OXIDATION OF D-FRUCTOSE WITH VANADIUM(V): A KINETIC APPROACH*†

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ABSTRACT

The kinetics of the oxidation of D-fructose with vanadium(V) in perchloric acid have been studied. The reaction is of first order with respect to the [Fructose], but the values of the rate constant increase slightly with increasing [V(V)]. In the range from 0.002–0.02M V(V), the inverse of the second-order rate constant is linearly related to the inverse of [V(V)]. Sodium hydrogensulfate and perchlorate accelerate the reaction, the effect of the former salt being greater. At a constant [H$^+$] and ionic strength, the reaction is of first order with respect to [HSO$_4^-$]. At constant ionic strength, the reaction is of third order with respect to [H$^+$]. The activation parameters have been determined. The data obtained have been compared with those for simpler mono- and poly-hydric alcohols. A possible three-step mechanism involving C–H bond fission and yielding glucosones as primary products has been suggested.

INTRODUCTION

Previously, we have reported[1-4] rate constants as well as the effects of [H$^+$], [NaClO$_4$], and [HSO$_4^-$] on the rate of the oxidations of several mono- and poly-hydric alcohols to aldehydes or ketones with [V(V)]. We now report on the corresponding reaction of D-fructose.

The kinetics of the oxidation of carbohydrates have been studied with various one-equivalent oxidants, such as Co(III)[5], Mn(III)[6], V(V)[7-9], and Ce(IV)[10,11]. Of these, V(V) is a versatile and potent oxidant[12] and it has been used in kinetic investigations of the oxidation of hexoses, including D-fructose[7-9]. However, the oxidation of D-fructose was studied almost exclusively in sulfuric acid media which can be expected to contain at least two catalysing species, namely, H$^+$ and HSO$_4^-$, which complicate the mechanism[2,3,8]. More information on the mechanism should be obtainable by using perchloric acid media.

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†Vanadium(V), Part XII. For Part XI, see ref. 1

EXPERIMENTAL

Ammonium metavanadate (analytical grade, Merck) and D-fructose (Fluka) were used without further purification.

Kinetic experiments. — (*a*) The principal method (1) involved analysis of un-reacted V(V) by quenching with aqueous ferrous sulfate following the addition of aqueous potassium thiocyanate, and determination of the absorbance at 450 nm with a Cary Model 16 spectrophotometer equipped with a Varian Model G-2510 chart-recorder[13].

(*b*) Alternatively (method 2), the reactions were carried out in the spectrophotometer with thermostated cells, and [V(IV)] was determined on the basis of the absorbance at 765 nm using a Beckman Model ACTA MIV spectrophotometer[14].

Both methods give the same values for the rate constant within the limits of experimental error (Table I), and V(V) is reduced quantitatively to V(IV). Method 1 was preferred because the correct temperature in method 2 was attained too slowly for the fast reactions.

All the rate constants were determined under pseudo-first-order conditions with D-fructose in excess, and they refer to the oxidation of the first alcohol group.

RESULTS

Tables I and II show that the rate of oxidation is of first order with respect to [Fructose]. Our results agree well with the value 1.2×10^{-4} $M^{-1}.s^{-1}$ calculated from the results of Pathak *et al.*[7] for k_{obs}/[Fructose] in M perchloric acid at 25°.

Although, in individual runs, V(V) disappeared by first-order kinetics and the correlation coefficient was close to unity, the data in Table II show that the rate constant increased slightly with increasing V(V). The same phenomenon was ob-

TABLE I

COMPARISON OF DIFFERENT METHODS FOR DETERMINING THE RATE CONSTANT FOR THE OXIDATION OF D-FRUCTOSE WITH V(V) AT 45°: [V(V)] = 0.006M, [HClO$_4$] = 0.981M

Method[a]	λ_{max} (nm)	[Fructose] (M)	k_{obs} (s^{-1})	r	k_{obs}/[Fructose] (M^{-1}.s^{-1})
1	450	0.0502	(7 46 ±0.30) × 10^{-5}	0.9986	(1.49 ±0.05) × 10^{-3}
2	765	0.0506	(7.65 ±0.07) × 10^{-5}	0.9983	(1 51 ±0 03) × 10^{-3}
1	450	0.1504	(2.48 ±0 17) × 10^{-4}	0.9953	(1 65 ±0.11) × 10^{-3}
2	765	0.1504	(2 41 ±0 01) × 10^{-4}	0 9999	(1.60 ±0.01) × 10^{-3}
1	450	0.3808	(5.38 ±0.16) × 10^{-4}	0 9983	(1 53 ±0.05) × 10^{-3}
2	765	0.3507	(5.80 ±0.06) × 10^{-4}	0.9999	(1 65 ±0.02) × 10^{-3}

[a]See Experimental.

