Kinetics and mechanism of the addition of triphenylphosphoniocyclopentadienide to tetrahalo-*p*-benzoquinones. Part V.[1–4] The disubstitution reaction of iodanil

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Iodanil reacts with an excess of triphenylphosphoniocyclopentadienide to yield exclusively the 2,5-disubstituted quinone through a second-order reaction. Kinetic data suggest that the reaction goes in two steps, involving pre-equilibrium formation of a betaine followed by an E1 type elimination of HI. The empirical rate law is derived from a multi-response non-linear least-squares analysis and the 2,6-/2,5-isomer ratio for tetrahalo-*p*-benzoquinone substitution is discussed for all the halogens. Finally, the synthesis and characterisation of 2-(triphenylphosphonio-3′-cyclopentadienyl)-3,5,6-trifluorocyclohexa-2,5-diene-1,4-dione (5, X = F) are also reported.

Introduction

Recently, it has been demonstrated that chloranil (**1**, X = Cl) and bromanil (**1**, X = Br) react with excess triphenylphosphoniocyclopentadienide **2** to give the 2,6- and 2,5-disubstitution products,[3] **3** and **4** respectively, whereas fluoranil[4] (**1**, X = F) yields exclusively the 2,6-isomer (**3**, X = F). The reaction proceeds through a pair of consecutive reactions that lead to the monosubstitution products **5** in a matter of seconds and to the disubstituted isomers over several hours. The addition of ylide to the quinone is the rate-limiting step for all monosubstition reactions,[1,2,5,6] whereas the disubstitution reactions are explained by assuming that the monosubstitution product and ylide may be in equilibrium with a σ-complex which yields the disubstitution product by means of an E1 halide elimination.[3] With fluoranil the formation of both the monosubstitution and disubstitution products occurs considerably faster than the analogous reactions with all the other haloquinones.[4]

The kinetics and mechanism of the disubstitution reaction of iodanil are reported in this work. The reaction of iodanil with the ylide is similar to that of chloranil and bromanil except that the 2,5-disubstitution isomer is the only disubstitution product formed. These systems exhibit unusual behaviour with respect to the position of substitution in the quinone ring. There is a large amount of experimental evidence indicating that, under forcing conditions, tetrahalo-*p*-benzoquinones normally undergo disubstitution[7] in positions 2,5- by nucleophilic agents such as aliphatic[8–10] and aromatic amines,[11] polyoxaethylenediamines,[12] azomethines[13] or hydroxide groups.[14] This behaviour has been rationalised by Hückel MO theory assuming that the second nucleophilic attack is directed towards position C(5) because of charge donation afforded by the mesomeric effect of the substituent. However, on reaction with **2**, tetrahalo-*p*-benzoquinones show a progressive change in the disubstitution pattern depending on the halogen used. Fluoranil appears to react exclusively in the 2,6-positions, chloranil and bromanil react in both the 2,5- and 2,6-positions in a ratio close to 1:1 and iodanil reacts exclusively in the 2,5-position. These experimental facts are discussed qualitatively in this work on the basis of the reaction mechanism and simple HMO theory. Finally, the structure of the monosubstitution product of fluoranil (**5**, X = F) is also reported since in previous work[4] it was inferred only on the basis of the structure of the disubstituted compound and the UV–VIS spectrum.

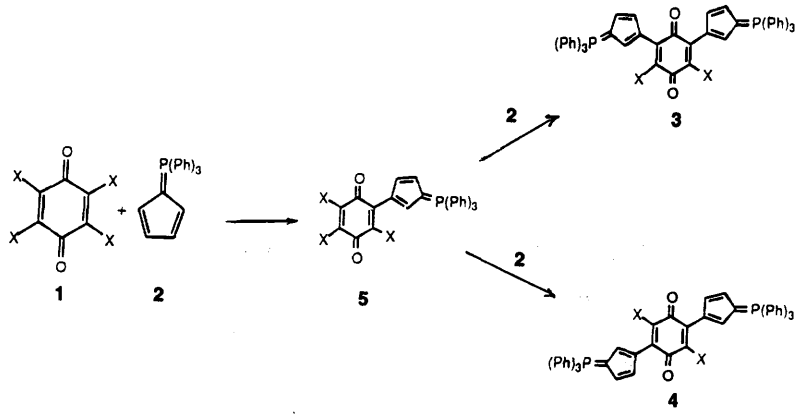
Experimental

Materials

Triphenylphosphoniocyclopentadienide was prepared by the method reported by Ramirez.[15] For kinetic runs further purification was carried out by flash chromatography on silica gel 60H using dichloromethane as eluent. The quality of the purified product (>99%) was checked by IR and ^{31}P NMR spectroscopy. 2,3,4,5-Tetradeuterio-1-triphenylphosphoniocyclopentadienide was prepared from **2** by H–D exchange in deuterioacetic acid–deuterium oxide medium.[16] The level of deuteriation as assessed by ^{1}H NMR was 88%. Commercial fluoranil was recrystallised twice from acetone and then sublimed to give bright yellow crystals, mp (sealed tube) 181 °C, lit.,[4] 181 °C. The quality of the product was checked by IR spectroscopy. Iodanil was prepared by the method of Jackson and Bolton[17] and was recrystallised twice from glacial acetic acid to give dark purple needles, mp (sealed tube) 279–281 °C, lit.,[17] 282 °C. The quality of the product was checked by IR spectroscopy. Commercial quinuclidine (Aldrich) was purified by sublimation and stored in a vacuum desiccator to avoid contact with atmospheric moisture. The quality of the product was checked by ^{1}H NMR and IR spectroscopy. Dichloromethane was dried by heating the solvent under reflux over CaH_2 for 24 h. Acetonitrile was dried with 4 Å molecular sieves and CaH_2 before distillation. Only freshly distilled solvent was used for kinetic runs.

Synthetic procedures

2,5-Disubstitution product of iodanil. A solution of ylide **2** (129 mg, 0.39 mmol) and quinuclidine (45 mg, 0.40 mmol) in acetonitrile (80 ml) was added to a solution of iodanil (60 mg, 0.1 mmol) in the same solvent (50 ml). The reaction mixture was then stirred for 30 h at room temperature. The product gradually precipitated on the walls of the reaction flask and the colour of the solution changed from dark blue to violet. The solution was evaporated to a third of its initial volume and the small violet microcrystals of the product (60% yield) were filtered, washed with cold acetonitrile, dried under vacuum at 4 mm Hg for 4 h and stored in a desiccator at room temperature. The purity of the product was >80% as assessed by multinuclear NMR, the monosubstituted quinone being the only significant impurity. The structure of the product was determined by a combination of spectroscopic techniques as detailed in Table 1.



