THE GAMMA—RAY—INDUCED RADIOLYSIS
OF PROPIONALDEHYDE IN THE LIQUID PHASE

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The gamma-ray-induced decomposition of propionaldehyde has been investigated. Products formed during the decomposition and their G-values were determined. To obtain more information about the role of the secondary processes of the radiolysis, the following factors were also investigated: (a) changes in the G-values of the products as a function of dose intensity, (b) concentration of the initial substance, (c) time of irradiation, and (d) the inhibiting effect of iodine and nitric oxide.

On the basis of experimental results it could be established that the decomposition takes place according to a chain mechanism, where, in certain steps, free radicals are involved. Increasing the dose, the role of the elementary steps involving free radicals becomes more dominant than that of the molecular steps.

Introduction

One of the fundamental problems in radiation chemistry is the elucidation of the role of primary processes in the determination of the mechanism of a given process. Some authors suggest the possibility of an ionic mechanism, according to others, however, it is the free radical mechanism that dominates. On the basis of recent results [1, 2, 3] the products obtained in the radiolysis of organic compounds were identical both qualitatively and near-quantitatively with those produced by photolysis. As is well known, the classical free radical reactions can be brought about also by irradiation and the effect of the inhibitors on these reactions is also similar in most cases.

In this laboratory the thermal decomposition and photolysis of several organic compounds have been studied. In connection with these investigations the radiolysis of propionaldehyde has been studied in the liquid phase in the presence and absence of nitric oxide and iodine as radical scavengers. The main purpose of these experiments was to get information about the role of free radicals produced by the radiolysis as well as to find out which elementary steps they are involved in. The result of these experiments is summarized in the present paper.
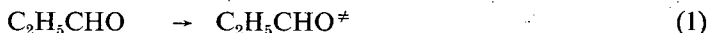
Experimental

Propionaldehyde was separated from impurities by subjecting it to repeated fractionated distillation under vacuum at low temperature. The purity of the propionaldehyde obtained in this manner was checked by gas chromatography. The pure propionaldehyde was introduced into a bottle kept in a dark place under vacuum. For the purpose of irradiation a given amount of propionaldehyde was transported from this container to the sample tubes, sealed off and kept at the temperature

of liquid air. When a gaseous radical scavenger was used the gas was let in at the appropriate pressure before sealing the sample tube containing the propional-dehyde. For the irradiation of the samples a 353 curie ^{60}Co source was used. The effect of the doses was determined by the method of FRICKE [4] and it varied between 1—3,7·10^5 rad/h.
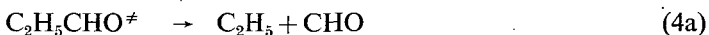
Having irradiated the samples, they were opened under vacuum and the gaseous products were separated from the liquid ones by means of a Toepler pump at $-110\,°C$. The gas analysis was carried out at 50 °C by a Carlo Erba Fractovap gas chromatograph Mod. C, fitted with a thermal conductivity detector, using a column filled with silica gel and Helium as carrier gas. The liquid products were analysed at 80 °C using a flame ionization detector and a column filled with Poly-ethyleneglycol supported on fire brick, and nitrogen as carrier gas.

Results

Experiments carried out so far by different authors in connection with the radiolysis of aldehyde were chiefly concerned with the determination of the main products only. PATRICK and BURTON [5], investigating the radiolysis of propional-dehyde, found carbon monoxide, ethane, and hydrogen as main products. On the basis of the products formed, they concluded that the mechanism of the radiolysis of propionaldehyde is essentially the same as that of its photochemical decomposition. They assumed, on the basis of works carried out by others [6, 7, 8, 9, 10], that the primary steps in this process are the formation of different excited molecules,

$$C_2H_5CHO \quad \rightarrow \quad C_2H_5CHO^{\neq} \tag{1}$$

being able to decompose in various ways

$$C_2H_5CHO^{\neq} \quad \rightarrow \quad C_2H_4 + H_2CO \tag{2}$$

$$H_2CO \quad \rightarrow \quad H_2 + CO \tag{2a}$$

$$C_2H_5CHO^{\neq} \quad \rightarrow \quad CH_4 + CH_2CO \tag{3}$$

$$C_2H_5CHO^{\neq} \quad \rightarrow \quad CH_3 + CH_2CHO \tag{3a}$$

$$C_2H_5CHO^{\neq} \quad \rightarrow \quad C_2H_6 + CO \tag{4}$$

$$C_2H_5CHO^{\neq} \quad \rightarrow \quad C_2H_5 + CHO \tag{4a}$$

This assumption was also supported later by KERR [11, 12].

