NOTES

The Radiolysis of Squalane ($C_{30}H_{62}$) from −196°C to 350°C

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The radiolysis of squalane at room temperature has been already studied by Yamazaki and Shida.[1] The present note will describe a study of the influence of the temperature on the γ-radiolysis of squalane. This substance is favorable for studying the effect of the temperature on radiolysis because of its characteristic nature of being liquid over a sufficiently wide range of temperature, i.e., −78.5 to 350°C or more. It was irradiated in vacuo at 350, 300, 250, 200, 150, 100, 0, −78.5 and −196°C by γ-rays with the total doses of 1.5×10^7 and 2.13×10^7 r.

Non-condensable gases at the temperature of liquid nitrogen, hydrogen plus methane, were collected in a micro gas burette mounted directly above a toepler pump until the sample tube was evacuated to 10^{-3} mmHg. The total volume of non-condensable gases was next measured, after which hydrogen was removed by a liquid nitrogen trap through a tube of cupric oxide heated to 270°C, at which temperature no methane was decomposed. The mass-spectrometric analysis of the residual non-condensable gas on several occasions showed it to consist of almost pure methane. The condensable gases were analyzed by gas chromatography. Each product was identified by using a mass-spectrometer. The *G*-values*1 obtained are given in Table I. In this table, it may be seen that the *G*-values of hydrogen production are nearly constant at 3.8 from −196°C to 100°C, but that they increase to 7.0 at 350°C. For the other products of hydrocarbon, the increases in *G*-values in the region from 150°C to 300°C are larger than those at lower temperatures.

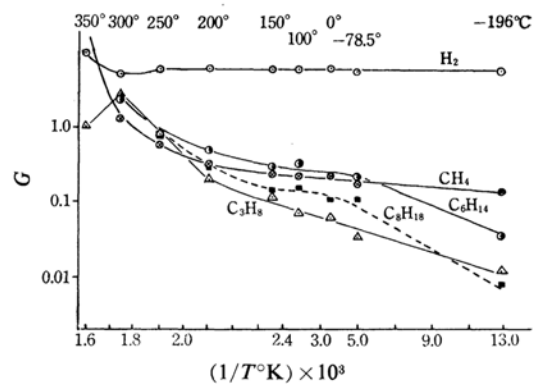

Fig. 1. Plots of log *G* against $1/T$°K.

The skeleton of squalane is as follows:

$$(C\text{-}\underset{\underset{C}{|}}{C}\text{-}C\text{-}C\text{-}\underset{\underset{C}{|}}{C}\text{-}C\text{-}C\text{-}\underset{\underset{C}{|}}{C}\text{-}C\text{-}C\text{-})_2$$

In this figure, the relation between the logarithmic *G*-values and $1/T$°K is plotted. It appears preferable to divide the temperature range into two parts, below and above 150°C.

Below 150°C.—In this region of temperature, the viscosity of squalane is so high that the molecular motion may be reduced, and the so-called cage effect seems to take place. The diffusion of radicals produced by γ-irradiation, therefore, must be greatly diminished. Under these circumstances, the radical reactions, which are expected to be abstraction, recombination and disproportionation, will be very much affected. Radicals that have diffused out of the cage are converted into products by abstracting hydrogen atoms from squalane molecules. On the other hand, those held in cages may react with each other, undergoing recombination and disproportionation to form original molecules and products consisting of aliphatic

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1) H. Yamazaki and S. Shida, *J. Chem. Phys.*, 32, 950 (1960).

*1 The *G*-value is defined as the number of species of a given kind reacting or produced per 100 eV. of radiation energy absorbed.

TABLE I. *G* VALUES OF EACH PRODUCT

°C	H_2	CH_4	C_3H_8	C_3H_6	i-C_4H_{10}	i-C_5H_{12}	C_6H_{12}	C_6H_{14}	C_8H_{18}
−196	3.4	0.12	0.01	0.006			0.03		0.007
− 78.5	3.4	0.16	0.03	0.022			0.2		0.1
0	3.7	0.2	0.055	0.053			0.2		0.1
100	3.7	0.21	0.063	0.02			0.3		0.14
150	4.22	0.28	0.14	0.015	0.025	0.036	0.44	0.27	0.22
200	4.07	0.35	0.17	0.013	0.037	0.088	0.043	0.29	0.26
250	4.07	0.55	0.79	0.045	0.118	0.63	0.82	0.43	0.93
300	3.61	1.21	2.66	—	0.44	2.88	2.15	0.34	—
350	7.0	12.0	1.0	—	0.7	2.4	—	—	—

or olefin. Therefore, the reactions in cages are thought to proceed in a relatively short time, before radicals diffuse out of the cages, i. e., to occur in a spur.[2] The products due to this instantaneous disproportionation reaction may be formed as soon as the C–C bonds are separated by γ-irradation. It should be, therefore, interpreted that a reaction like the so-called molecular detachment takes place in a liquid of high viscosity at a low temperature.[3] In this figure, it may be seen that the curve becomes steeper with the increasing molecular weight of the product. This may be due to the fact that the activation energy for diffusion becomes larger with the increasing molecular weight of the fragment. It may also be noted that near 150°C the slopes tend to be flat. These inflexion points of the curve may indicate some difference between the liquid states below and above 150°C. The pursuit of the discontinuity of this curve will be one of the objects of our later work.

Above 150°C.—Since no thermal cracking of free radicals takes place about 150°C,[4] the activation energies for each product were obtained from the curve above 150°C; they were estimated to be 15±1 kcal./mol. Large radicals, such as that of squalane, presumably, need lower activation energies for thermal cracking.

The rapid increase observed in this region may come simply from the cracking of free radicals produced by the γ-irradiation. It is necessary also to mention that the rupture of the C–C bonds of a radical by thermal cracking occurs at the β-position of free valence.[5] Since the *G*-values of hydrogen production are the largest of all, a lot of squalane radicals may be produded. Among them, the tertiary radicals will be predominant, and the products of their thermal cracking are expected to be C_4, C_5 and C_9. Actually the C_4 and C_5 were produced abundantly. Contrary to the expectation, however, the C_9 product was not observed. It seems, therefore, that the inner C–H bonds of a long molecule have less reactivity. This observation suggests that the "*intramolecular energy transfer*"[6] may take place in a long molecule. Thus, prior to the rupture of C–H bonds, the energy absorbed in a molecule is transferred to the end parts of the molecule and makes their reactivity large enough to separate the hydrogen atoms from the original molecule.

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