Scheme 1

Attempts to carry out the reaction in toluene failed and the use of dichloromethane, benzene/diethyl ether or benzene/acetonitrile as solvents, resulted in brown solutions with very poor yields of the 2,5-disubstitution product. Finally, attempts to purify diethyl ether/dichloromethane solutions of the product on silica gel 60H columns or TLC plates also resulted in extensive decomposition.

Monosubstitution product of fluoranil. Fluoranil (74 mg, 0.41 mmol) was dissolved in 200 ml of dry diethyl ether and cooled to −70 °C in a dry ice/acetone bath. A solution of ylide **2** (134 mg, 0.41 mmol) in benzene (75 ml) was added dropwise over 1 h. After the addition, anhydrous K_2CO_3 (50 mg) was added and the reaction mixture was stirred for 1 h. The solution was allowed to reach room temperature, filtered, the diethyl ether removed under vacuum and the remaining solution was stored at −5 °C for 24 h. The needle-like crystals which formed (70 mg, 35%) were filtered, avoiding contact with atmospheric water, washed with cold benzene, dried under vacuum (4 mm Hg) for 4 h and stored in a desiccator at 5 °C. The product was characterised by IR and multinuclear NMR spectroscopy, see Table 2.

A solid sample exposed to the laboratory atmosphere at room temperature decomposed over a period of days. Attempts to pass solutions of the products through chromatography silica gel columns or using flash chromatography again resulted in extensive decomposition.

NMR Experiments

2,5-Disubstitution product of iodanil. ^1H, ^{31}P and ^{13}C NMR spectra were recorded for dilute solutions containing 5 mg of product in 1.0 ml of CD_2Cl_2 at room temperature. Attempts to record spectra at higher temperature resulted in a decomposition of the sample and increasing the product mass over 20 mg resulted in broad NMR signals.

Monosubstitution product of fluoranil. ^1H, ^{31}P, ^{19}F, ^{13}C and $^1H,^1H$ COSY NMR spectra were recorded for dilute solutions containing 15 mg of the compound in 2 ml of C_6D_6 at 24 °C. Attempts to record the spectra in CD_2Cl_2 or $CDCl_3$ resulted in extensive decomposition of the sample.

Kinetic experiments

Reaction rate. In order to measure the reaction rates, stock dichloromethane (1.03×10^{-3} mol dm^{-3}) and acetonitrile (1.37×10^{-3} mol dm^{-3}) solutions of iodanil were prepared and then diluted by a factor of ten. Six reaction mixtures for each solvent were prepared by injecting 500 μl of the quinone solution into a UV-VIS cell containing a fresh thermostatted solution of ylide prepared *in situ* by introducing into the cells a weighed quantity of ylide ranging from 5 mg to 30 mg and 2.5 cm^3 of dichloromethane or a range of 1 mg to 5 mg of ylide and 2.5 cm^3 of acetonitrile.

The absorbance spectra of the six reaction mixtures were recorded between 400 and 800 nm at intervals of 7 min during 707 min for the dichloromethane solutions and at intervals of 6 min during 420 min for acetonitrile solutions with a Cary-3 UV-VIS spectrophotometer equipped with an automatic sample handler and controlled by a computer. The temperature was maintained constant to ±0.1 °C with the Peltier heater-cooler accessory. This procedure was repeated at 288.2, 293.2, 298.2, 303.2 and 308.2 K in dichloromethane, and at 288.2, 298.2, 308.2 and 318.2 K in acetonitrile.

Isotope effect. The procedure was repeated in dichloromethane at 298.2 K but using 2,3,4,5-tetradeuterio-1-triphenylphosphoniocyclopentadienide in order to determine the kinetic isotope effect.

Influence of basic species. The procedure was repeated but using dichloromethane containing quinuclidine (10^{-4} mol dm^{-3}) as solent in order to investigate the influence of base on the reaction rate. In addition, the concentration of ylide was maintained constant at 3.4×10^{-3} M and large amounts of solid quinuclidine were added to the spectrophotometer cells leading to quinuclidine concentrations ranging from 9×10^{-3} to 7×10^{-2} mol dm^{-3} in acetonitrile at 298.2 K.

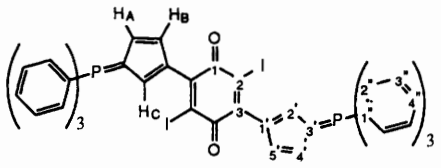
Results

Structure determination

2,5-Disubstitution product of iodanil. The mass spectrometry, multinuclear NMR, IR and UV-VIS spectroscopy data (Table 1) leave no doubt that the isolated compound is the 2,5-disubstitution product of iodanil. The ^{13}C NMR shows a single carbonyl signal at 181.1 ppm and the IR spectrum shows a single frequency at 1634 cm^{-1} for this group. The VIS electronic spectrum consists of a single band centred at 562 nm (CH_2Cl_2), similar in position and intensity to those of 2,5-disubstitution products[3] of chloranil and bromanil. Substitution in position C(3) on the cyclopentadiene ring is supported by the fact that the 2,5-product is formed from the monosubstitution product, whose $^1H,^1H$ COSY spectrum showed substitution in position C(3).[5] The compound also shows a single ^{31}P NMR peak indicating that both phosphorus atoms share the same chemical environment. Additionally, J_{PH} and J_{HH} calculated coupling constants are similar to those found for other compounds of the family and are therefore consistent with C(3)-substitution.

