KINETICS OF OXIDATION OF HYDROCARBONS BY QUINOLINIUM DICHROMATE

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Quinolinium dichromate (QDC) oxidizes hydrocarbons (toluenes and phenanthrenes) smoothly in dimethylformamide in the presence of acid. The rate of the reaction was first order in each substrate, oxidant and acid. The effects of variations in solvent composition and temperature were studied. The rate data obeyed Hammett's relationship and the values of ρ were -0.20 for toluenes and -1.79 for phenanthrenes. Induced polymerization of acrylonitrile and the reduction of mercury(II) chloride were not observed. For the oxidation of toluenes, a kinetic isotope effect, $k_H/k_D = 5.13$, was observed. The initial reaction for the oxidation of toluenes involved hydrogen abstraction, forming an intermediate which was rapidly converted to the product, the corresponding aldehyde. For the oxidation of phenanthrene, the experimental data have been rationalized in terms of a hydride ion transfer in the rate-determining step.

INTRODUCTION

The development of newer chromium(VI) reagents[1-7] for the oxidation of organic substrates continues to be a subject of interest. New procedures are emerging, involving 'non-aqueous' chromium(VI) reagents, with the general idea that anhydrous conditions are more conducive to mild oxidation. The reagent employed in this investigation, quinolinium dichromate (QDC), $(C_9H_7NH^+)_2Cr_2O_7{}^{2-}$, has been found to be a useful and versatile oxidant[8] that deserves further evaluation. The liquid-phase oxidation of toluenes to the corresponding aldehyde is an important process from an industrial point of view.[9] The oxidation of phenanthrene has yielded either phenanthroquinone or phenanthroic acid.[10-13] In our efforts to understand the mechanistic aspects of the oxidation of hydrocarbons, we report here the kinetic features of the oxidation of toluenes and phenanthrenes by QDC in acidic medium, using dimethylformamide as the solvent, under a nitrogen atmosphere.

EXPERIMENTAL

Materials and methods. Quinolinium dichromate (QDC) was prepared by the reported method[8] and its purity was checked by determining chromium(VI) iodometrically. Dimethylformamide (DMF) was of AnalaR grade from BDH, and was distilled under

reduced pressure before use. The acidity of all solutions was adjusted by using perchloric acid (Merck). The ionic strength was maintained constant ($\mu = 1.0$ M) by using sodium perchlorate (Fluka).

All the substrates were obtained from Merck and were purified by distillation or crystallization before use. The deuterated compounds were prepared using the method reported earlier.[14]

The reactions were performed under pseudo-first-order conditions by keeping a large excess of the substrate with respect to the oxidant (QDC). The reactions were carried out at constant temperature (± 0.1 K), and were followed by monitoring the absorption band at 440 nm spectrophotometrically (Model UV 26 instrument, Beckman). The rate constants were evaluated from the linear ($r > 0.993$) plots of log[QDC] against time. The values reported are the means of at least duplicate runs, and were reproducible to within $\pm 3\%$. The solvent was DMF unless stated otherwise. The reaction mixtures remained homogeneous in the solvent systems used. All reactions were performed under a nitrogen atmosphere.

Product analysis from toluene. Under the present reaction conditions, the corresponding aldehyde was formed. The 2,4-dinitrophenylhydrazone (DNP) derivative of the corresponding aldehyde was prepared, recrystallized from ethanol, dried and weighed. The product in each case was identical (m.p.) with an authentic sample of the DNP of the corresponding aldehyde. The yields of DNP after recrystallization were *ca* 75% for all the toluenes.

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For purposes of comparison, *p*-cymene was oxidized under the same reaction conditions. The product obtained was *p*-(2-propyl)benzaldehyde, which was characterized as the 2,4-dinitrophenylhydrazone derivative, after recrystallization from benzene as red needles in *ca* 75% yield (m.p. 241 °C).

Product analysis from phenanthrene. Freshly crystallized phenanthrene (0·01 M) and oxidant solution (0·001 M), taken in DMF containing perchloric acid (0·5 M), were mixed at 313 K and maintained under nitrogen for 24 h. The mixture was cooled, filtered and washed with water. The solid was suspended in ethanol, sodium metabisulphite solution (20 ml) was added and the mixture was allowed to stand. Water (50 ml) was added and the mixture was filtered. Saturated sodium carbonate solution was added to the filtrate and the precipitate was stirred, filtered and washed with water. The solid obtained (orange–yellow needles) was dried over calcium chloride in a desiccator (yield *ca* 60%, m.p. 209 °C; product 9,10-phenanthroquinone).

