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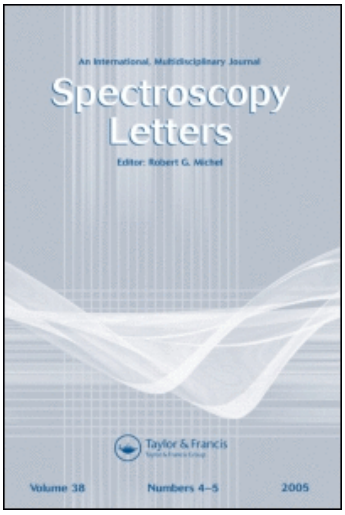

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectrophotometric Studies of the Energy Consumed During Oxidative Degradation of D-Fructose

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To cite this Article Ahmed, Seddique M.(2008) 'Spectrophotometric Studies of the Energy Consumed During Oxidative Degradation of D-Fructose', Spectroscopy Letters, 41: 5, 212 — 220
To link to this Article: DOI: 10.1080/00387010802134322
URL: http://dx.doi.org/10.1080/00387010802134322

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Spectroscopy Letters, 41:212–220, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010802134322

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Spectrophotometric Studies of the Energy Consumed During Oxidative Degradation of D-Fructose

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ABSTRACT Mechanistic investigation of the oxidative degradation of D-fructose (D-Fruc) has been studied by spectrophotometric technique. Molecular mechanics (MM+) calculations suggest that the potential energy (PE/kcal mol^{-1}) of the D-fruc (opening structure) is at least three (3.71) times more stable than the PE of the cycling structure of the same matrix. The oxidation constant (K_{ox}) of the anionic form of the D-Fruc (Fruc-NaOH) is about seven times greater than that of the protonated form (Fruc-H_2SO_4). Therefore, the anionic form is more highly oxidizable than is the cationic form of this matrix. The limit of detection can be as low as 18 ppm (mg L^{-1}) of D-Fruc. This is about 60 times lower than the blood sugar level (BSL) or 100 times lower than that reported previously. The proposed procedure was applied successfully for the oxidation of D-Fruc in uni-fructose powder. The anionic form of D-Fruc (Fruc-NaOH) has the ability to store energy about 744.72 kJ g^{-1} h at 608 nm in a condensed lightweight form. Kinetic parameters of the oxidative degradation of the anionic form of D-Fruc at different concentration were deduced. A number of models were used to evaluate the kinetic parameters. The mechanism of the degradation of D-Fruc is explained on the basis of kinetic parameters.

KEYWORDS D-Fructose, energy storage, kinetics, MM+ calculations

INTRODUCTION

Carbohydrate units are constituents of nucleic acids and play an important role in metabolism and in mammalian food supply. These are very attractive natural ligands for both toxic and essential metal ions. In contrast, the presence of excess of sugar in the blood gives evidence of serious malfunction of the human organism. Oxidative degradation of sugars by different oxidizing agents has been the subject of numerous investigations.[1–18] It has been established that the sugars, or their derivatives, play an important role in the chemistry of chromium, specially in the environment[1,8–10,16–19] and in the mechanism of chromium-induced cancer.[19] Chromium (VI) crosses the cell membrane and oxidizes cellular components in a process

Received 8 June 2007;
accepted 26 January 2008.

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that leads to cellular damage, including interference with the genetic machinery. The inhibitory/catalytic effect of organized structures (e.g., micelles) on the kinetics of a large number of reactions is well documented in the literature.[20] The kinetics of vanadium (V) oxidation of different monosaccharides in H_2SO_4, $HClO_4$, and HCl solutions has been the subject of much research.[9]

Many earlier studies indicated that the initial formation of a carbohydrate enediol, favored in alkaline medium, is essential for its further oxidation in the presence of metal ions.[21] However, most of those studies were carried out in drastic experimental conditions, using copper coordinated to weak ligands (aqua, phosphate, tartarate, citrate) and at very high concentrations (10^{-3} to 10^{-4} mol L^{-1}), when the metal is simultaneously precipitated as Cu(I) oxide.[14,21–24] Selective oxidation of alcohols, aldehydes, or some carbohydrate on metal catalysts has been reported.[25,26]

In our previous study, we have reported the oxidative polymerization of aniline hydrochloride, or 8-hydroxyquinoline in different media, and oxidative hydrolysis of 5-sulfosalicylic acid doped poly(*o*-tolidine) matrix.[27–29]

In the current study, oxidative degradation process of the anionic and cationic forms of D-fructose in synthetic solutions and uni-fructose powder was investigated by spectrophotometric technique. Molecular mechanics (MM+) calculations proved that the opening keto is more stable than the opening enol or cycling forms of D-Fruc. Activation parameters for the rate of oxidation of D-Fruc were computed and discussed.