Monosubstitution product of fluoranil. Mass spectrometry, multinuclear NMR, IR and UV-VIS spectroscopy data (Table 2), support the contention that the isolated compound is the 2-(triphenylphosphonio-3′-cyclopentadienyl)-3,5,6-trifluorocyclohexa-2,5-diene-1,4-dione (**5**, X = F) as expected. The IR spectrum shows two bands at 1679 and 1631 cm^{-1} and the ^{13}C NMR spectrum shows two signals at 181.3 and 170.3 ppm consistent with the existence of two carbonyl

Table 1 Spectroscopic data for 2,5-(triphenyl-phosphonio-3′-cyclopentadienyl)-3,6-diiodocyclohexa-2,5-diene-1,4-dione



^{13}C NMR spectrum[a]
C(n) δ/ppm (multiplicity, J_{P-C}/Hz)
C(1) 181.1 (s), C(2) 124.8 (d, 2.0), C(3) 129.3 (s), C(1′) 87.2 (d, 125.0), C(2′) 127.9 (d, 16.3), C(3′) 125.9 (d, 19.4), C(4′) 117.5 (d, 14.2), C(5′) 121.7 (d, 15.1), C(1″) 125.3 (d, 90.4), C(2″) 134.6 (d, 10.3), C(3″) 130.1 (d, 12.4), C(4″) 134.0 (d, 2.8)

^{1}H NMR spectrum[a]
δ/ppm H_A 6.88 (heptuplet), H_B 6.20 (quintuplet), H_C 7.01 (quintuplet). J/Hz J_{AB} = 4.6, J_{AC} = 2.1, J_{BC} = 2.1, J_{AP} = 5.0, J_{BP} = 2.4, J_{CP} = 4.6

^{31}P-NMR spectrum[a]
δ/ppm 14.52 (s)

FAB mass spectrum[b]
M 1008 (36.1%), M + 1 (100), M + 2 (58.7), M + 3 (36.1), M + 4 (11.5), M + 5 (6.8)

ν(KBr disc)/cm^{-1}
3053w (C–H stretch Ph), 2955w, 2925w and 2855w (C–H stretch cp ring), 1634m (C=O stretch), 1507s, 1458m, 1435s, 1327s, 1284w, 1203, 1181w, 1109vs, 1074m, 1026m, 996w, 921m, 843w, 805w, 748w, 719m, 692s, 668w, 641w, 603m, 557s, 531m, 510m

Visible electronic spectrum[c]
λ_{max} = 562 nm, ε_{max} = 16 000 ± 100 cm^{-1} dm^3 mol^{-1}

[a] Solvent CD_2Cl_2. [b] In *m*-nitrobenzyl alcohol as matrix. [c] Solvent CH_2Cl_2, 298 K.

groups. Additionally, the ^{19}F NMR spectrum shows three peaks and the VIS spectrum consists of a single broad band similar in position and intensity to those of monosubstitution products of chloranil,[1] bromanil[2] and iodanil.[2] The ^{1}H,^{1}H COSY spectrum (see Fig. 1) shows the typical coupling scheme observed for substitution in position C(3) of the cp ring with two weak-weak interactions of the proton at 7.8 ppm with the protons at 6.52 and 7.55 ppm, strong (at 6.52 ppm) and weak (at 7.80 ppm) interactions for the proton at 7.55 ppm and strong (at 7.55 ppm) and weak (at 7.80 ppm) interactions for the proton at 6.52 ppm. The ^{31}P spectrum consists of a single peak at 14.74 ppm with a chemical shift which is similar to those of the monosubstitution products of chloranil (15.04 ppm), bromanil (15.04 ppm) and iodanil (15.02 ppm).

Kinetic results

Reaction rates. The monosubstitution product of iodanil was formed in quantitative yield seconds after mixing as evidenced by UV–VIS spectroscopy which showed a single band at *ca.* 690 nm, and therefore its concentration was considered identical with that of the parent haloquinone. All kinetic runs were carried out with an excess of ylide.

The visible spectra of the reaction mixtures were similar to those observed in previous work for the disubstitution reactions of chloranil and bromanil[3] and consisted of an increasing band at 562 nm, attributed to the disubstitution product, and a decreasing band at 693 nm due to the monosubstitution product. The spectra also showed an isosbestic point at 669 nm indicating that the rate of disappearance of the monosubstitution product was correlated with the rate of appearance of the disubstitution product and consequently, stationary steady or equilibrium hypotheses could be applied to all the intermediates. The spectra at high temperature and/or high ylide concentrations showed the distortion due to the acid-catalysed oligomerisation of ylide previously reported[3] and it was noticed that acetonitrile reaction mixtures showed cleaner spectra than dichloromethane solutions under the same conditions of temperature and concentration of ylide.

Since evolution of the spectra of the iodanil reaction mixtures were found to be similar to those observed for chloranil and bromanil, the absorbance values at 458, 482, 560, 640 and 693 nm *vs.* time were, as in previous work,[3,4] fitted to empirical eqn. (1) minimising the least-square multiresponse surface with

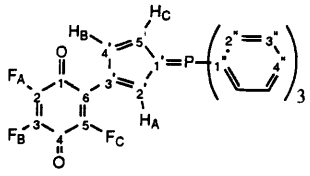
$$A_\lambda(t) = \beta_{\lambda 0} + \beta_{\lambda 1}e^{-kt} + \beta_{\lambda 2}e^{-\mu t} \quad (1)$$

respect to the set of adjustable parameters $\{\beta_i, k, \mu\}$ by means of the Davidon, Fletcher and Powell method[18] using a modified version of the OPKINE program.[19] The non-linear correlation coefficient was greater than 0.99 for all the fittings. The values of k, the first-order rate coefficients governing the appearance of the 2,5-disubstitution product, are given in Table 3. The μ values were always small compared to k values, especially when acetonitrile was used as solvent, and did not present a definite variation with respect to temperature. The first-order rate coefficients varied linearly with the concentration of ylide (Fig. 2) and the slopes of these straight lines with null intercept gave the second order rate constants $k^{(2)}$ at various temperatures. The variation of the $k^{(2)}$ values with temperature (Table 4) gave good Arrhenius plots ($r > 0.99$) for the kinetic runs carried out in both solvents (Fig. 3).

Isotope effect. The values of k and $k^{(2)}$ when using 2,3,4,5-tetradeuterio-1-triphenylphosphoniocyclopentadienide are reported in Tables 3 and 4 respectively. The ratio $k_H^{(2)}/k_D^{(2)}$ was found to be 0.40 at 298 K indicating a significant inverse isotope effect.

Effect of the addition of quinuclidine to the reaction mixtures and solvent effect. The values of k and $k^{(2)}$ for systems containing different amounts of quinuclidine are also reported in Table 3 and Tables 4 and 5. The ratio of the second order coefficient with and without quinuclidine was 1.0 in both dichloromethane (293 K) and acetonitrile (298 K) indicating that the presence of a stronger base than the ylide had no appreciable effect on the reaction rate. The reaction rate increased, however, on changing from dichloromethane to acetonitrile by a factor of 7 indicating a polar transition state relative to the ground state.