RESULTS AND DISCUSSION

The oxidation of all the substituted toluenes by QDC in DMF resulted in the formation of the corresponding aldehyde. Under the conditions used there was no further oxidation of the aldehyde. The oxidation of phenanthrene by QDC in DMF resulted in the formation of 9,10-phenanthroquinone.
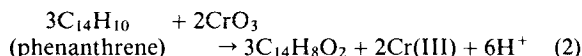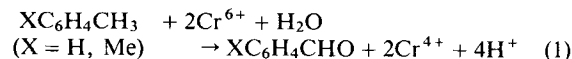
Stoichiometry

Stoichiometric experiments were carried out under nitrogen at 313 K under the conditions $[QDC]_0 > [substrate]_0$, at various acid concentrations. The disappearance of Cr(VI) was followed until the absorbance values became constant. The QDC concentration was determined. Stoichiometric ratios, $\Delta[QDC]/\Delta[substrate]$, of 1·09 for toluenes and 0·70 for phenanthrene (Table 1) were obtained, which

conformed to the overall equations:

$$XC_6H_4CH_3 + 2Cr^{6+} + H_2O$$
$$(X = H, Me) \rightarrow XC_6H_4CHO + 2Cr^{4+} + 4H^+ \quad (1)$$

$$3C_{14}H_{10} + 2CrO_3$$
$$(phenanthrene) \rightarrow 3C_{14}H_8O_2 + 2Cr(III) + 6H^+ \quad (2)$$

Rate law

Under pseudo-first-order conditions, the individual kinetic runs were first order with respect to QDC. Further, the rate constants were independent of the initial concentrations of QDC (Table 2). The reaction was of first order with respect to substrate concentration. The second-order rate constants, k_2, were obtained by dividing the pseudo-first-order rate constant (k_1) by the substrate concentration and were found to remain constant (Table 3). This indicated that the reaction was first order with respect to the substrate concentration.

The reaction was susceptible to change in acid concentration, and the dependence on acid was observed to be unity (Table 4). The linear increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step. There have been earlier reports of the involvement

Table 2. Dependence of reaction rate $[10^4 k_1 (s^{-1})]$ on oxidant concentration[a]

| Compound | 10^3[QDC] (M) | | | |
	0·1	0·50	0·75	1·0
p-Xylene	3·9	3·8	3·9	3·8
o-Xylene	3·5	3·5	3·4	3·5
m-Xylene	3·3	3·3	3·3	3·2
Toluene	3·0	3·0	3·0	3·0
Phenanthrene	1·6	1·8	1·7	1·8

[a] [Substrate] = 0·01 M; [HClO$_4$] = 0·75 M for toluenes and 0·50 M for phenanthrene; temperature = 313 ± 0·1 K.

Table 3. Dependence of reaction rate $[10^4 k_1 (s^{-1})]$ on substrate concentration[a]

| Compound | 10^2[substrate]/(M) | | | | |
	1·0	5·0	7·5	10·0	20·0
p-Xylene	3·8	18·5	27·0	38·0	75·0
o-Xylene	3·5	18·0	26·5	35·0	70·0
m-Xylene	3·2	16·2	23·0	32·5	64·0
Toluene	3·0	14·8	21·7	30·0	60·0
Phenanthrene	1·8	9·0	14·2	18·5	37·3
Phenanthrene[b]	1·80	1·80	1·89	1·85	1·87

[a] [QDC] = 0·001 M; [HClO$_4$] = 0·75 M for toluenes and 0·50 M for phenanthrene; temperature = 313 ± 0·1 K.
[b] $10^2 k_2$ (l mol^{-1} s^{-1}).

Table 1. Stoichiometry of the oxidation of substrates by QDC[a]

| Parameter | [HClO$_4$] (M) | | |
	0·10	0·25	0·50
10^2[QDC] (M)	2·50	2·60	2·70
$\Delta[QDC]/\Delta[p\text{-xylene}]$	1·18	1·10	1·02
$\Delta[QDC]/\Delta[phenanthrene]$	0·68	0·70	0·72

[a] [Substrate] = 0·005 M.

