Kinetics and Mechanism of the Addition of Triphenylphosphoniocyclopentadienide to Tetrahalogeno-*p*-benzoquinones. Part 4.[1-3] The Substitution Reactions of Fluoranil

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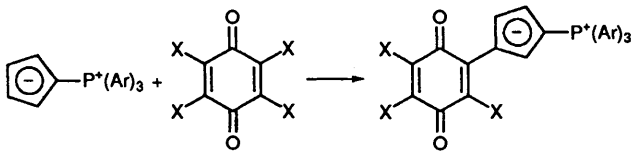
Fluoranil reacts with excess triphenylphosphoniocyclopentadienide to yield the monosubstituted and 2,6-disubstituted quinone derivatives through two parallel, irreversible, second-order reactions which are well separated in time. The rate of formation of the monosubstitution product was resolved using the stopped-flow technique and its half-life was found to be in the millisecond range. Kinetic data for the mono- and di-substitution products indicate that both reactions proceed in two steps involving rate-limiting addition to form a polar betaine intermediate followed by elimination of hydrogen halide through an E1 mechanism. The empirical rate law was established by carrying out a multi-response non-linear least-square analysis of the absorbance of the reaction mixtures.

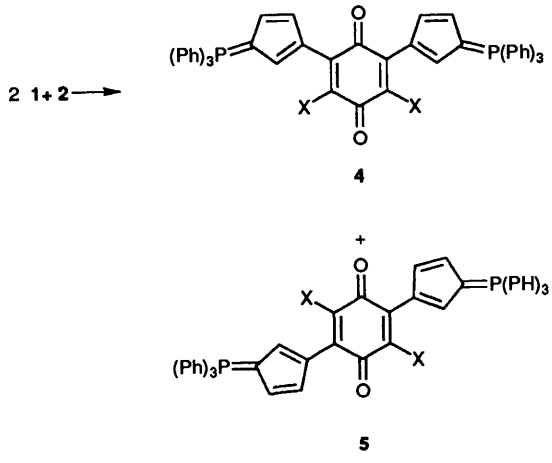
The reaction of triarylphosphoniocyclopentadienides **1** with tetrahalogeno-*p*-benzoquinones **2** proceeds in virtually quantitative yield to give monosubstitution products **3** which have been characterized by UV spectroscopy (λ = 700 nm), multinuclear NMR and X-ray crystallography.[4-6]



1 **2** **3**

One of the important conclusions of this work was the observation of substitution in position-3 of the cyclopentadiene ring of **1** in contrast to reactions with smaller electrophiles (*e.g.* aryl diazonium ions) which gave substitution in position-2 of the cyclopentadiene ring.[7,8] The kinetics and mechanism of this reaction have been studied intensively for X = Cl,[1] Br and I[2] and to a limited extent with X = F. It was concluded that the reactions proceed by rate-limiting addition of the ylide to the quinone, followed by elimination of hydrogen halide by either an E1, E2 or E1cB mechanism dependent upon the halide. It was suggested in fact, that with X = Cl, the mechanism of halide elimination was probably E1cB whereas with X = I, the mechanism was probably E1. With X = Br, the data were explained by either an E2 or E1cB mechanism with emphasis on the former. It was noted during these studies that the brilliant blue compounds formed by monosubstitution of the quinone, reacted further in the presence of excess ylide to form mixtures of compounds which were all intensely coloured. It is well known that the halogenoquinones undergo disubstitution (in the 2,5- or 2,6-positions)[9-11] and that under forcing conditions, multiple substitution may occur. The kinetics and mechanism of the disubstitution reactions of chloranil and bromanil to form **4** and **5** have also been investigated[3] and once again the reactions were shown to proceed by rate-limiting nucleophilic addition of the ylide to the monosubstituted quinone followed by elimination of hydrogen halide, apparently by an E1 mechanism.

The rate of reaction of the quinones with **1** was in the order F ≫ Cl ~ Br > I with fluoranil approximately 50 times faster than chloranil in CH_2Cl_2 and this element effect[12] was the



4 **5**

principal criterion used to establish rate-limiting attack by the nucleophile. This paper seeks to quantify the fluoranil reaction through a detailed mechanistic study of the monosubstitution reaction by stopped flow kinetics and a parallel kinetic study of the disubstitution reaction by conventional UV–VIS spectroscopy.

Experimental

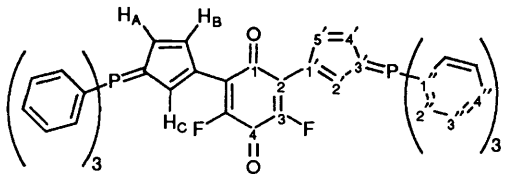
Materials.—Triphenylphosphoniocyclopentadienide **1a** was prepared according to the method reported by Ramirez and Levy.[13] For kinetic runs further purification was carried out by flash chromatography on silica gel 60H using dichloromethane as eluent. The quality of the purified product (>99%) was checked by IR, ^1H and ^{31}P NMR spectroscopy.

2,3,4,5-Tetradeuterio-1-triphenylphosphoniocyclopentadienide **1b** was prepared from **1a** by H–D exchange in deuterioacetic acid–deuterium oxide medium.[14] The level of deuteriation as assessed by ^1H NMR was 88%, the extent of deuteriation in position C(3) being larger than in position C(2) by a ratio of 1.05:1.00.

Commercial fluoranil **2** (Aldrich) product was recrystallized from acetone (× 2) to give lustrous yellow crystals, m.p. 181 °C. IR Grade dichloromethane was dried by refluxing over CaH_2 and was then distilled before use in kinetic runs.

