EXPERIMENTAL
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Conductivity Water:

Conductivity water was prepared by the following method: tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analyse" sulfuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). The conductivity water thus prepared was utilised for the preparation of all the solutions used in the kinetic determinations.

Perchloric Acid:

"Baker Analysed" reagent was used.

N,N-Dimethyl formamide:

Dimethyl formamide was purified by the following method: Anhydrous copper sulphate was prepared by heating copper sulphate (CuSO₄·5H₂O) until it turned white. The complete removal of water molecules was checked by its constant weight after repeated heating. Anhydrous copper sulphate was mixed with dimethyl formamide (SDS, AR grade), and the mixture was allowed to stand for 24 hours. The solution was filtered and the filtrate
was distilled under reduced pressure (b.p. 153°C). The
distillate thus collected was used as the solvent.

**Quinolinium dichromate (C₉H₇NH⁺)₂Cr₂O₇²⁻**

To a stirred solution of CrO₃ (100g) in water (100ml) cooled in ice, quinoline (86 ml) was added in small portions. The solution was diluted with acetone (400ml), cooled to -20°C, and the orange solid which separated out was filtered, washed with acetone, dried in vacuo and recrystallized from water (m.p. 160°C). The purity of the compound was further checked by spectral analysis. Infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730cm⁻¹, characteristic of the dichromate ion.

**Substrates:**

Toluene, xylenes, fluorene, substituted fluorenes, diphenylmethane, and triphenylmethane were E.Merck samples. Nitrotoluenes were obtained from Koch-Light Laboratories (U.K.). Naphthalene, substituted naphthalenes, phenanthrene and substituted phenanthrenes were BDH samples. All these substrates were purified by distillation or by repeated recrystallizations until their boiling points or melting points, respectively, were in agreement with literature values. The purity of each of the substrates
was checked by spectral analysis.

The methoxy toluenes were prepared by the following method:

A solution of 20g of sodium hydroxide in 200ml water and 30g of o-cresol were taken in a 500ml round bottom flask fitted with a separating funnel. The mixture was stirred well and cooled by immersing in an ice bath. 30ml of dimethyl sulphate was taken in the separating funnel and was added to the mixture, dropwise, during one hour, while the mixture was stirred vigorously. The mixture was refluxed, with stirring, for about 2 hours in order to complete the methylation. The mixture was cooled, transferred to a separating funnel, and the lower layer was removed. The upper layer was washed once with water, twice with dilute sulfuric acid, and again with water until the washings were neutral to litmus. The mixture was dried over anhydrous magnesium sulphate and the contents were distilled. The distillate (o-methoxytoluene) was collected at 171°C. The other isomers were prepared by using p-cresol and m-cresol respectively (b.p. of p-methoxytoluene = 174°C; m-methoxytoluene = 178°C). The purity of the three isomers was further checked by spectral analysis.

All ir spectra were recorded on an IR-297 (Perkin
Elmer spectrophotometer, UV spectra on an UV-26 (Beckman) spectrophotometer and nmr spectra on an EM-390 (Varian) 90MHz NMR spectrometer.

