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Original Research Article

Kinetic cerimetric estimation of aldoses

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Abstract

Kinetic Cerimetric estimations of D-Glucose D-Xylose and D-Erythrose has been carried out after elaborating the kinetic and mechanistic features of these indicator electron transfer reactions which can be expressed as $C_nH_{2n}O_n$ + 2nCe(IV) +H_2O → $C_{n-1}H_{2n-2}$ O_n+ nCe(III)+2H^+ +n HCOOH This reaction showed first order kinetics with respect to initial concentarations of reacting species cerium (IV), respective aldose and sulphuric acid under the experimental pseudo first order conditions.and a free radical mechanism producing lower aldose as initial reaction product. The observed decreasing absorbance with time at different initial concentrations of respective aldoses from 0.50 x 10^{-2} mol dm^{-3} to 3.0 x 10^{-2} mol dm^{-3} has been used for the. kinetic cerimetric estimations of simulated samples of respective aldose adopting (a) Rate constant, (b) variation of absorbance at fixed time (c) variation of time at fixed absorbance of (d) One point and (e) Two point methods. Using respective calibration plots. The consistency and reproducibility of these and earlier results have clearly showed that these kinetic cerimetric estimations of aldo sugars can be used as an alternative/additional analytical method to the existing traditional estimation methods in the present day laboratory conditions and also as advance laboratory experiments

Key Words: Kinetic estimation, Aldoses, Cerium (IV) oxidation, Electron transfer reaction.

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INTRODUCTION

Kinetic (reaction-rate) methods have undergone wide development in the last few years.[1] This development can be attributed to the need to analyze very small (trace) amount of substances in quicker time to get better understanding of reaction mechanism and controlled synthetic procedures. The reactions used for kinetic determination is known as "indicator reaction", which must be thermodynamically favoured and its mechanism and kinetic factors should be well explored. The rate data of indicator reactions thus obtained is then used for estimation by employing different computational methods.[2] The present report regarding estimation of aldoses (D-Glucose, D-Xylose and D—Erythrose) is a logical extension of earlier work of detailed kinetic and mechanistic studies of electron transfer reactions of metal ions including ceric sulphate with various reducing sugars and alditols.[3]

Experimental: The rate data of indicator electron transfer reaction between aldoses and ceric sulphate were obtained with using Shimadzu Pharmaspec-UV-1700, kinetic model spectrophotometer by measuring changing absorbance at 316 nm due to changing concentration of Cerium (IV) in sulphuric acid medium under pseudo first order conditions. In typical kinetic run, the reaction mixture (20.0 ml.), contains 2.0 ml of ceric sulphate (2.50 x 10^{-3} mol dm^{-3}), containing 2.0 mol dm^{-3} sulphuric acid, 5.0 ml of 5.0 mol dm^{-3} sulphuric acid and 2.0 ml of 0.5 mol dm^{-3} respective aldose solution is kept in temperature controlled water bath at 296 ± 0.5 K and then absorbance is noted after each 10.0 min using Shimadzu Pharmaspec-UV-1700,. The pseudo first order rate constant $k_{obs.}(s^{-1})$ has been calculated by semi log and stepwise methods using the integral form of the first order rate equation for the rate data obtained using varying kinetic experimental conditions which included variations of $k_{obs}(sec^{-1})$ with changing initial concentrations with Ce(IV),respective aldose, sulphuric acid, hydrogen ion, bisulphate ion and temperature.

RESULTS AND DISCUSSION

Reaction product analysis was done in the left over reaction mixture of kinetic run. Formation of HCOOH and respective lower aldose were confirmed by usual spot test and paper chromatography. Thus the general stoichiometric equation can be expressed as in equation (1)

$C_nH_{2n}O_n + 2Ce(IV) + H_2O \rightarrow C_{n-1}H_{2n-2}O_{n-1} + 2Ce(III) + HCOOH + 2H^+$ --(1)

The products formed in these indicator reaction were further confirmed by HPLC. Formation of respective intermediate C-centered free radical were confirmed by induced polymerization with acryl nitrile which is consistent with the earlier results of EPR spin trapping studies[4] Thus following reaction mechanistic steps involving the formation of intermediate C-centered free radical in slow rate determining step followed by fast reaction between free radical and Ce (IV) to form lower aldose and formic acid as initial reaction products.