TABLE II

VARIATION OF THE RATE CONSTANT WITH THE CONCENTRATION OF D-FRUCTOSE AND V(V) AT 25° IN WATER: [HClO$_4$] = 0.981M

| [V(V)] (M)	[Fructose] (M)	k$_{obs}$ (s^{-1})	r	k$_{obs}$/[Fructose] (M^{-1}.s^{-1})
0.0200	0.1207	(1.59 ±0.05) × 10^{-5}	0.9978	(1.32 ±0.04) × 10^{-4}
0.0200	0.3431	(4.19 ±0.10) × 10^{-5}	0.9986	(1.22 ±0.03) × 10^{-4}
0.0200	0.5969	(7.33 ±0.15) × 10^{-5}	0.9990	(1.23 ±0.03) × 10^{-4}
0.0200	1.029	(1.37 ±0.05) × 10^{-4}	0.9987	(1.33 ±0.05) × 10^{-4}
0.00200	0.5969	(3.61 ±0.60) × 10^{-5}	0.9613	(6.05 ±1.00) × 10^{-5}
0.00300	0.5969	(4.26 ±0.13) × 10^{-5}	0.9986	(7.14 ±0.22) × 10^{-5}
0.00400	0.5969	(4.87 ±0.11) × 10^{-5}	0.9986	(8.17 ±0.18) × 10^{-5}
0.00600	0.5969	(5.52 ±0.04) × 10^{-5}	0.9999	(9.25 ±0.10) × 10^{-5}
0.0100	0.5977	(6.84 ±0.09) × 10^{-5}	0.9996	(1.14 ±0.02) × 10^{-4}
0.0200	0.5969	(7.33 ±0.15) × 10^{-5}	0.9990	(1.23 ±0.03) × 10^{-4}
0.0300	0.5969	(7.83 ±0.15) × 10^{-5}	0.9993	(1.31 ±0.03) × 10^{-4}
0.0400	0.5969	(8.18 ±0.04) × 10^{-5}	1.0000	(1.37 ±0.01) × 10^{-4}
0.0600	0.5969	(8.56 ±0.09) × 10^{-5}	0.9998	(1.43 ±0.02) × 10^{-4}
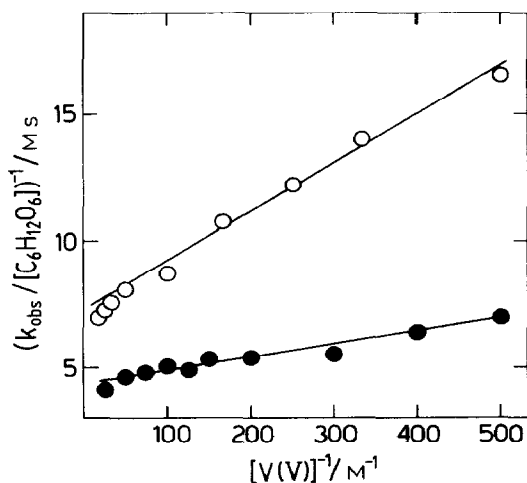
Fig. 1. Reciprocal plot for the reaction of D-fructose with V(V): 10^3(k$_{obs}$/[Fructose])$^{-1}$/M.s in 0.981M HClO$_4$ at 25° (—O—), 10^{-2}(k$_{obs}$/[Fructose])$^{-1}$/M.s in 1.5M H$_2$SO$_4$ at 30° (—●—; from ref. 7).

served by Pathak et al.[7] in the oxidation of D-fructose in sulfuric acid by sodium metavanadate, but no quantitative correlation was reported. In Fig. 1, the values of (k$_{obs}$/[Fructose])$^{-1}$ are plotted against [V(V)]$^{-1}$ and also for the values calculated from the results of Pathak et al.[7]. The increase of the rate constant in 0.981M perchloric acid at 25° in the range 0.002–0.02M V(V) follows Eq. 1,

$$(k_{obs}/[Fructose])^{-1}/M.s = (1.92 ±0.10) × 10 × [V(V)^{-1}/M^{-1} +$$
$$(7.27 ±0.28) × 10^3 \qquad 1$$