Table 2 Spectroscopic data for 2-(triphenyl-phosphonio-3′-cyclopentadienyl)-3,5,6-trifluorocyclohexa-2,5-diene-1,4-dione



^{13}C NMR spectrum[a]

Assignment	δ	Multiplicity	$^{n}J_{C-X}$/Hz[b]				
C(1)	181.3	d	—	—	$^{2}J_{CF}$ = 13.6	—	—
C(2)	123.6	d	—	—	$^{2}J_{CF}$ = 7.4	—	—
C(3)	142.7	dd	—	$^{1}J_{CF}$ = 258.4	—	$^{3}J_{CF}$ = 5.3	—
C(4)	170.3	t	—	—	$^{2}J_{CF}$ = 23.6	—	—
C(5)	143.0	dq	—	$^{1}J_{CF}$ = 270.8	$^{2}J_{CF}$ = 11.2	$^{3}J_{CF}$ = 6.1	—
C(6)	148.9	dq	—	$^{1}J_{CF}$ = 264.8	$^{2}J_{CF}$ = 11.2	—	$^{4}J_{CF}$ = 2.9
C(1′)	89.5	d	J_{CP} = 111.5	—			
C(2′)	128.8	dd	J_{CP} = 16.8	$^{4}J_{CF}$ = 8.9			
C(3′)	117.5	d	J_{CP} = 20.0	—			
C(4′)	121.9	dd	J_{CP} = 15.1	$^{4}J_{CF}$ = 9.3			
C(5′)	120.0	dd	J_{CP} = 14.2	$^{5}J_{CF}$ = 3.5			
C(1″)	126.6	d	J_{CP} = 90.3				
C(2″)	133.8	d	J_{CP} = 10.4				
C(3″)	129.2	d	J_{CP} = 12.4				
C(4″)	133.1	d	J_{CP} = 2.8				

^{1}H NMR spectrum[a]
δ/ppm H(Ph) 7.60 (multiplet 15 H), H_A 7.80 (d octuplet), H_B 7.55 (dt), H_C 6.52 (octuplet). J/Hz J_{AB} = 2.1, J_{AC} = 2.9, J_{BC} = 2.1, J_{AP} = 5.5, J_{BP} = 0.7, J_{CP} = 4.5, J_{AF} = 4.5, J_{BF} = 5.9

^{31}P NMR spectrum[a]
δ/ppm 14.74 (s)

^{19}F NMR spectrum[a]
δ/ppm F_A −145.4 (q), F_B −147.7 (q), F_C −134.0 (broad s). J/Hz J_{AB} = 8.5, J_{AC} = 0, J_{BC} = 2.5

FAB mass spectrum[c]
M − 2 (3%), M − 1 (6), M 486 (16), M + 1 (27), M + 2 (32), M + 3 (100)[e]

ν(KBr disc)/cm^{-1}
3242 (w), 3054 (w), 2918 (w), 1714m (F–C stretch), 1679m (C=O stretch), 1631 (C=O stretch), 1545 (s), 1453 (m), 1437 (m), 1329 (m), 1304 (s), 1288 (s), 1247 (s), 1196 (s), 1183 (s), 1155 (s), 1101 (s), 1043 (s), 999 (s), 939 (m), 910 (m), 824 (w), 777 (s), 751 (w), 720 (m), 691 (s), 650 (w), 618 (w), 606 (w), 589 (m), 561 (s), 532 (m), 510 (m), 494 (w), 462 (w).

Visible electronic spectrum[d]
λ_{max} = 700 nm, ε_{max} = 8180 ± 50 cm^{-1} dm^3 mol^{-1}

[a] Solvent: C_6D_6, 297 K. [b] d = Doublet, t = triplet, q = quadruplet, dd = doublet of doublets, dq = doublet of quadruplets. [c] In *m*-nitrobenzyl alcohol matrix. [d] Solvent CH_2Cl_2, 298 K. [e] Probably the reduced form of the quinone + 1 amu.

Discussion

It can be shown that the mechanism in Scheme 2 leads to eqn. (2) where ε_i refers to the molar extinction coefficient of species

$$\frac{A(t)}{a_0} = \{\varepsilon_v - \varepsilon_d\} + \left\{\varepsilon_a - \varepsilon_v + \frac{\varepsilon_d\mu - \varepsilon_p k}{k + \mu}\right\}e^{-kt} + \frac{k}{k + \mu}(\varepsilon_d + \varepsilon_p)e^{\mu t} \quad (2)$$

'i', l is the cell path length (1 cm) and a_0 is the initial concentration of the monosubstitution product. This equation has the same form as empirical eqn. (1). During the mathematical derivation of eqn. (2) it was assumed that the ylide was in excess and that steady state or equilibrium hypotheses could be applied to all the intermediates as discussed in previous work.[3,4]

Having established the empirical rate law, the second step is to propose a detailed mechanism of the reaction to explain the linear dependence of k on the initial concentration of ylide, the inverse isotope effect, the solvent effect and the failure of additional strong base to influence the reaction rate. Furthermore, it is necessary to explain the rate order for the formation of the disubstitution products (2,5 + 2,6) for the range of tetrahalo-*p*-benzoquinones which was: FA ≫ BA > CA > IA at 293 K in dichloromethane.

The formation of the disubstitution products proceeds by nucleophilic addition of the ylide to the electron deficient quinone ring followed by the elimination of HI. The elimination step is usually of the E1 or E1cB type and both mechanisms are shown in Scheme 3.