On the basis of the investigations of these authors the role of the elementary steps involving radicals could not exactly be determined. Therefore, during the experiments carried out in our laboratory we tried to determine all the other possible products besides the primary ones; thus, in addition to carbon monoxide, ethane, hydrogen as main gaseous products the presence of trace amounts of methane, ethylene propane and butane could be observed. Regarding other products in the liquid phase, formaldehyde, acetaldehyde, methyl-ethyl ketone, diethyl ketone, iso-butyl alcohol, iso-amyl alcohol and polymer products could be identified. In our experiments only the following products were analysed quantitatively: carbon monoxide, ethane, hydrogen, ethylene, methyl-ethyl ketone, diethyl ketone, iso-butyl alcohol and iso-amyl alcohol. The other products could be determined

only qualitatively because of the small conversion. The quantitative determination of methane was difficult due to the high yield of carbon monoxide present.

Changes in the G-values of the main products have been plotted against doses applied. The results can be seen in Fig. 1 and Fig. 2, as well as in Table I.
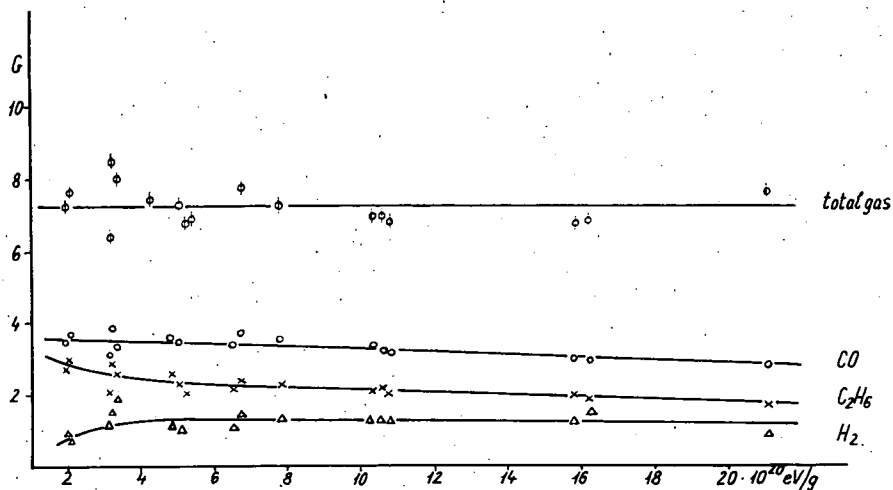

Fig. 1. Changes in the G-values of the total gas-, and the main gaseous products as a function of doses applied

The G-value of the total gaseous products as a function of dose does not seem to show any change within experimental error. Concerning the changes in the G-values of the various products shown in Fig. 1 and Fig. 2 the following can be
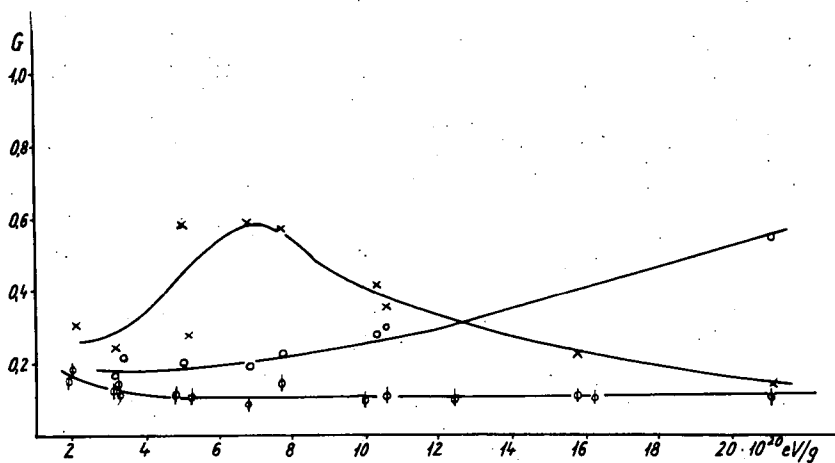

Fig. 2. Changes in the G-values of the main liquid products (methyl ketone (○), iso-butanol (×)), and those of $G_{C_2H_4}$ (∅) as a function of doses

