Radiation Chemical Studies with Cyclotron Beams. IV. The Effect of Water in the Heavy-ion Radiolysis of Liquid Acetone

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A study was made of the effect of water on the LET dependence of the product yields for liquid acetone. Acetone containing 2 wt% water was subjected to irradiation by energetic ^{4}He, ^{12}C, and ^{14}N ions as well as by ^{60}Co γ rays at room temperature; the LET range was up to 80 eV Å^{-1}. A significant effect of water was observed above 50 eV Å^{-1}, where $G(H_2)$ and $G(CO)$ showed continuous increases with an increase in LET. For pure acetone, $G(H_2)$ and $G(CO)$ showed their peak values at 50 eV Å^{-1}, indicating a saturation of decomposition in the ionization track, as has been reported previously. The present results may be interpreted in terms of the hydrogen-bonded network formed by the addition of water; this will expand the reaction zone outside the track and result in increases in the product yields without any waste of excessive energy in the high-LET region.

Radiolysis with heavy ions which have very high LET values is an interesting and important subject in radiation chemistry. Since the track structure of heavy ions differes appreciably from that of low-LET radiations, chemical reactions characteristic of high-LET radiations may be expected. However, few experimental studies have been carried out[1] despite the relatively extensive development of theories of the interaction of heavy ions with matter.[2–4]

In a previous paper of this series,[5] we reported the characteristic features of the radiolysis of liquid aliphatic ketones (acetone, methyl ethyl ketone, and diethyl ketone) with energetic C and N ions over a wide LET range. The most significant results reported in the preceding paper were: (1) the amount of major gaseous products (H_2 and CO) formed per unit track length tend to be constant, independent of the amounts of energy absorbed in the high-LET region (>*ca.* 60 eV Å^{-1}), and (2) the ratios of $G(H_2)$ to $G(CO)$ increase steadily with an increase in LET.

The first result indicates that the decomposition of ketones takes place only within a track core with a constant radius above a critical LET; therefore, $G(H_2)$ and $G(CO)$ apparently begin to decrease above this LET. The excessive energy thus accumulated within the track core may be supposed to increase the temperature of the core and induce some chemical reactions with high activation energies.

The second result can be explained in terms of such a thermal-spike effect in the track core; we assumed the thermal decomposition of free radicals to account for the increases in $G(H_2)/G(CO)$ as well as $G(H_2)$ and $G(CO)$ themselves. We also assumed the formation of highly excited states of ketone molecules which give product distributions different from those in the radiolysis with low-LET radiations.

Since these results are specific for pure ketones, and since no similar results have been observed for other organic liquids in the LET region studied, we plan to carry out a series of experiments which will lend further support to the assumptions presented above. This paper will report on one of them, presenting the radiolysis results obtained with liquid acetone containing a small amount of water over a wide LET range.

The γ-radiolysis of acetone as well as of other ketones in a liquid phase has been studied,[6] and the effect of water on the γ-radiolysis yields from liquid acetone has been demonstrated;[7,8] the resulting increase in $G(H_2)$ has been explained on the basis of ion-molecule reactions.[7] We have found that a small amount of water exerts a significant effect on the LET dependence of the product yields from acetone in the high-LET region. This effect, not explicable on the same basis as that in the γ-radiolysis, will be discussed in terms of a hydrogen-bonded network formed in the solution on the basis of the assumptions presented in the preceding paper.[5]

Experimental

The experimental procedures were essentially the same as those described previously;[5,9,10] only the essential points will, then, be mentioned. Ions of ^{4}He, ^{12}C, and ^{14}N were accelerated with the 160-cm cyclotron at the Institute of Physical and Chemical Research. Their energies and LET (represented by the energy-loss parameter defined as[5] $z = 1/E\int_0^E(-dE/dx)dE$) were 18.9 MeV, 6.7 eV Å^{-1}, 30.0—66.4 MeV, 54.4—39.2 eV Å^{-1}, and 18.0—47.5 MeV, 80.0—62.4 eV Å^{-1}, for He, C, and N ions, respectively. Irradiation was carried out at an ambient temperature.

Reagent-grade acetone (Wako Pure Chem. Ind.) was dried and distilled before use;[5] the water was triply distilled. The gaseous products from radiolyzed acetone were Toepler-pumped and were subjected to gas-chromatographic analysis.

Results

All the experiments reported in this paper were carried out with acetone containing 2 wt% H_2O. No differences beyond the experimental erros in the product yield were found between solutions containing 2 and 5 wt% H_2O either for the γ-radiolysis or for the heavy-ion radiolysis.