It can be shown[3] that with the appropriate assumptions (see below) both mechanisms lead to a linear dependence of the first order kinetic coefficient on the initial concentration of ylide [eqns. (3) and (4)].

$$v = k_3\frac{k_1}{k_2}y_0a = k^{(2)}a \qquad \text{(E1 mechanism)} \quad (3)$$

$$v = k_1y_0a = k^{(2)}a \qquad \text{(E1cB mechanism)} \quad (4)$$

In order to deduce eqns. (3) and (4) the steady state hypothesis was applied to all the σ-intermediates assuming that for the E1 mechanism the σ-complex and the reactants were either in equilibrium (*i.e.* $k_2 \gg k_3$) or at very low concentration

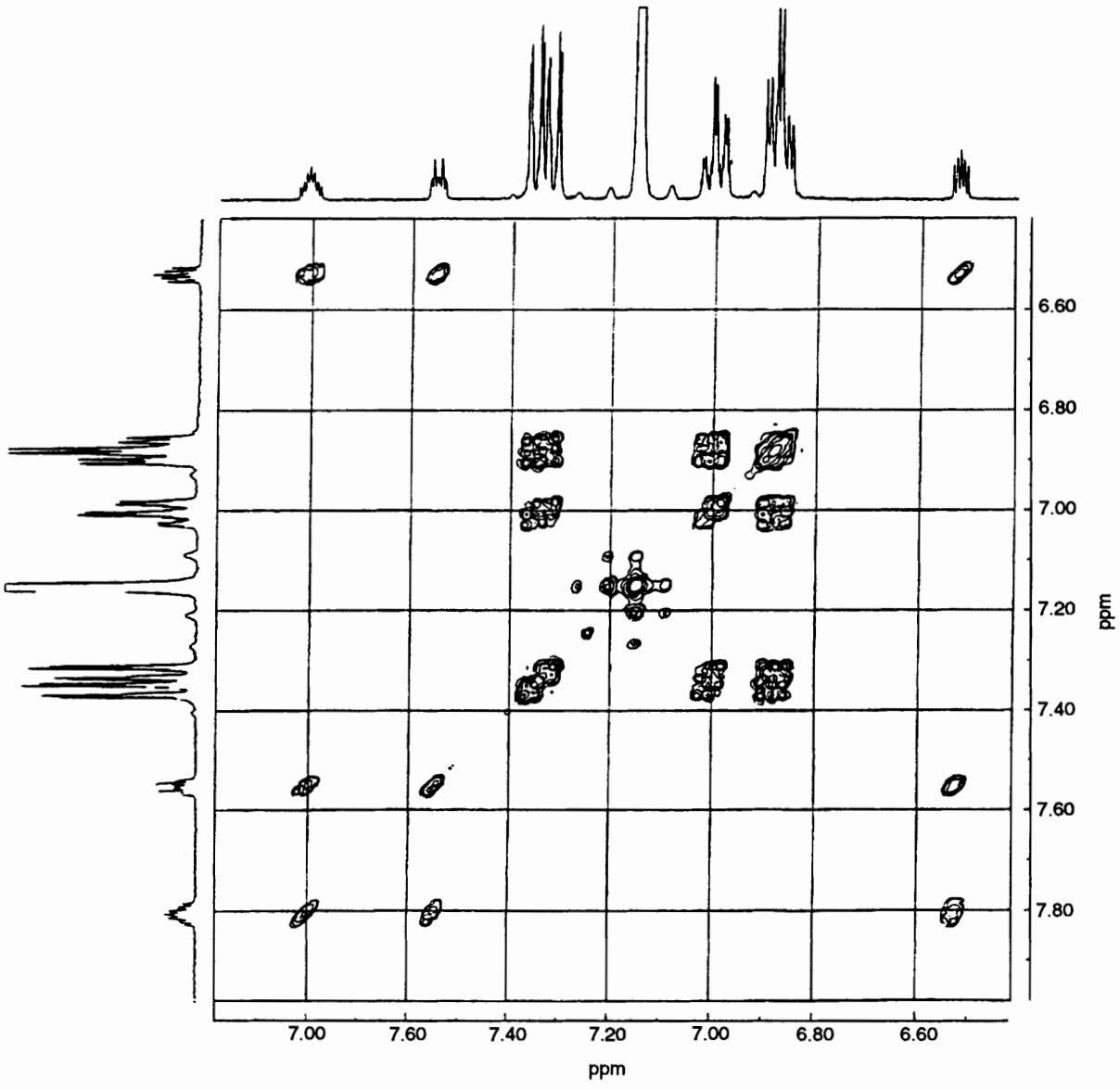


Fig. 1 $^1H,^1H$ COSY spectrum of **5** (X = F) in dichloromethane-d_2 at 297 K

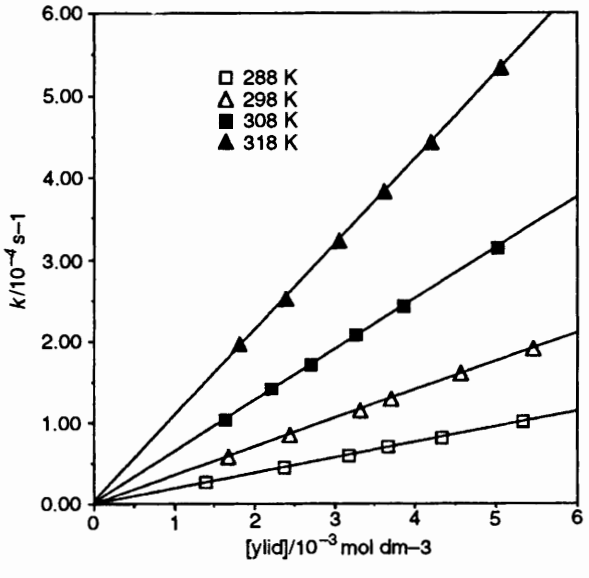


Fig. 2 Variation of the first order coefficient with initial concentration of ylide at various temperatures in acetonitrile

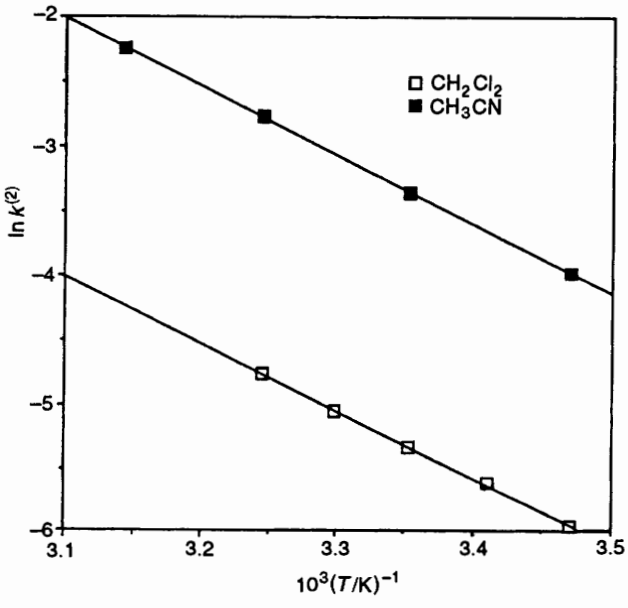


Fig. 3 Arrhenius plots in dichloromethane and acetonitrile for the disubstitution of iodanil by (2)

