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A STUDY ON THE γ RADIOLYSIS OF 2-FURANYL KETONES
IN 2-PROPANOL IN PRESENCE AND ABSENCE OF
ATMOSPHERIC OXYGEN

by

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دراسة على التحلل الكيميائي بالإشعاع لحاليل كيتونات ٢ - الفيروراتيل
في الكحول الأيزوبروبيل في وجود أو غياب أكسجين الهواء الجوي

د. إبراهيم جار العلم راشد

قسم العلوم الطبيعية

كلية الهندسة - جامعة المنصورة

د. محمد محمد الدسوقي

قسم الهندسة الكيميائية

الكلية الفنية العسكرية

خلاصة

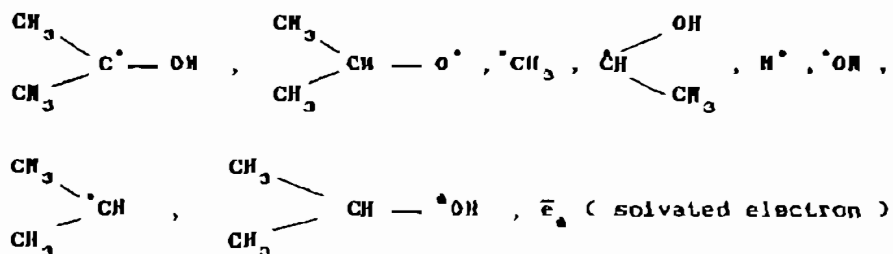
في هذا البحث تم دراسة تواتر التحلل الكيميائي الإشعاعي بأشعة جاما - في وجود أو غياب أكسجين الهواء الجوي -
لحاليل مختلفة من كيتونات ٢ - الفيروراتيل في الكحول الأيزوبروبيل . وتم تحديد أنواع وكميات التواتر التي تظهر من التحلل
الإشعاعي لكل مركب . وتم مناقشة ميكانيكيات تكون التواتر المختلفة في وجود أكسجين الهواء الجوي أو غيابه . وهذا البحث
يرضخ إمكانية التوقع المناسب للتواتر التي يمكن الحصول عليها عند تعرض مركبات أخرى لكيتونات الفيروران لأشعة جاما سواء
كان ذلك في وجود الأكسجين أو في غيابه كما يساعد على وضع ميكانيكيا ملائمة لتكون هذه التواتر .

ABSTRACT

The main radiolytic products obtained from the γ radiolysis
of some 2-furanyl ketones in presence or absence of atmospheric
oxygen are investigated. Their different radiolytic yields are
given. The general radiolytic mechanisms explaining the formation
of the detected radiolytic products - in presence or absence of
oxygen - are discussed. The present work enables to predict the
radiolytic products of the other 2-furanyl ketones either in
presence or absence of atmospheric oxygen, as well as their
possible radiolytic formation mechanisms.

INTRODUCTION

Since 2-propanol is usually utilized as a solvent in many radiolytic manipulations, several workers investigated the species formed during its radiolysis [1-7]. These species are:



Several studies showed the ability of some ketones to scavenge the hydrogen atoms, hydroxyl groups and solvated electrons. Examples of these ketones are benzophenone [8-11], cyclohexanone [12-14], and furanyl ketones [15-20].

During γ -radiolysis of a solution of 2-propanol and 2-furanyl ketones, solvated electrons, radicals and species evolved from them lead to the formation of their radiolytic products. The nature of these products depends upon the presence or absence of atmospheric oxygen. The studied series of ketones allows to predict the probable radiolytic products formed during radiolysis of similar other ketones in 2-propanol. The radiolytic mechanisms of formation of radiolytic products may be discussed in the view of the following principal mechanisms:

(a) Radical interaction mechanism interprets the formation of radiolytic products due to the interaction between the radicals formed from the solvent and ketones existed in the medium [1,3,7-31].

(b) Electron capture mechanism, which describes the reduction of carbonyl to give the corresponding alcohols and pinacols [22-32].

