

KINETICS OF CHROMIC ACID OXIDATION OF PHENANTHRENE
AND 3-SUBSTITUTED PHENANTHRENES

N.Narayanankutty and M.V.Bhatt

Department of Organic Chemistry, Indian Institute of Science,
Bangalore, India

(Received in UK 4 May 1971; accepted in UK for publication 13 May 1971)

Although chromic acid oxidation is the preferred synthetic method for the conversion of aromatic hydrocarbons to quinones, this reaction has not received attention from the point of view of mechanism.¹ Pioneering and incisive studies on the oxidation of alcohols and arylalkanes^{2,3} have revealed that a wide variety of mechanisms are possible with different substrates and experimental conditions and any conjecture on the mechanism based on analogy would be naive. Obviously oxidation of aromatic hydrocarbons by chromic acid follows a course different from that of sodium dichromate. The former yields quinones almost exclusively,^{4,5} whereas the latter oxidizes side chains to carboxylic acids in excellent yields (90-95%).⁶

Oxidation of hydrocarbons to quinones necessarily involves a number of steps. In view of the complex nature of the reaction, it is gratifying to find that the kinetics of oxidation of phenanthrene and 3-substituted phenanthrenes fit a first-order rate expression for the disappearance of chromic acid. The oxidation was studied in 91% acetic acid in the presence of perchloric acid and sodium perchlorate at constant ionic strength. The rate of reaction as a function of phenanthrene concentration was determined over a five-fold concentration variation. The second-order rate constants which were calculated were constant (Table 1), indicating that the reaction is first-order with respect to phenanthrene.

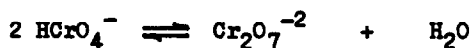
TABLE 1

Effect of changing phenanthrene concentration on the rate of
chromic acid oxidation of phenanthrene

[Phenanthrene], M	$k_1 \times 10^4, \text{sec.}^{-1}$	$k_2 \times 10^3, \text{M}^{-1} \text{sec.}^{-1}$
0.016	0.47	2.88
0.033	0.91	2.75
0.050	1.47	2.93
0.066	1.94	2.94
0.082	2.39	2.91

$[\text{HClO}_4] = 0.1\text{M}; [\text{NaClO}_4] = 0.2\text{M}; [\text{CrO}_3] = 0.0033\text{M};$
Solvent - 91% acetic acid; temp. 40.1°.

The rate constant decreased with increasing chromic acid concentration. This behaviour is analogous to that observed in the case of alcohols⁷ and aldehydes⁸ and arises from acid chromate-dichromate equilibrium. Only the acid chromate ion (HCrO_4^-) is involved in the rate expression.



The order with respect to perchloric acid was determined in the same way. The plot of $\log k$ against H_0 at constant ionic strength was linear with a slope of 0.96. It is possible to write the rate law as :

$$v = k[\text{Phenanthrene}][\text{HCrO}_4^-] h_0$$

TABLE 2

Effect of change in concentration of chromium trioxide on the rate constant of oxidation of phenanthrene

$[\text{CrO}_3], \text{M}$	$k_1 \times 10^4, \text{sec.}^{-1}$
0.0016	4.79
0.0023	2.32
0.0033	1.47
0.0041	1.06
0.0078	0.66

$[\text{Phenanthrene}] = 0.05\text{M}$;

$[\text{HClO}_4] = 0.1\text{M}$; $[\text{NaClO}_4] = 0.2\text{M}$

The rates were measured at two more temperatures (30.1° and 50.1°).

The plot of $\log k$ versus $1/T$ was a straight line. From the slope, E , ΔH^\ddagger and ΔS^\ddagger were calculated. The values obtained are given in Table 3.

TABLE 3

Temperature, $^\circ\text{C}$	$k_2 \times 10^3, \text{M}^{-1}\text{sec.}^{-1}$	$E, \text{k cal}$	$\Delta H^\ddagger, \text{k cal}$	$\Delta S^\ddagger, \text{e.u}$
30.1	1.71			
40.1	2.88	11.4	10.8	- 35.72
50.1	5.09			

$[\text{Phenanthrene}] = 0.033\text{M}$; $[\text{HClO}_4] = 0.1\text{M}$; $[\text{NaClO}_4] = 0.2\text{M}$; $[\text{CrO}_3] = 0.0033\text{M}$

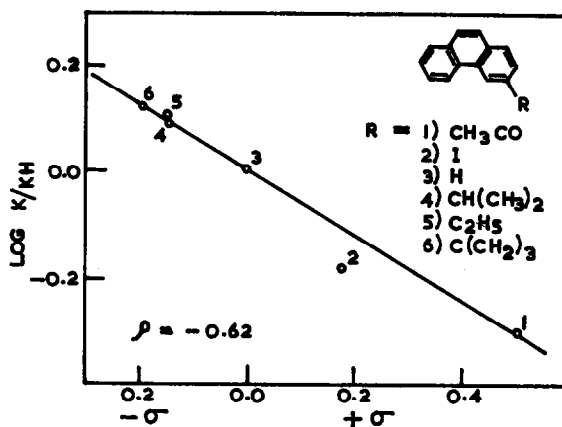


FIG. 1. SUBSTITUENT EFFECT ON THE RATE OF OXIDATION OF PHENANTHRENE WITH CHROMIC ACID.

We have found that the substituent effect data fits a linear free energy relationship with Hammett σ_p -values giving a ρ value of -0.62 (Correlation coefficient $r = 0.986$). This result is unexpected in view of the fact that the Hammett equation has not been applied, as far as we know, to reactions at the 9,10-positions of phenanthrene. Previous rate data⁹ on the addition of bromine to substituted phenanthrenes does not fit Hammett's plot. A negative entropy of activation shows that the transition state is rigid. The low ρ value of -0.62 is consistent only with an electrophilic or a radical attack not involving a highly charged transition state.

We are continuing this work with appropriate deuterated compounds with the object of delineating the mechanism of chromic acid oxidation of phenanthrenes and other polycyclic aromatic hydrocarbons.

References

1. K.B.Wiberg in Oxidations in Organic Chemistry ed. K.B.Wiberg, pp.69 Academic Press (1965).
2. A.Leo and F.H.Westheimer, J.Amer.Chem.Soc., 74, 4383 (1952).
M.Cohen and F.H.Westheimer, J.Amer.Chem.Soc., 74, 4387 (1952), and earlier papers cited therein.
3. K.B.Wiberg and R.J.Evans, Tetrahedron, 8, 313 (1960).
K.B.Wiberg and R.Eisenthal, Tetrahedron, 20, 1151 (1964).
4. J.Gason, Organic Reactions, 4, 305 (1948), John Wiley.
L.F.Fieser, W.P.Campbell, E.M.Fry and M.D.Gates Jr., J.Amer.Chem.Soc., 61, 3218 (1939).
K.H.Klipstein, Ind.Engg.Chem., 18, 1327 (1926).
5. We have determined the stoichiometry of the reaction by carrying out an experiment similar to that used for kinetic study and estimating the products. The yield of phenanthrene quinone was 85.5%.
6. L.Friedman, D.L.Fishel and H.Schechter, J.Org.Chem., 30, 1453 (1965).
7. A.Novik and F.H.Westheimer, J.Chem.Phys., 11, 506 (1943).
8. K.B.Wiberg and T.Mill, J.Amer.Chem.Soc., 80, 3022 (1958).
9. L.F.Fieser and C.C.Price, J.Amer.Chem.Soc., 58, 1838 (1936).
L.P.Hammett, Physical Organic Chemistry, pp.79, McGraw-Hill (1940).