MATERIALS AND METHODS

Chemicals and Solutions

D-Fructose (D-Fruc) was obtained from Merck Chemicals Co. (Darmstadt, Germany) Uni-fructose (uni-Fruc) powder was purchased from GalaxoSmithKline, Egypt S.A.E. Stock solutions of D-Fruc and potassium permanganate ($KMnO_4$, Aldrich, Milwaukee, WI) were prepared by dissolving the appropriate amounts of respective samples in doubly distilled water. The solution of $KMnO_4$ was standardized against oxalic acid.[30] The application of Beer's law for permanganate at about 526 nm had earlier been verified giving $\varepsilon = 2000 \pm 50\,dm^3\ mol^{-1}\ cm^{-1}$.[30] All of the other reagents used were of analytical reagent grade, and double-distilled water was used throughout.

The solution of uni fructose (uni-Fruc) powder for the oxidative degradation of D-Fruc was prepared in the following way. Appropriate amount from uni-Fruc powder was dissolved in double distilled water (100 mmol) and diluted to 100 ml in a volumetric flask with bidistilled water.

Instrumentation

A Perkin-Elmer Lambda35 (Gen Tech Scientific, Inc., USA) UV/Vis spectrophotometer (190–1100 nm) with 1.0 cm quartz cell (scan speed, 8.0 nm s^{-1}) was used for spectrophotometric measurements. A HETO, HOLTAN, A/S. GYAVANG 17–19, DK) thermostat (type HMT 200) was used for accelerated kinetic studies.

Procedure

Ten milliliters of 1.0 mmol L^{-1} solution of $KMnO_4$ (oxidant) in strong acid (1.2 mol, adjusted by H_2SO_4) or strong alkaline medium (adjusted by standard NaOH) (200 mmol L^{-1}) was placed in into a calibrated flask. The background spectrogram of this solution was recorded. Then, different amounts of the analyte (D-Fruc or uni-Fruc) were added into individual flasks by means of a micropipette (Voaco, UK). All presented absorption spectra are corrected for the blank reagent, which was prepared in a similar manner as the samples, however, not containing analyte. All measurements were carried out at room temperature (298 ± 1) K, except those used to assess the influence of temperature on the reaction rate of the oxidative degradation of D-Fruc or uni-Fruc sugars.

Method of Calculations

MM+ calculations including MM2 and MMP2 force field[25–32] were carried out assuming the investigated molecule in the gas phase. The values of potential and geometric energies as well as the dipole moment were obtained considering dPE = 0.42 J and the normal method.[31–35] The search for a minimum energy of the molecule geometry resulted in a 3D structure. MM+ calculations iteratively change the position of atoms towards the structure characterized by lower energy until the molecule internal energy has been minimized.

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The energy of a molecule is influenced by the atomic coordinates and could be calculated according to the equations.[31–35]

$$E(x) = E_{str} + E_{ang} + E_{stb} + E_{oop} + E_{tor} + E_{vdw} + E_{ele} + E_{sol} + E_{res} \quad (1)$$

$$E_{str} = \mathcal{W}_{str} \sum_{i=j} k_{ij}(r_{ij} - L_{ij})^2 + k'_{ij}(r_{ij} - L_{ij})^3 + k''_{ij}(r_{ij} - L_{ij})^4 \quad (2)$$

$$E_{ang} = \mathcal{W}_{ang} \sum_{i-j-k} k_{ijk} d_{ijk}^2 + k'_{ijk} d_{ijk}^3 + k''_{ijk} d_{ijk}^4 \quad (3)$$

$$E_{stb} = \mathcal{W}_{stb} \sum_{i-j-k} (k_{ijk}(r_{ij} - L_{ij}) + k_{kji}(r_{jk} - L_{jk}))d_{ijk} \quad (4)$$

$$E_{oop} = \mathcal{W}_{oop} \sum_{i:jkl} k_{i:jkl} X_{i:jkl}^2 \quad (5)$$

$$E_{tor} = \mathcal{W}_{tor} \sum_{i-j-k-1} \sum_{n=0}^{6} k_{n:ijkl} \cos(nT_{ijkl} - P_{n:ijkl}) \quad (6)$$

$$E_{vdw} = \mathcal{W} \sum_{kj} e_{ij} \left[\frac{(1+a)R_{ij}}{r_{ij} + aR_{ij}}\right]^{R_{ij}} \times \left[\frac{n_{ij}}{m_{ij}} \frac{(1+b)R_{ij}^{R_{ij}}}{r_{ij}^{R_{ij}} + bR_{ij}^{R_{ij}}} - \frac{m_{ij} + n_{ij}}{m_{ij}}\right] s(r_{ij}) T_{ij} I_{ij}^{vdw} \quad (7)$$

