Oxidation of Organic Compounds with Quinquevalent Vanadium. Part 15.[1] Oxidation of 2,6-Dimethylphenol

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The oxidation of 2,6-dimethylphenol by acid aqueous vanadium(v) solution has been studied in the presence both of added acetonitrile and of acetic acid. In the case of the former solvent the reaction can be followed by a conventional u.v. spectrophotometer, but the reaction in acetic acid is much faster and a stopped-flow spectrophotometer, constructed of oxidant- and acid-inert materials, was also used. Under both conditions the main products were monomeric and dimeric quinones, and the reactions are second order in vanadium(v). Under both conditions there is evidence for the initial formation of a vanadium(v)–phenol complex which is then further attacked by a further vanadium(v) species. The reactions are acid catalysed.

In an early survey of the oxidant power of acidified quinquevalent vanadium one of the present authors noted[2] that the reaction with phenols was rapid in aqueous media. No further studies were made at the time since then available techniques for following the reaction were too slow, and the then available stopped-flow apparatus was not adequately thermostatted or resistant to attack by the strongly acid oxidising reagent solutions. Two groups of workers[3,4] have since reported on the kinetics of the oxidation of simple phenols, but they do not agree either on their observations or their interpretations, and comparison is difficult owing to a lack of experimental detail. In addition studies have been made of the oxidation of a number of di- and tri-hydric phenols,[5–7] and several workers have provided evidence of transient V^V–phenol complexes. The present work was undertaken to clarify our understanding of the reaction with simple monohydric phenols, and to provide data on an oxidation of a phenol by a presumed inner-sphere or bonded electron-transfer mechanism for comparison with similar data on a known outer-sphere oxidation of the same phenol, 2,6-dimethylphenol (2,6-DMP).[8]

Results and Discussion

Products and Stoicheiometry.—In order to ensure the solubility of the reagents and the products two solvent systems were used, 25% acetonitrile–water and 75% acetic acid–water. The first was chosen to be comparable with previous oxidation work in aqueous solution, while the latter was chosen in order to achieve higher concentrations of reactants and products in order to observe complex formation directly. The main products in both systems were 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (TMDQ) and 2,6-dimethylbenzoquinone (DMBQ). Table 1 shows how the concentrations of products change with the extent of reaction, and it can be seen that TMDQ is the main product, but that when there is little phenol left in solution the proportion of the dimer being formed is rather less. Between 2.1 and 2.8 mol of vanadium(v) are used up per mol of phenol oxidant, the TMDQ slowly disappearing when left in contact with excess of oxidant, and this is consistent with the observed product ratio. A similar product ratio and stoicheiometry was observed in acetic acid solutions.

Reaction in Water–Acetonitrile.—Kinetic studies were made of the reaction by following the increase of the u.v. absorption (418 nm) of the major product TMDQ under conditions of excess oxidant, and a good first-order plot was obtained up to three half-lives. If oxidant was not in excess the slope of the logarithmic plot increased with time, suggesting that significant amounts of hydroquinones might be formed as intermediates. Table 2(a) demonstrates that the addition of acetonitrile has had little effect on the rate of reaction, and that the observed first-order rate constants are substantially independent of the initial concentration of 2,6-DMP. The values of the rate constants are of course based on the observed t_∞ values for the absorbance; the yield data shows that this t_∞ value is proportional to the initial concentration of 2,6-DMP, confirming that the reaction is first order in 2,6-DMP over a 10-fold range of initial concentrations. Table 2(b) demonstrates by a comparison between the first two columns that the order in oxidant is between 1 and 2, and it is found by plotting appropriate graphs that the data fit the equation $k_{obs} = kK[V]^2(1 + K[V])$ † rather better than the alternative equation $k_{obs} = a[V] + b[V^2]$. The latter equation corresponds to attack on the phenol *via* two paths, one of which is first and the other second order in vanadium(v). The former attributes the deviation from a strict second-order law to the kinetically significant formation of a 1 : 1 phenol–V^V complex [reactions (1) and (2)] where $K = 5$ l mol^{-1} and $k = 0.3$ l mol^{-1} s^{-1}.

