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Kinetics and Mechanism of Oxidation of D-Glucose and D-Fructose by Potassium Ferricyanide in the Presence of Ammonia

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The reaction rate is independent of the concentration of ferricyanide ion and directly proportional to both the reducing sugar and ammonia concentration. The reaction is of general basic catalysis in nature. The reaction rate is decreased with the addition of ammonium chloride due to common ion effect. The catalytic constants k_{OH^-} and k_{NH_3} have been calculated graphically. The reaction rate is, also, decreased with the gradual decrease in dielectric constant of the solvent and increased with the gradual increase in ionic strength. The rate expression obtained is as:

$$-\frac{d[\text{Fe y}^{3-}]}{dt} = k_1[\text{NH}_3]\ [\text{Reducing Sugar}]$$

Conant, Aston and Tonberg[1] have studied the oxidation quantitatively of four aldehydes and D-glucose, D-fructose and D-arabinose by alkaline molybdicyanide, tungsticyanide and ferricyanide potentiometrically. They found that more alkaline the solution the more rapid was the reaction. They have also considered that the initial stage of the oxidation of an organic substance by an electron abstracting agent might be fast, reversible and pH dependent. Speakman and Waters,[2] Hinshelwood and Shorter,[3] Drummond and Waters[4] have also reported the enolization to be necessary prior to oxidation of aldehydes and ketones. The most systematic study of the kinetics of oxidation of reducing sugars in alkaline medium by bivalent copper by Singh, Krishna and Ghosh[5] in the presence of complexing agents, Singh and Singh[6] in absence of complexing agents and by alkaline hexacyanoferrate(III) by Nath and Singh[7] has been done. They have reported the reaction rate to be independent of oxidizing agent and directly proportional to reducing sugar and alkali concentration. The similar results have been obtained by Srivastava, Nath and Singh[8a,8b] in the oxidation of aldopentoses and disaccharides.

The present study deals with the kinetics of

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[1] J. B. Conant, J. G. Aston and C. O. Tonberg, *J. Am. Chem. Soc.*, **52**, 407 (1930).

[2] P. T. Speakman, and W. A. Waters, *J. Chem. Soc.*, **1955**, 40.

[3] C. Hinshelwood and J. Shorter, *ibid.*, **1950**, 3276.

[4] A. Y. Drummond and W. A. Waters, *ibid.*, **1950**, 3425.

[5] M. P. Singh, B. Krishna and S. Ghosh, *Z. Physik. Chem.*, **204**, 1 (1955).

[6] S. V. Singh and M. P. Singh, *Z. Physik. Chem. (Frankfurt)*, **50**, 1/2 (1966).

[7] N. Nath and M. P. Singh, *J. Phys. Chem.*, **69**, 2038 (1965).

[8] a) R. K. Srivastava, N. Nath and M. P. Singh, This Bulletin, **39**, 833 (1966). b) R. K. Srivastava, N. Nath and M. P. Singh, *Tetrahedron*, **23**, 1189 (1967).

oxidation of D-glucose and D-fructose by potassium ferricyanide in the presence of weak base ammonia. The effect of solvent (dielectric constant) and ionic strength on the reaction rate has also been studied.

Experimental

The course of the reaction has been followed by estimating unreduced potassium ferricyanide at different intervals of time iodometrically. The reactions were started by mixing the fresh solution of reducing sugar with potassium ferricyanide and ammonia kept in a bottle in an electrically maintained thermostat at constant temperature which has an accuracy of ±0.1°C.

Potassium ferricyanide, sulphuric acid, sodium thiosulphate, potassium ferrocyanide and D-glucose used were of B.D.H. (Analar) grade. Ammonia, Ammonium chloride B.D.H. (L.R.) and E. Merck sample of potassium iodide and D-fructose were also used. The values for the dielectric constant of alcohol-water mixture were obtained with a cell of 1.68$\mu\mu$f capacity by a dielectrometer (Dielkometer Type TBK No. 53015) working on the principle of heterodyne beat method.

Results and Discussion

The kinetics of oxidation of D-glucose[9] has been done by us. The next series of experiments have been performed by following the kinetics of oxidation of D-fructose by potassium ferricyanide in the presence of ammonia. The results obtained are similar to that of D-glucose except that the D-fructose has a higher rate (4.8 times) of oxidation.

Order of Reaction with Respect to Ferricyanide Ion. The order of the reaction with respect to ferricyanide ion has been determined by keeping the concentration of D-fructose high. The standard zero-order velocity constant (k_s) has been calculated by multiplying k_0 ($\Delta x/\Delta t$) by the strength (s) of sodium thiosulphate used divided by aliquot (v) sucked *i. e.* $k_s = k_0 \times s/v$. The following Tables 1 and 2 and the summarized Table 3 show the same k_s values at increasing concentration of potassium ferricyanide at constant concentration of other reactants. This indicates that the reaction rate is independent of ferricyanide ion. Also, the results of Table 1 have been shown graphically in Fig. A, in which the molar concentration of remaining ferricyanide ion has been plotted against time t. A straight line after slight induction period is obtained. From the slope the k_s value comes out to be 6.66×10^{-5} mol $l^{-1}\cdot$ min^{-1} which is identical to the value of k_s calculated in Table 1. This further confirms that reaction rate is independent of ferricyanide ion.