(c) Excited state mechanism that explains the formation of radiolytic products due to the interaction between the excited molecules of ketones or solvent or both with each other to give products [22-33].

EXPERIMENTAL:**Materials:**

Pure 2-propanol was treated according to the method described by Gillies [3] to eliminate the traces of acetone. The studied 2-furanyl ketones were prepared by the method of Galli [34]. The prepared ketones were purified by different techniques. Liquid ketones were purified by several vacuum distillations and by thin layer chromatography, where the solid ones were purified by several recrystallization and thin layer chromatography. The purity of both synthesised ketones and purified 2-propanol was examined by gas chromatography using FID detector and different columns of different polarities. The prepared ketones were analysed by Perkin-Elmer-457 IR spectrophotometer and Varian T 60 NMR instrument. The radiolytic products were determined by Ribermag R 10-10 mass spectrometer coupled with HP 3390 A gas chromatograph.

Qualitative and quantitative determinations of radiolytic products were determined by HP 3390 A gas chromatograph with the optimum column of SP 1000 (10%), 60-80 mesh, L = 3 m, D = 2.5 mm, and t = 160-190 °C. The temperature of both detector and injector was 250 °C. The carrier gas was helium at a flow rate of 20-30 ml/min.

Methods:

3.5 ml pyrex glass ampoules were utilized as containers for irradiation of prepared solutions. The ampoules were first washed with chromic acid then rinsed thoroughly several times by P.28 bidistilled water. After the ampoules have been oven dried, they were γ -preirradiated for one hour. Solutions of 0.1 and 0.01 molar from the prepared ketones in 2-propanol were pipetted into each ampoule.

For studying γ -radiolysis of ketones in 2-propanol in absence of atmospheric oxygen, gasses in solution present in the ampoules were stripped off in a high vacuum line (10^{-5} - 10^{-6} torr) by the conventional freeze-melt technique of 4-5 cycles. Finally, the ampoules were sealed off under vacuum.

For investigating γ -radiolysis of ketones in 2-propanol in presence of atmospheric oxygen, the ampoules containing solutions were left open.

Irradiation of the sealed and open ampoules containing solutions were carried out using a ^{60}Co (Gamma cell type 220) source from Atomic energy of Canada Ltd (dose rate 0.305 KGy/h). The absorbed doses were determined using freshly prepared Frick dosimeter solutions [$G(\text{Fe}^{++})=19.6(100\text{eV})^{-1}$] [35].



After Irradiation of ketone solutions, qualitative and quantitative determinations of the radiolytic products were carried out. The quantitative determination was investigated through retention times and mass spectrometry for the formed radiolytic products, while the quantitative determination was performed via a standard curve.

RESULTS AND DISCUSSION

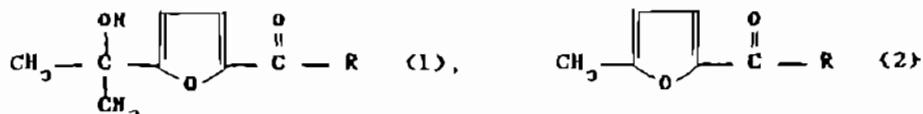
γ -radiolysis of 2-furyl ketones in 2-propanol was investigated. The investigated ketones have the general formula:

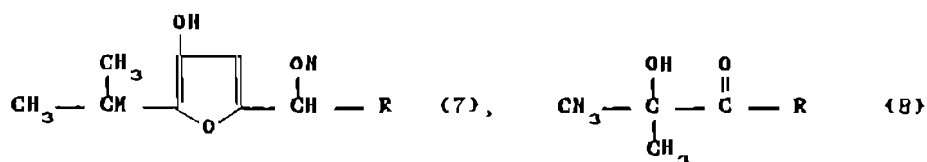
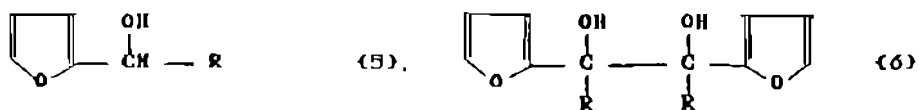
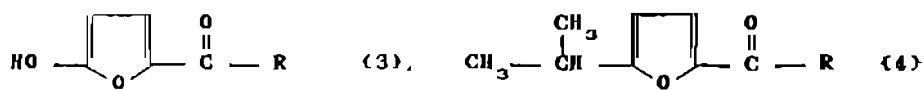