Table 1. Concentrations of organic reactants and products in the V^V oxidation[b] of 2,6-dimethylphenol as measured at various times after the start of the reaction

Time after mixing (min)	10^6[XOH][a]/ mol l^{-1}	10^6[DMBQ][a]/ mol l^{-1}	10^6[TMDO][a]/ mol l^{-1}
0	41 (100)[c]		
1.5	35 (85)		4.7 (25)
4.0	12 (30)	1.7 (4)	8.3 (43)
7.5	9.2 (23)	2.5 (6)	11.0 (56)
25.0	0.0 (0.0)	6.5 (16)	15.0 (76)

[a] XOH = 2,6-Dimethylphenol, DMBQ = 2,6-dimethylbenzoquinone, TMDQ = 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. [b] $[V^V]$ 3.7 × 10^{-2} mol l^{-1}, 25% CH_3CN–H_2O, [$HClO_4$] 1 mol l^{-1}. [c] Figures in parentheses represents the percentage of maximum theoretical yield.

$$V^V + 2,6\text{-DMP} \underset{}{\overset{K}{\rightleftharpoons}} V\text{-}2,6\text{-DMP} \qquad (1)$$

$$V\text{-}2,6\text{-DMP} + V^V \xrightarrow{k} \text{products} \qquad (2)$$

Table 2 includes (column e) the data calculated on this basis, and also (column f) the data calculated on the alternative

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† *i.e.* $d[TMDQ]/dt = k_{obs}\ [DMP] = kK[V^2][DMP]/(1 + K[V])$ at constant [H^+].

Table 2. Oxidation of 2,6-dimethylphenol by V^V in a 25% acetonitrile–water

(a) Effect of substrate concentration on the pseudo-first-order rate constant for the oxidation of 2,6-dimethylphenol by V^V at 11.5 °C

10^5[XOH] [a]/ mol l^{-1}	10^4k_{obs} [b]/s^{-1}	% Yield of TMDQ [a]
	25% CH_3CN–H_2O	
2.7	4.2	59
5.3	4.5	62
10.7	5.1	62
21.4	5.6	64
	No added CH_3CN	
5.3	4.6 [c]	
10.7	5.1 [c]	

(b) Effect of oxidant concentration on the pseudo first-order rate constant for oxidation of 2,6-dimethylphenol by V^V at 11.4 °C

$10^3[V^V]$/ mol l^{-1}	10^4k_{obs} [d]/ s^{-1}	$10^4k_{calc}/s^{-1}$		% Yield of TMDQ
		e	*f*	
9.6	1.28	1.32	1.48	60
18.9	4.46	4.89	4.66	61
19.3	5.14	5.10	4.84	62
37.2	17.3	17.5	15.9	59
59.5	41.0	41.5	38.8	
74.4	58.0	60.5	59.6	55

(c) Effect of acidity on the pseudo-first-order rate constant for the oxidation of 2,6-dimethylphenol by V^V at 25.0 °C

$[H^+]$/mol l^{-1}	10^5k_{obs} [g]/s^{-1}	$10^5k_{calc}/s^{-1}$ [h]	% Yield of TMDQ
0.10	9.2	9.0	50
0.19	18	18.1	50
0.37	39	38.8	51
0.55	63	63.1	52
0.73	90	90.8	54
1.00	140	139	56

[a] See Table 1. [b] Measured at λ 418 nm (appearance of TMDQ); average of three kinetic runs ±5% error; $[V^V]$ 1.93 × 10^{-2} mol l^{-1}; $[HClO_4]$ 1 mol l^{-1}. [c] *T* 12.0 °C. [d] Measured at λ 418 nm (TMDQ appearance); average of three kinetic runs ±5% error; [XOH] 1.07 × 10^{-4} mol l^{-1}, solvent 25% CH_3CN–H_2O, $[HClO_4]$ 1.03 mol l^{-1}. [e] Value of *k* calculated on the basis of complex formation. [f] Value of *k* calculated on the basis of mixed first- and second-order kinetics. [g] λ 418 nm; average of three determinations; $[V^V]$ 2.08 × 10^{-2} mol l^{-1}, [XOH] 7.35 × 10^{-5} mol l^{-1}, ionic strength 1.10 mol l^{-1} ($NaClO_4$); 25% CH_3CN–H_2O. [h] Calculated from $k_1[H^+] + k_2[H^+]^2$, see text.

Table 3. Oxidation of 2,6-dimethylphenol by V^V in 75% acetic acid–water at 25 °C

(a) Effect of substrate concentration on the pseudo-first-order rate constant, k_{obs}

10^5[XOH]/mol l^{-1}	10^3k_{obs} [a]/s^{-1}
0.52	2.85
1.03	2.93
2.06	2.98
3.09	2.97
4.12	2.80
5.15	2.87

(b) Effect of oxidant concentration on k_{obs}

$10^3[V^V]$/mol l^{-1}	k_{obs} [b]/s^{-1}	$10^3k_{o2s}/[V^V]^2$
4.1	0.093	5.53
8.0	0.2	4.53
16.5	0.99	3.64
24.5	2.2	3.67
33	3.8	3.49
41	5.5	3.27

