

NOTE

Kinetics of Oxidation of Furfural by 1-Bromobenzimidazole

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The kinetics of oxidation of furfural with 1-bromobenzimidazole (BBI) has been studied in binary solvent mixture of acetic acid and water. The reaction shows uni order dependence each with respect to oxidant, substrate and H^+ concentration. Addition of benzimidazole has no effect on the reaction rate. $BBIH^+$ has been postulated as the reactive oxidizing species. Increase in ionic strength has no effect on the reaction rate. The reaction rate increases with increase in percentage of acetic acid. The reaction fails to initiate polymerization of acrylonitrile. The reaction rates were determined at different temperatures and the activation parameters have been calculated. A mechanism in consistent with the kinetic data has been proposed.

Key Words: 1-Bromobenzimidazole (BBI), Furfural, Kinetics, Oxidation, Potentiometry.

In recent years, the kinetics studies on the oxidation as well as halogenations of organic compounds by N-halo compounds is gaining importance due to their application in organic synthesis and also due to the kinetic aspects¹⁻⁶. In all these N-halo compounds, N-X bond is highly polar and they produce positive halogen (X^+) in polar solvents due to protonation. This positive halogen acts as powerful electrophile. In the present investigation the reaction kinetics of furfural with 1-bromobenzimidazole (BBI) has been studied in presence of perchloric acid and mercury(II) acetate.

1-Bromobenzimidazole (BBI) was prepared and purified by the literature method⁷. Furfural was distilled and the fraction collected at 162 °C was used. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected. All other chemicals were analar grades of purity. Double distilled water was used throughout the study.

Kinetic measurements: Pseudo-first order conditions were maintained by keeping a large excess (10 folds) of furfural over 1-bromobenzimidazole (BBI). Mercury(II) acetate was added to each reaction mixture to prevent liberation and further reaction of bromine⁸. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reaction were followed potentiometrically⁹ up to 70 % completion, by following the potentials of the reaction mixture containing varying concentrations of [BBI]/[BI] couple at regular time intervals using a platinum-saturated calomel electrode assembly. The pseudo-first order rate

constant, k was computed from the linear ($r > 0.997$) plots of $\log (E_1 - E_0)$ versus time. When the kinetic run was done by iodometry, the same results were obtained with $k \pm 4 \%$. Preliminary experiments showed that the reaction was not sensitive to change in ionic strength; hence no attempt was made to keep it constant.

Stoichiometry: To determine the stoichiometry, furfural was treated with an excess of 1-bromobenzimidazole (BBI). When the reaction was complete, unreacted BBI was determined iodometrically. Estimation of the unreacted oxidant showed that one mole of oxidant react with one mole of furfural. The product analysis shows the presence of furoic acid (furan-2-carboxyl acid) as the product which is confirmed by spectral analysis and TLC.

The kinetics oxidation of furfural by BBI was investigated at several initial concentrations of the reactants. The reaction was carried at different concentrations of BBI. The fact that the plots of $\log [BBI]$ versus time were straight lines even beyond 75 % completion of the reaction indicates that the reaction is first order with respect to BBI. However, the pseudo-first order rate constants decrease with increase in concentration of gross BBI (Table-1). Similar observations have been made earlier in different oxidation studies¹⁰⁻¹². The oxidation was also carried out with various concentration of furfural, keeping other solution variables as constant at 303 K. An increase in the concentration of furfural increases the rate of oxidation (Table-1) and a plot of $\log k$ versus $\log [\text{furfural}]$ was linear

TABLE-1
EFFECT OF VARYING [SUBSTRATE], [OXIDANT]
AND [H⁺] ON REACTION RATE

Acetic acid = 70 %, [mercury(II) acetate] = 1.0×10^{-2} mol dm³

[BBI] × 10 ³	[Furfural] × 10 ²	[H ⁺] × 10 ²	k _{obs} × 10 ⁴
1.6	4.4	9.95	4.97
2.4	4.4	9.95	4.78
3.2	4.4	9.95	4.53
4.0	4.4	9.95	4.28
4.8	4.4	9.95	4.15
3.2	2.2	9.95	2.55
3.2	3.3	9.95	3.34
3.2	4.4	9.95	4.53
3.2	5.5	9.95	5.83
3.2	6.6	9.95	7.02
3.2	4.4	4.98	2.13
3.2	4.4	9.95	4.53
3.2	4.4	14.93	6.95
3.2	4.4	19.90	9.40
3.2	4.4	24.85	11.87

with unit slope showing the first order dependence on the substrate. The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentration of perchloric acid and keeping the concentration of the other reactants are constant. The rate increases proportionally with increase in [H⁺]. Acidity dependence is first order throughout the range of reactions.

The effect of mercury(II) acetate in present study showed negligible effect on the reaction rate but found its utility to fix bromide ion during the course of the reaction and avoiding the oxidation of the latter to molecular bromine¹³. The addition of benzimidazole has no effect on the reaction rate. Polymerization is not observed when acrylonitrile is added to the reaction mixture.

The effect of varying dielectric constant of reaction rate was studied (Table-2) by varying concentration of acetic acid from 60-90 %. It is found that the rate of reaction increases with increase in acetic acid content of the solvent mixture and the plot of log *k* versus 1/*D* was linear.

