

A catalytic oxidation of sugar by vanadium(IV)

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Abstract

Platinum and other noble metals have been found to catalyze the complete oxidation of sucrose and other sugars by vanadium(IV) in acid environments. As the redox potential of vanadium(IV)/vanadium(III) differs substantially from that of dioxygen/water, it might be possible to use this reaction to construct a redox type of fuel cell. In the present paper, the requirements on the catalyst are discussed, especially those that give full conversion of the oxidation reaction. Various sugars such as fructose, glucose, xylose and arabinose have been investigated and found to yield essentially the same results. A provisional model is proposed that might describe the processes on the catalyst surface.

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Keywords: Wet oxidation of sugars; Vanadium(IV); Platinum black

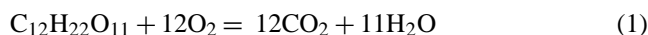
1. Introduction

In some previous papers [1–3], we have studied the catalytic oxidation of formic acid, formaldehyde and methanol in acid solution using vanadium(IV) as the oxidant. The aim of that research was to construct a redox fuel cell where the difficulties with methanol as a fuel in a ‘direct cell’ would be circumvented.

One draw-back with such a redox cell, at least as concerns methanol, is that methanol is a volatile substance, precluding the use of high temperatures. As sugars are non-volatile compounds, we have, therefore, tested the oxidation of sugars, primarily sucrose, with the same or similar catalyst systems and with vanadium(IV) as the oxidant.

The reason for choosing vanadium is that the redox potential for the couple vanadium(IV)/vanadium(III) is quoted as 0.36 V [4] and thus relatively close to that for sugar–CO₂, would it have been reversible. This latter potential can be calculated from thermodynamic data [4,5].

For the reaction



$$\Delta G = -1358.5 \text{ kcal/mol} = -5684 \text{ kJ/mol} \quad (2)$$

$$\Delta H = -1349.0 \text{ kcal/mol} = -5644 \text{ kJ/mol} \quad (3)$$

Consequently, the corresponding cell voltage would be determined by

$$48EF = -5684 \text{ kJ/mol} \quad (4)$$

where F is the Faraday constant. Thus,

$$E = 1.23 \text{ V} \quad (5)$$

and the normal potential of the sugar/CO₂ couple 0.00 V, i.e. very close to the H⁺/H₂ couple. Obviously, the closer the potential of the oxidative couple to the sugar–CO₂ couple, the more energy can be extracted in a redox type fuel cell. Concurrent with this, more demands are put on the catalyst system.

Incidentally, one notes that the theoretical efficiency of a hypothetical fuel cell driven directly by sugar and oxygen would be

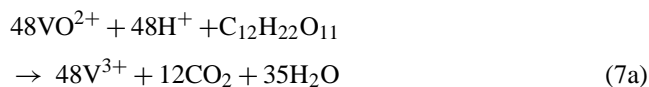
$$\eta = \frac{\Delta G}{\Delta H} = 101\% \quad (6)$$

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We found in surveying experiments that platinum black and also finely dispersed platinum on suitable carriers and some other noble metals similarly dispersed, were useful to promote the complete oxidation of sucrose to carbon dioxide at about 90 °C with no appearance of carbon monoxide.

This finding and a suitable catalytic system for the oxidation of vanadium(IV) to vanadium(V) makes it possible to construct a sugar powered fuel cell system [6]. In this paper, we will report on the fundamental reaction, the catalytic oxidation of sugar.



The oxidation of VO^{2+} , required to complete formula (7a) to formula (1), will be dealt with in a forthcoming paper.



2. Conditions of reaction

To the best of our knowledge, the reaction (7a) is not previously described [7]. The oxidation of sugar using platinum catalysts is described, but in this case, molecular oxygen has been the oxidant [8,9]. As indicated above such a reaction is of course unsuitable if the goal is to extract some of the free energy stored in the sugar–dioxygen pair. The basic condition for the reaction must be that it is performed in an acidic medium that will expel the carbon dioxide formed. Secondly, one should like to perform the reaction with as high concentrations of vanadium salts as possible, cf. the use of vanadium in accumulator systems [10], to reach a high exchange current density at the electrodes of a redox cell.

Thirdly, the temperature of reaction is limited to just below the boiling point of the electrolyte solution.

In order to be able to use a catalyst system, as reproducible as possible, we have selected commercial preparations of platinum black for the surveying investigations of this reaction.

3. Experimental

The experiments were performed so that the reaction medium, e.g. 200 ml of sulphuric acid containing vanadyl sulphate, was heated in a three-necked bottle, with a suitable thermostating arrangement, together with a specified amount of platinum black (Johnson Matthey, ca. 5 m²/g). The vessel was closed by a condenser stoppered at the top. A certain volume of a standard sugar solution was added such that the sugar concentration of the experiment was achieved, e.g. 1.03 mM or 2.06 mM. The moment when this was done was regarded as the starting point of the reaction. An inert atmosphere was kept in the vessel by pure nitrogen that was circulated in a loop leading down in the reaction mixture.