Table I

G-Values of products at different doses

Dose in eV/g	G-Values/number of molecules formed (100eV absorbed)					
	CO	C_2H_6	H_2	C_2H_4	C_3H_8	total gas
$1,928 \cdot 10^{20}$	3,477	2,700	0,932	0,153	not anal.	7,263
$2,003 \cdot 10^{20}$	3,640	2,995	0,762	0,187	not anal.	7,568
$3,180 \cdot 10^{20}$	3,020	1,978	1,170	0,127	not anal.	7,586
$3,260 \cdot 10^{20}$	3,372	2,568	1,128	0,114	not anal.	7,382
$4,817 \cdot 20^{20}$	3,614	2,582	1,125	0,116	not anal.	7,438
$5,004 \cdot 10^{20}$	3,433	2,273	1,042	0,086	not anal.	7,219
$6,477 \cdot 10^{20}$	3,534	2,148	0,825	0,068	not anal.	6,394
$6,677 \cdot 10^{20}$	3,880	2,400	1,584	0,071	not anal.	7,936
$7,718 \cdot 10^{20}$	3,549	2,295	1,365	0,158	not anal.	7,368
$10,545 \cdot 10^{20}$	3,233	2,242	1,338	0,119	not anal.	6,932
$15,818 \cdot 10^{20}$	2,967	2,005	1,325	0,115	not anal.	6,412
$16,192 \cdot 10^{20}$	2,923	1,880	1,076	0,099	not anal.	6,609
$21,091 \cdot 10^{20}$	2,845	1,635	0,691	0,096	0,316	7,728
	methyl-ethyl--ketone		diethyl--ketone		i-butyl--alcohol	i-amyl--alcohol
$2,003 \cdot 10^{20}$	0,614		0,016		0,971	0,063
$3,180 \cdot 10^{20}$	0,132		0,002		0,318	0,016
$3,210 \cdot 10^{20}$	0,238		0,002		0,236	0,016
$5,004 \cdot 10^{20}$	0,206		0,003		0,617	0,002
$5,148 \cdot 10^{20}$	0,494		0,003		0,263	0,021
$6,677 \cdot 10^{20}$	0,257		0,005		0,656	0,037
$7,718 \cdot 10^{20}$	0,222		0,006		0,572	0,038
$10,545 \cdot 10^{20}$	0,308		0,009		0,358	0,044
$15,818 \cdot 10^{20}$	0,416		0,011		0,220	0,050
$21,091 \cdot 10^{20}$	0,548		0,015		0,137	0,061

noticed: (*a*) the G values of hydrogen and ethylene are nearly constant at greater dose values, while (*b*) carbon monoxide and ethane show only a slight decrease. This, however, is compensated, at greater doses, by the appearance of propane in an appreciable amount, which was detectable only in traces in the case of small doses.

Fig. 2 shows the changes in the G-values of the two main products, namely those of methyl ketone and iso-butanol as a function of dose. One has to mention that the changes in the G-values of diethyl ketone and iso-amyl alcohol show a similar curve to that obtained for methyl-ethyl ketone; however, their G-values are smaller by 1 and 2 orders of magnitude respectively.

Changes in the G-values of the aldehyde decomposed were also plotted against various dose intensities. These are illustrated in Fig. 3.

The G-values of the aldehyde decomposed are approximately ten-fold of what could be expected on the basis of the G-values of the products. This enormous difference can possibly be attributed to the formation of polymers of considerable amount. Polymers of various degree of polymerization of the aldehyde were found

