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A STUDY ON RADIOLYSIS OF  
2- PROPANOL IN THE PRESENCE OF  
FURANIC KETONES

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دراسة تشعيع الكحول الأيزوبروبيلي في وجود  
كيتونات الفيروران

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خلاصة

يتناول هذا البحث دراسة تشعيع الكحول الأيزوبروبيلي باشعة جاما في وجود تراكيزات مختلفة من كيتونات الفيروران

وهذه الكيتونات إشتملت على كيتونات : ٢ - فيورانيل - ٤ - ميثيل الفينيل ، ٢ - فيورانيل الفينيل ، ٢ - فيورانيل - ٤ - ميثوكسي الفينيل ، ٢ - فيورانيل البيوتيل ، ٢ - فيورانيل البنثيل ، ٢ - فيورانيل الميثيل . ودرست تأثير الجرعة الممتصة من الإشعاعات على تصاعد غازي الهيدروجين والميثان وكذلك تم دراسة ومناقشة ميكانيكيات تشعيع الكحول الأيزوبروبيلي في وجود تلك الكيتونات وذلك في وجود أو غياب لكسجين الهواء الجوى .

**ABSTRACT:**  $\gamma$ -radiolysis of 2-propanol has been studied in the presence of different concentrations of some furanic ketones. The studied furanic ketones were: 2-furanyl-4-methyl phenyl ketone, (FM), 2-furanyl phenyl ketone, (FP), 2-furanyl-4-methoxyphenyl ketone, (FMP), 1(2-furanyl)-1-pentanone, (FP), 1-(2-furanyl) 1-ethanone, (FE). The effect of the absorbed dose on the liberated hydrogen and methane was studied. The mechanisms of  $\gamma$ -radiolysis of 2-propanol in presence of the mentioned ketones are discussed in the presence or absence of atmospheric oxygen.

## INTRODUCTION

2-Propanol is utilized as a solvent in many radiation manipulations. Several studies have been made to investigate the effect of scavengers of radicals and electrons on its yields [1-9]. The kinetics of radiolysis differs in the presence of atmospheric oxygen from its absence [4-9]. In this communication, attempts are made to investigate the general behaviour of 2-propanol containing different concentrations of some furanic ketones during its  $\gamma$ -radiolysis in presence or absence of atmospheric oxygen. This investigation helps the prediction of the behaviour in future studies with other scavengers either in presence or absence of atmospheric oxygen.

## EXPERIMENTAL

Firstly, 2-propanol must be purified from acetone by the method described by Gille [10]. The ketone must be purified or synthesized by one of the three methods described elsewhere [4]. The purity of both 2-propanol and ketones was examined by gas chromatography using columns with different polarities.

3.5 ml Pyrex glass ampoules were utilized for irradiation of prepared solutions. The ampoules were first washed with chromic acid and rinsed thoroughly several times by redistilled water. The ampoules were oven dried, then they were  $\gamma$ -preirradiated for one hour.

Solutions of ketones in 2-propanol were prepared in concentrations of 0.1 and 0.01 molar. 2.5 ml of each solution were pipetted into ampoules.

In case of  $\gamma$ -radiolysis in absence of atmospheric oxygen, gases in solutions were stripped off in a high vacuum line ( $10^{-5}$ - $10^{-6}$  torr) by the conventional freeze melt technique up to 5 cycles. Finally the ampoules were sealed off under vacuum. In case of  $\gamma$ -radiolysis of 2-propanol in presence of atmospheric oxygen, the ampoules were directly irradiated after the solution had been pipetted without any other treatment.

Irradiation of the sealed or open ampoules containing solutions were carried out using a  $^{60}\text{Co}$  (Gamma cell type 220) source from Atomic Energy of Canada Ltd dose rate (0.305 KGy/h) and dose rate of (1.07 14 M Gy/h) by "Egypt Mega Cell". The absorbed dose was determined using freshly prepared Frick dosimeter solutions [ $G(\text{Fe}^{+++}) = 15.6 (100 \text{ ev})^{-1}$ ] [11].

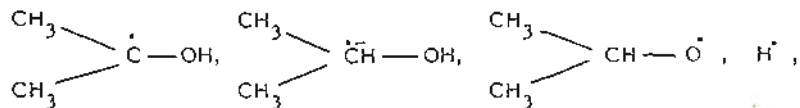
Qualitative and quantitative determinations of hydrogen and methane were determined by gas chromatography using a column of molecular sieve 5 A°, L=3m, D=2.5 mm with cathorometer,  $t_{\text{column}} = 80-100 \text{ }^\circ\text{C}$ ,  $t_{\text{injector}} = 250 \text{ }^\circ\text{C}$ ,  $t_{\text{detector}} = 250 \text{ }^\circ\text{C}$ , flow rate of carrier gas ( $\text{N}_2$ ) = 20 ml/min.

