

EFFECT OF LET ON THE RADIOLYSIS OF CYCLOPENTANE

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Received 4 June 1992

Accepted 10 June 1992

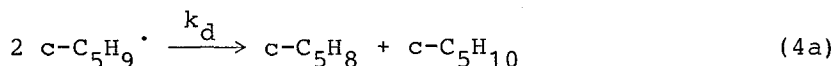
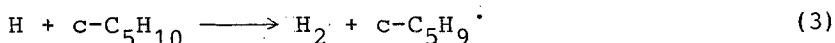
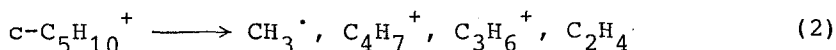
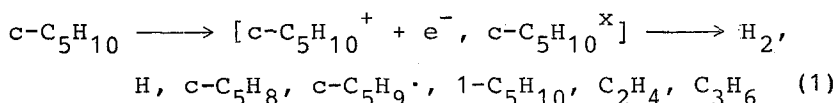
The γ - and α -radiolysis of cyclopentane were compared in the presence and absence of iodine scavenger. The G-values of the main hydrocarbon products, cyclopentene and bicyclopentyl are 2.22 and 0.56 molecule/100 eV in α -radiolysis and 3.25 and 1.23, respectively, in γ -radiolysis. During high LET α -irradiation the yields of products formed by a radical mechanism are much smaller ($G = 1.18$) than in γ -radiolysis ($G = 2.68$), whereas "unimolecular" cyclopentene formation is hardly influenced by LET ($G = 1.8$ and 1.6 , respectively).

INTRODUCTION

Although cyclohexane¹ is the most commonly investigated alkane in radiation chemistry, the reactions of cyclopentane irradiated with low ionization density (low linear energy transfer, LET) radiations have also often been studied and the product spectra published¹.

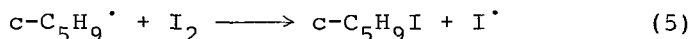
In liquid phase, primary chemical reactions of excited cyclopentane molecules (produced primarily or as

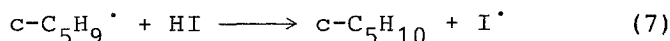
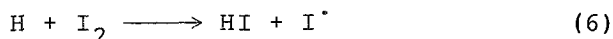
a result of electron-ion recombination) involve not only atomic and molecular eliminations of hydrogen, yielding cyclopentene and bicyclopentyl as end products [$G(\text{c-C}_5\text{H}_8) = 2.9\text{--}3.1$ and $G(\text{c-C}_5\text{H}_9)_2 = 1.2\text{--}1.3$], but also opening of the C_5 ring, resulting in 1-pentene ($G = 0.7$) and decompositions in ethene, propene and cyclopropane ring scission products [$G(\text{ring scission}) = 0.5$]. Ionic fragmentation also takes place with low yield ($G = 0.15$):



In the presence of iodine considerable decrease both in the cyclopentene and bicyclopentyl yields was found together with formation of cyclopentyl iodide in high yield. The G -values of the latter are 3.0 (dose 5 kGy^2), 2.6 (dose 10 kGy^3) or 1.95 molecule/100 eV (dose 50 kGy^4). By means of $^{14}\text{C}_2\text{H}_5\cdot$ radical sampling technique, Holroyd and Klein⁵ measured a cyclopentyl radical yield of 4.0.

The effect of iodine at low concentrations is radical scavenging:





In liquid cyclopentane, cyclopentyl radicals react with iodine in a diffusion controlled process⁶ ($k_5 = 1.9 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$), and the same is expected for scavenging of H atoms according to Reaction 6. At higher than 1 mmol dm^{-3} concentrations of iodine the interaction of iodine with cationic species of radiolysis should also be taken into account^{1,7}.

There are no data on the radiolysis of cyclopentane at high ionization density. In the radiolysis of cyclohexane using α -rays (average energy of 3 MeV, LET = 200 eV nm^{-1}) instead of γ -rays (average energy of 1.2 MeV, LET = 0.2 eV nm^{-1}), there is a considerable effect in the product distribution: the initial yields of dehydrogenation products become lower in neat cyclohexane and radical scavengers become less effective. These findings are explained in terms of competition of particle-particle reactions in the track (or its core) of ionizing particles and the diffusion of intermediates out (and back) of the track and their reaction in the bulk with the additive⁷.

EXPERIMENTAL

The cyclopentane used was a Fluka product. The LET-value of the 3 MeV effective average energy ^{210}Po α -radiation is ca. 200 and that of ^{60}Co γ -radiation 0.2 eV nm^{-1} . The doses were 2.5–5.5 kGy (250–550 krad). Other technical details are described elsewhere⁸.

