# The Correlation of Kinetic Isotope Effects with Reaction Orders to Establish the Mechanism of the Hydroxylation of Thianthrene Cation Radical in Acetonitrile

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We find that in the presence of 2,6-lutidine (L), the hydroxylation of the thianthrene (Th) cation radical in acetonitrile (AN) is first order in water. This result is in sharp contrast to those reported in neutral AN in which case the reaction was observed to be third order in water.[1] We have been able to verify an approximate third order in $H_2O$ under some conditions but find the reaction order complex and not to fit into a reasonable simple mechanistic scheme. It has been pointed out that the mechanism proposal of Evans and Blount[1] is inconsistent with their experimental rate law.[2] We have now been able to clarify the mechanism by correlating deuterium kinetic isotope effects ($k_H/k_D$) with reaction orders.

$$2\mathrm{Th}^{\cdot +} + \mathrm{H_2O} \rightarrow \mathrm{ThO} + 2\mathrm{H}^+ + \mathrm{Th} \qquad (1)$$

The kinetics of the hydroxylation of $\mathrm{Th}^{\cdot +}$ which has the stoichiometry shown in eqn. (1), were studied by derivative cyclic voltammetry[3] using the reaction order approach.[4] The essence of the method is that $v_{\frac{1}{2}}$, the voltage sweep rate necessary for the derivative peak ratio to equal 0.500, is directly proportional to the apparent rate constant. Any changes in reaction conditions, such as substrate concentration ($C_A$) or isotopic content of the reactants, which affect the reaction rate are directly reflected in $v_{\frac{1}{2}}$.[4] The data shown in Table 1 are from six different reaction series in which $C_A$ was varied in the range 0.5 to 2.0 mM. The data reported are for $C_A$ equal 1.0. The basic buffer consisted of $CF_3CO_2^-LH^+$ (3.3 mM) and L (7.5 mM) while the acidic buffer contained $CF_3CO_2^-LH^+$ (3.4 mM) and $CF_3CO_2H$ (12.9 mM). The $k_H/k_D$ and reaction orders ($R_{A/B}$) are listed in Table 2. The $R_{A/B}$ reflect both the contribution of $\mathrm{Th}^{\cdot +}$ (B) and Th (A) to the overall reaction rate.[4]

*Table 1.* Derivative cyclic voltammetry kinetics of the hydroxylation of the thianthrene cation radical in acetonitrile.

| X | $C_X$/M | Conditions | $v_{\frac{1}{2}}$/V s$^{-1}$ |
|---|---|---|---|
| $H_2O$ | 2.09 | Neutral | 91.8 |
| $D_2O$ | 2.09 | Neutral | 9.64 |
| $H_2O$ | 1.11 | Basic buffer | 26.2 |
| $D_2O$ | 1.11 | Basic buffer | 12.6 |
| $H_2O$ | 1.11 | Acidic buffer | 102.9 |
| $D_2O$ | 1.11 | Acidic buffer | 101.0 |

The data are consistent with a mechanism consisting of steps (1) to (4) where we do not specify the base, but this may be $H_2O$, L or $CF_3CO_2^-$. Under neutral conditions $R_{A/B}$ approaches 1. This is consistent with the orders in $\mathrm{Th}^{\cdot +}$ and Th being 2 and −1, respectively. The rate law for this extreme case is (5). The large value of $k_H/k_D$ under these conditions arises from both (2) and (4). We point out that the observed value of $R_{A/B}$ was 1.3 indicating that the limit represented by rate law (5) was not observed. We also do not specify a base in reaction (4) and this is because the kinetics indicate first order in both L and $H_2O$. Reaction (4) may be subject to general base catalysis where the solvent can also act as the base.

