

## Acid Catalysed Prototropy of Substituted Acetonaphthones— Kinetics of Perchloric Acid Catalysed Bromination & Phenyl Iodosoacetate Oxidation

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Enolisation rates of several 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones at three different temperatures in acetic acid-water mixture (95 %, v/v) in perchloric acid catalysed bromination and phenyl iodosoacetate (PIA) oxidation reactions correlate very well with Hammett  $\sigma_p$  constants. Acetonaphthones with 4- and 6-OCH<sub>3</sub> substituents deviate from the corresponding Hammett plot for PIA oxidation. From basicity data deprotonation rate constants ( $k_d$ ) have been evaluated for bromination and PIA oxidation reactions.

The acid catalysed prototropy of substituted acetophenones has been extensively studied employing several reactions<sup>1-3</sup>. No systematic prototropy study has been carried out so far on substituted acetonaphthones. In order to understand the electronic effects of the substituents in the enolisation reaction in naphthalene system, we have determined the rates of perchloric acid catalysed bromination and phenyliodosoacetate (PIA) oxidation of several 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones in acetic acid-water mixture (95 %, v/v).

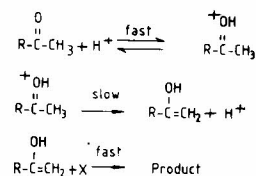
### Materials and Methods

All the acetonaphthones were prepared and purified by literature methods<sup>4</sup>. Acetophenone (BDH) was purified by preparing its semicarbazone and regenerating it. Perchloric acid (BDH) was employed as a source of H<sup>+</sup> ions. Purified acetic acid was used. Phenyl iodosoacetate was prepared by the modified procedure of Venkatasubramanian *et al.*<sup>5</sup> All the kinetic runs were carried out under pseudo-first order condition: [ketone] >> [bromine] or [PIA]. The course of the reaction was monitored by estimating the unreacted bromine or PIA by standard iodometric procedure. From the pseudo-zero order rate constants ( $k_0$ ), pseudo-first order rate constants ( $k_1$ ) and enolisation rate constants ( $k_e$ ) were evaluated as usual<sup>6</sup>. All the rate constants are reproducible within  $\pm 2.0\%$ . All the data were treated by the method of least squares.

The reaction products were isolated for 1- and 2-acetonaphthones under experimental conditions and found to be  $\omega$ -bromoacetonaphthones for bromination reaction and  $\omega$ -acetoxyacetonaphthones for PIA oxidation.

### Results and Discussion

The results of kinetic studies show that in bromination and oxidation reactions the order in [bromine] and [PIA] is zero each. In both bromination and oxidation reactions the order in [H<sup>+</sup>] and [ketone] is also one each. These observations indicate enolisation of the protonated ketone in the rate-limiting step. Both the reactions, therefore, proceed through the same mechanism as shown in Scheme 1. This mechanism accounts for zero order dependence in [bromine] and [PIA]. These observations are similar to those reported earlier<sup>7,8</sup>.



Scheme 1

The rate data for perchloric acid catalysed bromination and PIA oxidation of several substituted 1- and 2-acetonaphthones are given in Tables 1 and 2 together with thermodynamic activation parameters. Examination of the rate data reveals that electron-releasing substituents in naphthalene ring increase the rate while electron-withdrawing ones decrease it. The validity of Hammett equation in these reactions has been tested by statistical correlation of the rate constants with  $\sigma_p$  constants<sup>9</sup>. The results of regression analysis are presented in Table 3. The small negative  $\rho_c$  observed for the enolisation step is due to the difference in the  $\rho$  values of the two consecutive steps namely the equilibrium protonation of the carbonyl oxygen and deprotonation at  $\alpha$ -carbon atom. Therefore it follows that