Synthetic Procedure.—A solution containing fluoranil (23

Table 1 Spectroscopic characterization of the 2,6-disubstituted derivative of fluoranil



^{13}C NMR spectrum (room temperature)

Assignment	δ	Multiplicity	J/Hz
C(1)	170.80	t	^3J_F 89.2
C(2)	125.23	m	not resolved
C(3)	148.97	q	^1J_F 265.7, ^3J_F 10.9
C(4)	190.10	t	^2J_F 13.6
C'(1)	119.08	d	^3J_P 25.6
C'(2)	125.46	d	^2J_P 8.0
C'(3)	87.84	d	^1J_P 111.5
C'(4)	118.22	d	^2J_P 14.0
C'(5)	116.60	d	^3J_P 19.5
C''(1)	123.79	d	^1J_P 90.5
C''(2)	133.62	d	^2J_P 9.4
C''(3)	129.18	d	^3J_P 12.4
C''(4)	133.27	d	^4J_P 2.3

^{31}P NMR spectrum at 248 K

δ 14.52 (s)

^1H NMR spectrum at 248 K

Assignment	δ	Multiplicity	Relative intensity
Ph protons	7.60	m	15
H_A and H_C	6.79	m	2
H_B	6.24	m	1

ν(KBr disc)/cm^{-1}
3056w (C–H stretch Ph), 2951, 2925 and 2864w (C–H stretch cpd ring), 1670w and 1610m (C=O stretch), 1559s, 1461s, 1435s, 1297vs, 1237m, 1198w, 1136w, 1105s, 1014s, 918w, 842w, 811w, 783w, 752w, 721m, 695s, 639w, 611w, 557s, 532m, 512m

FAB mass spectrum in *m*-nitrobenzyl alcohol matrix
M 792 (16%), M + 1 (72), M + 2 (67), M + 3 (100), M + 4 (51), M + 5 (51), M + 6 (5), M + 7 (7)

$\lambda_{max}(CH_2Cl_2)$/nm
484 (ε_{max}/dm^3 mol^{-1} cm^{-1} = 8600 ± 100), 710 (ε_{max}/dm^3 mol^{-1} cm^{-1} 12260 ± 100)

mg, 0.13 mmol) in dichloromethane (25 cm^3) was prepared and cooled to 5 °C. A solution containing ylide (85 mg, 0.25 mmol) and quinuclidine (56 mg, 0.50 mmol) was added slowly at the same temperature. The reaction mixture was then allowed to react for 2 h. During the addition, a transient blue colour developed instantly which then changed gradually to green–violet.

Isomer Separation.—The reaction mixture was evaporated to dryness, redissolved in 3 cm^3 of dichloromethane and poured onto a 60H silica gel chromatographic column previously equilibrated with diethyl ether. Two coloured bands developed after passing a mixture of dichloromethane (10% v/v) and diethyl ether (90% v/v) as eluent which were collected as separate fractions, concentrated, poured into hexane, and then, evaporated to dryness again. The composition of the crude products was checked by multinuclear NMR.

The first red fraction (40 mg) contained mainly hydrolysis products of the 2,6-disubstitution product of fluoranil whilst the second greenish fraction (35 mg) contained mainly the disubstitution product. The green fraction was re-chromatographed using the same procedure to yield virtually pure 2,6-disubstitution product which was characterized by multinuclear NMR (see Table 1). The overall yield of the procedure was *ca* 30%, the major part of the product being lost by hydrolysis on the silica gel during the separation process.

Equilibrium Experiments.—Stoichiometry of the monosubstitution and disubstitution reaction. The stoichiometry of the monosubstitution reaction was investigated by the Job–Foster technique by measuring the final absorbance of solutions prepared by mixing x cm^3 of fluoranil and $(3.5 - x)$ cm^3 of ylide, x ranging from 0.5 to 2.5 cm^3, and 6.5 cm^3 of solvent from stock solutions of fluoranil (1.1×10^{-3} mol dm^{-3}) and ylide (1.2×10^{-3} mol dm^{-3}) in CH_2Cl_2 and toluene.

The stoichiometry of the disubstitution reaction was investigated by following the same procedure. A stock solution of monosubstitution product (1.5×10^{-3} mol dm^{-3}) prepared *in situ* by mixing equivalent quantities of ylide and fluoranil was used instead of the solution of fluoranil. Under these experimental conditions the disubstitution reaction was slow so the absorbance was measured 3 h after the reaction mixtures were prepared.

Kinetic Experiments.—Study of the monosubstitution reaction. Stock solutions of fluoranil (1.3×10^{-3} mol dm^{-3}), quinuclidine (6.2×10^{-3} mol dm^{-3}), ylide (3.2×10^{-3} mol dm^{-3}) and deuteriated [$^2H_4$]ylide (3.2×10^{-3} mol dm^{-3}) were prepared in dry dichloromethane. For a typical kinetic experiment the fluoranil stock solution was diluted to 3.0×10^{-5} mol dm^{-3} ($\approx$ 1/30) and five ylide solutions ranging from 1.3×10^{-3} to 3.2×10^{-3} mol dm^{-3} were prepared.

The absorbance at 706 nm of the reaction mixtures, prepared by mixing the diluted solution of fluoranil with the ylide solutions in 1 : 1 ratio, was measured at intervals of 1 ms during 200 ms at 288, 298, 303 and 311 K with a Durrum-Gibson stopped flow spectrophotometer attached to a PC *via* a DAS-800 A/D converter. In order to calculate the magnitude of the deuterium isotope effect, a similar experiment was carried out at 298 K but using [$^2H_4$]ylide instead of ylide.

Finally, in order to estimate the effect of a strong base on the rate of reaction, a series of five solutions of ylide (1.0×10^{-3} mol dm^{-3}) and quinuclidine ranging from 1.0×10^{-3} to 2.0×10^{-3} mol dm^{-3} were prepared and mixed with the dilute solution of fluoranil at 298 K. The change in absorbance with time was monitored as described above.

