Monatshefte für Chemie 121, 571 – 576 (1990)

Monatshefte für Chemie
Chemical Monthly

Kinetics and Mechanism of Oxidation of Acetanilide by Quinquevalent Vanadium in Acid Medium

Reeta Gupta*

Chemistry Laboratories, Government Science College, Rewa-486001, India

Summary. The kinetics of the oxidation of acetanilide with vanadium(V) in sulphuric acid medium at constant ionic strength has been studied. The reaction is first order with oxidant. The order of reaction in acetanilide varies from one to zero. The reaction follows an acid catalyzed independent path, exhibiting square dependence in H^+. A Bunnett plot indicates that the water acts as a nucleophile. The thermodynamic parameters have been computed. A probable reaction mechanism and rate law consistent with these data are given.

Keywords. Acetanilide; Kinetics; Mechanism; Oxidation; Vanadium(V).

Kinetik und Mechanismus der Oxydation von Acetanilid mit fünfwertigem Vanadium in saurem Medium

Zusammenfassung. Es wurden kinetische Untersuchungen der Oxydation von Acetanilid mit Vanadium(V) in schwefelsaurem Medium bei konstanter Ionenstärke durchgeführt. Gegenüber dem Oxidans ist die Reaktion erster Ordnung, die Reaktionsordnung gegenüber Acetanilid variiert zwischen 1 und 0. Die Reaktion folgt einem von der Säurekatalyse unabhängigen Weg, wobei die Abhängigkeit von H^+ quadratisch ist. Ein Bunnett-Plot zeigt, daß das Wasser als Nucleophil wirkt. Die thermodynamischen Parameter wurden berechnet. Ein möglicher Reaktionsmechanismus und ein Geschwindigkeitsnetz, das mit diesen Daten in Einklang ist, wird angegeben.

Introduction

Anilides are the N-phenyl derivatives of amide of either aliphatic or aromatic acids. The literature survey reveals that the oxidation of acetanilide, an important medicinal compound, has been very little studied both quantitatively and kinetically. In this report, kinetics and mechanism of oxidation of acetanilide by vanadium(V) in sulphuric acid medium have been discussed.

Experimental

A solution of acetanilide (S. M.) was prepared by dissolving in the predetermined amount of glacial acetic acid (B. D. H.). The oxidant solution was prepared by dissolving ammonium meta vanadate (Reidal) in sulphuric acid. The precise concentration of the resulting solution was estimated by usual methods. All the other chemicals used were of standard grade.

---

* For correspondence: 4926 Deep Creek Road, Fremont, CA 94555, USA

The kinetic measurements were made at constant ionic strength by adding either sodium sulphate or sodium perchlorate. The mixture was allowed to equilibrate at the required temperature (30 ± 0.1°). Kinetics of the reaction were monitored by estimating unconsumed vanadium(V) against standard ferrous ammonium sulphate solution using N-phenyl anthranilic acid as an indicator.

The stoichiometric investigations revealed that 1 mol of acetanilide reacts with 4 mol of vanadium(V) yielding *p*-benzoquinone as a product and it also produces ammonia and acetic acid. The oxidation reaction may thus be represented as shown below:

$$C_8H_9ON + 4\,V(V) + 3\,H_2O \rightarrow C_6H_4O_2 + 4\,V(IV) + 4\,H^+ + NH_3 + CH_3COOH.$$

Results and Discussion

The dependence of rate on the concentration of the oxidant was studied by varying the initial concentration of the vanadium(V) at constant ionic strength. It has been observed that for all the concentrations of vanadium(V) the initial ($\approx$ 15%) reaction is very fast and the remaining reaction follows first order kinetics. The average constant values of the pseudo first order rate constant at different initial concentrations of the oxidant were found to decrease with increase in the concentration of vanadium(V) in acetanilide (Table 1). Therefore, it is concluded that the concentration order of the reaction is one. The equifractional change method also confirms the first order dependence on vanadium(V). In the differential method the slope value of the linear plot of $\log \mathrm{d}c/\mathrm{d}t$ vs. $\log C$ was obtained as 0.70 (Fig. 1). Hence, the time order obtained for acetanilide is less than the concentration order which indicates that the reaction is autocatalyzed [1].

An increase in [Acetanilide] increased the reaction rate (Table 2) at constant [Vanadium(V)] and tended to attain a limiting value indicating complex kinetics. The plot of k_1 vs. [Acetanilide] showed a deviation from a straight line behavior at higher concentrations of acetanilide, suggesting that the order in substrate varies from unity to zero (Fig. 2).

