TRENDS IN PHOTOCHEMICALLY INDUCED STRIPPING OF PALM OIL.

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ABSTRACT

Photochemical investigations on palm oil show a behaviour which hitherto appears not to have been reported in the literature. Low energy photolysis of palm oil at room temperature showed a drastically reduced concentration of free acids and the formation of products of which glycerol and carbondioxide were identified. The reaction was found to be first order kinetically with respect to the oil concentration. Acetone-sensitisation of the reaction resulted in a near 100-fold reaction rate enhancement, based on the determined reaction rate constants.

INTRODUCTION

Vegetable oils are important for various purposes. As food, their stability, which is quite often affected by environmental factors, has been studied quite extensively. The often observed deterioration of vegetable oils, generally associated with poor storage, has been shown to be attributable to the formation of peroxides[1]. Studies have shown the peroxide formation to involve molecular oxygen and the carbon atom alpha to an unsaturated carbon of the fatty acid moiety[2]. Free radicals[3,4] as well as singlet oxygen[5,6] have been implicated in the peroxide formation reaction. Studies also appear to show the reaction to be sensitised by dyes and pigments present in the oils[7,8]. Light-induced as well as non-light induced reactions have been observed[2]. Reactions involving the hydrolytic cleavage of vegetable oil esters to give glycerol and fatty acids in acidic and basic medium are known. Photoextrusion of CO_2 in diesters and tetraesters have been reported[9]. A search of literature, however, revealed no photo-induced equivalent of these hydrolytic and decarboxylation processes in vegetable oils. Several low energy irradiations of samples of the Nigerian variety of palm oil in our laboratory consistently showed CO_2 and glycerol to be formed along with other yet to be determined products. Both products (CO_2 and glycerol) were identified in non-sensitised[10] as well as acetone sensitised[11] reactions. These observations form the subject of this paper.

EXPERIMENTAL

Reagents and apparatus

The reagents (e.g. NaOH, $Na_2S_2O_3$, KI, Wij's solution) and solvents (ethanol, acetone, chloroform and carbon tetrachloride) were all of analytical grade and were used as bought without further purification. The apparatus for the irradiations was set up as shown in Fig. 1. It consisted of a low energy

Figure 1: Photo-reaction Apparatus
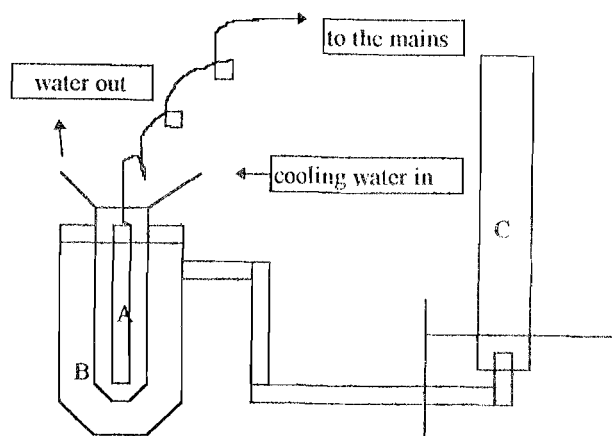
A = Low-energy fluorescent lamp,

B = Reaction chamber and C = Gas collection unit.

fluorescent lamp (product of Philips Company, Holland) immersed in a jacketed tube with circulating cooling water. The lamp/cooler unit dipped into the reaction chamber. A gas collection unit in the form of an inverted water-filled burette was connected by a rubber tubing to the reaction chamber. The lamp, 23.4 x 1cm, of irradiation intensity comparable to that of a typical household fluorescent lamp, was connected to the main power supply through a voltage regulator.

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Samples and storage

Palm oil samples were the local type, processed by the common Eastern Nigeria traditional methods[12]. The samples were purchased at different locations in the open market within the Jos metropolis. The samples were decanted and stored in the dark in a freezer prior to each study.

Chemical characterization of samples

Acid Value (AV) was determined in accordance with the American Society of Testing and Materials (ASTM) method D1980-87; Iodine Value (IV) was determined using the IUPAC (1976)[13] method 2.205 and the Peroxide Value (PV) determination was done according to the IUPAC/AOCS (1992)[14] method 2.501. Saponification Value (SV) and the Ester Value (EV) were determined as described by Cooks and Van Rede[15]. The results of chemical characterization of samples before and after various treatments are summerised in Table 1.

