

## Chemical Storage of Solar Energy Using Hydrazones

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### Abstract

Hydrazones derived from 4- phenoxybutanoic acid were reprepared and their oxidation potentials in Micellar-Ethanol solution were measured using cyclic voltammetric technique. These compounds were used as photosensitizers in three component system containing methyl viologen ( $MV^{2+}$ ) and  $Na_2EDTA$ . Different behaviors of the hydrazones were observed as photosensitizers depending on their oxidation potential values and their stability in irradiation solution. Rate constants of methylviologen reduction by the photochemical active hydrazones were recoded and hydrogen was photoproduced using  $TiO_2$  as catalyst.

**Keywords:** Photochemical Conversion of Solar Energy, Photosensitizer,  $Na_2EDTA$ ,  $MV^{2+}$

### الخرن الكيمياوي للطاقة الشمسية باستخدام الهيدروزونات

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### الخلاصة

تم تحديد جهود التأكسد لسلسلة من الهيدروزونات المشتقة من حامض 4- فينوكسي بيوتانويك والمحضرة سابقا، في محلول ايثانول مايسلر باستخدام تقنية الفولتكرام الحلقي. استخدمت هذه المواد كمحفزات ضوئية في نظام ثلاثي مكون من مثيل الفايلولوجين ، و  $Na_2EDTA$  ، والمحفز الضوئي (الهيدرازون). تفاوت اداء الهيدروزونات في اختزال مثيل الفايلولوجين اعتمادا على جهود تأكسدها واستقراريتها في محاليل الايثانول- مايسلر. تم حساب ثابت السرعة للهيدروزونات التي نجحت كمحفزات ضوئية ، وتبين بان البعض منها لها القدرة على الخرن الكيمياوي للطاقة الشمسية، وذلك بانتاج الهيدروجين من تجزئة الماء باستخدام ثاني اوكسيد التيتانيوم المبلتن  $Pt/TiO_2$  كعامل مساعد

**الكلمات الدالة:** التحويل الكيمياوي الضوئي للطاقة الشمسية ، المحفزات الضوئية،  $Na_2EDTA$ ،  $MV^{2+}$

### Introduction

Energy is the most important issue of the 21<sup>st</sup> century. About 85% of our energy comes from fossil fuels, a finite resource unevenly distributed beneath the Earth's surface. Reserves of fossil fuels are progressively decreasing, and their continued use produces harmful effects such as pollution that threatens human health and greenhouse gases associated with global warming. Prompt global action to solve the energy crisis is therefore needed [1]. The search for future alternative energy options that are renewable and environmentally friendly is of great importance and solar energy is one of these options [2].

One of the final goals of current research of the photochemical conversion and storage of solar energy is photoproduction of hydrogen, the most abundant element in nature, from water. Many workers postulated and put in order various systems in the way of achieving this

target [3,4,5,6,7,8,9,10]. However, the most popular and best studied model system for the photosensitized reduction of water has been the one containing  $\text{Ru}(\text{bpy})_3^{+2}$  (bpy=2,2 bipyridine) as the photosensitizer, methyl viologen (1,1 dimethyl -4,4- bipyridinium dication;  $\text{MV}^{2+}$ ) as electron relay, and EDTA as sacrificial electron donor [6,11,12, 13,14,15,16, 17,18]. Although many other exciting approaches and schemes (eg. Methylporphyrines and some well-known organic dyes) have been attempted and tried as photosensitizers in light induced electron transfer; it is fair to state the other practical system for photolysis of water to hydrogen have yet to be found [15,19,20,21].

Accordingly the increasing interest in the chemistry of hydrazones induced the author aims to prepare new compounds of this class to use them as new photosensitizers.

