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NEIGHBORING GROUP PARTICIPATION IN SOLVOLYSIS. IX.[1]
METHYL PARTICIPATION IN SOLVOLYSIS OF PINACOLYL BROSYLATE

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Pinacolyl brosylate (3,3-dimethyl-2-butyl *p*-bromobenzenesulfonate, **1**) is a key substance in the controversy of the solvolysis mechanism of secondary alkyl substrates. From study on deuterium isotope effects and behavior of olefins in trifluoroacetic acid, Shiner and his coworkers proposed the use of **1** as a reference compound whose solvolysis proceeds by way of rate-determining ionization with neither neighboring (k_Δ) nor solvent nucleophilic (k_s) assistance.[2] After taking into account the inductive effects, small rate ratios (*e.g.*, < 0.1) of secondary alkyl brosylates relative to pinacolyl brosylate are attributed to the internal return of intimate ion-pairs (hidden return), while larger ones (> 1) to some cause of acceleration such as strain release, solvent participation, or neighboring group participation.

$(CH_3)_3CCH(CH_3)OSO_2C_6H_4Br\text{-}p$ **1**

Bentley, Schleyer, and their coworkers criticized Shiner's proposals and argued that solvolysis of **1** is accelerated not by inhibition of such hidden return but entirely or almost entirely by inductive-hyperconjugative effects.[3] On the other hand, Harris pointed out the possibility of methyl participation in pinacolyl solvolysis with, in our opinion, insufficient evidence.[4] Nordlander was in favor of Shiner's proposals,[5] and Pross claimed a small solvent nucleophilic assistance in pinacolyl solvolysis.[6]

Recently, we demonstrated the usefulness of carbon-14 kinetic isotope effects as a tool to detect neighboring methyl participation in solvolysis of neopentyl and related *p*-nitrobenzenesulfonates.[1,7] The present paper describes the successful application of this technique for elucidation of the mechanism of pinacolyl solvolysis.

Solvolysis of **1** and its labeled compounds was conducted in acetic acid at 55 °C and in 97% 2,2,2-trifluoroethanol at 25 °C both at 0.05 M concentration. Carbon-14 isotope effects were calculated by use of Eq. 1 for **1**-α-^{14}C and Eq. 2 for **1**-γ-^{14}C, in which x is the fraction of reaction, and A_0 and A_x are the specific activities of the recovered esters at $x = 0$ and $x = x$, respectively.[1] Results are shown in Table 1.

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

$$\log A_x = \log A_0 - 1/3[1 - (k^{14}/k^{12})]\log(1-x) \qquad (2)$$

Table 1. Kinetic Isotope Effects in Solvolysis of Pinacolyl Brosylate

Solvent	CH_3CO_2H	97% CF_3CH_2OH
$10^5k/s^{-1}$	$5.05\pm0.04^{a,d}$	$7.76\pm0.12^{b,e}$
k^{12}/k^{14} at α	1.031 ± 0.004^{c}	1.059 ± 0.002^{c}
k^{12}/k^{14} at γ	1.061 ± 0.009^{d}	1.063 ± 0.005^{d}

[a] Determined titrimetrically. [b] Determined conductometrically. [c] Values from single runs. Standard deviations were calculated from errors in the slope of Eq. 1. [d] Average of two runs. [e] Average of three runs.

Large carbon-14 isotope effects at γ confirm the bonding change of this carbon at the transition state of the reaction. Methyl participation in the pinacolyl solvolysis has thus been verified.[1]

Larger γ-effects in this secondary alkyl solvolysis (*ca.* 6%) as compared with those in primary solvolysis such as neopentyl or 2-methyl-2-adamantylmethyl (4-5%)[1,7] are difficult to explain at present. The participating methyl has a composite character of bond-breaking and bond-forming, which are antagonistic to each other with respect to the contribution to the magnitude of the kinetic isotope effects. Triplicated errors inherent in the isotope effects of **1**-γ-^{14}C also restrict the discussion.[1]

Smaller effects at the α-carbon (3-6%) in **1** than that in the neopentyl ester (*ca.* 7%),[7] and the different solvent dependencies of the α- and γ-carbon-14 effects, are just mentioned as the apparent results of this study. A detailed discussion on them must await a further study.

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