The boiling points, melting points and the spectral data obtained for each of the substrates used, are summarized in Table 1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Boiling points or melting points (°C)</th>
<th>UV (nm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td>110</td>
<td>261(H)</td>
</tr>
<tr>
<td>p-xylene</td>
<td>137.5</td>
<td>260(H)</td>
</tr>
<tr>
<td>o-xylene</td>
<td>144</td>
<td>262(M/W)</td>
</tr>
<tr>
<td>m-xylene</td>
<td>139</td>
<td>264 (M/W)</td>
</tr>
<tr>
<td>p-methoxy tolune</td>
<td>174</td>
<td>224 (A)</td>
</tr>
<tr>
<td>o-methoxy tolune</td>
<td>171</td>
<td>227 (A)</td>
</tr>
<tr>
<td>m-methoxy tolune</td>
<td>178</td>
<td>222 (A)</td>
</tr>
<tr>
<td>p-nitrotoluene</td>
<td>54 (m.p.)</td>
<td>217,285(A)</td>
</tr>
<tr>
<td>o-nitrotoluene</td>
<td>221</td>
<td>202,266,325(W)</td>
</tr>
<tr>
<td>m-nitrotoluene</td>
<td>232</td>
<td>203,273,315 (W)</td>
</tr>
<tr>
<td>Diphenylmethane</td>
<td>264</td>
<td>260(A)</td>
</tr>
<tr>
<td>Benzydrol</td>
<td>68.5 (m.p)</td>
<td>259(CH)</td>
</tr>
<tr>
<td>Triphenyl methane</td>
<td>95 (m.p.)</td>
<td>262(A)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>117.5 (m.p.)</td>
<td>206,260,301(A)</td>
</tr>
<tr>
<td>2-methoxyfluorene</td>
<td>108 (m.p.)</td>
<td>271,303(A)</td>
</tr>
<tr>
<td>2-methylfluorene</td>
<td>103 (m.p.)</td>
<td>265,305(A)</td>
</tr>
<tr>
<td>2-bromofluorene</td>
<td>114 (m.p.)</td>
<td>260, 290(A)</td>
</tr>
</tbody>
</table>
2-chlorofluorene 96 (m.p.) 266,295 (A)
2-nitrofluorene 157 (m.p.) 233 (A)
9-fluorenol 152 (m.p.) 270,305 (A)
Naphthalene 358 (m.p.) 220,275,301 (A)
1-methylnaphthalene 244 220,281 (H)
1-methoxynaphthalene 269.5 231,293 (cH)
1-nitronaphthalene 61 (m.p.) 333 (A)
Phenanthrene 102 (m.p.) 250,293,346 (A)
9-methylphenanthrene 90 (m.p.) 252,297,331 (A)
9-bromophenanthrene 63 (m.p.) 256,302,334 (cH)
9-nitrophenanthrene 116 (m.p.) 207,243,250 (A)
9-methoxyphenanthrene 96 (m.p.) 247,274,305 (A)

* A = alcohol; W = water; cH = cyclohexane; H = hexane; M/W = methanol-water mixture.

**Deuterated Compounds:**

All the deuterated compounds used were obtained from Isotopes Inc., USA.

(a) ArCD₃(Ar=X-Ph, where X was -CH₃, -OCH₃, -NO₂). The nmr spectrum of each of the samples in CCl₄ did not show any absorption for the methyl protons.

(b) 9,9-dideuteriofluorene: the nmr spectrum of this sample in CCl₄ did not show the absorption for the protons at the 9-position.

(c) Naphthalene-d₈: nmr analysis did not show the absorption for the proton at the 8-position.
(d) Diphenylmethane-d$_2$ was prepared by the known method(1), and its purity was checked by nmr analysis.

**Acrylonitrile**

The monomer (BDH) was washed with 5% sodium hydroxide solution to remove the inhibitor (hydroquinone), and then with 3% orthophosphoric acid to remove any basic impurities. It was then washed with water, dried over anhydrous calcium chloride, and distilled under reduced pressure in an atmosphere of nitrogen. The middle fraction was collected (b.p. 77°C) and used.

**Other reagents**

All other reagents used were of Analar grade, and were purified before use, and their boiling points/melting points were checked, and found to agree with those given in the literature.

**Kinetic Method:**

All the standard flasks and reaction vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered conical flasks which were painted black on the outside to prevent any photochemical change. All the glass apparatus used were tested for loss
of solvent, and the loss was found to be negligible. The standard flasks, reaction vessels and the pipettes used were standardised, using conductivity water, and the correction was found out and applied.

An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperature accurately, with fluctuations of not more than ±0.1°C. The temperatures were recorded by means of an accurate sensitive thermometer, reading to tenths of a degree. The bath-liquid was water, covered with a layer of liquid paraffin to minimise evaporation of water and loss of heat due to radiation.

Spectrophotometers

For absorption measurements, the spectrophotometers used were: (a) Digital spectrophotometer Type 106 (Systronics), and (b) UV26 (Beckman) UV-Visible spectrophotometer.

(a) The Type 106 Digital spectrophotometer was a single beam spectrophotometer having a grating of
600 lines/mm, and a wavelength range from 340nm to 960nm. The nominal spectral slit width was 20nm, constant over the entire range. The full scale deflection could be obtained over the wavelength range of 340nm to 600nm. By the addition of a red filter and interchanging of the phototube, the range could be extended to 960nm. In order to ensure maximum sensitivity of the instrument, and to minimize the errors in measurements of optical density due to fluctuations in voltage, the spectrophotometer was connected to the mains through an external voltage stabilizer. This was in addition to the in-built voltage stabilizer within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The instrument was calibrated, as specified in the instruction manual, over the range of concentrations of \( \text{K}_2\text{CrO}_4 \) in KOH solutions, so as to verify Beer's law at 370nm.