Table 4. Dependence of reaction rate [$10^4 k_1 (s^{-1})$] on acid concentration[a]

Compound	[HClO$_4$] (M)				
	0·25	0·50	0·75	1·0	1·25
p-Xylene	1·3	2·7	3·8	5·5	6·5
o-Xylene	1·2	2·5	3·5	5·0	6·1
m-Xylene	1·1	2·3	3·2	4·5	5·5
Toluene	1·0	2·1	3·0	4·2	5·0
Phenanthrene	0·9	1·8	2·6	3·7	4·6

[a] [Substrate] = 0·01 M; [QDC] = 0·001 M; temperature = 313 ± 0·1 K.

of such Cr(VI) species in chromic acid oxidations.[15a] Protonated Cr(VI) species have been observed in the presence of p-toluenesulphonic acid in nitrobenzene–dichloromethane mixtures.[16] The observed rate law is therefore

$$v = k[\text{substrate}] [\text{QDC}] [\text{H}^+] \qquad (3)$$

Effect of solvent

The dielectric constants for dimethylformamide–water mixtures were estimated approximately from the dielectric constants of the pure solvents and are recorded in

Table 5. A plot of log k_1 against the inverse of the dielectric constant was linear ($r = 0.990$), with a positive slope. This suggested an interaction between a positive ion and a dipole,[17] and was in consonance with the observation that in the presence of an acid the rate-determining step involved a protonated Cr(VI) species.

Effect of temperature

The reactions were studied at different temperatures and from the plots of log k_1 versus the reciprocal of temperature (Figure 1) the activation energies and other parameters were evaluated (Table 6) by the standard procedure.[18] The enthalpies and entropies of activation for the oxidation reaction were linearly related ($r = 0·988$). The correlation was tested and found to be valid by applying Exner's criterion.[19] The isokinetic temperature, obtained from the plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 359 K. Even though not much physical significance is attached to isokinetic temperatures, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a requirement for the validity of the Hammett equation.

Linear free energy relationship

An attempt was made to obtain a free energy relationship of the Hammett equation type in order to correlate

Table 5. Dependence of reaction rate [$10^4 k_1 (s^{-1})$] on solvent composition[a]

	DMF:H$_2$O				
	100:0 ($D^b = 37·6$)	95:5 ($D = 39·7$)	90:10 ($D = 41·8$)	85:15 ($D = 43·9$)	80:20 ($D = 46·1$)
p-Xylene	3·8	3·5	3·0	2·4	2·2
o-Xylene	3·5	2·6	2·2	1·9	1·7
m-Xylene	3·2	2·4	2·0	1·8	1·6
Toluene	3·0	2·3	1·9	1·7	1·5
Phenanthrene	1·8	1·4	1·1	0·9	0·7

[a] [Substrate] = 0·01 M; [QDC] = 0·001 M; [HClO$_4$] = 0·75 M for toluenes and 0·50 M for phenanthrene; temperature = 313 ± 0·1 K.
[b] Dielectric constant.

Table 6. Activation parameters[a]

Substrate	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
p-Xylene	51	– 149	98
o-Xylene	59	– 122	97
m-Xylene	61	– 117	98
Toluene	64	– 109	98
Phenanthrene	32	– 213	99
9-Methylphenanthrene	30	– 220	98
9-Methoxyphenanthrene	25	– 232	98
9-nitrophenanthrene	36	– 202	99