(c) Effect of acidity on k_{obs}

$[H^+]$/mol l^{-1}	k_{obs} [c]/s^{-1}
0.55	4.2
0.76	6.8
1.00	8.0

[a] λ 418 nm; $[V^V]$ 5.0 × 10^{4} mol l^{-1}, $[HClO_4]$ 1.0 mol l^{-1}. [b] λ 418 nm; [XOH] 1.0 × 10^{-5} mol l^{-1}, $[HClO_4]$ 1.0 mol l^{-1}. [c] λ 418 nm; $[V^V]$ 4.7 × 10^{-2} mol l^{-1}, [XOH] 3.05 × 10^{-5} mol l^{-1}, ionic strength 1.07 mol l^{-1} ($NaClO_4$).

basis using $a = 0.0058$ l mol^{-1} s^{-1} and $b = 1.0$ l^2 mol^{-1} s^{-1}. The value of *K* observed is comparable with that quoted for reaction of *p*-dihydroxybenzene, and, not surprisingly, is much less than that observed for *o*-dihydroxybenzenes.[5]

Table 2(c) shows that the reaction is strongly acid dependent and that the observations are compatible with the equation $k_{obs} = k_1[H^+] + k_2[H^+]^2$ when $k_1 = 8.5 \times 10^{-4}$ l mol^{-1} s^{-1}, $k_2 = 5.4 \times 10^{-4}$ l^2 mol^{-2} s^{-1}.* The data do not fit an equation derived on the assumption that *K* found above is significantly acid dependent, though the extent of complexing of the 2,6-DMP is *ca.* 10%. Addition of vanadium(IV) (5 × 10^{-2} mol l^{-1}) to a reaction containing 2.5 × 10^{-2} mol l^{-1} vanadium(V) had no significant effect on the rate of reaction, in contrast to the effect of $IrCl_6^{3-}$ in oxidations of 2,6-DMP by $IrCl_6^{2-}$.[8]

The above data are consistent with a mechanism in which a complex is formed reversibly between 2,6-DMP and the predominant vanadium(V) species VO_2^+, and that the complex is then further attacked by a further vanadium(V) species, by two parallel rate-limiting steps, one of which includes one extra proton, and the second of which includes two. The product of such a redox process will have the oxidation level of the 2,6-dimethylphenoxonium cation, and could therefore readily give rise to either of the principal products, any possible polyhydric intermediates being readily further oxidised to the quinonoid forms.[5] The absence of a term in $[2,6\text{-DMP}]^2$ indicates that the formation of the dimeric product occurs subsequently to the rate-limiting step (*cf.* ref. 8).

Reaction in Acetic Acid–Water.—It was not possible to increase the concentrations significantly in the water–acetonitrile medium in order to demonstrate complex formation more directly, and there was visual evidence of transient green colours when the reagents were mixed in acidified acetic acid media, so further studies were undertaken in this solvent. The reaction was found to be much faster. Initially the formation of the product was monitored (417 nm) with oxidant in excess, as before.

Table 3(a) demonstrates that the dependence on 2,6-DMP is still first order, while Table 3(b) shows that the reaction is second order in vanadium(V). There is no clear evidence for a first-order term. It should be noted that the concentration of oxidant is considerably lower than that used in water–acetonitrile, so complexing ought to be kinetically negligible if *K* has a similar value to that found above. Similarly, if the previ-

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* *i.e.* $d[TMDQ]/dt = k_{obs}$ [DMP] $= (k_1[H^+] + k_2[H^+]^2)$[DMP] at constant $[V^V]$.

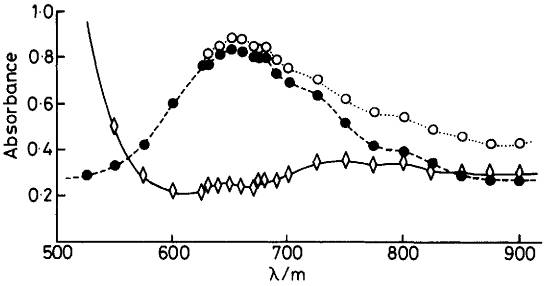


Figure 1. Spectra of intermediates in the V^V oxidation of 2,6-dimethylphenol in 70% acetic acid. [V^V] 5 × 10^{-2} mol l^{-1}, [XOH] 5.6 × 10^{-3} mol l^{-1}, [$HClO_4$] 1.0 mol l^{-1}. ●, *t* 0 (directly after mixing); ○, *t* 10 ms (maximum); ◇, *t* 3 s (infinity)

Table 4. (a) Observed and calculated absorbance values for (C_{650}) complex on mixing V^V and 2,6-dimethylphenol in 75% acetic acid–water at 25 °C ([$HClO_4$] 1.0 mol l^{-1})