by carrying out the analysis of the samples. Some of the light polymers could be identified by gas chromatography; the heavier ones were observed at the bottom of the sample tube in the form of white crystals. The decrease in the G-values of CH_3CH_2CHO observed with the increase of dose cannot really be explained on the basis of the data obtained by the analysis of the products. This has also been observed by other authors in the radiolysis of different organic compounds and interpreted by the assumption that at higher doses the deactivation of the excited aldehyde molecule is rather considerable.
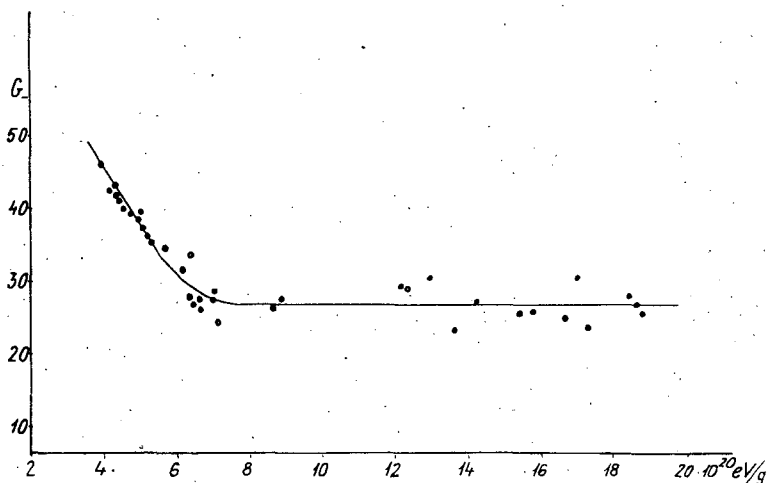
Fig. 3. Changes in the G-values of aldehyde decomposed as a function of doses
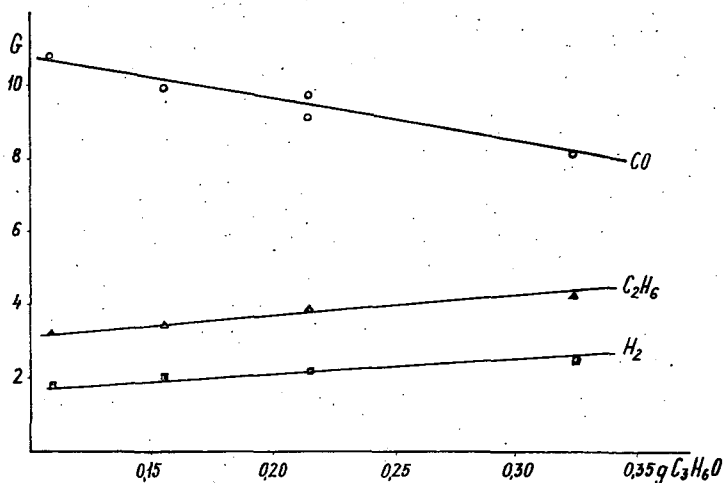
Fig. 4. Changes in the G-values of the main products as a function of initial concentration of propionaldehyde

Changes in the G-values of the products as a function of the concentration of aldehyde are shown in Fig. 4. G-values of ethane and hydrogen show a near identical increase, and this fact supports the assumption that the decomposition of propionaldehyde shows no change in quality as the concentration of aldehyde varies; it is only the number of molecules decomposed that increases proportionally, as the number of molecules absorbing the energy of irradiation increases. (see Fig. 5.)
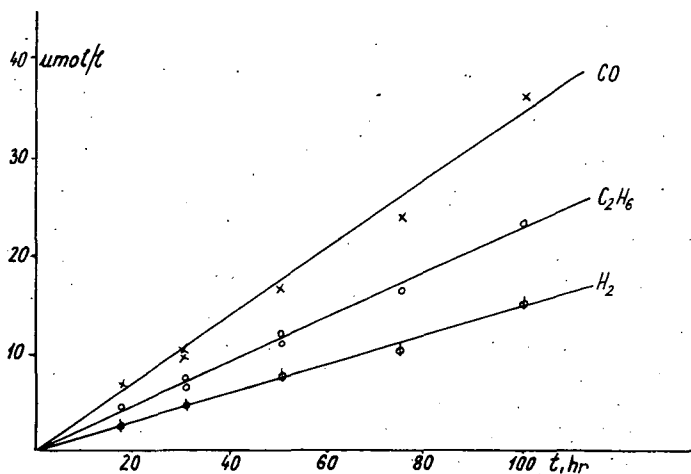

Fig. 5. Changes in the yield of the main gaseous products as a function of irradiation time (at $3,38 \cdot 10^5$ rad/hr dose intensity)

Plotting the G-values of the products against the time of irradiation the result is almost always a straight line; this is not found so only in the case of very small doses of irradiation. (See Fig. 6 and Fig. 7.) In order to explain this finding it has been assumed that, in the range of lower doses, the space distribution of the activated particles (radicals, ions, atoms) formed at the irradiation of the initial substance is more favourable from the point of view of some of the secondary reactions.

In connection with the radiolysis of hydrocarbons it is almost generally assumed that the hydrogenation of unsaturated compounds by thermal hydrogen atoms in this dose range occurs throughout the volume, not in the spurs. The other dominant elementary reaction claimed in this dose range is the abstraction of a hydrogen atom from the parent molecule

$$RH + H \rightarrow H_2 + R$$
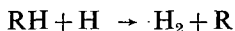
Effect of iodine on the radiolysis of propionaldehyde

The applicability of iodine as a radical scavenger is accounted for by the fact that it can easily react with free radicals without requiring any activation energy. Thus, it fundamentally alters the role of free radicals in a given process, manifesting its overall effect in inhibition. The inhibiting effect of iodine under constant total dose was investigated by altering the concentration of iodine in the range of 10^{-3} to

