EXPERIMENTAL
PURIFICATION OF MATERIALS

Conductivity water:

Conductivity water used for the preparation of standard solution and in runs for freezing the aliquots was prepared by the following method.

Tap water was distilled first with alkaline potassium permanganate and then distilled with Merck "pro analyse" sulphuric acid from all glass vessel. This was followed by boiling off the dissolved carbon dioxide.

Acetic acid:

Acetic acid BDH (AR) was refluxed with chromic anhydride with addition of a quantity of acetic anhydride corresponding to the water content of acetic acid. The solid that had separated out was filtered off and the acid was distilled from an all glass apparatus. Large head and tail fractions were rejected and the fraction distilling at 118°C was collected (Orton and Bradfield 1924,1927) b.p. 118°C, nD 30 1.368, d430 1.038.

Toluene: AR grade toluene was first treated with anhydrous calcium chloride, filtered, placed over sodium wire and then redistilled, b.p. 110.6°C, nD 30 1.496, d430 0.87.

P-xylene: BDH (AR) sample was used, b.p. 144.4°C nD 30 1.507, d430 0.897.

m-xylene: E.Merck (German) analar grade sample was used. b.p. 139°C, nD 30 1.499, d430 0.87.

m-bromotoluene: Fluka sample was used as such after distillation using an air condenser b.p. 180 183°C.
p-bromotoluene: p-bromotoluene was prepared by the method of vogel. A solution of cuprous bromide was prepared by refluxing 31.5 gms of crystallised copper sulphate, 10 gms of copper turning, 77 gms of sodium bromide, 8.2 c.c. of concentrated sulphuric acid and 500 c.c. of water in a 2.5 lit. round bottomed flask over a flame for four hours until the solution pertained a yellowish colour. A small quantity of sodium bisulphite was added to complete the reduction.

To 53.5 gms of p-toluidine and 400 ml of water in a one lit. flask 53 c.c. of concentrated sulphuric acid was added and warmed till the solid disappeared. The contents were cooled in ice and some crushed ice was added to accelerate the cooling. To this solution (0 to 5°C) a solution of sodium nitrite (35 gms in 60 c.c. water) was added with constant stirring till a slight excess of sodium nitrite was present. Temperature was maintained below 10°C.

The 2.5 lit. flask containing the cuprous solution was equipped for steam distillation. A separatory funnel containing p-tolyldiazonium sulphate was fitted to it. The cuprous bromide solution was heated to boiling and p-tolyldiazonium sulphate solution was added in small lots. The steam distillation was continued until no more of organic matter distilled out.

The steam distillate was made alkaline with 20% sodium hydroxide solution and p-bromotoluene was separated out. The crude product was washed with
50 c.c. of warm (30°C) concentrated sulphuric acid, then with water, sodium hydroxide solution and finally with water. It was dried over anhydrous magnesium sulphate and distilled through an air cooled condenser.

b.p. 182 - 184°C

p-chlorotoluene: BDH sample was distilled before use.
 b.p. 162.5°C.

m-chlorotoluene: BDH sample was distilled before use.
 b.p. 162°C.

Phenol: BDH(AR) sample, b.p. 182°C was used after distillation.

p-cresol: BDH sample was used after distillation
 b.p. 201.9°C.

m-cresol: BDH sample was used after distillation
 b.p. 202.7°C.

p-nitrophenol: BDH sample was used m.p. 114°C.

Glycine: Loba (GR) sample was used as such.

L-phenylalanine: BDH sample was used as such.

L-Leucine: BDH sample was used as such.

L-Valine: BDH sample was used as such.

L-alanine: BDH sample was used as such.