Table 3 First order kinetic coefficients[a]

Solvent: CH_2Cl_2

T/K 288.2 ± 0.1			T/K 293.2			T/K 298.2			T/K 303.2			T/K 308.2		
$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$
5.04	3.16	1.27 ± 0.1	5.52	2.97	2.0 ± 0.2	5.39	3.14	2.6 ± 0.2	5.51	3.12	3.6 ± 0.2	5.00	3.06	4.2 ± 0.2
10.10	3.18	2.5 ± 0.2	10.92	2.99	3.9 ± 0.2	10.01	3.16	4.8 ± 0.2	9.62	3.09	6.4 ± 0.2	9.74	3.05	8.2 ± 0.2
14.98	3.18	3.7 ± 0.2	15.03	2.97	5.4 ± 0.2	14.45	3.13	6.9 ± 0.2	14.27	3.07	9.1 ± 0.2	14.92	3.06	12.6 ± 0.2
19.98	3.17	5.0 ± 0.2	19.06	3.01	6.8 ± 0.2	19.20	3.15	9.1 ± 0.2	19.09	3.08	12.2 ± 0.2	19.03	3.04	16.1 ± 0.2
24.57	3.18	6.1 ± 0.2	24.73	2.98	8.9 ± 0.2	24.79	3.13	11.8 ± 0.2	24.31	3.10	15.6 ± 0.2	24.02	3.05	20.3 ± 0.3
30.10	3.13	7.6 ± 0.2	28.93	2.99	10.4 ± 0.2	29.94	3.12	14.4 ± 0.2	29.14	3.09	18.4 ± 0.2	28.75	3.06	24.3 ± 0.3
			5.35[b]	3.14	2.0 ± 0.2	1.54[c]	3.13	1.8 ± 0.2						
			9.87	3.13	3.9 ± 0.2	2.90	3.11	3.4 ± 0.2						
			14.96	3.09	5.3 ± 0.2	4.75	3.11	5.6 ± 0.2						
			19.33	3.16	6.9 ± 0.2	4.94	3.08	5.8 ± 0.2						
			24.74	3.14	8.8 ± 0.2									
			29.18	3.15	10.4 ± 0.2									

Solvent: CH_3CN

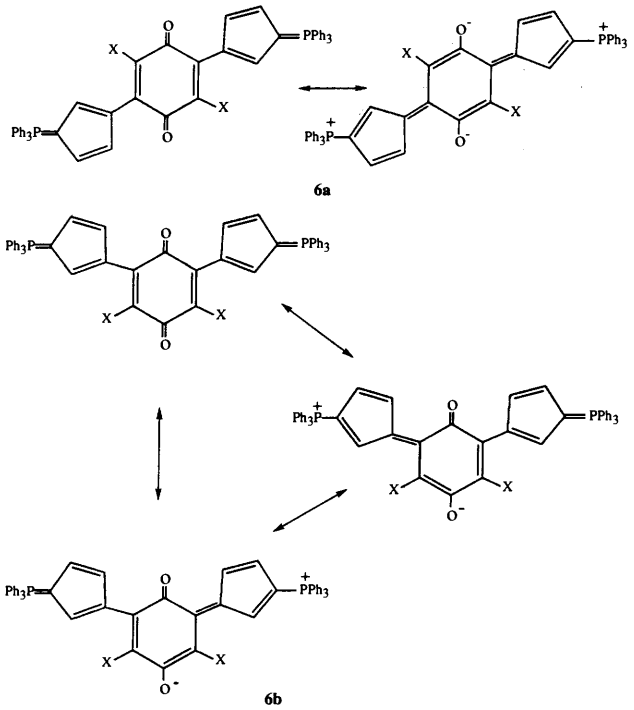
T/K 288.2 ± 0.1			T/K 298.2			T/K 308.2			T/K 318.2		
$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$	$y \times 10^3$	$q \times 10^5$	$k \times 10^5$
1.38	2.41	2.5 ± 0.2	1.66	3.01	5.6 ± 0.2	1.63	2.30	10.1 ± 0.2	1.81	2.30	19.5 ± 0.5
2.37	2.42	4.3 ± 0.2	2.43	3.02	8.3 ± 0.2	2.21	2.33	13.9 ± 0.2	2.38	2.30	24.9 ± 0.7
3.17	2.39	5.7 ± 0.2	3.31	3.03	11.2 ± 0.2	2.70	2.34	16.9 ± 0.3	3.05	2.31	32 ± 1
3.66	2.42	6.7 ± 0.2	3.71	2.99	12.6 ± 0.2	3.27	2.34	20.5 ± 0.5	3.62	2.29	38 ± 1
4.34	2.43	7.8 ± 0.2	4.57	3.02	15.6 ± 0.3	3.86	2.30	23.9 ± 0.5	4.19	2.30	44 ± 2
5.33	2.24	9.6 ± 0.2	5.45	3.03	18.5 ± 0.5	5.01	2.36	31 ± 1	5.05	2.29	53 ± 2

y = Initial concentration of ylide in mol dm^{-3}, k = first order kinetic coefficient in s^{-1}. [a] Errors are the standard deviations of k values obtained by fitting, using the least-square procedure, the absorbance *vs.* time data of a single kinetic run to the eqn. (2) (see D. M. Himmelblau, *Process Analysis by Statistical Methods*, Wiley, New York, 1968). Since the number of data points was greater than 50, the s values were not corrected by using the t-student. For more details concerned with the calculation of k see ref. 3. [b] Initial concentration of quinuclidine 1×10^{-4} mol dm^{-3}. [c] Use of 2,3,4,5-tetradeuterio-1-triphenylphosphoniocyclopentadienide.

($k_3 \gg k_2$) but for the E1cB mechanism $k_2 \ll (k_3 y_0 + k_b b_0)$. These assumptions lead to a linear dependence of k on y_0 and a zero order dependence on b_0 for both mechanisms.