$$\mathrm{Th}^{\cdot +} + \mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Th}^{\cdot}-\overset{+}{\mathrm{O}}\mathrm{H_2} \qquad (1)$$

$$\mathrm{Th}^{\cdot}-\overset{+}{\mathrm{O}}\mathrm{H_2} + \mathrm{Base} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Th}^{\cdot}-\mathrm{OH} + \mathrm{BaseH}^+ \qquad (2)$$

$$\mathrm{Th}^{\cdot}-\mathrm{OH} + \mathrm{Th}^{\cdot +} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Th}^{+}-\mathrm{OH} + \mathrm{Th} \qquad (3)$$

$$\mathrm{Th}^{+}-\mathrm{OH} \xrightarrow{k_4} \mathrm{ThO} + \mathrm{H}^+ \qquad (4)$$

$$\mathrm{Rate} = 2k_4K_1K_2K_3[\mathrm{Th}^{\cdot +}]^2[\mathrm{H_2O}][\mathrm{Base}]/[\mathrm{Th}][\mathrm{BaseH}^+] \qquad (5)$$

*Table 2.* Correlation of reaction orders with kinetic isotope effects observed during the hydroxylation of the thianthrene cation radical in acetonitrile.

| Reaction conditions | $k_H/k_D$ | $R_{A/B}$ |
|---|---|---|
| Neutral | ~10 | 1.3 |
| Basic buffer | 2.1 | 1.75 |
| Acidic buffer | 1.0 | 2.0 |

0302-4369/82/020133-02$02.50

In the acidic buffer $k_H/k_D$ was 1 and $R_{A/B}$ was 2. Under these conditions the reaction order in $Th^{\cdot +}$ is apparently 2 and that for Th is 0. The rate law consistent with the data is (6). Thus, in acidic buffer

$$\text{Rate} = 2k_3K_1K_2[\text{Th}^{\cdot +}]^2[\text{H}_2\text{O}][\text{Base}]/[\text{BaseH}^+] \tag{6}$$

reaction (2) can be considered in equilibrium giving rise to a small value of $k_H/k_D$ and the electron transfer step (3) is rate limiting.

The reactions carried out in basic buffer represent the intermediate case between the two extremes outlined above with observed values of $k_H/k_D$ of about 2 and $R_{A/B}$ about 1.75. This situation can be described by rate law (7). The fractional reaction

$$\text{Rate} = 2k_4K_1K_2K_3[\text{Th}^{\cdot +}]^2[\text{H}_2\text{O}][\text{Base}]/[\text{BaseH}^+](k_4/k_{-3} + [\text{Th}]) \tag{7}$$

order is due to the competition of back reaction (3) with product forming reaction (4). The reactions in the basic buffer are considerably slower than those in either neutral solution or acidic buffer. This means that trifluoroacetate is a more effective base in reaction (2) than is 2,6-lutidine.

It seems highly unlikely that the presence of L in low concentrations can have a drastic effect on the overall mechanism of the reaction. It is more likely that in the absence of L the overall mechanism is the same but that the role of water is complex. For example, if Base in step (2) is $H_2O$ and $H_2O$ is implicated in step (4) an approximate third order in water could be expected under conditions outlined above where either rate law (5) or (7) applies. The work reported here has bearing on related studies[1,2,5-9] and the new approach, that of correlating kinetic isotope effects with reaction orders, may prove to be of value in clarifying other complex mechanisms of the reactions of ion radicals.

1. Evans, J. and Blount, H. *J. Org. Chem. 42* (1977) 976.
2. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 43.
3. Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem. 121* (1981) 57, 73.
4. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 233.
5. Cheng, H. Y., Sackett, P. H. and McCreery, R. L. *J. Am. Chem. Soc. 100* (1978) 962.
6. Hammerich, O. and Parker, V. D. *Acta Chem. Scand, B 36* (1982) 59.
7. Svanholm, U., Hammerich, O. and Parker, V. D. *J. Am. Chem. Soc. 97* (1975) 101.
8. Svanholm, U. and Parker, V. D. *J. Am. Chem. Soc. 98* (1976) 997.
9. Svanholm, U. and Parker, V. D. *J. Am. Chem. Soc. 98* (1976) 2942.

Received November 16, 1981.