Kinetics of Ceric Ion Oxidation of Naphthalene and Its Derivatives. Formation of the Radical Cation Intermediate in the Rate Limiting Step

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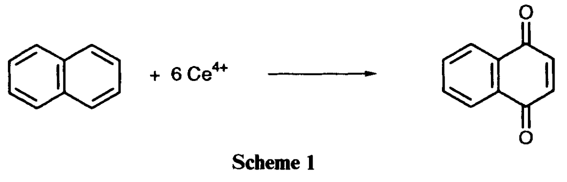
Ceric ammonium sulfate, CAS, oxidizes naphthalene to 1,4-naphthoquinone in essentially quantitative yield in CH_3CN–dil. H_2SO_4. Stoichiometric studies indicate that 6 mol of CAS are required for the oxidation of 1 mol of naphthalene to 1,4-naphthoquinone. Kinetic investigations reveal that the reaction takes place through initial formation of a 1 : 1 complex of naphthalene and cerium(IV) in an equilibrium step followed by slow decomposition of the complex to naphthalene radical cation. Kinetic results on the effects of acid strength, polarity of the medium, temperature and substituents are in accordance with this mechanism. Further conversion of the radical cation into 1,4-naphthoquinone takes place in fast steps involving a further 5 mol of cerium(IV) and 2 mol of H_2O.

Even though kinetics of ceric ion oxidation of organic substrates such as alcohols, ketones, glycols and aromatic side chains have been fairly well studied,[1] data on the kinetics of cerium(IV) oxidation of aromatic rings are meagre. Trahanovsky and Brixius investigated the ceric ammonium nitrate, CAN, oxidation of substituted 1,2-diphenylethanes by competition experiments and found that the products are benzaldehydes, benzyl alcohols and benzyl nitrates.[2] They have obtained a Hammett ρ value of -4.61 and concluded that the reaction goes through the formation of the corresponding radical cation in the rate limiting step. Gorbachev and Vabel reported that the ceric sulfate oxidation of naphthalene in acetic acid–sulfuric acid mixture exhibited first-order dependence on each reactant with an activation energy of 14 kcal mol^{-1}.[3] Product analysis and stoichiometry of the reaction were not studied, rendering the kinetic data of doubtful mechanistic significance.

In the course of our efforts towards oxidation of aromatic rings with single electron-transfer oxidants,[4–7] we have undertaken a detailed kinetic investigation of the ceric ion oxidation of naphthalene and its derivatives. We describe the results of this investigation here.

Results and Discussion

Stoichiometry.—We have previously observed that 1,4-naphthoquinone is obtained in 90–95% yield in the oxidation of naphthalene using 6 mol proportion of ceric ammonium sulfate, CAS, in 2 mol dm^{-3} sulfuric acid and CH_3CN.[4] Also, stoichiometric studies have been carried out under conditions similar to those followed for kinetic studies by taking naphthalene in excess over CAS in 70% CH_3CN–H_2O, 0.2 mol dm^{-3} H_2SO_4 at 30 °C (see Experimental section for details). The amount of 1,4-naphthoquinone formed and cerium(IV) utilized are summarized in Table 1.[8] The results are in accordance with the stoichiometry as given in Scheme 1.