Study of the disubstitution reaction. Stock solutions of fluoranil (8×10^{-4} mol dm^{-3}) and quinuclidine (3.7×10^{-4} mol dm^{-3}) in dry dichloromethane were prepared. Five reaction mixtures were prepared by injecting 500 μl of the fluoranil solution into a UV–VIS cell containing a weighed quantity of ylide, ranging from 5 to 30 mg, and 2.5 cm^3 of dichloromethane. The absorbance spectra of the five reaction mixtures were recorded between 400 and 800 nm at intervals of 10 s during 600 s with a Hewlett-Packard 8452A diode array spectrophotometer and the measurements were repeated at 288, 291, 299, 305 and 311 K. In order to calculate the magnitude of the deuterium isotopic effect, a similar experiment was carried out at 298 K using [$^2H_4$]ylide instead of ylide.

Finally, in order to estimate the influence of a strong base on the reaction rate, similar experiments were performed at 298 K but using 2.5 cm^3 of a solution of quinuclidine (at 1.9×10^{-3}, 2.6×10^{-3} and 3.7×10^{-3} mol dm^{-3}) instead of the pure solvent.

Results and Discussion

Structure Determination.—The spectroscopic information dealing with the isolated compound is collected in Table 1. The

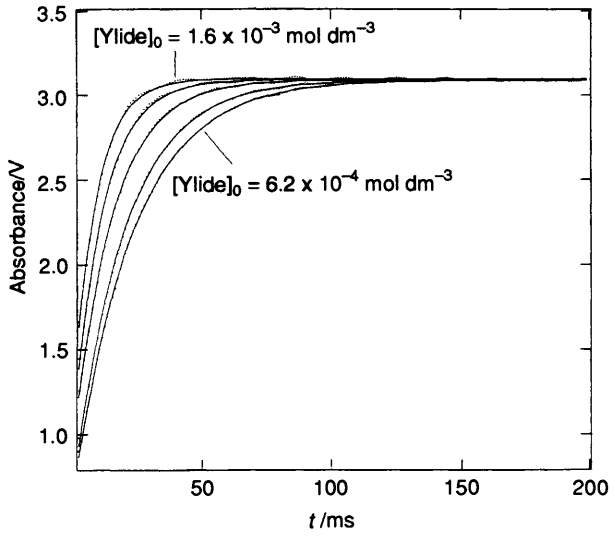


Fig. 1 Average oscilloscope traces for the monosubstitution reaction of fluoranil for reaction mixtures ranging from 6.2 × 10^{-4} mol dm^{-3} to 1.6 × 10^{-3} mol dm^{-3} in ylide

NMR data are entirely consistent with the formation of the 2,6-disubstituted derivative of fluoranil. The ^{13}C spectrum showed two signals at 170.8 and 190.1 ppm assigned to the carbonyl groups, the second signal being strongly coupled with fluorine and displaced down field as expected for a C=O group with two adjacent fluorine atoms. Only one carbonyl signal would be expected from the 2,5-disubstitution. This data correlated with the appearance of two C=O stretching bands in the IR spectrum at 1610 and 1670 cm^{-1} and also with the presence of two bands in the UV–VIS spectrum as observed for the 2,6-disubstitution products of chloranil and bromanil.[3]

The substitution in position C(3) of the cyclopentadiene (cpd) ring was confirmed by the ^1H NMR spectrum which showed a band integrating for two cpd protons at 6.79 ppm and a band at higher field integrating for one proton. Finally, the mass spectrum showed the molecular ion peak at 792 mu as expected for a disubstituted compound.

All attempts to isolate the monosubstitution product failed. However, the transient blue colour observed must be attributed to this compound since the final product obtained is just the disubstituted one. This supposition is also supported by the visible spectra of the reaction mixtures during the first 10 s of reaction which show a broad band (λ_{max} = 706 nm, ε_{max} = 7100 ± 100 dm^3 cm^{-1} mol^{-1} in dichloromethane) analogous in position and intensity to the bands observed for the monosubstitution products of chloranil,[1] bromanil and iodanil.[3]

Kinetic Data.—Rate law for the monosubstitution reaction. As the reactants do not absorb in the 500 to 800 nm region, all the absorbance at 706 nm was attributed to the monosubstitution product. The average oscilloscope traces obtained during a typical stopped-flow kinetic experiment where the concentration of the quinone and temperature remained constant and the concentration of ylide was gradually increased are shown in Fig. 1. Each curve is the result of averaging between six to eight oscilloscope traces. The average trace was corrected for the base line which was greater as the temperature increased. The experiments were designed in such a way that the ylide was in a 40 to 100 fold excess with respect to the concentration of fluoranil thus ensuring that first order conditions were maintained throughout.

Under these experimental conditions, all the absorbance curves could be explained by a first order kinetic model since when they were fitted directly to expression (1) by means of a

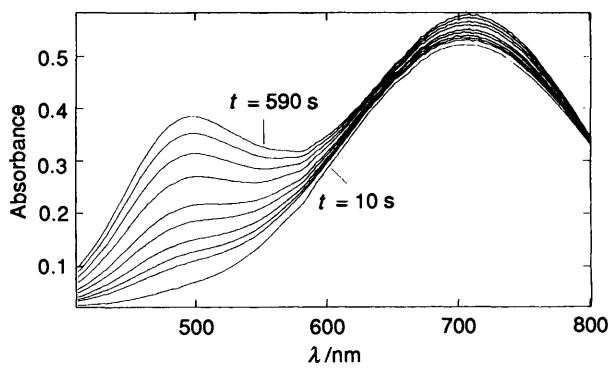


Fig. 2 Typical kinetic run for a reaction mixture 4.98 × 10^{-3} mol dm^{-3} in ylide at 299 K showing the changes in the visible spectrum during the disubstitution reaction

$$A = \alpha_0 + \alpha_1 e^{-k_{obs}t} \quad (1)$$

non-linear square procedure using a modified version* of program OPKINE[15] they gave, in all cases, good non-linear correlations ($r > 0.999$). The values of k_{obs} as a function of the initial concentration of ylide (y_0) and temperature are shown in Table 2.