Table 1—Enolisation Rate Constants and Activation Parameters for Perchloric Acid Catalysed PIA Oxidation of Substituted Acetonaphthones in Acetic Acid-Water (95%, v/v)

| Sl No.                          | Substituent      | $10^5 k_e$ (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> ) |      |       | $\Delta H^\ddagger$<br>(kJmol <sup>-1</sup> ) | $-\Delta S^\ddagger$<br>(JK <sup>-1</sup> mol <sup>-1</sup> ) | log $\rho_z$ |
|---------------------------------|------------------|-----------------------------------------------------------------|------|-------|-----------------------------------------------|---------------------------------------------------------------|--------------|
|                                 |                  | 25°                                                             | 30°  | 35°   |                                               |                                                               |              |
| 4-Substituted 1-acetonaphthones |                  |                                                                 |      |       |                                               |                                                               |              |
| 1                               | OCH <sub>3</sub> | 42.4                                                            | 57.3 | 104.0 | 49                                            | 146                                                           | 5.6          |
| 2                               | CH <sub>3</sub>  | 9.7                                                             | 16.1 | 24.5  | 58                                            | 127                                                           | 6.6          |
| 3                               | H                | 7.8                                                             | 13.2 | 21.3  | 73                                            | 78                                                            | 9.2          |
| 4                               | F                | 7.4                                                             | 11.4 | 20.0  | 74                                            | 77                                                            | 9.3          |
| 5                               | Cl               | 4.9                                                             | 8.3  | 14.9  | 82                                            | 51                                                            | 10.6         |
| 6                               | Br               | 4.8                                                             | 8.1  | 14.8  | 83                                            | 49                                                            | 10.7         |
| 6-Substituted 2-acetonaphthones |                  |                                                                 |      |       |                                               |                                                               |              |
| 7                               | OCH <sub>3</sub> | 274                                                             | 491  | 707   | 44                                            | 146                                                           | 5.6          |
| 8                               | CH <sub>3</sub>  | 13.4                                                            | 20.7 | 32.2  | 64                                            | 104                                                           | 7.8          |
| 9                               | H                | 11.1                                                            | 18.8 | 30.9  | 76                                            | 67                                                            | 9.8          |
| 10                              | F                | 10.3                                                            | 17.9 | 29.4  | 77                                            | 62                                                            | 10.0         |
| 11                              | Cl               | 9.5                                                             | 16.3 | 28.8  | 82                                            | 47                                                            | 10.8         |
| 12                              | Br               | 9.0                                                             | 16.0 | 28.6  | 86                                            | 37                                                            | 11.4         |

For acetophenone the values of 10<sup>5</sup> *k<sub>e</sub>* (mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>) are 11.1 and 18.8 at 25° and 30° respectively.

Table 2—Enolisation Rate Constants and Activation Parameters for Perchloric Acid Catalysed Bromination of Substituted Acetonaphthones in (95%, v/v) Acetic Acid-Water

| Substituent                     | $10^5 k_e \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$ |      |      | $\Delta H^\ddagger$<br>(kJmol <sup>-1</sup> ) | $-\Delta S^\ddagger$<br>(JK <sup>-1</sup> mol <sup>-1</sup> ) | log $\rho_z$ |
|---------------------------------|------------------------------------------------------------------|------|------|-----------------------------------------------|---------------------------------------------------------------|--------------|
|                                 | 30°                                                              | 35°  | 40°  |                                               |                                                               |              |
| 4-Substituted 1-Acetonaphthones |                                                                  |      |      |                                               |                                                               |              |
| CH <sub>3</sub>                 | 19.4                                                             | 34.7 | 52.7 | 77                                            | 63                                                            | 9.9          |
| H                               | 14.5                                                             | 23.0 | 41.8 | 81                                            | 51                                                            | 10.6         |
| F                               | 13.0                                                             | 22.2 | 40.0 | 87                                            | 33                                                            | 11.5         |
| Cl                              | 9.4                                                              | 15.8 | 26.8 | 89                                            | 29                                                            | 11.7         |
| Br                              | 9.2                                                              | 15.4 | 26.4 | 89                                            | 28                                                            | 11.8         |
| 6-Substituted 2-Acetonaphthones |                                                                  |      |      |                                               |                                                               |              |
| CH <sub>3</sub>                 | 24.2                                                             | 40.9 | 68.8 | 80                                            | 49                                                            | 10.7         |
| H                               | 21.2                                                             | 36.5 | 62.5 | 83                                            | 42                                                            | 11.0         |
| F                               | 20.5                                                             | 35.8 | 62.0 | 85                                            | 36                                                            | 11.4         |
| Cl                              | 18.3                                                             | 30.7 | 51.8 | 84                                            | 37                                                            | 11.2         |
| Br                              | 18.0                                                             | 30.0 | 52.0 | 84                                            | 41                                                            | 11.1         |