10^{-1} mol/l. Changes in the G-values of gaseous products as an effect of various iodine concentration can be seen in Fig. 8 and Fig. 9. Since in the presence of iodine the yield of carbon monoxide is greatly decreased, methane could also be determined quantitatively and its changes are shown in Fig. 9.
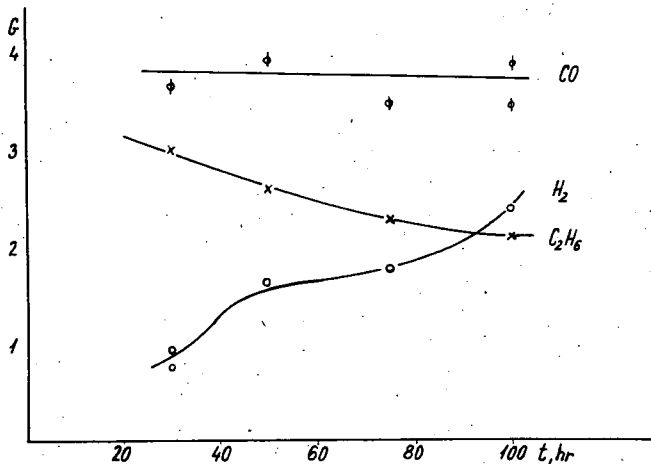

Fig. 6. Changes in the G-values of the main products as a function of irradiation time (at $1,07 \cdot 10^5$ rad/hr dose intensity)
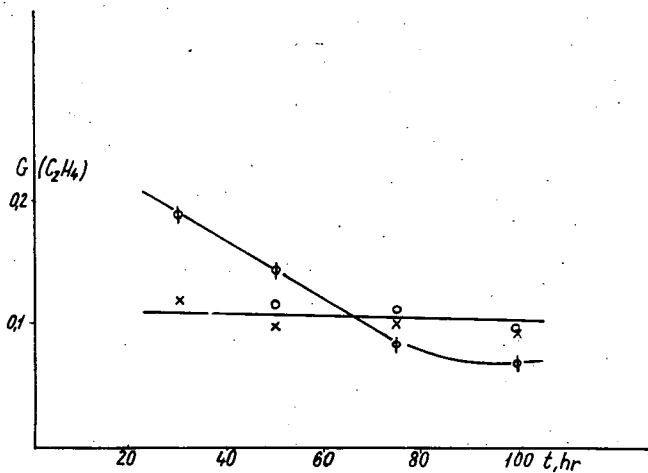

Fig. 7. Changes in the G-values of ethylene as a function of irradiation time ($\varnothing$: 10,7; o: 1,65; $\times$: $3,68 \cdot 10^5$ rad/hr dose intensity)

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The inhibiting effect of iodine in the case of the radiolysis of propionaldehyde manifests itself in the fact that it can easily react with radicals R, RCO, and H,
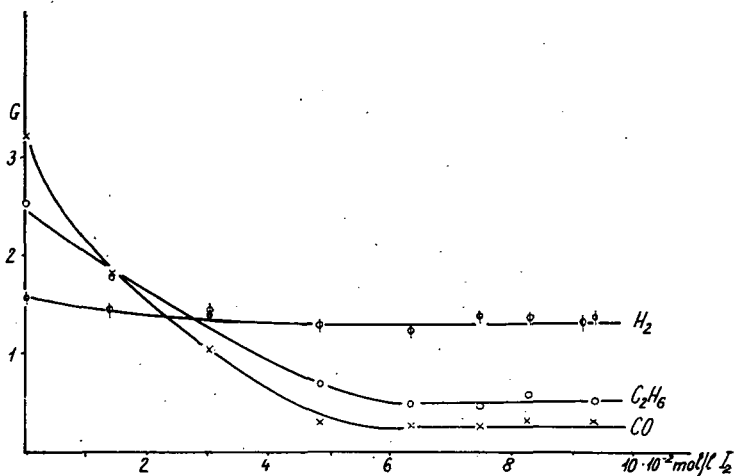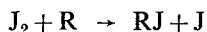
$$J_2 + R \rightarrow RJ + J$$

