Radiation Chemical Studies with Cyclotron Beams. III. The Heavy-ion Radiolysis of Liquid Aliphatic Ketones

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The liquid-phase radiolysis of acetone, methyl ethyl ketone, and diethyl ketone with ^{4}He–, ^{12}C–, and ^{14}N–ions was carried out with the intention of discovering the specific reactions taking place in a very high LET region. The heavy ions were accelerated at various energies with an IPCR cyclotron, the LET of which was up to 80 eV/Å. The radiolytic yields of the main gaseous products, hydrogen and carbon monoxide, were found to increase appreciably with an increase in the LET and to reach the maximum values in the LET region between 50 and 70 eV/Å. The ratios of the two yields, $G(H_2)/G(CO)$, also increase substantially with an increase in the LET. These results, as well as the variations in the yields of saturated and unsaturated hydrocarbons, appear to indicate a thermal-spike effect which may bring about the thermal decomposition of free radicals, giving rise to the enhanced $G(H_2)$ and $G(CO)$ values in the high LET region.

We have been studying the radiolysis with heavy charged particles, helium, carbon, and nitrogen ions, accelerated with an IPCR 160 cm cyclotorn, the LET of which was in the range up to 80 eV/Å. In previous papers[1,2] the results of the heavy-ion radiolysis of aerated aqueous solutions of ferrous sulfate (Fricke solution) have been reported. The same procedures have also been applied to some neat organic liquids.

The aim of the present experiments is to elucidate the specific reactions induced by the interaction of energetic heavy ions with matter. Although no systematic studies of radiolysis with heavy ions have been reported, some unique results seem to reflect the specific reactions going on in the high LET region. For instance, as we[3] and other investigators[4,5] have found, the radiolytic yields of hydrogen from several organic liquids increase significantly in the high LET region, above several tens of eV/Å, irrespective of the variation in the yields in the lower LET region.[4,5]

These characteristic increases in the hydrogen yields seem not to be explainable solely on the basis of the spur-diffusion model nor the specific interaction near the end of the heavy-ion tracks.[4] Burns and his colleagues[5a] explained the increases in the decomposition yield of liquid benzene as being due to the bimolecular reaction between excited molecules which becomes important with an increase in the LET. This may be a reasonable explanation for the radiolysis in a medium LET region. On the basis of Burns' hypothesis, Voltz[6] explained a complementary correlation of the LET dependences of the radioluminescence and the radiolytic yield of liquid toluene.

In a very high LET region, the production of the energetic electrons by the knock-on collision of heavy ions may also affect the chemistry, as was suggested by Mozumder *et al.*[7] This effect has been demonstrated by us[3] to be effective in the interpretation of the discontinuities of the LET-dependence curves of $G(Fe^{3+})$ for the radiolysis of a Fricke solution with different kinds of heavy ions.

Another important effect which has been assumed, but not been definitely demonstrated, in the liquid-phase radiolysis with high LET radiations is the thermal-spike effect.[8] This effect, in fact, has occasionally been assumed in interpreting significant LET effects on the radiolysis of liquid aromatic compounds[9] and polycrystalline alkali nitrates,[10a] sodium chlorate,[10b] amino acids, and proteins.[11]

In γ radiolysis, the temperature at the center of a spur is assumed to be approximately 50—100° above the ambient temperature, and the duration of the heat may be less than 10^{-9} s, according to Magee,[12] who calculated using macroscopic parameters for the heat conductivity and the specific heat.

In a similar manner, Burns and Barker[13] estimated the temperature rise not only in a spherical spur but also in a cylindrical track, suggesting substantial thermal effects on the reactions in the very high LET region.

In this paper, we will report the results of our product analysis for the radiolysis of liquid acetone, methyl ethyl ketone, and diethyl ketone with carbon and nitrogen ions; these results suggest that the thermal-spike effect plays a role in the very high LET region.