From time to time, an aliquot was sampled from the nitrogen atmosphere and analyzed for carbon dioxide (and any other gas) in a gas chromatograph. The temperature of the reaction medium was kept at 90 °C in all experiments described here.

It was also arranged so that samples could be withdrawn from the reaction medium and analyzed with respect to the light absorption spectrum, a band at ca 800 nm being indicative of the remaining VO^{2+} .

4. Results

4.1. Influence of sugar concentration

We measured the rate as the initial rate, i.e. the limiting conversion per time unit when the time approached zero. The amount of carbon dioxide formed was recalculated to the equivalent number of moles of vanadium(IV) lost by the reaction as given in formula (7a). In Fig. 1, we give the results of such measurements for sucrose and a specified concentration of vanadium(IV). The measurements were performed at different concentrations of sulphuric acid or phosphoric acid. It is immediately clear that the use of phosphoric acid is the better choice. Furthermore one observes that in all cases there is a maximum for the rate at a certain sugar concentration. In the case of phosphoric acid as electrolyte, this maximum occurs at the point when we have stoichiometric equivalence between the vanadium concentration and the sugar concentration. (0.1 M vanadium \approx 48 \times 0.002 M sugar.) This relation is probably accidental. In the case of sulphuric acid as the

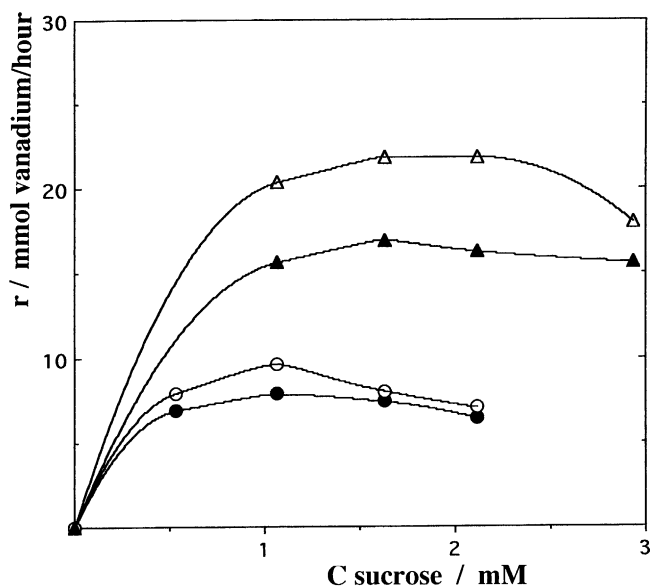


Fig. 1. Initial rate of the sugar oxidation (expressed in mmol vanadium/h, calculated from measured CO_2) as a function of the initial sugar concentration. Initial vanadium concentration, $C(\text{VO}^{2+}) = 0.1$ M; catalyst, 250 mg Pt black; denotations: 1 M H_2SO_4 (●), 3 M H_2SO_4 (○), 1 M H_3PO_4 (▲), 5 M H_3PO_4 (Δ).

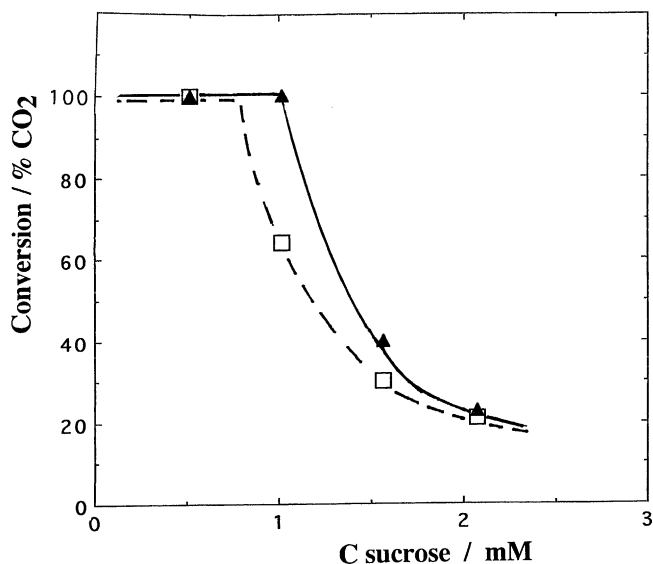


Fig. 2. Conversion (%CO₂ formed of the theoretical value) as a function of the initial sugar concentration: 1 M H₂SO₄ (□); 3 M H₂SO₄ (▲). C(VO²⁺) = 0.1 M; 250 mg Pt black.

electrolyte, the corresponding maximum appears at a much smaller value of the sugar concentration.