$CH_2OH(CHOH)_nCH(OH)_2 + Ce(IV) \underset{\text{Fast}}{\rightleftharpoons} [C_6H_{12}O_6 Ce(IV)]^{\neq}$

$[C_6H_{12}O_6 Ce(IV)]^{\neq} \xrightarrow{k} CH_2OH(CHOH)_n C^{\bullet} HOH + Ce(III) + H_3O^+ + HCOOH$ (2) slow

$CH_2OH(CHOH)_nC^{\bullet}HOH + Ce(IV) \xrightarrow{\text{Fast}} CH_2OH(CHOH)_{n-1}CHO + Ce(III) + H^+$ (3)

The linear dependence of pseudo first order rate constant $k_{obs.}(s^{-1})$ with initial concentrations of D-glucose, D-xylose and D-erythyrose (Table 1-3) have been used for kinetic estimations of these aldoses using following methods.

Rate constant method The rate of present indicator reaction has been determined by observing decreasing concentration of Ce(IV) in terms of absorbance with time at constant temperature as

$d[Ce(IV)]/dt = k_s [Ce(IV)] [\text{Aldose}] [H_2SO_4]_0 = k_0 [A_0] [\text{Aldose}]_0$ at constant $[H_2SO_4]_0$

Thus $k_{obs} = k_0 [\text{D-Aldose}]_0$ (4)

Calibration plots were obtained between $k_{obs.}$ and [D-glucose] in each case and the concentration of simulated samples of D-glucose was determined from the "best fit " regression equations.

Fixed time method: The concentration of Ce(IV) i.e. changing absorbance $\Delta[A_t]$ with finite time interval can be expressed in terms of equation (5)

$\Delta [\text{Absorbance}]_t / \Delta t = k_0 [\text{Aldose}]$ (5)

Thus, $[\text{Absorbance}]_t = k [\text{Aldose}]_0$ (6)

Calibration plots were then obtained between absorbance at 20 min, 40 min, and 60min and Aldose concentrations in the respective kinetic runs. The concentration of simulated samples of Aldose was determined from the "best fit" regression equations.

Fixed absorbance (concentration) method: Rearranged equation (5)can be expressed as:

Time = $k [\text{Aldose}]]_0^{-1} = k [\text{Absorbance}]^{-1}$ (7)

Calibration plots were obtained between fixed concentration of Aldose in terms of 1.1, 0.9 and 0.7 absorbance observed at different time intervals during individual kinetic run. Concentration of simulated samples of Aldose was then estimated from the "best fit" regression lines in each case.

One point (fixed absorbance) method: It is always not possible to perform large number of kinetic runs when a small amount of sample is available for estimation. Then simplified kinetic estimation of Aldose was also employed. Reaction mixtures with known and simulated sample of Aldose were taken and at fixed absorbance 1.1, 0.9 and 0.7 at respective time intervals were determined.

Thus $(\text{time})_{known} \propto [\text{Aldose}]]^{-1}$ or $(\text{Absorbance})^{-1}$

and $(\text{time})_{simulated} \propto [\text{Aldose}]]^{-1}$ or $(\text{Absorbance})^{-1}$

$(\text{time})_{known} / (\text{time})_{simulated} = (\text{Absorbance})_{simulated} / (\text{Absorbance})_{known}$ (8)

Two point (Difference in Absorbance) method: This method can yield better estimation results as this requires determination of change in absorbance at fixed time intervals of 20min, 40min, and 60 min for the known and simulated samples of D-glucose.

Thus $(\Delta \text{ time})_{known} \propto \Delta[\text{D-glucose}]^{-1}$ or $(\Delta\text{Absorbance})^{-1}$

And $(\Delta \text{ time})_{simulated} \propto \Delta[\text{D-glucose}]^{-1}$ or $(\Delta\text{Absorbance})^{-1}$

$(\Delta \text{ time})_{known} / (\Delta \text{ time})_{simulated} = (\Delta\text{Absorbance})_{simulated} / (\Delta\text{Absorbance})_{known}$ (9)

Following are the "Best fit" regression equations obtained and estimated concentration value of simulated samples of all the three aldoses using all these five methods (A-E) and respective rate data (table 1-3)