Such fractional dependence on the substrate has also been reported for the oxidation of acetanilide and substituted acetanilide by $HClO_4$-phenyl iodosyl acetate system [2]. This dependence of rate on [Acetanilide] makes the formation of an intermediate complex likely, prior to the rate limiting step. This presumption was also confirmed by the linearity and positive intercept on the double reciprocal plot of k_1 vs. [Acetanilide].

Table 1. Effect of varying [Vanadium(V)] on reaction rate: [Acetanilide] = $2.50 \cdot 10^{-2} M$; $[H_2SO_4] = 5.0\,M$; $HAc-H_2O$ = 10% (*v*/*v*); $\mu = 5.01\,M$; temperature = 30°C

[Vanadium(V)] ($10^3 M$)	$10^3 k_1$ (min^{-1})
1.25	11.53
2.00	11.21
2.50	10.07
3.33	9.76
5.00	8.69

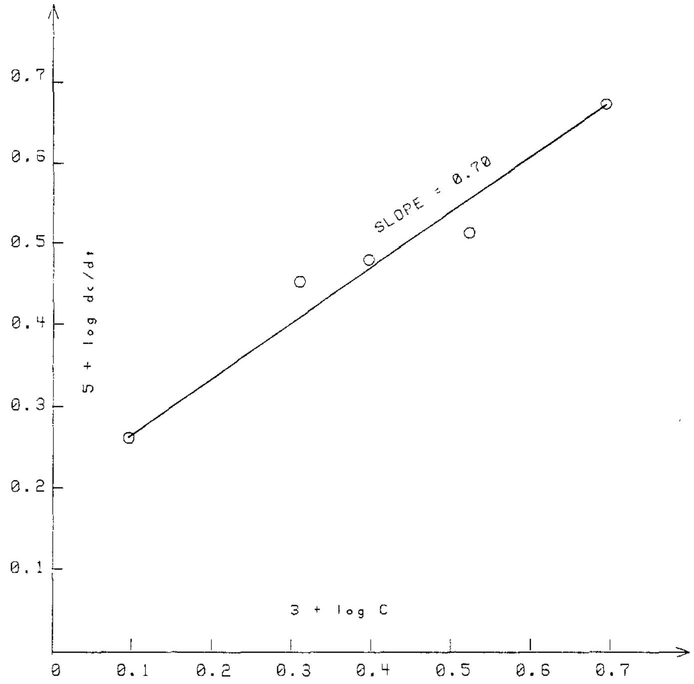


Fig. 1. Plot of log d*c*/d*t* vs. log *C*. [Acetanilide] = $2.50 \cdot 10^{-2} M$; [H_2SO_4] = $5.0 M$; H*Ac*$-H_2O$ = 10% (*v*/*v*); μ = $5.01 M$; temperature = 30°C

Table 2. Effect of varying [Acetanilide] on reaction rate: [Vanadium(V)] = $2.50 \cdot 10^{-3} M$; [H_2SO_4] = $5.0 M$; H*Ac*$-H_2O$ = 10% (*v*/*v*); μ = $5.01 M$; temperature = 30°C

[Acetanilide] ($10^2 M$)	$10^3 k_1$ (min^{-1})	k_2 ($l\,mol^{-1}\,min^{-1}$)
1.00	4.06	4.06
1.25	5.25	4.20
2.00	8.28	4.14
2.50	10.07	4.02
3.33	13.46	4.04
5.00	17.94	3.58

In the case of acetanilide, the plot of k_1 vs. $[H^+]^2$ was a straight line passing through the origin, suggesting that the reaction involves an acid catalyzed independent path. Also, the rate was directly proportional to the square of the concentration of sulphuric acid. Zucker-Hammett plots [3] i.e. log k_1 vs. $-H_0$ and log k_1 vs. log [acid] were linear with a slope less than unity.

In an attempt to correlate the rate with acid concentration, Bunnett's hypothesis, in addition to the Hammett acidity function, was tested. Bunnett found that plots of (log $k_1 + H_0$) vs. log a_{H_2O} (where H_0 is the Hammett activity function and a_{H_2O} is the activity of water in a given solvent mixture) are generally linear. The slopes of the linear plots obtained are certainly useful in providing a method of