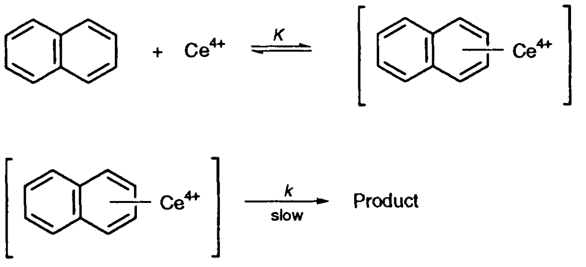


Scheme 1

Kinetics.—In most of the kinetic studies, a 70 : 30 mixture of acetonitrile–water (by volume) was used as solvent at a sulfuric acid concentration of 0.2 mol dm^{-3}. Naphthalene was taken in excess (20–30 times) to that of cerium(IV) concentration and the progress of the reaction was followed by determining the change in concentration of cerium(IV) with time. It was observed that plots of $\log(C_t)$ against time, where C_t is the concentration of cerium(IV) in the reaction mixture, measured at time t, are linear, indicating the first-order dependence on cerium(IV). Correlation coefficients of 0.998–0.999 were obtained for such plots under various conditions. No curvature was observed over 80% of the reaction. The rate law of the reaction can be described by eqn. (1), where k_1 stands for the pseudo-first-order

$$\frac{-d[Ce^{4+}]}{dt} = k_1[Ce^{4+}] \qquad (1)$$

rate constant. The observed rate constant k_1 was constant over a 0.0005–0.0030 mol dm^{-3} range of $[Ce(IV)]_0$. The variation of k_1 with $[naphthalene]_0$ levelled off at higher concentrations, suggesting a pre-equilibrium such as shown in Scheme 2.[9,10]



Scheme 2

The rate law for Scheme 2 can be derived to give the expression shown in eqn. (2).[11] Comparison of eqn. (2) with the experimental rate eqn. (1) gives the eqns. (3) and (4).

$$\frac{-d[Ce^{4+}]}{dt} = \frac{kK[\text{Naphthalene}][Ce^{4+}]}{1 + K[\text{Naphthalene}]} \qquad (2)$$

$$k_1 = \frac{kK[\text{Naphthalene}]}{1 + K[\text{Naphthalene}]} \qquad (3)$$

$$\frac{1}{k_1} = \frac{1}{kK[\text{Naphthalene}]} + \frac{1}{k} \qquad (4)$$

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Table 1 CAS oxidation of naphthalene—stoichiometric analysis

			1,4-Naphthoquinone		
Entry	Ce^{4+}/mol dm^{-3}	OD[a]	g dm^{-3}	mol dm^{-3}	Ce^{4+}/1,4-naphthoquinone
1	0.002 0	0.19	0.051 39	0.000 325 2	6.15
2	0.002 5	0.24	0.064 91	0.000 410 8	6.09
3	0.004 0	0.38	0.102 77	0.000 650 4	6.15
4	0.006 0	0.57	0.154 16	0.000 975 6	6.15

[a] Optical density, at 347 nm, of the solution obtained by dissolving the product isolated from 25 cm^3 of the reaction mixture in 100 cm^3 of methanol (see Experimental section for details).

Table 2 CAS oxidation of naphthalene at different concentrations of H_2SO_4[a]

Entry	$[H_2SO_4]/[Li_2SO_4]$ (mol dm^{-3})	10^4 k/s^{-1}	K/dm^3 mol^{-1}
1	0.20/0.10	3.68	12.54
2	0.23/0.07	6.14	11.13
3	0.26/0.04	10.50	8.53
4	0.29/0.01	21.07	6.08

[a] [Cerium(IV)] = 0.001 mol dm^{-3}; CH_3CN, 50%; H_2O, 50%; T = 30 °C.

Table 3 CAS oxidation of naphthalene—effect of water present in the medium[a]

Entry	$\%CH_3CN/\%H_2O$ (v/v)	10^4 k/s^{-1}	K/dm^3 mol^{-1}
1	75/25	4.69	7.16
2	70/30	5.50	6.93
3	65/35	7.07	6.65
4	60/40	7.76	7.26

[a] [Cerium(IV)] = 0.0025 mol dm^{-3}; $[H_2SO_4]$ = 0.20 mol dm^{-3}; T = 30 °C.