### Experimental

Hydrazones were reprepared according to some previously published [22,23]. UV- visible spectra were recorded on CECIL type CE 599 spectrophotometer. Infrared spectra were recorded on a Perkin – Elmer 983 GIR spectrophotometer. Cyclic voltammetric experiments were carried out using a three-electrodes system (a reference electrode SCE, a platinum wire auxiliary electrode and working electrode, glassy carbon electrode GC). This system was connected with a CV-27 BAS scanning potentiostat supplied with a cell stand type C1B-240 and x-y recorder type Omnigraphic, Houston instrument. Irradiation experiments for sensitization and hydrogen production reactions were performed with a 250 W- Xenone arc lamp (Applied photophysics, LTD). Photochemical reactions were held in 4 mL size quartz cell supplied with 3-cm-neck. Photocatalytic hydrogen production experiments were carried out using a cylindrical 30 mL pyrex cell equipped with a 2 cm<sup>2</sup> diameter quartz irradiation window surrounded by a water- cooling jacket. Hydrogen gas analyses were carried on a Pyeunicam 304 gas chromatography supplied with a carbosieve 5 A column 1/8" in diameter, and 3 ft length with thermal conductivity detector, TCD. Column temperature was fixed at 60 °C, injection temperature 80 °C, detection temperature 100 °C and flow rate 20 mL min<sup>-1</sup>.

### Results and Discussion

Hydrazones (Ia-e, II, and III) derived from substituted 4- phenoxybutanoic acid was prepared according to [23]. The reprepared hydrazones and  $\lambda$  max values of their  $1 \times 10^{-4}$  M Ethanol- Micellar solution (CTAB) are shown in table (1).

**Table (1):  $\lambda$  max of the prepared and used compounds measured in Ethanol- Micellar solution at  $1 \times 10^{-4}$  M concentrations**



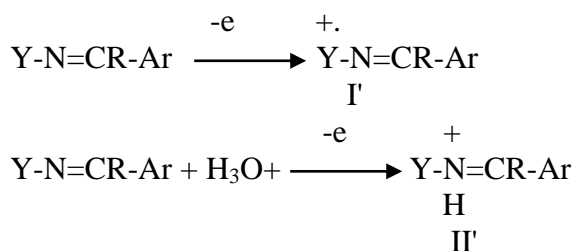
compound No	X	Ar	R	$\lambda$ max
Ia	H	4- CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	398
Ib	H	4- OH-C <sub>6</sub> H <sub>4</sub>	H	402
Ic	H	2-C <sub>10</sub> -H <sub>7</sub>	H	415
Id	H	2,4-(OCH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	H	420
Ie	H	3,4-(OCH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	H	417
II	Cl	2,4-(OCH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	H	414
III	Cl	4-CH <sub>3</sub> -CH <sub>3</sub>	CH <sub>3</sub>	411

The presence of electron rich fragment C=N in the hydrazones motivated us to use them as photosensitizers. This was done to photoproduce methyl viologen in a three-component system containing ethylenediaminetetraacetic acid disodium salt, Na<sub>2</sub>EDTA as a sacrificial electron donor in the way of producing hydrogen from Ethanol-Micellar solution mixture in the presence of platinized titanium dioxide (Pt/TiO<sub>2</sub>). Since the photoproducing activity of photosensitizers toward methyl viologen (MV<sup>2+</sup>), with reduction potential 0.69 V[24,25], depend on the closeness of their oxidation potential to that of hydrazones, so these potentials have to be measured. Cyclic voltammetry technique was chosen for this purpose and the first run of the solution containing ( $4.8 \times 10^{-4}$  M hydrazones, 0.1M KCl as supporting electrolyte) at pH=5 showed irreversible two oxidation peaks at the region (1.01-1.20 V) and (1.44-1.50V) respectively. The full details of the data collected are shown in table (2)

**Table (2): anodic oxidation of hydrazones (Ia-e, II, III) ( $4.8 \times 10^{-4} \text{M}$ ) in 20% (V/V) ethanolic micellar solution containing 0.1M  $\text{K}_2\text{SO}_4$  at scan rate (0.08-0.1 V/S)**