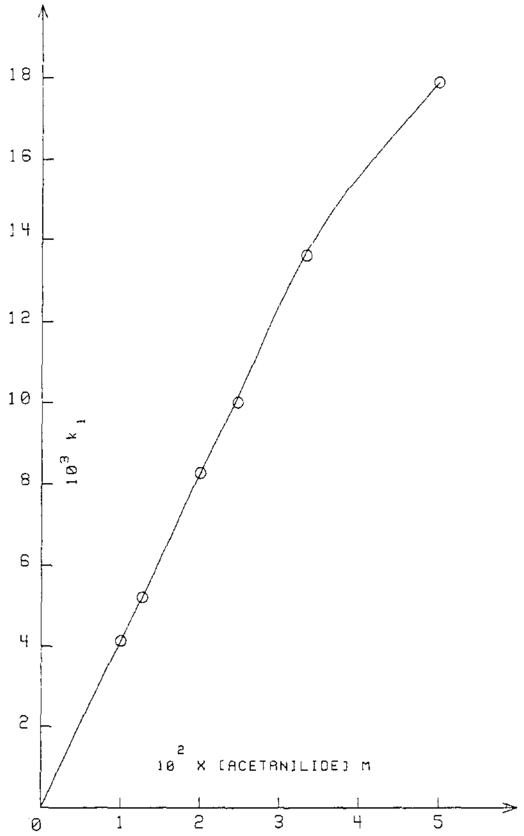


Fig. 2. Plot of k_1 vs. [Acetanilide]. [V(V)] = $2.50 \cdot 10^{-3}$ *M*; [H_2SO_4] = 5.0 *M*; μ = 5.01 *M*; H*Ac*−H_2O = 10% (*v*/*v*); temperature = 30°C

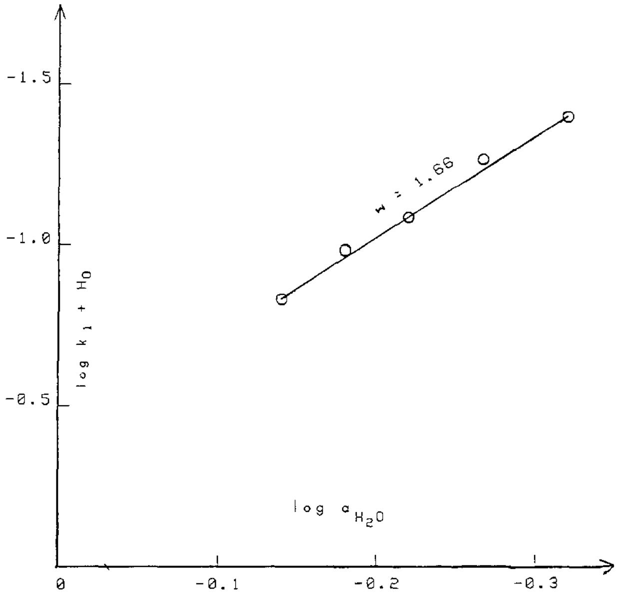


Fig. 3. Plot of log k_1 + H_0 versus log a_{H_2O}. [V(V)] = $2.50 \cdot 10^{-3}$ *M*; [Acetanilide] = $2.50 \cdot 10^{-2}$ *M*; H*Ac*−H_2O = 10% (*v*/*v*); temperature = 30°C

empirical classification of acid catalyzed reactions. According to Bunnett [4] the slopes of the linear plots of ($\log k_1 + H_0$) vs. $\log a_{H_2O}$ defines a parameter "w". The w values of -2.5 to zero indicate non-participation of water molecules in the transition state. The values between $+1.2$ to $+3.3$ indicate that water acts as a nucleophile and the values greater than $+3.3$ indicate that water acts as a proton abstracting agent.

In the present investigation, the Bunnett plot has been found to be linear (Fig. 3). The w value ($+1.66$ in sulphuric acid) indicates that during the course of the reaction water acts as a nucleophile in the rate controlling step.

The value of the pseudo first order rate constant is not effected by an addition of sodium bisulphate, suggesting that the active species of vanadium(V) does not involve the bisulphate ion. The addition of $NaClO_4$ and Na_2SO_4 shows a negligible increase in the value of the rate constant. The effect of variation of the acetic acid–water ratio was examined and it was found that the values of k_1 increase with the decrease in dielectric constant (D) of the medium. A positive slope from the linear plot of $\log k_1$ vs. $1/D$ and the results of salt effects indicate that the reaction is of an ion-dipole type.

The temperature dependence of the reaction was studied at four different temperatures (30°, 35°, 40°, 45°C). The plot of $\log k_1$ vs. $1/T$ for different [Acetanilide], was found to be straight lines showing that the reaction obeys an Arrhenius temperature dependence. The values of E, A, and $\Delta S^{\neq}$ are $86.17 \pm 5.7\,\mathrm{kJ\,mol^{-1}}$, $5.55 \pm 0.9 \cdot 10^{10}\,\mathrm{s^{-1}}$ and -39.57 ± 0.3 e.u. respectively.

An induced polymerization of acrylonitrile took place within a short interval of time when it was added to the reaction mixture. This indicates that free radicals are formed during the course of the reaction as a result of one electron transfer.