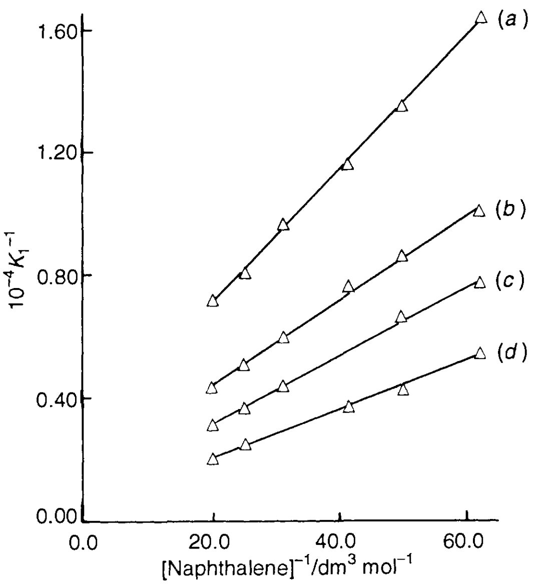

Fig. 1 CAS oxidation of naphthalene at various concentrations of H_2SO_4: $[H_2SO_4]$/mol dm^{-3} 0.20 (*a*), 0.23 (*b*), 0.26 (*c*), 0.29 (*d*)

Reasonable linear correlations (correlation coefficient 0.995–0.998) have been observed under various conditions (*e.g.* Fig. 1). From the slope ($1/kK$) and intercept ($1/k$), the rate constant k in units of s^{-1} and the equilibrium constant K in units of dm^3 mol can be calculated (see entry 1, Table 2). We have undertaken kinetic investigations under various conditions in order to obtain information about the nature of the intermediates involved in the reaction.

Effect of Acid Strength.—The effect of change in acid concentration was studied in 50% acetonitrile, in the sulfuric acid concentration range of 0.20–0.29 mol dm^{-3}. Precipitation of cerium salts occurred when the sulfuric acid concentration was less than 0.20 mol dm^{-3}. Lithium sulfate was added so that the total concentration of sulfuric acid and lithium sulfate was 0.30 mol dm^{-3}. Plots of $1/k_1$ *vs.* $1/[\text{naphthalene}]_0$ at various $[H_2SO_4]$ are shown in Fig. 1. The values of k and K are given in Table 2.

The cerium(IV) species exist as sulfated complexes in sulfuric acid. It has been reported that in the range of acidity used in the present work (0.20–0.29 mol dm^{-3}), the di- and tri-sulfated complexes, $Ce(SO_4)_2$ and $[Ce(SO_4)_3]^{2-}$ are predominant.[12] These species will be in a series of equilibria with H^+ as follows.[13,14]

$$[Ce(SO_4)_3]^{2-} + H^+ \rightleftharpoons [HCe(SO_4)_3]^-$$

$$[HCe(SO_4)_3]^- + H^+ \rightleftharpoons [H_2Ce(SO_4)_3]$$

$$[H_2Ce(SO_4)_3] + H^+ \rightleftharpoons [H_3Ce(SO_4)_3]^+$$

The increase in acid concentration would increase the concentrations of protonated forms of cerium(IV) species. Since the net positive charge of the cerium(IV) will be increased in this way, the transfer of electron from the aromatic ring to the cerium(IV) would take place more readily. Hence, increase of acid concentration increases the rate of decomposition, k, of the naphthalene–Ce^{4+} complex where the electron transfer from naphthalene to Ce^{4+} takes place. Since Ce^{4+} is a one-electron oxidant this decomposition product would most probably be the corresponding radical cation. However, the reason for decrease in the equilibrium constant with increase in acid concentration is not clearly understood.

Effect of Water Present in the Medium.—Kinetic studies were carried out at the CH_3CN compositions of 60%, 65%, 70% and 75%. In all cases, plots of 1/[naphthalene] against $1/k_1$ give good linear relationships. The values of K and k obtained are given in Table 3. It is apparent from the data that increase in water concentration of the medium (*i.e.* 75% to 60% CH_3CN) does not alter the equilibrium constant, K, of the association step but facilitates decomposition of the complex to Ce(III) and naphthalene radical cation.