TABLE III

VARIATION OF THE RATE CONSTANT WITH [NaClO$_4$] AND [HSO$_4^-$] FOR THE OXIDATION OF D-FRUCTOSE WITH
V(V) AT 25°: [V(V)] = 0.02M, [FRUCTOSE] = 0.1M, [HClO$_4$] = 0.49M

[NaClO$_4$] (M)	[NaHSO$_4$] (M)	k$_{obs}$ (s^{-1})	r	k$_{obs}$/[Fructose] ($M^{-1} s^{-1}$)
—	—	$(6.91 \pm 0.28) \times 10^{-6}$	0.9958	$(6.90 \pm 0.28) \times 10^{-5}$
1.000	—	$(9.11 \pm 0.45) \times 10^{-6}$	0.9940	$(9.10 \pm 0.45) \times 10^{-5}$
2.000	—	$(1.30 \pm 0.05) \times 10^{-5}$	0.9978	$(1 30 \pm 0.05) \times 10^{-4}$
3.000	—	$(1.78 \pm 0.07) \times 10^{-5}$	0 9986	$(1 78 \pm 0.07) \times 10^{-4}$
4.000	—	$(2.74 \pm 0.11) \times 10^{-5}$	0.9975	$(2.74 \pm 0 11) \times 10^{-4}$
—	4.000	$(6.67 \pm 0.05) \times 10^{-4}$	0.9998	$(6 66 \pm 0.05) \times 10^{-3}$
1.000	3.000	$(5.36 \pm 0.07) \times 10^{-4}$	0 9997	$(5.35 \pm 0.07) \times 10^{-3}$
2.000	2 000	$(3.83 \pm 0.07) \times 10^{-4}$	0.9995	$(3.83 \pm 0.07) \times 10^{-3}$
3.000	1 000	$(2.09 \pm 0.02) \times 10^{-4}$	0 9998	$(2.09 \pm 0.02) \times 10^{-3}$
4 000	—	$(2.74 \pm 0 11) \times 10^{-5}$	0.9975	$(2 74 \pm 0 11) \times 10^{-4}$

TABLE IV

VARIATION OF THE RATE CONSTANT WITH [HClO$_4$] AT A CONSTANT IONIC STRENGTH OF 3.69M FOR THE
OXIDATION OF D-FRUCTOSE WITH V(V) AT 25°· [V(V)] = 0.02M, [FRUCTOSE] = 0.1M

[HClO$_4$] (M)	k$_{obs}$ (s^{-1})	r	k$_{obs}$/[Fructose] ($M^{-1} s^{-1}$)
1.06	$(7.57 \pm 0.15) \times 10^{-5}$	0 9993	$(7.56 \pm 0 15) \times 10^{-4}$
1.79	$(7 80 \pm 0.17) \times 10^{-5}$	0.9990	$(7.79 \pm 0 17) \times 10^{-4}$
2.77	$(1.04 \pm 0.01) \times 10^{-4}$	0.9998	$(1.04 \pm 0.01) \times 10^{-3}$
3 15	$(1.32 \pm 0 01) \times 10^{-4}$	0.9999	$(1 31 \pm 0.01) \times 10^{-3}$
3 41	$(1.52 \pm 0.02) \times 10^{-4}$	0 9997	$(1.52 \pm 0.02) \times 10^{-3}$
3.42	$(1.55 \pm 0.02) \times 10^{-4}$	0 9996	$(1.54 \pm 0.02) \times 10^{-3}$
3.61	$(1.72 \pm 0 03) \times 10^{-4}$	0.9995	$(1 72 \pm 0.03) \times 10^{-3}$
3 69	$(1.80 \pm 0.02) \times 10^{-4}$	0 9997	$(1 80 \pm 0 02) \times 10^{-3}$

with a correlation coefficient of 0.9945. Equation 2 is for the rate constant in 1.5M
H$_2$SO$_4$ at 30°, calculated using the reported[7] data with a correlation coefficient of
0.9726.

$$(k_{obs}/[Fructose])^{-1}/M.s = (5.12 \pm 0.43) \times 10^{-1} \times [V(V)]^{-1}/M^{-1} +$$
$$(4.35 \pm 0.11) \times 10^2 \qquad 2$$

The addition of sodium perchlorate accelerates the rate (Table III). The in-
crease of the rate constant in 0.49M perchloric acid follows Eq. 3, with a correlation
coefficient of 0.9979.