$$E_{ele} = \begin{cases} \frac{w_{ele} e^2}{4\pi\varepsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{r_{ij} + b_{ele}}\right] s(r_{ij}) T_{ij} I_{ij}^{ele} & \text{Coulomb} \\ \frac{w_{ele} e^2}{4\pi\varepsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{(r_{ij} + b_{ele})^2}\right] s(r_{ij}) T_{ij} I_{ij}^{ele} & \text{Distance-dependent dielectric} \\ \frac{w_{ele} e^2}{4\pi\varepsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{r_{ij} + b_{ele}} - \frac{\omega_{ij}^2}{R_c} - \frac{(1-\alpha)}{R_c}\right] s(r_{ij}) T_{ij} I_{ij}^{ele} & \text{Reaction field, } \alpha = \frac{d - d_x}{d + 2d_x} \end{cases} \quad (8)$$

$$E_{wi} = w_{sol} W(d^{-1} - d_x^{-1}) \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^{n} \sum_{j=1}^{n} \times \frac{q_i q_j \sqrt{G_i G_j}}{\sqrt{y_{ij} + \exp(-y_{ij})/4}} \times s(r_{ij}) T_{ij}, \quad y_{ij} = r_{ij}^2 G_i G_j. \quad (9)$$

The amount of charge transferred at each iteration is damped with an exponentially decreasing scale factor. The amount of charge transferred between atoms i and j at each iteration when $X_i > X_j$ is

$$dq = \frac{1}{2} \frac{X_i - X_j}{X_j^+} \quad (10)$$

E_{str} is the bond stretch, E_{ang} is the bond angle bend; E_{stb} is the stretch-bend, E_{oop} is the out-of-plane, E_{tor} is the torsion, E_{vdw} is the van der Waals force, E_{ele} is electrostatic, E_{sol} is the implicit solvation, E_{res} is restraint energy, and X_j^+ is the electronegativity of the positive ion of atom j.

RESULTS AND DISCUSSION

Molecular Mechanics Calculations

MM+ calculations can be used to calculate the PE and OMG energies and dipole μ of the molecular (MG) and optimum molecular geometric (OMG) structure of D-Fruc (opening keto- and opening enol- and cycling forms) as shown in Table 1. These calculations showed that the PE of the OMG structure of the keto form of D-Fruc (Scheme 1b) is lower (stable) by at least four (4.98×10^4) orders of magnitude than the MG of the same matrix (Scheme 1). These calculations are important for understanding the stability of this matrix. Moreover, the PE of the OMG structure of the opening keto form is more stable by about three (3.71) or two (1.97) times than the cycling or opening enol forms under the same conditions. Therefore, the opening keto form structure is a more favorable form for the oxidative degradation than the opening enol or cycling forms.

Absorption Spectra of the Oxidative Degradation of D-Fruc

Absorption spectra of the oxidant ($KMnO_4$) in strong acidic medium (pH 1.2, adjusted by H_2SO_4) is shown in Fig. 1a. The absorbance at $\sim$525 nm decreased with an increasing of the D-Fruc concentration at

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TABLE 1 MG and OMG Energies of D-Fruc in Different Forms

System/parameter	PE/(KJ mol L^{-1})	OMG/(KJ mol L^{-1})	μ (Debye)
D-Fruc open keto (MG)	2.54×10^5	—	4.42
D-Fruc open keto (OMG)	−5.095	−0.919	8.45
D-Fruc-open enol (MG)	924.407	—	3.43
D-Fruc open enol (OMG)	4.940	5.643	3.98
D-Fruc cycling (MG)	205.456	—	8.09
D-Fruc cycling (OMG)	3.314	3.74	5.17
D-Fruc opening-H_2SO_4 (MG)	6.20×10^4	—	9.21
D-Fruc opening-H_2SO_4 (OMG)	− 4.47	−9.465	4.11
D-Fruc opening-NaOH (MG)	6.607×10^4	—	11.38
D-Fruc opening-NaOH (MG)	−3.356	−1.160	19.26

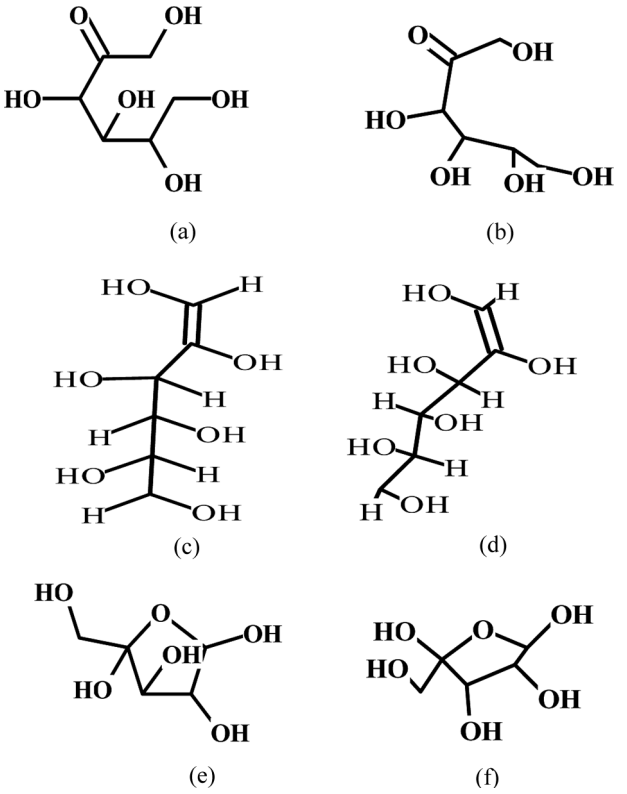
constant oxidant ($KMnO_4$, 1.0 mmol L^{-1}). The data were analyzed using linear regression program,[27] according to the following equation:

$$A = a + bC \tag{11}$$

where A and C are the absorbance and concentration of the analyte (D-Fruc), and a and b are the intercept and slope of the straight line, respectively. Statistical data, regression coefficient, and relative standard deviation are given in Table 2. The slope of this straight line corresponds with the oxidation constant (K_{ox}) as shown in Table 2. The lower K_{ox} was found in neutral medium (Table 2) and the higher K_{ox} in H_2SO_4. These observations indicate that the K_{ox} is highly dependent on the strength of the acidity of the medium. The intercept (Table 2) of the straight line (a) is attributed to the initial absorbance of the oxidant ($KMnO_4$) alone (without addition of D-Fruc). This value is consistent well with the corresponding experimental value.

The complete discoloration (λ of about 525 nm) of the oxidant (Mn(VII)) in strong acidic medium (H_2SO_4, 1.2 mol L^{-1}) was recorded at the ratio of 5:1 (oxidant:D-Fruc). These observations could be explained by the following equation:

$$5C_6H_{12}O_6 + 24KMnO_4 + 36H_2SO_4 \longrightarrow 30CO_2 + 66H_2O + 12K_2SO_4 + 24MnSO_4. \tag{12}$$



SCHEME 1 Molecular (a, c, e) (MG) and optimum (b, d, f) molecular geometric (OMG) possible configuration structures of D-Fruc, in keto (a, b), enol (c, d), and cycling (e, f) forms, using MM+ calculations.

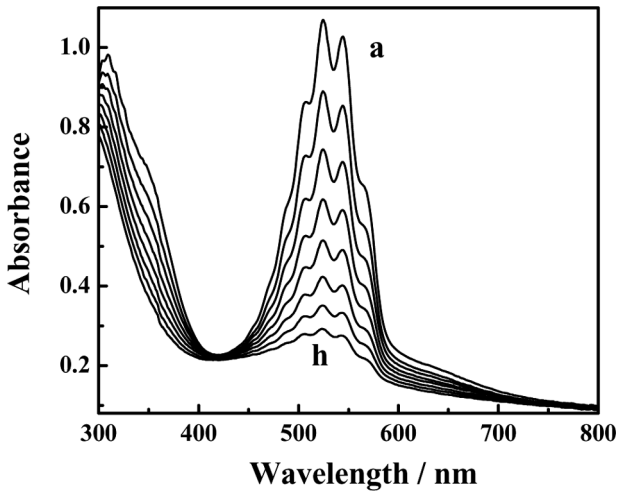


FIGURE 1 Absorption spectra of the oxidant ($KMnO_4$, 1.0 mmol L^{-1}) in strong acid medium (H_2SO_4, 1.2 mol) after addition of D-Fruc (a–h) as: 0.0, 2, 4, 5, 6, 8, 9, and 10 mmol L^{-1}, respectively.

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TABLE 2 Calibration Plot Data of the Absorbance versus D-Fruc Concentration

System/parameter	K_{ox}	a	r	RSD $\times 10^{-3}$
At $\lambda = 525$ nm				
D-Fruc-H_2SO_4	116.20	1.270	0.991	8.551
Uni-Fruc-H_2SO_4	59.344	1.39	0.984	16.531
D-Fruc-NaOH	904.92	1.40	0.985	1.089
Uni-Fruc-NaOH	537.93	1.34	0.981	1.712
At $\lambda = 608$ nm				
D-Fruc-NaOH	649.32	0.286	0.995	1.531
Uni-Fruc-NaOH	323.94	0.247	0.978	2.991

The electronic absorption spectra of oxidant ($KMnO_4$, 1.0 mmol L^{-1}) were scanned (Fig. 2a) in strong alkaline solution (KOH, 200 mmol L^{-1}). It was found also, that the absorbance of the oxidant at $\sim$525 nm decreases rapidly with increasing the concentration of D-Fruc sugar. The K_{ox} for the anionic form (D-Fruc-NaOH) was found to be at least seven (7.81) times greater than the K_{ox} of the cationic form of the same matrix (Table 2). These observations indicate that the anionic form is more highly reactive for the oxidation than the cationic form.