Table 3—Hammett Reaction Constants at 30°

| Reaction    | Series     | $\rho_c$ | $\rho_p$ | $\rho_d$ |
|-------------|------------|----------|----------|----------|
| Bromination | 4 $\alpha$ | -0.80    | -2.24    | 1.44     |
| Oxidation   | 4 $\alpha$ | -0.77    | -2.24    | 1.50     |
| Bromination | 6 $\beta$  | -0.31    | -1.74    | 1.43     |
| Oxidation   | 6 $\beta$  | -0.27    | -1.74    | 1.47     |

$$k_d = K_1 k_e \quad \dots (1)$$

where *k<sub>d</sub>* is the rate constant for the deprotonation at  $\alpha$ -carbon atom of the conjugate acid, *k<sub>e</sub>* is the measured enolisation rate constant and *K<sub>1</sub>* is acid dissociation constant of the protonated carbonyl group.

It is not possible to evaluate *k<sub>d</sub>* unless *K<sub>1</sub>* is known. We have assumed this unknown quantity to be the same as that for dissociation of the conjugate ketones in water<sup>7</sup>. The basicity data of Ananthakrishna Nadar *et al.*<sup>10</sup> were correlated with  $\sigma_p$  constants, from which  $\rho_p$

(reaction constant for protonation of carbonyl oxygen),  $\rho_d$  (reaction constant for deprotonation at the  $\alpha$ -carbon atom of the conjugate acid) (Table 3), and *k<sub>d</sub>* (Table 4) were evaluated for bromination and PIA oxidation reactions. In all the cases the magnitude of electronic effect of substituents is higher in the protonation step rather than in the deprotonation at  $\alpha$ -carbon atom. The electronic effects of substituents operate in opposite directions in these two processes, thereby making the overall electronic effect in enolisation as small negative  $\rho_c$ . Hence the overall reactivity of ketone is determined by the electron density at carbonyl oxygen.

Analysis of data in Tables 1 and 2 reveals that the enolisation rate of 1-acetonaphthone is less than that of 2-acetonaphthone or acetophenone. This may be due to the presence of *peri*-H in 1-acetonaphthone, which forces the acetyl group to move out of the plane of