Pentavalent vanadium, a metal cation oxidant, is amphoteric and exists only in cationic form in solution of acidity greater than $0.5\,M$ [5],

$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O.$$

The cationic vanadium(V) species can change its form depending on the acid type and concentration range. This VO_2^+ species has been described as $V(OH)_4^+$ [6] in accordance with the tetrahedral structure of vanadium compounds [7]. The participation of the active species $[VO_2(H_2SO_4)_2]^+$ in the reaction in presence of sulphuric acid has been established [8]. The nitrogen atom and the carbonyl oxygen of the acetanilide molecule coordinate with electrophilic vanadium(V) species yielding an electron deficient complex, which in the rate determining step suffers nucleophilic attack of water molecules leading to the formation of a free radical intermediate. These free radicals then undergo hydrolytic fission in a fast step and give anilinium free radicals. In the light of these evidences, the following probable mechanism is being proposed:

$$V(OH)_4^+ \text{ or } [VO_2(H_2O)_2]^+ + 2H_2SO_4 \overset{K_1}{\rightleftharpoons} [VO_2(H_2SO_4)_2]^+ + 2H_2O, \qquad (1)$$

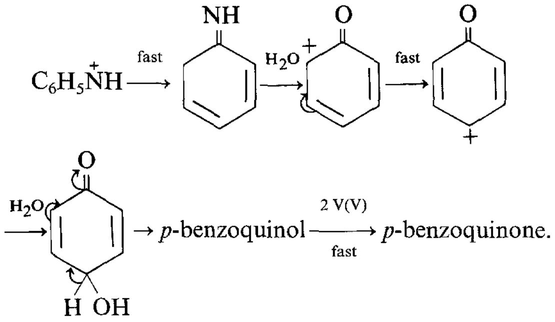
$$[VO_2(H_2SO_4)_2]^+ + C_6H_5NHCOCH_3 \overset{K_2}{\rightleftharpoons} \text{complex}^+, \qquad (2)$$

$$\text{complex}^+ + H_2O \underset{\text{slow}}{\overset{k}{\rightarrow}} C_6H_5\dot{N}COCH_3 + [VO_2(H_2SO_4)_2] + H_3O^+, \qquad (3)$$

$$C_6H_5\dot{N}COCH_3 + H_2O \xrightarrow{\text{fast}} C_6H_5\dot{N}H + HOAc. \qquad (4)$$

p-Benzoquinone was identified as the product of oxidation. Its formation from the anilinium free radical ($C_6H_5\dot{N}H$) can be explained as follows:

$$C_6H_5\dot{N}H + V(V) \xrightarrow{\text{fast}} C_6H_5\overset{+}{N}H + V(IV) \tag{5}$$



The mechanism leads to the rate law:

$$k_{\text{obs}} = \frac{k K_1 K_2 [\text{Acetanilide}] [H_2SO_4]^2}{1 + K_1 [H_2SO_4]^2 + K_1 K_2 [\text{Acetanilide}] [H_2SO_4]^2} . \tag{6}$$

According to Wells and Kuritsyn [9] the equilibrium constant for the formation of $V(OH)_3^{2+}$ is very much less than one and so K_1 may also be assumed to be less than one and thus Eq. (6) becomes

$$k_{\text{obs}} = \frac{k K_1 K_2 [\text{Acetanilide}] [H_2SO_4]^2}{1 + K_1 K_2 [\text{Acetanilide}] [H_2SO_4]^2} .$$

The above mechanism is compatible with all experimental results.

Acknowledgement

I am thankful to Dr. Kusum Sharma and Dr. V. K. Sharma of Government Science College, Rewa (India) for their valuable support and discussions through this work.

References

[1] Laidler K. J.: Chemical Kinetics, 2nd edn. Tata McGraw-Hill, p. 17
[2] Radhakrishnamurti P. S., Sasmal B. M., Patnaik D. P. (1985) Indian. J. Chem. **24**(A): 106
[3] Zucker L., Hammett L. P. (1939) J. Am. Chem. Soc. **61**: 2791
[4] Bunnett J. F. (1961) J. Am. Chem. Soc. **83**: 4956
[5] Littler J. S., Waters W. A. (1959) J. Chem. Soc.: 254
[6] Coryeel C. D., West D. M. (1933) J. Am. Chem. Soc. **55**: 1909
[7] Mulligan W. O., Vernon I. W. (1952) J. Phys. Chem. **56**: 145
[8] Sengupta K. K., Pal B. S., Mukherjee D. C. (1974) J. Chem. Soc.: 226
[9] Wells C. F., Kuritsyn L. V. (1970) J. Chem. Soc.: 1372

Received August 29, 1989. Accepted November 2, 1989