TABLE-2

EFFECT OF VARYING [ACETIC ACID] ON REACTION RATE
[BBI] = 3.2×10^{-3} mol dm³, [H⁺] = 9.95×10^{-2} mol dm³, [furfural] = 4.4×10^{-2} mol dm³, acetic acid = 70 %, [mercury(II) acetate] = 1×10^{-2} mol dm³, temperature = 303 K

Acetic acid (%)	D	1/D	k _{obs} × 10 ⁴
60	35.14	2.84	2.77
70	27.90	3.58	4.53
80	20.67	4.83	6.60
90	13.44	7.44	8.68

The rate constants were measured at three different temperatures (Table-3) and activation parameters have been calculated from the linear Eyrings plot of ln *k*/*T* versus 1/*T* by the least square method.

Mechanism and rate law: In acidified aqueous acetic acid solution of BBI, the possible oxidizing species are BBI itself, BBIH⁺, HOBr, H₂OBr⁺ and Br₂. The strict first order dependence of reaction rate on BBI rules out the possibility of molecular bromine as oxidizing species. The dependence on

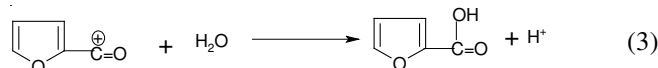
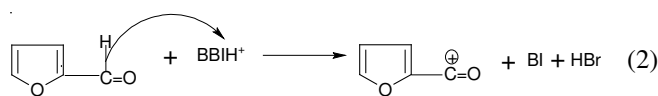
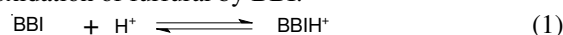
TABLE-3
EFFECT OF VARYING TEMPERATURE ON REACTION RATE

[BBI] = 3.2×10^{-3} mol dm³, [H⁺] = 9.95×10^{-2} mol dm³,
[furfural] = 4.4×10^{-2} mol dm³, acetic acid = 70 %, [mercury(II) acetate] = 1×10^{-2} mol dm³

Temperature	k _{obs} × 10 ⁴	1/T × 10 ³	ln <i>k</i> / <i>T</i>
293	2.38	3.41	-14.02
303	4.53	3.30	-13.41
313	9.08	3.19	-12.75

ΔH* = 47.99 KJ mol⁻¹, ΔS* = -150.519 JK mol⁻¹, ΔG* = 93.59 KJ mol⁻¹.

reaction rates on [H⁺] ions precludes the involvement of BBI as such or HOBr as active oxidizing species and suggesting BBIH⁺ the most probable oxidizing species. This is also evidenced by the absence of any effect of benzimidazole on the reaction rate. The following scheme has been proposed for the oxidation of furfural by BBI.



The above mechanism leads to the following rate law.

$$\text{Rate} = -d[\text{BBI}]/dt = k_2[\text{furfural}][\text{BBIH}^+] \quad (4)$$

From eqn. 4,

$$k_1[\text{BBI}][\text{H}^+] = k_{-1}[\text{BBIH}^+]$$

or

$$k_a = k_1/k_{-1} = [\text{BBIH}^+]/[\text{BBI}][\text{H}^+]$$

$$[\text{BBIH}^+] = k_a[\text{BBI}][\text{H}^+] \quad (5)$$

Substituting eqn. 5 in 4,

$$\text{Rate} = k_2 k_a [\text{furfural}][\text{BBI}][\text{H}^+] \quad (6)$$

$$k_2 k_a = k_{\text{obs}}$$

$$\text{Rate} = k_{\text{obs}}[\text{furfural}][\text{BBI}][\text{H}^+] \quad (7)$$

Conclusion

The kinetics of oxidation of furfural by 1-bromobenzimidazole (BBI) in aqueous acetic acid medium clearly shows that the order with respect to BBI, furfural and H⁺ ion are unity. The product analysis shows the presence of furoic acid as the major product. The mechanism proposed for this oxidation kinetics is in accordance with the observed kinetic facts.

REFERENCES

- N. Nanda, B.S. Sheshdri and S.M. Mayanna, *React. Kinet. Catal. Lett.*, **67**, 35 (1999).
- N.A. Mohamed Farook, *J. Sol. Chem.*, **36**, 435 (2007).
- K. Chowdhury and K.K. Banerji, *J. Org. Chem.*, **55** (1990).
- S. Negi and K.K. Banerji, *Indian J. Chem.*, **21B**, 846 (1982).
- N.S. Srinivasan and N. Venkatasubramanian, *Indian J. Chem.*, **10**, 1014 (1972).
- B. Ramkumar, *Asian J. Chem.*, **14**, 463 (2002).
- B. Ramkumar, *Asian J. Chem.*, **13**, 777 (2001).
- J. Mukherjee and K.K. Banerji, *J. Org. Chem.*, **46**, 2323 (1981).
- B. Ramkumar, *Afinided*, **60**, 257 (2003).
- K.B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York, 69 (1965).
- M.K. Pillay and Thirunavukkarasu, *Indian J. Chem.*, **20B**, 583 (1981).
- M.K. Pillay and A.A. Jameel, *Indian J. Chem.*, **31A**, 46 (1992).
- S. Srivastava, A. Awasthi and K. Singh, *Int. J. Chem. Kinet.*, **37**, 275 (2005).