Effect of Temperature.—The temperature dependence of the cerium(IV) oxidation of naphthalene was studied in 70% CH_3CN and 0.20 mol dm^{-3} H_2SO_4 at 20, 26, 30 and 35 °C. The values of K and k obtained from the reciprocal plots are summarized in Table 4. The values of the equilibrium constant K decreases with increase in temperature as expected. From the Arrhenius plot of $1/T$ *versus* log k and assuming $E_a = \Delta H + RT$, the values $E_a = 24.35 \pm 1$ kcal mol^{-1}, $\Delta H = 23.75 \pm 1$

Table 4 Effect of temperature on the CAS oxidation of naphthalene[a]

Entry	T/K	$10^4\,k/\text{s}^{-1}$	$K/\text{dm}^3\,\text{mol}^{-1}$
1	293	1.43	8.08
2	299	3.03	7.75
3	303	5.50	6.93
4	308	10.87	5.32

[a] [Cerium(IV)] = 0.0025 mol dm^{-3}; [H_2SO_4] = 0.20 mol dm^{-3}; CH_3CN, 70%; H_2O, 30%.

Table 5 CAS oxidation of substituted naphthalenes[a]

Entry	Naphthalene	$10^4\,k/\text{s}^{-1}$	$K/\text{dm}^3\,\text{mol}^{-1}$
1	2-Methyl	18.74	11.02
2	2-*tert*-Butyl	4.56	15.08
3	2-Chloro	1.18	2.07
4	1-Methyl	17.53	6.19
5	1-Phenyl	52.21	1.87
6	1-Bromo	0.915	4.87

[a] [Cerium(IV)] = 0.0025 mol dm^{-3}; [H_2SO_4] = 0.20 mol dm^{-3}; CH_3CN, 70%; H_2O, 30%; T = 30 °C.

kcal mol^{-1}, $\Delta G^{\ddagger} = 21.65 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6.88 \pm 0.5$ cal mol^{-1} K^{-1} were evaluated.*[,15] The positive value of entropy of activation indicates that the rate limiting step is dissociative in nature. This result is in accordance with the suggested mechanism (Scheme 2) involving the decomposition of the cerium(IV)–naphthalene complex in the rate determining step and could be a consequence of a less ordered transition state.

Effect of Substituents.—Substituted naphthalenes on CAS oxidation give mixtures of quinones, through oxidation of the ring carrying the substituents and also the unsubstituted ring. Kinetic data on the cerium(IV) oxidation of 1- and 2-substituted naphthalenes reveal that in all cases the Michaelis–Menten kinetic behaviour is observed (Scheme 2). The values of the equilibrium constants K and the rate constants k obtained for various substituted naphthalenes are given in Table 5. The data indicate that the decomposition of the cerium(IV)–naphthalene complex is facilitated by electron-donating substituents, in accordance with the transfer of an electron from naphthalene ring to Ce^{4+} in this step. The reactions of 1-nitro- and 1-cyanonaphthalene are too slow to measure the rate and with 1- and 2-methoxynaphthalene, the reactions are too fast.

Isotopic Effect.—In order to examine whether there is any C–H bond breaking in the transition state, we employed [1,4-$^2H_2$]naphthalene for kinetic studies. We have found that the K and k values obtained in this case are essentially the same as those observed for naphthalene, indicating the absence of C–H bond breaking in the transition state.

Conclusions

The results of the kinetic investigations reveal that the reaction proceeds by initial complex formation between cerium(IV) and naphthalene followed by decomposition of the complex in the slow step. Since cerium(IV) is a single electron oxidant, the decomposition product of the cerium(IV)–naphthalene complex should be the naphthalene radical cation. Results of various kinetic investigations undertaken to probe the nature of the transition state of the rate limiting step are also in accordance with this interpretation.