The absorbance of the band at $\sim$608 nm (green coloration) due to (Mn(VI)) was increased with increasing concentration of D-Fruc (Fig. 2). This absorption is due to the transformation of permanganate (MnO_4^-) to manganate (MnO_4^{2-}) through a one-electron reduction according to the mechanism

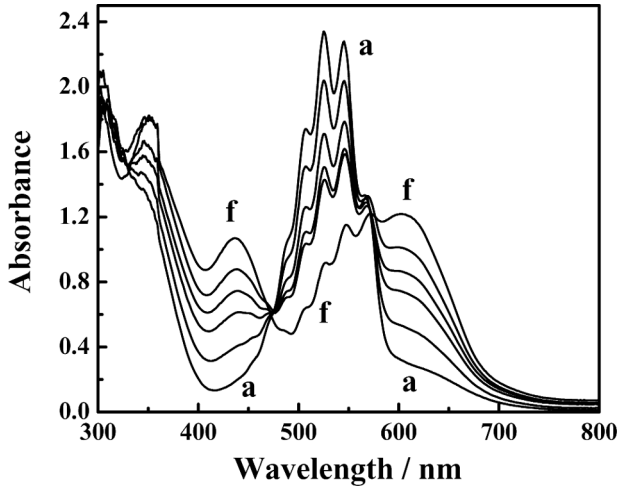

FIGURE 2 Absorption spectra of the oxidant ($KMnO_4$, 1.0 mmol L^{-1}) in strong alkaline medium (NaOH, 200 mmol L^{-1}) after addition of D-Fruc (a–f) as: 0.0, 0.4, 0.6, 0.8, 1.0, and 1.4 mmol L^{-1}, respectively.

illustrated in equation (13):

$$C_6H_{12}O_6 + 24KMnO_4 + 24KOH \longrightarrow 6CO_2 + 24K_2MnO_4 + 18H_2O. \quad (13)$$

Moreover, the K_{ox} for the decomposition of the oxidant (at $\sim$525 nm) is higher than the K_{ox} at $\sim$608 nm.

Acid or Base Catalyzed for Oxidation of D-Fruc

The K_{ox} of D-Fruc or uni-Fruc is listed in Table 3. From these calculations, it was found that the K_{ox} in alkaline medium of the uni-Fruc (anionic form) is about three orders (1.74×10^3) of magnitude greater than the K_{ox} in acidic medium (H_2SO_4). It is confirmed that the anionic form of the analyte (D-Fruc) is more highly reactive for the oxidation than is the cationic form. First-derivative plots of the absorbance against pH (Fig. 3) showed that the maximum pHs in acidic and alkaline media are 0.85 and 11.20, respectively.

Absorption Spectra of the Oxidation of D-Fruc in Uni-Fruc Powder

The absorption spectra of the oxidant ($KMnO_4$, 1.0 mmol) is shown in Fig. 1a. This absorbance decreases (at $\sim$525 nm) also, with increasing the concentration of uni-Fruc in strong acid or alkaline media. The K_{ox} was found to be lower by about two times in magnitude than that of the standard D-Fruc in strong acid or alkaline media (Table 2), revealing again that the anionic form of D-Fruc in uni-Fruc sample is also profitable for oxidation. The value of K_{ox} of the uni-Fruc (real sample) is lower than the K_{ox} in synthetic medium (Table 2).

TABLE 3 Calibration Plot Data of the Absorbance versus H^+ or OH (at $\lambda = 525$ nm)

System/parameter	K_{ox} [H^+]	a	r	RSD $\times 10^{-3}$
D-Fruc-H_2SO_4	0.4258	1.783	0.984	0.411
Uni-Fruc-H_2SO_4	0.344	1.74	0.932	0.186
D-Fruc-NaOH	7.395×10^2	1.638	0.997	1.346
Uni-Fruc-NaOH	9.673×10^2	1.73	0.921	0.951