Experimental

Materials. Reagent-grade acetone (Wako Pure Chem. Ind.), methyl ethyl ketone (Junsei Pure Chem. Co.), and diethyl ketone (Koso Chem. Co.) were dried and purified by distillation in the presence of $CaSO_4$ using a 50 cm stainless steel helix-packed column. Since a trace of water has been shown to affect the product yields,[14-16] meticulous care was taken to remove the water as completely as possible. The purified ketones were degassed thoroughly and distilled into a storage bulb through a tube filled with Molecular Sieve 4A.

Irradiation Cells. The irradiation cell shown in Fig. 1 was made of Pyrex glass and had a thin aluminum-foil (13—70 μ) window for heavy-ion irradiation which was fixed in place with a screwed brass keeper. A platinum lead was connected to the ground through a current integrator. The sample was then placed in the reservoir side of the cell by distillation *in vacuo* and was then further degassed by conventional freezing-pumping-thawing cycles before being transferred into the cell. For ^{60}Co-γ irradiation, Pyrex glass tubes (1.0 cm in O.D. and 20 cm high) were used.

Irradiation. The irradiation arrangement and the experimental procedure for the cyclotron experiments were essentially the same as those described previously.[2,3] The charged particles used were helium, carbon, and nitrogen ions accelerated with the IPCR 160 cm cyclotron. The energies of these particles entering the samples were:[17]

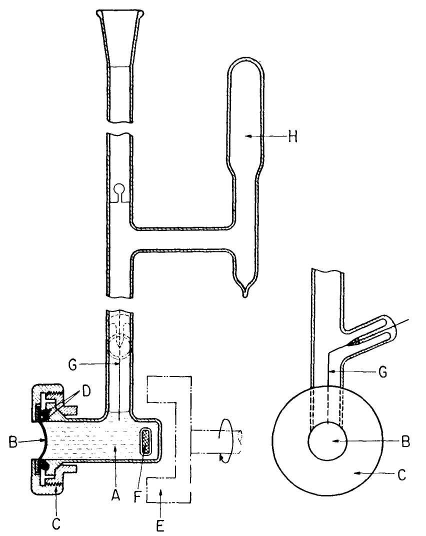

Fig. 1. Irradiation cell. A: Sample, B: Aluminum-foil window, C: Screwed brass keeper, D: Teflon rings, E: Rotating magnet, F: Stirrer, G: Platinum lead, H: Reservoir.

6.9—21.3 MeV for helium ions, 22.0—67.3 MeV for carbon ions, and 18.0—68.0 MeV for nitrogen ions, corresponding to the initial LET between 6—80 eV/Å. The current intensities were usually ~1 nA, and the total doses were in the range of (3—10) × 10^{19} eV. The samples were stirred vigorously during irradiation by means of a magnetic stirrer. The ambient temperature was ~22 °C.

γ-Irradiation was carried out using a 10 kCi ^{60}Co source at a dose rate of 4.66×10^{17} eV/g min and at a total dose of up to 4.5×10^{19} eV/g.

Analysis. Gaseous products from irradiated samples were collected by using a Toepler pump. Since the hydrocarbons were found not to be degassed completely from the irradiated samples by conventional freezing-pumping-thawing cycles, we used a micro-refluxing column cooled with ice, through which the hydrocarbons were pumped out. Gas chromatographic analyses were applied to the gaseous products, H_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and n-C_4H_{10}; analyses of the liquid products were not performed.

Energy-loss Parameter. In the present paper, the product yields are represented as a function of the energy-loss parameter, z, defined as:

$$z = \frac{1}{E}\int_0^E \left(-\frac{dE}{dx}\right) dE$$

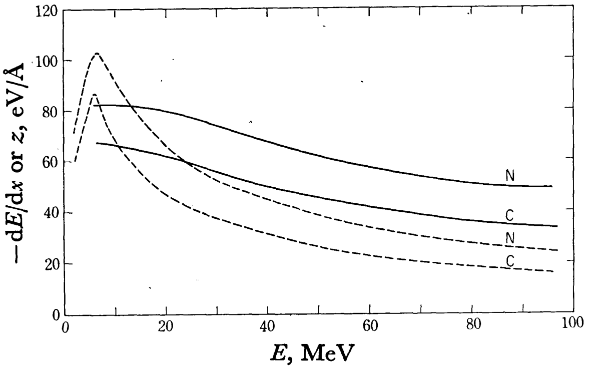

Fig. 2. Instantaneous LET (broken lines) and energy-loss parameter, z, (solid lines) for liquid acetone (20 °C) as a function of particle energy.