Since eqn. (1) is obeyed the reaction is obviously first order with respect to the quinone. Plots of k_{obs} against the concentration of ylide, gave good lines with null intercept whose slopes (k_Q^2) are shown in Table 3. Thus, the reaction is also first order with respect to the ylide.

Since the mechanism for chloranil,[1] bromanil[2] and iodanil[2] implied the cleavage of an H atom from the cpd ring, the effect of the addition of a strong base on the reaction rate and the deuterium isotopic effect were investigated. The concentrations of fluoranil and ylide were held constant and the concentration of an inert base, quinuclidine, was raised in such a way that it was the predominant Brønsted base in the system. The values of k_{obs} are shown in Table 4 and it is apparent that k_{obs} is independent of the concentration of amine; the small differences between the values of k_{obs} may be attributed to small changes in the concentration of ylide between the experiments.

The values of k_{obs} for a series of kinetic runs carried out at 298 K where deuteriated [$^2H_4$]ylide was used instead of ylide are shown in Table 5. The value of k_D^2 was almost identical to that obtained with protonated ylide so we can conclude that there is no isotope effect for this system.

From the results of the experiments described it is clear that the empirical rate law for the monosubstitution reaction is as shown in eqn. (2), where q is the concentration of the

$$-\dot{q} = k_Q^2 yq \quad (2)$$

haloquinone and y is the concentration of ylide. This conclusion was also reached for the chloranil and bromanil systems. It is also clear from the magnitude of the isotope effect and from the influence of other bases on the reaction rate that the rate-determining step of the reaction should be the addition of the ylide nucleophile and that the subsequent cleavage of the hydrogen or fluorine atoms must be relatively fast.

Rate Law for the Disubstitution Reaction.—As has been stated in the preceding sections, the blue colour of a reaction mixture of fluoranil and ylide is transient and in a matter of minutes the solutions change from deep blue to green–violet. The change in the absorbance during the reaction can be seen in a typical kinetic run obtained with a diode array spectrophotometer, see

* C language version available on request.

Table 2 First order rate constants for the monosubstitution of fluoranil[a]

T/K							
288.2.0 ± 0.1		298.2 ± 0.1		303.2 ± 0.1		308.2.0 ± 0.1	
y_o	k_{obs}	y_o	k_{obs}	y_o	k_{obs}	y_o	k_{obs}
0.65	39.4 ± 0.1	0.63	43.3 ± 0.1	0.65	47.0 ± 0.1	0.61	46.8 ± 0.2
0.75	45.0 ± 0.1	0.73	50.4 ± 0.1	0.75	55.0 ± 0.2	0.71	57.4 ± 0.2
0.97	57.8 ± 0.1	0.94	65.6 ± 0.1	0.96	73.3 ± 0.2	0.88	73.1 ± 0.4
1.33	78.7 ± 0.1	1.24	86.8 ± 0.3	1.30	98.3 ± 0.4	1.23	99.0 ± 1.2
1.62	93.9 ± 0.1	1.57	109.6 ± 0.5	1.61	120.7 ± 0.6	1.54	126.5 ± 1.2

[a] y_o = Initial concentration of ylide 10^3 mol dm^{-3}; k_{obs} = first order rate constant/s^{-1}.

Table 3 Second order rate coefficients for the substitution of fluoranil[a]

Monosubstitution		Disubstitution	
T/K	$k^2/10^{-4}$	T/K	k^2
288.2 ± 0.1	5.67 ± 0.07	287.8 ± 0.1	0.190 ± 0.006
298.0	7.02 ± 0.02	290.9	0.218 ± 0.004
303.2	7.62 ± 0.15	299.2	0.306 ± 0.007
308.2	8.38 ± 0.25	304.9	0.409 ± 0.008
		311.4	0.511 ± 0.005

[a] $k_{obs} = h + k^2 y_o$, all $h \approx 0$, k^2/dm^3 s^{-1} mol^{-1}.

Table 4 First order rate constants for the monosubstitution of fluoranil in the presence of quinuclidine at 298 K

$y_o/10^{-4}$ mol dm^{-3}	$a_o/10^{-3}$ mol dm^{-3}	k_{obs}/s^{-1}
5.06	0.00	35.0 ± 0.1
5.07	0.93	32.5 ± 0.1
5.04	1.12	34.5 ± 0.1
5.10	1.32	35.6 ± 0.1
5.06	1.50	35.3 ± 0.1
5.05	1.88	34.8 ± 0.1

Table 5 Rate coefficients for the monosubstitution with [$^2H_4$]ylide at 298 K

Monosubstituted Product		Disubstituted Product	
[[$^2H_4$]ylide]$_o$[a]	$k_{D.obs}$/s^{-1}	[[$^2H_4$]ylide]$_o$[a]	$k_{D.obs}/10^{-3}$ s^{-1}
0.66	51.2 ± 0.04	5.14	1.88 ± 0.01
0.77	59.9 ± 0.03	11.4	3.73 ± 0.01
0.99	73.9 ± 0.02	14.7	4.85 ± 0.01
1.32	96.5 ± 0.06	24.9	7.90 ± 0.01
1.66	193.0 ± 0.12		
k_D^2[b]	(6.94 ± 0.11) × 10^4		0.305 ± 0.004
k_H^2/k_D^2	1.01		1.00

[a] 10^3 mol dm^{-3}. [b] s^{-1} mol^{-1} dm^3.

Fig. 2. In the first few seconds the visible spectrum is essentially that of the monosubstitution product and during the last minutes the spectrum conforms to that of the 2,6-disubstituted product, see Fig. 3. At intermediate times, the spectra are a combination of the spectra of monosubstituted and disubstituted products.