Iodine was used as a free-radical scavenger for the γ and He-ion radiolyses; in the presence of iodide, one could obtain "molecular" yields, which may be regarded as the yields of the products formed inside radiation spurs or tracks.

In the C- and N-ion radiolyses, iodine was not used, since the yields of H_2 and CO in these cases are little affected by scavengers and, therefore, may be regarded as being practically equal to the molecular yields. In the present study, emphasis has been placed on the characteristic reactions taking place inside the densely ionizing tracks formed with heavy ions of high LET.

Figure 1 shows the variations with the LET (given by z) of $G(H_2)$ and $G(CO)$ determined for acetone containing 2 wt% H_2O (solid lines); these yields were obtained using He, C, and N ions accelerated to various energies. In contrast to the previous results obtained with pure acetone (dotted lines), [5] no peaks of $G(H_2)$ and $G(CO)$ were observed with aqueous acetone. $G(H_2)$ and $G(CO)$, which are lower than the corresponding values for pure acetone in the low-LET region, increase steadily with an increase in LET, and in the high-LET region they become even higher.

For comparison with earlier results,[7,8] the effect of water in the γ-radiolysis was also studied. In the absence of iodine, 2 wt% H_2O increases the total yields of H_2, CO, CH_4, and C_2H_6, but exerts no effect on those of C_2H_2 and C_2H_4. The molecular yields of these products obtained with iodine added at 1.8×10^{-3} M are lower for H_2 and CO and higher for saturated hydrocarbons than those for pure acetone; the molecular yields of unsaturated hydrocarbons are, however, practically unaffected. The effects of water on the total yields, except for the case of CO, are in qualitative agreement with the results obtained by Barker and Noble,[7] who determined the yields with acetone containing 0.4 wt% H_2O.

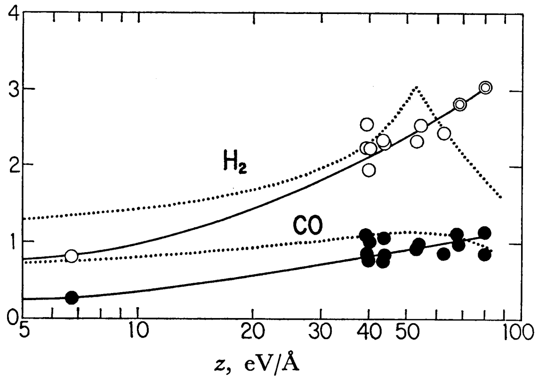

Fig. 1. LET dependence of $G(H_2)$ (○) and $G(CO)$ (●) for acetone containing 2 wt% H_2O.
LET dependence for pure acetone is shown by dotted lines for comparison (Ref. 5).

Discussion

Extensive studies of the primary processes in irradiated liquid acetone have been carried out by pulse radiolysis; they have revealed the formation of excited states[11-14] and molecular ions[11-19] in relatively high yields.

Electrons ejected by ionization attach to parent acetone molecules to form molecular anions; the total yield of the acetone cation and anion thus formed was determined and found to be approximately $G=1.5$.[13] Molecular anions will undergo recombination with cations to form excited states and neutral free radicals.

Earlier mass-spectrometric studies have shown that a rapid proton transfer does occur:[20,21]

$$(CH_3)_2CO^+ + (CH_3)_2CO \rightarrow (CH_3)_2COH^+ + CH_2COCH_3 \qquad (1)$$

Sieck and Ausloos[19] suggested an important role of the ion–molecule reaction (1) as well as other reactions in liquid-phase radiolysis. However, in view of the fact that the transient absorptions of the acetone cation and anion are observable in the pulse radiolysis,[16,18] the rate constant of Reaction (1) may not necessarily be rapid in a condensed phase. Thus, there still remains an ambiguity concerning the ionic reactions taking place in liquid ketones.

A relatively high yield, $G=1.3\pm0.1$, has been reported for the excited states of acetone in a liquid phase; the excited states may be produced by direct excitation or by ion recombination.[14] Robinson and Rodgers[14] have also suggested, from their pulse-radiolysis study of acetone solutions, that the geminate recombination of ion pairs may produce excited states, too. In the radiolysis with heavy ions having high LET values, most of the initial ionic species are neutralized by the recombination inside densely ionizing tracks to form excited states.

