y. Murata, *J. Org. Chem.*, 1973, **95**, 6158.