The values of the stopping power, $-dE/dx$, for ketones were obtained by multiplying those for water calculated by Northcliffe[18,19] by the densities of the ketones. The integration was carried out graphically; examples of z as a function of the particle energy are shown in Fig. 2.

Results

Some typical data of the product yields determined for the helium, carbon, and nitrogen ions are listed in Table 1, along with those for γ rays. The yields of the two main products, H_2 and CO, from three γ-radiolyzed ketones are reduced by 20 and 10% respectively in the presence of I_2(10^{-2} M). These results, consistent with the results obtained by other workers,[15,20a] indicate that H_2 and CO are formed principally within the γ-ray spurs; therefore, in the radiolysis with carbon and nitrogen ions of high LET's, they may reasonably be assumed to be formed mostly within dense ionization tracks.

In the γ radiolysis, neither a dose nor a dose-rate

TABLE 1. TYPICAL DATA OF THE PRODUCT YIELDS FOR ALIPHATIC KETONES

(a) ACETONE

Radiation	^{60}Co-γ		He-ions		C-ions	N-ions
E, MeV			6.9	11.0	67	65.7
z, eV/Å	0.02		13.1	9.25	39	55.3
$[I_2]$, M	0	8×10^{-3}	0	1.5×10^{-2}	0	0
$G(H_2)$	0.96	0.79	1.47	1.19	2.36	2.71
$G(CO)$	0.56	0.48	0.80	0.73	1.05	1.22
$G(CH_4)$	1.76	0.35	0.97	0.56	0.99	0.96
$G(C_2H_6)$	0.30	0.27	0.50	0.35	0.56	0.64
$G(C_2H_2)$	0.02	0.03	—	—	—	—
$G(C_2H_4)$	0.04	0.06	0.12	0.08	0.21	0.24

(b) METHYL ETHYL KETONE

Radiation	^{60}Co-γ	He-ions		C-ions	N-ions
E, MeV		7.8	12.0	46.5	29.9
z, eV/Å	0.02	10.8	8.6	46.2	72.8
$[I_2]$, M	1.5×10^{-2}	0	7×10^{-3}	0	0
$G(H_2)$	1.23	1.86	1.86	3.36	3.41
$G(CO)$	0.67	0.92	0.82	1.26	1.31
$G(CH_4)$	0.23	0.52	0.36	0.60	0.55
$G(C_2H_6)$	0.26	0.65	0.44	0.66	0.54
$G(C_3H_8)$	0.24	0.34	0.30	0.39	—
$G(C_2H_2)$	0.03	0.11	0.09	0.38	—
$G(C_2H_4)$	0.51	0.76	0.70	1.11	0.77

(c) DIETHYL KETONE

Radiation	^{60}Co-γ		He-ions		C-ions	N-ions
E, MeV			22	22	53.5	36.0
z, eV/Å	0.02		6.2	6.2	46.0	71.2
$[I_2]$, M	0	$(3.5—7)\times10^{-3}$	0	7×10^{-3}	0	0
$G(H_2)$	1.18	1.07	1.48	1.45	2.61	4.01
$G(CO)$	0.94	0.95	1.09	0.92	1.62	2.27
$G(CH_4)$	—	0.05	0.08	0.04	0.18	0.21
$G(C_2H_6)$	—	0.22	0.52	0.26	0.36	0.80
$G(C_3H_8)$	—	0.01	—	0.03	—	—
$G(C_2H_2)$	—	0.05	—	0.09	—	—
$G(C_2H_4)$	—	0.44	0.67	0.46	0.75	1.22

dependence was observed in the ranges under study for any ketone. A detectable dose-rate dependence was not observed at intensities between 1 and 3 nA in the heavy-ion radiolysis, either.