Fig. 2 represents some very important results. It shows that the yield, that should be 100% according to the statement in Section 1, is not always so. The yield strongly depends on the concentration of sugar. In want for better data, we have drawn the lines so as to indicate a breaking point up to which the yield is 100% and such that it is <100% beyond the sugar concentration of that point. The question to be asked is; why is the appearance of the two parts of the curve so distinctly different for just a doubling of the sugar concentration?

4.2. Influence of catalyst

In order to determine the conditions under which a complete combustion took place, we investigated the rate and the conversion as a function of the amount of catalyst. This investigation was performed on pure fructose. Figs. 3 and 4 give the variation of rate and conversion as function of the amount of catalyst. One observes (Fig. 4) that, at the concentration parameter values used, a certain critical amount of catalyst is needed to obtain a complete oxidation. One must conclude that under conditions such that the rate, measured through the amount of CO₂ formed, is not sufficiently high, other side reactions are taking place, probably resulting in only partial oxidation of the sugar.

4.3. Influence of the vanadium concentration

Using the same technique as above, we investigated the variation of the initial rate with the total vanadium concentration. The experimental results are presented in Figs. 5 and 6, showing a decline in rate with the vanadium concentration.

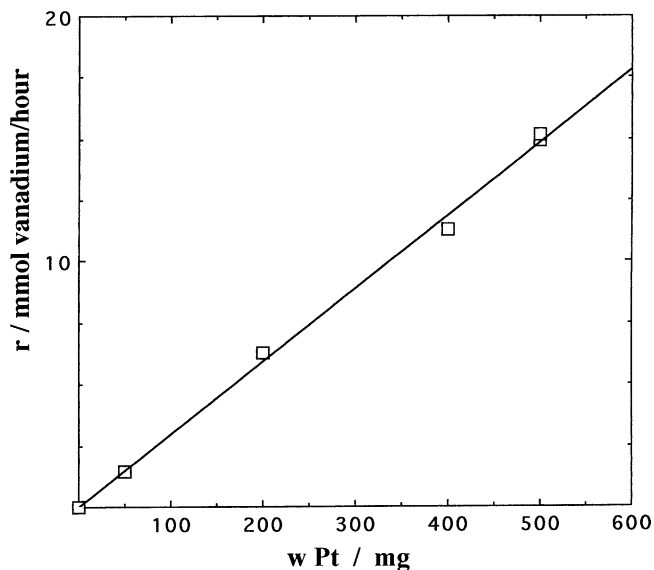
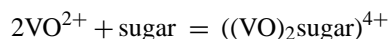


Fig. 3. Initial rate of the oxidation of fructose as a function of the amount of Pt black: C(fructose) = 2.055 mM; C(H₂SO₄) = 1.0 M; C(VO²⁺) = 0.1 M.

The reason for this decline is probably very complex. There might be a pre-equilibrium, e.g.



where the complex is the species that carries the reaction.

One must, however, also consider the increase in ionic strength of the solution when the vanadium(IV) concentration is increased. This problem will be further discussed in the next section.

One further notes (Fig. 6) that the plot of rate versus the square root of the vanadium concentration yields a straight

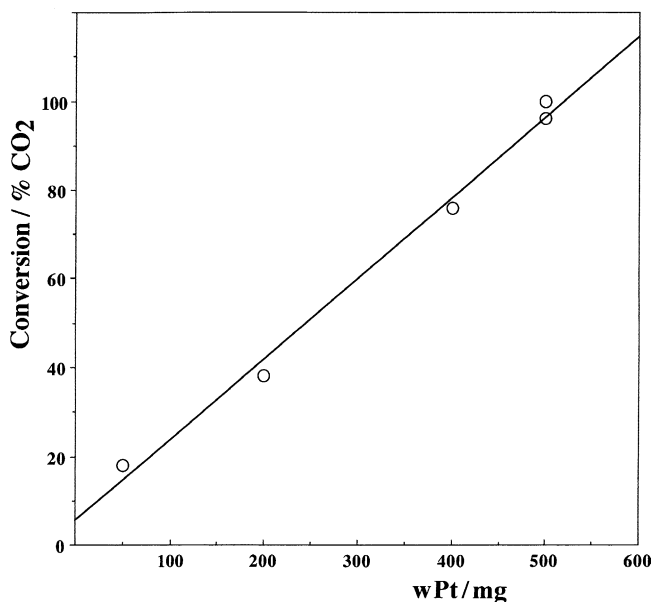


Fig. 4. Conversion (%CO₂ formed) of the oxidation of fructose as a function of the amount of catalyst: C(fructose) = 2.055 mM; C(H₂SO₄) = 1.0 M; C(VO²⁺) = 0.1 M.