Fig. 8. Changes in the G-values of the main products as a function of the concentration of iodine
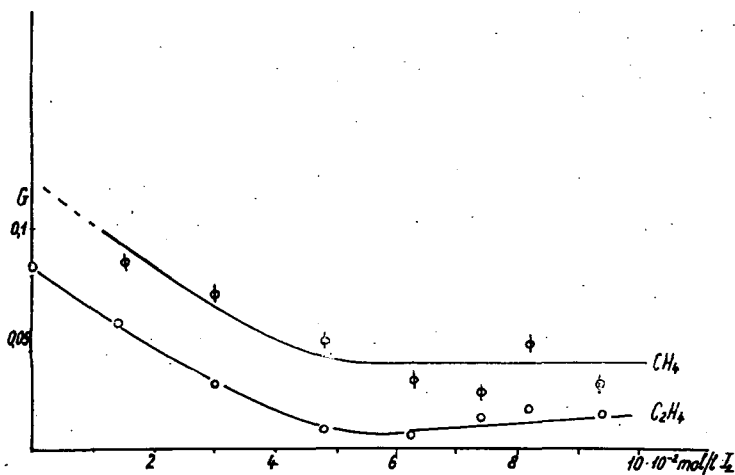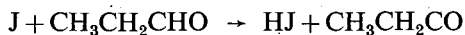

Fig. 9. Changes in the G-values of methane and ethylene as a function of the concentration of iodine

Moreover, one has to take into consideration the hydrogen atom abstraction by the iodine atoms,

$$J + CH_3CH_2CHO \rightarrow HJ + CH_3CH_2CO$$

From the hydrogen iodide formed it may be assumed that the formation of hydrogen is the only possible way for a reaction and thus the decrease in the yield of hydrogen is not so considerable. The iodine atom-stabilized RCO radicals of lower reactivity disappear in recombination reactions producing ketones. For the liquid products only qualitative analysis was carried out in the presence of iodine. It was observed that the yield of ketone increased considerably, while that of the other products did not change essentially.

Effect of NO on the radiolysis of propionaldehyde

By increasing the concentration of nitric oxide, the values of G of the products are decreased (see Fig. 10), since nitric oxide reacts with radicals H and R producing
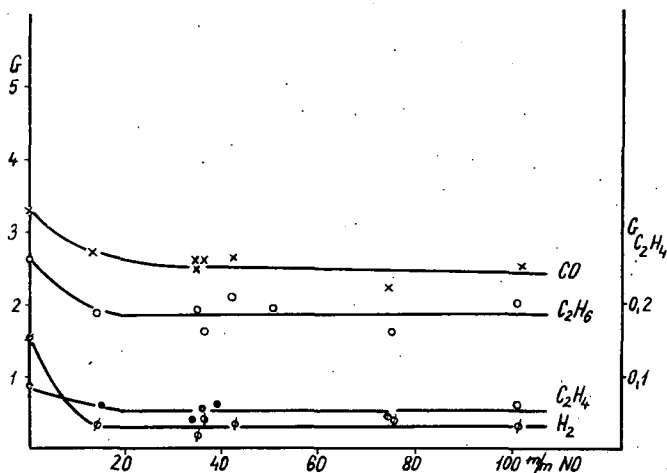

Fig. 10. Changes in the G-values of the main gaseous products as a function of the concentration of nitric oxide

HNO and RNO radicals respectively. As a result of the recombination of HNO radicals, nitrous oxide and water are formed instead of hydrogen. Consequently it can be understood why the yield of hydrogen decreases to a greater extent in this case than in the presence of iodine. RNO radicals can further produce methane, ethane by abstracting hydrogen atoms, and, therefore, no considerable decrease in the yield of these products occurs. Out of the liquid products only the polymers showed some change, namely they increased as the concentration of nitric oxide was increased. The inhibiting effect of nitric oxide is summarized in Table II.

Discussion

Gaseous products formed during the radiolysis of propionaldehyde are almost identical with those produced by thermal decomposition. A similarity can mainly be observed in connection with the main products. Ethane and carbon monoxide are the main products both in the case of radiolysis and thermal decomposition

Table II

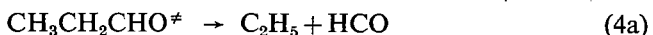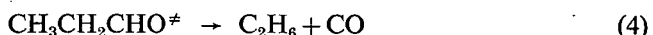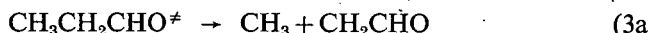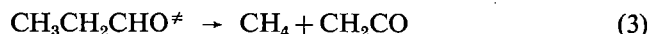*Products of the Radiolysis of Propionaldehyde*

Conditions	G-Values/number of molecules formed (100eV absorbed)						
	H_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4H_{10}
Pure C_2H_5CHO	1,58	3,23	0,118	2,52	0,083	0,01	0,01
$C_2H_5CHO + NO$	0,32	2,50	—	1,82	0,054	0,01	0,01
$C_2H_5CHO + J_2$	1,36	0,28	0,036	0,557	0,028	0,01	0,01

of propionaldehyde [13]. Therefore, it can be assumed that, in the case of liquid-phase radiolysis too, the products are formed mainly in chain reactions involving free radicals. This assumption seems to be substantiated by the experimental fact that the yield of products formed showed a decrease in the presence of radical scavengers applied.