$$\log \{(k_{obs}/[Fructose])/M^{-1}.s^{-1}\} = (1.49 \pm 0.06) \times 10^{-1} [NaClO_4]/M +$$
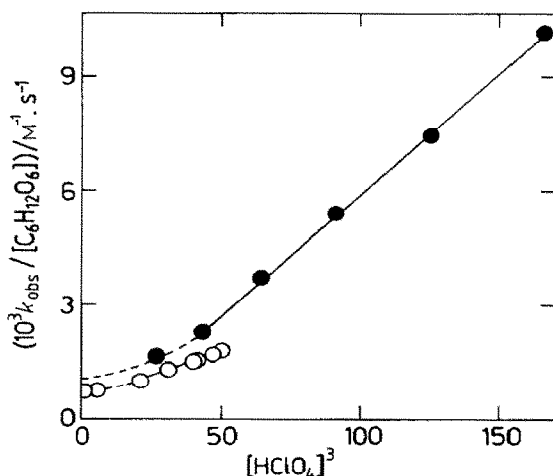$$(-4.18 \pm 0.02) \qquad 3$$

Fig. 2. Dependence of the rate constant on the third power of $[HClO_4]$ at constant ionic strength: $[HClO_4]$ = 1.06–3.69M, I = 3.69M (—○—); $[HClO_4]$ = 3.0–5.5M, I = 5.51M (—●—: from ref. 7).

TABLE V

EFFECT OF TEMPERATURE ON THE RATE CONSTANT OF THE OXIDATION OF D-FRUCTOSE WITH V(V) IN WATER: $[V(V)]$ = 0.02M, [FRUCTOSE] = 0.1M AT 25°

t (°)	$[HClO_4]$ (M)	k_{obs} (s^{-1})	r	$k_{obs}[Fructose]$ ($M^{-1}.s^{-1}$)
25	0.490	(6.91 ±0.28) × 10^{-6}	0.9958	(6.90 ±0.28) × 10^{-5}
35	0.488	(2.81 ±0.13) × 10^{-5}	0.9945	(2.82 ±0.13) × 10^{-4}
45	0.487	(1.04 ±0.04) × 10^{-4}	0.9981	(1.05 ±0.04) × 10^{-3}
50	0.485	(1.93 ±0.04) × 10^{-4}	0.9990	(1.95 ±0.04) × 10^{-3}

At a constant ionic strength maintained by variation of $[NaClO_4]$ and $[NaHSO_4]$, the rate is linearly proportional to the latter (Table III), as given by Eq. 4 with a correlation coefficient of 0.9979.

$$(k_{obs}/[Fructose])/M^{-1}.s^{-1} = (1.60 ±0.06) \times 10^{-3} [HSO_4^-]/M + (4.34 ±1.49) \times 10^{-4} \qquad 4$$

The effect of the acid concentration was studied by partial neutralisation of perchloric acid with sodium hydroxide to maintain a constant ionic strength (Table IV). The plot of the rate constant against the acid concentration or its second power is clearly curved; with the third power of the acid concentration, the dependence is linear and, in the range 2.8–3.7M perchloric acid, follows Eq. 5 with a correlation coefficient of 0.9995. The results are shown in Fig. 2 together with the values calculated from the results of Pathak et al.[7] at higher concentrations of perchloric acid and higher ionic strength of 5.51M. Taking the positive salt effect into considera-

tion, the data agree well and the dependence on the third power of $[HClO_4]$ is found in both cases, but the slope is considerably higher, *i.e.*, $\sim 6.4 \times 10^{-5}$, at the higher ionic strength.

$$(k_{obs}/[\text{Fructose}])/\text{M}^{-1}.\text{s}^{-1} = (2.60 \pm 0.04) \times 10^{-5} \, [HClO_4]^3/\text{M}^3 + $$
$$(4.95 \pm 0.16) \times 10^{-4} \qquad 5$$

The effect of temperature on the rate of oxidation is shown in Table V. The value of 107.1 ± 0.2 kJ.mol^{-1} for the enthalpy of activation and the value of 37.7 ± 0.7 J.K^{-1}.mol^{-1} for the entropy of activation at 25° have been evaluated from $k_{obs}/[\text{Fructose}]$.

DISCUSSION

D-Fructose can exist in solution as pyranose, furanose, and open-chain forms. Kinetically, it can be considered to be a polyol in which the reactivities of the alcohol groups are affected by the carbonyl group.