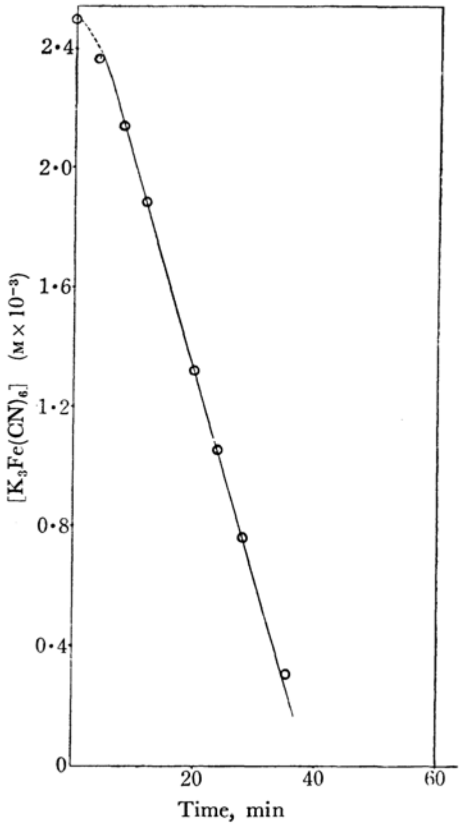

Fig. A

Temperature 40°C
Zero order plot
$[K_3Fe(CN)_6] = 2.50 \times 10^{-3}$M
[D-Fructose] $= 1.00 \times 10^{-2}$M
$[NH_3] = 1.00 \times 10^{-1}$N
Frome slope
$k_s = 6.66 \times 10^{-5}$ mol l^{-1} $^{-1}$mn^{-1}

Table 1

Temp.: 40°C
$[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$M, $[NH_3] = 1.00 \times 10^{-1}$N
[D-Fructose] $= 1.00 \times 10^{-2}$M

Time min	N/752 hypo ml	$k_0 = \frac{\Delta x}{\Delta t}$
0	9.40	—
4	8.90	0.125
8	8.06	0.210
12	7.10	0.240
20	5.00	0.262
24	4.00	0.250
28	2.88	0.280
35	1.20	0.240
∞	0.00	

Mean k_0 0.247
(Neg. 1st constant)

$k_s = 6.56 \times 10^{-5}$ moll^{-1}min

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[9] K. C. Gupta and M. P. Singh, *Z. Physik, Chem.*, **232**, 289 (1966).

TABLE 2

Temp.: 40°C

$[K_3Fe(CN)_6]=3.33\times10^{-3}$M, $[NH_3]=1.00\times10^{-1}$N

[D-Fructose] $=1.00\times10^{-2}$M

Time min	N/752 hypo ml	$k_0=\frac{\Delta x}{\Delta t}$
0	12.46	—
5	11.54	0.184
10	10.60	0.188
15	9.20	0.280
20	8.20	0.200
25	7.20	0.200
30	6.00	0.240
45	3.00	0.200
55	1.50	0.150
∞	0.00	

Mean k_0 0.224

(Neg. 1st two and last constant)

$k_s=5.95\times10^{-5}$ mol l^{-1} min^{-1}

TABLE 3

Temp.: 40°C

$[NH_3]=1.00\times10^{-1}$N, [D-Fructose] $=1.00\times10^{-2}$M

$[K_3Fe(CN_6)]$ M$\times10^3$	μ M	$k_s\times10^5$ mol l^{-1} min^{-1}
2.50	0.015	6.56
3.33	0.020	5.95
4.00	0.024	6.01
5.00	0.030	6.01

TABLE 4

Temp.: 40°C

$[K_3Fe(CN_6)]=2.50\times10^{-3}$M, $[NH_3]=1.00\times10^{-1}$N

[D-Fructos]$=1.00\times10^{-2}$M

$[K_4Fe(CN_6)]$ M$\times10^3$	$k_s\times10^5$ mol l^{-1} min^{-1}
2.50	6.15
3.33	6.78
5.00	6.80
10.00	7.27

Table 4 shows the effect of variation of potassium ferrocyanide on the reaction rate at constant concentration of other reactants. Practically the same k_s values indicate that the reaction rate is not affected by the concentration of the ferrocyanide ion. The slight increase in k_s value at its higher concentration is due to increase in ionic strength.

Order of Reaction with Respect to D-Fructose. In order to determine the order of the reaction with respect to D-fructose, its concentration has been varied keeping the concentration of other reactants constant. The results have been given in summarized form in Table 5. It is observed that zero order velocity constant increases proportionately with the increase in concentration of D-fructose. In the third column, the k_s/[D-fructose] value has been calculated which is fairly uniform. This indicates that the reaction rate is directly proportional to D-fructose concentration.