Table 1: Variation absorbance with d-glucose concentration

10^{-2}Time (sec)	----------10 [D-glucose] in (mol dm^{-3})----------					
	0.50	0.75	1.00	1.25	1.50	1.75
0	1.318	1.318	1.318	1.318	1.318	1.318
6	1.242	1.214	1.187	1.163	1.137	1.115
12	1.176	1.113	1.076	1.031	0.983	0.946
18	1.114	1.055	0.975	0.917	0.854	0.800
24	1.053	0.981	0.880	0.810	0.735	0.677
30	0.996	0.909	0.796	0.723	0.634	0.565
36	0.938	0.842	0.721	0.639	0.538	0.485
42	0.878	0.774	0.647	0.560	0.452	0.402
48	0.830	0.718	0.581	0.495	0.386	0.337
54	0.782	0.663	0.517	0.436	0.332	0.288
60	0.728	0.613	0.460	0.385	0.283	0.244
66	0.677	0.560	0.404	0.355	0.241	0.205
$10^5 k_{obs}$ (s^{-1})	9.663 ±0.03	12.830 ±0.05	17.122 ±0.04	20.331 ±0.03	25.005 ±0.06	28.027 ±0.02
$10^3 k_o$ *	1.930	1.715	1.667	1.711	1.635	1.675

10^4 [Ce (IV)] = 2.5 mol dm^{-3} [H_2SO_4] = 1.45 mol dm^{-3} Temperature = 296 ± 0.5 K λ =316 nm.

Table 2:

10^{-2}Time (sec)	----------10 [D-glucose] in (mol dm^{-3})----------				
	2.00	2.25	2.50	2.75	3.00
0	1.318	1.318	1.318	1.318	1.318
6	1.091	1.068	1.046	0.991	0.953
12	0.904	0.870	0.834	0.760	0.698
18	0.744	0.702	0.659	0.579	0.511
24	0.615	0.568	0.519	0.436	0.364
30	0.494	0.447	0.404	0.327	0.257
36	0.412	0.366	0.322	0.248	0.180
42	0.332	0.292	0.254	0.187	0.125
48	0.268	0.238	0.209	0.138	0.091
54	0.222	0.191	0.161	0.091	0.057
60	0.180	0.150	0.116	0.061	0.036
66	0.140	0.110	0.076	0.040	0.022
10^5 $k_{obs.}$ (s^{-1})	32.520 ±0.08	35.695 ±0.01	39.350 ±0.01	47.764 ±0.02	55.921 ±0.02
10^3 k_o *	1.705	1.602	1.631	1.712	1.623

*10^3 k_o = $k_{obs.}$/[D-glucose] (mol^{-1} dm^{-3} s^{-1})

Kinetic Estimation of D-Glucose: (A) Rate constant method Regression Equation 10^5 $k_{obs.}$ = 17.429 [D-glucose] - 0.962 Corr. Coeff. = 0.98

Table 3:

10[simulated -1] (mol dm^{-3})	1.04(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm^{-3})	2.00(Calculated): 2.00 (Actual)

Fixed time method__and (C) Fixed absorbance (concentration) method

Regression Equations: A_{1200} = -0.180 [D-glucose] + 1.259 Corr. Coeff. = 0.99

A_{2400} = -0.267 [D-glucose] + 1.165 Corr.Coeff. = 0.99

A_{3600} = -0.293 [D-glucose] + 1.036 Corr. Coeff. = 0.99

$t_{1.1}$ = - 57.83 [D-glucose] + 182.08 Corr.Coeff. = 0.86

$t_{0.9}$ = -119.18[D-glucose] + 388.86 Corr.Coeff. = 0.85

$t_{0.7}$ = -114.04 [D-glucose] + 435.14 Corr.Coeff. = 0.98

Table 4:

10[simulated -1] (mol dm^{-3}) (Fixed Time Method)	1.05 ± 0.02 (Calculated): 1.00 (Actual)
10 [simulated -2] (mol dm^{-3})	2.04 ± 0.04 (Calculated): 2.00 (Actual)
10[simulated -1] (mol dm^{-3}) (Fixed Abs. Method)	1.02 ± 0.04 (Calculated): 1.00 (Actual)
10[simulated -2] (mol dm^{-3})	2.05 ± 0.02(Calculated): 2.00 (Actual)

(D) One Point Method

Table 5:

Fixed Absorbance	10^{-2}Time (sec.)	10[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (t_2 C_2/t_1)$
0.7	t_1 = 31.0	C_2 = 1.5	C_1 = 1.05 (C_{Actual} = 1.00)
	t_2 = 21.7		
	t_1 = 16.8	C_2 = 1.5	C_1 = 1.94 (C_{Actual} = 2.00)
	t_2 = 21.7		
	t_1 = 24.8	C_2 = 1.5	C_1 = 0.99 (C_{Actual} = 1.00)
0.9	t_2 = 16.6		
	t_1 = 12.9	C_2 = 1.5	C_1 = 1.93 (C_{Actual} = 2.00)
	t_2 = 16.6		
	t_1 = 11.8	C_2 = 1.5	C_1 = 1.04 (C_{Actual} = 1.00)
1.1	t_2 = 8.2		
	t_1 = 5.9	C_2 = 1.5	C_1 = 2.08 (C_{Actual} = 2.00)
	t_2 = 8.2	C_2 = 1.5	

Table 6:

10 [simulated -1] (mol dm^{-3})	1.03 ± 0.02 (Calculated): 1.00 (Actual)
10 [simulated -2] (mol dm^{-3})	1.98 ± 0.06 (Calculated): 2.00 (Actual)

(E) Two Point Method

Table 7:

10^{-2} Time (sec.)	Absorbance ΔA	10[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (\Delta A_1 C_2 / \Delta A_2)$
12	ΔA_1 = 0.242	C_2 = 1.5	C_1 = 1.08 (C_{Actual} = 1.00)
	ΔA_2 = 0.335		
	ΔA_1 = 0.444	C_2 = 1.5	C_1 = 1.98 (C_{Actual} = 2.00)
	ΔA_2 = 0.335		
24	ΔA_1 = 0.392	C_2 = 1.5	C_1 = 1.01 (C_{Actual} = 1.00)
	ΔA_2 = 0.583		
	ΔA_1 = 0.763	C_2 = 1.5	C_1 = 1.97 (C_{Actual} = 2.00)
	ΔA_2 = 0.583		
36	ΔA_1 = 0.530	C_2 = 1.5	C_1 = 1.02 (C_{Actual} = 1.00)
	ΔA_2 = 0.780		
	ΔA_1 = 1.076	C_2 = 1.5	C_1 = 2.07 (C_{Actual} = 2.00)
	ΔA_2 = 0.780		

Table 8:

10[simulated-1] (mol dm^{-3})	1.04 ± 003 (Calculated): 1.00 (Actual)
10[Simulated-2] (mol dm^{-3})	2.01 ± 0.04 (Calculated): 2.00 (Actual)

Table 9: Variation of absorbance with d-xylose concentration

10^{-2} Time (sec.)	----------10 [D-xylose] (mol dm^{-3}) --------					
	0.50	0.75	1.25	1.50	1.75	2.25
0	1.321	1.321	1.321	1.321	1.321	1.321
1.2	1.271	1.245	1.198	1.214	1.125	1.044
2.4	1.238	1.197	1.116	1.116	1.009	0.926
3.6	1.209	1.152	1.047	1.029	0.915	0.797
4.8	1.184	1.107	0.988	0.950	0.834	0.722
6.0	1.158	1.068	0.934	0.875	0.764	0.640
7.2	1.133	1.033	0.885	0.820	0.700	0.574
8.4	1.111	0.998	0.837	0.758	0.644	0.514
9.6	1.088	0.964	0.791	0.700	0.591	0.461
10.8	1.068	0.930	0.750	0.657	0.542	0.415
12.0	1.048	0.898	0.710	0.617	0.498	0.375
13.2	1.028	0.867	0.670	0.579	0.459	0.339
14.4	1.008	0.839	0.632	0.540	0.424	0.308
15.6	0.988	0.808	0.592	0.499	0.393	0.280
16.8	0.968	0.781	0.557	0.461	0.363	0.256
18.0	0.948	0.753	0.525	0.432	0.335	0.235
$10^5 k_{obs.}(s^{-1})$	21.53 ±0.04	34.89 ±0.06	57.27 ±0.01	66.01 ±0.03	89.77 ±0.03	118.6 ±0.09

10^4 [Ce (IV)] = 2.5 mol dm^{-3} [H_2SO_4] = 1.45 mol dm^{-3} Temperature = 296 ± 0.5 K λ =316 nm

Table 10:

10^{-2} Time (sec.)	----------10 [D-xylose] (mol dm^{-3}) -------				
	2.50	2.75	3.00	simulated -1	simulated -2
0	1.321	1.321	1.321	1.321	1.321
1.2	0.993	0.961	0.922	1.218	1.096
2.4	0.864	0.836	0.789	1.146	0.978
3.6	0.742	0.717	0.677	1.087	0.841
4.8	0.665	0.630	0.579	1.033	0.760
6.0	0.579	0.543	0.502	0.985	0.691
7.2	0.514	0.460	0.434	0.939	0.630
8.4	0.457	0.402	0.375	0.897	0.574
9.6	0.410	0.350	0.325	0.857	0.527
10.8	0.370	0.308	0.283	0.820	0.483
12.0	0.332	0.271	0.244	0.787	0.446
13.2	0.300	0.239	0.212	0.753	0.412
14.4	0.275	0.203	0.185	0.721	0.391
15.6	0.251	0.179	0.162	0.691	0.353
16.8	0.220	0.160	0.143	0.665	0.323
18.0	0.198	0.144	0.127	0.638	0.295
$10^5 k_{obs.}(s^{-1})$	133.8±0.02	150.5±0.06	162.6±0.05	**47.64±0.08**	**102.3±0.03**

Kinetic Estimation of D-Xylose Rate constant method **Regression Equation** 10^5 $k_{obs.}$ = 57.521 [D-xylose] – 10.736 Corr. Coeff. = 0.99

Table 11:

10[simulated -1] (mol dm^{-3})	1.01(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm^{-3})	1.97(Calculated): 2.00 (Actual)

(B and C) Fixed Time and Fixed Absorbance Method

Regression Equations

A_{240} = -0.1832 [D-xylose] + 1.336 Corr. Coeff. = 0.99

A_{360} = -0.2455 [D-xylose] + 1.289 Corr.Coeff. = 0.99

A_{720} = -0.2859 [D-xylose] + 1.241 Corr. Coeff. = 0.97

$t_{1.1}$ = - 1.9132 [D-xylose] + 5.473 Corr.Coeff. = 0.87

$t_{0.9}$ = - 4.273 [D-xylose] + 12.837 Corr.Coeff. = 0.86

$t_{0.7}$ = - 4.782 [D-xylose] + 16.720 Corr.Coeff. = 0.96

Table 12:

10 [simulated -1] (mol dm^{-3}) (Fixed Time Method)	1.03 ± 0.02 (Calculated): 1.00 (Actual)
10 [simulated -2] (mol dm^{-3})	2.07 ± 0.07 (Calculated): 2.00 (Actual)
10 [simulated -1] (mol dm^{-3})	1.04 ± 0.01 (Calculated): 1.00 (Actual)

(Fixed Abs. Method) 10 [simulated -2] (mol dm^{-3})	2.06 ± 0.03 (Calculated): 2.00 (Actual)

(D) One Point Method

Table 13:

Fixed Absorbance	10^{-2} Time (sec.)	10[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (t_2 C_2/t_1)$
0.7	t_1 = 3.3 t_2 = 2.1	C_2 = 1.5	C_1 = 0.96 (C_{Actual} = 1.00)
	t_1 = 1.6 t_2 = 2.1	C_2 = 1.5	C_1 = 2.02 (C_{Actual} = 2.00)
0.9	t_1 = 8.4 t_2 = 5.1	C_2 = 1.5	C_1 = 0.91 (C_{Actual} = 1.00)
	t_1 = 3.7 t_2 = 5.1	C_2 = 1.5	C_1 = 2.07 (C_{Actual} = 2.00)
1.1	t_1 = 15.0 t_2 = 9.6	C_2 = 1.5	C_1 = 0.96 (C_{Actual} = 1.00)
	t_1 = 7.0 t_2 = 9.6	C_2 = 1.5	C_1 = 2.05 (C_{Actual} = 2.00)

Table 14:

10[simulated -1] (mol dm^{-3})	0.94 ± 0.02 (Calculated): 1.00 (Actual)
10[simulated -2] (mol dm^{-3})	2.05 ± 0.02 (Calculated): 2.00 (Actual)

(E) Two Point Method

Table 15:

10^{-2} Fixed Time (sec.)	Absorbance ΔA	10[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (\Delta A_1 C_2 / \Delta A_2)$
2.4	ΔA_1 = 0.175 ΔA_2 = 0.249	C_2 = 1.5	C_1 = 1.05 (C_{Actual} = 1.00)
	ΔA_1 = 0.343 ΔA_2 = 0.249	C_2 = 1.5	C_1 = 2.07 (C_{Actual} = 2.00)
4.8	ΔA_1 = 0.288 ΔA_2 = 0.403	C_2 = 1.5	C_1 = 1.07 (C_{Actual} = 1.00)
	ΔA_1 = 0.561 ΔA_2 = 0.403	C_2 = 1.5	C_1 = 2.09 (C_{Actual} = 2.00)
7.2	ΔA_1 = 0.382 ΔA_2 = 0.523	C_2 = 1.5	C_1 = 1.09 (C_{Actual} = 1.00)
	ΔA_1 = 0.691 ΔA_2 = 0.523	C_2 = 1.5	C_1 = 1.98 (C_{Actual} = 2.00)