[a] Error limits: $\Delta H^{\neq}$ ±2 kJ mol^{-1}; $\Delta S^{\neq}$ ±3 J K^{-1} mol^{-1}; $\Delta G^{\neq}$ ±2 kJ mol^{-1}.
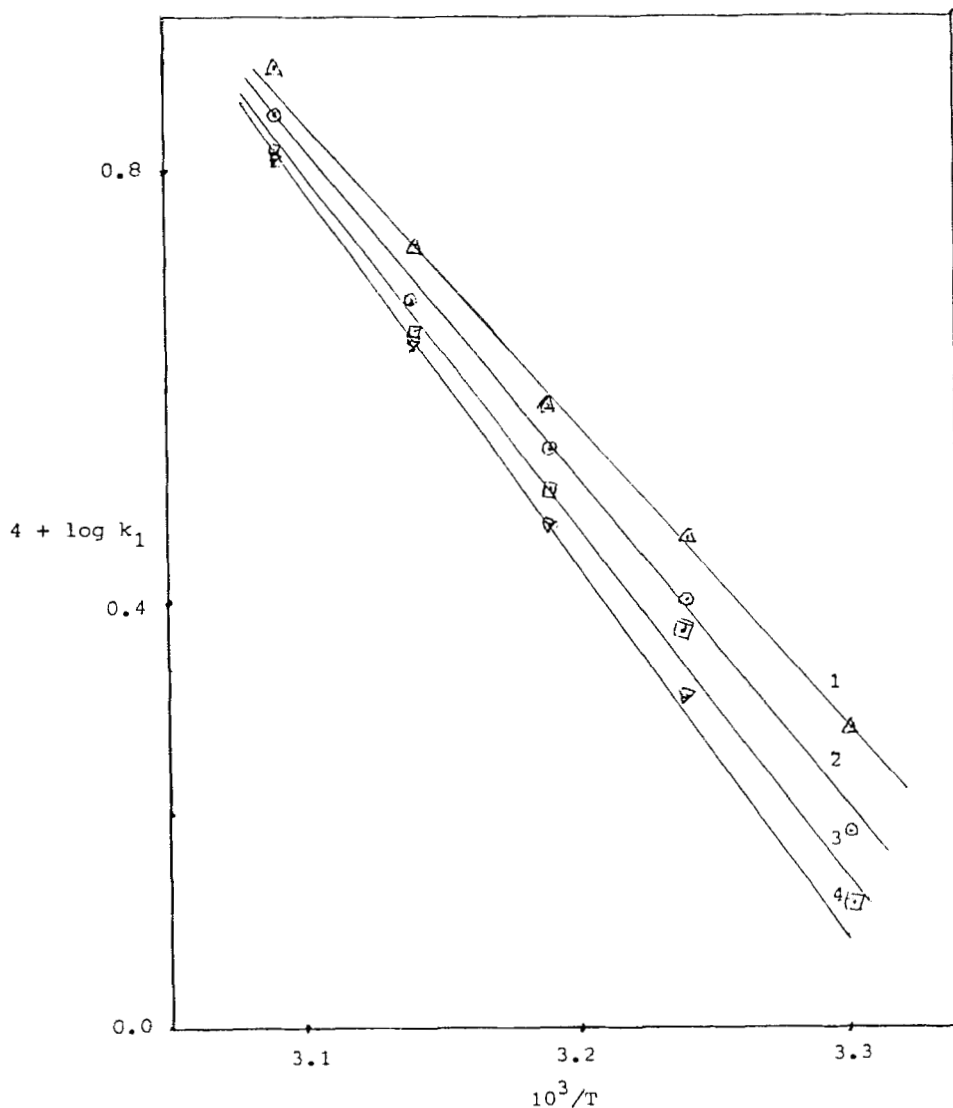
Figure 1. Plots of log k_1 versus inverse of temperature for (a) toluenes (1 = p-xylene; 2 = o-xylene; 3 = m-xylene; 4 = toluene) and (b) phenanthrene

the reactivity with the substituent constant.[20a] A plot of log k_1 versus the σ values of substituents (Figure 2) was linear ($r = 0.995$). The values of the reaction constants (ρ) were -0.20 for toluenes and -1.79 for phenanthrenes. For most hydrogen abstraction reactions the reaction constants (ρ) have small magnitudes.[20b]

Kinetic isotope effect

The kinetic isotope effect ($k_H/k_D = 5.13$) indicated the cleavage of the carbon–hydrogen bond of the methyl

group attached to the arene ring. The data are recorded in Table 7.

