

## OXIDATION OF 1- AND 2-ACETYLNAPHTHALENES BY IODATE — A KINETIC STUDY

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Kinetics of oxidation of 1- and 2-acetylnaphthalenes by iodate in the presence of sulphuric acid in aqueous methanol has been studied. The reaction is first order with respect to both [iodate] and [acetylnaphthalene]. Solvent effect indicates a cation-dipole type of interaction in the rate limiting step. A mechanism is proposed with a slow attack of  $\text{IO}_2^+$  on enol form of acetylnaphthalene forming an intermediate carbonium ion, which ultimately gives corresponding  $\omega$ -hydroxyacetylnaphthalene. The higher reactivity of 2-acetyl isomer is attributed to the greater stability of the corresponding carbonium ion than that of 1-acetyl isomer.

The present study aims at getting information on the effect of naphthalene ring on the rate of oxidation since a limited work is carried out in the oxidation of naphthalene system especially from the kinetic viewpoint. In continuation of our earlier work on the oxidation of organic substrates by iodate<sup>1-5</sup>, we have studied the kinetics of oxidation of 1- and 2-acetylnaphthalenes. The oxidation of these substrates by Ce(IV), Cr(VI), and V(V) have been reported in the literature<sup>6-8</sup> and the products isolated are corresponding  $\omega$ -hydroxyacetylnaphthalene in the case of Ce(IV) (ref.<sup>6</sup>) and Cr(VI) (ref.<sup>7</sup>) and acetylnaphthol with V(V) (ref.<sup>8</sup>).

### EXPERIMENTAL

All the experiments were conducted under the conditions [acetylnaphthalene]  $\gg$   $[\text{IO}_3^-]$  in 50% (v/v) aqueous methanol medium at 45°C in the presence of 4M- $\text{H}_2\text{SO}_4$ . The course of the reaction was followed by estimating the unreacted iodate iodometrically. The pseudo first order rate constants were obtained by plotting  $\log (\text{IO}_3^-)_t$  vs time.

*Materials.* 1- and 2-acetylnaphthalenes were Fluka AG samples. They were used as such after checking their b.p. and m.p. Potassium iodate, methanol, potassium iodide, sulphuric acid and sodium thiosulphate were of BDH grade. Water was distilled twice before use.

### RESULTS AND DISCUSSION

The  $k_{\text{obs}}$  values obtained at different  $[\text{IO}_3^-]$  and [acetylnaphthalene] (Tables I and II) indicate that the reactions are first order with respect to both  $[\text{IO}_3^-]$  and [acetyl-

naphthalene]. Reactions studied at different  $\text{H}_2\text{SO}_4$  indicate that the reaction is acid-catalysed (Table III).

TABLE I

Effect of  $[\text{IO}_3^-]$  on  $k_{\text{obs}}$  (in  $\text{mol l}^{-1} \text{s}^{-1}$ ); [acetylnaphthalene] = 0.05 mol/l,  $[\text{H}_2\text{SO}_4]$  = 4.0 mol/l, 318 K, 50% (v/v) aq. MeOH

| Naphthalene derivative | $k_{\text{obs}} \cdot 10^4$ at $[\text{IO}_3^-]$ , mol/l |       |       |       |       |
|------------------------|--|-------|-------|-------|-------|
|                        | 0.001  | 0.002 | 0.004 | 0.008 | 0.010 |
| 1-Acetyl               | 1.567  | 1.599 | 1.535 | 1.567 | 1.599 |
| 2-Acetyl               | 2.203  | 2.225 | 2.289 | 2.255 | 2.301 |

TABLE II

Effect of [acetylnaphthalene] on  $k_{\text{obs}}$  (in  $\text{mol l}^{-1} \text{s}^{-1}$ );  $[\text{IO}_3^-]$  = 0.002 mol/l,  $[\text{H}_2\text{SO}_4]$  = 4.0 mol/l, 67% (v/v), aq. MeOH, 318 K

| Naphthalene derivative | $k_{\text{obs}} \cdot 10^4$ at [acetylnaphthalene], mol/l |       |       |       |
|------------------------|---|-------|-------|-------|
|                        | 0.010   | 0.025 | 0.050 | 1.000 |
| 1-Acetyl               | 0.836   | 2.058 | 3.946 | 8.156 |
| 2-Acetyl <sup>a</sup>  | 0.452   | 1.247 | 2.255 | 4.374 |

<sup>a</sup> 50% (v/v) aqueous methanol.