TABLE 5. EFFECT OF VARIATION OF AMMONIA ON THE REACTION RATE

Temp.: 40°C

$[K_3Fe(CN)_6]=2.50\times10^{-3}$M, $[NH_3]=5.00\times10^{-2}$N

[D-Fructose] M$\times10^2$	$k_s\times10^5$ mol l^{-1} min^{-1}	k/[D-Fructose] $\times10^3$
0.666	2.50	3.75
1.000	3.87	3.87
1.250	4.01	3.20
2.000	6.22	3.11

Table 6 shows the effect of increasing concentrations of ammonia on the reaction rate under identical condition of other reactants at two different temperatures, *i. e.*, 40°C and 35°C. It is observed that k_s value gradually increases with the increasing concentrations of ammonia. Also, the k_s values have been calculated for normal concentration of ammonia. These values gradually decrease with the increase in concentration of ammonia and decrease in hydroxyl ion concentration.

Further, these results have been shown graphically (Fig. 1) by plotting k_s against the concentration of ammonia. It is observed that at lower con-

TABLE 6

$[K_3Fe(CN)_6]=2.50\times10^{-3}$M, [D-Fructose]$=1.00\times10^{-2}$M

Temp. : 40°C			Temp. : 35°C	
$[NH_3]$ N$\times10^2$	$k_s\times10^5$ mol l^{-1} min^{-1}	$k_s/[NH_3]$ $\times10^4$	$k_s\times10^5$ mol l^{-1} min^{-1}	$k_s/[NH_3]$ $\times10^4$
2.00	1.84	9.20	—	—
3.33	2.89	8.67	1.60	4.80
5.00	3.87	7.74	2.10	4.20
10.00	6.56	6.56	3.57	3.57
20.00	9.04	4.52	5.30	2.65

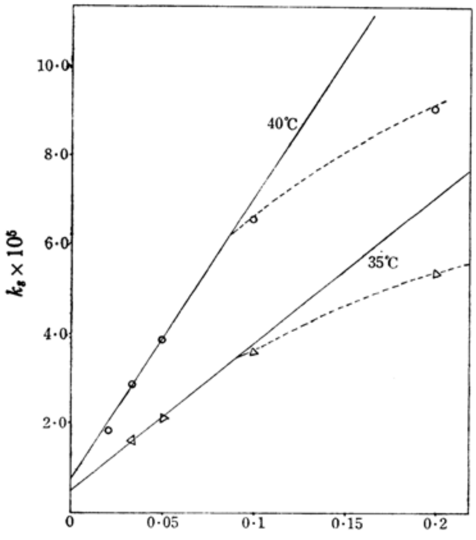

Fig. 1
Variation of NH_3 Conc.
$[K_3Fe(CN)_6] = 2.50 \times 10^{-3}$ M
[D-Fructose] $= 1.00 \times 10^{-2}$ M

centration of ammonia, there is direct proportionality; but at higher concentration there is deviation due to the decrease in dissociation of ammonia.

Common Ion Effect and Catalytic Constants. For reactions involving catalysis by bases there is a secondary salt effect which has to do with the effect of ionic strength on the dissociation of weak bases. Thus the actual degree of dissociation of a weak base such as ammonia can be changed by changing the concentration of salts in solution. Since the rate of reaction depends on the concentration of hydroxyl ions obtained from ammonia, it is clear that the rate of reaction will depend on the salt concentration. Table 7 shows the results at increasing concentrations of ammonium chloride on the reaction rate at constant concentration of other reactants. Due to common ion effect the hydroxyl ion concentration decreases with the increase in ammonium chloride concentration; which leads to gradual decrease in zero order velocity cononstant.

Table 7
$[K_3Fe(CN_6)] = 2.50 \times 10^{-3}$M, [D-Fructose] $= 1.00 \times 10^{-2}$M
$[NH_3] = 10.00 \times 10^{-2}$N

		Temp.: 35°C	Temp.: 40°C
$[NH_4Cl]$ M $\times 10^2$	pH	$k_s \times 10^5$ mol l^{-1} min^{-1}	$k_s \times 10^5$ mol l^{-1} min^{-1}
0.00	—	3.57	6.56
0.25	10.4	2.29	4.10
0.50	10.2	1.66	2.63
1.00	10.0	1.20	1.87
2.00	9.7	0.67	1.22

The reaction between ferricyanide ion and D-glucose (*loc. cit.*) and D-fructose is of general basis catalysis in nature. In order to confirm this the following experiments have been performed at varying concentrations of ammonia and ammonium chloride by keeping their ratio constant. The results have been given in summarized form in Tables 8 and 9.