The γ-radiolytic yields of H_2 and CH_4 from acetone containing a small amount of water were found to be substantially higher than those for dried acetone reported here, in agreement with those obtained by Barker and Noble;[14] the detailed results over a wide LET range will be communicated elsewhere.

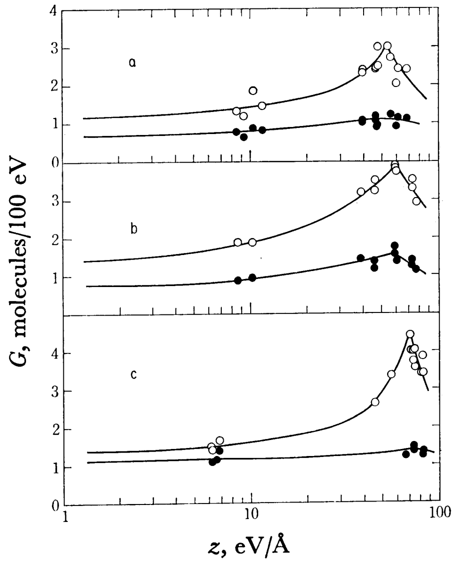

Fig. 3. Variations of $G(H_2)$ and $G(CO)$ with z. Open circles: H_2, closed circles: CO. a: acetone, b: methyl ethyl ketone, c: diethyl ketone. Yields in the vicinity of 10 eV/Å obtained with He-ions and those in the higher region with C- and N-ions.

Figure 3 shows the dependences with z of the yields of H_2 and CO for the three ketones. The yields for the γ and helim-ion radiolysis are those obtained with iodine solutions ($(3.5—7.0)\times10^{-3}$ M) in ketones; all the other yields are those with neat ketones. It should be noted that the maximum yields of H_2 and CO appear for every ketone in the very high LET region.

Discussion

Radiolysis studies of liquid acetone have been carried out by many workers,[14—16,20—25] and the ionic and the free-radical reaction mechanisms have been pointed out to be of importance. For higher ketones, one can expect reactions analogous to those of acetone.[24] Based on the reaction mechanisms proposed so far, one can reasonably assume the pathways producing hydrogen and carbon monoxide to be as follows.

A large portion of these main gaseous products are apparently formed, as may be seen from the results described above, *via* "molecular" mechanisms, even in the γ radiolysis; that is, they are formed in the spur or track region without any influence of radical scavengers. Hydrogen is presumably produced by the abstraction reaction of the hot and/or thermal hydrogen atoms which are formed by the fragmentation of the excited ketone molecules and excited ionic species resulting from the ion-molecule reactions. As will be mentioned below, hydrogen atoms are considered to be produced also by the decomposition of free radicals inside the tracks of the high LET radiations.

According to the results of photochemical studies of acetone, the excited states dissociate by these reactions:[26)]

$$CH_3COCH_3^* \begin{cases} \longrightarrow CH_3CO + CH_3 & (1) \\ \longrightarrow 2CH_3 + CO & (2) \\ \longrightarrow CH_2COCH_3 + H & (3) \end{cases}$$

Carbon monoxide may also be produced if acetyl radicals undergo dissociation:

$$CH_3CO \longrightarrow CH_3 + CO \qquad (4)$$

Reaction (4), however, will proceed only at high temperatures because of its relatively high activation energy (13—18 kcal mol^{-1} [27,28]). Ionic reaction mechanisms producing carbon monoxide have not yet been elucidated.

As is shown in Fig. 3, both $G(H_2)$ and $G(CO)$ increase with an increase in z, reaching their maximum values at z=50, 60, and 70 eV/Å respectively for acetone, methyl ethyl ketone, and diethyl ketone. The increases in $G(H_2)$ and $G(CO)$ below the peak z's may be explained at least partly in terms of the increasing contributions of the reactions between excited ketone molecules in the dense radiation tracks, which have been proposed by Burns and his co-workers[5] for the radiolysis of benzene with high LET radiations. It should, however, be noted that, in the present study, the ratios of $G(H_2)$ to $G(CO)$ also increase from about 2(at z= 10—20 eV/Å) to about 3(at z=70—80 eV/Å) with an increase in z for the three ketones investigated. This result cannot be explained completely by the spur-diffusion model, which is based on a simple competition between the diffusion and the reaction of radicals or excited ketone molecules formed in an LET-independent step.