TABLE III

Effect of  $[\text{H}_2\text{SO}_4]$  on  $k_{\text{obs}}$  (in  $\text{mol l}^{-1} \text{s}^{-1}$ ); [acetylnaphthalene] = 0.05 mol/l,  $[\text{IO}_3^-]$  = 0.002 mol/l, 50% (v/v) aq. MeOH, 318 K

| Naphthalene derivative | $k_{\text{obs}} \cdot 10^4$ at $[\text{H}_2\text{SO}_4]$ , mol/l |       |       |       |
|------------------------|--|-------|-------|-------|
|                        | 2.0  | 3.0   | 4.0   | 4.5   |
| 1-Acetyl               | 0.203  | 0.595 | 1.599 | 2.741 |
| 2-Acetyl               | 0.359  | 0.815 | 2.255 | 3.321 |

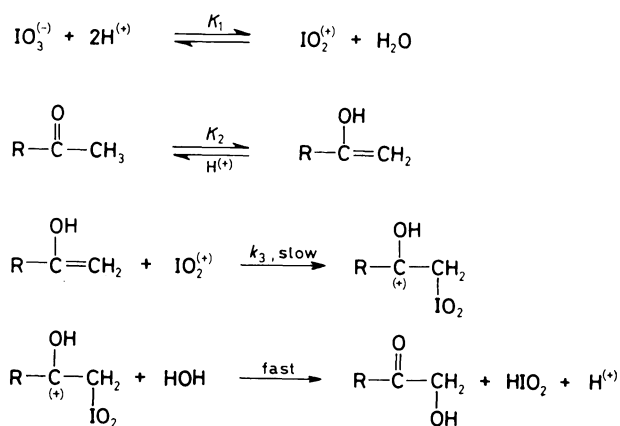
A correlation of  $\log k_{\text{obs}}$  with Hammett's acidity function<sup>9</sup>  $H_0$  gives a linear plot with a slope of nearly unity in each case. The magnitude of the slope indicates the absence of water molecule participation in the rate determining step. These results suggest a rate law of the type (1).

$$\frac{-d[\text{IO}_3^-]}{dt} = K[\text{acetylnaphthalene}][\text{IO}_3^-]h_0 \quad (1)$$

Rate measurements made at constant  $[\text{H}_2\text{SO}_4]$  and temperature in MeOH-water mixtures of different compositions (v/v), (Table IV) show that a medium of low dielectric constant is favourable for the present oxidation process. Treatment of rate data with dielectric constant of the medium according to Amis-Jaffe equation<sup>10</sup> gives linear plots with slopes of +59.0 and +52.5 with 1- and 2-acetylnaphthalenes, respectively. The magnitude and sign of the slope are suggestive of cation-dipole type of interaction between oxidant and substrate. In an independent study of iodination of these two substrates in 50% (v/v) aqueous methanol at 45°C at an acidity of 0.02M- $\text{H}_2\text{SO}_4$ , the iodination rate constants are found to be  $2.05 \cdot 10^{-2} \text{ mol l}^{-1} \cdot \text{s}^{-1}$  and  $1.08 \cdot 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$  with 1- and 2-acetylnaphthalenes, respectively. These rates are much higher than the oxidation rates.

The product isolated was identified to be the corresponding  $\omega$ -hydroxyacetylnaphthalene from IR data.

In view of these observations a plausible mechanism for the oxidation can be given as shown in Scheme 1 (R stands for naphthyl).



SCHEME 1

It is established that iodination of acetylnaphthalenes proceeds via slow enolization steps. Since in the present case the iodination rates are found to be much higher than

the oxidation rates, the possibility of enolisation of the acetylnaphthalene being the rate determining step has been ruled out. Literature survey shows that in acid medium the present oxidant  $\text{IO}_3^-$  exists either as the neutral form  $\text{HIO}_3$  or as the cationic form<sup>11,12</sup>  $\text{IO}_2^+$ . Since the solvent effect on the present oxidation suggests a cation-dipole type of interaction between the oxidant and substrate, a slow attack of  $\text{IO}_2^+$  on the methylene carbon of enol form of acetylnaphthalene is proposed. This results in the formation of an intermediate carbonium ion which undergoes hydrolysis giving the product  $\omega$ -hydroxyacetylnaphthalene. The second product,  $\text{HIO}_2$  produced, being a potential oxidant<sup>13</sup> oxidizes two more moles of substrate and ultimately reduces to  $\text{I}^-$ , which has been identified. The rate expression (2) derived from this mechanism is in consonance with the proposed rate law (1).