Table 8
$[K_3Fe(CN_6)] = 2.50 \times 10^{-3}$M, [D-Glucose] $= 5.00 \times 10^{-2}$M

$[NH_3]$ N $\times 10^2$	$[NH_4Cl]$ M $\times 10^2$	Temp.: 40°C $k_s \times 10^5$ mol l^{-1} min^{-1}	Temp.: 35°C $k_s \times 10^5$ mol l^{-1} min^{-1}
3.3	0.33	1.01	0.694
		pH 10.0	
5.0	0.50	1.22	0.787
10.0	1.00	1.66	1.07
20.0	2.00	1.99	1.28
3.3	0.166	1.45	0.942
		pH = 10.2	
5.0	0.250	1.70	1.09
10.0	0.500	2.20	1.38
20.0	1.000	3.15	1.90

In Tables 8 and 9 the concentrations of ammonia and ammonium chloride have been gradually increased, keeping their ratios constant (10 : 1 and 20 : 1) in each case at 40°C and 35°C. These results are at constant pOH because pOH of the system is related by the following equation.

Table 9
$[K_3Fe(CN)_6] = 2.50 \times 10^{-3}$M, [D-Fructose] $= 1.00 \times 10^{-2}$M

$[NH_3]$ N $\times 10^2$	$[NH_4Cl]$ M $\times 10^2$		Temp.: 40°C $k_s \times 10^5$ mol l^{-1} min^{-1}	Temp.: 35°C $k_s \times 10^5$ mol l^{-1} min^{-1}
2.00	0.200		1.02	—
3.33	0.333	pH = 10.0	1.17	0.763
5.00	0.500		1.44	0.926
10.00	1.000		1.87	1.200
20.00	2.000		2.34	1.340
3.33	0.166		1.68	1.11
5.00	0.250	pH = 10.2	1.93	1.22
10.00	0.500		2.63	1.66
20.00	1.000		3.85	2.26

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} \tag{1}$$

where $pK_b = \log 1/K_b$, K_b being dissociation constant of the base which is related with the equilibria

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

From the above equation it is clear that the increase in k_s values is only due to the increase in

TABLE 10.

	$[K_3Fe(CN_6)]=2.50\times10^{-3}$M [D-Glucose]$=5.00\times10^{-2}$M		$[K_3Fe(CN)_6]=2.50\times10^{-3}$M [D-Fructose]$=1.00\times10^{-2}$M	
	k_{OH^-} mol l^{-1} min^{-1}	k_{NH_3} mol l^{-1} min^{-1}	k_{OH^-} mol l^{-1} min^{-1}	k_{NH_3} mol l^{-1} min^{-1}
40°C	6.77×10^{-2}	1.13×10^{-4}	7.31×10^{-2}	1.47×10^{-4}
35°C	4.50×10^{-2}	0.71×10^{-4}	5.02×10^{-2}	0.87×10^{-4}

undissociated ammonia. This shows that the reaction is of general basic catalysis in nature and in these experiments the total rate (k_s) is governed by the following equation.

$$k_s = \mathrm{kOH}^-\cdot[\mathrm{OH}^-]+k_{\mathrm{NH_3}}\cdot[\mathrm{NH_3}] \qquad (2)$$

where k_{OH^-} and k_{NH_3} are the catalytic constants of OH^- and NH_3 respectively. In order to show the validity of Eq. (2) the results of these Tables have been shown graphically in Figs. 2, 3, 4 and 5 by plotting k_s against ammonia concentration and the catalytic constant of OH^- (k_{OH^-}) has been calculated from the value of the intercept of the ordinate and the value of k_{NH_3} has been calculated from the slope of the straight line. The values obtained are given in Table 10.

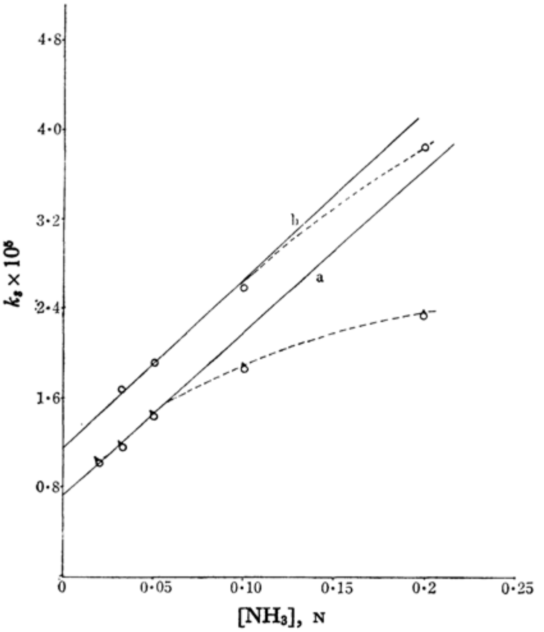

Fig. 2

Tempeature 40°C
Variation of NH_4Cl at fixed ratio
$[K_3Fe(CN)_6]=2.50\times10^{-3}$ M
[D-Fructose]$=1.00\times10^{-2}$ M
a$=10:1$, pH$=10.0$
$k_{KH_3}=1.45\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=7.3\times10^{-2}$ mol l^{-1} min^{-1}
b$=20:1$, pH$=10.2$
$k_{NH_3}=1.5\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=7.32\times10^{-2}$ mol l^{-1} min^{-1}

