

PATHWAYS IN AROMATIC OXIDATIONS BY PIA

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A kinetic study of the oxidation of phenanthrene and acenaphthene by phenyliodosoacetate (PIA) in aqueous acetic acid-perchloric acid medium is reported. The order with respect to oxidant, substrate(s) and acid is each unity. A suitable mechanism is proposed and a corresponding rate law derived.

Описывается кинетическое исследование окисления фенантрена и фенилиодозоацетата в среде водной, уксусной и перхлорной кислоты. Порядок по отношению к окислителю, субстрату (ам) и кислоте каждый равен единице. Приводится вероятный механизм и выводится соответствующее уравнение скорости.

INTRODUCTION

The kinetics and mechanism of oxidation of diols /1/; α -hydroxyacids, aromatic amides /2/ sugars /3/ and organic sulfides /4/ by PIA have been reported earlier. While in case of all the substrates except sulfides a slow breakdown of the initial complex of the substrate and $\text{Ph-I}^+-\text{OAc}$ has been invoked, a simultaneous attack of H_2O and $\text{Ph-I}^+-\text{OAc}$ on the protonated sulfur atom occurs in the rate determining step in case of the sulfides. As regards to aromatic hydrocarbons, our investigations revealed that benzenoid and side chain substituted benzenoid hydrocarbons are resistant to oxidation by PIA, but hydrocarbons like phenanthrene and acenaphthene underwent facile oxidation under mild conditions. Hence a kinetic study of the oxidation of the hydrocarbons by PIA is undertaken to get an insight into the mechanism.

EXPERIMENTAL

Phenanthrene and acenaphthene were recrystallized and their melting points checked before use. Perchloric acid and acetic acid were of (BDH) AnalaR grade. Phenyliodosoacetate was prepared by the modified method of Boesekin and Schneider /5/. The progress of the reaction was monitored by estimating the unreacted PIA iodometrically at various intervals of time.

RESULTS AND DISCUSSION

The reaction is first order with respect to PIA as evidenced from the linearity of the $\log(a-x)$ vs. time plots and constancy of the pseudo first order rate constants ($10^3 \times k_1 = 2.2 \pm 0.2 \text{ sec}^{-1}$ and $0.72 \pm 0.02 \text{ sec}^{-1}$) within four fold variation in the concentrations of phenanthrene and acenaphthene, respectively. The k_1 value increases with increase in the concentration of substrate. Plots of $\log k_1$ vs. $\log [\text{substrate}]$ yield slopes of 1 for both compounds proving the first order dependence on the substrates. There is an acceleration with the increase in the concentration of HClO_4 at constant ionic strength ($\mu = 0.1 \text{ M}$). The plots of $\log k_2$ vs. $\log [\text{H}^+]$ are linear with slopes of 1 indicating first order dependence on the acidity (Table). Whereas in presence of sodium acetate the reaction with phenanthrene doesn't proceed even after many days, that with acenaphthene proceeds very slowly. Enhancement in rate is observed on increasing the ionic strength of the medium. At 0.01 and 0.05 M perchlorate concentrations the $10^3 \times k_1$ for phenanthrene and acenaphthene are 2.85; 3.34 and 0.86; 1.20 sec^{-1} , respectively. The rate of the reaction increases on increasing the percentage (V/V) of acetic acid in the reaction mixture, i.e. decreasing the dielectric constant of the medium. For phenanthrene the $10^3 \times k_1$ values at 75%, 80%, 85% and 90% acetic acid are 1.98, 2.63; 3.98 and 6.46 sec^{-1} and for acenaphthene 0.57; 0.75; 1.12; 1.63 sec^{-1} , respectively. The results of the effect of ionic strength and dielectric constant leads us to believe that the reaction occurs between a positive ionic species and a dipole or a neutral molecule.

The reactions have been carried out at three different temperatures and the Arrhenius activation parameters are computed ($\Delta E^\ddagger = 47.8 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta H^\ddagger = 45.3 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$; $\log_{10} A = 7.8 \pm 0.4$; $\Delta S^\ddagger = 104.2 \pm 5.2 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$ for phenanthrene and $63.8 \pm 3.2 \text{ kJ} \cdot \text{mol}^{-1}$; $61.2 \pm 3.0 \text{ kJ} \cdot \text{mole}^{-1}$; 10 ± 0.5 and $-52.2 \pm 3 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$ for acenaphthene.

Of the two compounds studied, phenanthrene is found to be more reactive than acenaphthene, obviously because of the presence of a reactive double bond in the 9, 10 position, which is in conjugation with the two benzene rings. In addition to this, the $\sigma - \sigma$ and $\sigma - \pi$ hyperconjugation of the hydrogen present at either of the two positions accounts for its higher activity. Acenaphthene has two active methylene groups conjugated separately with the two benzene rings and has a $\sigma - \sigma$ hyperconjugation effect of the hydrogen present on one methylene group over the other, thus making the C-H bond labile. Acenaphthene, even with the structural advantage of labile hydrogens is less reactive than phenanthrene where the 9, 10 positions are very active.

