SHORT COMMUNICATIONS

Isotope Effects on the Hydrogen Formation Reaction in the Radiolysis of Cyclopentanone

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Hydrogen gas has been found to be one of the major products of the radiolysis of cyclopentanone in the liquid phase[2,3] but not in the photolysis,[4] while there are many common major reaction products in the two processes. The uniqueness of the hydrogen formation in this sense led us to study the reaction in detail in the hope of acquiring a knowledge of the excited species in the radiolysis different from the well-defined ones in the photolysis.[4,5]

Either a degassed sample, containing 0.5—1 *ml* each of cyclopentanone, cyclopentanone-d_8, and 2,2,5,5-cyclopentanone-d_4, or a mixture of cyclopentanone and cyclopentanone-d_8, was sealed into a reaction vessel and irradiated with γ-rays from a cobalt-60 source at a dose rate of 3.7×10^6 rad/hr. The amount of hydrogen formed was proportional to the absorbed dose, as has been reported previously.[2] The isotopic composition of the hydrogen gas was analyzed by means of a mass spectrometer.

The mechanism of the hydrogen formation may be summarized as:

$$\text{cyclopentanone} \xrightarrow{\Phi} (\text{cyclopentanone}^*)$$

$$\begin{cases}\rightarrow \text{hydrogen gas} + \text{residue} & (1)\\ \rightarrow \text{hydrogen atom} + \text{residue} & (2)\end{cases}$$

$$\text{hydrogen atom} + \text{cyclopentanone} \rightarrow \text{hydrogen gas} + \text{residue} \quad (3).$$

The yields of protium, $G(H_2)$, from cyclopentanone and of deuterium, $G(D_2)$, from cyclopentanone-d_8 were 0.60 ± 0.12 and 0.22 ± 0.04 respectively. The $G(H_2)/G(D_2)$ ratio was about 3, apparently indicating that such a rate constant as Φ is about three times larger in cyclopentanone than in cyclopentanone-d_8.

The $H_2 : D_2 : HD$ ratio in the hydrogen formed from the 1 : 1 mixture of cyclopentanone and cyclopentanone-d_8 was 5.6 : 1.0 : 3.6 It can readily be shown[6] that, in the mixture, if the isotope effects do not exist in such steps as (3), the ratio of $H_2 : D_2 : HD$ will range from approximately 3.0 : 1.0 : 2.0 to 3.0 : 1.0 : 0, depending on the magnitude of the molecular hydrogen contribution, *i. e.*, such second steps as are shown in reaction (1). The deviation of these values from the experimental value indicates the existence of such an isotope effect as well as the molecular hydrogen contribution. The ratio of $H_2 : D_2 : HD$ in the hydrogen formed from 2,2,5,5-cyclopentanone-d_4 was 1.5 : 1.0 : 2.9.*1 It can also be shown[6] that the ratio will be 1.0 : 1.0 : 2.0 if no such isotope effect, no molecular hydrogen formation, and no difference in the reactivities between hydrogens attached to α and β positions to the carbonyl group are assumed. The difference between the ratio found and that predicted in the partially-deuterated cyclopentanone suggests the existence of the isotope effect also or of different reactivities in addition to the isotope effect. Although the contribution of molecular hydrogen is indicated by the presence of 2-cyclopentenone among the radiolysis products[2b] as well as by the analytical results mentioned above, the contribution of "hot hydrogen" is also suggested by the fact that a relatively large amount of HD was found in the mixture of cyclopentanone and cyclopentanone-d_8, as well as by the fact that the amount of hydrogen reduced by the addition of such radical scavengers as DPPH was rather small.[2b]

1) Communications should be addressed to M. K.
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*1 This ratio is different from that (1 : 0.37 : 1.26) reported in Ref. 2b. The difference may be attributed to the greater degree of deuterium substitution in the present studies.