Further conversion of the naphthalene radical cation to 1,4-naphthoquinone, involving a further 5 mol of cerium(IV) takes place through fast steps. We have previously reported 1,2-shifts of substituents (^{2}H, Br and Ph) in the cerium(IV), manganese(III) and anodic oxidation of 1- and 1,4-di-substituted naphthalenes to the corresponding 2- and/or 2,3-di-substituted 1,4-naphthoquinones which throw light on the mechanism of the conversion of the radical cation to the 1,4-naphthoquinone.[4–7] These results also help in the understanding of the NIH shift observed in the hydroxylation of aromatic rings with certain monooxygenases.[16–19]

Experimental

Methods and Materials.—Naphthalene used for the kinetic investigations was purified by column chromatography (silica gel; eluent, hexane) and sublimed twice and further crystallized twice (ethanol) and dried *in vacuo*; m.p. 80 °C; $\lambda_{\max}$(hexane)/nm 221 (log ε 5.08) and 275 (log ε 3.81). Substituted naphthalenes were prepared following cited procedures. All reagents used were of reagent grade. Acetonitrile was purified by distilling over anhydrous P_2O_5 after keeping over anhydrous sodium sulfate for 48 h. Distilled water was further distilled twice over $KMnO_4$; it was distilled again before use.

Kinetics.—Solutions of naphthalene in acetonitrile and sulfuric acid were taken in the reaction flask and closed with a stopper. Ceric ammonium sulfate, $2(NH_4)_2SO_4{\cdot}Ce(SO_4)_2{\cdot}2H_2O$, in sulfuric acid was kept in a separate flask. Both the flasks were kept in a thermostat maintained at the required temperature to within ±0.1 °C. The solutions were given 1 h to attain thermal equilibrium. Reactions were started by adding a known volume of CAS solution into the reaction flask. Aliquots were pipetted out at regular intervals into conical flasks containing known volume of excess of standard ferrous ammonium sulfate in H_2SO_4 (1 mol dm^{-3}). The contents were then diluted to 25 cm^3 with water and titrated against standard CAS in H_2SO_4 (1 mol dm^{-3}) using ferroin as indicator; 2 drops of 0.0001 mol dm^{-3} ferroin solution, end point being red to colourless. Subtracting the titre value for a particular time from the value required for the known excess of ferrous ammonium sulfate solution, the titre value equivalent to the cerium(IV) content in the reaction mixture was determined. The cerium(IV) concentrations at different times were then graphically analysed for the order of the reaction. Calculations of rate constants and other kinetic parameters were carried out using a least squares linear curve fitting program. The rate constants k_1 are results of duplicate runs and are reproducible within ±3%.

Stoichiometry.—Stoichiometric studies were carried out under conditions similar to those used in kinetics, by taking naphthalene in considerable excess over that of CAS in 70% CH_3CN, 0.20 mol dm^{-3} H_2SO_4 at 30 °C. After completion of 30–40 half-lives (~30 h), a known volume of the reaction mixture was extracted with ether, successively four or five times. The ether extracts were combined, washed twice with water, dried over anhyd. Na_2SO_4 and the solvent was removed under reduced pressure. The amount of 1,4-naphthoquinone present in the mixture was determined by dissolving it in methanol and measuring the absorbance at 347 nm (ε 2339).[8] Blank estimates showed that naphthalene did not interfere with the absorbance of 1,4-naphthoquinone at this wavelength. The amount of 1,4-naphthoquinone was calculated from the relation

$$\text{Naphthoquinone (g dm}^{-3}) = \frac{A^{347}}{14.79 \times b}$$

where A^{347} is the absorbance (optical density) and b is the

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* 1 cal = 4.18 J.

thickness of the cell used (1 cm). The factor 14.79 is the specific absorptivity of 1,4-naphthoquinone at 347 nm, obtained by dividing the value of molar absorptivity, ε, by the molecular weight. The stoichiometric analysis carried out in this way is summarized in Table 1.

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