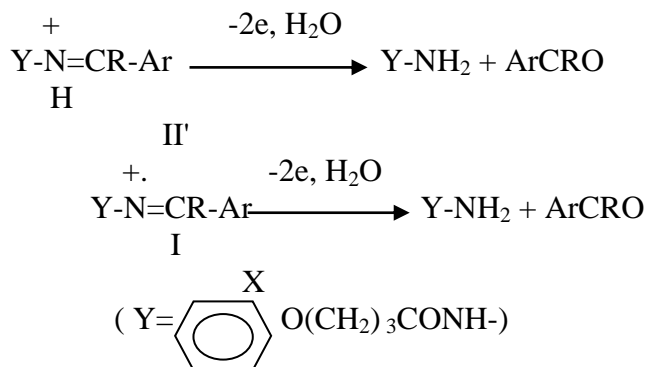
Cpd No.	Type of Micellar Soln.	$E_{p1}/\text{V}$	$I_{p1}/\text{mA}$	$E_{p2}/\text{mA}$	$I_{p2}/\text{mA}$
Ia	Lauryl Sulfate	1.089	0.030	-	-
	CTAB	1.121	0.031	-	-
	CTAB	1.161	0.030	-	-
Ib	Lauryl Sulfate	1.050	0.036	-	-
	CTAB	1.068	0.042	-	-
	CTAB	1.082	0.039	-	-
Ic	Lauryl Sulfate	1.098	0.044	-	-
	CTAB	1.190	0.051	-	-
	CTAB	1.172	0.049	-	-
Id	Lauryl Sulfate	1.010	0.020	1.451	0.055
	CTAB	1.018	0.025	1.480	0.070
	CTAB	1.090	0.031	1.430	0.060
Ie	Lauryl Sulfate	1.121	0.040	1.500	0.100
	CTAB	1.180	0.052	1.492	0.090
	CTAB	1.160	0.043	1.440	0.087
II	Lauryl Sulfate	1.170	0.037	1.410	0.120
	CTAB	1.150	0.055	1.471	0.112
	CTAB	1.191	0.041	1.430	0.079
III	Lauryl Sulfate	1.200	0.039	-	-
	CTAB	1.290	0.033	-	-
	CTAB	1.200	0.029	-	-
- Unidentified Wave					

The first peak ( $E_{p1}$ ) was attributed to the oxidation of the hydrazones to form the cationic radical (I') via one electron process which is in the anodic reaction of traces of acid could be turned to the formation of the species (II'). The following scheme (1) describes the anodic reaction of these compounds at the first wave [25,26].



**Scheme 1: Anodic Reaction of the Hydrazones at the First Wave.**

The second peak  $E_{p2}$  at (1.44 - 1.50V) was assigned to the further oxidation of the cationic radical (I') via two electron process followed by the hydrolysis of the intermediate forming the corresponding carbonyl compounds (aldehydes, ketones) and amines by any of the pathways shown below,(scheme 2).



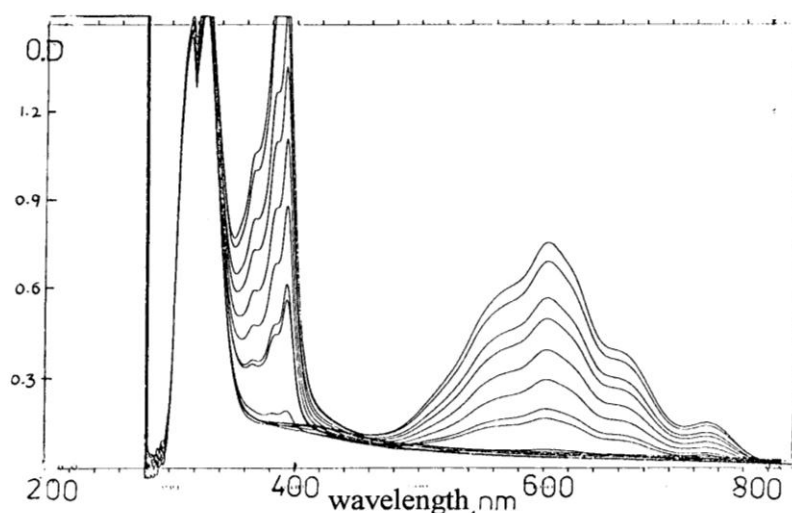
**Scheme 2: Oixdation of Cationic Radica (I) Via Two Election Process Follwed by Hydrolysis Of The Intermediate.**