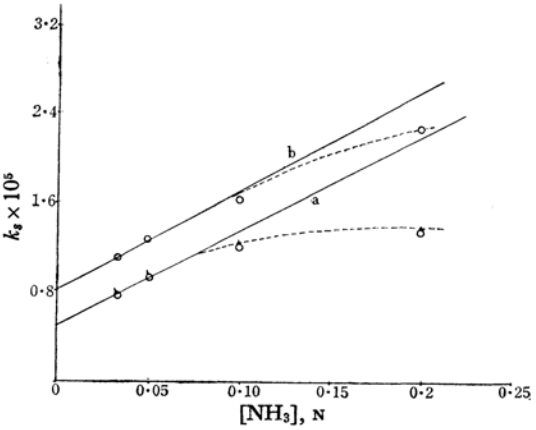

Fig. 3

Temperarure 35°C
Variation of NH_4Cl at fixed ratio
$[K_3Fe(CN)_6]=2.50\times10^{-3}$ M
[D-Fructose]$=1.00\times10^{-2}$ M
a$=10:1$, pH$=10.0$
$k_{NH_3}=0.86\times10^{-4}$ mol l^{-1}min^{-1}
$k_{OH^-}=5.0\times10^{-2}$ mol l^{-1} min^{-1}
b$=20:1$, pH$=10.2$
$k_{NH_3}=0.89\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=5.10\times10^{-2}$ mol l^{-1} min^{-1}.

From the graph it is clear that linearity is obtained only at lower concentrations of the base and the electrolyte. The deviation at higher concentrations is due to the fact that Eq. (2) is valid only at low ionic strength.

Effect of Dielectric Constant and Ionic Strength. In the reaction between ion-dipolar molecule the logarithm of the velocity constant is a linear function of ionic strength (μ) instead of square root of μ as in the case of reaction between ion-ion. This is only valid when there is a large variation in ionic strength, because under such conditions Debye-Hückel term disappears and only the Hückel term ($b\mu$) becomes prominent. On the other hand, the activity of the hydroxyl ion can be increased by the addition of the neutral salt, and thus the catalytic influence of the hydroxyl ion becomes a function of the concentration of the salt. This is also called a secondary salt effect. In order to show the validity of the above conclusion the effect of varying dielectric constant (by adding ethanol or methanol by volume) and ionic strength on the reaction rate has been studied. The results have been given in the Tables 11, 12

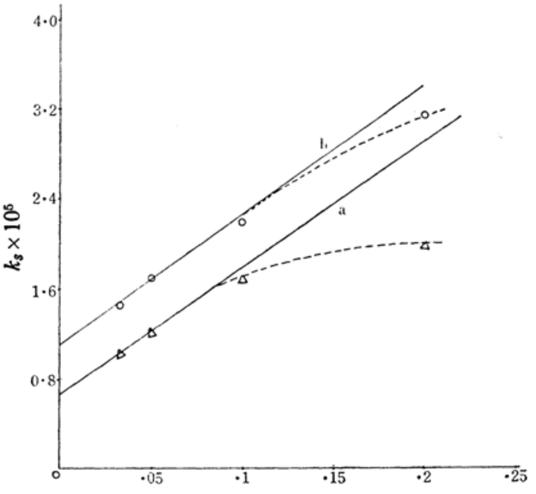

Fig. 4

Temperature 40°C
Varition of NH$_4$Cl at fixed ratio
[K$_3$Fe(CN)$_6$]$=2.50\times10^{-3}$ M
[D-Glucose]$=5.00\times10^{-2}$ M
a$=10:1$, pH$=10.0$ $k_{NH_3}=1.12\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=6.6\times10^{-2}$ mol l^{-1} min^{-1}
b$=20:1$, pH$=10.2$ $k_{NH_3}=1.14\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=6.94\times10^{-2}$ mol l^{-1} min^{-1}