Table 7. Kinetic isotope effects for toluenes at 313 ± 0.1 K

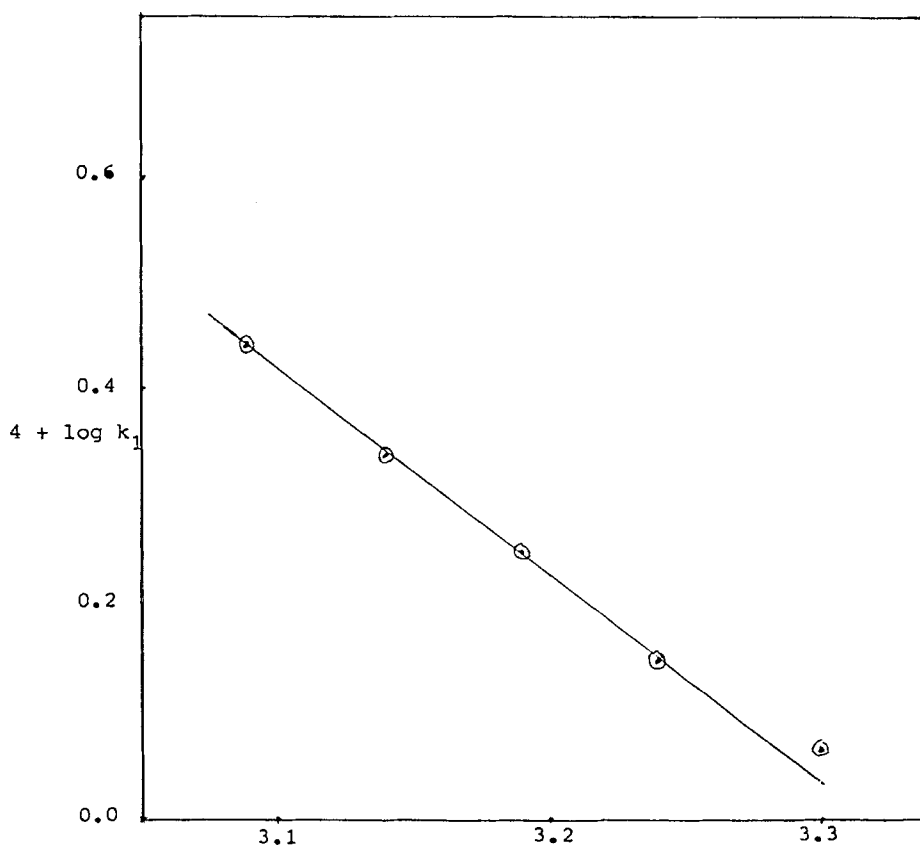| Substrate	$10^4 k_1$ (s^{-1})		
	ArCH$_3$ (k_H)	ArCD$_3$ (k_D)	k_H/k_D
p-CH$_3$C$_6$H$_4$—	3·8	0·73	5·2
o-CH$_3$C$_6$H$_4$—	3·5	0·70	5·0
m-CH$_3$C$_6$H$_4$—	3·2	0·62	5·2

Figure 1. (Continued)

Induced polymerization

As all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile or reduction of mercury(II) chloride.[21] Further, no ESR signals could be detected in each of the reactions studied (Model E-4 instrument, Varian). These results do not rule out free radical intermediates; they simply do not provide evidence that radicals are formed. This may be due to the high rate of oxidation of the free radicals. Control experiments were performed in the absence of the substrate. The concentration of QDC did not show any appreciable change.

Mechanism

Based on the observed experimental data, the mechanistic pathway of the reaction has to be considered. Although the reaction did not give any ESR signals and there was no evidence for the induced polymerization of acrylonitrile or the reduction of mer-

cury(II) chloride, the possibility of a hydrogen abstraction mechanism cannot be completely excluded. The radical formed initially would react rapidly with the Cr^{5+} species formed in the initial step, similarly to what has been observed in the oxidation of saturated hydrocarbons by chromium(VI) compounds.[15b] The significant kinetic isotope effect observed suggests considerable carbonium ion character in the transition state. The transition state could be considered as involving a carbon atom which would exist with both radical and carbonium ion character. Such types of intermediates have been reported in earlier investigations.[22-25] This resonance hybrid would possess lower energy than either the radical or the carbonium ion, which would account for the stability of the intermediate. The negative values of the reaction constant (ρ) observed in the oxidation reactions clearly indicated the possibility of a hydrogen abstraction mechanism. A cleavage of the carbon–hydrogen bond in the rate-determining step of the reaction was supported by the observed kinetic isotope effect, $k_H/k_D = 5 \cdot 13$ (Table 5).

