J. Indian Chem. Soc.,
Vol. LX, June 1983, pp. 554-556

Ceric-Cerium Oxidation of *ortho*-Cresol

R. G. VARMA*

P.M.B. Gujarati Science College, Indore

and

R. L. YADAV

Holkar Science College, Indore

Manuscript received 11 May 1982, revised 8 November 1982, accepted 19 March 1983

Ceric-cerium and *ortho*-cresol have been found to form an 1 : 1 complex with λ_{max} at 440 mμ. The thermodynamic parameters of kinetics of the oxidation have been evaluated. The experimental findings are consistent with the postulate that the rate determining step in the reaction involves the disproportionation of a coordinate complex formed by the reactants, giving rise to products through free radical formation.

THE oxidation of cresols by various oxidants in different media has been studied previously[1-9]. Literature reveals that the kinetics of oxidation of *ortho*-cresol by cerium(IV) has been almost overlooked. The present investigation was, therefore, undertaken to elucidate the kinetics of *ortho*-cresol oxidation by cerium(IV).

Experimental

Materials : The chemical used were either of AnalaR or E. Merck G. R. quality. Triple distilled water was used throughout the investigation.

Kinetics measurements :

Equal volumes (25 ml) of ceric ammonium sulphate solution (in 2 *N* H_2SO_4) and *ortho*-cresol solution (in 30% HAc), both of known concentration were brought to the temperature of the thermostat and then rapidly mixed. At regular intervals, 5 ml samples of the reaction mixture were withdrawn into a conical flask containing ice-cold water to quench the reaction. The amount of unchanged oxidant in the reaction mixture was estimated volumetrically with standard Mohr's salt solution using 2-4 drops of Ferroin as indicator.

Stoichiometry and product analysis :

To study the overall oxidation product, a reaction mixture containing a known excess of ceric-cerium over the organic substrate was kept for 48 hr. The unreacted oxidant was estimated. It was found that one mole of *ortho*-cresol required two mols of ceric sulphate for complete oxidation.

$$CH_3C_6H_4OH + 2Ce(IV) + H_2O = CH_3C_6H_4O_2 + 2Ce(III) + 3H^+$$

It was observed that on mixing the reactants, the initially yellow colour mixture turns light orange in colour which becomes dirty green and ultimately the solution becomes blackish brown. The change in colour suggests that the oxidation of *ortho*-cresol proceeds through different stages of oxidation. The reaction mixture containing one gram of the organic substrate was steam distilled after oxidation when a yellow compound distilled over. This was extracted with ether and crystallised in a vacuum desiccator. This compound was identified as *p*-toluquinone, yield 0.8630 g, m.p. 71°. TLC with an authentic sample also confirms the product. The yield was approx. 75% which is slightly lower than the theoretical calculated value. Besides this, three unidentifiable products (tlc) were also obtained.

Test for organic free radical :

Ceric-cerium with many organic substrates have been reported to act as redox initiators for vinyl polymerisation[10-13], though ceric-cerium alone can initiate polymerisation of methylmethacrylate (MMA). In the present investigation ceric-cerium solution, in presence or in absence of organic substrate, was flushed with nitrogen to expel oxygen from the system, before the addition of MMA[14]. It was visually observed that the rate of polymerisation markedly enhanced and the viscosity increase with lapse of time was more in the ceric-cerium-*ortho*-cresol redox system than in the system without the organic substrate. No quantitative estimation was carried out.

Complex formation :

It was found that a blackish brown colour developed when the oxidant and the organic subs-

---

* Author for correspondence ; Address : 4/2, Parsi Mohalla, Indore-452 001.

trate were mixed together. This has a maximum optical density of 0.70 in comparision to the optical density of 0.16 at λ_{max} 440 mμ, of the light yellow oxidant. Job's method of continuous variation[15] showed the formation of 1 : 1 complex.

Results and Discussion

It was observed that the rate of oxidation in the given range of concentration [Ce(IV) : 0.869-1.00$\times 10^2 M$; *o*-cresol : 12.50-14.28$\times 10^4 M$] proceeded satisfactorily at measurable rate, but became kinetically immeasurable if an attempt was made to increase or decrease the concentration range of either the oxidant or the organic substrate. The experimental results indicate a significant retarding effect of cerium(III) specially in the lower concentration of the organic substrate and higher concentration of oxidant. This was further confirmed in a separate experiment in which cerous salt was added from outside. The duplicate rate measurements were found to be reproducible within ±2%.

The reaction obeys first order rate law with respect to cerium(IV) and the organic substrate. Because of the limitations of the rate measurable concentrations, a large variation in concentration of oxidant or organic substrate was not possible though the values in any particular run were found to be fairly constant. However, the slight deviation in values of rate constant in any particular run may be attributed to the retarding effect of cerium(III) and some side reactions which may progressively slow down with the formation of the complex.

Influence of temperature on rate constant :

The reaction velocities were measured at four different temperatures. The Arrhenius equation was found to be valid in the temperature range studied. The values of thermodynamic parameters are recorded in Table 1.