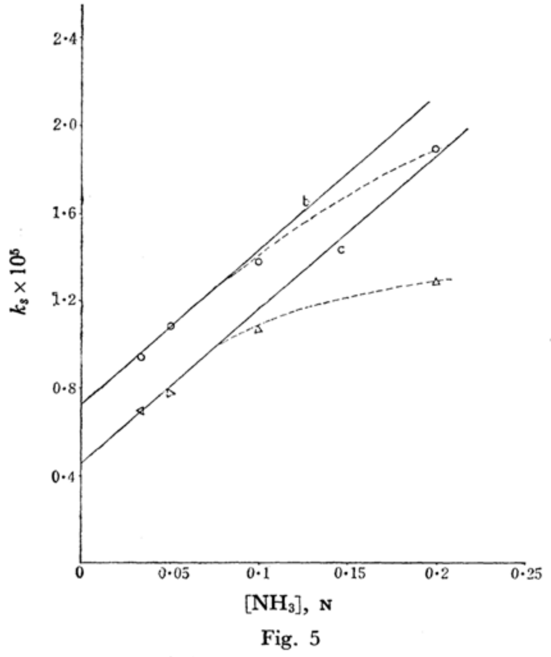

Fig. 5

Temperature 35°C
Variation of NH$_4$Cl at fixed ratio
[K$_3$Fe(CN)$_6$]$=2.50\times10^{-3}$ M
[D-Glucose]$=5.00\times10^{-2}$ M
a$=10:1$, pH$=10.0$ $k_{NH_3}=0.7\times10^{-4}$ mol l^{-1} min^{-1}
$k_{OH^-}=4.5\times10^{-2}$ mol l^{-1} min^{-1}
b$=20:1$, pH$=10.2$ $k_{NH_3}=0.72\times10^{-4}$, mol l^{-1} min^{-1}
$k_{OH^-}=4.5\times10^{-2}$ mol l^{-1} min^{-1}

and 13. In the case of ammonia the reaction rate decreases with the decrease in dielectric constant, but in the case of strong base sodium hydroxide enhanced reaction rates with the decrease in dielectric constant are obtained. On the other hand when neutral salt (KCl) is added at particular dielectric constant the reaction rate increases with the gradual increase in ionic strength.

In the case of ion-ion reactions, the effect of ionic strength and dielectric constant on the reaction rate is expressed by Brönsted-Christiansen-Scatcherd[10] equation. A similar relationship is expressed by Amis and Joffé[11] and Laidler and Eyring[12] in the case of reaction between ion-dipolar molecule. Both the above equations show that logarithm of velocity constant varies as ionic strength instead of square root of ionic strength as in the case of ion-ion reactions. In order to show the validity of the data the log k_s has been plotted against μ (Fig. 6). A straight line with slight deviation at low ionic strength (due to complication of secondary salt effect) is obtained. Further, ln k_0' varies as $1/D$, where k_0' is the velocity constant at zero ionic strength and D is the dielectric constant of the solution. These two equations lead to contradictory results[13] which have been described in the following lines.

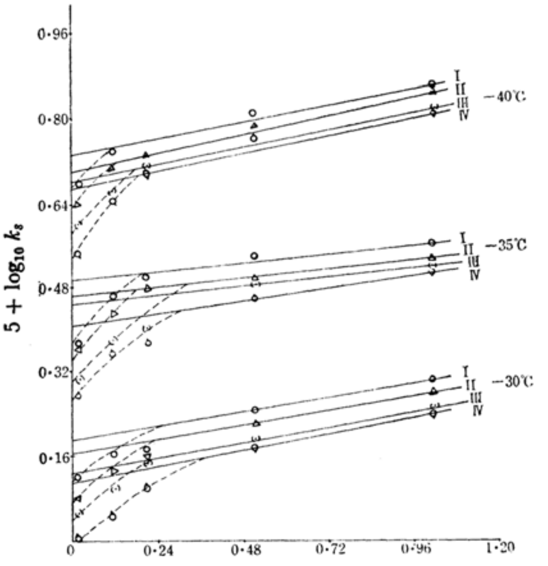

Fig. 6

Variation of ionic strength
[K$_3$Fe(CN)$_6$]$=2.50\times10^{-3}$ M
[NH$_3$]$=1.00\times10^{-1}$ N
[D-Glucose]$=5.00\times10^{-2}$ M

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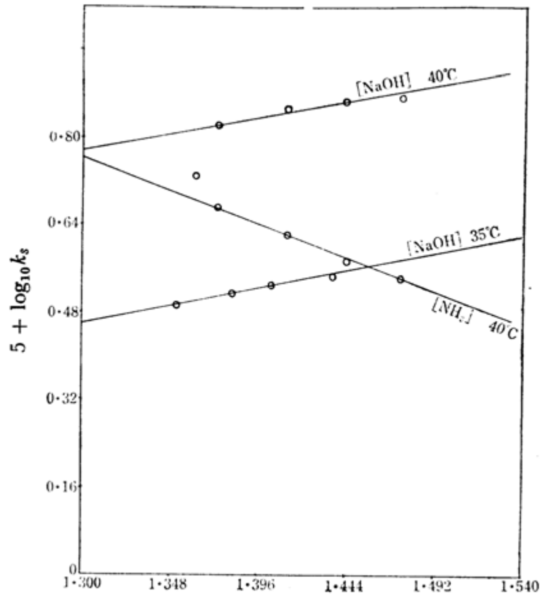
[10] Edawrd S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Company, N. Y. (1949), p. 77.

[11] Edward S. Amis and H. H. Jaffé, *J. Chem. Phys.*, **10**, 598 (1942).

[12] K. J. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, **39**, 299 (1940).