10^3[V^V]/ mol l^{-1}	10^3[XOH]/ mol l^{-1}	Observed absorbance	Calculated absorbance [a]
0.0	0.0	0.00	0.00
4.8	5.0	0.23	0.24
9.5	5.0	0.46	0.45
14	5.0	0.67	0.66
19	5.0	0.86	0.85
24	5.0	1.04	1.03
29	5.0	1.20	1.20
33	5.0	1.32	1.37
38	5.0	1.43	1.52
43	5.0	1.60	1.67
48	5.0	1.69	1.80
5.0	5.0	0.21	0.24
5.0	10.0	0.43	0.47
5.0	15	0.66	0.69
5.0	20	0.88	0.89
5.0	25	1.11	1.08
5.0	30	1.32	1.26
5.0	35	1.50	1.42
5.0	40	1.65	1.58
5.0	45	1.78	1.73
5.0	50	1.95	1.87

(b) Observed and calculated absorbance values measured at λ 850 nm directly after mixing V^V and 2,6-dimethylphenol in 75% acetic acid–water at 25 °C ([$HClO_4$] 1.0 mol l^{-1})

10^3[V^V]/ mol l^{-1}	10^3[XOH]/ mol l^{-1}	Observed absorbance	Calculated absorbance [b]
0.0	0.0	0.00	0.00
4.8	5.0	0.06	0.07
9.5	5.0	0.13	0.14
14	5.0	0.20	0.21
19	5.0	0.28	0.27
24	5.0	0.34	0.32
29	5.0	0.40	0.37
33	5.0	0.47	0.43
38	5.0	0.56	0.47
43	5.0	0.58	0.52
48	5.0	0.66	0.56
5.0	5.0	0.02	0.08
5.0	10	0.09	0.15
5.0	15	0.15	0.21
5.0	20	0.19	0.28
5.0	25	0.25	0.34
5.0	30	0.32	0.39
5.0	35	0.37	0.44
5.0	40	0.40	0.49
5.0	45	0.45	0.54
5.0	50	0.52	0.58

Table 4 (*continued*)

(c) Observed and calculated values for the change in absorbance at 850 nm as measured from mixing to the maximum value attained

10^3[V^V]/ mol l^{-1}	10^3[XOH]/ mol l^{-1}	Observed absorbance ($O.D._{max.}$ − $O.D._{t=0}$)	Calculated absorbance difference [c]
0.0	0.0	0.00	0.00
5.0	5.0	0.04	0.04
5.0	10	0.05	0.06
5.0	15	0.07	0.08
5.0	20	0.08	0.09
5.0	25	0.09	0.10
5.0	30	0.09	0.10
5.0	35	0.10	0.10
5.0	40	0.11	0.11
5.0	45	0.10	0.11
5.0	50	0.12	0.11
4.8	5.0	0.03	0.04
9.5	5.0	0.07	0.06
14	5.0	0.08	0.08
19	5.0	0.09	0.09
24	5.0	0.11	0.09
29	5.0	0.11	0.10
33	5.0	0.11	0.11
43	5.0	0.12	0.11
48	5.0	0.10	0.11

(d) Effect of acidity on the absorbance of complexes [d]

[$HClO_4$]/mol l^{-1}	Maximum absorbance at 650 nm	Absorbance difference at 850 nm ($O.D._{max.}$ − $O.D._{t=0}$)
0.55	0.48	0.07
0.76	0.78	0.07
1.00	1.19	0.07

(e) Effect of solvent on complexes [e]

% Acetic acid in solvent	Maximum absorbance at 650 nm	Absorbance difference at 850 nm ($O.D._{max.}$ − $O.D._{t=0}$)	k_{obs}^{650} decay/ s^{-1}
50	V. small	V. small	
55	0.16	0.02	
60	0.22	0.05	
65	0.44	0.06	2.2
70	0.77	0.07	3.9
75	1.67	0.10	9.0

[a] *K* 7.5 ± 2 l mol^{-1}, ε 1 100 ± 200 l mol^{-1} cm^{-1}, derived from a non-linear least squares computer fit to the observed data. [b] *K* 8 ± 3 l mol^{-1}, ε 330 ± 200 l mol^{-1} cm^{-1}, calculated fit to the observed data. [c] *K* 110 ± 30 l mol^{-1}, ε 21 ± 5 cm^{-1} l mol^{-1}, calculated fit to the observed data. [d] [V^V] 3.7 × 10^{-2} mol l^{-1}, [XOH] 3.1 × 10^{-3} mol l^{-1}, ionic strength 1.07 mol l^{-1} ($NaClO_4$), solvent 75% HOAc–H_2O. [e] [V^V] 4.8 × 10^{-2} mol l^{-1}, [XOH] 5.0 × 10^{-3} mol l^{-1}, [$HClO_4$] 1.0 mol l^{-1}, *T* 25 °C.