As a primary step, the formation of an excited molecule can be considered. According to the MAGEE hypothesis [14] these molecules are excited to various states of energy by the radiation
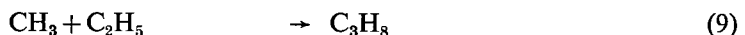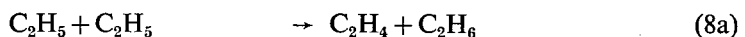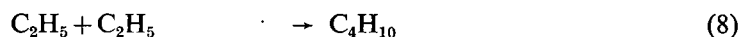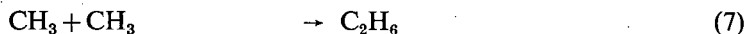
$$CH_3CH_2CHO \quad \rightarrow \quad CH_3CH_2CHO^{\neq} \tag{1}$$

being able to decompose in different ways

$$CH_3CH_2CHO^{\neq} \rightarrow C_2H_4 + H_2CO \tag{2}$$

$$H_2CO \quad \rightarrow \quad H_2 + CO \tag{2a}$$

$$CH_3CH_2CHO^{\neq} \rightarrow CH_4 + CH_2CO \tag{3}$$

$$CH_3CH_2CHO^{\neq} \rightarrow CH_3 + CH_2CHO \tag{3a}$$

$$CH_3CH_2CHO^{\neq} \rightarrow C_2H_6 + CO \tag{4}$$

$$CH_3CH_2CHO^{\neq} \rightarrow C_2H_5 + HCO \tag{4a}$$
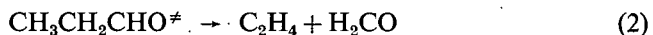
On the basis of results obtained with the photolysis of propionaldehyde [7, 8] it can be established that steps (3) and (3a) as well as steps (4) and (4a) are simultaneous steps of the decomposition, having identical kinetic features, and all are to be taken into consideration. If, however, products were formed only in this way, the formation of liquid products and that of propane and butane could not be interpreted and neither could the dependence of the products on doses and the effect of the inhibitor. Therefore, the additional reactions of the radicals formed in the primary steps must also be taken into consideration.

Methyl and ethyl radicals formed in reaction steps (3a) and (4a) can enter into a recombination reaction or abstract hydrogen from the parent molecule as follows

$$CH_3 + CH_3CH_2CHO \quad \rightarrow \quad CH_4 + CH_3CH_2CO \tag{5}$$

$$C_2H_5 + CH_3CH_2CHO \quad \rightarrow \quad C_2H_6 + CH_3CH_2CO \tag{6}$$

$$CH_3 + CH_3 \quad \rightarrow \quad C_2H_6 \tag{7}$$

$$C_2H_5 + C_2H_5 \quad \rightarrow \quad C_4H_{10} \tag{8}$$

$$C_2H_5 + C_2H_5 \quad \rightarrow \quad C_2H_4 + C_2H_6 \tag{8a}$$

$$CH_3 + C_2H_5 \quad \rightarrow \quad C_3H_8 \tag{9}$$
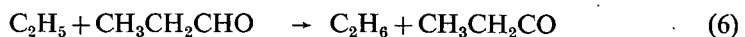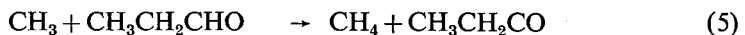
The occurrence of reaction step (9) is much more likely than that of step (7) or (8), which is proved by the increasing yield of propane. Both radicals can enter into reaction with the ethylene formed in step (2), requiring an activation energy of 4—7 Kcal/mol,
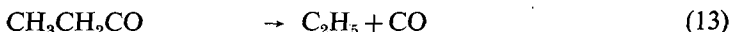
$$CH_3 + C_2H_4 \rightarrow C_3H_7 \tag{10}$$

$$C_2H_5 + C_2H_4 \rightarrow C_4H_9 \tag{11}$$
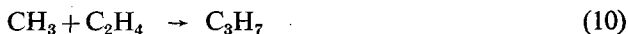
Hydrogen can be formed not only in molecular step (2a), but also by the decomposition of radicals CH_2CHO and CHO formed in steps (3a) and (4a) respectively.
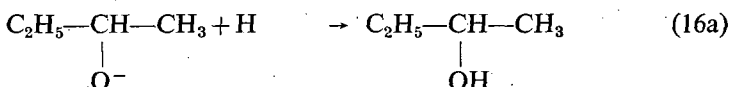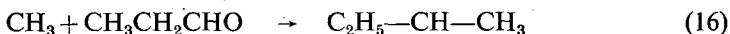
The radical CH_2CHO may produce acetaldehyde, too, in a secondary reaction