Table 16:

10[simulated -1] (mol dm^{-3})	1.07 ± 0.01(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm^{-3})	2.04 ± 0.04 (Calculated): 2.00 (Actual)

Table 17: Variation of absorbance with d-erythrose concentration

10^{-2}Time (sec.)	--------- 10^2 [D-erythrose] (mol dm^{-3}) ------					
	0.50	0.75	1.25	1.50	1.75	2.25
0	1.347	1.347	1.347	1.347	1.347	1.347
1.2	1.273	1.265	1.232	1.206	1.178	1.109
2.4	1.228	1.199	1.139	1.106	1.060	0.948
3.6	1.192	1.153	1.066	1.017	0.962	0.828
4.8	1.165	1.115	1.004	0.944	0.879	0.732
6..0	1.139	1.080	0.954	0.887	0.814	0.655
7.2	1.115	1.046	0.905	0.832	0.753	0.583
8.4	1.090	1.012	0.858	0.780	0.696	0.522
9.6	1.067	0.981	0.813	0.729	0.643	0.470
10.8	1.046	0.951	0.769	0.681	0.594	0.422
12.0	1.026	0.924	0.732	0.641	0.551	0.380
13.2	1.007	0.898	0.696	0.602	0.513	0.344
14.4	0.988	0.875	0.662	0.563	0.475	0.313
15.6	0.970	0.854	0.632	0.527	0.440	0.283
16.8	0.950	0.832	0.602	0.491	0.408	0.259
18.0	0.936	0.813	0.576	0.462	0.378	0.236
10^5 $k_{obs.}$ (s^{-1})	25.80 ±0.06	33.83 ±0.01	52.85 ±0.02	64.32 ±0.07	77.34 ±0.05	110.3 ±0.09

10^4 [Ce (IV)] = 2.5 mol dm^{-3} [H_2SO_4] = 1.45 mol dm^{-3} Temperature = 296 ± 0.5 K λ =316 nm.

Table 18:

10^{-2}Time (sec.)	------- 10^2 [D-erythrose] (mol dm^{-3}) ------				
	2.50	2.75	3.00	Unknown-1	Unknown-2
0	1.347	1.347	1.347	1.347	1.347
1.2	1.072	1.020	0.973	1.257	1.151
2.4	0.892	0.827	0.771	1.171	1.014
3.6	0.763	0.680	0.615	1.115	0.907
4.8	0.658	0.567	0.494	1.064	0.815
6..0	0.576	0.473	0.396	1.020	0.741
7.2	0.491	0.399	0.324	0.977	0.673
8.4	0.426	0.335	0.255	0.934	0.611
9.6	0.372	0.284	0.207	0.894	0.556
10.8	0.326	0.236	0.162	0.854	0.506
12.0	0.287	0.197	0.128	0.820	0.461
13.2	0.253	0.164	0.101	0.787	0.423
14.4	0.227	0.143	0.079	0.759	0.386
15.6	0.202	0.122	0.062	0.735	0.351
16.8	0.183	0.110	0.052	0.711	0.322
18.0	0.167	0.100	0.045	0.687	0.292
10^5 $k_{obs.}$ (s^{-1})	132.2 ±0.03	162.0 ±0.08	194.7 ±0.01	**42.64 ±0.04**	**92.05 ±0.04**

Kinetic Estimation of D-Erythrose Rate Constant Method Regression Equation $10^5 k_{obs.}$ = 64.912 [D-erythrose] – 22.357 Corr. Coeff. = 0.95

Table 19:

10^2[simulated -1] (mol dm^{-3})	1.00(Calculated): 1.00 (Actual)
10^2[simulated -2] (mol dm^{-3})	1.96(Calculated): 2.00 (Actual)