Table 1: Summary of results of the chemical characterisation of samples before and after various treatments.

Sample	Acid value (AV)	Iodine value (IV)	Saponication value (SV)	Ester value	Peroxide value (PV)	% Moisture content
Crude palm oil (CPO)	19.50	54.20	147.30	127.80	0.08085	0.14
Lab extracted PO	6.90	54.40	53.30	46.50	0.07540	0.11
Photolysed CPO (1hr)	10.50	51.40	119.10	99.90	0.2393	-
Acetone sensitized Photo-CPO	3.34	53.30	99.43	80.77	0.2409	-

Sample irradiation and product analysis

For a typical run, the weighed oil sample was introduced into the reaction chamber, the lamp/cooler unit inserted and the mains switched on. In the case of acetone-sensitised reaction, each oil sample was dissolved in a quantity of acetone in the ratio of 2:3 (v/w), acetone to oil, before being introduced into the reaction chamber. Reaction

progress was monitored by measuring the evolving gas volume and periodic withdrawal of sample for physical and chemical analysis. At the end of each run, the solid product was separated from the unreacted oil and weighed. The solid product which, from preliminary studies, contained glycerol was extracted with 3% chloroform. The chloroform was subsequently distilled off and the glycerol residue dried and weighed. The solid residue from the glycerol extraction was also dried and weighed. The results are shown in Tables 2 and 3 for the non-sensitised and the acetone-sensitised reactions. respectively.

Table 2: Product yields in a 2 hour palm oil photolysis (unsensitized)

Weight of oil (g)	Weight of solid product (g)	Weight of CO_2 evolved (g)	Weight of extracted glycerol (g)	Glycerol as % of photolised oil
60	24.10	1.642×10^3	6.5	10.83
80	38.26	2.385×10^3	8.7	10.88
100	42.10	2.834×10^3	10.9	10.90
120	49.95	3.578×10^3	13.1	10.92

Table 3: Product yields in a 2 hour palm oil photolysis (Acetone-sensitised)

Weight of oil (g)	Weight of solid product (g)	Weight of CO_2 evolved (g)	Weight of extracted glycerol (g)	Glycerol as % of photolised oil
60	43.20	1.118×10^2	6.6	11.00
80	47.26	1.181×10^2	8.9	11.13
100	49.42	1.505×10^2	11.2	11.20
120	54.51	1.760×10^2	13.5	11.25

The evolved gas was collected through a tube into an inverted burette by downward displacement of water. The gas was rechanelled through a water adsorbent, anhydrous calcium chloride[16] and a pre-weighed carbon dioxide adsorbent, soda lime. Glycerol was identified spectroscopically (IR) and by its reaction with $KHSO_4$ to form acrolein[15].

Kinetic analysis of data

The measured gas volumes were converted to moles of gas assuming ideal gas behaviour and correcting for both elevation (Jos is about 1500 metres above sea level) and the partial pressure of water vapour at room temperature at the location of the experiment. The analysis assumed the rate law:

$$R = k[A]^n$$

where R is the reaction rate, [A] the concentration of the oil (substituted with CO_2 concentration using the relation given below), n the reaction order and k the reaction rate constant. The apparent first-order rate constants, k_1 for the product (CO_2) yield, have been estimated based on the equation

$$W_t = W_o(1 - e^{-k_1 t})$$

where W_o is the maximum amount of the product that would be obtained at infinite time and W_t is the amount of the product generated at any given time, t. Experimental data obtained were plotted and analysed with the aid of the Microsoft Excel, version 5.0. The results are presented in Figures 4 and 5 and Tables 4 and 5.