Where, R indicates the following different radicals

- R : $-\text{CH}_3$ (2-furyl methyl ketone) (I)
- : $-\text{CH}_2-\text{CH}_3$ (2-furyl ethyl ketone) (II)
- : $-(\text{CH}_2)_2\text{CH}_3$ (2-furyl n-propyl ketone) (III)
- : $-(\text{CH}_2)_3\text{CH}_3$ (2-furyl n-butyl ketone) (IV)
- : $-(\text{CH}_2)_4\text{CH}_3$ (2-furyl n-pentyl ketone) (V)
- :  (2-furyl n-phenyl ketone) (VI)
- :  CH_3 (2-furyl p-methylphenyl ketone) (VII)

Results showed that in absence of atmospheric oxygen, the general radiolytic products obtained were as follows: (22-25)





In presence of atmospheric oxygen, the following radiolytic products were detected [21,24]:

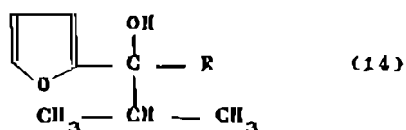
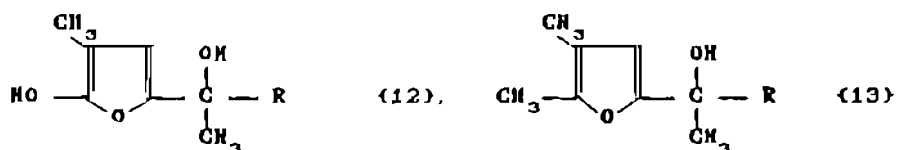
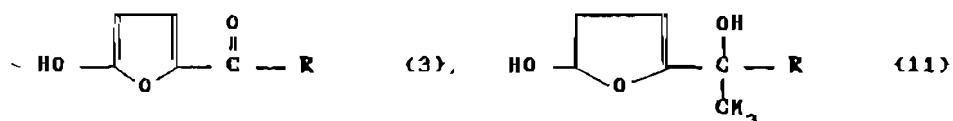
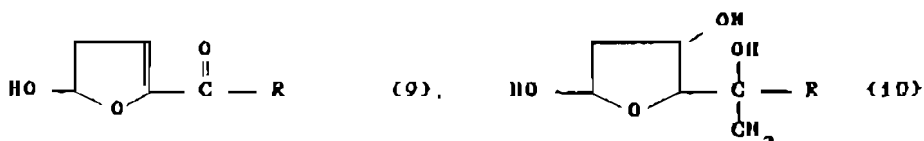
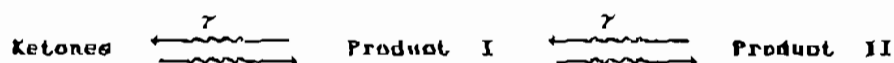
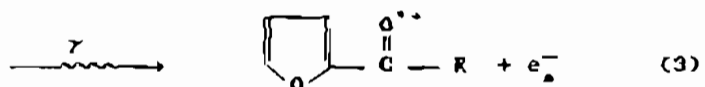
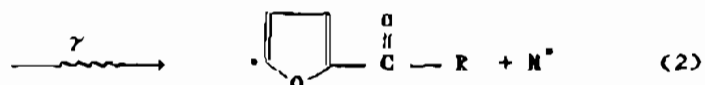