This behaviour of the absorbance is different to that observed for the disubstitution of chloranil and bromanil[3] which show maximum intensity around 550 nm and an isosbestic point at 660 nm. The behaviour of the fluoranil system can be understood by taking into account that there is no evidence for the formation of the 2,5-disubstituted isomer, responsible for the absorbance at 550 nm, and the molar absorption coefficient of the 2,6-disubstituted (ε_D) compound in the interval 400 to 800 nm is always greater than that of the monosubstitution compound (ε_M) and, therefore, the isosbestic condition for this system ($\varepsilon_M = \varepsilon_D$) is never reached in this wavelength range.

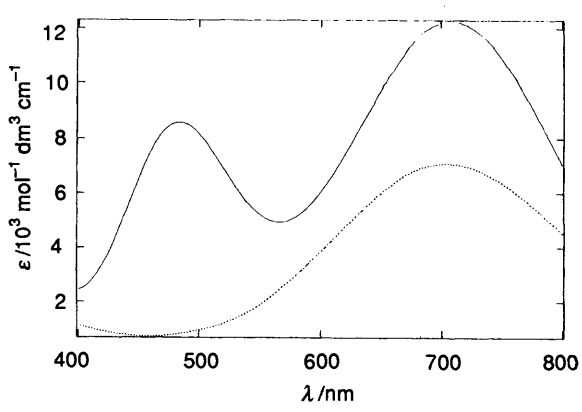


Fig. 3 Molar extinction coefficients for the monosubstituted and disubstituted products of fluoranil between 400 and 800 nm at 298 K

The isosbestic condition can be derived by assuming that the main reaction occurring in the system is reaction (3), where M

$$M \xrightarrow{Y(excess)} D + (YH^+,F^-) \quad (3)$$

and D are the monosubstituted and disubstituted product, respectively. The experiments were designed in such a way that the ylide was in a 100 to 400 fold excess with respect to the concentration of fluoranil to ensure first order conditions were maintained. If we assume that k_{obs} is the kinetic coefficient of the process then the reaction rate can be expressed by eqn. (4),

$$-\dot{m} = \dot{d} = k_{obs}m \quad (4)$$

whose integration leads to eqns. (5) and (6). Introducing (5)

$$m = m_o e^{-k_{obs}t} \quad (5)$$

$$d = m_o(1 - e^{-k_{obs}t}) \quad (6)$$

and (6) into the absorbance equation one obtains eqn. (7).

$$A/m_o = \varepsilon_D + (\varepsilon_M - \varepsilon_D)e^{-k_{obs}t} \quad (7)$$

Equating the time derivative of eqn. (7) to zero the isosbestic condition, $\varepsilon_M = \varepsilon_D$, is reached. Since the absorbance data were well represented by eqn. (7) the experimental absorbance data were analysed according to eqn. (8), where the subscript λ refers

$$A = \beta_{o\lambda} + \beta_{1\lambda}e^{k_{obs}t} \quad (8)$$

to a definite wavelength. For each kinetic run the absorbance

Table 6 First order rate constants for the disubstitution of fluoranil[a]

T/K									
287.8 ± 0.1		294.9 ± 0.1		299.2 ± 0.1		304.9 ± 0.1		311.4 ± 0.1	
y_o	k_{obs}	y_o	k_{obs}	y_o	k_{obs}	y_o	k_{obs}	y_o	k_{obs}
0.69	1.38 ± 0.01	0.45	1.62 ± 0.01	0.50	2.06 ± 0.01	0.48	3.12 ± 0.01	0.53	4.05 ± 0.01
1.03	2.01	1.01	2.88	0.96	3.43	0.56	3.43	0.68	6.29
1.49	3.06	1.43	3.85	1.50	5.29	0.91	4.86	1.47	8.78
1.92	3.75	2.00	5.08	1.92	6.54	1.39	6.86	1.86	10.76
2.42	4.65	2.45	5.97	2.60	8.43	2.20	9.86	2.36	13.45
						2.67	12.24		

[a] k_{obs} = First order rate constant/10^{-3} s^{-1}; y_o = initial concentration of ylide/mol dm^{-3}.

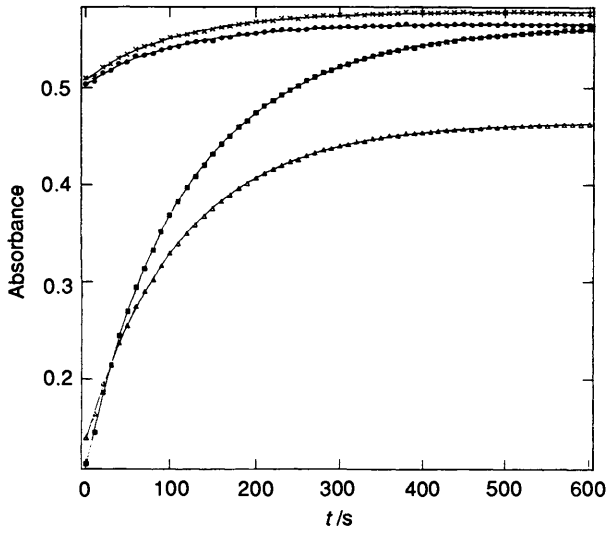


Fig. 4 Absorbance *vs.* time for a reaction mixture containing 2.60 × 10^{-2} mol dm^{-3} ylide at 299 K: ■ 484 nm; ▲ 536 nm; ● 690 nm; × 710 nm