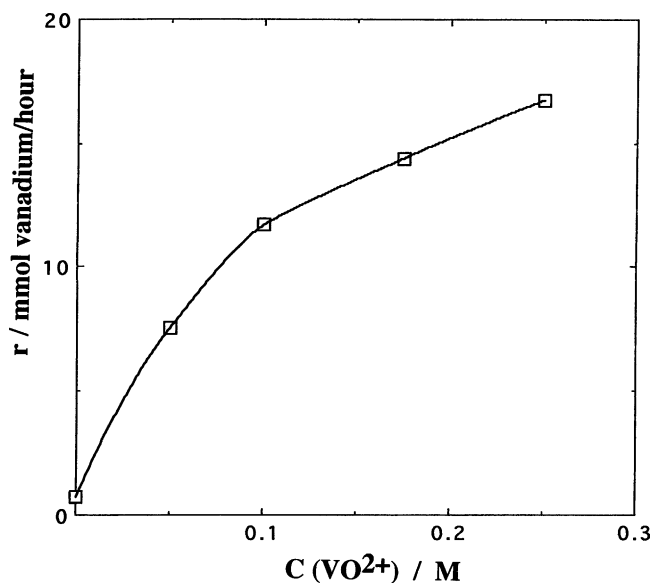


Fig. 5. Initial rate (r) of the oxidation of sucrose as a function of the concentration of vanadium(IV) sulphate, $C(\text{VO}^{2+})$. $C(\text{H}_2\text{SO}_4) = 1.0 \text{ M}$; $C(\text{sugar}) = 2.055 \text{ mM}$; 500 mg Pt black.

line within the experimental accuracy. This line, surprisingly at first, gives a positive intercept on the ordinate axis. By separate experiments with $C_{\text{vanadium(IV)}} = 0$, this observation was verified (cf. Fig. 5).

4.4. Investigations of different kinds of sugar

Once the original discovery was made that sucrose was completely oxidized by vanadium(IV), we have screened a number of other sugars for their reactivity in the same sense. It appears that, so far, all sugars behave the same, with only

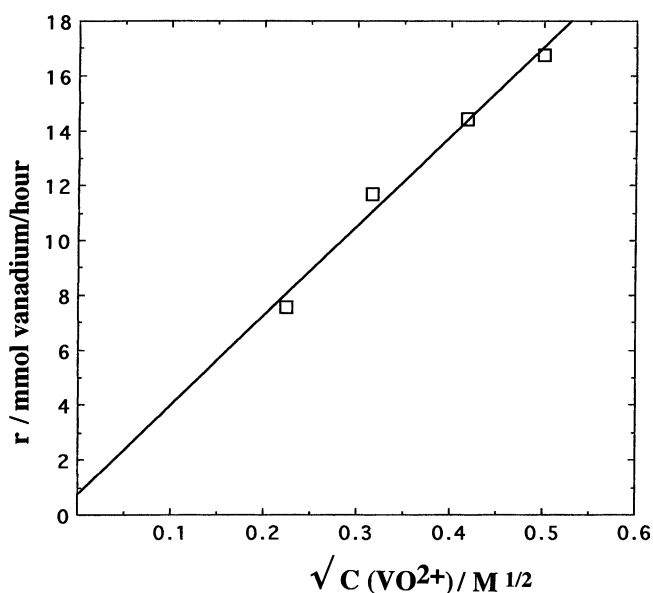


Fig. 6. Initial rate (r) of the oxidation of sucrose as a function of $(C(\text{VO}^{2+}))^{1/2}$. Conditions as in Fig. 5.