The mechanistic pathway of the oxidation process

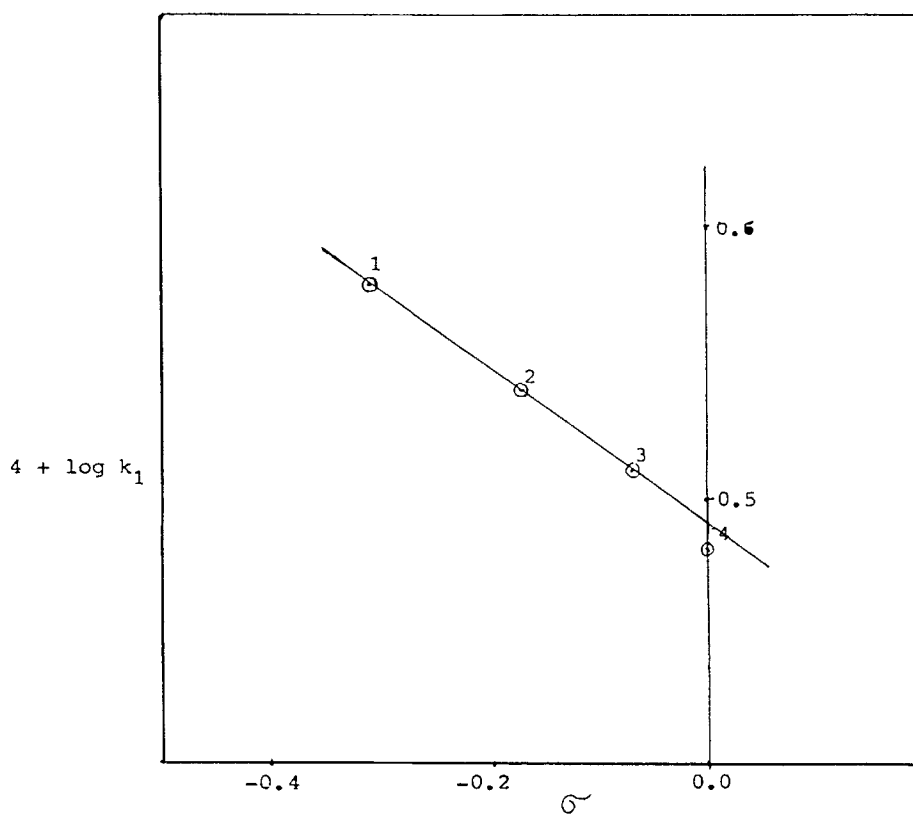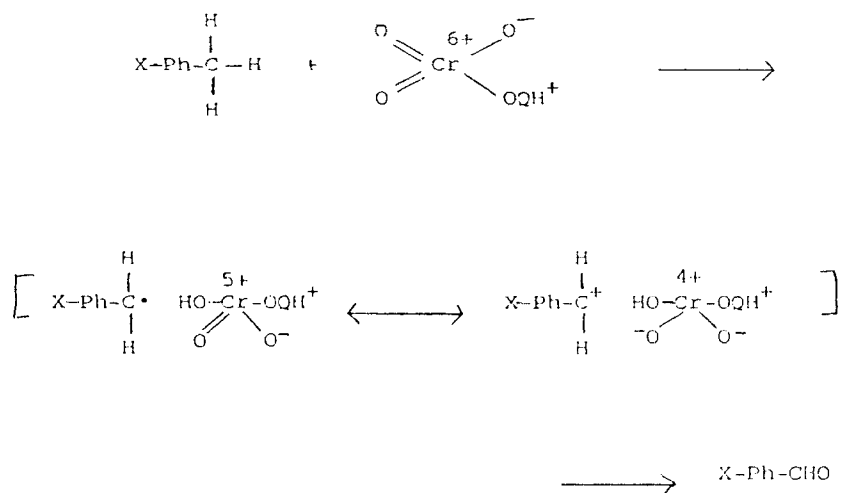Figure 2. Hammet plots for (a) toluenes (1 = p-xylene; 2 = o-xylene; 3 = m-xylene; 4 = toluene) and (b) phenanthrenes (1 = 9-methoxyphenanthrene; 2 = 9-methylphenanthrene; 3 = phenanthrene; 4 = 9-nitrophenanthrene
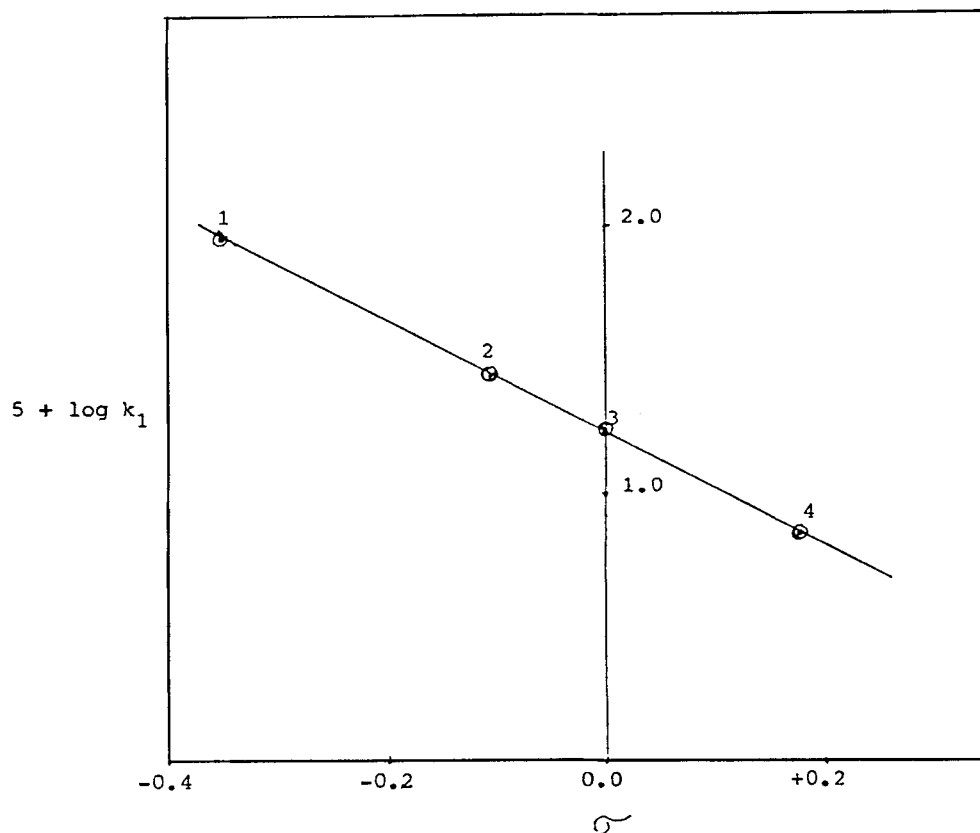

