

A Kinetic Assessment of the Rapid Iodination of Pyrrole in Aqueous Medium by Molecular Iodine using Hydrodynamic Voltammetry

Borkar V.T.*, Dangat V.T., Bonde S.L., Bhadane R.P. and Yadav Keerti

Department of Chemistry, Nowrosjee Wadia College, Pune, INDIA

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Abstract

The quantitative study of the rapid iodination of pyrrole in aqueous medium using molecular iodine at 7 pH has been carried out at five different temperatures. The reaction was found to be very rapid and of second order having a half-life of 40 seconds and velocity constant $5000 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C . The rapidity of the reaction necessitated the use of a special technique, hydrodynamic voltammetry, to follow the course of the reaction. The energy of activation, entropy of activation and pre-exponential factor 'A' for the reaction are evaluated as $56.16 \text{ kJ mol}^{-1}$, $-64.35 \text{ J K}^{-1} \text{ mol}^{-1}$ and $6.96 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively at 30°C and 7 pH. The kinetic and related thermodynamic data obtained elucidate the high reactivity of the heterocycle under study.

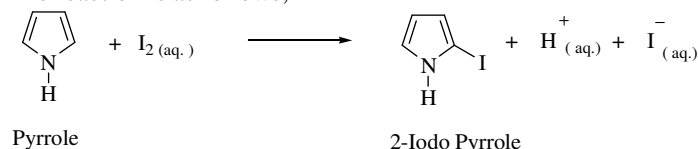
Keywords: Pyrrole, Iodination, Hydrodynamic voltammetry.

Introduction

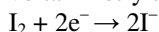
Iodination of aromatic substrates are known to be electrophilic substitution reactions and are rapid in aqueous medium devoid of iodide ions¹. Iodo derivative of aromatic substrates are known to have several pharmaceutical applications². Hence rates and mechanisms of the formation of these derivatives are important³. In aqueous solutions, halogenations of aromatic substrates follow rapid kinetics necessitating special techniques to measure such reaction rates. These include temperature jump, competition technique and stopped flow and pulse radiolysis technique^{4,5}.

We have herein adopted a relatively simple yet efficient technique, hydrodynamic voltammetry to monitor the course of the fast iodination of pyrrole in aqueous medium^{6,7}.

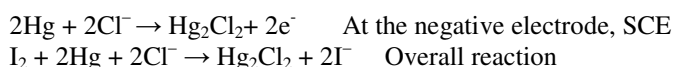
The reaction is as follows;



The aqueous solutions used are necessarily very dilute due to the rapidity of the reaction and green chemistry principles are inherent in this study⁸. Iodine being the only species in the reaction that is electroreducible at the cathode, its change in concentration during the reaction is followed by measuring the nano-current at a platinum microelectrode that rotates at 600 rpm. The following are the two half-cell reactions at the two electrodes in the galvanic cell used in this hydrodynamic voltammetry technique.



At the positive electrode, RPE



The use of a large concentration of the supporting electrolyte, KNO₃ ensures linear proportionality of the diffusion limited current at the RPE due to the iodine concentration in the cell.

Material and Methods

Chemicals: AR grade samples of pyrrole, iodine, sodium dihydrogen phosphate, disodium hydrogen phosphate and potassium nitrate were used to prepare the required stock solutions in double distilled water.

Electrodes: The cathode [RPE] is a platinum electrode fused to a glass tube rotated at 600 rpm with the aid of a motor. The anode [SCE] is a saturated calomel electrode.

Calibration: The RPE and SCE are dipped in 50.0 cm³ of $5 \times 10^{-4} \text{ M}$ KNO₃ - the supporting electrolyte. A potential of +0.1 V Vs the SCE is applied at the RPE. Zero deflection is adjusted on the scale with the help of a shunt. KNO₃ solution is then replaced by $5 \times 10^{-6} \text{ M}$ iodine solution containing hundred fold concentration of the supporting electrolyte. The galvanometer deflection is adjusted to be at a maximum value on the scale. The diffusion current in terms of the galvanometer deflection, is noted for different iodine concentrations. The graph of diffusion current Vs [I₂] is obtained (figure-1). The calibration readings are carried out at five different temperatures.