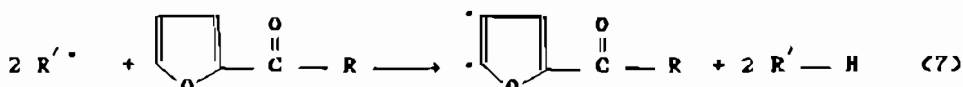
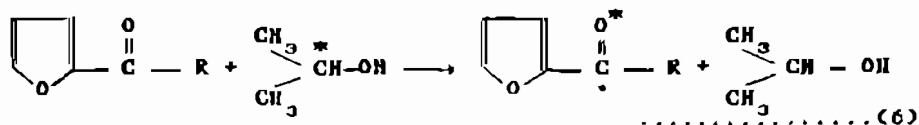
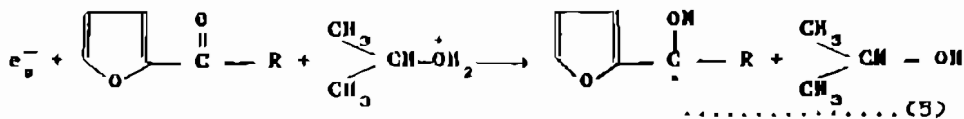
Table (1) shows the radiation yields (G) of some radiolytic products for some studied 2-furanyl ketones in 2-propanol in absence or presence of atmospheric oxygen. As the concentration

of ketone decreases, the detected and measured radiolytic products decreases due to less concentration of ketone species. It was also found that the radiation yields (G) decreased as the absorbed dose increased. This may be interpreted as follows: At the beginning of radiolysis the concentration of the radiolytic product was null, therefore, the tendency to form radiolytic products was high at low doses, similar to ordinary reversible reactions. Consequently the rate of formation of radiolytic products may be higher at the beginning of radiolysis and decrease with the approach to the equilibrium state at higher doses. Moreover, the formed radiolytic products had a tendency in the irradiated medium to form other radiolytic products. This may be illustrated as follows:



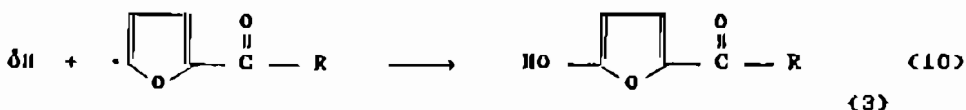
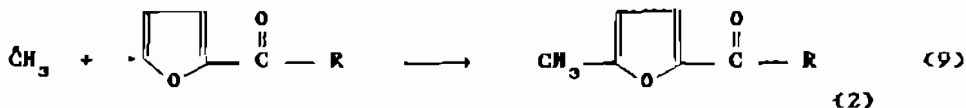
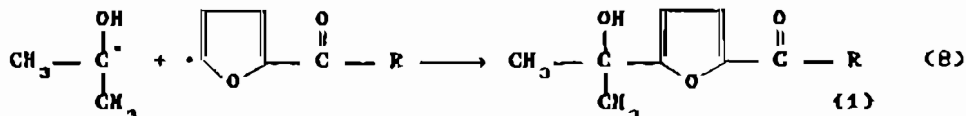
The main species that are formed from the radiolysis of 2-furanyl ketones - in the absence of atmospheric oxygen - according to the three mechanisms discussed before, may be illustrated as follows (21,29):