(b) The UV-26 (Beckman) UV-Visible spectrophotometer was a single monochromator, having a filter grating of 1200 lines/mm, and a wavelength range from 190nm to 900nm. This spectrophotometer had a thermostatic control arrangement and the absorbance value was displayed directly on the digital display and on the recorder. Photometric linearity was checked over the range of...
concentrations of $K_2CrO_4$ in KOH solutions, as specified in the instruction manual, so as to verify Beer's law at 370nm.

**Absorption cells**

The absorption cells were of 'Corning' glass and of 8ml capacity for the spectrophotometer Type 106 (Systronics). Quartz cells of 5ml capacity were used for spectral determinations with the UV-26 spectrophotometer (Beckman). All the cells were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken to see that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

**Rate measurements**

A known amount of the substrate was weighed accurately into a 10ml standard flask, dissolved and made up with the requisite quantities of dimethyl formamide, so as to make the solutions of the required molarity. Quinolinium dichromate was accurately weighed out into a 10ml standard flask, dissolved and made up in dimethyl formamide. Sufficient time was allowed
to compensate for any change of heat during dilution. A known volume of perchloric acid was taken in a 10ml standard flask and made up with distilled water so as to make the solution of required strength. The three solutions were separately thermostated at the required temperature for 1 h, under a nitrogen atmosphere. Equal volumes of the two solutions of oxidant and perchloric acid were mixed. An equal volume of the substrate solution was then introduced, and the reaction mixture mixed well. The reaction mixture was homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of Cr(VI). Readings were taken at regular intervals of time, by noting the decrease in optical density at 440nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or in triplicate, and the rate constants which were determined were found to be reproducible to within ±3%. All reactions were performed under a nitrogen atmosphere. Since the reactions were performed at high concentrations of acid, the ionic strength was not maintained constant.
Calculations

(a) Rate constants:

For all the kinetic determinations, pseudo-first-order reaction conditions have been used, wherein the concentration of the substrate has been taken in a very large excess over that of the concentration of the oxidant.

The pseudo-first-order rate constant, \( k_1 \), expressed as \( \text{sec}^{-1} \), were calculated from the equation (2):

\[
 k_1 = \frac{2.303}{t} \log \frac{D_0}{D_t} \tag{1}
\]

where \( D_0 \) was the initial optical density of the reaction mixture, and \( D_t \) was the optical density at time \( t \).

The logarithmic plots of optical density against time were linear, and extrapolation to zero time gave the values of \( D_0 \).

The values of the second order rate constant, \( k_2 \), expressed in \( \text{M}^{-1}\text{s}^{-1} \), were computed by dividing the pseudo-first-order rate constant (\( k_1, \text{s}^{-1} \)) by the concentration of the substrate (M).

All values of rate constants were the average of two or more experiments, with agreement being within ±3%.
(b) **Thermodynamic activation parameters:**

These parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows:

(i) **Activation energy (E):**

From the linear plot of \( \log k_1 \) against the reciprocal of temperature \( T \),

\[
\text{Slope} = -\frac{E}{2.303R}
\]

\[
E = -\text{Slope} \times 2.303R \quad (\text{kJ mol}^{-1})
\]

(ii) **Enthalpy of activation \((\Delta H^\#)\)**

\[
\Delta H^\# = E - RT
\]

\((\text{kJ mol}^{-1})\)

(iii) **Entropy of activation \((\Delta S^\#)\)**

\[
k_1 = \frac{kT}{h} e^{\frac{\Delta S^\#}{R}} e^{-\frac{\Delta H^\#}{RT}}
\]

\[
\Delta S^\# = 2.303R \left[ \log k_1 + \frac{\Delta H^\#}{2.303RT} - \log \frac{kT}{h} \right]
\]

\((\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\)

where \( k \) is the Boltzmann constant, \( h \) is the Planck's constant, and \( R \) is the gas constant.
(iv) **Free energy of activation** ($\Delta G^\neq$):

$$\Delta G^\neq = \Delta H^\neq - T\Delta S^\neq$$

(kJmol$^{-1}$)

**Stoichiometry**

The stoichiometric experiments were carried out under nitrogen at 313K, under the conditions of $[\text{QDC}]_0 > [\text{Substrate}]_0$, at varying acid concentrations. The disappearance of Cr(VI) was followed, until the absorbance values became constant. The $[\text{QDC}]_\infty$ was estimated.