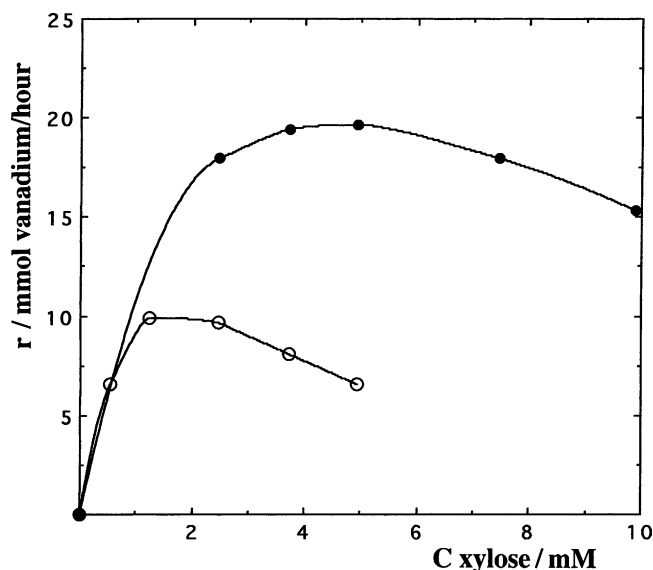


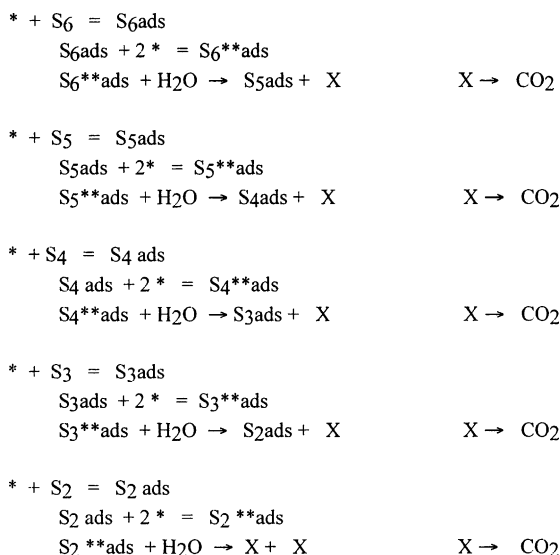
Fig. 7. Initial rate (r) of the oxidation of xylose as a function of the xylose concentration: 1 M H_2SO_4 (○); 1 M H_3PO_4 (●); $C(\text{VO}^{2+}) = 0.1 \text{ M}$; 250 mg Pt black.

some small differences in the absolute values of rates; sucrose, fructose, glucose, arabinose, xylose, all behave the same. Fig. 7 gives some experimental results for xylose. Implicit in this finding is, that also those carbohydrates that can be hydrolyzed to glucose in acidic environments are likely candidates to reduce vanadium(IV). This was verified in the case of starch. The result for xylose is of obvious importance as wood material can be degraded to pentoses, such as xylose and arabinose.

5. Discussion

One might possibly regard it as premature to suggest a detailed mechanism of the reaction based on the limited and rather qualitative information so far achieved. What is said below must, therefore, be taken 'cum grana salis'. We intend, however, to mark some relevant issues.

1. The first one is that all carbohydrates react likewise and with a very similar rate. This must mean that there is a common, drastic degradation of the carbohydrate molecules to simple species, probably adsorbed on the surface of the catalyst metal. One is tempted to suggest the formation of Pt–C and Pt–H bonds in analogy with the gas phase reactions of alkanes where such species are formed on noble metal surfaces [11].
2. Secondly, the observation that complete formation of CO₂ is not always achieved (paragraph 2, above) indicates that there are parallel reactions occurring. Of these, the formation of carbon dioxide is the slowest step at least in the sense that it is most demanding for catalyst assistance. Only to exemplify the type of issues at hand, one could suggest that there is on the catalyst surface a stepwise



Scheme 1.

degradation of C6 sugars to C5 sugars, etc. down to C3, C2 and C1 species (Scheme 1). Thus formation of formic acid, oxalic acid, etc. might be expected.

Actually, in collaboration with Prof. C. Lamy, University of Poitiers [12], the species remaining in the reacting solution were measured by HPLC. For three solutions where we, from GC measurements, deemed the reaction as complete, no new species were detected. For three other solutions, where we achieved only about 40, 50 and 60% conversion, several other species were detected, such as gluconic acid (ca. 33%), tartaric acid (ca. 3%), formic

acid (ca. 3%) and about an equal amount of unidentified species.

- The third observation that carries relevant information for a discussion on mechanisms is the dependence of the rate constant (k) on the ionic strength. In Table 1, we have calculated the ionic strength (I) of a series of solutions with varying vanadium concentrations.

The rate constant, k , is defined from the equation dw/dt (mmol/h) = $kC(VO^{2+})$. As $C(VO^{2+})$ is given in mol/l (Tables 1 and 2) k is presented here in the dimension of ml/h.

When plotting (Fig. 8), the result as $\log k$ versus \sqrt{I} , a straight line with slope -1.07 is found for 2 mM sugar and -2.23 when 1 mM sugar was used.

In another series of measurements, the ionic strength was built up from both vanadium(IV) and vanadium(III) sulphate (Table 2). The composition of the solutions was such that the sugar was always in an equivalent amount of the vanadium(IV) sulphate. In this experiment, the slope of $\log k$ versus \sqrt{I} was found to be -2.30 (Fig. 8).

Although we work at salt concentrations of such a magnitude that the laws of Debye and Hiickel are not exactly obeyed, it might be informative to note that the coefficient of the $\log k$ versus \sqrt{I} is of the sign that should be expected for a reaction between a positive and a negative ion in dilute solutions. For very dilute solutions, it holds [13] that

$$\log k = \log k_0 + 2Az_1z_2\sqrt{I} \quad (7)$$

where z_1 and z_2 are the charges of the reacting ions. The parameter A contains besides natural constants the temper-

Table 1
Influence on the rate from the ionic strength formed by increasing $C(VO^{2+})$

$C(VO^{2+})$ (M)	Initial rate (mmol/h)	Rate constant, k (ml/h)	$\log k$	Ionic strength, I (M)	\sqrt{I} (\sqrt{M})
$C(\text{sugar}) = 2.06$ mM					
0.05	7.3	146	2.16	1.20	1.10
0.10	11.6	116	2.06	1.40	1.18
0.175	14.4	82	1.92	1.70	1.30
0.25	16.8	67	1.83	2.00	1.41
$C(\text{sugar}) = 1.03$ mM					
0.025	10.5	420	2.62	1.10	1.05
0.05	12.8	256	2.41	1.20	1.10
0.10	15.5	155	2.19	1.40	1.18
0.20	17.2	86	11.93	1.80	1.34

Catalyst: 500 mg platinum black; volume of reactor = 200 ml.