	For positive ion effect of increasing		For negative ion effectof increasing	
	dielectric constant	ionic strength	dielectric constant	ionic sterngth
Author	decrease	increase	increase	decrease
Amis and Jaffé Laidler and Eyring	decrease	increase	decrease	increase

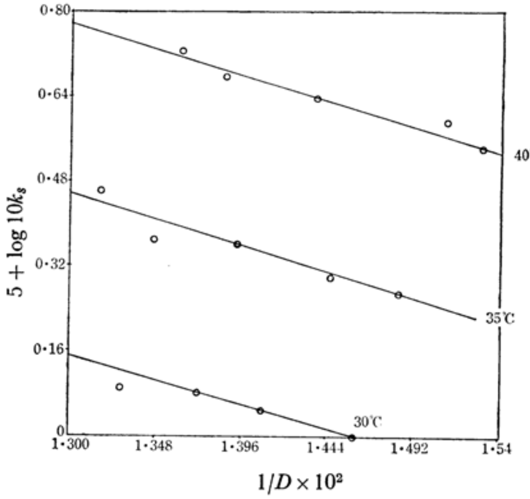
From the above results it is clear that both the equations predict the same results in the case of reaction between positive ion and dipolar molecule, but there is difference in the case of reaction between negative ion and dipolar molecule. Now in the present reaction between negative ion and dipolar molecule (reducing sugar) in presence of ammonia the effect of variation of ionic strength on the reaction rate is in agreement with the result predicted by Laidler and Eyring. Now, when the dielectric constant has been decreased, an increase in the reaction rate is observed in the presence of sodium hydroxide and decrease in the presence of ammonia. Thus the results obtained in the case of sodium hydroxide are again in agreement with Eyring's equation. The contradictory result obtained in the presence of ammonia is due to the fact that the decrease in the dielectric constant of the medium results in the decrease in hydroxyl ion and increase in NH_3 concentration. This has been shown graphically in Fig. 7 by plotting log k_s against $1/D$. A straight line with relative slope



$1/D \times 10^2$

Fig. 7

Variation of dielectric (Methanol) constant
$[K_3Fe(CN)_6]=2.50\times10^{-3}$ M
[D-Glucose]$=5.00\times10^{-2}$ M
$[NH_3]=1.00\times10^{-1}$ N



$1/D \times 10^2$

Fig. 8

Variation of dielectric (Ethanol) Constant
$[K_3Fe(CN)_6]=2.50\times10^{-3}$ M
$[NH_3]=1.00\times10^{-1}$ N
[D-Clucose]$=5.00\times10^{-2}$ M
$\mu=0.015$ M

TABLE 11

Temp.: 40°C
$[K_3Fe(CN_6)]=2.5\times10^{-3}$M $[K_3Fe(CN_6)]=2.5\times10^{-3}$M
$[NH_3]=1.00\times10^{-1}$N $[NaOH]=6.66\times10^{-3}$N
[D-Glucose]$=5.00\times10^{-2}$M [D-Glucose]$=1.00\times10^{-2}$M
$\mu=0.015$ M $\mu=1.0216$ M

Percentage of methanol by vol.	D	$k_s\times10^5$ mol l^{-1} min^{-1}	$k_s\times10^5$ mol l^{-1} min^{-1}
5	72.77	4.70	6.62
10	70.83	4.17	7.10
15	69.21	3.72	7.30
20	67.82	3.48	7.51

TABLE 12

Temp. : 35°C
$[K_3Fe(CN)_6]=2.5\times10^{-3}$M, $[NaOH]=6.66\times10^{-3}$N
[D-glucose]$=1.00\times10^{-2}$M
$\mu=0.0616$ M

Percentage of methanol by vol.	D	$k_s\times10^5$ mol l^{-1} min^{-1}
5	73.93	3.13
10	72.33	3.26
15	71.23	3.39
20	69.59	3.51

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13) Edward S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Company, N. Y. (1949), p. 174.

TABLE 13

$[K_3Fe(CN_6)] = 2.50 \times 10^{-3}$M, $[K_3Fe(CN)_6] = 2.5 \times 10^{-3}$M, $[NH_3] = 1.00 \times 10^{-1}$N, $[NH_3] = 1.00 \times 10^{-1}$N, [D-Glucose] $= 5.00 \times 10^{-2}$M, [D-Fructose] $= 1.00 \times 10^{-2}$M