$$\frac{-d[\text{IO}_3^-]}{dt} = K_1 K_2 k_3 [\text{IO}_3^-] [\text{acetylnaphthalene}] h_0 \quad (2)$$

TABLE IV

Effect of solvent composition on  $k_{\text{obs}}$  (in  $\text{mol l}^{-1} \text{s}^{-1}$ ); [acetylnaphthalene] = 0.05 mol/l,  $[\text{IO}_3^-]$  = 0.002 mol/l,  $[\text{H}_2\text{SO}_4]$  = 4.0 mol/l, 318 K

| Naphthalene derivative | $k_{\text{obs}} \cdot 10^4$ at % (v/v) aq. MeOH |       |       |       |
|------------------------|---|-------|-------|-------|
|                        | 40  | 50    | 60    | 70    |
| 1-Acetyl               | 0.978   | 1.599 | 2.303 | 3.946 |
| 2-Acetyl               | 1.766   | 2.255 | 3.791 | 6.141 |

TABLE V

Effect of temperature (in K) on  $k_{\text{obs}}$  (in  $\text{s}^{-1}$ ) and calculated thermodynamic parameters ([acetylnaphthalene] = 0.05 mol/l,  $[\text{IO}_3^-]$  = 0.002 mol/l,  $[\text{H}_2\text{SO}_4]$  = 4.0 mol/l, 50% (v/v) aq. MeOH)

| Naphthalene derivative | $k_{\text{obs}} \cdot 10^5$ at |       |       |       | $\Delta H^\ddagger$<br>kJ mol <sup>-1</sup> | $\Delta S^\ddagger$<br>J K <sup>-1</sup> mol <sup>-1</sup> | $\Delta G^\ddagger$<br>kJ mol <sup>-1</sup> |
|------------------------|--------------------------------|-------|-------|-------|---|--|---|
|                        | 306 K                          | 313 K | 318 K | 323 K |   |  |   |
| 1-Acetyl               | 6.24                           | 10.08 | 15.99 | 22.51 | 56.75                                       | -178   | 113.30                                      |
| 2-Acetyl               | 7.97                           | 15.43 | 20.38 | 31.25 | 68.50                                       | -139   | 112.70                                      |

Of the two naphthalenes studied, 2-acetyl derivative appears to be more reactive than 1-acetyl derivative. In general, in 1-naphthyl type of substrates the *peri* interaction with the hydrogen of the adjacent ring restricts the attainment of planarity and these compounds react relatively slowly, while in 2-naphthyl systems, in which little steric opposition is offered for the formation of planar carbonium ion, reactions proceed at normal rates<sup>14</sup>. In the present case the rate limiting attack involves an electrophilic attack of  $\text{IO}_2^+$  on methylene carbon atom. Therefore the substituents which make the attacking centre less negative would naturally react slower. The electron attracting nature of 2,3-benzo substituent (1-naphthyl) is higher than that of 3,4-benzo substituent (2-naphthyl group) as evidenced by their Hammett's  $\sigma$  values, which are measures of electron withdrawing capacities of the substituents on the benzene ring. For 1- and 2-naphthyl groups these values are +0.50 and +0.04, respectively<sup>15</sup>. And also the carbonium ion formed in the slow step in 2-acetylnaphthalene is more resonance-stabilized than that of 1-acetyl derivative. Though there is much difference between the  $\sigma$  values of these two substrates, the observed rate constants  $k_{\text{obs}}$  do not appear to be much different from each other. This is attributed to the fact that  $k_{\text{obs}}$  is a composite rate constant which is the product of  $K_1K_2k_3$ . Though the enolization constant  $K_2$  of 1-acetyl derivative is greater than that of 2-acetyl derivative, the overall rate constant  $k_{\text{obs}}$  of 2-acetylnaphthalene is greater than that of 1-acetylnaphthalene, suggesting that the true rate constant  $k_3$  may be considerably larger in the case of 2-acetyl derivative compared to 1-acetyl derivative.

Thus, though the enolization is faster with 1-acetyl derivative, the attack of  $\text{IO}_2^+$  is more facile and the carbonium ion formed is more stabilized with 2-acetyl derivative and it reacts faster than the 1-acetyl derivative.

The thermodynamic parameters computed are given in Table V. The same value of free energy of activation ( $\Delta G^\ddagger = 113.0 \text{ kJ mol}^{-1}$ ) indicates the operation of similar mechanism with the two naphthalenes studied. The entropy of activation  $\Delta S^\ddagger$  is highly negative, suggesting that the transition state is more polar, hence more solvated than the reactant.

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