ously observed deviation from second order had been due to a first-order term the first-order term would now have dominated the process, provided that the relative rate constants were not significantly changed by the solvent change. Table 3(c) shows a first-order dependence on acidity; the accessible range was limited by the insolubility of vanadium(v) at the lower acidities. In order to study the transient colour changes higher concentrations of a reagent were necessary, and the faster reactions resulting from this necessitated the use of the

Table 5. (a) Pseudo-first-order rate constants for complex decay in 75% acetic acid-water at 25 °C: effect of substrate concentration

10^3[XOH]/ mol l^{-1}	k_{obs}^{650} decay [a]/s^{-1}	k_{obs}^{850} decay [b]/s^{-1}
0.51	9.1	10.7
1.02	9.7	10.5
1.52	9.6	10.0
2.54	10.0	11.6
4.00	9.8	13.0
5.00	9.3	13.0

(b) Effect of oxidant concentration on k_{obs}

10^3[V^V]/ mol l^{-1}	k_{obs}^{650} decay [c]/ s^{-1}	k_{obs}^{850} decay [d]/s^{-1}	k_{obs}^{850} formation/ s^{-1}	k_{calc}^{650}/s^{-1} [d]
29	4.3, 4.1 [e]	5.3	380	4.45
33	5.1, 5.5 [e]	6.3	400	5.55
38	6.8, 6.8 [e]	7.9	500	7.03
43	8.1, 8.5 [e]	9.1	550	8.63
48	9.2, 9.6 [e]	10.1	560	10.32

(c) Effect of acidity on k_{obs} [f]

[H^+]/mol l^{-1}	k_{obs}^{650} decay/ s^{-1}	k_{obs}^{850} decay/ s^{-1}	k_{obs}^{850} formation/s^{-1}
0.55	4.2	6.6	380
0.76	6.2	7.3	450
1.00	7.7	8.5	600

[a] λ 650 nm; [V^V] 4.8 × 10^{-2} mol l^{-1}, [$HClO_4$] 1.0 mol l^{-1}. [b] λ 850 nm; concentrations as in note *a*. [c] λ 650 nm; [XOH] 2.5 × 10^{-3} mol l^{-1}, [$HClO_4$] 1.0 mol l^{-1}, solvent 75% HOAc–H_2O; *T* 25.0 °C. [d] λ 850 nm; conditions as in note *c*. [e] Conditions as in note *c* but [XOH] 1.02 × 10^{-3} mol l^{-1}. [f] [V^V] 3.7 × 10^{-2} mol l^{-1}, [XOH] 3.05 × 10^{-3} mol l^{-1}, ionic strength 1.07 mol l^{-1} ($NaClO_4$), solvent 75% HOAc–H_2O.

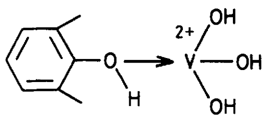
stopped-flow apparatus. Repeated flow experiments demonstrated changes illustrated in Figure 1. An absorbance peak is formed immediately on mixing at *ca.* 650 nm, which decays exponentially to the products. At 850 nm however, the initially generated absorption increases over *ca.* 10 ms to a higher value, and then slowly decays. It was clear therefore that two intermediates are being detected, which we will refer to as C_{650} and C_{850}, and studies were made of the formation and decay of these complexes by monitoring the absorption at 650 and 850 nm.