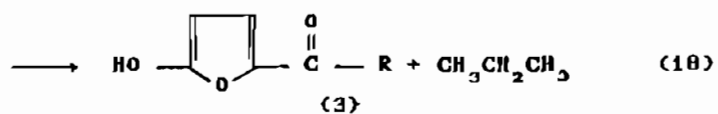
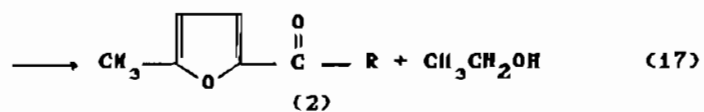
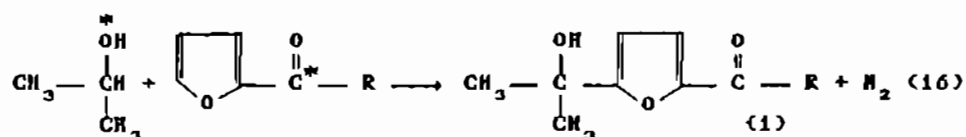
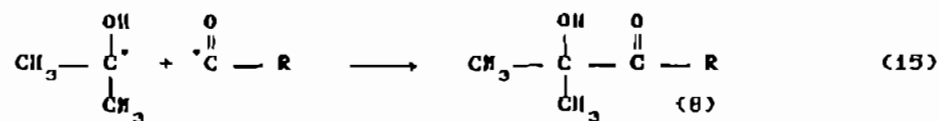
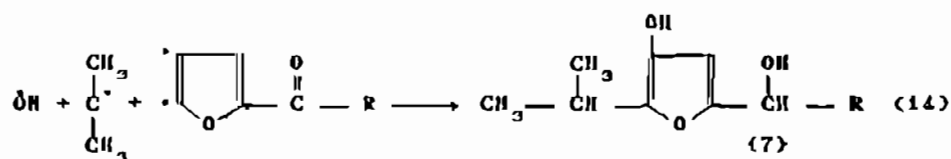
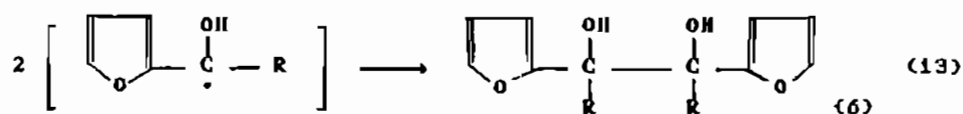
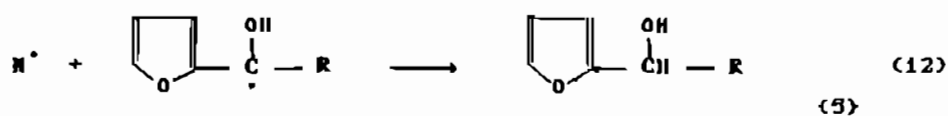
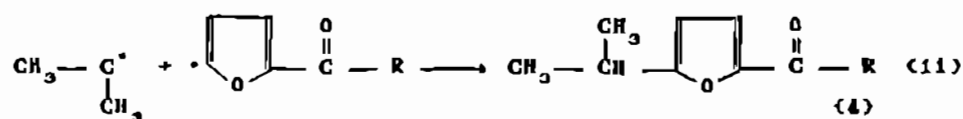


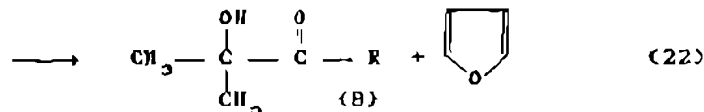
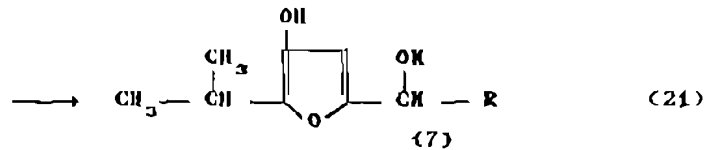
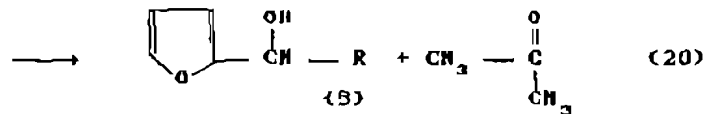
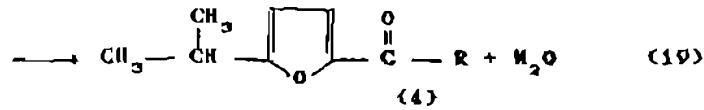


Where R' may be: H[•], [•]CH₃, [•]OH, $\begin{matrix} \text{CH}_3 \\ | \\ \text{C} - \text{OH} \\ | \\ \text{CH}_3 \end{matrix}$, $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH} - \delta \\ | \\ \text{CH}_3 \end{matrix}$, $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH} - \text{OH} \\ | \\ \text{CH}_3 \end{matrix}$