Table 4: Initial rates obtained from different initial weights of palm oil (Unsensitised)

Weight of oil	n_{CO_2} (moles)	Initial rates (mols/min)	$\log (n_{CO_2})$	$\log$ (oil wt)	$\log$ (rate)
60.00	3.73×10^{-5}	4.9×10^{-7}	-4.4283	1.7782	-6.3036
80.00	4.74×10^{-5}	6.32×10^{-7}	-4.3242	1.9031	-6.1993
100.00	6.10×10^{-5}	8.13×10^{-7}	-4.2147	2.0000	-6.0899
120.00	7.45×10^{-5}	9.93×10^{-7}	-4.1278	2.0792	-6.0029

Table 5: Initial rates obtained from different initial weights of palm oil (Acetone-sensitised)

Weight of oil	n_{CO_2} (moles)	Initial rates (mols/min)	$\log (n_{CO_2})$	$\log$ (oil wt)	$\log$ (rate)
60.00	2.20×10^{-4}	2.933×10^{-6}	-3.6576	1.7782	-5.5327
80.00	2.71×10^{-4}	3.613×10^{-6}	-3.5670	1.9031	-5.4421
100.00	3.12×10^{-4}	4.160×10^{-6}	-3.5058	2.0000	-5.3809
120.00	3.73×10^{-4}	4.973×10^{-6}	-3.4283	2.0792	-5.3034

RESULTS AND DISCUSSION

Tables 2 and 3 show the yield of glycerol as a function of the initial oil concentration for the sensitised and unsensitised reactions. Figures 2 and 3 are graphs of amounts of CO_2 (in moles) evolved versus time for different weights of palm oil. The results from Tables 2 and 3 and Figures 2 and 3 show the formation of glycerol/CO_2 to be oil concentration dependent. It is also observable from the results that CO_2 and glycerol formation tend towards an equilibrium value as the time and oil concentration

Figure 2: A graph of amount (in mols) of CO_2 evolved versus time during photolysis of various weights of palm oil (unsensitized)
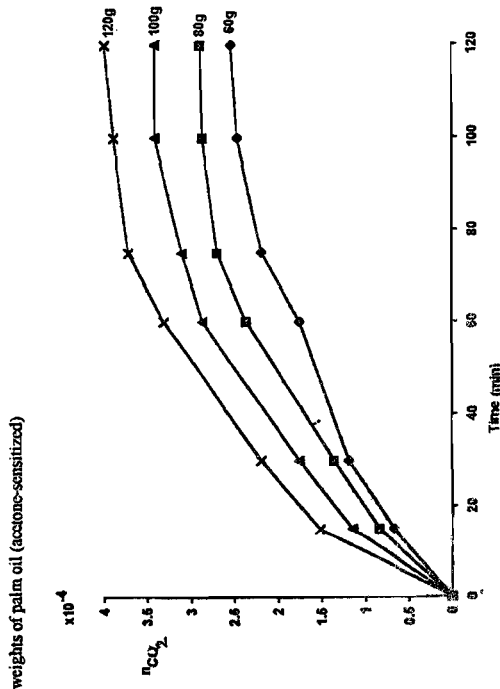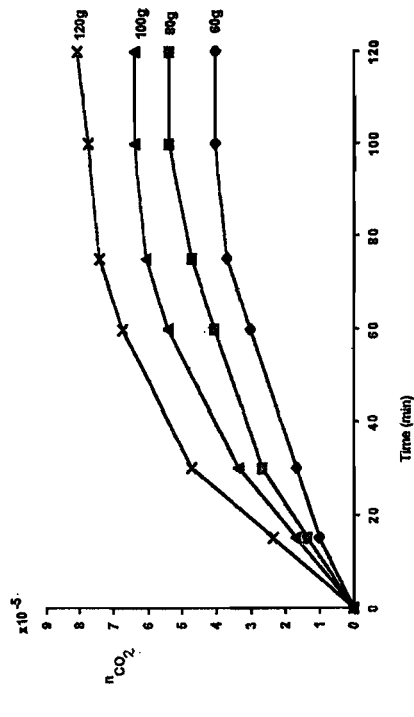

Figure 3: A graph of amount (in mols) of CO_2 evolved versus time during photolysis of various weights of palm oil (acetone-sensitized)

increase, respectively. The approach of glycerol equilibrium concentration is evidently more rapid in the sensitised than the unsensitised reactions. In Table 2, glycerol has a nearly constant value averaging 10.88% of the total oil photolysed. In Table 3, the percentage of glycerol is significantly higher, averaging 11.19%. These results imply that

the reaction or reactions leading to the formation of product or products is enhanced by the presence of acetone. Tables 4 and 5 give the initial rates obtained from different initial weights of palm oil. The relevant plots that enabled the determination of the kinetic parameters (n,k) are given in Figures 4 and 5. The analysis shows the reactions to be first order with respect to the oil/CO_2 concentration in both systems. Thus the substrate-photon collisional step of the photochemical process, leading to the formation of an excited substrate must essentially be faster than the subsequent unimolecular decarboxylation process, the latter being the rate determining step. The rate of reaction of the unsensitised compared with the sensitised reaction (Figure 6) shows the latter reaction to be approximately 100-fold faster than the former. Noticeably, the acid number (representative of the amount of free fatty acid present in the oil originally) decreases from an initial value of 19.50 (Table 1) to a final value of 5.60 for the unsensitised and 2.20 for