$$CH_2CHO + CH_3CH_2CHO \rightarrow CH_3CHO + C_2H_5CO \tag{12}$$

The radical CH_3CH_2CO may decompose, but it is more likely that it reacts with radical R producing ketone

$$CH_3CH_2CO \qquad \rightarrow C_2H_5 + CO \tag{13}$$

$$CH_3CH_2CO + CH_3 \rightarrow CH_3CH_2COCH_3 \tag{14}$$

$$C_2H_5 + CH_3CH_2CO \rightarrow (CH_3CH_2)_2CO \tag{15}$$

The radicals R may possibly enter into reaction with the aldehyde molecule according to the following reaction steps, too

$$CH_3 + CH_3CH_2CHO \rightarrow C_2H_5\!-\!\overset{\displaystyle |}{\underset{\displaystyle O^-}{CH}}\!-\!CH_3 \tag{16}$$

$$C_2H_5\!-\!\overset{\displaystyle |}{\underset{\displaystyle O^-}{CH}}\!-\!CH_3 + H \rightarrow C_2H_5\!-\!\overset{\displaystyle |}{\underset{\displaystyle OH}{CH}}\!-\!CH_3 \tag{16a}$$

With a similar reaction the ethyl radical can produce iso-amyl radical.

In Fig. 1 and Fig. 2 changes in the G-values of the products can be seen as a function of doses applied. The decrease of ethane is compensated by approximately the same amount of increase in hydrogen. However, the decreasing of ethane cannot be explained by the fact that it decomposes to hydrogen and ethylene, since, while this explanation would be acceptable as regards the hydrogen, it could not be accepted for the ethylene, because the latter decreases. This decreasing of ethane, as the dose increases, can presumably be attributed to the fact that the minor part of the ethyl radicals formed in step (4a) is converted to ethane since the reactions of the ethyl radicals with methyl-, and C_2H_5CO radicals are much more favoured. This is supported by the fact that the amount of liquid products and that of propane increases with increased doses. In addition, it must also be taken into consideration that only the minor part of the radical C_2H_5CO results in an ethyl radical; the major part of it becomes a liquid product. On the whole, all these processes are unfavourable for the formation of ethane. The G-value of ethane decreases by 0,8, while the amount of propane, methyl-ethyl ketone and that of iso-butanol increases. The material balance of these processes is as follows:

$$-\Delta G C_2H_6 \cong \Delta G(C_3H_8) + \Delta G(CH_3COC_2H_5) + \Delta G \text{ (iso-butanol)}$$

$$0,8 \cong \quad 0,32 \quad + \qquad 0,3 \quad + \quad 0,3$$

The decrease in the G-values of carbon monoxide is 0,6, which is compensated by the increase in the G-values of the liquid products

$$-\Delta G(CO) \cong \Delta G[CH_3COC_2H_5] + \Delta G(\text{iso-butanol})$$

$$0,6 \quad \cong \quad 0,3 \quad + \quad 0,3$$

The observed effect of the different dose intensities on the yield of various products can only be interpreted by assuming that, as the dose is increased, the role of the processes involving radicals becomes more important. So, for example, the growing importance of reaction step (3a) is indicated by the increased yield of propane on the one hand. Another such proof is the formation of C_2H_4 by the recombination of CH_2 radicals formed by the decomposition of radical CH_2CHO, ensuring a near-constant G-value for ethylene when greater doses are used. The effect of the two inhibitors applied was not the same, which can be understood if their different reactivities towards the radicals are taken into consideration.

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РАДИОЛИЗ ПРОПИОНАЛЬДЕГИДА В ЖИДКОЙ ФАЗЕ СТИМУЛИРОВАННЫЙ ГАММА ИЗЛУЧЕНИЕМ

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Изучался процесс разложения пропиональдегида под влиянием ^{60}Со-гамма излучения. Были определены их Г-значения. Чтобы лучше раскрыть частичные процессы радиолиза изучались изменения Г-значений продуктов в зависимости от дозирования, концентрации исходного вещества и времени излучения, а также проследили ингибиторный эффект J_2 и No.

В свете экспериментальных данных выяснилось что разложение имеет место по цепному механизму в отдельных шагах которого принимают учатие свободные радикалы. Увеличивая дозы роль реакций имеющих место с участием свободных радикалов была намного больше чем та же молекулярных шагов.