The stoichiometric ratio, $\Delta[\text{QDC}] / \Delta[\text{Substrate}]$ was obtained, for each oxidation reaction studied. The individual stoichiometric equations have been shown along with the reactions of each of the substrates with the oxidant.

**Product analysis**

The reactions were carried out in a manner similar to the kinetic experiments (using an excess of the substrate) and were allowed to proceed to completion, keeping the reaction mixture for about 24 hours, in an atmosphere of nitrogen. The products obtained from the reaction of the various substrates with the oxidant were isolated as follows:
(a) **Product from the oxidation of toluene, xylenes, methoxytoluenes, nitrotoluenes, diphenylmethane, triphenylmethane and fluorene:**

At the end of the reaction, the reaction mixture was diluted with ice-water saturated with sodium chloride, neutralised with NaHCO$_3$, and was extracted several times with ether. The ether extract was washed with water, dried over anhydrous MgSO$_4$, and then concentrated. The characterization of the products was carried out as follows:

(i) Spotting on TLC plates showed two spots for the products obtained from the oxidation of toluene, xylenes, methoxy toluenes and nitrotoluenes. Separation was effected on an alumina column, using varying proportions (100:0 to 70:30, v/v) of hexane and chloroform as the eluant. The product obtained with lesser proportions of chloroform was tested for the aldehyde by TLC, in the case of toluene and all the substituted toluenes. One spot was obtained when the chromatogram was sprayed with 2,4-dinitrophenyl hydrazine. An aliquot (5ml) was pipetted into 50ml of 2N HCl saturated at 0°C with 2,4-dinitrophenyl hydrazine. The aldehyde was converted to the 2,4-dinitrophenyl hydrazone, which was filtered, washed, dried and weighed. The yields were calculated from the amounts of the 2,4-dinitrophenyl-
hydrazone formed, and were found to vary between 75-85% for all the substrates. The melting points of the corresponding 2,4-dinitrophenylhydrazones were determined after one or more recrystallizations from ether. The corresponding m.p.'s of the 2,4-DNP derivatives thus prepared are shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Oxidation product</th>
<th>Melting point (°C) of 2,4-DNP derivatives prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>Benzaldehyde</td>
<td>235</td>
</tr>
<tr>
<td>p-xylene</td>
<td>p-tolualdehyde</td>
<td>232</td>
</tr>
<tr>
<td>m-xylene</td>
<td>m-tolualdehyde</td>
<td>193</td>
</tr>
<tr>
<td>o-xylene</td>
<td>o-tolualdehyde</td>
<td>192</td>
</tr>
<tr>
<td>p-methoxytoluene</td>
<td>p-methoxy benzaldehyde</td>
<td>253</td>
</tr>
<tr>
<td>m-methoxytoluene</td>
<td>m-methoxy benzaldehyde</td>
<td>244</td>
</tr>
<tr>
<td>o-methoxy toluene</td>
<td>o-methoxy benzaldehyde</td>
<td>250</td>
</tr>
<tr>
<td>p-nitrotoluene</td>
<td>p-nitro benzaldehyde</td>
<td>318</td>
</tr>
<tr>
<td>m-nitrotoluene</td>
<td>m-nitro benzaldehyde</td>
<td>290</td>
</tr>
<tr>
<td>o-nitrotoluene</td>
<td>o-nitro benzaldehyde</td>
<td>264</td>
</tr>
</tbody>
</table>

Further proof for the formation of the corresponding aldehyde was obtained by isolating the aldehyde, using the standard method(3). IR analysis gave a sharp band at 1700cm\(^{-1}\), which was characteristic of the carbonyl stretching for an aldehyde group attached to an aryl ring. Two weak bands at 2850cm\(^{-1}\) and 2750cm\(^{-1}\) were
characteristic of the C-H stretching.

The second product, obtained in about 5-10\% yield, was a polymeric material, which could not be characterized.

(ii) Spotting on TLC plates showed two spots for the product obtained from the oxidation of fluorene. The crude product was chromatographed on a silica gel column using varying proportions (100:0 to 70:30, v/v) of hexane and chloroform for elution. The product obtained with lesser proportions of chloroform was found to be identical with 9-fluorenone (m.p.=82\(^{\circ}\)C), which was further characterized by IR (absorption at 1750cm\(^{-1}\)) and UV analyses (in cyclohexane, absorption at 257nm, 295nm and 378nm). The yield of the product, 9-fluorenone, was \(\sim 85\%\). The product obtained with higher proportions of chloroform was coloured, and could not be analyzed further, since it underwent polymerization. An analysis of the products of the reaction mixture did not show the presence of fluorenol or of any ketal.