In order to find clues for the explanation of these significant results, the values of $G(H_2)\times z$ and $G(CO)\times z$ are plotted as a function of z in Fig. 4. The $G\times z$-value gives a measure of the number of molecules produced per 100 Å of a radiation track (G is the number of molecules produced per an absorbed energy of 100 eV). Figure 4 apparently indicates that the values of $G(CO)\times z$ almost level off above the given z's for the three ketones, whereas those of $G(H_2)\times z$ do not do so. The plateau values for $G(CO)\times z$ are estimated to be 100±20.

The number of CO molecules produced should obviously not exceed the number of ketone molecules decomposed. In the γ radiolysis of liquid acetone, some oxygen-containing compounds other than carbon monoxide are produced, and their yields are greatly reduced in the presence of a radical scavenger (I_2),[15] indicating that these products are formed in the bulk. In the higher LET region, the yields of these compounds must decrease, and presumably carbon monoxide will be the main oxygen-containing product.

If this assumption is accepted, the number of CO molecules produced in the very high LET region can be said to be approximately equal to the number of

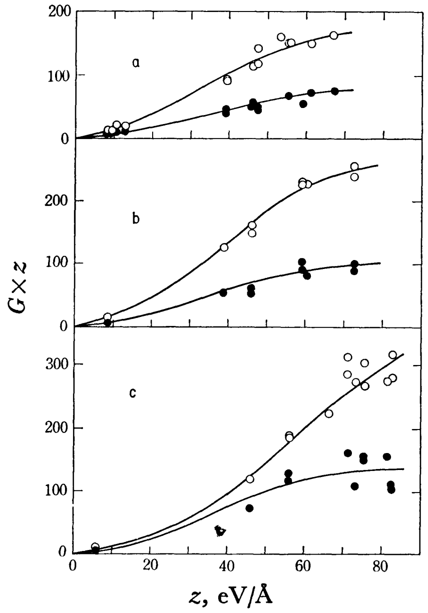

Fig. 4. Plots of $G \times z$ *vs.* z. Symbols have the same meaning as for Fig. 3.

ketone molecules decomposed. The nearly saturated curves of $G(CO) \times z$ in Fig. 4 thus indicate that the numbers of ketone molecules decomposed are limited above the given z-values: *ca.* one molecule of ketone per Å of a radiation track. The appearance of the maximum $G(CO)$ and $G(H_2)$ in Fig. 3 may be explained on the basis of such a saturation phenomenon, which has not been observed for other compounds.

The different behavior of the $G(H_2) \times z$-curves from that of $G(CO) \times z$ in Fig. 4 implies that the formation of hydrogen is still taking place more or less even after the decomposition producing carbon monoxide is "saturated." The fact that the $G(H_2)/G(CO)$ ratios increase steadily with an increase in z may support the above arguments.

Although we have not yet reached a definite conclusion, the thermal decomposition of alkyl radicals in the high temperature zones within the tracks (thermal spikes) or the formation of highly excited states of ketone molecules, thus giving rise to more hydrogen, seems to account for the increases in $G(H_2)/G(CO)$ in the high LET region.

In fact, the activation energies of the decomposition of alkyl radicals ($C_nH_{2n+1} \rightarrow C_nH_{2n} + H$) are known to be ~30 kcal mol^{-1},[28] much higher than those of $C_nH_{2n+1}CO$ ($\rightarrow C_nH_{2n+1} + CO$). Therefore, the decomposition of alkyl radicals, if any, should be expected to take place only in the very high LET region where excess energies are dissipated as heat, giving rise to the formation of more hydrogen as well as that of unsaturated hydrocarbons.

The alternative explanation is the probable formation of highly (vibrationally or electronically) excited states which may form in the very high LET region and may decompose differently from the lower excited states produced in the lower LET region. The present results do not provide decisive information which can distinguish between these two proposed mechanisms; further studies are, therefore, in progress along these lines.

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