Table 4(a) shows the dependence of the absorption observed immediately on mixing at 650 nm, on reagent concentrations. The absorption is essentially proportional to the product [V][2,6-DMP] but as each reagent is used in excess the proportionality constant drops, though a sharp limit is not seen in the accessible range. The data were fitted by computer to the model of a 1 : 1 V^V–DMP complex, and a value of *K* of 7.5 l mol^{-1} and ε 1 100 was found to fit the data. A similar fit to the Table 4(b) of the initial absorbance at 850 nm gave *K* 8 l mol^{-1} and ε 330, confirming that the initial absorbance at 850 nm is probably due to the same species. The further change in absorbance at 850 nm taking place in the first 10 ms after mixing was also fitted similarly [Table 4(c)]; the change in the concentration of C_{650} during this time was very small, so its contribution to the change at 850 nm could be neglected. The accuracy with which the further change at 850 nm could be measured was limited since it only consisted of *ca.* 20% of the absorption, but it indicated that the C_{850} species may also be a 1 : 1 complex formed reversibly, but with a rather higher association constant (*K ca.* 110 ± 30, ε *ca.* 21 ± 5). Table 4(d) shows that the absorbance of the C_{650} is proportional to the acidity, though that of C_{850} appears unchanged, and 4(e) shows that both the absorption and the rate of reaction is strongly dependent on the composition of the solvent. The kinetics of the formation of C_{650} were too fast for observation, but the rate of the decay of C_{650} (k_d 650), decay at 850 (k_d 850), and the change in the first 10—20 ms at 850 (k_f 850) were studied as a function of initial reagent concentration. k_d 850 should of course include a large component of k_d 650, and no attempt has been made to remove it. An initial comparison showed that the rate of formation of TMDQ (500 nm) gave the same first-order rate constants as k_d 650 in a run with oxidant in excess. As in the studies of TMDQ appearance, these reaction curves gave good first-order plots for 2—3 half lives when oxidant was in excess, but they were slower and apparently of higher order when 2,6-DMP was in excess, indicating that free oxidant is necessary to hasten the decomposition steps k_d. However as the kinetics were not first order no further studies were carried out with excess of DMP. Table 5(a) shows that the decay processes under conditions of excess oxidant are unaffected by further addition of phenol, showing that no extra phenol molecule is involved in this step, while Table 5(b) confirms this, while also showing that k_d (both) and k_f are dependent on vanadium(v) concentration, the dependence being consistent with the equation $k_{obs} = kK[V]^2/(1 + K[V])$ from which the calculated values are derived. Note that *K* (13 ± 5 l mol^{-1}) is comparable with the value estimated for the equilibrium study of C_{650} formation above. A value of 560 ± 100 l mol^{-1} s^{-1} is used for *k*. Similarly Table 5(c) shows that the reactions are substantially first order in hydrogen ion concentration. The above observations are consistent with reactions (3) (where $K' = K/[H^+]$) and (4). These are quite similar to

$$V^V + 2,6'DMP + H^+ \overset{K'}{\rightleftharpoons} C_{650} \qquad (3)$$

$$C_{650} + V^V \xrightarrow{k} \text{products} \qquad (4)$$

the mechanism proposed for the reaction in aqueous acetonitrile, but there is no evidence here for a reaction path second order in hydrogen ion, and the hydrogen ion dependence observed undoubtedly arises in the complex formation stage. A possible structure for C_{650} is (1). The green colour may be due to an internal charge transfer transition, and the marked effect of acetic acid on the reaction may be an indication that it is specifically involved in the transition state.



(1)

The nature of the C_{850} species is less clear; the reaction resulting in the increase of absorption at 850 nm shows the same dependences on initial concentration as does the much slower direct decrease of absorbance at 650 nm, though the absorbance at 850 nm attributable to the complex seems to be independent of acidity. It may therefore be a second V^V–DMP complex which does not include an extra proton, though the acid dependence of its k_f values suggests that its formation is acid catalysed. One possibility is that $C_{650} \longrightarrow C_{850} + H^+$ and that the reaction is not as fast as the formation of C_{650} because it is not a simple proton loss process. The long wavelength of the absorption of C_{850} suggests that it is due to an easy charge-transfer process, possibly even in a phenoxyl radical–V^{IV} complex, but there is no clear evidence whether or not the C_{850} species is a precursor complex, a successor complex, or even not in any way involved with the main path of the oxidation. To summarise, the reaction in aqueous acetic acid follows equation (5), where $kK' = 3.3 \times 10^3$ l^3 mol^{-3} s^{-1} [from the data in Table 3(b)] and $K' \approx 8$ l^2 mol^{-2}.

$$d[\mathrm{TMBQ}]/dt = kK[\mathrm{V^V}]^2[2,6\text{-}\mathrm{DMP}][\mathrm{H^+}]/(1 + K[\mathrm{V^V}][\mathrm{H^+}] \quad (5)$$

The reaction rate for the decomposition of the complex k is therefore some two orders of magnitude larger in acetic acid than in acetonitrile, even after allowing for the difference in the temperature at which the measurements were taken.

The other major affect of the solvent change is the effect on the acid dependence. Although even in acetonitrile–water the acid independent term predominates at $[\mathrm{H^+}] = 1$ the second-order term is quite perceptible; it is however not detectable in the acetic acid mixture. This may be a consequence of the lower stability of a doubly charged species in the medium of lower dielectric constant; in neither case does the acid dependence appear to relate to the protonation (or deprotonation) of the phenol. There is no evidence for the participation of the phenoxide anion; this would be both inconsistent with the observed acid and vanadium dependence, and it would require a rate-limiting elementary redox process consisting of an electron transfer with a rate constant of *ca.* 10^6 l mol^{-1} s^{-1}. In addition no evidence could be found by e.s.r. (both direct and using spin traps) of the intermediacy of free radical species, though in the earlier work [1] there was some evidence of induced polymerisation of acrylonitrile in the oxidation of phenol.

