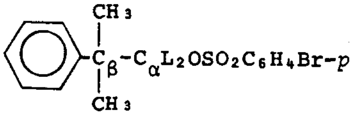
Tetrahedron Letters No. 48, pp 4767 - 4770. Pergamon Press. Printed in Great Britain.

NEIGHBORING GROUP PARTICIPATION IN SOLVOLYSIS. V.[1]
CARBON-14 AND DEUTERIUM ISOTOPE EFFECTS IN SOLVOLYSIS OF NEOPHYL *p*-BROMOBENZENESULFONATE

Hiroshi Yamataka, Sueng-Geon Kim, Takashi Ando† and Yasuhide Yukawa
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka, Japan

(Received in Japan 11 September 1973; received in UK for publication 15 October 1973)

In the previous papers of this series, we reported that the magnitude of the carbon-14 isotope effect at the phenyl-1 position observed in solvolysis of neophyl brosylate (I) was similar to those of 2-arylethyl nosylates proceeding exclusively with participation by a neighboring aryl group.[1-3] The result supports the familiar idea that the neophyl system can be a good model for the k_Δ solvolysis.[4] In order to characterize the transition state of the process, therefore, it is useful to measure the kinetic isotope effects at the various other positions of I, in which absence of ion-pair return must not cause any trouble for the measurement.



$C_6H_5C_\beta(CH_3)_2-C_\alpha L_2OSO_2C_6H_4Br\text{-}p$

Ia : L=H
b : phenyl-1-^{14}C, L=H
c : α-^{14}C, L=H
d : β-^{14}C, L=H
e : L=D

The labeled esters, Ic, d, and e, were prepared by the ordinary method[5] using sodium cyanide-^{14}C, benzoic acid-*7*-^{14}C, and lithium aluminum deuteride, respectively. Acetolysis was followed titrimetrically and trifluoroacetolysis was done spectrophotometrically. For radioassay, the unreacted I was recovered six or seven times at several fractions of reaction, ranging from 0 to 80%.

The samples of the ester were purified by repeated recrystallization and oxidized in a combustion furnace. The radioactivity of the carbon dioxide generated was measured by the ionization chamber counting method with a good reproducibility.[6] The kinetic isotope effect was calculated by the least squares method using eq 1;

$$\log A_x = \log A_0 - (1-k^{14}/k^{12})\log(1-x) \qquad (1)$$

where x is the fraction of reaction and A is the specific activity of the recovered I. The data showed good linearity without any trend with x. The results are summarized in Table I. Standard deviations and correlation coeffecients reflect the accuracy of the measurement.

Table I. Isotope Effects in Solvolysis of Neophyl *p*-Bromobenzenesulfonate

	CH_3CO_2H, 75°C	CF_3CO_2H, 0°C
k, sec^{-1} (Ia)	6.99×10^{-5}	7.62×10^{-5}
k^{12}/k^{14} at phenyl-1 (Ib)[a]	1.0234±0.0010[c] (0.996)[d]	1.0353±0.0007 (0.998_7)
k^{12}/k^{14} at α (Ic)	1.0931±0.0032 (0.997)	1.1411±0.0010 (0.999_8)
k^{12}/k^{14} at β (Id)	1.0137±0.0007 (0.993)	1.0142±0.0006 (0.995)
k_H/k_D at α (Ie)[b]	1.214±0.002	1.247±0.008

[a] reference 1. [b] per d_2, the average of two determinations. [c] standard deviations, s. [d] correlation coefficients, r.

The small and positive carbon-14 isotope effects observed at the β-position (Id) are in contrast with the negligible deuterium effects at the same position so far reported for the k_Δ solvolysis of the 2-arylethyl system.[7] The fact suggests that some change in the bonding of the β-carbon may occur in the transition state, although an alternate possibility derived from the fractionation factor can not be rejected here without an exact calculation on the system.[8] In any event, no change in the bonding should be concluded after coincidence of both results of carbon and deuterium effects, as either one of them could happen to be unity because of some compensation.

Very large isotope effects observed at the α-carbon are interesting, as a large effect at a reaction center is usually considered as an indication of an S_N2 reaction. The value of $k^{12}/k^{14} = 1.093$ in acetolysis of Ic is a typical one for a direct substitution, and the value of 1.141 in trifluoroacetolysis is equal to the maximum one ever reported for the S_N2 reaction.[9] The result suggests that the neighboring phenyl group plays an important role in the reaction as an external nucleophile does in a direct substitution, and that the vibrational character of the reacting carbon is similar to that in the S_N2 reaction. No additional bonding, either by resonance or by hyperconjugation, is possible for the system. A large carbon-14 isotope effect is expected for such a case just like as an S_N2 reaction.

The secondary deuterium isotope effects at the alpha to the reacting carbon in this system, $k_H/k_D = 1.21$ for acetolysis and 1.25 for trifluoroacetolysis, are typical ones for the k_Δ process,[10] which are in between those for a direct substitution ($k_H/k_D = 1.0$)[11] and those for a limiting reaction ($k_H/k_D = 1.22$ per D).[12] These fairly large α-deuterium effects in the process seem to be incompatible with the large α-carbon effects discussed above. This apparent discrepancy, however, can be interpreted based on the special geometry of the transition state of the process. A neighboring aryl group attacks the α-carbon from the direction close to the β-carbon and distant from the α-hydrogens. In such a distorted transition state the force constants for the bending motions including the α-C-H bond are smaller than those in a usual S_N2 reaction. Fairly large effects can reasonably be expected for this type of a transition state.

In conclusion, the isotope effects observed at the various positions in solvolysis of neophyl brosylate have been in good accord with the postulated geometry of the transition state of the k_Δ process, which in turn has been characterized as a nucleophilic substitution including a concerted ionization with a similar nature as S_N2 at the reacting α-carbon.

REFERENCES AND FOOTNOTES

1. Part IV: Y. Yukawa, S.-G. Kim, and H. Yamataka, *Tetrahedron Lett.*, 373 (1973).
2. Y. Yukawa, T. Ando, K. Token, M. Kawada, and S.-G. Kim, *ibid.*, 2367 (1969).
3. Y. Yukawa, T. Ando, M. Kawada, K. Token, and S.-G. Kim, *ibid.*, 847 (1971).
4. A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968); M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969).
5. R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).
6. A Takeda-Riken TR-84M vibrating reed electrometer with a TR-6515D digital voltmeter was used.
7. (a) W. H. Saunders, Jr., S. Ašperger, and D. H. Edison, *J. Amer. Chem. Soc.*, **80**, 2421 (1958); (b) W. H. Saunders, Jr. and R. Glaser, *ibid.*, **82**, 3586 (1960); (c) T. Ando, N. Shimizu, S.-G. Kim, Y. Tsuno, and Y. Yukawa, *Tetrahedron Lett.*, 117 (1973); (d) K. Tsuji, unpublished results.
8. S. R. Hartshorn and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **94**, 9002 (1972).
9. M. L. Bender and D. F. Hoeg, *ibid.*, **79**, 5649 (1957).
10. D. E. Sunko and S. Borčić in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand Reinhold, New York, N. Y., 1970, p. 160.
11. A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p. 172.
12. (a) V. J. Shiner, Jr. and W. Dowd, *J. Amer. Chem. Soc.*, **93**, 1029 (1971); (b) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971); (c) V. J. Shiner, Jr. and R. D. Fisher, *ibid.*, **93**, 2553 (1971).