Qualitative and quantitative determinations of radiolytic products were determined by gas chromatograph using FID detector and suitable columns (SP 1000 10%, OV 275 10% and SE 30 10%), L = 3m, D = 2.5 mm,  $t_{\text{column}} = 150-200 \text{ }^\circ\text{C}$ ,  $t_{\text{detector}} = 250^\circ\text{C}$ ,  $t_{\text{injector}}$

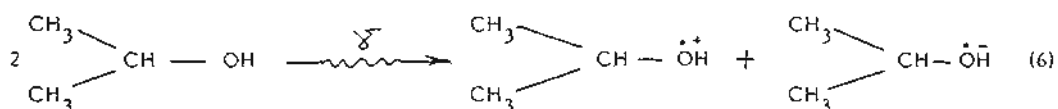
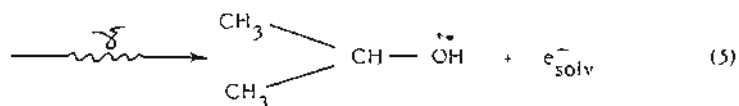
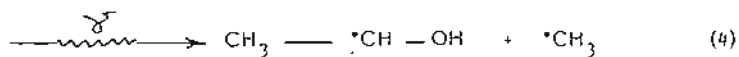
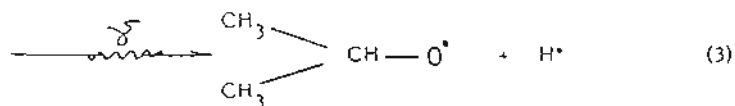
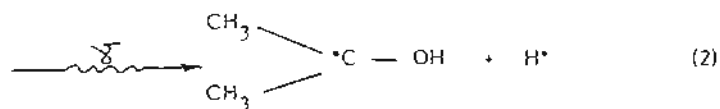
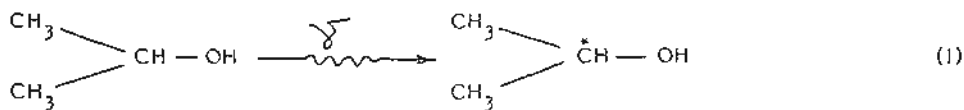
= 250°C , flow rate of carrier gas (He) 20 ml/min.

## RESULTS AND DISCUSSION

The principal radiolytic products of 2-propanol are, [ 12 - 14]:



$\text{CH}_3 - \dot{\text{C}}\text{H} - \text{OH}$  and  $\dot{\text{C}}\text{H}_3$ . The mechanisms of formation of the above mentioned products were investigated by different authors [ 10,13,15 - 25] as follows :



The different-species formed as a result of 2-propanol radiolysis, which are illustrated in equations (1-6) may be represented by R.

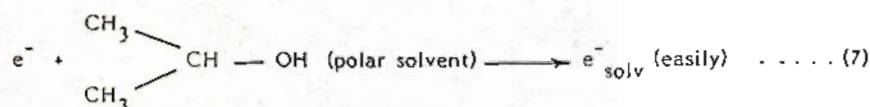
The described intermediate principal radiolytic products react in solution to produce permanent radiolytic products with yields G shown in Table (1). The radiolytic mechanisms to produce each product are explained elsewhere [3]. The three principal mechanisms to interpret the production of these products are:

- (a) Molecular excited state mechanism, in which the excited molecule interacts either with solvent molecules, with the existing solute or with itself to produce the radiolytic products.
- (b) Free radical mechanism, in which the free radicals formed due to deexcitation of the excited molecules or due to degradation interact with themselves, with the solute or with the solvent molecules to produce the radiolytic products.
- (c) Solvated electron mechanism, in which the solvated electron interacts with reducible centers such as carbonyl groups to reduce them to alcoholic groups or to react with positive ion molecules to produce excited ones which behave similarly to the mechanism given in (a).

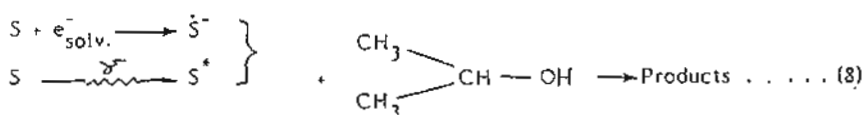
The three mechanisms participate simultaneously to produce the radiolytic products, the preponderant ones depend on the following:

- The nature of solvent.
- The nature of solute.
- Presence or absence of oxygen.
- Dose absorbed and dose rate.
- Temperature and pH of solutions.

The nature of solvent depends on whether it is polar or not. Polar solvents facilitate the rapid formation and stabilization of solvated electrons and make them more efficient for reduction [2,3].