Cinnamic Acid: BDH sample was recrystallised from hot water preserved in dark m.p. 133°C.

m-methyl cinnamic Acid: Fluka sample was used as such.
Other substituted Cinnamic Acids:

The substituted cinnamic acids were prepared according to the method of Vogel. 0.33 mole of the corresponding aromatic aldehyde and 0.72 mole of malonic acid previously dried at 90 to 100°C for two hours were mixed in 150 c.c. of dry pyridine and 2.5 c.c. of piperidine contained in a 500 c.c. round bottomed flask and heated under reflux for six to fortyeight hours. Finally the reaction was completed by boiling the reaction mixture for some time. The contents were cooled and poured in to excess of water containing hydrochloric acid to combine with pyridine. The solid that separated was filtered off, washed with water and dried. It was finally recrystallised.

p-methyl cinnamic acid: from p-tolualdehyde, heated for six hours, recrystallised from glacial acetic acid
m.p. 172°C.

m-nitro cinnamic acid: from m-nitrobenzaldehyde, heated for 48 hours, recrystallised from alcohol m.p. 205°C.

p-bromocinnamic acid: from p-bromobenzaldehyde, refluxed for 48 hours, recrystallised from glacial acetic acid, m.p. 247°C (decomposes).

p-chlorocinnamic acid: from p-chlorobenzaldehyde, refluxed for 48 hours, recrystallised from glacial acetic acid, m.p. 250°C.
m-chloro cinnamic acid: from m-chlorobenzaldehyde, refluxed for 48 hours, recrystallised from glacial acetic acid, m.p. 161°C.

Ferrous ammonium sulphate:
BDH (AR) sample was used for preparing the solution.

Potassium dichromate:
BDH (AR) sample was used for standardisation.

Perchloric acid:
E.Merck (GR) sample (70%) was used as such after standardisation. For low acid concentration, stock solutions were prepared with distilled water and from this, the required volumes were used for obtaining acid concentration.

Potassium iodide:
BDH (AR) reagent was used as such.

Sodium thiosulphate:
BDH (AR) reagent was used.

Starch:
BDH (AR) grade (soluble) sample was used.

Sulphuric acid:
BDH (AR) reagent was used.

Ceric ammonium nitrate:
BDH (AR) sample was used for preparing the solution.

Ru(III) chloride:
Ru(III) chloride (Johnson Mathey, London) analar sample was dissolved in water containing very dilute hydrochloric acid. The solution was standardised by the method of Houriuchi et al.

An aqueous solution containing 0.1 to 3.5 mg of Ru(III) per 100 c.c. was treated with an excess of EDTA, adjusted the
PH 4 to 4.5 with 1(N) HNO₃ and 20% ammonium acetate and heated to 100°C for 10 minutes. Then it was cooled and adjusted to pH 1.8 and the excess of EDTA was titrated with Bi⁺³ solution in presence of xylenol orange as indicator.

From the standard stock Ru(III) solution exact volumes were taken with a standard micropipette so that desired concentration could be maintained in the reaction mixture.

Preparation of solvent mixtures:

Solvent mixtures were prepared by mixing known volumes of the solvents. The volume of each solvent mixture thus prepared was enough to permit all kinetic runs to be performed using the same batch and thus errors due to possible variations in composition were avoided. The dielectric constants of the various binary solvent mixtures have been computed assuming linearity in the range of solvent composition in the present work. Such assumptions have been made by previous workers (Wiberg and Evans 1958). Variation of dielectric constants with temperature has been taken into consideration. For acetic acid water mixtures the values of Smyth and Rogers (1930) were used.

Kinetic method:

All the standard flasks and reaction bottles were of pyrex glass with well ground stoppers. To prevent photochemical reactions the reaction vessels were painted black from outside. All of them were tested for loss of solvent and the loss was found to be negligible. The volumetric apparatus i.e. the pipettes, burettes and the standard flasks were standardised by the usual method taking conductivity water. Corrections were found out and applied.
An electrically operated thermostatic waterbath operating through a Jumo GKU 10 relay and a Jumo (German) contact thermometer was used. It was provided with sufficient thermal lagging, suitable heaters and mechanical stirrers with proper cooling arrangements for continuous work. The bath temperature was maintained constant with minimal fluctuations of not more than ±0.02°C. Temperature was recorded by means of an accurate sensitive thermometer reading to tenth of a degree.

The bath liquid was water covered with a thick layer of liquid paraffin to minimise the evaporation of water and loss of heat due to radiation.

Velocity measurement:

A known amount of the substrate was accurately weighed into a 100 ml standard flask and made up with solvent or solvent mixtures to achieve the required molar concentration.