Table 1

Variation of substrate and acid concentrations. Temp: 35 °C,
Solvent: 80% HOAc + 20% water

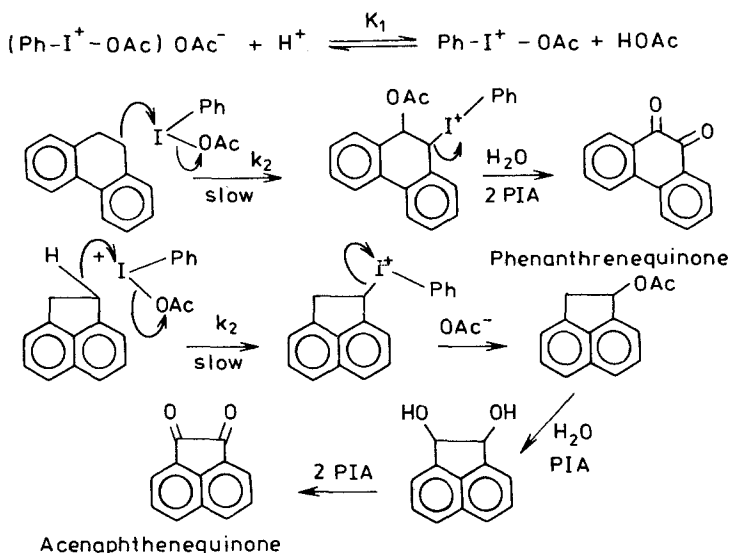
[O] × 10 ⁴ (Molarity)	[S] × 10 ³	[H ⁺] × 10 ²	[NaClO ₄] × 10 ²	k ₁ × 10 ³ (sec ⁻¹)		
Phenanthrene	1.8			0.97		
		3.8		2.04		
	5.00	5.0	4.0	—	2.63	
		7.5			4.16	
		10.0			5.57	
	5.00		2.0	7.0	1.85	
		5.00		3.0	6.0	2.62
				4.0	5.0	3.34
				5.0	4.0	4.68
Acenaphthene	1.30			0.21		
	5.0	2.53	4.0	—	0.36	
		5.00			0.75	
		8.02			1.43	
	5.0		1.0	8.0	0.24	
			2.0	7.0	0.46	
			4.0	5.0	1.20	
			6.0	3.0	2.15	

The phenyliodosoacetate in acid medium dissociates to Ph-I⁺-OAc which acts as an active species. Humffray and Imberger /4/ have also predicted the same species in the oxidation of organic sulfides by PIA. The 9 and 10 positions of phenanthrene containing an active double bond, are the positions susceptible for attack by the Ph-I⁺-OAc species. In case of acenaphthene the methylene groups act as reaction sites for the incoming Ph-I⁺-OAc species. The overall mechanism of the reaction is depicted in the scheme.

An increase in the percentage of acetic acid in the mixture can increase the overall acidity of the system, apart from decreasing the dielectric constant of the medium. Both the above changes will enhance the reaction. Had acetic acid acted only by the change of the acidity of the system, such remarkable change of rate (for 10% increase in acetic acid, the rate is doubled) would not be expected. Hence probably it is the cumulative enhancing effect of acidity and dielectric constant of the medium which causes such a sharp change in the rates by the change of acetic acid content in the mixture. This supports the view that the reaction occurs between a positive ion and a dipole or a neutral molecule, where the positive ion is the active Ph-I⁺-OAc species. Phenanthrene and acenaphthene

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are neutral molecules and the former can also act as a dipole. The linear plot of $[S]$ vs. k_1 , passing through the origin, rules out the possibility of the formation of a precursor complex. Hence it is the attack of the $\text{Ph-I}^+-\text{OAc}$ on the reactive carbon centre of the substrate which is rate determining. This is followed by the rapid elimination of Ph-I and subsequent rearrangement to diacetoxy and monoacetoxy compounds for phenanthrene and acenaphthene, respectively. These are the products under the experimental condition employed, as a large excess of substrate over the oxidant is always maintained, though the final products are the corresponding quinones as evidenced by the stoichiometry of 1 : 3 and 1 : 4 (substrate : oxidant) for phenanthrene and acenaphthene, respectively.



The rate law explains all the observed orders with respect to oxidant, substrate and acid.

REFERENCES

1. K. H. Pausacker: *J. Chem. Soc.* 107 (1953).
2. N. Venkatasubramania and K. Swaminathan: *J. Chem. Soc., Perkin Trans. 2*, 1161 (1975).
3. S. C. Pati and R. C. Mohapatra: *Proc. Ind. Acad. Sci.*, Vol. 88A(I) 382 (1981).
4. A. A. Humffray and H. E. Imberger: *J. Chem. Soc., Perkin Trans. 2*, 382 (1981).
5. J. Boeseken and G.C.C.C. Schneider: *J. Prakt. Chem.*, 131, 285 (1931).