Thus we have a system in which formation of the intermediate σ-complex may be reversible or irreversible and in order to clarify the situation it is necessary to address the problem of the isomers formed during the disubstitution reaction through the series from fluoranil to iodanil. With fluoranil, only the 2,6-isomer is formed and with iodanil only the 2,5-isomer is observed. With chloranil and bromanil an intermediate situation prevails which gives a mixture of 2,5- and 2,6-disubstitution products in both cases as shown in Table 6 which also gives a summary of the relative rates, deuterium isotope effects and activation parameters for all the haloquinones. If we then assume that the correct mechanism is an E1 process, an explanation for all the results in terms of kinetic *versus* thermodynamic control appears through a consideration of the relative rates of halide departure (represented by k_3) and the reverse of σ-complex formation (represented by k_2).

Consider the relative stabilities of the two disubstitution products. At first sight one might anticipate that the 2,5-isomer



$$A + Y\,(\text{excess}) \xrightarrow{k} V + P \qquad \text{(main reaction)}$$

$$\left.\begin{array}{l} P + Y \rightleftharpoons I \longrightarrow D + H \\ Y + H \rightleftharpoons P \end{array}\right\} \qquad \text{(secondary reaction)}$$

Scheme 2 A = Monosubstitution product of iodanil, V = 2,5-disubstitution product of iodanil, P = protonated species of ylide, I = intermediate, H = form of the free proton in the solvent, D = product responsible for the absorbance of 405 nm at high temperature

Table 4 Second order kinetic coefficients.

$k_i = h_i + k_i^{(2)}[y]_o$, $h_i \approx 0$, $k_i^{(2)} \times 10^3/\text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$ (all r > 0.99)

Solvent: CH_2Cl_2		Solvent: CH_3CN	
Temperature/K	$k^{(2)} \times 10^3$	Temperature/K	$k^{(2)} \times 10^3$
288.2 ± 0.1	2.53 ± 0.10	288.2 ± 0.1	18.1 ± 0.5
293.2	3.58 ± 0.04	298.2	34.0 ± 0.5
293.2[a]	3.48 ± 0.08	298.2[c]	33.8 ± 0.8
298.2	4.78 ± 0.15	308.2	62 ± 3
293.2[b]	11.9 ± 0.1	318.2	105 ± 4
303.2	6.3 ± 0.3		
308.2	8.47 ± 0.04		
$k_H^{(2)}/k_D^{(2)} = 0.40$		$k^{(2)}/k_{amine}^{(2)} = 1.00$	
$k^{(2)}/k_{amine}^{(2)} = 0.97$			

Errors are given as confidence limits at 99.5% of probability and four degrees of freedom for the standard deviation of the slope of a line obtained from a single least-square fit of k values *vs.* initial concentration of ylide data. The subindices refer to the second order rate coefficient ratios obtained by using normal ylide (H), deuteriated ylide (D) at 298 K, and in the presence of quinuclidine (amine) at 293 K for CH_2Cl_2 and at 298 K for CH_3CN. [a] Initial concentration of quinuclidine was 1×10^{-4} mol dm^{-3}. [b] Use of 2,3,4,5-tetradeuterio-1-triphenylphosphoniocyclopentadienide. [c] See Table 5.

Table 5 First and second order kinetic coefficients in acetonitrile in the presence of quinuclidine at 298 K[a,b,c]

$y \times 10^3$/mol dm^{-3}	$q \times 10^5$/mol dm^{-3}	$Q \times 10^2$/mol dm^{-3}	$k \times 10^4$/s^{-1}	$k^{(2)}$/s^{-1} mol^{-1} dm^3
3.30 ± 0.01	2.39 ± 0.01	6.95 ± 0.01	1.12 ± 0.02	0.034_0
3.31	2.37	2.53	1.13 ± 0.02	0.034_0
3.41	2.38	2.04	1.15 ± 0.02	0.033_7
3.41	2.38	0.94	1.15 ± 0.02	0.033_8
3.47	2.37	4.70	1.18 ± 0.02	0.033_8
3.51	2.38	3.66	1.20 ± 0.02	0.034_1
			average = (3.39 ± 0.03) × 10^{-2}	

[a] y Initial concentration of ylide, q initial concentration of iodanil, Q initial concentration of quinuclidine. k First order kinetic coefficient. $k^{(2)} = k/y$ is the second order kinetic coefficient. [b] For more information about the errors quoted for k see Table 3. [c] Error of the average is given as the confidence interval of the mean at 99.5% of probability and 5 degrees of freedom.

Table 6 A summary of relative rates, deuterium isotope effects and activation parameters for the disubstitution of tetrahaloquinones by triphenylphosphoniocyclopentadienide in CH_2Cl_2 at 298 K

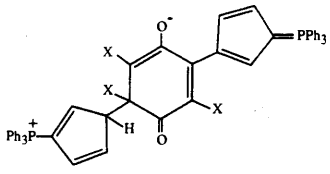
	Tetrahaloquinone			
	Fluoranil	Chloranil	Bromanil	Iodanil
$10^3 k^2$ (dm^3 s^{-1} mol^{-1}) 2/5:	—	3.50	7.66	4.83
$10^3 k^2$ (dm^3 s^{-1} mol^{-1}) 2/6:	305	4.33	6.83	—
k_H/k_D	1.0	—	—	0.40
E_A (kJ mol^{-1}) 2/5	—	40	42	42
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}) 2/5	—	−129	−116	−151
E_A (kJ mol^{-1}) 2/6	30	36	41	—
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}) 2/6	−157	−142	−121	—

Table 7 π-Hückel MO energies and charge values on C(5) and C(6)

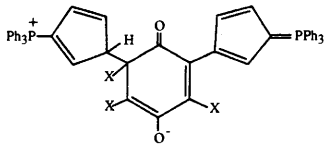
Compound	π-Charge/e		Free valence	
	C(5)	C(6)	C(5)	C(6)
5 (X = F)	0.082	0.037	0.33	0.34
5 (X = Cl	0.087	0.038	0.35	0.36
5 (X = Br)	0.087	0.038	0.36	0.39

	3 (X = F)	**4** (X = F)	**3** (X = Cl)	**4** (X = Cl)	**3** (X = Br)	**4** (X = Br)
E_π	−39.5812	−39.5992	−35.4496	−35.4756	−33.4322	−33.4458
ΔE_π		−0.018		−0.026		−0.0136