The oxidising/brominating agent along with required amount of supplement chemicals (including a definite amount of the catalyst in case of catalysed reactions) was taken in another 100 c.c. flask. Desired acid concentration and ionic strength were maintained by adding requisite amount of HClO₄, H₂SO₄ and NaClO₄ to this flask and the solutions were made up with desired solvent/solvent mixtures. Sufficient time was allowed to compensate for any change due to heat during dilution. The flasks containing the substrate, oxidising/brominating agent along with the clean and dry reaction vessels were thermostated for at least two hours before mixing the reactants. Correction for solvent expansion was applied in both the cases while calculating the molarity.
50 c.c. of each of the solutions was used for the experiment. First the substrate solution was pipetted out into the reaction vessel by means of a calibrated standard 50 c.c. pipette. After allowing a little more time to compensate for slight temperature variations 50 c.c. of the oxidising/brominating solution (standardised just before mixing) was added with a standard rapid delivery pipette, the instant of half delivery being noted as zero time. The vessels were stoppered and shaken well. The progress of the reaction was followed by withdrawing 5 c.c. aliquots at various time intervals, discharging into a known excess of appropriate freezing solution and then analysing the contents. Self decomposition of the oxidant/brominating agent due to solvent was also routinely checked and corrections, where ever necessary were applied.

For fast runs accurate stop watches were used.

The pseudo first order rate constants expressed as
were calculated from the integrated expression,

\[ k_{obs} = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \]

where 'a' is the initial molar concentration of the oxidant/brominating agent and 'x' is the concentration reacted at time 't' i.e., (a-x) is the residual concentration at time 't'.

For reactions zero order in the oxidant, the zero order rate constants \( k_0 \) = \( x/t \), where 'x' is the concentration reacted at time 't'.

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All the experiments were carried out in duplicate to ensure reproducibility and the results were reproducible within 3% error. For fast runs, the experiments were repeated at least thrice and the mean value of the rate data not differing by more than 5% was taken into record.

**Analytical method**

**Bromination/Oxidation with NBA**

In acid medium NBA was estimated iodometrically in accordance with the equation,

\[ \text{CH}_3\text{CONHBr} + 2\text{I}^- + \text{H}^+ = \text{CH}_3\text{CONH}_2 + \text{Br}^- + \text{I}_2. \]

5 c.c. aliquot of NBA solution was dumped into a mixture of iodate free potassium iodide solution containing a pinch of sodium bicarbonate and 2N H\textsubscript{2}SO\textsubscript{4}. It was allowed to stand in dark for three minutes. The liberated iodine was titrated against standard thiosulphate solution to the conventional starch iodine end point.

**Oxidation by Ce(IV)**

5 c.c. aliquot of Ce(IV) solution was dumped into a measured volume of standard ferrous ammonium sulphate solution in presence of 25 c.c. of 4 N H\textsubscript{2}SO\textsubscript{4}. The residual ferrous ions were titrated against a standard dichromate solution using N-phenylanthranilic acid as indicator.

**Oxidation by Lead tetra acetate**

5 c.c. aliquot of Pb (IV) solution was dumped in to 10 c.c. of 5% potassium iodide solution containing 1 gm of (AR) Sodium acetate. The liberated iodine was titrated against standard thiosulphate solution to a starch end point.
Thermodynamic functions of activation

According to the theory of absolute reaction rate (Glasstone, Laidler and Eyring, 1941) the following expression may be written for the rate co-efficient $k_r$ of a reaction.

$$k_r = \frac{kT}{h} K^+ e^{-\left(\frac{\Delta F^+}{RT}\right)}$$

$$= \frac{kT}{h} e^{-\frac{\Delta H^+}{RT}} \frac{\Delta S^+/R}{e^{\frac{\Delta H^+}{RT}}}$$

where $k$ = Boltzmann constant

$K^+$ = Constant for equilibrium between the reactants and the activated complex.

$\Delta F^+$ = Standard free energy of activation

$\Delta H^+$ = Enthalpy of activation

$\Delta S^+$ = Entropy of activation.

It has been assumed that the transmission co-efficient is unity. For reactions in solution the heat and entropy of activation can be calculated from the experimentally determined values of parameters of Arrhenius equation.

$$\Delta H^+ = E_a - RT$$

and $$\Delta S^+ = R \left[ \ln \frac{A_h}{kT} \right]$$

The standard state with respect to which the thermodynamic constants have been calculated is one mole per liter.