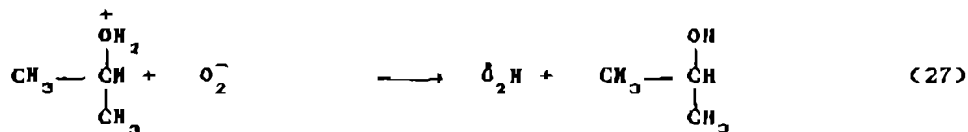
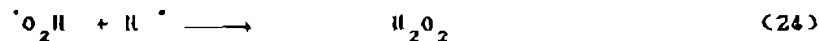
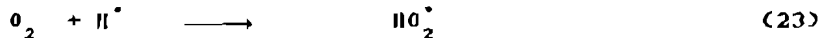
Therefore the formation of radiolytic products during radiolysis of 2-furanyl ketones in 2-propanol (in absence of atmospheric oxygen) which were indicated before (numbered from 1 to 8) may be interpreted as a result of interaction between species from 2-propanol and those formed from ketones according to the following equations [22,23,25,26,29] :







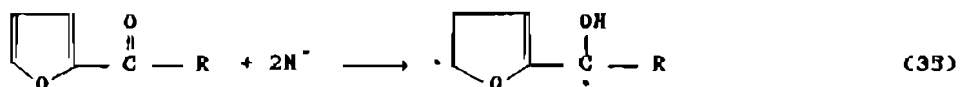
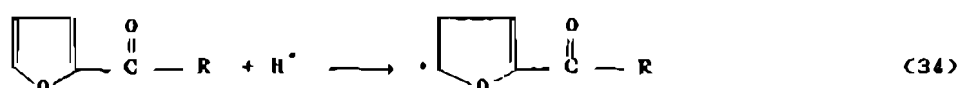
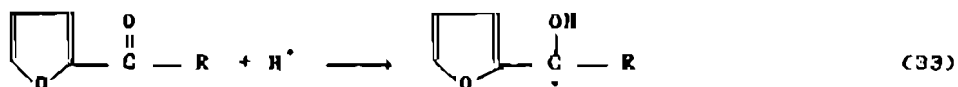
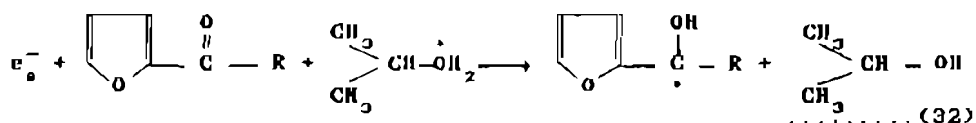
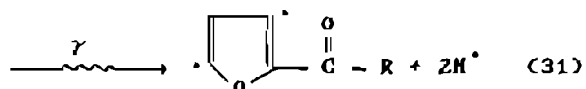
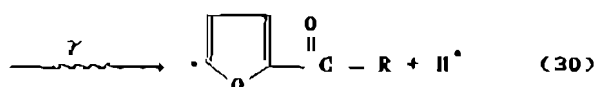
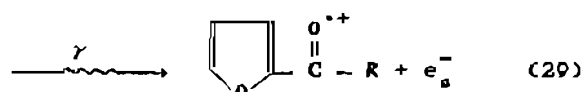
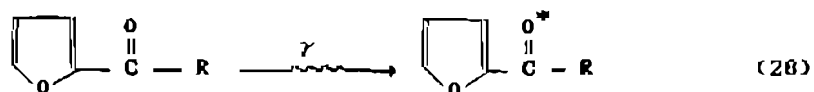
In the presence of atmospheric oxygen, the hydrogen radicals and solvated electrons that are produced during radiolysis of 2-propanol may be scavenged according to the following reactions [24]:

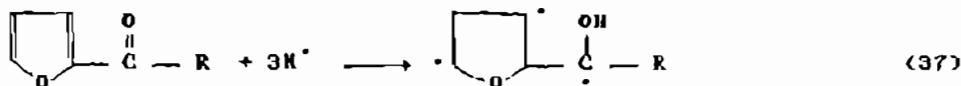
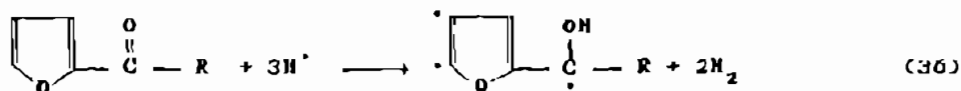


In the presence of atmospheric oxygen, the principal formed radicals as a result of radiolysis of 2-propanol are those formed in absence of oxygen in addition to those given in equation (23-27). The presence of atmospheric oxygen increases the

tendency of formation of hydroxyl radicals. Similar results for radiolysis of polar solutions found that the presence of oxygen increases the formation of hydroxyl radicals (37-47).

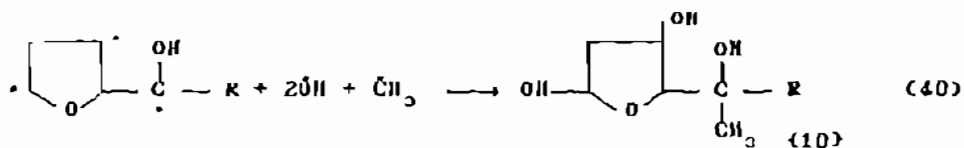
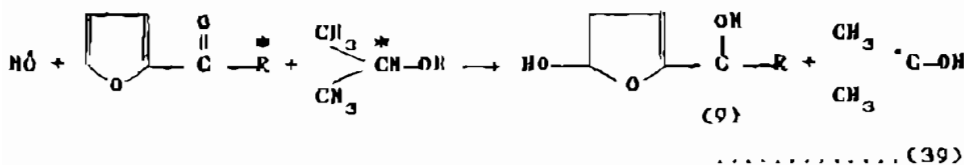
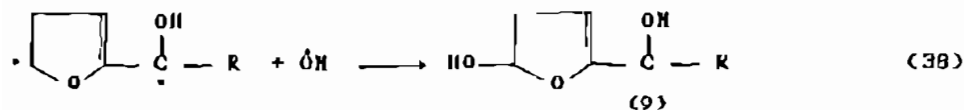
The main formed species during radiolysis of 2-furanyl ketones in 2-propanol in the presence of atmospheric oxygen through the different noted mechanisms may be shown via the following equations (21-24).