E_π: Total π-electronic energy in β units. $\Delta E_\pi = E_\pi(\mathbf{4}) - E_\pi(\mathbf{3})$ in β units. Phosphorus Hückel parameters: $\alpha_{C-P} = -0.1$, $\alpha_P = -1.71$, $k_{C-P} = -0.875$.[20,21]



7a



7b

$$A + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sigma, \quad \sigma \xrightarrow{k_3} \sigma^+ + I^-, \quad \begin{cases} \sigma^+ + Y \xrightarrow{k_4} V + YH^+ \\ \sigma^+ + B \xrightarrow[\text{Fast}]{k_b} V + YH^+ \end{cases} \quad (E_1 \text{ mechanism})$$

$$A + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sigma, \quad \begin{cases} \sigma + Y \xrightarrow{k_3} \sigma^- + YH^+ \\ \sigma + B \xrightarrow{k_b} \sigma^- + BH^+ \end{cases}, \quad \sigma^- \xrightarrow{k_4} V + I^- \quad (E_1cB \text{ mechanism})$$

Scheme 3 σ = Ylide-monosubstitution product addition complex; σ^+ = addition complex after losing I^-; σ^- = addition complex after losing a proton. B = base (quinuclidine).

(**6a**) would be the most stable as suggested (albeit only barely so) by the HMO data of Table 7, since delocalisation of charge occurs over both carbonyl groups affording a 2 × 8 π-electron system which minimises the dipole moment. On the other hand, the 2,6-isomer offers a second, less obvious mode of delocalisation between the cyclopentadiene systems which gives a 1 × 8 π-electron delocalised system combined with a 1 × 12 π-delocalised system (**6b**) which also disperses charge. Thus it is not unreasonable to conclude that in fact, the 2,6-isomer is thermodynamically more stable than the 2,5. When one considers the intermediate σ-complexes (**7a** and **7b**) formed during the disubstitution reaction, however, it is easy to see that the intermediate (and therefore the TS) leading to the 2,5-isomer would be the more stable because the charges involved are distributed between two carbonyl groups whereas for 2,6-disubstitution the charge delocalisation from both ylide structures terminates on one carbonyl. Thus, if the reaction is thermodynamically controlled, one might expect a reaction profile as shown in Fig. 4(*a*) (where $k_2 > k_3$) and this is apparently the case for fluoranil. With the reaction under kinetic control, Fig. 4(*b*) is appropriate ($k_3 > k_2$) and this applies in the case of the disubstitution of iodanil. The intermediate situations for chloranil and bromanil are then explained by an energy profile in which k_2 and k_3 are very similar in magnitude.

This interpretation of the mechanism is consistent with the observed rate sequence from fluoranil to iodanil since the overall energy change ($\Delta G^\ddagger_1 + \Delta G^\ddagger_3 - \Delta G^\ddagger_2$) is probably dominated by initial nucleophilic attack of the ylide on the quinone and hence must follow the rate sequence FA > CA ~ BA > IA. It is also consistent with the observed isotope effects provided we assume the latter are secondary in origin. If a trigonal carbon bearing hydrogen becomes tetrahedral in the rate limiting step of a reaction a small inverse isotope effect ($k_H/k_D < 1$) is usually observed.[20] Nucleophilic addition of the ylide to the quinone obviously causes a change from sp^2 to sp^3 carbon in the cp ring but in the case of fluoranil we have already argued that this step is reversible ($k_3 < k_2$) and hence $k_H/k_D = 1$, as observed. With iodanil, however, addition of the ylide is rate-limiting ($k_3 > k_2$) and hence $k_H/k_D < 1$ as shown in Table 6. Isotope effects on the intermediate situations with chloranil and bromanil were not investigated but it is worth noting that in monosubstitution k_H/k_D (CA) = 0.9 and k_H/k_D (BA) = 0.7, which is consistent with the idea of a gradual change of relative values of k_2 and k_3 across the series of haloquinones.

Activation parameters. The activation parameters derived

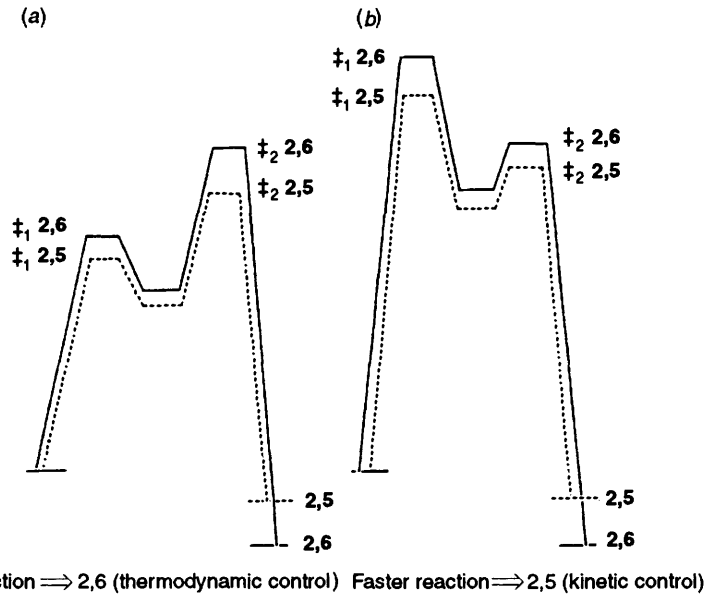


Fig. 4 Free energy diagram for the formation of the 2,5- and 2,6-disubstitution products of tetrahaloquinones

from the $k^{(2)}$ rate coefficients in dichloromethane and acetonitrile are reported in Table 6.

It is difficult to interpret the activation energy data with great confidence but certain trends are evident in Table 6. In the formation of the thermodynamically controlled products (2,6) it is clear that there is a significant rise in the enthalpy of activation across the series and a concurrently less negative entropy of activation. With the 2,5-isomer formation, however, the enthalpy term is fairly constant but the entropy term becomes more negative across the series implying a much more highly organised TS for the iodanil reaction.

In conclusion, it seems that the disubstitution of haloquinones by triphenylphosphoniocyclopentadienylide proceeds by a two-step mechanism involving nucleophilic attack by the ylide on the quinone to form an intermediate σ-complex which eliminates halide ion by an E1 mechanism. The intermediate may be formed reversibly or irreversibly dependent on the halide ion which exerts kinetic or thermodynamic control to determine the isomer ratio of the disubstitution products.

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