Table 2
Influence on the rate from the ionic strength formed by increasing $C(V^{3+})$ and/or $C(VO^{2+})$

$C(VO^{2+})$ (M), $C(V^{3+})$ (M)	Initial rate (mmol/h)	Rate constant, k (ml/h)	$\log k$	Ionic strength, I (M)	\sqrt{I} (\sqrt{M})
0.025, 0.025	2.7	105	2.02	1.29	1.14
0.05, 0.05	4.8	96	1.98	1.59	1.26
0.1, 0.1	3.0	30	1.48	2.19	1.48
0.1, 0	17.0	187	2.27	1.37	1.17
0.05, 0	10.0	220	2.34	1.18	1.09

The sugar concentration was made equivalent to the concentration of V(IV), e.g. 1 mM for $C(VO^{2+}) = 0.05$ M; 2 mM for $C(VO^{2+}) = 0.1$ M; volume of reactor = 200 ml.

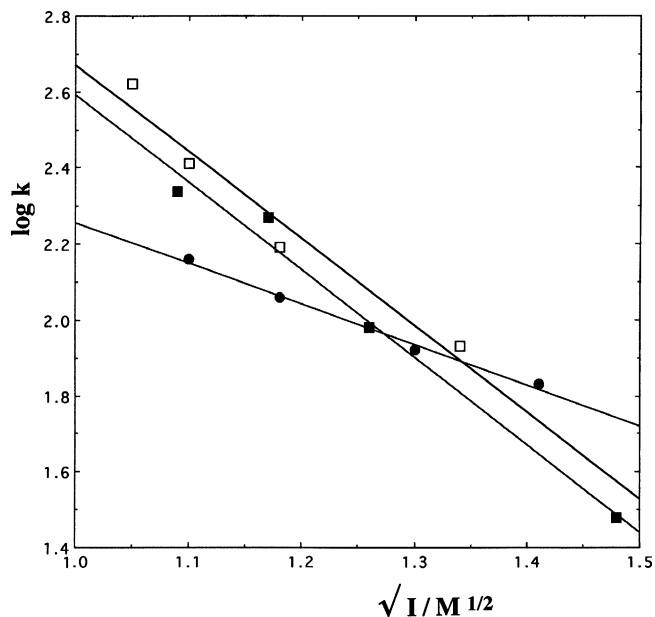
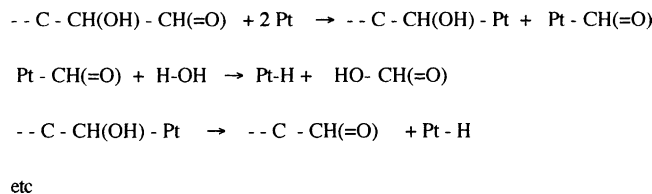


Fig. 8. $\log k$ plotted against $\sqrt{I/M}^{1/2}$. Data from Tables 1 and 2. $C(\text{sugar}) = 2.06 \text{ mM}$; 500 mg Pt black (●); $C(\text{sugar}) = 1.03 \text{ mM}$; 500 mg Pt black (□); $C(\text{sugar})$ equivalent to $C(\text{VO}^{2+})$, vide Table 2. Additional vanadium(III) cf. rows 2–5 in Table 2. Silica supported catalyst corresponding to about 800 mg Pt (■).

ature and the dielectric constant of the solution as $(DT)^{-3/2}$. It is well known [13] that $A = 0.51$ at room temperature and in dilute aqueous systems. At 90°C and in $1 \text{ M H}_2\text{SO}_4$, A is roughly 0.54, as the dielectric constant of water is decreasing with temperature [14], almost compensating the increase of temperature. The factor $2Az_1z_2$ is then = 1.08. If these calculations hold true, the results described just above should indicate a reaction between two univalent ions of different charge, or between one divalent ion and one univalent one, respectively. It is, however, very questionable if the rules for homogeneous reactions should hold for reactions where at least one of the partners is adsorbed on a surface.

What is interesting, though, is the observation that the two cases where there probably is ample space on the surface give a distinctly different slope, compared to the case where free sites are probably not easily available. One might compare the different patterns for sugar concentrations 1 mM and 2 mM, respectively, that are depicted in Fig. 2.

4. Two other effects of the ionic strength that can affect the reaction rate must be mentioned. The first one is that the adsorption of electrolyte, e.g. HSO_4^- ions on the platinum surface is ionic strength dependent. It is well known that the electrolyte adsorption on the electrode surfaces can strongly influence the current from, e.g. a fuel cell. The other effect is the influence of the ionic strength on a pre-equilibrium governing the concentration of the reactive species on the catalyst surface.



Scheme 2.