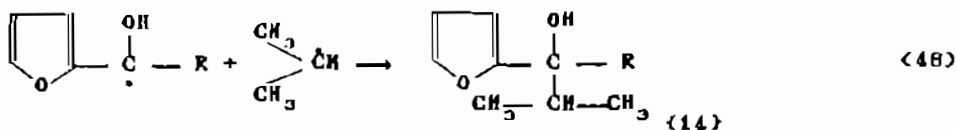
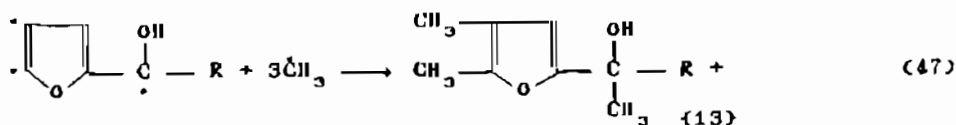
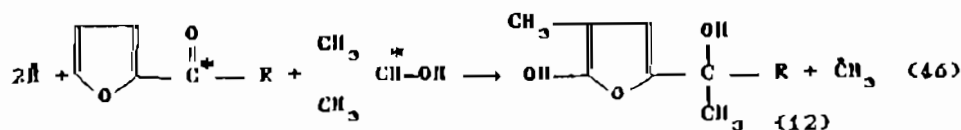
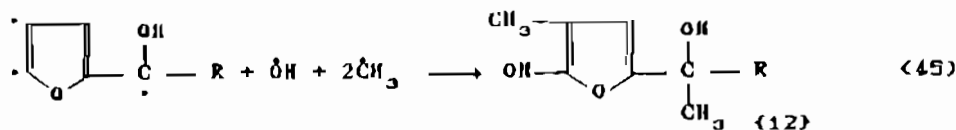
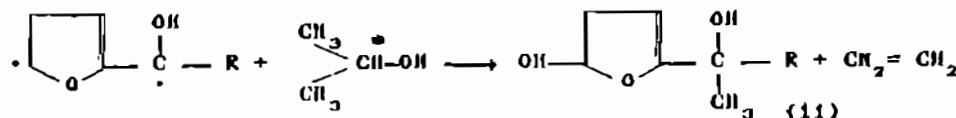
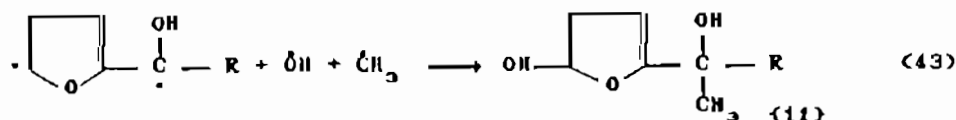
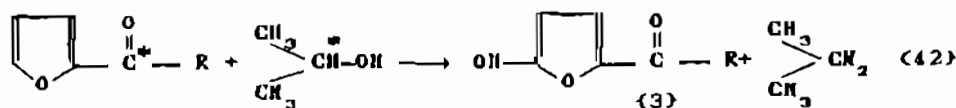
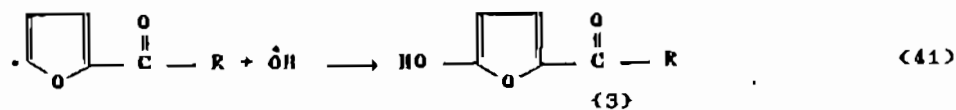


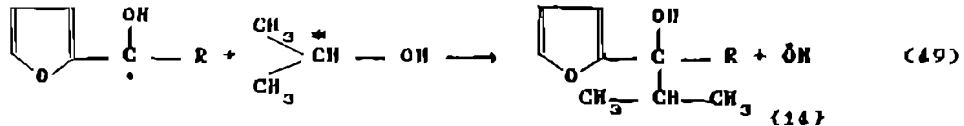


Similar species were formed during γ -radiolysis of five-membered heterocyclic compounds in acidic and basic media [15-20].

The formation of radiolytic products due to γ -irradiation of solution of 2-furanyl ketones in 2-propanol (in the presence atmospheric oxygen) may be interpreted as due to the interaction of species formed from those ketones that represented by the equations (34-42) and those of 2-propanol that represented by equations (1-5, 29-33) through the three noted mechanisms (free radical, electron-capture and excited state mechanisms). Therefore, the formation of radiolytic products (in the presence of atmospheric oxygen) may be represented by the following reactions:







As shown in the free radical mechanisms, the radiolytic products were formed as a result of interaction between radicals formed from 2-propanol and ketones during radiolysis. The nature of these radicals depends upon presence or absence of the atmospheric oxygen. Similar mechanisms were given elsewhere [48,49].

In the electron capture mechanism, the carbonyl group (C=O) of 2-furanyl ketones and the oxygen molecules scavenge the formed solvated electrons (e_s^-) to form anions. These anions attract hydrogen ions to form active radicals which react with hydrogen and other radicals forming hydroxy radiolytic products. Therefore, this mechanism interprets, clearly, the reduction of ketones to their corresponding alcohols and pinacols in the medium when atmospheric oxygen is present [21,37-47]. The proposed mechanisms by electron capture mechanism in this study are in accordance with that suggested elsewhere [11,48].

In the participation of excited state mechanism, the excited molecules of solvent or ketones interacted to produce either principal radicals or final product. The excited molecules of solvent or ketone may react with other excited species in the medium to produce final products that were detected in the medium. Similar mechanisms of participation of the excited state were suggested by several authors to form similar radiolytic products [27,28,48,49].

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