

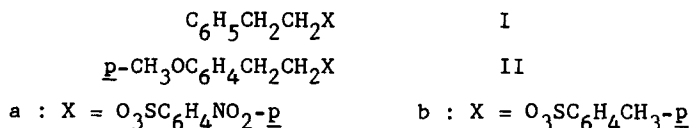
CARBON-14 ISOTOPE EFFECTS IN THE ACETOLYSIS OF 2-ARYL-
(ARYL-1-¹⁴C)-ETHYL *p*-NITROBENZENESULFONATES

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In recent years much interest in the solvolysis of 2-arylethyl systems has developed in connection with the non-classical phenonium ion problems (1). Although a number of techniques including secondary deuterium isotope effects (2) have been utilized to prove the structures of the rate-determining transition states, there are considerable ambiguities concerning the reaction. The participation of aryl groups, in our opinion, has been postulated without a reliable evidence. In this communication we report the primary carbon-14 isotope effects in the acetolysis of phenyl-1-¹⁴C labeled 2-arylethyl esters, and present a definite evidence of neighboring 4-methoxyphenyl (anisyl) participation in the transition state.

2-Phenyl-(phenyl-1-¹⁴C)-ethyl *p*-nitrobenzenesulfonate (Ia) was prepared from benzoic acid-(phenyl-1-¹⁴C), and 2-(4-methoxyphenyl-(phenyl-1-¹⁴C))-ethyl *p*-nitrobenzenesulfonate (IIa) from toluene-(phenyl-1-¹⁴C) via the long sequence



of reactions. Ia and IIa were acetolyzed at 100 and 60°C, respectively, by the usual sealed ampoule technique. After the reaction mixtures were quenched and

poured into ice-water, the precipitated esters were recovered quantitatively. Carbon-14 isotope effects were calculated from the fraction of reaction and the specific activity of the recovered esters (Table I).

Table I
Carbon-14 Isotope Effects in the Acetolysis of 2-Aryl-
(aryl-1-¹⁴C)-ethyl p-Nitrobenzenesulfonates

Reactant	Time, min	%reaction	Specific Activity ^{a)}	k^{12}/k^{14}
	0	0	2.068	
Ia ^{b)}	185	39.0	2.068	1.000
	335	59.3	2.066	1.000
	435	69.2	2.079	1.004
	590	80.6	2.082	1.004
			mean value	1.002 ± 0.001 ^{d)}
IIa ^{c)}	0	0	1.751	
	325	39.4	1.777	1.030
	580	59.3	1.791	1.025
	780	70.4	1.814	1.030
	1030	80.3	1.829	1.027
		mean value	1.028 ± 0.001 ^{d)}	

a) mCi mol⁻¹. b) 100.00±0.02°C, c=0.065 mol l⁻¹, $k_1 = 4.52 \times 10^{-5} \text{sec}^{-1}$.

c) 60.00±0.02°C, c=0.059 mol l⁻¹, $k_1 = 2.59 \times 10^{-5} \text{sec}^{-1}$. d) Probable error of the mean.

No carbon isotope effect observed in the acetolysis of Ia indicates that the major portion of this reaction proceeds without phenyl participation in the transition state. This is in accord with the practical absence of scrambling (4.6%) between α - and β -carbons in the acetolysis of Ib (3). The small or negligible secondary α -deuterium effect ($k_H/k_D=1.03$) of Ib (2) is also attributed to Sn2 character of the reaction.

Our observation of the small but definite carbon-14 isotope effect at the position of phenyl-1 of IIa confirms some change of the bonding of this carbon

atom in the transition state. This strongly suggests the importance of the anisyl participation, and is consistent with complete scrambling (50%) between α - and β -carbons in the reaction of IIb (4). Although the secondary α -deuterium effect observed in the acetolysis of IIb ($k_H/k_D=1.18$) might be regarded as a result of anisyl participation (2), it seems to be still an indirect evidence.

Additional information concerning α - and β -carbon isotope effects are necessary to clarify the structure of the transition state, but we feel phenyl-1 carbon isotope effects would be sensitive to the nature of the transition states (5). Further investigation on this line is now in progress.

REFERENCES

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5. We are currently investigating phenyl-1 carbon isotope effects in the Beckmann and pinacol rearrangements and the effects of reagent change on the isotope effects. It will be reported in near future.