Photoproduction of methyl viologen,  $MV^{+2}$  was held by irradiation mixtures of  $3.4 \times 10^{-4}$  M hydrazones (Ia-e, II, III),  $3.4 \times 10^{-3}$  M  $Mv^{+2}$ ,  $10^{-2}$  M  $\text{Na}_2$  EDTA in 20% ethanolic micellar solution (V/V), buffered to pH=5 using white light ( $2980 \text{ w/m}^2$ ). The photoreduction of  $MV^{+2}$  was monitored against time of irradiation by the classical build up of  $MV^{+2}$  radical ion.

Hydrazones (Ia-e, II, and III) showed different behavior in photoreducing activity depending on their stability toward hydrolysis. Compounds (Ib,c ,II, III) were totally failed in reducing  $MV^{+2}$  regardless the time of irradiation and type of micellar solution been used (Lauryl sulfate, cetyltetraammonium bromide(CTAB), cetyltetraammonium chloride (CTAC). Whereas compounds (Id,e) showed, rather positive results in photoreducing methylviologen in the above mentioned micellar solution [7,14]. Table (3) reveals the value of rate constants of photoproducing reaction achieved using compounds(Id &Ie). Whereas Figure (1) shows the spectrum revealing the classical build up of  $MV^{+2}$  radical ion using Id as photosensitizer.

**Table (3): Values of Rate Constants of Reduction of  $MV^{2+}$  by Hydrazones (Id and Ie) at 25 °C**

Compd No.	Type of Micellar Soln.	rate constant, $k \text{ s}^{-1}$
Id	Lauryl sulfate	$4.3 \times 10^{-4}$
Id	CTAB	$8.0 \times 10^{-4}$
Id	CTAC	$1.0 \times 10^{-4}$
Ie	Lauryl sulfate	$4.5 \times 10^{-4}$
Ie	CTAB	$5.8 \times 10^{-4}$
Ie	CTAC	$8.8 \times 10^{-4}$



**Fig.(1): UV- visible spectrum revealing the classical build up of  $MV^{+2}$  radical ion using Id as photosensitizer.**

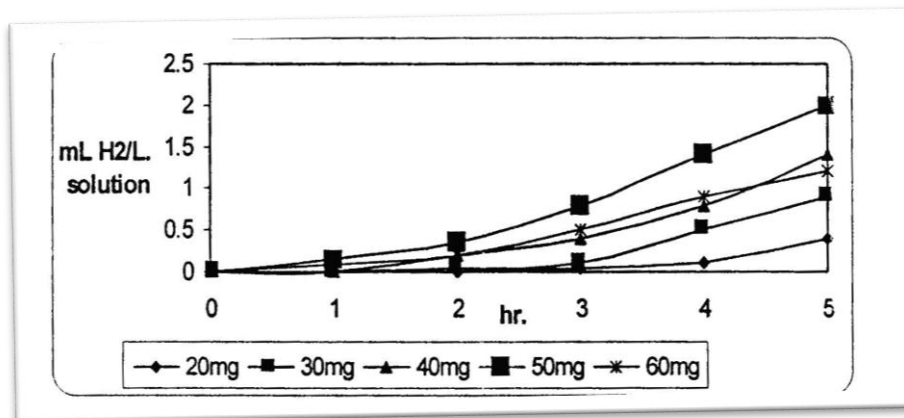
These reactions was found to fit good first order kinetics by plotting in  $(A_{\infty} - A_t)$  against  $t$ , according to Lambert- Beer law derivation of the first order equation [25].

$$\ln (A_{\infty} - A_t) = \ln A - kt$$

$A_{\infty}$  = absorbance of  $Mv^{+}$  at which values remains unchanged regardless time of irradiation.