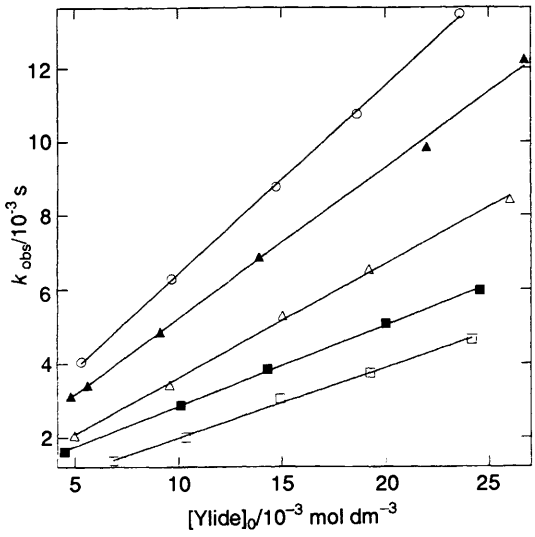


Fig. 5 Dependence of the first order kinetic coefficients on the ylide concentration and temperature for the disubstitution reaction: □ 281.8 K; ■ 294.9 K; △ 299.2 K; ▲ 304.9 K; ○ 311.4 K

curves at 484, 536, 690 and 710 nm were fitted simultaneously to eqn. (8) by means of the modified version of OPKINE program using the Davidon–Fletcher–Powell algorithm.[16] A typical set of fitted data is shown in Fig. 4 and all cases gave good non-linear correlation coefficients (r > 0.999). The values of k_{obs} obtained for the kinetic runs are shown in Table 6.

The fact that eqn. (8) is obeyed leads to the conclusion that the disubstitution reaction is again first order with respect to the halogenoquinone. In order to investigate the order with respect to the ylide, the values of k_{obs} were plotted against y_o. Good lines with null intercept were obtained for all temperatures, see Fig. 5, indicating that the reaction was again first order in the ylide, and the second order rate constants, k_M^2, are also shown in Table 3.

As the disubstitution reaction also involves a C–H bond cleavage, the effect of the addition of a strong base, and the deuterium isotope effect were also investigated. Table 7 shows the effect of the addition of amine for a series of three experiments where the concentration of quinuclidine was gradually increased. The value of k_M^2 in the presence of amine was approximately 0.275 dm^3 s^{-1} mol^{-1} and in the absence of quinuclidine this value was 0.298 dm^3 s^{-1} mol^{-1} (interpolated from the Arrhenius plot). In addition, the value of k^2 appeared to be independent of the amine concentration within experimental error. These facts indicate that the amine has little or no effect on the reaction rate.

The discrepancy between the values of k_M^2 can be attributed to a minor parallel reaction of the amine with the fluoranil rather than an effect of the amine on the system under investigation. A blank experiment carried out in the absence of ylide resulted in an increase of absorbance at 535 nm, which is responsible for the red colour of the solution. No further kinetic investigation was performed on this parallel reaction.

The results of the kinetic studies using tetradeuteriated ylide are shown in Table 5 from which it is clear that the disubstitution reaction also does not present a deuterium isotope effect (k_H^2 = 0.298 ± 0.005 and k_D^2 = 0.305 ± 0.005 dm^3 s^{-1} mol^{-1}). Thus, the results obtained from the disubstitution reaction are very similar to those obtained for the monosubstitution reaction and the empirical rate law may be written as eqn. (9), where m is the concentration of the

$$-\dot{m} = k_M^2 ym \quad (9)$$

monosubstitution species. The effect of the amine addition and the isotope effect allow the conclusion that the rate determining step is the addition of the ylide to the halogenoquinone, the subsequent cleavage of the C–H bond being relatively fast.

Dependence of Kinetic Coefficients on Temperature.—The values of ln (k_i^2) for the monosubstitution (k_Q^2) and disubstitution (k_M^2) reactions were plotted against $1/T$ to give good linear correlations in both cases, see Fig. 6.

Stoichiometry.—The Job–Foster plots for the monosubstitution reaction in dichloromethane are shown in Fig. 7(*a*). The plot for the monosubstitution reaction showed a maximum for a volumetric fraction of fluoranil equal to 0.52 in agreement with an irreversible reaction of 1 : 1 stoichiometry.

The Job plot for the disubstitution reaction [Fig. 7(*b*)] also showed maximum concentration of the 2,6-disubstitution

Table 7 First and second order rate constants for the disubstitution of fluoranil in the presence of quinuclidine at 298 K[a]

	$a_0/10^{-3}$ mol dm^{-3}					
	0.31		1.63		2.17	
	y_0	k_{obs}	y_0	k_{obs}	y_0	k_{obs}
	4.56	1.95	6.92	2.25	5.59	2.09
	10.1	3.27	10.3	3.16	10.2	3.27
	18.0	5.45	16.9	4.99	21.5	6.44
	30.8	9.02	29.9	8.53	30.4	8.97
k^2/dm^3 s^{-1} mol^{-1}	0.271 ± 0.005		0.273 ± 0.005		0.278 ± 0.003	

[a] y_0 = Initial concentration of ylide/10^3 mol dm^{-3}; a_0 = initial concentration of quinuclidine; k_{obs} = first order reaction constant/10^3 s^{-1}.

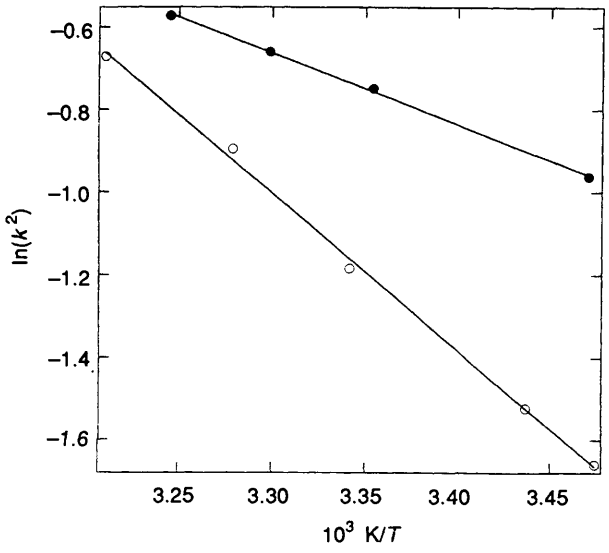


Fig. 6 Arrhenius plot of the second order kinetic coefficients for the monosubstitution (●) and disubstitution (○) reactions of fluoranil

product for a volumetric fraction of monosubstitution product close to 0.50 again in agreement with a 1:1 stoichiometry. In this case, however the plot was curved and the concentration of the disubstituted product was lower than expected, which may be attributed to a parallel equilibrium between the ylide and/or the product and the HF liberated during the formation of the monosubstitution product.