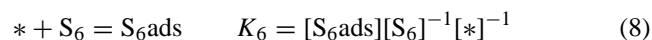
6. Provisional mechanism

The reaction pattern of the hydrocarbons adsorbed on the catalyst surface must be very complex. For most parts, the reactions steps are irreversible in the sense that the reconstruction of the ordered structure of the starting material is very unlikely. In spite of the restraints given in the previous section, and as a basis for further work, we should like to suggest the scheme put forward above (Scheme 1). We exemplify with a hexose molecule, denoted by S_6 .

The first reaction is the adsorption in which it is assumed that one adsorption site is needed (cf. also Scheme 2). The thus adsorbed S_6 species reacts by splitting a C–C bond for which is needed two adsorption sites. By a concurrent addition of a water molecule a C1 species is formed. This species we denote by X here and there are good reasons to believe that it is formic acid. The formate ion adsorbs on the platinum surface, analogously to what is the case in the gas phase decomposition of formic acid over metals [15], and is in its turn oxidised by an VO^{2+} ion as suggested in our previous paper [2]. We assume that the reaction of X to form CO_2 is the rate determining step as the above considerations on the rate dependence on the ionic strength seemed to indicate a reaction between oppositely charged ions.

Scheme 1 is too complicated to allow an analysis based on the relatively limited data that we present here. We, therefore, concentrate on the interpretation of the initial rates. This means that we neglect all rows but the first one.

Thus the adsorption equilibrium is described as



where (*) denotes a free surface site and the concentration of adsorbed species and free sites are expressed in a convenient way so that

$$Y = [S_{6\text{ads}}] + [*] \quad (9)$$

where Y is a measure of the *totally available sites*, or of the platinum surface, expressed in another way.

Introducing (8) into (9) we get

$$Y = [*](1 + K_6 [S_6]). \quad (10)$$

Then, a reaction occurs (cf. Scheme 2) involving the breaking of a C–C bond.



with the rate

$$\frac{d[S_6^{**}]}{dt} = k'[S_6\text{ads}][*]^2 \quad (12)$$

where k' is defined by this relation (12).

If we now introduce Eqs. (8) and (10) into (12)

$$\frac{d[S_6^{**}]}{dt} = \frac{k'K_6[S_6]Y^3}{(1 + K_6[S_6])^3} \quad (13)$$

Thereafter, follows a rapid reaction step



And if also X reacts rapidly

$$\text{rate} = \frac{d[CO_2]}{dt} = k'K_6[S_6]Y^3(1 + K[S_6])^{-3} \quad (15)$$

As we consider, the very first moments of the reaction for which the rate is measured as ‘initial rate’, r_0 , $[S_6]$ will approximately equal C_S , the total sugar concentration in the aqueous phase.

$$r_0 = \frac{d[CO_2]}{dt} = k'K_6C_S Y^3(1 + K_6C_S)^{-3} \quad (16)$$

Some interesting relations follow from this formulation and will be described below.

(a) Forming the expression $(C_S/r_0)^{1/3}$, one will find a linear relation in C_S

$$\left(\frac{C_S}{r_0}\right)^{1/3} = (1 + K_6C_S)Y^{-1}(k'K_6)^{-1/3} \quad (17)$$

In Fig. 9, we exemplify this relation by data for the oxidation of sucrose and xylose, respectively.

The ratio between slope and intercept of the line yields the adsorption equilibrium constant K_6 . From this, it is

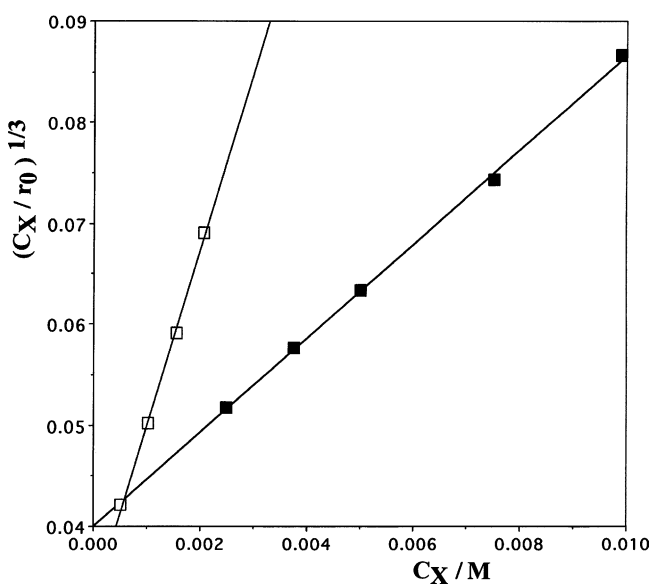


Fig. 9. Graphs according to Eq. (17) for the oxidation of sucrose in 1 M H_2SO_4 with 250 mg Pt (\square) and of xylose in 1 M H_3PO_4 and 250 mg Pt (\blacksquare).

