Primary Kinetic Isotope Effect for Phenylation with Phenyl Radical[1]

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Primary kinetic hydrogen isotope effect has been observed in the homolytic phenylation of aromatic compounds with the phenyl radical generated from benzoyl peroxide ($k_H/k_D=6.6$),[2] but no primary isotope effect has been reported in the formation of biphenyls from the decomposition of phenylazotriphenylmethane or *N*-nitrosoacetanilide in deuteriobenzene. The isotope effect in the case of benzoyl peroxide has been attributed to the occurrence of disproportionation between phenylcyclohexadienyl radicals and the absence of isotope effect in the other two cases has been attributed to the non-occurrence of the disproportionation of phenylcyclohexadienyl radicals, which instead have suffered abstraction of hydrogen by triphenylmethyl radicals or phenylazooxide radicals.[3]

TABLE 1. KINETIC ISOTOPE EFFECT FOR THE HOMOLYTIC AROMATIC PHENYLATION*

Run	Compound	k_H/k_D for the formation of substituted biphenyls		
		2-	3-	4-
1	PhCl-d_5[a]	1.10	1.13	1.23
2	PhNO$_2$-d_5[b]	1.46	1.16	1.01
3	PhNO$_2$-d_5[c]	2.3[illegible]	—	1.06
		2,4-	2,6-	
4	*m*-Dinitrobenzene-d_5[d]	1.54	1.55	

* All reactions were carried out at room temperature (20±3°C).

a) k_H/k_D was calculated from the partial rate factors which were determined gas-chromatographically from the competitive phenylations of C_6H_6-$C_6H_5NO_2$ and of C_6H_6 - $C_6D_5NO_2$.

b) k_H/k_D was determined by a mass spectrometer connected directly to the exit of a gas chromatograph to which nitrobiphenyl isomers obtained from the competitive phenylation of $C_6H_5NO_2$ - $C_6D_5NO_2$ were fed.

c) See text for method of determination.

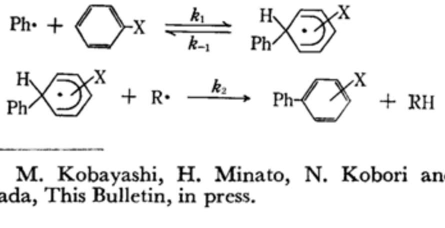
d) The biphenyl isomers obtained from the competitive phenylation of *m*-dinitrobenzene - *m*-dinitrobenzene-d_4 were analyzed by the same method as that used for Run 3.

Our previous paper described the formation of phenyl radical from benzenediazonium tetrafluoroborate and sodium nitrite.[4] We investigated the reaction with deuterated aromatics, and observed primary kinetic isotope effect in the phenylation with phenyl radical. Results are summarized in Table 1. The experimental procedure is described by use of Run 3 as an example. To a solution of nitrobenzene (40 mmol), pentadeuterionitrobenzene (40 mmol) and sodium nitrite (120 mmol) in DMSO (150 g), a solution of benzenediazonium tetrafluoroborate (34 mmol) in DMSO (70 g) was added at room temperature (20±3°C). A mixture of nitrobiphenyls obtained was separated to pure components by chromatography on an alumina column, and k_H/k_D was determined from the ratio of the parent peaks of a nitrobiphenyl and a tetradeuterionitrobiphenyl by mass spectrometry.

Quaterphenyls were not found in the product mixtures. The absence of the dimerization (and oxidation) product of phenylcyclohexadienyl radical must be due to efficient abstraction of hydrogen from phenylcyclohexadienyl radical.

The data in Table 1 may be explained on the basis of the steric effect. The larger values of k_H/k_D were observed for the formation of 2-nitrobiphenyl and 2,4- and 2,6-dinitrobiphenyls, all of which had a substituent at ortho position.

Another possible explanation is that with those substituents capable of stabilizing the intermediate phenylcyclohexadienyl radical by resonance the activation energy for the addition of phenyl radical to substituted benzene is lower and the addition step proceeds faster, and consequently the step of hydrogen abstraction makes greater contribution in the overall kinetic rate. It seems that in principle the isotope effect exists in the aromatic phenylation with phenyl radical and the isotope effect is observable only when the substituent is large enough and/or stabilizes the intermediate phenylcyclohexadienyl radical by resonance. We wish to propose the following mechanism, in which the addition of phenyl radical is reversible.



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[1] Aromatic Arylation with Aryl Radicals. II.

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