Kinetic Measurements: 25 cm³ of $1 \times 10^{-5} \text{ M}$ pyrrole containing $1 \times 10^{-3} \text{ M}$ KNO₃ and 25cm³ of $1 \times 10^{-5} \text{ M}$ iodine containing of $1 \times 10^{-3} \text{ M}$ KNO₃ containing the buffer components (Na₂HPO₄ and NaH₂PO₄) are kept in a thermostat at the desired

temperature. The reactants are then mixed in a container in which the SCE is dipped and the RPE is rotating. A stop-clock is started at the moment of mixing. As the reaction proceeds, the galvanometer deflection decreases steadily and is recorded at every 10 seconds until 80 seconds. The above procedure of calibration and kinetic measurements is repeated for ascertaining the reproducibility of the galvanometer readings and is found to be precise within 0.2 nA. The unreacted iodine concentration at different instants is then computed using the calibration curve.

A plot of $[I_2]^{-1}$ Vs time is found to be linear (figure-2). Hence the reaction is inferred to be of the second order. The slope of this plot gives the velocity constant 'k'. These studies are carried out at different temperatures from which the energy of activation for the reaction is evaluated.

Further, the frequency factor, A and the entropy change, ΔS^\ddagger for the reaction are also evaluated.

Constant parameters in the reaction under study:

Potential applied at the RPE Vs SCE.	$1.0 \times 10^{-1}V$
Initial concentration of iodine	$5.0 \times 10^{-6}M$
Initial concentration of pyrrole	$5.0 \times 10^{-6}M$
Concentration of KNO_3	$5.0 \times 10^{-4}M$
Total reaction mixture volume	50.0 cm^3
Concentration of Na_2HPO_4	2.6 m mol
Concentration of NaH_2PO_4	2.4 m mol

Results and Discussion

The observations are presented in tables 1-3 and figure 1-3.

Table-1
Calibration readings of the diffusion current of molecular iodine at various temperatures

$[I_2]/10^{-6}M$	Diffusion Current/ nA				
	10.1°C	15.2°C	20.0°C	25.4°C	30.0°C
1	4.0	5.2	6.1	7.5	8.2
2	8.2	10.1	12.0	14.4	16.4
3	12.1	15.3	18.3	22.0	24.1
4	16.3	20.1	24.1	28.1	32.2
5	20.0	25.0	30.0	37.5	41.0

Table-2
Kinetics of iodination of pyrrole at 30.0°C by molecular iodine

Time/s	Diffusion current /nA	$[I_2]/10^{-6}M$	$[I_2]^{-1}/10^5 M^{-1}$
0	41.0	5.0	2.0
10	33.0	4.0	2.5
20	27.0	3.3	3.0
30	23.0	2.8	3.5
40	21.0	2.5	4.0
50	18.0	2.2	4.5
60	17.0	2.0	5.0
70	15.0	1.8	5.5
80	14.5	1.7	6.0

Table-3
Variation of velocity constant of iodination of pyrrole by molecular iodine with temperature

T / K	$[T]^{-1}/10^{-3}[K^{-1}]$	$k/M^{-1}s^{-1}$	log k
303	3.30	5000	3.698
298	3.35	3750	3.574
293	3.41	2500	3.397
288	3.47	1875	3.273
283	3.53	1231	3.096

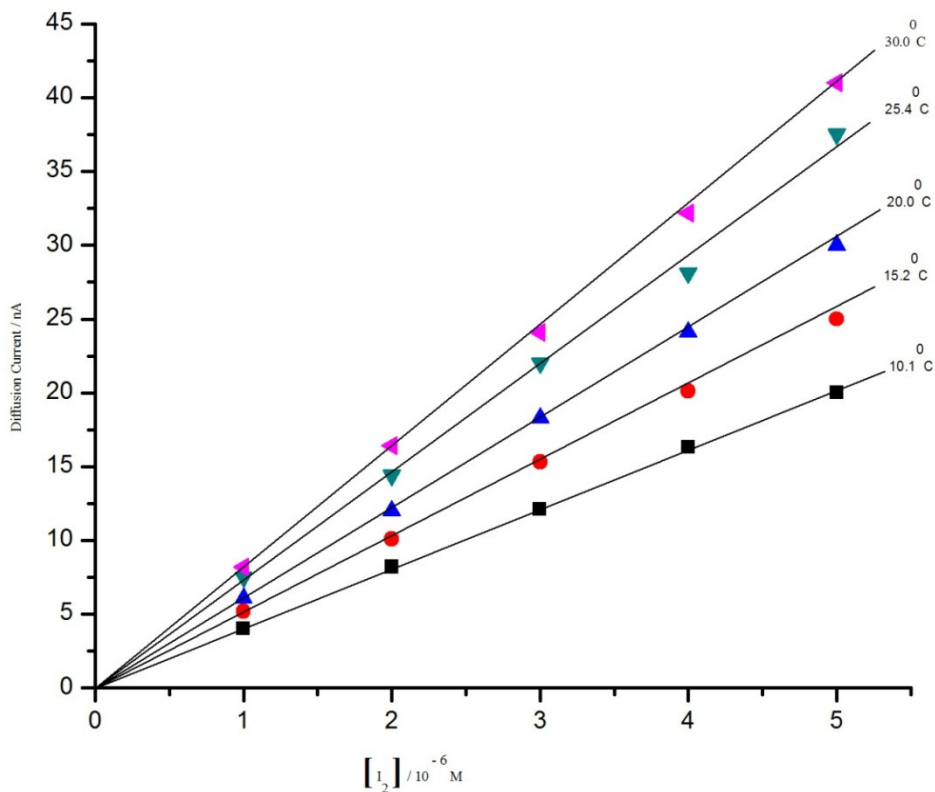


Figure-1
Calibration plots of the diffusion current of $[I_2]$ at various temperatures for iodination of pyrrole

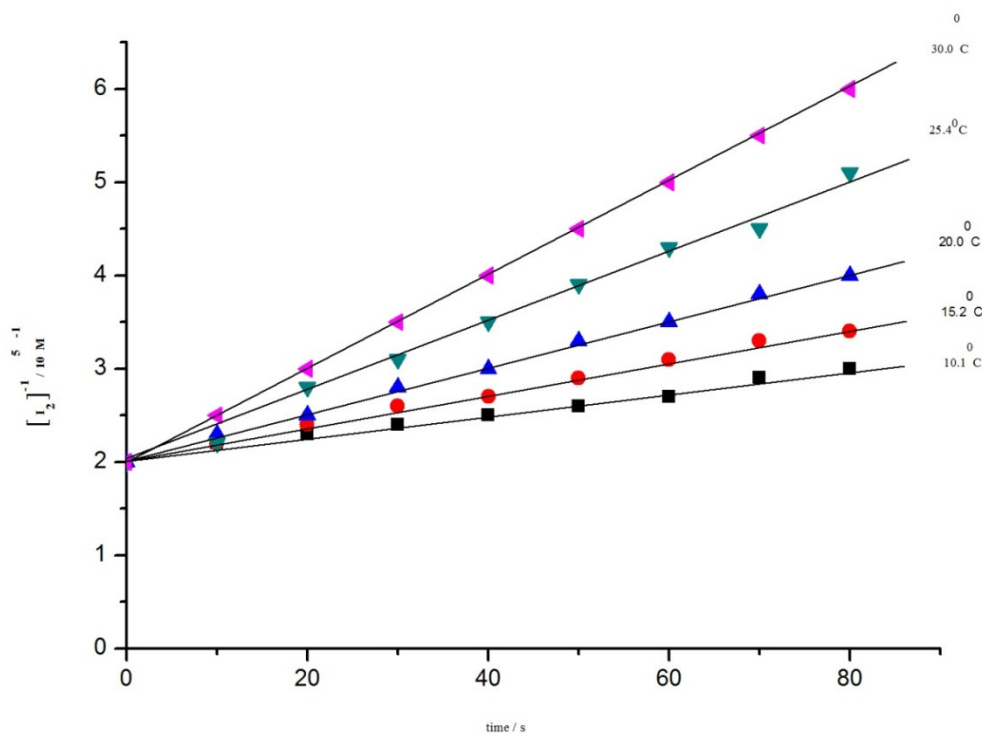


Figure-2
Kinetic plots for iodination of pyrrole at various temperatures by molecular iodine

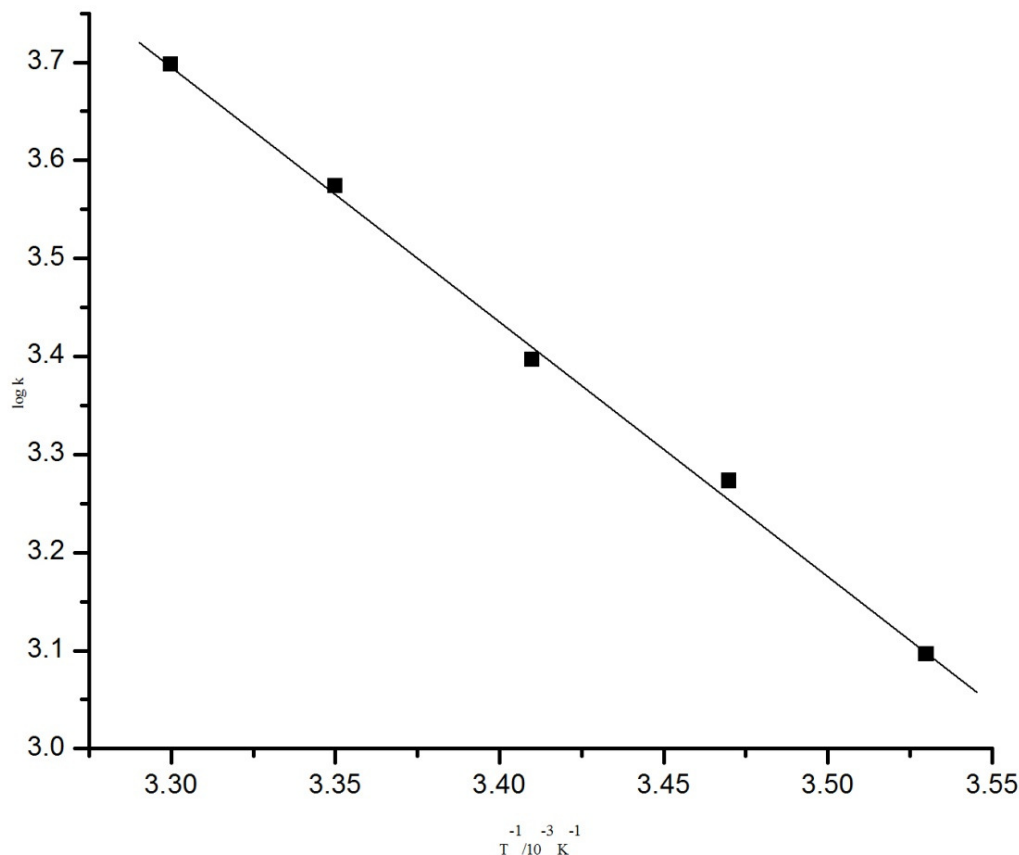
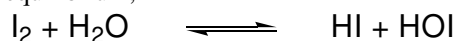


Figure-3
 Arrhenius plot for the reaction under study

Molecular iodine is the sole iodinating reagent in the reaction in view of the thermodynamic equilibrium constant for the equilibrium,

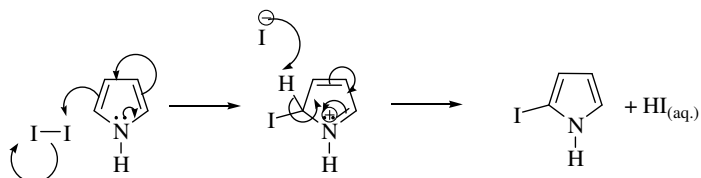


which is predominantly shifted to the left in view of the low hydrolysis constant (2.0×10^{-13}) and since hypiodous acid is known to be a very weak electrophile⁹.

From the current recorded at the RPE Vs the SCE for various concentrations of iodine, a calibration plot of diffusion current Vs $[I_2]$ is prepared. From the kinetic measurements, a plot of $[I_2]^{-1}$ Vs time using the calibration curve is obtained and is linear confirming that the reaction has an overall order of two. The velocity constant k is obtained from the slope of this figure. The reaction is fast but its half-life is extended by diluting the solutions. This leads to very low initial concentrations of the reactants which further attenuate during the reaction. Yet, it is possible to follow the course of the reaction using hydrodynamic voltammetry as this technique can detect very low concentration of an electro-reducible species. In the reaction under study, only iodine among the products and reactants is electro-reducible, hence the technique is applicable.

The reaction is carried out at five different temperatures from which data, the energy of activation, entropy of activation and pre-exponential factor 'A' for the reaction are evaluated as $56.16 \text{ kJ mol}^{-1}$, $-64.35 \text{ J K}^{-1} \text{ mol}^{-1}$ and $6.96 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively at 30°C and 7 pH.

Mechanism



Conclusion

The value of the velocity constant obtained for the iodination of pyrrole in aqueous medium indicates that the substrate being a five member heterocycle, is less aromatic than benzene derivatives leading to greater reactivity and higher iodination rate. Further, the frequency factor, A and the entropy change, ΔS^\ddagger for the reaction are also evaluated¹⁰. Thus the speculated reactivity of pyrrole in the iodination reaction using aqueous molecular iodine has been herein quantitatively ascertained.

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