(B and C) Fixed Time and Fixed Absorbance Method

Regression Equations

A_{240} = -0.1832 [D-erythrose] + 1.336 Corr. Coeff. = 0.99

A_{360} = -0.2455 [D-erythrose] + 1.289 Corr.Coeff. = 0.99

A_{720} = -0.2859 [D-erythrose] + 1.241 Corr. Coeff. = 0.97

$t_{1.1}$ = - 1.9132 [D-erythrose] + 5.473 Corr.Coeff. = 0.87

$t_{0.9}$ = - 4.273 [D-erythrose] + 12.837 Corr.Coeff. = 0.86

Table 20:

10 [simulated -1](mol dm^{-3}) (Fixed Time Method)	1.05 ± 0.02 (Calculated): 1.00 (Actual)
10 [simulated -2] (mol dm^{-3})	2.07 ± 0.07 (Calculated): 2.00 (Actual)
10 [simulated -1](mol dm^{-3}) (Fixed Abs. Method)	0.94 ± 0.32 (Calculated): 1.00 (Actual)
10 [simulated -2](mol dm^{-3})	2.09 ± 0.03 (Calculated): 2.00 (Actual)

(D) One Point Method

Table 21:

Fixed Absorbance	10^{-2} Time (sec.)	10^2[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (t_2 C_2/t_1)$
0.7	t_1 = 3.3	C_2 = 1.5	C_1 = 0.94
	t_2 = 2.1		(C_{Actual} = 1.00)
	t_1 = 1.5	C_2 = 1.5	C_1 = 2.10
	t_2 = 2.1		(C_{Actual} = 2.00)
0.9	t_1 = 7.7	C_2 = 1.5	C_1 = 0.99
	t_2 = 5.1		(C_{Actual} = 1.00)
	t_1 = 3.7	C_2 = 1.5	C_1 = 2.06
	t_2 = 5.1		(C_{Actual} = 2.00)
1.1	t_1 = 15.0	C_2 = 1.5	C_1 = 0.97
	t_2 = 9.6		(C_{Actual} = 1.00)
	t_1 = 6.9	C_2 = 1.5	C_1 = 2.08
	t_2 = 9.6		(C_{Actual} = 2.00)

Table 22:

10^2[simulated -1] (mol dm^{-3})	0.97 ± 0.02(Calculated): 1.00 (Actual)
10^2[simulated -2] (mol dm^{-3})	2.08 ± 0.02 (Calculated): 2.00 (Actual)

(E) Two Point Method

Table 23:

10^{-2} Fixed Time (sec.)	Absorbance ΔA	10[Standard] mol dm^{-3}	10[Simulated Sample] mol dm^{-3} $C_1 = (\Delta A_1 C_2 / \Delta A_2)$
2.4	ΔA_1 = 0.175	C_2 = 1.5	C_1 = 1.05
	ΔA_2 = 0.249		(C_{Actual} = 1.00)
	ΔA_1 = 0.343	C_2 = 1.5	C_1 = 2.07
	ΔA_2 = 0.249		(C_{Actual} = 2.00)
4.8	ΔA_1 = 0.288	C_2 = 1.5	C_1 = 1.07
	ΔA_2 = 0.403		(C_{Actual} = 1.00)
	ΔA_1 = 0.561	C_2 = 1.5	C_1 = 2.09
	ΔA_2 = 0.403		(C_{Actual} = 2.00)
7.2	ΔA_1 = 0.382	C_2 = 1.5	C_1 = 1.09
	ΔA_2 = 0.523		(C_{Actual} = 1.00)
	ΔA_1 = 0.691	C_2 = 1.5	C_1 = 1.98
	ΔA_2 = 0.523		(C_{Actual} = 2.00)

Table 24:

10^2[simulated -1] (mol dm^{-3})	1.07 ± 0.01(Calculated): 1.00 (Actual)
10^2[simulated -2] (mol dm^{-3})	2.04 ± 0.04 (Calculated): 2.00 (Actual)

The outcome of kinetic estimation of aldoses by oxidation with ceric sulphate in simulated samples has been logically extended to use these kinetic experimental conditions of indicator reactions for the estimation of D-glucose in available industrial pharmaceutical samples. An attempt has been made to validate the present cerimetric estimation of D-glucose on the basis of following typical analytical performance characteristics described in most of the standard international documents including ICH (International Conference of Harmonization-1996) guidelines. The validated kinetic cerimetric method for the estimation of D-glucose in simulated samples has been now applied for the estimation of D-glucose in four locally available pharmaceutical sample under the identical kinetic run conditions used for simulated samples estimations. The observed absorbance at 316nm with time for all samples is given in Table- 4. The amount of D-glucose in these samples was calculated by using rate data and best fit regression equations obtained from the calibration plots.