In the γ-radiolysis of acetone, the effect of water on the product yields was explained by Barker and Noble[7] on the basis of the ion-molecule reaction (1). In fact, water is believed to react with the cation and anion of acetone molecules as follows:[16,18]

$$(CH_3)_2CO^+ + H_2O \rightarrow CH_3COCH_2 + H_3O^+ \qquad (2)$$

$$(CH_3)_2CO^- + H_2O \rightarrow (CH_3)_2COH + OH^- \qquad (3)$$

These reactions are probably responsible for the removal of the transient absorptions of the cation and anion by water; therefore, their rate constants must be higher than that of Reaction (1). However, since there is limited information available on the mechanism of ionic reactions taking place in the bulk, no further discussion can be made of the effect of water in the γ-radiolysis.

In the heavy-ion radiolysis, H_2 and CO are produced mostly inside the dense tracks and the ionic reactions are of less importance than in the γ-radiolysis. Water would interact with the excited states of the acetone molecules, which may be produced favorably in the heavy-ion radiolysis, as has been mentioned above.

It has been suggested that water may form a hydrogen-bonded network among acetone molecules, through which a rapid energy transfer may be expected to take place.[22] The significant effects of water on the product yields and their LET dependence in the heavy-ion radiolysis seem to be explainable in terms of the hydrogen-bonded network, as will be discussed below.

The previous results with pure ketones[5] indicate that, above the critical LET (50 eV Å^{-1} for acetone), decomposition takes place only within the tracks of the limited radii. The excessive energy deposited in the tracks above the critical LET was assumed to cause the thermal decomposition of the free radicals with high activation energies, or to promote the formation of highly excited states of ketone molecules, resulting in more production of H_2 and CO. Under these conditions, however, some amounts of energy must be wasted not to form products, depending upon the amounts of energy deposited per unit track-length; therefore, the yields are reduced with an increase in LET, as is shown in Fig. 1 (dotted lines).

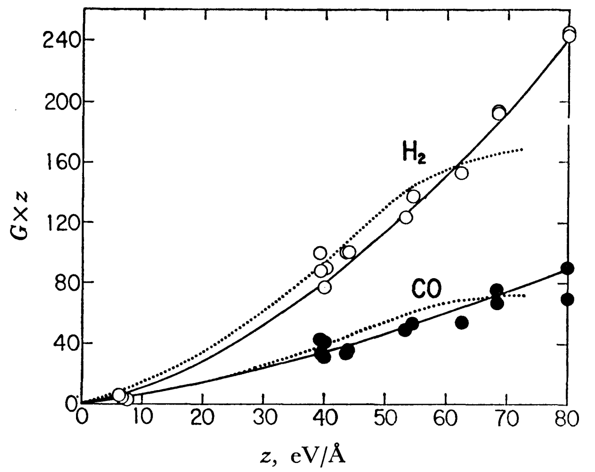

Fig. 2. Plots of Gz *vs.* z.
○, H_2; ●, CO. Dotted lines are for pure acetone (Ref. 5).

If the hydrogen-bonded network formed by water added to acetone could serve to transfer the excessive energy from the track outward the bulk, the reaction zone[23] in which acetone molecules can decompose would accordingly expand outside the track core.

Thus, the excessive energy, which would be wasted within the limited volume of the track in pure acetone at LET above 50 eV $Å^{-1}$, may be consumed efficiently and the yields may be expected to increase continuously with an increase in LET, as is shown in Fig. 1 (solid lines). In such expanding reaction zones, however, the occurrence of the thermal decomposition of free radicals or the formation of highly excited states will be more or less reduced, and the yields at LET below 50 eV $Å^{-1}$ will be reduced compared with those for pure acetone. The experimental results are consistent with those expectations.

Figure 2 shows the plots of Gz *vs.* z, where Gz gives a measure of the number of molecules produced per 100 Å of track length. By comparing these plots (solid lines) with those for pure acetone (dotted lines),[5] one may see a steady expansion of the reaction zone with an increase in the LET; the plots for pure acetone show a saturation in the high-LET region.

The hydrogen-bonded network will also be operative to some extent in the radiolysis with low-LET radiations. The decreases in the molecular yields of H_2 and CO observed in the γ-radiolysis of aqueous acetone may be ascribed to the dissipation of energy from spurs to the bulk through the hydrogen-bonded network; the importance of this effect increases in liquid ketones with an increases in LET.

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References and Notes

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23) A track-core radius is given by the maximum impact parameter that can excite an electronic state (Ref. 2) and is considered to be constant for charged particiles of low energies although it expands with an increase in energy. (Refs. 2 and 3) We assumed here that a rapid transfer of energy from the track core may result in the formation of a reaction zone outside the core.