The rate constant[15] for the oxidation of glycol in 3.5M perchloric acid at 25° is 6.4×10^{-6} M^{-1}.s^{-1} and that of glycerol in 2.9M perchloric acid at 25° is 7.2×10^{-6} M^{-1}.s^{-1}. The reactivity of D-fructose is higher by much more than a statistical quantity $\{k_{obs}/[\text{Fructose}]$ is $\sim 1.6 \times 10^{-3}$ M^{-1}.s^{-1} (Table IV)$\}$ and shows the importance of the carbonyl group for the reaction rate and site.

It can be estimated[8,16] that, in 2M perchloric acid, the rate of mutarotation of D-glucose is $\sim 33,000$ times higher than the rate of oxidation with V(V). Therefore, it is highly probable that the mutarotation equilibrium for D-fructose is immediately attained.

The rate constant[17] for the oxidation of D-glucose in 1.5M perchloric acid at 25° is 1.0×10^{-5} M^{-1}.s^{-1}. As the rate constant for D-fructose in M perchloric acid and in otherwise comparable conditions is 1.3×10^{-4} M^{-1}.s^{-1}, the reactivity of D-fructose is more than ten times higher than that of D-glucose.

The order of reactivity of sugars in both aqueous perchloric and sulfuric acids is fructose > xylose > arabinose > galactose > mannose > glucose[8]; in aqueous 30% acetic acid containing sulfuric acid, it is fructose >xylose > arabinose > galactose > glucose > mannose[9]. For aldoses, these orders are almost the same as those[18] for the proportions of open-chain forms. Thus, it has been concluded that the sugars are oxidised mainly through the open-chain forms[8,9] and it is also clear that the conversion of fructose *via* the enol form does not interfere under acidic solutions.

The reaction is acid-catalysed (Fig. 2). From Fig. 2 and Eq. 5, it is seen that, at relatively high concentrations of acid, the rate constant correlates well with $[HClO_4]$, but the slope is dependent on the ionic strength. As the concentration of acid decreases, the slope tends towards zero. The intercept is positive and shows that, apart from the acid-catalysed reactions, an uncatalysed reaction also functions.

TABLE VI

COMPARISON OF SALT EFFECTS AND CATALYSIS BY HYDROGENSULFATE ION FOR COMPOUNDS WHICH UNDERGO C–H BOND FISSION IN AQUEOUS PERCHLORIC ACID

Compound	t (°)	Salt effect[a]	I^c (M)	HSO_4^--catalysis[b]	I^c (M)	Ref.
C–H bond fission						
TEAH[+d]	60	2.08×10^{-1}	3.09–7.03	2.74×10^{-3}	7.03	3
TMM[e]	50	1.83×10^{-1}	2.11–6.07	1.63×10^{-4}	6.07	4
DEPD[f]	50	1.99×10^{-1}	3.26–5.24	5.9×10^{-5}	5.24	4
C–C bond fission						
Glycolic acid	50	2.12×10^{-2}	0.23–4.19	1.19×10^{-2}	4.19	1
Lactic acid	50	1.86×10^{-2}	0.23–4.19	9.14×10^{-3}	4.19	1
Fission to be tested						
D-Fructose	25	1.49×10^{-1}	0.49–4.49	1.60×10^{-3}	4.49	

[a]Slope when $\log_{10}\{(k_{obs}/[\text{compound}])/\text{M}^{-1}.\text{s}^{-1}\}$ is plotted against [NaClO$_4$] at different ionic strength. [b]Slope when $(k_{obs}/[\text{compound}])/\text{M}^{-1}.\text{s}^{-1}$ is plotted against [HSO$_4^-$] at constant ionic strength. [c][HClO$_4$] + [NaClO$_4$] and/or [NaHSO$_4$]. [d]Triethanolammonium ion. [e]Tetramethylol methane. [f]2,2-Diethyl-1,3-propanediol.

The pK_a values for various simple alcohols[19] are ~ -3. The carbonyl group is much less basic[20], but its presence makes D-fructose more basic than simple alcohols. Therefore, it is likely that D-fructose is partly protonated in most of the solutions studied here. If this protonation facilitates the formation of complexes or reactivity, the dependence of the oxidising species will be on [HClO$_4$]^2. A linear dependence of the rate constant on [HClO$_4$]^2 has been found for the oxidation of the primary alcohols 1,3-propanediol[21], 1,3-butanediol[22], 1,4-butanediol[21], and triethanolammonium ion[2] with V(V).