The concentration of the 2,6-disubstituted product was obtained directly from the spectra of the reaction mixtures by using the Gaussian deconvolution method previously described.[3]

Mechanism of Reaction.—At this stage of the analysis it is evident that the overall reaction mechanism consists of two consecutive second order irreversible reactions whose kinetic rate coefficients are well separated in magnitude (k_Q^2/k_M^2 = 2.3 × 10^5), see Scheme 1.

$$Q + Y \xrightarrow{k_Q^2} M + (YH^+, F^-)$$

$$M + Y \xrightarrow{k_M^2} D + (YH^+, F^-)$$

Scheme 1

Following the guidelines of earlier work [1-3] we propose an E1 or an E1cB mechanism to explain the empirical rate laws, see Scheme 2, where Q = fluoranil, M = monosubstitution product, σ = sigma complex, σ$^-$ = σ-complex after the loss of

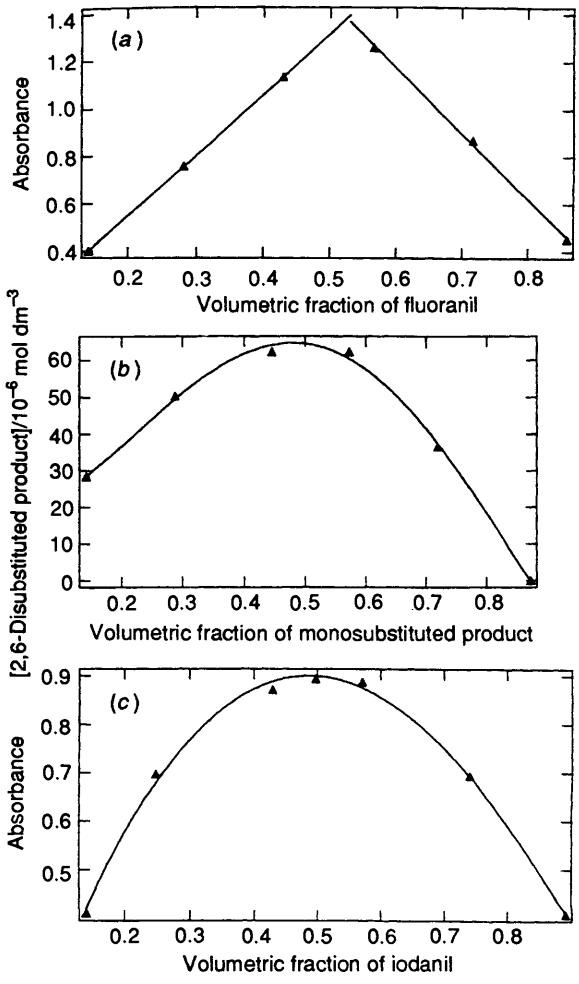


Fig. 7 Job plots for the monosubstitution (*a*) and disubstitution (*b*) reactions of fluoranil in dichloromethane and for iodanil in toluene (*c*)

$$Q + Y \underset{k_2}{\overset{k_1(rls)}{\rightleftharpoons}} \sigma \xrightarrow{k_3(fast)} M + HF \qquad (E1)$$

$$HF + Y \underset{k_5}{\overset{k_4}{\rightleftharpoons}} (YH^+F^-)\ (equilibrium)$$

$$Q + Y \underset{k_2}{\overset{k_1(rls)}{\rightleftharpoons}} \sigma$$

$$\begin{cases} \sigma + Y \xrightarrow{k_3} \sigma^- + YH^+ \\ \qquad\qquad (fast) \\ \sigma + B \xrightarrow{k_b} \sigma^- + BH^+ \end{cases} \qquad (E1cB)$$

$$\sigma^- \xrightarrow{k_4} M + F^-\ (fast)$$

Scheme 2

a proton, and B = organic base (rls = rate limiting step). Identical schemes may be proposed for the formation of the disubstitution product by replacing M by A and denoting the final disubstitution product as D.

Applying the steady stationary hypothesis to σ and σ$^-$ and taking into account that the ylide is in a great excess, the rate equations (10) and (11) can be derived for each mechanism. If

$$\dot{m} = \frac{k_1 k_3}{k_2 + k_3} y_0 q = k_{obs} q \quad (E_1) \qquad (10)$$

Table 8 Activation parameters for substitution of fluoranil

	Monosubstituted		Disubstituted
	CH_2Cl_2	Toluene	CH_2Cl_2
E_A/kJ mol^{-1}	14.4 ± 0.4	23 ± 1	31.6 ± 0.1
$\Delta H^{\ddagger}$/kJ mol^{-1}	11.9 ± 0.4	21 ± 1	29.2 ± 0.7
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	−112 ± 1	−97 ± 1	−157 ± 3
$\Delta G^{\ddagger}$/kJ mol^{-1}	45.4 ± 0.6	55 ± 1	76 ± 1

Table 9 Stoichiometry (halogenoquinone:ylide) for the formation of monosubstitution products

System	Fluoranil	Chloranil	Bromanil	Iodanil
Dichloromethane	1:1	1:2	1:2	1:2
Toluene	1:1	1:1	1:2	1:1

$$\dot{m} = \frac{k_1k_3y_o^2 + k_1k_bb_oy_o}{k_2 + k_3y_o + k_bb_o}q = k_{obs}q \quad \text{(E1cB)} \qquad (11)$$