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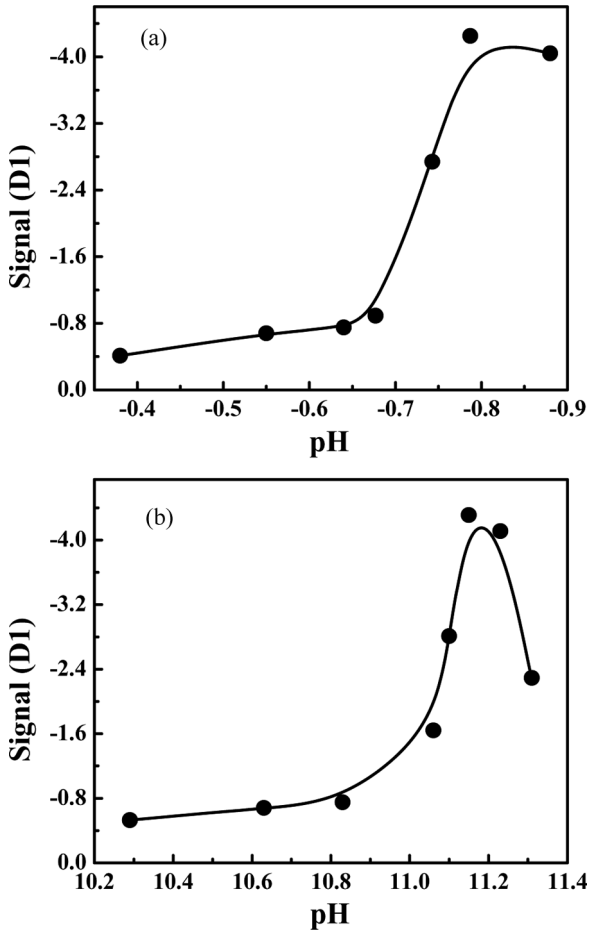

FIGURE 3 First derivative (D1) calculations of the absorbance (at 525 nm) versus pH for oxidation of D-Fruc (10 μmol L^{-1}) in acidic (H_2SO_4, a), and in basic (NaOH, b) medium.

Kinetic Study

Figure 4 represents the variation of the absorbance ($\lambda \sim 608$ nm) of the oxidant ($KMnO_4$, 0.5 mmol L^{-1}) with time at different initial concentration of D-Fruc in strong alkaline medium (NaOH, 200 mmol L^{-1}) by keeping other parameters constant. Computer-oriented kinetic analysis was carried out for each set of absorbance versus time data assuming variant kinetic equations.[28] It was found that the Ginstling–Bronstein equation (D4) gives the best fit of the experimental data with the correlation coefficient (r) close to unity and low relative standard deviation. The Ginstling–Bronstein equation (D4) can be expressed as:

$$(1 - \frac{2}{3}A) - (1 - A)^{\frac{2}{3}} = kt \qquad (14)$$

where A is the absorbance, k is the rate constant, and t is the oxidation time.

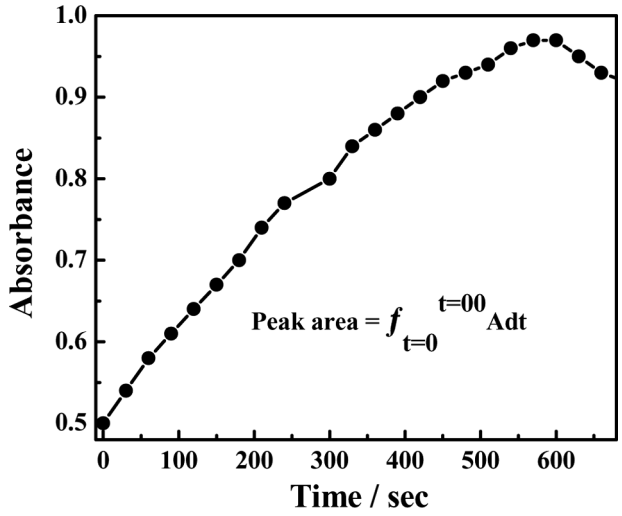

FIGURE 4 Computer drawing of the absorbance ($\lambda \sim 608$ nm) vs. oxidative degradation time (min) of D-Fruc (100 μmol L^{-1}) by $KMnO_4$ (1.0 mmol L^{-1}), (Temperature 20°C).

Based on the fitting of experimental data obtained, for example, when oxidative degradation of D-Fruc (100 μmol L^{-1}) by $KMnO_4$ (1.0 mmol L^{-1}) was carried out in the presence of NaOH (200 mmol L^{-1}), reaction rate constant $k = 2.207 \times 10^{-4}\,s^{-1}$ was computed and the values of statistical parameters $r = 0.989$ and RSD $= 2.23 \times 10^{-4}$ were obtained. It is interesting to note from these calculations that the rate constant (k) value calculated by the (D4) models is about 3, 4, 5, 11, 20, and 107 times lower than the k values obtained by applying D1, D2, and D3 (one-, two-, or three-dimensional diffusion), or first- (F1), second- (F2), and third-order (F3) kinetics under the same conditions.

The limit of detection can be as low as 18 ppm (mg L^{-1}) of D-Fruc, suggesting the possible application of this procedure for the determination of D-Fruc in real samples. This is lower by about 60 times than the blood sugar level (BSL) or by 100 times than the previously reported.[3]

Reproducibility (98–101%) of the oxidative degradation reaction of D-Fruc was calculated for five independent measurements.[36,37]

Energy Storage of D-Fruc in Alkaline Medium

The fundamental property of an electrically activated chromogenic material[38] is that it exhibits a large change in optical properties upon a change in either electrical field or injected or ejected charge.