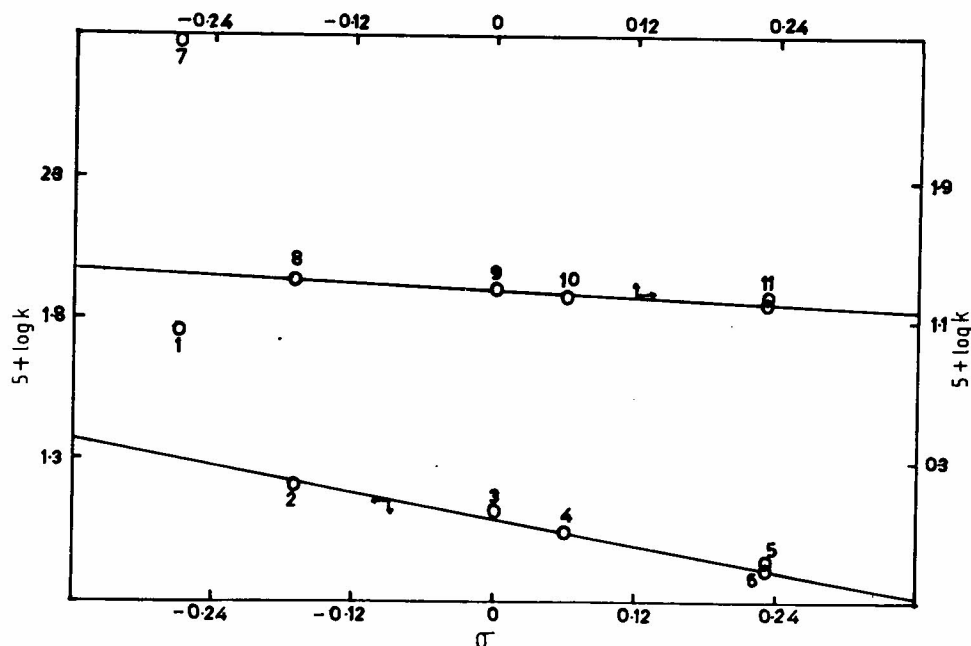


Fig. 1—Hammett plot for PIA oxidation of substituted acetonaphthones in acetic acid-water mixture (95%, v/v) at 30° [Arabic numerals on the curve refer to the 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones listed in Table I]

Table 4—Deprotonation Rate Constants Calculated from Basicity Data for Substituted Acetonaphthones at 30°

| Constant                                           | Substituent     |     |     |      |      |
|----------------------------------------------------|-----------------|-----|-----|------|------|
|                                                    | CH <sub>3</sub> | H   | F   | Cl   | Br   |
| 4-Substituted 1-acetonaphthones                    |                 |     |     |      |      |
| $-pK_{BH^+}$                                       | 6.3             | 6.7 | 6.8 | 7.2  | 7.2  |
| $10^{-2}k_d$ (PIA) (s <sup>-1</sup> )              | 3.2             | 6.6 | 7.2 | 13.2 | 12.8 |
| $10^{-2}k_d$ (Br <sub>2</sub> ) (s <sup>-1</sup> ) | 3.9             | 7.3 | 8.2 | 14.9 | 14.6 |
| 6-Substituted 2-acetonaphthones                    |                 |     |     |      |      |
| $-pK_{BH^+}$                                       | 5.8             | 6.3 | 6.4 | 6.5  | 6.6  |
| $10^{-2}k_d$ (PIA) (s <sup>-1</sup> )              | 1.3             | 3.8 | 4.5 | 5.2  | 6.4  |
| $10^{-2}k_d$ (Br <sub>2</sub> ) (s <sup>-1</sup> ) | 1.5             | 4.2 | 5.1 | 5.9  | 7.2  |

naphthalene ring and inhibits the resonance between the ring and carbonyl group thereby decreasing the electron density at the carbonyl oxygen compared to that in 2-acetonaphthone or acetophenone wherein such inhibition of resonance is absent.

In the statistical correlation of the enolisation rates with  $\sigma_p$  constants, the methoxy group is omitted as it deviates considerably from the linear plots constituted by the other substituents (Fig. 1). Being an electron-releasing substituent, the methoxy group is involved in extended conjugation with the protonated carbonyl group. In 4-methoxy-1-acetonaphthone, the methoxy group has to assume a preferred orientation *trans*- to *peri*-H in order to enter into enhanced mesomeric interaction with protonated acetyl group. But due to steric interaction between *peri*-H and protonated

acetyl group the extent of mesomeric interaction between protonated acetyl group and  $-OCH_3$  group through naphthalene ring is much less in 4-methoxy-1-acetonaphthone than that in 6-methoxy-2-acetonaphthone where *peri*-H interaction is absent. The magnitude of resonance interaction energy  $\Delta\Delta G$ , for 4-methoxy substrate (2,500 J mol<sup>-1</sup>) and 6-methoxy substrate (7,100 J mol<sup>-1</sup>), in the PIA oxidation reaction is in accordance with the above facts.

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