Table 3

Adsorption constants and rate parameters for some combinations of catalyst masses, acids and carbohydrates

Carbohydrate	Acid	Catalyst (mg Pt)	K (M^{-1})	kY^3 ($mmol\ h^{-1}\ sites^3\ g\ Pt^{-3}$)
Sucrose	1 M H_2SO_4	500	580	103
	1 M H_2SO_4	250	535	53
Sucrose	3 M H_2SO_4	250	561	61
Sucrose	1 M H_3PO_4	250	259	115
Sucrose	5 M H_3PO_4	250	342	149
Xylose	1 M H_2SO_4	250	284	66
Xylose	1 M H_3PO_4	250	118	133
Arabinose	1 M H_3PO_4	250	111	102

possible to obtain the quantity kY^3 . The latter quantity is not possible to split further.

In Table 3, we have collected the quantities K_6 and kY^3 for some carbohydrates, acids and catalyst mass.

(b) From Table 3, one notes that for sucrose in sulphuric acid, K is constant, $K = 560 \pm 20\ M^{-1}$.

One further notes that kY^3 is proportional to the catalyst mass (as long as one and the same catalyst preparation is used, as is the case here).

Thirdly, one can note that kY^3 (related to the rate constants) is almost the same for sucrose and for xylose.

(c) It is easily deduced that the maximum of the function $C_S(1 + K_6C_S)^{-3}$ appears at $C_S = (2K_6)^{-1}$. Hence, using for the combination sucrose/sulphuric acid, the value $K = 560 \pm 20\ M^{-1}$ one finds that $(C_S)_{\max} = 0.89\ mM$; i.e. the position we find from Fig. 1. Similarly, for 5 M phosphoric acid and sucrose, $K = 342\ M^{-1}$ and $(C_S)_{\max} = 1.46\ mM$ in relatively good agreement with the maximum of Fig. 1. This is perhaps not so astonishing as the parameters involved were derived from data, such as those of Fig. 1.

(d) More noteworthy is a reconsideration of Eq. (8). It follows that the ratio between free sites and sites occupied by the reacting sugar molecule is

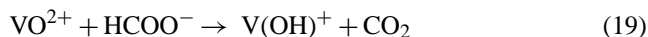
$$\frac{[*]}{[S\text{ads}]} = (K[S])^{-1} \quad (18)$$

As the reaction scheme suggests that two free sites are required for the reaction to proceed, it is important to know for which value of $[S]$ that the ratio $[*]/[S\text{ads}] \geq 2$. For sulphuric acid, this condition is $[S] \leq 1/(2 \times 560) = 0.89\ mM$. For phosphoric acid, the variation in K is rather large, so we must treat the two sets of data separately. For 1 M H_3PO_4 , the same condition is $[S] \leq 1/(2 \times 260) = 1.9\ mM$ and for 5 M H_3PO_4 one gets $[S] \leq 1/(2 \times 340) = 1.5\ mM$. These values are in rough agreement with the break points of Fig. 2, which can be estimated as 1.7 mM for both the concentrations of acid.

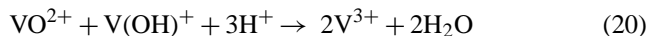
The important lesson to be learnt from this comparison is that in order to have a complete, 100% oxidation of the carbohydrate one must use sugar concentrations low enough to allow for a sufficient number of free sites per carbohydrate molecule to be available on the catalyst surface.

We can now also comment on the finding on the increment term of the rate when $C_{\text{vanadium(IV)}}$ is zero (Figs. 5 and 6).

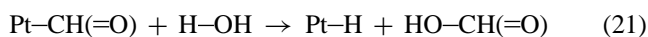
If the intermediate X in the reaction Scheme 1 is indeed the formate ion, we can expect [2] that the last reaction (19) is



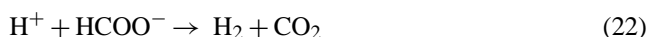
followed by



However, in the system, there is also another oxidizing agent, viz. the proton itself. Considering the second reaction of Scheme 2,



producing formic acid, we have another reaction in analogy to (19) that also produces carbon dioxide, viz.



It is the reaction (22) that is producing the carbon dioxide that is measured also in the absence of vanadium(IV).

One can finally point out that the Pt-H produced in Eq. (21) is the other cause of vanadium(III):



As vanadium(IV) has a much higher oxidation potential than the proton, Eqs. (19) and (23) will be the dominating ones.

7. Conclusions

It has been demonstrated that many carbohydrates can reduce vanadium(IV) to vanadium(III) under suitable conditions, favourably a suitable ratio between oxidant and the sugar.

In this paper, platinum black has been used throughout. In order to achieve a working fuel cell, further work is needed on the preparation of a well dispersed noble metal catalyst and also the development of good anode materials.

Mechanistically we suggest that, in order to reach 100% combustion, the sugar concentration must not be higher than that at least two surface sites per adsorbed carbon residue are always free and available.

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