(iii) Spotting on TLC plates showed one spot each for the products obtained from the oxidation of diphenylmethane and triphenylmethane.
Product from diphenylmethane: An aliquot (5ml) was pipetted into 50ml of 2N HCl saturated at 0°C with 2,4-DNP. The product was filtered, washed, dried and weighed. The yield was calculated from the amount of 2,4-dinitrophenylhydrazone formed. The melting point was taken after one or more recrystallizations from ether (m.p. = 236°C). Yield ~85%.

The remainder of the solution was taken in 20ml benzene. The benzene layer was separated, washed with 5% NaOH, then with water, and dried over anhydrous MgSO₄. The excess benzene was removed by distillation and the product was collected. On solidification, a white solid was obtained (m.p. = 48°C). The IR spectrum exhibited a carbonyl band at 1670 cm⁻¹ and certain other bands characteristic of benzophenone(4).

Product from triphenylmethane: This product was identified as the tertiary alcohol, triphenylcarbinol. The IR spectrum gave sharp bands, at 3620 cm⁻¹ (O-H stretching), 1360 cm⁻¹ (C-O stretching), and 1150 cm⁻¹ (O-H bending), characteristic of triphenylcarbinol. Yield ~80%.

Product from the oxidation of Naphthalene

The reaction mixture was neutralized with NaHCO₃, extracted with chloroform, washed with water, dried
over anhydrous MgSO$_4$ and concentrated. Spotting on TLC plates showed two spots. The crude product was chromatographed over a neutral alumina column, using hexane and benzene in varying proportions (100:0 to 70:30, v/v) as the eluant. The product obtained with increasing proportions of benzene was found to be identical with 1,4-naphthoquinone (m.p. = 124°C). IR analysis showed sharp bands at 1690 and 1680 cm$^{-1}$, characteristic of the carbonyl stretching for polynuclear quinones. There was approximately 60-70% conversion of the naphthalene to the product. The second product was the starting naphthalene (~30%), indicating that the actual yield of the product was higher than the percent conversion.

**Product from the oxidation of Phenanthrene**

The reaction mixture was cooled, filtered, and washed with water. The solid obtained was suspended in ethanol, 20ml of sodium metabisulfite solution was added, and the mixture allowed to stand for 30 minutes. 50ml of water was added, and the mixture was filtered. To the filtrate, saturated sodium carbonate solution was added. The precipitate was stirred, filtered, and washed with water. The solid obtained (orange yellow needles) was dried over calcium chloride in a desiccator.
(yield ~60%, m.p.=209°C; product: 9,10-phenanthroquinone).

Tests for Radical formation

Many of the oxidation reactions investigated were observed to proceed via radical intermediates formed in the rate-determining step of these reactions. The presence of these radical intermediates was observed by the following tests:

(a) Reduction of inorganic ions,

\[ R. + M^{(n+1)+} \rightarrow R^+ + M^{n+1} \]

Mercuric chloride was easily reduced by these radicals to insoluble mercurous chloride, which was relatively inert towards reoxidation by the oxidant \( M^{n+} \).

(b) Polymerization of an added olefinic monomer, such as acrylonitrile.

1ml acrylonitrile (0.02M) and 2ml of substrate solution (0.2M) in DMF and \( \text{HClO}_4 \) (1.5M) were placed in the lower part of a Thunberg tube(5). 2ml of oxidant solution (0.02M) in DMF was placed in the upper part of the tube. The system was evacuated, and filled with dry nitrogen. The two solutions were mixed and allowed to stand at 313K for 30 minutes. There was the formation
of a white opalescence indicating the formation of a polymer. Each experiment was accompanied by a blank control.

ESR measurements

The presence of radical intermediates formed in the slow step of the reaction was detected and confirmed by ESR measurements.

Using the requisite reaction conditions, the radicals were generated, in a flow system (E-4, Varian), by mixing the substrate and oxidant, by volume, in an esr sample tube just outside the cavity of the spectrometer. The mixture was placed under high vacuum, in order to expel dissolved oxygen and the sample tube was placed in the cavity of the spectrometer. The conditions for obtaining the spectrum at 77K were as follows:

Scan range 4000G, field set 3300G, modulation amplitude 6.3G, microwave frequency 9.45GHz, time constant 0.3 sec, scan time 4 minutes.
REFERENCES