The comparison of the present results with the earlier kinetic work on oxidation of monohydric phenols by vanadium(V) is difficult, as both the earlier groups concentrated on oxidation of unsubstituted or monosubstituted phenols, which are notorious for the complexity of their oxidation products. Neither group found kinetic evidence for complex formation, though Yatsimirskii and Nikolov [3] found evidence from initial rate measurements for second-order dependence on vanadium(V) in acidified aqueous solution. Radhakrishnamarti and Panda,[4] working on acetic acid mixtures, did not report second-order dependence on vanadium(V) but they did not explore the effect of varying the initial concentration of that reagent. They did however evaluate a Hammett ρ value (−4.3) suggesting that the rate-limiting step may involve formation of a phenoxonium cation or similar species, though this was inconsistent with their reported kinetics. Some of the differences between the earlier reports appear to be due to their different choice of solvents.

Comparison of the present results with those observed in the oxidations of 2,6-DMP by iridium(IV) [8] shows that although the products are very similar the mechanisms are very different. The differences arise naturally from the bonded or non-bonded nature of the initial electron transfer; in the case of iridium(IV) this gives rise reversibly to phenoxyl radicals, while in the present system no such active intermediate need be liberated.

Experimental

2,6-Dimethylphenol was recrystallised from hexane and freshly sublimed shortly before use. Acetonitrile was Fluka purissima grade, shown to be stable towards the oxidant. Perchloric acid (AnalaR) and sodium perchlorate (recrystallised) were also checked to be free from reducing materials. Vanadium(V) solutions were made up by the cautious acidification of warm solutions of sodium or ammonium metavanadate in water by concentrated perchloric acid. The acetonitrile was added with the phenolic component of the reaction mixture, but in the case of acetic acid solutions some acetic acid was added slowly with stirring to the acidified vanadium(V) solutions. The solutions were standardised by reduction with $\mathrm{Fe^{II}}$ and back-titration against standard cerium(IV) solution.

Oxidation Products.—Organic products from the reaction of vanadium(V) (0.2M) with equimolar solutions of phenols were extracted with diethyl ether and examined by t.l.c. Phenol gave several yellow bands, one of which had the same R_F value as *p*-benzoquinone. 2,6-DMP gave DMBQ and TMBQ as the only products. 2,4,6-Tri-t-butylphenol was also oxidised in aqueous acetic acid, as it is known to readily give a deep-blue phenoxyl radical, or (in the presence of oxygen) a dimeric peroxide. No phenoxyl radical or peroxide was observed, but the major product was 2,6-di-t-butylbenzoquinone. Kinetics were carried out in a thermostatted cell holder in a SP 800 or SP 1700 u.v. recording spectrometer, thermally pre-equilibrated reagents being mixed in the silica cuvette for reactions with half-lives >30 s. Reactions were also carried out under nitrogen with de-oxygenated solutions, but no change of rate resulted. The concentrations of the product quinones were established spectrophotometrically; the extinction coefficients were confirmed to be $\lambda_{\max.}$ 254 (ε 21 600 l mol^{-1} cm^{-1}) for 2,6-dimethylbenzoquinone and $\lambda_{\max.}$ 417 nm (ε 70 200) for TMDQ (prepared by the oxidation of the phenol by manganese dioxide).[9]

The stopped-flow apparatus was designed in the laboratory to be usable with highly corrosive materials, and to be capable of being thermostatted. The apparatus (Figure 2) is constructed vertically in blocks, held together under pressure, without any use of adhesives, by steel bolts extending from top to bottom of the apparatus. It can be totally immersed to the stopping syringe block in a thermostat bath for accurate temperature control. Inlets for the hydraulic drive and the reagents pass through gaskets in the side of the thermostat. Kel-F (polytrifluorochloroethylene) was used for parts requiring mechanical strength and PTFE (polytetrafluoroethylene) for gaskets and seals. The mixer was of the eight-jet type with the liquid entering tangentially from four jets in each direction, giving efficient mixing. The quartz-windowed observation cell was 1.275 cm in length and calculated to be 2.2 cm from the mixing chamber. The driving ' syringes ' were of a somewhat unusual design [10] consisting of cavities of capacity 5 ml divided by a two-layer diaphragm, Teflon on the reagent side, neoprene on the oil side. Oil is forced in from one side, displacing the membrane and expelling the reagent from the other. These were filled *via* three-way Teflon taps. These diaphragm syringes were driven hydraulically by silicone oil which was itself propelled by a pair of pistons activated by compressed air for smooth reproducible action. The ' push ' was initiated by opening a solenoid valve in the air supply line. The stopping syringe also consists of two stages, a 1 ml diaphragm syringe which the reagents enter and from which they expel oil, and a conventional piston, driven by the oil against a mechanical stop. The movement of the piston interrupts a light beam, providing a signal to trigger the data collection device. The output from the amplifier was either displayed directly on a storage cathode ray oscilloscope, or, more accurately, recorded on a Datalab transient recorder and plotted on to a pen-recorder. It could also be recorded using a computer-based data collection unit.[11]

Since this was a new apparatus, its performance figures were tested, using the iron(III)–thiocyanate reaction [12] and other test solutions. The mixing ratio was tested, using water and dichromate, and hydroxide and phenolphthalein solutions were used to check for any premature mixing or

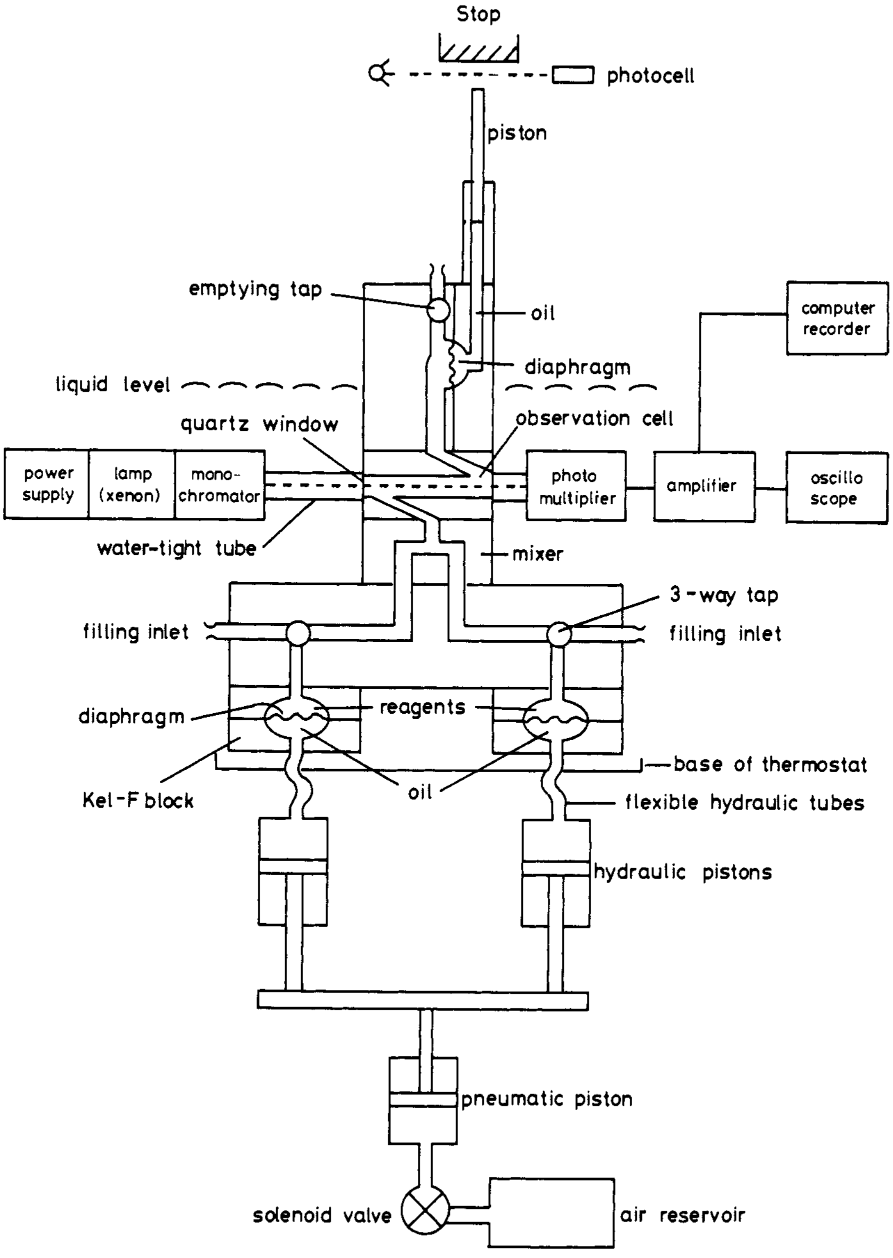


Figure 2. Stopped flow apparatus

diffusion in the apparatus. From the tests with Fe^{3+}–SCN^-, reproducible runs were obtained under a hydraulic pressure of 45 lb in^{-2} of compressed air. The total dead time of the apparatus was measured as 2.5 ms, and the mixing dead time as 1.1 ms.

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