Scheme 1
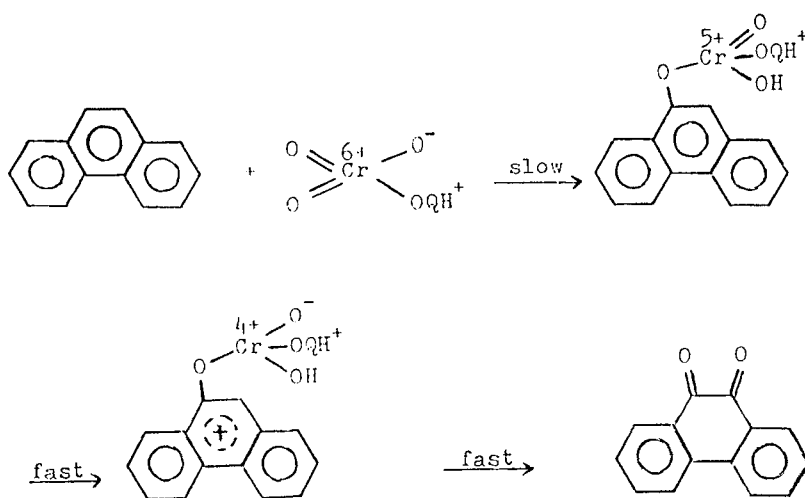
Figure 2. (*Continued*)

Scheme 2

would thus involve a cleavage of the carbon–hydrogen bond of the substituted group of the side-chain (for toluenes), followed by a rapid conversion of the resulting intermediate to give the product, the corresponding aldehyde (Scheme 1). The oxidation of *p*-cymene to *p*-(2-propyl)benzaldehyde indicates the selective oxidation of the methyl group to the aldehyde under the present reaction conditions. This also supports the proposed mechanism of the oxidation reaction.

The experimental results for the oxidation of phenanthrene point to a hydride ion transfer in the rate-determining step. The hydride ion transfer can occur directly or may involve the prior formation of a chromate ester (Scheme 2). The similarity in rate laws with that observed for chromic acid oxidation[15a] favours the formation of a chromate ester.

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