TABLE 1—EFFECT OF TEMPERATURE ON RATE CONSTANT

10^4 [*ortho*-cresol] = 12.50 *M* ; 10^2 [Ce (IV)] = 1.0 *M* ; [HAc] = 30% (v/v) ; [H_2SO_4] = 1.0 *M*

Temp. K	10^2 k_1 min^{-1}	ΔS e.u.	pZ$\times 10^4$ min^{-1}	ΔH kcal/mol.	ΔF kcal/mol.	ΔE kcal/mol.
298	1.05±0.01	−43.89	1.833	6.600	20.280	
303	1.46±0.01	−43.66	2.091	6.590	20.440	7.196
308	1.68±0.01	−43.81	1.978	6.580	20.690	(mean)
313	2.30±0.01	−43.63	2.192	6.570	20.840	

The results of ceric-cerium oxidation of *ortho*-cresol are interesting. The frequency factor for unimolecular decomposition processes is usually more than 10^{10} sec^{-1}. The low value of the frequency factor observed in the present investigations suggests that the activated complex is more rigid than the initial stage. This is also evident from the negative value of the entropy of activation. This may be compared with the values obtained in the case of catechol[16]. This further suggests that a free radical is involved in the reaction mechanism. In fact, the negative value of entropy of activation and high value of the free energy shows that the rate of reaction is immeasurably slow but it is coupled with low value of activation energy which makes the reaction rate measurable.

Inhibiting effect of sulphuric acid :

It is observed that the values of rate constant decrease on increasing the sulphuric acid concentration. The decrease in rate with increase in [H_2SO_4] is due to the existence of various complexes in solution (Eq. 1)

$$Ce^{4+} + x\,HSO_4^- \rightleftharpoons Ce(SO_4)_x^{4-2x} + x\,H^+ \quad \ldots (1)$$

In addition, equilibrium (2) will also be operating

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \quad \ldots (2)$$

The sulphatocerate complex being less active, there is retardation as observed. It is reported[17] that if the [sulphate ion] is constant and if [H_2SO_4] is increased above the [sulphate], there will be increase in rate as the equilibrium (1) is shifted to the left and the equilibrium (2) is negligibly affected.

It appears that the inhibiting effect observed on increasing [H_2SO_4] may be mainly due to bisulphate ion by forming the species[18] $H.Ce(SO_4)_3^-$.

Effect of solvent composition on rate constant :

It is observed that the values of rate constant increases with increasing percentage of acetic acid. This may be attributed to the fact that an increase in acetic acid content decreases the dielectric constant of the solvent[19] and increases the protonation which suppresses the formation of bisulphate ion responsible for removing active oxidant species from the reaction field.

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^-$$

Effects of salts on rate constant :

The effect of inorganic salts on reaction rate was found to be insignificant. It was, therefore, not felt necessary to keep the ionic strength constant.

All the experimental observations lead to the fact that the reaction proceeds through the formation of a complex which slowly decomposes to give reaction products through free radical.

$$\begin{tikzcd} \mathrm{Ce(IV)} + ortho\text{-cresol} \arrow[r, rightleftharpoons, "\text{fast}"] & \text{Complex} \arrow[d, "\text{slow}"] \\ & \text{Products} \end{tikzcd}$$

References

1. R. G. R. BACON, R. GRIME and D. J. MUNRO, *J. Chem. Soc.*, 1954, 2275.
2. A. SEIGEL and F. ANTONY, *Monatsh*, 1955, **86**, 292.
3. D. H. R. BARTON, FLOURING and O. E. EDWARDS, *J. Chem. Soc.*, 1956, 530.
4. G. V. KHARITONOV, *Tekh. Nauk*, 1958, 111.
5. YA. A. AARANA, K. R KIISLER and V. T. PALUOYA, *Tallinsk Polytekh. Inst.*, Ser. A, 1958, No. 153-66-77.
6. H. I. JOSCHEK and S. I. MILLER, *J. Amer. Chem. Soc.*, 1966, **88**, 3273.
7. U. KEISO, K. KUIV and M. GUBERGRITS, *Zh. Prikl. Khim.*, 1967, **40**, 1583.
8. U. GLABISZ, *Chem. Tech. (Berl.)*, 1967, **19**, 352.
9. G. ZEMPLEN and L. KISFALUDY, *Chem. Ber.*, 1960, **93**, 1125.

10. A. A. Katyal, V. K. Kulshrestha and R. H. Marchessault, *J. Polymer Sci.*, 1955, C-2, 403.
11. M. Santappa and V. S. Annathanarayan, *Proc. Indian Acad. Sc.*, 1965, 62, 105.
12. S. V. Subramanian and M. Santappa, *Current Science*, 1966, 35, 437.
13. S. K. Saha and A. K. Choudhary, *J. Polymer Sci.*, 1971, A-1, 1505.
14. P. Levesley and W. A. Waters, *J. Chem. Soc.*, 1955, 217; 1956, 215.
15. P. C. Job, *Annals Chim.*, 1928, 9, 113.
16. R. L. Yadav and R. G. Varma, *J. Indian Chem. Soc.*, 1981, 58, 768.
17. R. C. Mehrotra and S. K. Mishra, *J. Indian Chem. Soc.*, 1967, 44, 927.
18. T. J. Hardwick and Robertson, *Cand. J. Chem.*, 1951, 29, 828.
19. F. H. Westheimer and A. Novic, *J. Chem. Phys.*, 1943, 11, 506.