SHORT COMMUNICATIONS

Identification of Polyphenyls Formed in the Radiolysis of Biphenyl by Reverse Isotope Dilution Analysis

By Hiroaki Kōyama*, Gen-ichi Tsuchihashi
and Akibumi Danno

(Received January 22, 1962)

The radiolysis of polyphenyls has been studied by many workers[1-4] in order to elucidate the decomposition mechanism of organic coolant-moderator, however no datailed study on the identification of radiolytic products of high molecular weight has hitherto been carried out. The present work aimed to obtain a precise information concerning the radiolytic mechanism for biphenyl, the simplest polyphenyl. Here, reverse isotope dilution analysis by using ^{14}C-labeled compound was applied to determine the yields of terphenyls and quaterphenyls produced by the radiolysis of biphenyl.

Biphenyl-(phenyl-^{14}C) (33.2 mc/mol.)[5,6] was irradiated at 100±5°C in vacuum by gamma-rays (2.60×10^5 r/hr., 150 hr.)[7]. After the compound was irradiated, each carrier component was added to the irradiated sample and was homogeneously mixed using anisole as a homogenizer. Unchanged biphenyl-(phenyl-^{14}C) was removed by sublimation. Each compound was isolated by liquid elution chromatography on activated alumina with petroleum ether and then recrystallized from a suitable solvent several times to give a constant specific activity. Radioactivity of the purified product was determined using a Tri-Carb liquid scintillation spectrometer or an ionization chamber-vibrating reed electrometer.

Table I. *G*-Values for the formation of polyphenyls in the radiolysis of biphenyl

Product	Number of recryst.	Specific activity μc/mol.	*G*-Value	Ratio of *G*-value
o-Terphenyl	5 6	1.62 1.58	0.0063	7.6
m-Terphenyl	7 8	0.109 0.108	0.0012	1.4
p-Terphenyl	4 5	0.0194 0.0200	0.00083	1.0
o,o'-Quaterphenyl	4 5	0.348 0.350	0.0049	5.9
m,m'-Quaterphenyl	4 5	0.576 0.576	0.0051	6.1
p,p'-Quaterphenyl	4 5	1.30 1.60	0.0104	12.5

Table I shows *G*-values for formation of polyphenyls in the radiolysis of biphenyl. The following are a few interesting features drawn from the present results:

1) The formation of polyphenyl in the

---

* Present address: Central Research Institute of Electric Power Industry, Komae-cho, Kitatama-gun, Tokyo.

[1] W. G. Burns, W. Wild and T. F. Williams, "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy", **29**, 266 (1958).

[2] K. L. Hall and F. A. Elden, *J. Chem. Phys.*, **31**, 1420 (1959).

[3] R. A. Boxter and R. T. Keen, NAA-SR-3154 (1959).

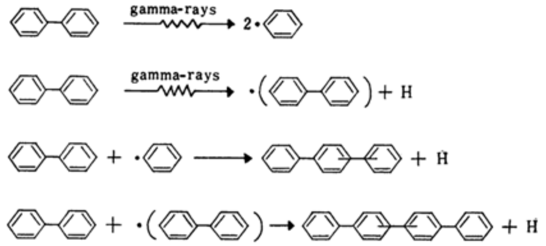
[4] W. W. West, AECU-4699 (1960).

[5] H. Kōyama, N. Morikawa, T. Migita, R. Itō and G. Tsuchihashi, *Radioisotopes*, **9**, 113 (1960).

[6] H. Kōyama, N. Morikawa and G. Tsuchihashi, ibid., in press.

[7] A. Danno et al., The 7th Hot Laboratories and Equipment Conference, Cleveland, p. 399 (1959).

radiolysis of biphenyl is assumed to occur according to the following equations:



$$H + H \longrightarrow H_2$$

Each molecule of terphenyl or quaterphenyl is presumed to be formed by the attach of a phenyl radical (ion) or a biphenyl radical (ion), respectively on biphenyl while radicals (ions) are undoubtedly produced directly in the primary process of the irradiation. Although we did not determine G-values for the formation of the three remaining unsymmetrical quaterphenyls, they would probably be of the same magnitude as those for the symmetrical ones. Then, the sum of G-values for quaterphenyl formation becomes several times as large as that for terphenyl. Therefore, the number of C–H bond ruptures becomes about ten times as large as that of C–C (phenyl-phenyl) bond ruptures. The ratio of these numbers agrees with that of the numbers of C–H and of C–C (phenyl-phenyl) bonds in biphenyl. Consequently, the rate of the rupture C–H bond in biphenyl by gamma-rays is of the same magnitude as that of C–C (phenyl-phenyl) bond.

2) If it is assumed that (1) the radical formation by gamma-rays and the following substitution reaction with these radicals take place at all the positions of biphenyl with equal ease and (2) o, o'-quaterphenyl can exist only as trans form due to steric hindrance, one would expect that the ratios of G-values of o-, m-, p-terphenyl and o, o'-, m, m'-, p, p'-quaterphenyl should be 2 : 2 : 1 and 2 : 4 : 1. However this was not the case. Accordingly, it seems that there is an orientation effect in the substitution reaction of biphenyl with these radicals which were produced initially by the irradiation and then thermalized. We are currently investigating the significance of this large G-value for p, p'-quaterphenyl formation.

Details of this study will be published later.

Radiation Application Division
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken