

Kinetics of Acid Hydrolysis of Furfural Semicarbazone: A Polarographic Study in Acid Medium

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Kinetics of hydrolysis of furfural semicarbazone has been studied polarographically in acid medium. The products of hydrolysis are identified as furfural and semicarbazide. The effects of the concentrations of (a) acid (HCl), (b) substrate, (c) furfural, (d) semicarbazide, (e) neutral salt (KCl), (f) solvents and (g) temperature on the rate of hydrolysis have also been studied. An A-2 type of mechanism involving the participation of protonated semicarbazone is found operative in acid hydrolysis. It is proposed that the species protonated at position-5 in the furan ring and at azomethine nitrogen is kinetically significant.

Alpokankanpera and coworkers¹⁻³ and Garst *et al.*⁴ reported that furan ring undergoes acid-catalysed hydrolytic cleavage in aqueous solutions. The nature of the products and the mechanism of the reaction depend on furan derivative. Garst *et al.*⁴ also proposed that 2-methoxyfuran can undergo hydrolysis involving protonation at position-5 (route-A) or position-3 (route-B). Route-A involves a tetrahedral intermediate adduct which breaks down mainly into the products with furan ring intact. On the other hand in route-B the tetrahedral intermediate breaks down solely by furan ring cleavage.

During the polarographic studies on furfural derivatives in our laboratories it was observed that the limiting current of furfural semicarbazone in acid solutions decreased with time and this was established as due to hydrolysis of the substrate. We have, therefore, studied polarographically the kinetics of acid hydrolysis in detail and the results are reported in this paper.

Materials and Methods

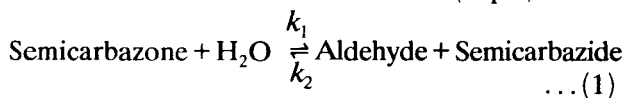
Polarographic measurements

A known volume of stock solution of hydrochloric acid (5 mol dm^{-3}) was taken in the polarographic cell, diluted to 22.5 ml with conductivity water, thermostated for sufficient time at the desired temperature and to this were added 5 or 6 drops of gelatin as maximum suppressor. An aliquot (2.5 ml) of stock solution of the substrate in aqueous ethanol was separately thermostated for sufficient time at the same temperature and then pipetted out into the polarographic cell containing the acid solution. The

time when the pipette was half empty was recorded, the reaction mixture purged with purified hydrogen and the polarograms were recorded at different time intervals.

Results and Discussion

An inspection of the polarograms in Fig. 1, shows that the height of the semicarbazone wave ($E_{1/2} = -0.78 \text{ V}$) progressively decreases with time, and a new wave at more negative potential ($E_{1/2} = -0.965 \text{ V}$) whose height progressively increases with time appears. The $E_{1/2}$ of the new wave is the same as that of furfural under identical experimental conditions. This suggests that the semicarbazone in the presence of the acid is progressively converted into the aldehyde. It is also observed that after a lapse of time, the height of the semicarbazone wave attains a constant value without showing further decrease with time. Polarograms of the reaction mixture recorded after 48 hr confirm that under the experimental conditions the semicarbazone is converted into the aldehyde and possibly semicarbazide. Cabello⁵ has reported that furfural decomposes to succinic aldehyde in the presence of acids at 120° to 130° under reflux conditions. But polarograms of furfural in 0.2 mol dm^{-3} HCl recorded at different time intervals show that at the temperature of study, furfural is stable. This suggests that the aldehyde group stabilises the furan ring, unlike the alkyl and alkoxy groups. The attainment of constancy in wave height suggests that the reaction under study is not going to completion and is an equilibrium process involving the hydrolysis and possibly the reformation of the semicarbazone (Eq. 1).



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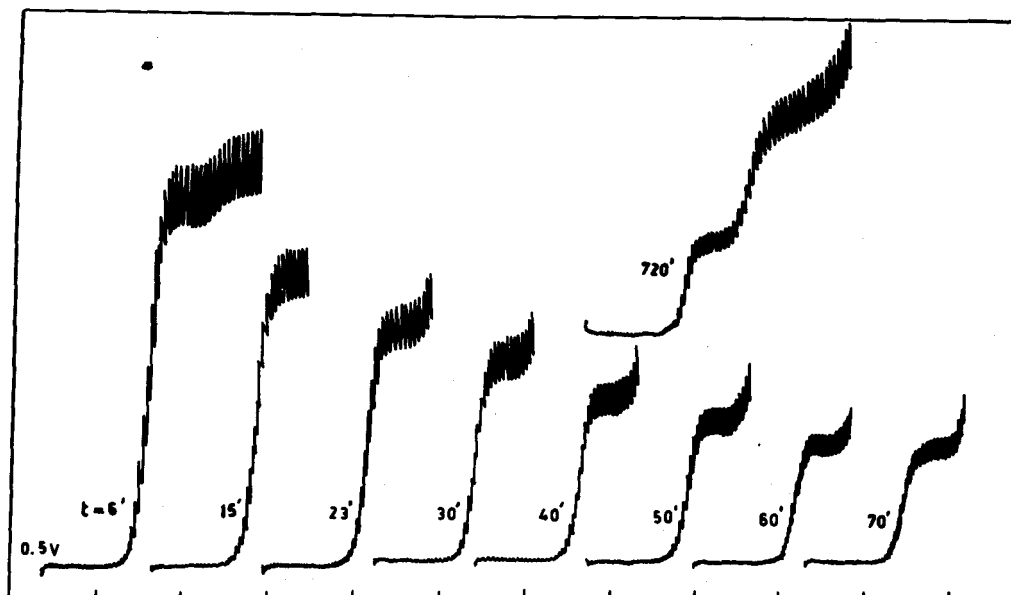


Fig. 1—Hydrolysis of furfural semicarbazone (FAS) ($0.2 \text{ mol dm}^{-3} \text{ HCl}$). [Each polarogram starts at 0.5 V versus Hg pool and time noted; [Semicarbazone] = $10^{-3} \text{ mol dm}^{-3}$]

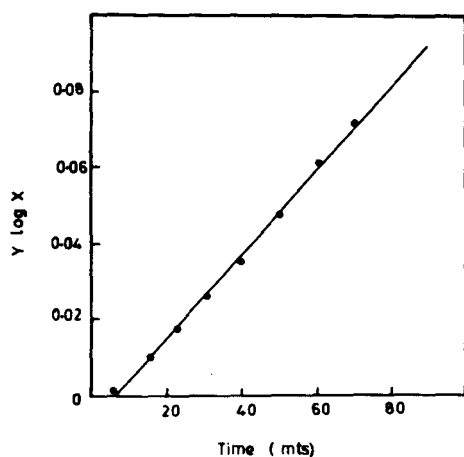


Fig. 2— $y \log x$ versus time plot $\left[x = \frac{[\text{SC}]_0^2 / [\text{SC}]_a - [\text{SC}]}{[\text{SC}] - [\text{SC}]_a} \cdot \frac{[\text{SC}]_a}{[\text{SC}]_0} \right]$

$$y = \frac{[\text{SC}]_a}{[\text{SC}]_0^2 - [\text{SC}]_a^2} \times 2.303 \quad \left. \right\}$$

Calculation of rate constants

The height (h) of the polarogram of the semicarbazone at any time is taken as a measure of the concentration of the semicarbazone at that time since the polarographic reduction of the semicarbazone is established to be diffusion-controlled. The rate constants k_1 (hydrolysis) and k_2 (formation) are calculated from Eqs (2) and (3) proposed by Egberink and Vanheerden⁶ for equilibrium processes.

$$k_2 t = \frac{[\text{SC}]_a}{[\text{SC}]_0^2 - [\text{SC}]_a^2} \ln \frac{[\text{SC}]_0^2 / [\text{SC}] - [\text{SC}]}{[\text{SC}] - [\text{SC}]_a} \cdot \frac{[\text{SC}]_a}{[\text{SC}]_0} \quad \dots (2)$$

$$\frac{k_2}{k_1} = \frac{[\text{SC}]_a}{([\text{SC}]_0 - [\text{SC}]_a)^2} \quad \dots (3)$$

In Eqs (2) and (3), $[\text{SC}]_0$ = initial concentration (initial height) of the semicarbazone; $[\text{SC}]_a$ = equilibrium concentration (equilibrium height of the semicarbazone); and $[\text{SC}]$ = concentration at any time (height at any time) of the semicarbazone.

A linear plot is obtained when right hand side of Eq. (2) is plotted against time. Typical plot is shown in Fig. 2. k_1 is calculated from the slope of the linear plot k_2 from the Eq. (3).

The rate constants obtained in the presence of different concentrations of (a) acid, (b) furfural semicarbazone, (c) added furfural, (d) added semicarbazide and (e) added neutral salt have also been calculated.

Results in Table 1 indicate that k_1 increases with increase in [acid]. Plot of $\log k_1$ versus $\log [\text{HCl}]$ is linear with slope = 0.80 (≈ 1), indicating that the order in [acid] is unity. The rate constant decreases with increase in [substrate]. For example at initial [substrate] of 8.0×10^{-4} , 12.0×10^{-4} , 16.0×10^{-4} and $20 \times 10^{-4} \text{ mol dm}^{-3}$, $10^2 k_1$ are 2.54, 2.42, 2.02 and 1.70 s^{-1} respectively. This implies that the active species involved is governed by some pre-equilibrium process. Upto four-fold excess, the added semicarbazide has only marginal effect on the rate. At [semicarbazide] of $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ the $10^2 k_1$ is 2.90 s^{-1} while at $40.0 \times 10^{-4} \text{ mol dm}^{-3}$, $10^2 k_1$ is 2.72 s^{-1} . Added furfural has no appreciable effect on k_1 upto a concentration equal to that of furfural

Table 1—Rate Constants for Acid Hydrolysis of Furfural Semicarbazone (FAS) at Different [HCl]

[FAS] = 1×10^{-3} mol dm ⁻³ ; temp. = 32°C		
[HCl] (mol dm ⁻³)	$10^2 k_1$ (s ⁻¹)	$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
0.2	2.62	1.11
0.4	4.63	1.14
0.6	6.78	1.23
0.8	7.70	1.30
1.0	8.94	1.46
1.2	10.92	1.52
1.4	12.70	1.65
1.6	16.60	1.91

Table 2—Effect of Varying Furfural Concentration on Rate Constant

[HCl] = 0.2 mol dm ⁻³ ; [FAS] = 1×10^{-3} mol dm ⁻³ ; temp. = 32°C		
10^4 [Furfural] (mol dm ⁻³)	$10^2 k_1$ (s ⁻¹)	$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
2	2.00	1.08
6	1.90	1.85
10	2.00	2.84
40	1.06	5.64
60	1.02	38.70

semicarbazone (Table 2). However at higher concentration k_1 decreases.

The results reveal the following facts.

(i) The rate constant diminishes with increase in organic cosolvent, i.e. with decrease in dielectric constant (Table 3).

(ii) Addition of neutral salt, such as KCl in the concentration range 0.04 to 0.20 mol dm⁻³ does not affect the rate constant. At [KCl] = 0.02, $10^2 k_1 = 2.6$ s⁻¹ while at 0.2 mol dm⁻³, $10^2 k_1 = 2.7$ s⁻¹.

(iii) Increase in temperature increases the rate constant and the activation parameters ($E_a = 40.13$ kJ mol⁻¹; $\Delta S^\ddagger = -152$ JK⁻¹ mol⁻¹) show that the hydrolysis is a bimolecular reaction.

Mechanism

The experimental results thus suggest that the protonated furfural semicarbazone undergoes hydrolytic cleavage to furfural and semicarbazide in a bimolecular reaction. The protonation equilibrium involves species protonated at the azomethine nitrogen as well as at different sites in the ring.

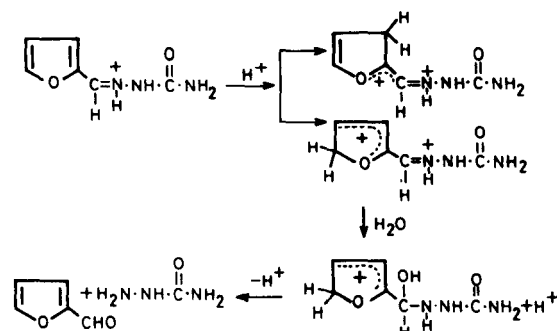
The polarogram of the reaction mixture after long periods of time (48 hr) shows that under the present experimental condition, furan ring remains intact. Hence it is proposed that the species protonated at position-5 is kinetically significant. Increase in [sub-

Table 3—Effect of Solvent on Rate Constant

[HCl] = 0.2 mol dm ⁻³ ; [FAS] = 1×10^{-3} mol dm ⁻³ ; temp. = 32°C				
Solvent	$k_1 \times 10^2$ (s ⁻¹) in aquo-organic medium			
	10%	20%	30%	40%
Methanol	2.50	1.95	1.38	1.01
Acetonitrile	1.60	1.01	0.56	0.19
Dimethylformamide	1.38	0.89	0.47	0.08

strate] thus possibly favours the intermediate with protonation at position-3. This explains the decrease in rate with increase in [substrate].

The decrease in log k_1 with increase in $1/D$ suggests that the reaction occurs between two ions of the same charge or a positive ion and a dipole. Further support to this is provided by the fact that added neutral salt does not affect k_1 much. Based on these observations, the reaction is classified as the reaction between a positive ion (protonated furfural semicarbazone) and a dipole (water), as shown in Scheme 1.



Scheme 1

Acknowledgement

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