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The change in optical properties can be in the form of absorbance, reflectance, or scattering. This optical change results in a transformation from a highly transmitting state to a partly reflecting or absorbing state. This change can be either totally or partly over the visible and solar spectrum. Typically it is over some portion of the spectra.

The theoretical capacity (kJ g^{-1}) of the energy (E) can be calculated if the weight or molecular weight (Mwt, g^{-1}) of the analyte is known:

$$E = \frac{N_A hc}{\lambda} \tag{15}$$

where $N_A = 6.022 \times 10^{23}\,\mathrm{mol}^{-1}$, $h = 6.625 \times 10^{-34}\,\mathrm{J\,s}$, and $c = 2.997 \times 10^{8}\,\mathrm{m\,s}^{-1}$ (N_A, h, c, and λ are Avogadro's number, Planck' constant, velocity of light, and the wavelength, respectively).

If the applied wavelength (λ, nm) during oxidation is known, the E could be determined via integration of the peak area (Eq. (16)) of the absorbance (A) versus discoloration time according to the following.

$$\text{Peak area} = \int_{t=0.0}^{t=00} A dt. \tag{16}$$

The E of D-Fruc also could be calculated experimentally using the following equation:

$$E = \frac{N_A hc}{\lambda} \int_{t-0}^{t=00} A dt, \tag{17}$$

where A is the absorbance and t is the oxidation time.

The anionic form of D-Fruc (Fruc-NaOH) has the ability to store energy about $744.72\,\mathrm{kJ\,g}^{-1}\,\mathrm{h}$ at 608 nm in a condensed lightweight form. The E storage in the sugar is very useful as a biofuel cell.

Activation Parameters

The rate constant of the oxidative degradation of D-Fruc sugar in strong alkaline medium (NaOH, $200\,\mathrm{mmol\,L}^{-1}$) were determined within the temperature range 283–323 K by keeping all the other experimental conditions unaltered. The corresponding activation parameters (Table 4) were computed using Arrhenius and Eyring.[27–29] Both Arrhenius and Eyring plots showed a close fit of experimental data (Fig. 5). The values of activation parameters calculated for experimental runs with different concentrations of D-Fruc sugar are summarized in Table 4.

TABLE 4 Activation Parameters for the Oxidative Degradation of D-Fruc in Strong Alkaline (NaOH, 200 mmol) Medium

D-Fruc (μmol L^{-1})	E_a/ (KJ mol^{-1})	$\Delta H^{\#}$/ (KJ mol^{-1})	$-\Delta S$/(J K^{-1} mol^{-1})	$\Delta G^{\#}$/(KJ mol^{-1})
100	31.337	31.645	279.756	115.021
150	34.170	33.190	250.876	107.951
200	35.826	34.134	206.876	93.403
250	37.934	36.279	185.258	91.485
300	38.953	38.243	184.193	93.13
350	39.165	39.369	160.205	87.110

These moderate values of activation energy supported the proposed mechanism of the oxidative degradation of the sugar under investigation.

Variation of $\Delta H^{\#}$ with $\Delta S^{\#}$ for the series of experiments represented by a straight line (r about 0.979), as shown in Fig. 6, suggests the compensation or isokinetic effect occurs. Several authors suspect the presence of isokinetic phenomena.[29,39,40] The most important application of the compensation and/or isokinetic effect is that such behaviors constitute evidence for a dominant mechanism throughout the correlated series chemical catalysis, cooperative relaxation kinetics in thermally simulated process, the sorption and browning of garlic,[39–41] and so forth. A higher positive value of $\Delta G^{\#}$ indicates that the transition state is highly solvated. A negative value of $\Delta S^{\#}$ within the range of radical reactions has been ascribed to the nature of electron pairing and electron unpairing processes and to the loss of degree of freedom, formerly available to the reactions on the formation of rigid transition state. Also,

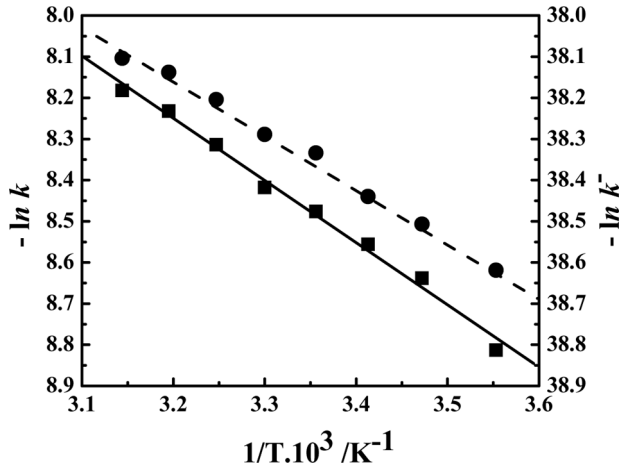

FIGURE 5 Plot of: -ln k (Arrhenius, dashed line) and -ln k' (Eyring, solid line) plots versus (1/T) (K) of the oxidative degradation of D-Fruc.