Figure 4: A plot of log(initial Rate) versus log n_{CO_2}

for the unsensitized reaction
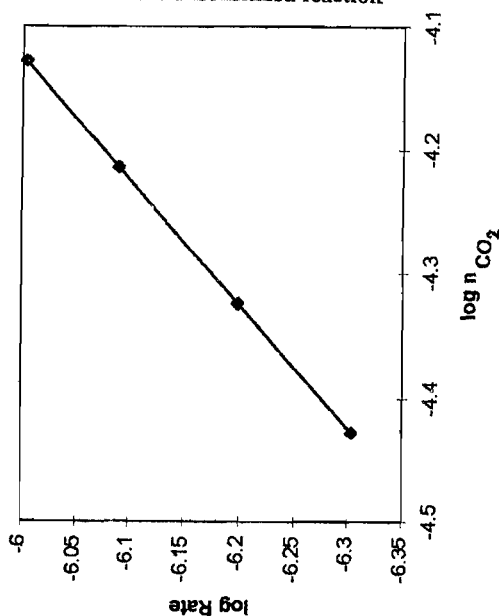
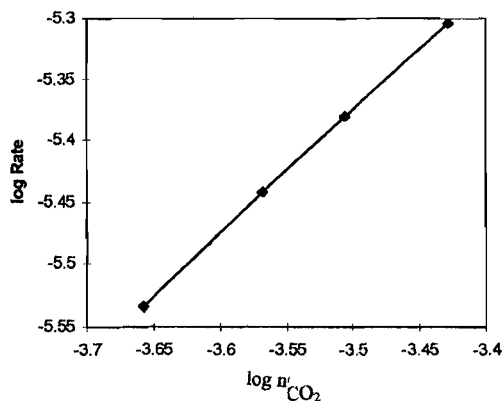Slope (i.e order of reaction) = 1.0

Intercept = -1.87309 thus k_1 = 0.01339399 min⁻¹

Correlation coefficient = 1.0

Figure 5: A plot of log(initial Rate) versus log n_{CO_2}
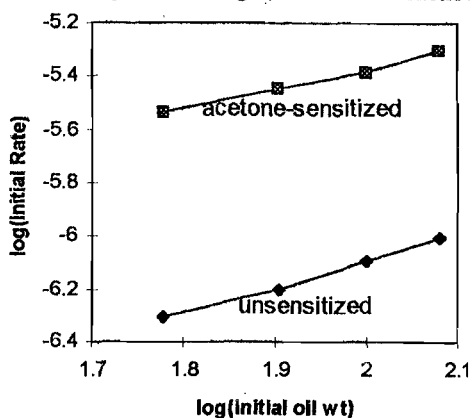
for the acetone-sensitized reaction

Slope (i.e order of reaction) = 1.0

Intercept = -1.8751 thus k_1 = 0.013335214 min⁻¹

Correlation coefficient = 1.0

Figure 6: A plot of log(initial Rate) versus

log (initial weight) for the two reactions.

the sensitised reactions during a 4-hour interval. Since glycerol is a product of hydrolysis, these results imply the decarboxylation not only of the free fatty acid present originally in a given amount of oil but also the free fatty acids formed in the process of the triglyceride stripping. It is however not possible to say how the hydrolysis and decarboxylation reactions are related in this study. More so that the amount of CO_2 recorded in these experiments suggests only partial decarboxylation, even after taking into account O_2 intake for the peroxide formation. On the other hand, the iodine number remained practically unchanged. This result suggests that the unsaturation of the oil is most probably unaffected in these reactions. Studies are

continuing to identify the other reaction products and to also relate the processes of hydrolysis, peroxidation and decarboxylation. It is hoped that the results of the ongoing studies will throw more light on the attempts to elucidate the mechanism of these reactions.

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