RESULTS AND DISCUSSION

The G-values of cyclopentene and bicyclopentyl in γ -radiolysis of neat cyclopentane were found to be 3.25 and 1.23 molecule/100 eV in good agreement with most of the former results. In the presence of iodine, at the 5.3 kGy dose applied, the cyclopentene and bicyclopentyl yields decrease sharply below about 2 mmol dm^{-3} , however, with increasing additive concentration they tend to level off at constant values of $G = 1.8$ and 0.14 . The cyclopentyl iodide yield found in our experiments is $G = 3.4$ (Fig. 1). Applying this G-value, the iodine consumption is around 2 mmol dm^{-3} .

The change in the scavenging curve above ca. 2 mmol dm^{-3} iodine content is due to the fact that at the dose applied the iodine concentration is sufficient to scavenge practically all the radicals that escape the spur into the bulk even at the end of the irradiation. The slow decrease in the yield above this concentration of iodine is probably due to reactions of H atoms and the ionic type interactions with iodine mentioned earlier: these ionic type reactions, however, may play only a minor role in the diminishing of yields.

In Figure 1 we show the also the cyclopentyl radical yields calculated on the basis of the decrease of cyclopentene and bicyclopentyl yields in the presence of iodine: $G(\text{c-C}_5\text{H}_9^\bullet) = 2/(\Delta G(\text{c-C}_5\text{H}_8) + \Delta G(\text{c-C}_5\text{H}_9)_2)/\cdot$. These yields are higher than those of radicals giving cyclopentyl iodide. The maximal difference between the two curves is $G \approx 1.8$.

We suppose that the difference is basically due to H atom scavenging (Reaction 6) diminishing the probability of Reaction 3 and the subsequent H atom transfer (Reaction 7). The yield of scavengeable H atoms has

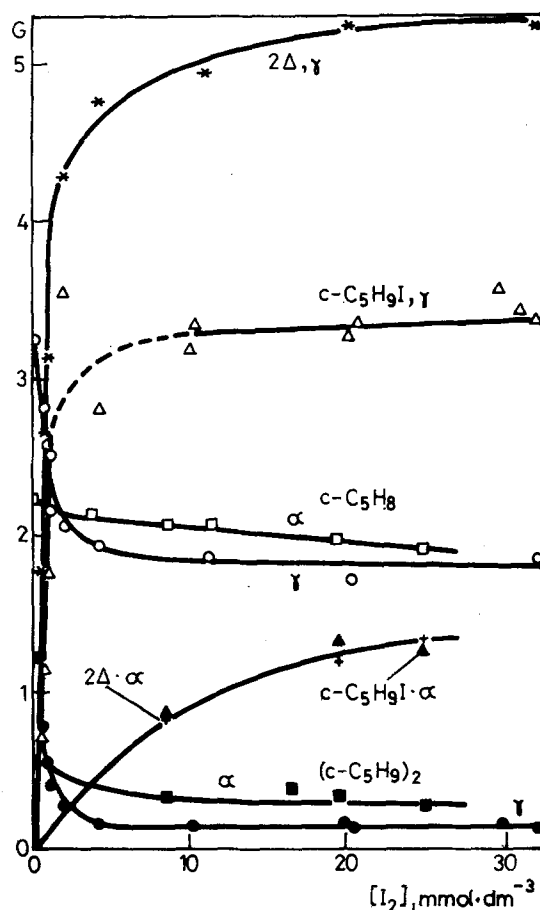
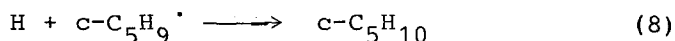


Fig. 1. G-values of cyclopentene, bicyclopentyl, cyclopentyl iodide and cyclopentyl radicals (2Δ , calculated on the basis of the decrease of yields in the presence of iodine) as a function of iodine concentration in α - and γ -radiolysis of cyclopentane

been reported to be between 1.6 and 1.96 and only in one work was it¹ 2.9 molecule/100 eV. The HI yield was found^{1,2,4} to be low ($G \approx 0.1$) due to Reaction 7.

In α -radiolysis of neat cyclopentane the cyclopentene and bicyclopentyl yields are much smaller (2.22 and 0.56

molecule/100 eV) than in γ -radiolysis, and the yields decrease less and more smoothly in the presence of iodine (Fig. 1). The limiting yields are around $G = 1.9$ and 0.3 , respectively. Here the cyclopentyl radical yields calculated on the basis of the decrease in dehydrogenation product G -values practically coincide with G -values of cyclopentyl iodide. This is probably due to the fact that under high LET conditions a considerable proportion of H atoms disappears in the back reaction in the spur (core):



Correspondingly, the number of H atoms available for reactions with iodine is considerably lower than in γ -radiolysis.

Another possible reason for the difference found between γ - and α -radiolysis can be the lower yield of H atoms at higher LET: this hypothesis will be described later in connection with triplet-triplet interactions.

