

HYDROGEN KINETIC ISOTOPE EFFECTS IN SULFONYLOXYLATION AND AROYLOXYLATION OF ARENES¹

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Hydrogen kinetic isotope effects in the reactions between arenes and *m*-nitrobenzenesulfonyl peroxide and aroyl *p*-toluenesulfonyl peroxides have been investigated. In ionic sulfonyloxylations, no primary isotope effect was observed, whereas in free-radical sulfonyloxylations and aroyloxylations, some primary isotope effect was observed.

Kinetic isotope effect in aromatic substitutions is useful for determination of the rate-determining step.² In ionic substitutions, primary kinetic isotope effect is usually not observed, but k_H/k_D is 1.1 - 2.8 in sulfonation,³⁻⁵ and Friedel-Crafts sulfonylation.⁶ Such k_H/k_D values indicate that the rate-determining step is not the first (formation of cyclohexadienyl cation) but second step (removal of a proton). Studies on isotope effect in free-radical substitutions on arenes are not so many. k_H/k_D values of 2 - 6 were reported for phenylation with benzoyl peroxide,⁷ phenylation with benzenediazonium salt and sodium nitrite,⁸ phenylation with phenylazo *p*-tolyl sulfone,⁹ and isopropyloxycarbonyloxylation induced with oxygen.¹⁰

We have studied isotope effect in sulfonyloxylation and aroyloxylation with sulfonyl peroxide and aroyl sulfonyl peroxide, and compared the rate-determining steps in ionic and free-radical substitutions on aromatics.

As a sulfonyl peroxide, *m*-nitrobenzenesulfonyl peroxide (NBSP) was used. This peroxide reacts almost instantaneously with benzene at room temperature, forming phenyl *m*-nitrobenzenesulfonate.¹¹ A dichloromethane solution (62 ml) of NBSP (1.29 mmol) was added to an equimolar mixture (89 mmol each) of benzene and benzene- d_6 , and the mixture was allowed to react for 2 hr at 20°C. The phenyl *m*-nitrobenzenesulfonate formed was isolated, and the isomer ratio was determined by mass spectrometry. The k_H/k_D value found was 0.91, which shows secondary isotope effect. Since the formation of cyclohexadienyl cation is expected to be very rapid for benzene and NBSP, the reaction between nitrobenzene and NBSP was studied. A mixture of NBSP (1.53 mmol), nitrobenzene (78 mmol) and nitrobenzene- d_5 (78 mmol) was allowed to react for 3 days at 30°C, and the products were separated by chromatography; an isotopic mixture of *m*-nitrophenyl *m*-nitrobenzenesulfonate was obtained in 50-70 mol%. Almost no *o*-, or *p*-nitrophenyl sulfonate was detected by gas chromatography, and this finding shows that the *m*-nitrobenzenesulfonyloxylation of nitrobenzene is not a free-radical reaction but an ionic reaction. Mass-spectrometric analysis of the *m*-nitrophenyl *m*-nitrobenzenesulfonate yielded $k_H/k_D = 1.02$.

When NBSP was irradiated in nitrobenzene, free-radical decomposition of NBSP did take place, but the main product was phenyl (not *m*-nitrophenyl) *m*-nitrobenzene-sulfonate.¹² The yield of the *m*-nitrophenyl ester was only 4%, and it was not possible to separate the mixture of isomers for the determination of isotope effect.

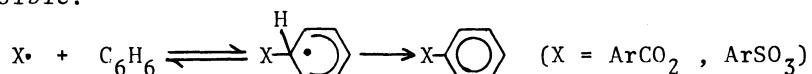
Aroyl sulfonyl peroxides yield sulfonyloxy radicals, and form aryl sulfonates when decomposed in arenes.¹³⁻¹⁴ Benzoyl p-toluenesulfonyl peroxide (BTP; 2.7 mmol) was allowed to decompose in benzene (100 mmol) and benzene-d₆ (100 mmol) in the presence of MgO (12-25 mmol; for the prevention of acid-catalyzed heterolysis) for 15.3 hr at 45°C, and the phenyl benzoate and phenyl p-toluenesulfonate were separated by column chromatography. Isotope effects for the formation of these esters were determined by mass spectrometry. In a similar manner, p-chlorobenzoyl p-toluene-sulfonyl peroxide (CTP; 1.28 mmol) was allowed to decompose in benzene (113 mmol) and benzene-d₆ (113 mmol) at 50°C, and the phenyl p-toluenesulfonate and phenyl p-chlorobenzoate were separated for mass-spectrometric determinations. The results are summarized in Table 1.

Table 1. Hydrogen Isotope Effect in Sulfonyloxylation and Aroyloxylation

Peroxide	Substrate	Product	k_H/k_D
NBSP	$C_6H_6 - C_6D_6$	phenyl m-nitrobenzenesulfonate	0.91
NBSP	$C_6H_5NO_2 - C_6D_5NO_2$	m-nitrophenyl m-nitrobenzenesulfonate	1.02
BTP	$C_6H_6 - C_6D_6$	phenyl p-toluenesulfonate	(1.37)*
		phenyl benzoate	1.39
CTP	$C_6H_6 - C_6D_6$	phenyl p-toluenesulfonate	1.12
		phenyl p-chlorobenzoate	1.57

*Since some of this ester may be formed by cage-recombination,¹³ this value should be regarded as the maximum.

Table 1 shows that in ionic sulfonyloxylation with NBSP no primary isotope effect was observed and the first step (formation of cyclohexadienyl cation) must be the rate-determining step. In free-radical sulfonyloxylations and aroyloxylations with BTP and CTP, primary kinetic isotope effect is observable, and the values are greater in aroyloxylations. These k_H/k_D values suggest that in the reactions with BTP and CTP, the second step (removal of hydrogen) is probably rate-determining, and the first step is reversible.



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