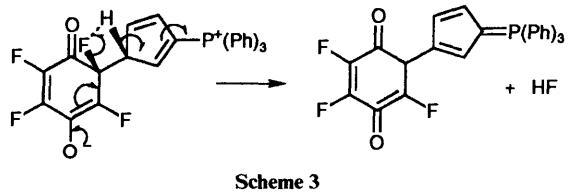
$k_3 \gg k_2$ or $k_3y_o + k_bb_o \gg k_2$ eqns. (10) and (11) reduce to eqn. (12).

$$\dot{m} = k_1y_oq \qquad (12)$$

The conclusion is that either the E1 or the E1cB mechanisms can explain the empirical rate equations and, regardless of the mechanism under consideration, the kinetic coefficient k^2 can be interpreted as the kinetic constant of the addition step of the ylide to the halogenoquinone (or monosubstitution product) to form the σ-complex.

Since F^- is a poorer leaving group than Cl^- or Br^- one might have expected the E1cB mechanism for the monosubstitution reaction. If such a mechanism were followed, however, a stoichiometry of 1:2 (fluoranil:ylide) would be observed since one molecule of ylide would attack the quinone ring and another would remove a proton from the σ complex prior to the elimination. This situation was found for the monosubstitution of chloranil in dichloromethane.[1] The observed stoichiometry for the fluoranil system is, however, 1:1 as assessed by the Job plots, see Fig. 7(*a*). The only way to achieve this stoichiometry in excess of quinone is for the σ-complex to undergo dissociation with the elimination of fluoride ion and as a consequence the E1 mechanism is probably followed.

This suggestion is consistent with the fact that F^- is more basic than Cl^- or Br^- and hence direct proton transfer through the F–C–C–H bond of the σ-complex may be favoured in the case of F^-, as shown in Scheme 3.



Scheme 3

Activation Parameters.—The activation parameters for the monosubstitution and disubstitution reactions are shown in Table 8. The activation enthalpy for the monosubstitution reaction in dichloromethane is similar to those observed with other halogenoquinones (11.9 compared with 13.6, 11.6 and 12.6 kJ mol^{-1} for chloranil,[1] bromanil and iodanil,[2] respectively). However, the activation entropy is markedly less negative for the fluoranil system, at −112 J mol^{-1} K^{-1} compared with −140, −148 and −158 J mol^{-1} K^{-1} for chloranil, bromanil and iodanil, respectively. The pattern found for $\Delta S^{\ddagger}$ values for the halogenoquinones in the less polar solvent toluene is just the opposite (−97, −95, −81 and −78 J mol^{-1} K^{-1}, respectively) and the activation enthalpies are considerably higher at 21, 30, 35 and 39 kJ mol^{-1}, respectively. These facts suggest that in toluene, solvation factors are far less important than in dichloromethane so that the degree of bond formation in the transition state is the feature dominating the relative reaction rates which means that the entropy of activation in toluene has the highest negative value with fluoranil where bond formation is highest.

The differences in reactivity among the halogenoquinones in dichloromethane appear to be related to solvation factors. Since the addition step assumes the localization of a certain amount of charge on the carbonyl oxygen, which can interact with the positive end of the solvent dipole, the higher the charge on the oxygen the higher the expected solvent interaction leading to a more negative entropy of activation. As the electronegativity of the halogen atom increases, the charge on the oxygen would be decreased by the inductive effect of the halogen and consequently the activation entropy would be less negative as observed for the series studied.

The slower rate of the disubstitution reaction compared with monosubstitution is principally due to the high activation energy (29.2 *vs.* 11.9 kJ mol^{-1}), which is probably related to the lower electrophilic character of the monosubstituted ring compared with the reactivity of the parent halogenoquinone.

E1 vs. *E1cB Mechanisms for the Monosubstitution Reaction.*—The stoichiometries for the monosubstitution reaction as determined from the Job–Foster plots for the four tetrahalogeno-*p*-benzoquinones in dichloromethane and toluene are shown in Table 9. Since the addition of the ylide to the halogenoquinone is the rate limiting step for all systems a stoichiometry of 1:1 is indicative of an E1 elimination mechanism but a stoichiometry of 1:2 can be explained either by an E1, E2 or an E1cB mechanism.

For fluoranil an E1 mechanism is observed in both solvents in which the F^- anion is basic enough to affect direct proton transfer as proposed in Scheme 3 possibly by a concerted mechanism. In this case it seems clear that a second molecule of ylide is not involved in either removing the proton or in forming a salt with HF, possibly due to strong intermolecular hydrogen bonding of the latter in the aprotic solvents.

For chloranil, the kinetic data strongly suggest that an E1cB mechanism is followed in dichloromethane but an E1 mechanism is followed in toluene indicating that the basicity of Cl^- is raised in the less polar toluene and the direct proton transfer is favoured. For bromanil, the kinetic data again suggest an E1cB or an E2 mechanism in dichloromethane and, possibly, the same occurs in toluene since Br^- is not basic enough and consequently a base (*i.e.* ylide) is always needed for the removal of a proton from the σ-complex. Finally, the kinetic data suggest an E1 elimination in both solvents for iodanil.[2] In dichloromethane, however, the stoichiometry is 2:1 (ylide:quinone) which suggests that a second mole of ylide is required to remove the proton whereas in toluene a 1:1 stoichiometry is observed implying that the ylide is no longer necessary for the removal of the proton. However, there is no doubt that the mechanism in dichloromethane is of type E1 when comparing the found empirical rate law with the theoretical rate law applicable to this mechanism.[2]

This situation is different to that of fluoranil. Since I^- is a good leaving group, elimination of the anion from the σ-complex is probably favoured and is followed by a proton transfer to a second molecule of ylide which explains why an equilibrium pattern is found in toluene for the Job–Foster plot with iodanil, see Fig. 7(*c*).

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