Table 4: Estimation of D-Glucose In Pharmaceutical Samples

10^2 Time sec	Prem Pharmaceuticals	D.J.Laboratories Pvt.Ltd.	Inven Pharmaceuticals	Wockhard Ltd.
0	1.325	1.325	1.325	1.325
6	1.116	1.137	1.126	1.130
12	0.953	1.006	0.995	0.975
18	0.826	0.862	0.865	0.833
24	0.698	0.745	0.744	0.735
30	0.595	0.638	0.630	0.645
36	0.522	0.550	0.540	0.552
42	0.424	0.468	0.447	0.477
48	0.359	0.405	0.385	0.425
54	0.300	0.352	0.330	0.356
60	0.246	0.299	0.275	0.302
66	0.194	0.246	0.225	0.250
10^5 $k_{obs.}$ (s^{-1})	27.43±0.08	24.50±0.07	25.36±0.024	24.82±0.09

(A)Variation of Absorbance with Time: 10^4 [Ce (IV)] = 350 ppm [H_2SO_4] = 1.45 mol dm^{-3} Temperature = 296 ± 0.5 K λ =316 nm

Table 5: Estimation Of D-Glucose Using "BEST FIT" Regression Equation obtained from Calibration Plots.

Name of manufacturer	10^5 $k_{obs.}$ (s^{-1})	Absorbance at 10^{-2} fixed time 12	24	36	Time at fixed abs 1.1	0.9
Prem Pharmaceuticals [samples] (in %)	27.43	0.953	0.698	0.522	66	147
	10.85	11.33	11.66	11.66	11.33	13.53
D.J.Laboratories Pvt.Ltd. [samples] (in %)	24.50	1.006	0.745	0.550	69	159
	9.73	9.40	10.47	11.01	11.00	12.86
Inven Pharmaceuticals [samples] (in %)	25.36	0.995	0.744	0.540	78	162
	10.06	9.8	10.53	11.26	11.10	11.66
Wockhard Ltd.	24.82	0.975	0.735	0.552	72	153

es] (in %)	9.86	10.53	10.73	11.00	10.66	11.20	10.53

10^5 k_{obs} = 17.429 [D-glucose] - 0.962 Corr. Coeff. = 0.98
A_{1200} = -0180 [D-glucose] + 1.259 Corr. Coeff. = 0.99
A_{2400} = -0.267 [D-glucose] + 1.165 Corr. Coeff. = 0.99
A_{3600} = -0.293 [D-glucose] + 1.036 Corr. Coeff. = 0.99
$t_{1.1}$ = - 57.83 [D-glucose] + 182.08 Corr. Coeff. = 0.86
$t_{0.9}$ = -119.18[D-glucose] + 388.86 Corr. Coeff. = 0.85
$t_{0.7}$ = -114.04 [D-glucose] + 435.14 Corr. Coeff. = 0.98

The results of these kinetic cerimetric estimations are comparable with the estimations carried out by the method described in pharmacopeia which is followed for these samples routinely in their respective organizations.

(C) Comparison of D-Glucose Estimation Using,
(a) Indian Pharmacopoeia method * **(b)** Present kinetic method

Table 6:

Sr. No.	Name of manufacturer	(a)	(b)	Actual value of % D-glucose mentioned on sample
1	Prem Pharmaceuticals	10.80	10.60±0.87	10.00
2	D.J.Laboratories Pvt.Ltd.	10.33	10.30±1.10	10.00
3	Inven Pharmaceuticals	10.13	10.10±0.92	10.00
4	Wockhard Ltd.	10.86	11.12±0.98	10.00

Actual value of D-glucose mentioned on sample = 10.00 % w/v

CONCLUDING REMARKS

The present report is a part of detailed study to use rate data obtained during electron transfer reactions between aldoses and other reducing sugars including alditols with one equivalent metal ions (ceric sulphate in present case) for their estimations in simulated /real samples. The results of present report show clearly the pseudo first order kinetic conditions can be successfully employed for the kinetic cerimetric estimations of aldoses with possible extensions of kinetic estimations of various metal ion oxidants and other organic compounds particularly pharmaceutical samples. These studies have the potential to develop a simple, inexpensive but accurate laboratory procedure for kinetic estimations using various electron transfer indicator reactions involving metal ions and organic/inorganic substrates.

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