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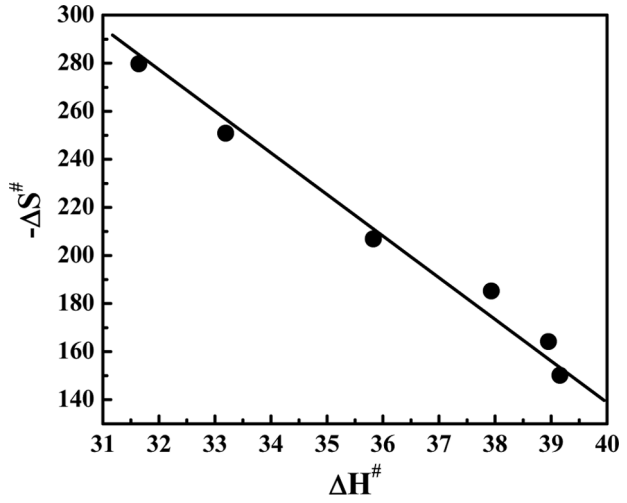

FIGURE 6 **Plot of $\Delta S^{\#}$ versus $\Delta H^{\#}$ for the oxidative degradation of D-Fruc.**

this is consistent with an SN_1 or dissociative mechanism in the transition state. Moreover, the negative entropy of activation indicates the presence of an ionic transition state as suggested by Stewat.[41] Dash and Mishra[42] have pointed out that many reactions show an isokinetic relationship, $\Delta H^{\#} = C + B\Delta S^{\#}$, and $\Delta H^{\#}$ and $\Delta S^{\#}$ values are with an isokinetic temperature (318 K). The computed value of B at 289.2 K is lower than at its experimental value at 303 K, indicating enthalpy as controlling factor.

The linearity ($r \approx 0.991$) of the previous relationship indicates that the mechanism of oxidation of D-Fruc is a suitable mechanism. The constancy of the values of free energy ($\Delta G^{\#}$) indicates the similar mechanism is operative in the oxidation of D-Fruc by inorganic oxidizing agent ($KMnO_4$).

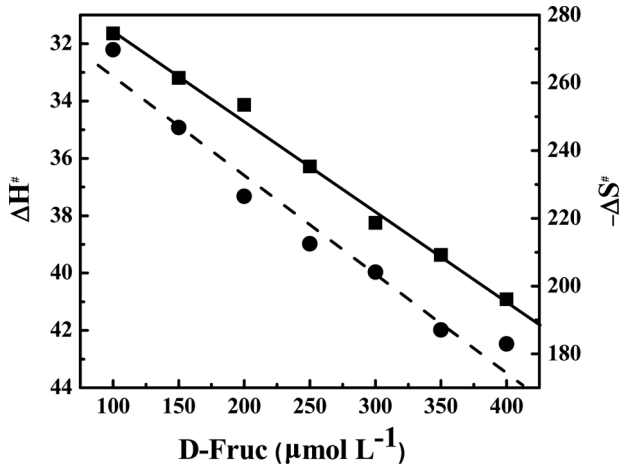

FIGURE 7 **Plot of $\Delta H^{\#}$ (solid line) and $\Delta S^{\#}$ (dashed line) vs. D-Fruc (μmol).**

On plotting $\Delta H^{\#}$ and $\Delta S^{\#}$ against D-Fructose concentration (Fig. 7) and extrapolating to $C = 0.0$, $\Delta H^{\#0}$ and $\Delta S^{\#0}$ values were obtained and hence $\Delta G^{\#0}$ was computed at any given temperature. The values seem to be almost independent of D-Fruc concentration. These values are 108.16 ± 0.1 at 25°C and 68.352 ± 0.3 kJ mol^{-1} for $\Delta H^{\#0}$ and $\Delta G^{\#0}$, respectively. The value of $\Delta S^{\#0}$ is equal to $-133.599 \pm 0.5\,J\,mol^{-1}$.

CONCLUSIONS

Oxidative degradation processes of D-Fruc was studied experimentally using spectrophotometric technique and substantiated computationally using molecular mechanics (MM+) calculations. The proposed procedure was followed successfully for the oxidative degradation of D-Fruc in synthetic solutions and in uni-Fruc powder. It was observed that the proposed method was simple, precise, inexpensive, and required neither sophisticated instrumentation such as spectroelectrochemical equipment nor transparent electrodes (such as metal oxide anodes of the type indium-doped tin oxide–coated glass-working electrode). The results obtained encourage the applicability of the proposed method for oxidation of some organic compounds in different fields such as wastewater treatment rather than the Fenton or electro-Fenton processes.[43] Both of these methods require the addition of ferricchloride ($FeCl_3$) to the solution, which, in turn, invokes consecutive separation steps.

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