Percentage of ethanol by vol.	D	μ M	$k_s \times 10^5$ mol l^{-1}· min^{-1}	$k_s \times 10^5$ mol l^{-1}· min^{-1}
Temp: 40°C				
0	73.38	0.015	5.35	6.56
5	72.06	0.015	4.78	5.75
I		0.115	5.52	6.61
		0.215	—	7.02
		0.515	6.47	7.52
		1.015	7.27	8.28
10	69.53	0.015	4.36	4.92
II		0.115	5.10	5.86
		0.215	5.42	6.35
		0.515	6.12	7.03
		1.015	7.10	8.20
15	66.16	0.015	3.95	4.31
III		0.115	4.64	5.36
		0.212	5.16	5.91
		0.515	6.16	6.61
		1.015	6.63	7.50
20	65.32	0.015	3.51	3.83
IV		0.115	4.48	5.01
		0.212	5.03	5.69
		0.515	5.84	6.43
		1.015	6.46	7.23
Temp.: 35°C				
0	76.03	0.015	2.90	3.57
5	74.15	0.015	2.35	3.06
I		0.115	2.92	3.60
		0.215	3.21	3.84
		0.515	3.47	4.40
		1.015	3.66	4.93
10	71.67	0.015	2.30	2.72
II		0.115	2.69	3.43
		0.215	3.02	3.72
		0.515	3.13	4.32
		1.015	3.44	4.60
15	69.36	0.015	2.01	2.40
III		0.115	2.36	3.12
		0.215	2.52	3.26
		0.515	3.08	3.86
		1.015	3.32	4.21
20	67.32	0.015	1.87	2.16
IV		0.115	2.26	2.92
		0.215	2.34	3.15
		0.515	2.87	3.63
		1.019	3.24	3.92
Temp.: 30°C				
0	77.25	0.015	1.50	2.01
5	75.15	0.015	1.32	1.74
I		0.115	1.47	1.91
		0.215	1.49	2.20
		0.515	1.75	2.40
		1.015	2.01	2.57
10	72.83	0.015	1.21	1.68
II		0.115	1.36	1.74
		0.215	1.44	2.02
		0.515	1.66	2.22
		1.015	1.91	2.45
15	70.95	0.015	1.12	1.51
III		0.115	1.25	1.68
		0.215	1.41	1.82
		0.515	1.55	2.03
		1.015	1.80	2.31
20	68.44	0.015	1.00	1.37
VI		0.115	1.11	1.49
		0.215	1.25	1.65
		0.515	1.50	1.92
		1.015	1.73	2.17

is obtained. This fact is supported by Harned.[14] He has reported in the case of acetic acid that logarithm of ionization constant varies as $1/D$. Thus in our case there would have been an increase with the decrease in dielectric constant as observed in the case of sodium hydroxide (Fig. 8) and the decrease in the reaction rate observed is only due to decrease in dissociation constant.

Mechanism of the Reaction

A careful study of the oxidation of reducing sugars (D-glucose and D-fructose) indicates that the rate expression is of the form:

$$-\frac{d[\text{Fe y}^{3-}]}{dt} = k[NH_3][s] \tag{1}$$

where [s] represents the concentration of reducing sugar and [Fe y^{3-}] the ferricyanide ion. The above equation indicates that the reaction velocity is independent of the concentration of ferricyanide ion and directly proportional to both the ammonia and reducing sugar concentration. For any given concentration of alkali, if the concentration of reducing sugar is comparatively larger than ferricyanide ion, the rate expression takes the form

$$-\frac{d[\text{Fe y}^{3-}]}{dt} = k_s = \frac{\Delta x}{\Delta t}$$

where

$$k_s = k[NH_3][s] \tag{2}$$

where k_s is the standard zero velocity constant and k the specific rate constant.

From the results it appears that first step involves the action of alkali on the reducing sugar (*loc. cit.*)

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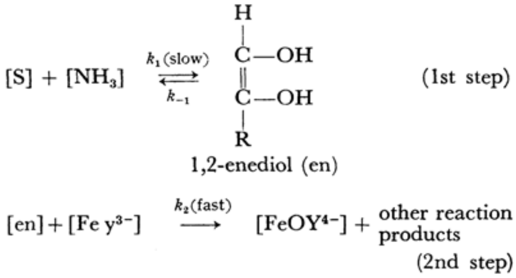
[14] H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1939).

forming an intermediate 1,2-enediol, which is subsequently oxidized by the ferricyanide ion. The latter being a comparatively faster process, so that the reaction becomes independent of ferricyanide ion concentration.

Thus



$$[\mathrm{S}] + [\mathrm{NH_3}] \underset{k_{-1}}{\overset{k_1\,(\text{slow})}{\rightleftharpoons}} \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C{-}OH} \\ \| \\ \mathrm{C{-}OH} \\ | \\ \mathrm{R} \end{array} \qquad \text{(1st step)}$$

1,2-enediol (en)

$$[\mathrm{en}] + [\mathrm{Fe\,y^{3-}}] \xrightarrow{k_2(\text{fast})} [\mathrm{FeOY^{4-}}] + \text{other reaction products} \qquad \text{(2nd step)}$$

considering the stationary state for enediol and $k_2 \gg k_{-1}$ the final rate expression comes out to be

$$-\frac{\mathrm{d}[\mathrm{Fe\,y^{3-}}]}{\mathrm{d}t} = k_1[\mathrm{NH_3}][\mathrm{S}] \qquad (3)$$

where k_1 is identical with k of Eq. (1). Equation (3) confirms our experimental findings. Further, this leads to the conclusion that the rate of enolization is the rate of oxidation of the reducing sugar.

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