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THE MECHANISM OF OXIDATION OF ALKYLAROMATIC COMPOUNDS BY METAL IONS. II.RELATIVE REACTIVITIES IN THE REACTION OF POLYMETHYLBENZENES WITH CERIC AMMONIUM NITRATE IN ACETIC ACID.[1]

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Recently we have determined orientation and positional selectivity in the side-chain oxidation of alkylaromatic compounds by ceric ammonium nitrate (CAN).[1] In this note we report on the substrate selectivity of the same reaction.

The oxidation reactions of some polymethylbenzenes promoted by CAN were investigated in acetic acid, at 20°, in the dark and under nitrogen. A careful product study showed that under these conditions the reaction leads exclusively to the formation of side-chain substituted products, nitrates and acetates. The sole exception was the reaction of mesitylene, where nuclear acetoxylation (~25%) was also observed. With one hydrocarbon (hexamethylbenzene) the stoichiometry of the reaction was determined. We found that 2 moles of CAN are necessary to oxidize one mole of substrate. Kinetics were carried out in the thermostatted cell compartment of a Beckman DBGT spectrophotometer and the disappearance of Ce(IV) was followed at 400 nm (ϵ 9.7 x 10^2 M^{-1} cm^{-1}). The concentration of the hydrocarbon (between 2 x 10^{-3} and 4 x 10^{-1} M, depending on its reactivity) was always in excess with respect to that of CAN (1-2 x 10^{-3} M).

Although first order in aromatic compound, the reaction does not follow a simple kinetic law since the apparent order in Ce(IV) is larger than 1 and increases as the CAN concentration increases. Moreover the reaction is subject to strong salt effects. Thus, the times for 5% of reaction, at constant initial CAN concentration, were used to evaluate the relative rates of oxidation reported in the Table.

The reaction is very sensitive to the electronic effects of substituents, a strong accelerating effect being produced by the progressive introduction of methyl groups. Hexamethylbenzene is revealed as ca. 10^5 fold more reactive than

Table

Kinetic data for the oxidation reactions of some polymethylbenzenes with CAN in acetic acid at 20°C

Substrate	$[CAN]=1.04\times10^{-3}$M		$[CAN]=2.11\times10^{-3}$M	
	$10^3\ t_{5\%}\,[RH]^a$ sec M	k_{rel}^b	$10^3\ t_{5\%}\,[RH]^a$ sec M	k_{rel}^b
Hexamethylbenzene	2.9×10	3.3×10^2	1.1×10	3.2×10^2
Pentamethylbenzene	9.2×10^2	1.0×10		
Durene	9.6×10^3	1	3.5×10^3	1
Isodurene	4.3×10^4	2.2×10^{-1}		
Pseudocumene	1.6×10^6	6.0×10^{-3}		
Mesitylene	2.0×10^6	4.8×10^{-3}		

(a) Time at 5% of reaction ($t_{5\%}$) multiplied by the concentration of substrate. Each value is the average of several determinations. The average error is ±4%.

(b) Rate relative to durene.

mesitylene. Thus, in spite of the relatively low positional selectivity[1], the oxidation reaction by Ce(IV) appears characterized by high substrate selectivity.

Interestingly, a good linear relationship (r = 0.998) is obtained when $-RT\ln k_{rel}$ ($\Delta G^{\neq}_{rel}$) for the oxidation of polymethylbenzenes is plotted against the charge-transfer transition energies ($h\nu_{CT}$) of the corresponding TCNE-complexes[2] (Figure). The high value of the slope (0.7)[3] indicates that a substantial amount of electron transfer has taken place in the transition state and therefore suggests that radical cations are involved in the reaction mechanism[4]. The remarkable difference between substrate and positional selectivity clearly indicates that, in the oxidation by CAN, rate and products are determined in different steps. While any mechanism involving a direct attack of Ce(IV) on the CH_3 group can be ruled out[5], our data might be consistent with the mechanism reported in the following scheme[6] if step (1) is rate determining:

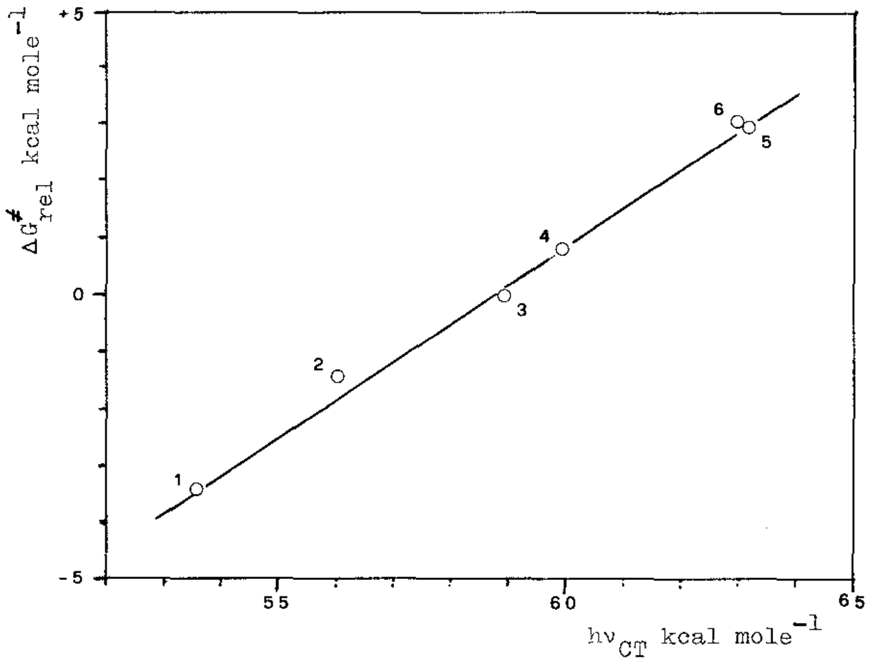

Figure. $\Delta G^{\neq}_{rel}$ for the oxidation by Ce(IV) of: (1) hexamethylbenzene; (2) pentamethylbenzene; (3) durene; (4) isodurene; (5) pseudocumene; (6) mesitylene, against charge-transfer transition energies of the corresponding TCNE-complexes.

$$ArCH_3 + Ce(IV) \rightleftharpoons ArCH_3^{+\cdot} + Ce(III) \qquad (1)$$

$$ArCH_3^{+\cdot} \longrightarrow ArCH_2\cdot + H^+ \qquad (2)$$

$$ArCH_2\cdot + Ce(IV) \longrightarrow \text{Products} \qquad (3)$$

and one assumes (in order to rationalize the order in Ce(IV) larger than 1) the intervention of dimeric and (or) polymeric forms of Ce(IV)[7]. Further work aimed at obtaining information in this respect is in progress.

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(3) If the rate data are plotted against the vertical ionization potentials[2] (which are linearly related to $h\nu_{CT}$) a slope of 0.56 is obtained.

(4) Formation of radical cations has been also recently suggested in the oxidation of alkylbenzenes by $Ce(OCOCF_3)_4$ in CF_3COOH (R.O.C. Norman, C.B. Thomas and P.J. Ward, J.Chem.Soc. Perkin I, 2914 (1973)), a reaction which leads mostly to the formation of biaryls and diarylmethanes, and in the oxidation of 1,2-diarylethanes by CAN in H_2O-CH_3CN (W.S. Trahanovsky and D.W. Brixius, J.Am.Chem.Soc., 95, 6778 (1973)). In the latter reaction the radical cation undergoes fragmentation to a benzyl radical and a benzyl cation instead of losing an α-proton.

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