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RECOIL CARBON-14 LABELING OF NAPHTHALENE, PHENANTHRENE AND ANTHRACENE UNDER NEUTRON IRRADIATION

Shigeru Oae*, Naomichi Furukawa, Yoshio Otsuji and Masayuki Hamada
Radiation Centre of Osaka Prefecture, Sakai, Osaka, Japan
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We wish to report here the results of C^{14}-labeling of naphthalene phenanthrene and anthracene by means of nuclear recoil.

This investigation has been initiated with a hope to see whether or not high energy C^{14} fragments formed by nuclear recoil favor or discriminate any particular position in product formations since a few scattered data have indicated such discriminations in bond formations.[1,2]

We have irradiated naphthalene and phenanthrene both in the form of picrate, and in 2-methylpyradine solution and anthracene only as its picrate, since anthracene is sparingly soluble in 2-methylpyradine. The reactor for the irradiation used in this investigation was the Brookhaven Reactor U.S.A. and the conditions of irradiation were shown in Table I.

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* Present address : Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Osaka, Japan.

[1] J.Y.Yang & A.P.Wolf ; J.Am.Chem.Soc. 82,3315(1960)

[2] a) M.Wald ; b) S.Oae ; c) A.P.Wolf ; Works done at Brookhaven Natl. Lab.

Table I

Irradiation Conditions

Compound	Neutron Flux		Time	
Naphthalene	7.3×10^{12}	n.cm.$^{-1}$sec.$^{-1}$	65 hrs	a)
"	1.4×10^{13}	"	"	b)
Phenanthrene	6.9×10^{12}	"	"	a)
"	"	"	"	b)
Anthracene	"	"	"	

a) Irradiated as picrates

b) Irradiated as 2-methylpyradine solutions

After the irradiations, these samples were radiochemically purified either by gas-liquid-chromatography or by repeated sublimations and recrystallizations. Their specific activities were determined by counting with a Packard Tri-curb liquid scintilation spectrometer, using internal standards. In the case of naphthalene, both α- and β-methylnaphthalene were added as carriers, and these " synthesized " products were separated and radiochemically purified by gas-liquid chromatography.

The specific activities and radiochemical yields of the " re-entry " products and of " synthesized " methylnaphthalenes were calculated and are shown in Table II.

The results indicate the radiochemical yields in the case of picrates were higher than those of 2-methylpyradine solutions both for naphthalene and phenanthrene.

Table II

Radiochemical Yields of Irradiated Compounds

Compounds		Total Activities c)	Radiochemical Yields
Naphthalene	a)	0.21 uc	1.59 %
"	b)	0.11	0.08
α-Methylnaphthalene	a)	0.026	0.19
"	b)	0.14	0.10
β-Methylnaphthalene	a)	0.02	0.15
"	b)	0.071	0.05
Phenanthrene	a)	1.59	7.79
"	b)	1.78	2.27
Anthracene		0.43	0.85

a) Irradiated as picrates
b) Irradiated as 2-methylpyradine solution
c) Total activities produced as each compounds

To determine the relative ratios of the C^{14} distributions in the respective compounds, the samples were degraded chemically as mentioned below.

1. Naphthalene was degraded by oxidizing to phthalic anhydride using V_2O_5 [3] as a catalyst at first, then the phthalic anhydride was converted to phthalimide [4] which was further rearranged to anthranilic acid. [5] By measuring activities of naphthalene,phthalic anhydride and anthranilic acid, the relative ratios of the C^{14} distribution in naphthalene were obtained.

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[3] C.R.Kinney & I.Pincus ; Ind.Eng.Chem. 43, 2880 (1951)

[4] W.A.Noyes & P.K.Porter ; Org.Synthesis Collective Vol 1, 457 (1956)

2. Phenanthrene was oxidized with CrO_3 to phenanthraquinone [6] which was then converted to diphenic acid. [7] Diphenic acid was further converted to 9-fluorenone [8] by heating to phthalic anhydride with V_2O_5 [3]. From these degradations the activities of 9,10 positions of both phenanthrene and anthracene were determined.

The results are given in Table III and Table IV.

The remarkable feature deduced from the degradation data are the following : (1) higher distributions of C^{14} were found in the positions where the localizations of electrons are known to be higher ; i.e. a-position of naphthalene, 9,10 positions of both phenanthracene and anthracene ; (2) the re-entry of C^{14} into angular positions were very small, probably due in part to the steric hindrance and also to the fact that more ruptures and formations of carbon-carbon bonds are necessary for labeling C^{14} at the angular than the other positions ; (3) the difference of phase did effect the yield but not the distributions of C^{14} in the products. The results clearly contradict to the well-known random knock-on

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(5) S.Yamaguchi ; Experimental Organic Chemistry, 8th Eddition, Nankodo Tokyo (1943)

(6) R.Wendland & J.Lalonde ; Org.Synthesis, 34, 76 (1954)

(7) S.Kato & H.Shioda ; Yuki Gosei Kagakukyokaishi 15, 637 (1957)

(8) E.H.Huntress, E.B.Heshberg & I.S.Cliff ; J.Am.Chem.Soc. 53, 2720 (1931)

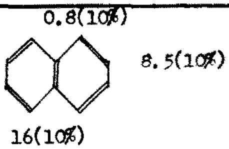
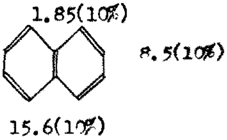
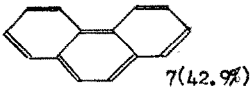
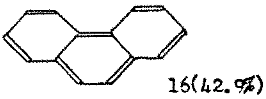
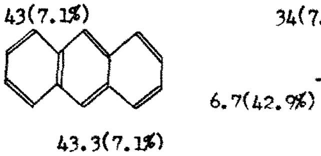
Table III

Specific Activities of the Degradation Products

Product	Specific Activities (dpm/m.mole)	
	Picrates	2-Methyl Pyradine Solution
Naphthalene	1.99×10^4	2.89×10^3
Phthalic anhydride	1.65 "	2.40 "
Anthranilic acid	1.34 "	1.95 "
Phenanthrene	9.01 "	6.86 "
9-Fluorenone	5.15 "	4.55 "
Anthracene	9.75 "	———
Phthalic anhydride	9.10 "	———

Table IV

Ratios of the Activities in the Molecule

Compounds	**Picrates**	**2-Methyl Pyradine solution**
Naphthalene		
Phenanthrene		
Anthracene		34(7.1%) ———

mechanism by Libby et al, [9] who assumed that the C^{14} produced by the reaction $N^{14}(n,p)C^{14}$ would be distributed statistically into the molecule.

Our results seem to suggest that the C^{14} atoms produced would lose most of their energy nearly down to the thermal region before attacking the molecules, giving preferentially thermodynamically more favored products, depending upon the states of chemical bondings concerned in any particular molecule.

It is interesting to note that the radiochemical yield of α-derivative was higher than that of β-isomer synthesis products isolated. The result also indicates that the replacement of hydrogen atoms by recoil C^{14} is also favored at α-position than at β-position.

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[9] W.F.Libby ; Science 93 283 (1941)