In Figure 2 G -values of cyclopentene are plotted as a function of those of bicyclopentyl. Comparison of the slopes of the straight lines obtained in γ - and α -radiolysis indicates slightly different ratios of disproportionation to combination reactions, $k_d/k_c = 1.15$ and 1.05 . As an average, we accept 1.1 . The same ratio during γ -radiolysis in gas phase was found to be⁹ 0.73 , in aqueous solutions¹⁰ 1.4 , whereas formerly in liquid cyclopentane we found⁴ 1.0 .

The limiting dimer yields, according to the existing theories¹, are due to fast reactions of radicals formed in each other's neighborhood. Therefore, the intercepts of the straight lines with the ordinate can be taken as the yields of "unimolecularly" produced cyclopentene.

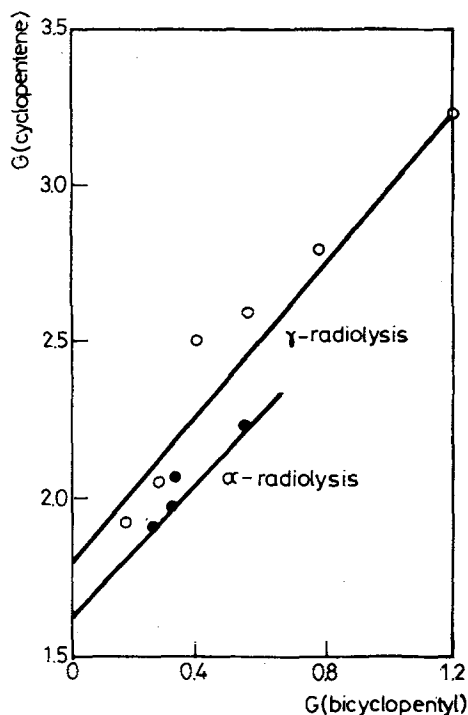


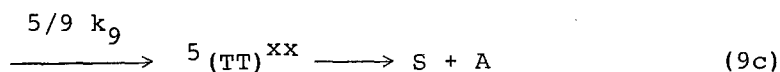
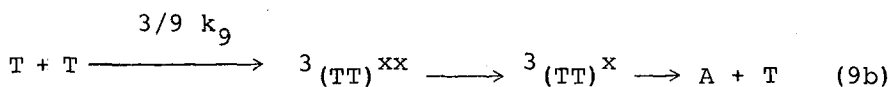
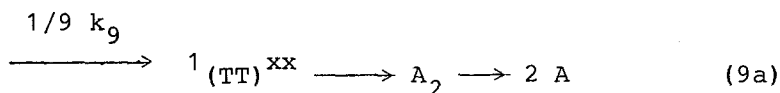
Fig. 2. $G(\text{cyclopentene})$ as a function of $G(\text{bicyclopentyl})$ in α - and γ -radiolysis of cyclopentane

There is only a slight difference in the G -values in γ - and α -radiolysis: $G(\text{c-C}_5\text{H}_8)_{\text{unimol.}} = 1.8$ and 1.6 , respectively. This result does not correspond with that of the $\text{C}_7\text{-C}_8$ -cycloalkanes^{8,11}, where changing from γ - to α -radiation the G -values of "unimolecular" alkene formation were found to decrease considerably, reflecting differences in the early physicochemical processes¹¹.

In contrast to the apparently uniform contribution of "unimolecular" dehydrogenation to product formation, the yield of dehydrogenation reaction by a radical mechanism differs considerably in γ - and α -irradiated

cyclopentane: $G(\text{C-C}_5\text{H}_8)_{\text{radical}} + G(\text{C-C}_5\text{H}_9)_2 = 1.45 + 1.23 = 2.68$ and $0.62 + 0.56 = 1.18$. This might be considered as evidence that the LET effect in α -irradiated cyclopentane manifests itself basically in the reduced yield of dehydrogenation through a radical mechanism.

The "unimolecular" alkene production is the typical decomposition channel of low energy singlet alkanes, whereas the radicals in radiolysis form, to a significant extent, in decomposition of triplet excited molecules¹². Although alkane triplet molecules are thought to be extremely short-lived, the direct triplet-triplet interaction in the track of high LET irradiation cannot be excluded. Saltiel and co-workers¹³ suggest nine spin states produced in the interaction of two triplet molecules which ultimately yield singlet (S), triplet (T) and ground state (A) molecules:



Such interaction can lead to dissipation of the triplet excitation energy without decomposition and to conversion of triplet molecules to singlet ones.

CONCLUSIONS

The effect of LET in the radiolysis of cyclopentene is similar to that found for cyclohexane. While the G-values of cyclopentene produced in "unimolecular" H_2 -elimination are close to each other under α - and γ -irradiation, there is a decrease in the efficiency of bicyclopentyl and cyclopentene formation through radical reactions in α -radiolysis. With increase of the ionization density (LET) the yields of processes giving radicals become smaller. This decrease can partly be due to deactivation of triplet molecules (the main source of radicals in radiolysis) through their direct interactions with each other.

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The authors wish to acknowledge the financial support of the Hungarian Research Fund (OTKA No. 1889).

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