$A_t$  = absorbance at any time.

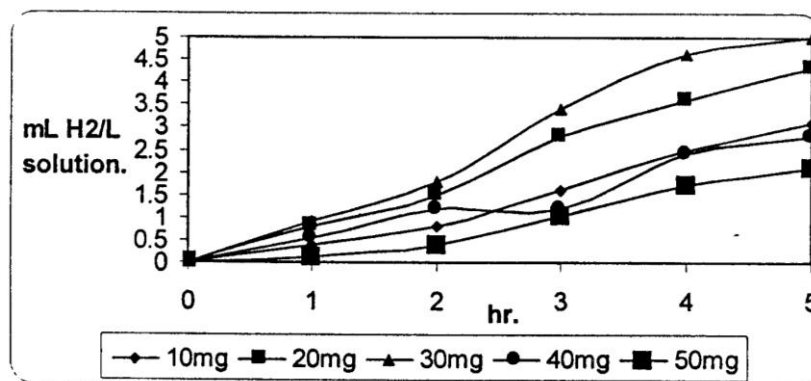
It was deduced from kinetic results shown in table (3) that compound Id with rate constant  $1 \times 10^{-3} \text{ s}^{-1}$  in CTAC and  $8.8 \times 10^{-4} \text{ s}^{-1}$  in CTAC where shown to be promising candidates in storage system by photoreducing  $H_2$  from water molecule [5,6,7,11,12,14,19,20,21]. Irradiation experimental using mixture of 25 mL comprising  $3.4 \times 10^{-4} \text{ M}$  of (Id & Ie)  $3.4 \times 10^{-3} \text{ M } MV^{+2}$ .  $10^{-2} \text{ M } Na_2EDTA$  in the presence of (20, 30, 40, 50, 60 mg) of 200 micron Pt /  $TiO_2$  in micellar solution at  $pH=5$  using white light were held for 5 hr. Only compound (Id) in CTAC showed 2mL  $H_2$  per one liter of irradiated solution at 50 mg of Pt/ $TiO_2$  loading, whereas the remaining compounds totally failed in photoproducing hydrogen regardless the time of irradiation and type of Pt/ $TiO_2$  loadings. Figure (2) shows the gradual increment of hydrogen volume during 5 hr of irradiation.



**Fig. (2): Hydrogen production mL/L solution using Hydrazone (Id) as photosensitizer in different loading Pt/TiO<sub>2</sub> (200 μ) at pH=5**

The inactivity of compounds (Ie) in evolving H<sub>2</sub> may be attributed to its relative lower rate constants which prepare sufficient amount of MV<sup>+</sup> on the surface of TiO<sub>2</sub> to reduce water molecule in sufficient rate [3,21,24,27].

To investigate the effect of particle size on the production of hydrogen, the previous experiments were repeated using (10, 20, 30, 40, 50 mg of 45 mic. Pt/TiO<sub>2</sub>). However, the same compounds (Id) in CTAC, showed only 5 mL hydrogen at 20 mg of Pt/TiO<sub>2</sub> after 5 hr irradiation. Figure (3) illustrates the total volume of hydrogen production. The shift of the optimum value for hydrogen production from 50 mg (200μ) to 20 mg (45 μ) may also be ascribed to screening effect caused by finely divided higher amount of Pt/TiO<sub>2</sub> [24].



**Fig.(3): Hydrogen production mL/L solution using Hydrazone (Id) as photosensitizer in different loading Pt/TiO<sub>2</sub> (45 μ) at pH=5**

The particle size is believed to be strongly correlated with the size of active surface of semiconductor, in other words for a given photocatalyst, the smaller the size of the semiconductor particle, the larger the volume of space charge layer, where electrons and holes were separated sufficiently. Electrons and holes easily reach the surface with their lifetime when the diffusion length (10<sup>4</sup> Å) for TiO<sub>2</sub> [24] is larger than the radius of the particle.

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