In slightly acidic solutions, V(V) exists[23] as VO_2^+, with pK_a 3.70 at 25°. At higher concentrations of acid, $V(OH)_3^{2+}$ and $V(OH)_2^{3+}$ are assumed to exist[24]. Madic *et al.*[25] reported that the aquadioxovanadium(V) ion forms a dimer with a central $V_2O_3^{4+}$ group in concentrated perchloric acid.

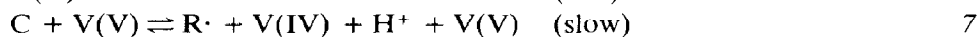For the catalysis by hydrogensulfate, we refer to earlier discussion of the formation of different oxidising species[2].

Most primary and secondary alcohols undergo C–H bond fission, but 2-hydroxycarboxylic acids[1,26] and hydroxy compounds which do not contain an α-hydrogen atom[27,28] undergo C–C bond fission. The fission of C–H bonds is associated with a considerably higher ionic strength effect and lower hydrogensulfate catalysis than fission of C–C bonds[1]. This test for the type of reaction associated with D-fructose is applied in Table VI, and the data indicated C–H bond fission.

The oxidation of alcohols *via* fission of C–H bonds has been assumed[2] to progress through a three-step process. In the first rapid pre-equilibrium step, a stable coordination complex C is formed between the substrate S and V(V). In the second step, the complex decomposes unimolecularly in the rate-determining step,

forming a free-radical R· and V(IV). In the third step, R· is rapidly oxidised, forming the reaction products P and V(IV).

In this study, a linear dependence was found between $k_{obs}/[\text{Fructose}])^{-1}$ and $[V(V)]^{-1}$ (Fig. 1, Eqs. 2 and 3). This dependence was found from our experimental results and from the results reported by Pathak et al.[7]. To our knowledge, such dependence has not been reported hitherto for the oxidation of alcohols by V(V). Kinetically, this observation can be explained by assuming that V(V) participates in the rate-determining step.

Taking into consideration all the above-mentioned aspects, the following mechanism can be proposed to explain, in a simplified form, the experimental data and the earlier observations on the acid-catalysed part of the oxidation.

$$V(V) + SH^+ \rightleftharpoons C \qquad\qquad\qquad\qquad (\text{fast}) \qquad\qquad 6$$
$$C + V(V) \rightleftharpoons R\cdot + V(IV) + H^+ + V(V) \quad (\text{slow}) \qquad\qquad 7$$
$$R\cdot + V(V) \rightarrow P + V(IV) + H^+ \qquad\qquad (\text{fast}) \qquad\qquad 8$$

In Eqs. 6–8, $k_{-6} \gg k_6$ and $k_{-6} \approx k_7[V(V)]$, and V(V) denotes the oxidising species preponderant at a particular acidity. The mechanism leads to the rate law

$$\text{Rate} = k_7[C][V(V)] \qquad\qquad\qquad\qquad\qquad\qquad 9$$

$$= \frac{k_6 k_7 [V(V)]}{k_{-6} + k_7[V(V)]} [V(V)][SH^+]. \qquad\qquad 10$$

Further,

$$\frac{1}{k_{obs}/[SH^+]} = \frac{1}{k_6} + \frac{k_{-6}}{k_6 k_7} \times \frac{1}{[V(V)]}. \qquad\qquad 11$$

and, at a constant acid concentration, $(k_{obs}/[\text{Fructose}])^{-1}$ is linearly related to $[V(V)]^{-1}$.

The rate constant[28] for the oxidation of acetoin [MeCH(OH)COMe] to 2,3-butanedione is $\sim 1.5 \times 10^{-2}$ $M^{-1}.s^{-1}$ in 0.5M perchloric acid at the ionic strength of 3.1M at 25°. The rate constant for the oxidation of D-fructose under comparable conditions is $\sim 1.5 \times 10^{-4}$ $M^{-1}.s^{-1}$ (Table III). This difference in rate by a factor of 10^2 suggests that at least the major part of the oxidation of D-fructose involves the open-chain form, the concentration of which is <1% of the total concentration. The marked effect of the carbonyl group noted above is also understandable if D-fructose reacts mainly as the open-chain form. It is also acceptable that the complexing ability of this form is greater than that of the cyclic forms.

Thus, D-fructose is most probably oxidised mainly through the open-chain form, via a three-step process by C–H bond fission, to yield glucosones as primary products. D-Fructose has been oxidised to glucosones by A. roseum[20], [60]Co γ-radia-

tion[30], and with oxygen under u.v. irradiation in the presence of metal oxides[31], including V_2O_5. Studies of this oxidation are in progress.

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