The mechanisms of radiolysis are directed according to the nature of solute. If solute scavenge electrons other mechanisms will affect on the solvent and the scavenging solute will be reduced. The ketone solute, S, may scavenge also radicals or absorb energy (e.g. Fluorescent, phosphorescent or aromatic materials) and interact with the solvent to produce radiolytic products as follows:



The detailed mechanisms of formation of radiolytic products S-R are discussed elsewhere [1-3]. These mechanisms show the scavenging effect of ketones S for R\* and solvated electrons that were utilized in case of radiolysis pure 2-propanol to produce hydrogen and methane. Therefore, the addition of S (furanic ketones) caused a decrease in the radiation yield (G) for hydrogen and methane as obvious from Tables (1,2). Lowering the ketone con-

centration cause an effective utilization of radiation energy for production of more radiolytic products (as the energy lost for excitation and deexcitation of conjugated used ketones is smaller in low concentrations than in higher ones). This interpret the higher negative G value for ketone at low concentration as shown in Table (2).

The dose rate and absorbed dose mainly affect the radiation yields due to rapidity of some reactions than others. For example, the physical and physicochemical changes are more effective at high dose rates due to their short period of reaction, where as the chemical stage reactions are effective at moderate or low doses [3]. The variations in working conditions (such as absorbed dose and dose rate) interpret the differences of G values of hydrogen and methane obtained from different studies conducted on radiolysis of 2-propanol as illustrated in Table (1).

Oxygen has an important role to play in mechanism selection. It reacts with  $H^\bullet$  to form  $\dot{O}_2H$  radicals and changes the nature of the final radiolytic products. Also, it can scavenge easily solvated electrons to form  $\bar{O}_2$  which reacts with  $H^\bullet$  to form  $\dot{O}_2H$  which forms  $H_2O_2$  as follows:



This interprets why in the presence of atmospheric oxygen the main radiolytic reactions are due to the attack of  $\dot{OH}$  radicals [5,26-34] and the formation of different radiolytic products that are identified in details in other work [35].

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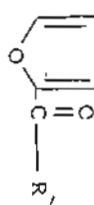
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Table (1): Radiolytic products of 2-propanol (pure).

Ref	dose rate (K Gy/hr)	dose (K Gy)	G(H <sub>2</sub> )	G(CH <sub>4</sub> )	G(C <sub>2</sub> H <sub>6</sub> )	G(C <sub>3</sub> H <sub>8</sub> )	G(C <sub>3</sub> H <sub>6</sub> )	G(CH <sub>3</sub> CH <sub>2</sub> O)	G( $\begin{matrix} \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{matrix}$ -C=O)
2	0.37	10 - 500	4.52 - 2.52	2.0 - 1.0					
3	0.305-0.240	10 - 300	6.4 - 3.5	2.1 - 1.65					
33	3.4	1.2 - 7.2	3.7	1.90			0.9	3.0	
23	6.3	1.6 - 12.4	3.3	1.69				2.75	
4	5.5	0.0304	4.5						
24	5.5	0.0304	4.9						
25	3.7	0.064	3.7 - 4.0						
30	44	83	3.33	1.66			1.15	2.89	
32	0.18	0.006-0.112	3.8	1.6	0.026	0.003	0.0013	1.10	3.4
26	6.3	0.0016-14.2	3.7	1.8	0.12	0.1	0.22	0.89	3.2

Table (2): Radiolytic products of 2-propanol with Furanyl Ketones at different concentrations and absorbed doses.



Ref	R	concentration (molar)	dose rate (KGy/hr)	dose (KGy)	G (H <sub>2</sub> )	G(CH <sub>4</sub> )	-G(ketone)
1		0.01	0.302	20 - 300	4.7 - 3.2	1.75 - 1.5	
		0.1			4.2 - 2.8	1.95 - 1.25	
2		1.6 x 10 <sup>-3</sup>	0.37	10 - 500	4.2 - 2.3	2.2 - 1.2	
		3.6 x 10 <sup>-1</sup>			2.3 - 1.4	1.2 - 1.1	
		1.558			1.2 - 0.9	0.6 - 0.7	
3		1.06 x 10 <sup>-2</sup>	0.305 - 0.24	20 - 300	5.45 - 3.6	1.65 - 1.4	
		1.06 x 10 <sup>-1</sup>			3.95 - 2.25	1.3 - 1.2	
3,4		1.162 x 10 <sup>-2</sup>	0.305 - 0.24	20 - 300	5.2 - 3.5	1.9 - 1.7	20 - 5
		1.62 x 10 <sup>-1</sup>			4.2 - 3	1.5 - 1.4	
		1.001			2.2 - 1.8	1.1 - 0.75	
5		0.01	0.3	20 - 300	4.7 - 2.7	2.1 - 1.1	
		0.1			3.2 - 2.1	1.4 - 0.9	
7		0.01	0.25	20 - 300	4.3 - 3.0	1.75 - 1.6	
		0.1			3.3 - 2.5	1.65 - 1.3	