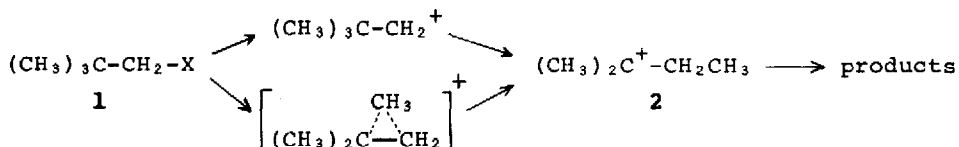# NEIGHBORING GROUP PARTICIPATION IN SOLVOLYSIS. VI.[1]
METHYL PARTICIPATION IN ACETOLYSIS OF NEOPENTYL p-NITROBENZENESULFONATE

Takashi Ando*, Hiroshi Yamataka, Junjiro Kuramochi,

Junko Yamawaki, and Yasuhide Yukawa

The Institute of Scientific and Industrial Research,

Osaka University, Suita, Osaka, Japan

Solvolysis of neopentyl derivatives (1) proceeds with rearrangement to yield substitution and elimination products derived from the t-amyl cation (2).

$$(CH_3)_3C-CH_2-X \quad \begin{array}{c} \nearrow (CH_3)_3C-CH_2^+ \searrow \\ \searrow \left[\substack{CH_3 \\ (CH_3)_2C\!-\!CH_2} \right]^+ \nearrow \end{array} (CH_3)_2C^+-CH_2CH_3 \longrightarrow products$$

$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

The timing of the ionization and rearrangement steps has long been a matter of controversies. Evidence for and against methyl participation has been accumulated from kinetic and stereochemical researches.[2] Even studies using kinetic isotope effects, which are usually the most decisive tool in such a case, were so far ineffective. Negligible intermolecular isotope effects in hydrolysis[3] and trifluoroacetolysis[4] of neopentyl-d_9 derivatives, and large intramolecular effects in the trifluoroacetolysis (CH_3 vs. CD_3) led Schubert and Henson to a conclusion that the rearrangement occurs after the ionization.[4] However, Schleyer pointed out that the negligible intermolecular effects could be brought about by normal effects of a migrating methyl group compensated by inverse effects of nonmigrating methyl groups.[5] He supported the concerted mechanism from the stereochemistry of acetolysis of 1-adamantyl-carbinyl-1'-d tosylate.[6]

We report here that our study using carbon-14 kinetic isotope effects gave decisive evidence for methyl participation at the rate-determining ionization in acetolysis of neopentyl p-nitrobenzenesulfonate (1a-d).

$$\begin{array}{l} CH_3 \\ | \\ CH_3\text{-}\overset{|}{C}\text{-}CL_2OSO_2C_6H_4NO_2\text{-}p \\ | \\ CH_3 \end{array}$$
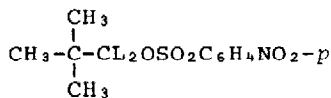
1a : L = H
b : 3-^{14}C, L = H
c : 1-^{14}C, L = H
d : L = D

In analogy with our previous study on the 2-phenylethyl system, the successive labeling technique was applied to the neopentyl system.[1]

The labeled compounds, **1b**, **c**, and **d**, were prepared from methyl iodide-^{14}C, barium carbonate-^{14}C, and lithium aluminum deuteride, respectively. Experimental procedures for kinetics and radioassays were similar to those reported earlier.[1] Results are summarized in Table I. Data on neophyl brosylate (**3**) are also included in comparison.

Table I.   Kinetic Isotope Effects in Acetolysis of Neopentyl
            Nosylate (**1**) and Neophyl Brosylate (**3**)

	1, 100°C	**3**, 75°C
k, sec^{-1}	$(2.82\pm0.01) \times 10^{-5}$	6.99×10^{-5}
k^{12}/k^{14} at γ	1.050 ± 0.001 *(methyl)*	1.023 *(phenyl-1)*
k^{12}/k^{14} at α	1.074 ± 0.002	1.093
k_H/k_D at α	1.187 ± 0.001	1.214

A fairly large effect at the γ-methyl-^{14}C (**1b**) clearly verifies that the bonding of this carbon is changing at the transition state of the reaction. This is the first observation of a positive isotope effect at the participating carbon of a σ-type. The effect detected at the α-carbon (**1c**) was also large and similar to those observed at the α-position in the neophyl system. The α-deuterium effect observed here (**1d**) is a typical value for the k_Δ solvolysis and about halfway in between the S_N1 and S_N2 reactions.[1,7]

In order to reinforce the conclusion, a γ-deuterium effect of a nonmigrating CD_3 was determined in acetolysis of neophyl-γ-d_6 brosylate (**4**) at 75°C.

$$Ph\text{-}C(CD_3)_2CH_2OSO_2C_6H_4Br\text{-}p \qquad \textbf{4}$$
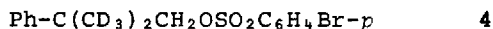
Although the effect was small, it was really inverse as expected; $k_H/k_D = 0.959\pm0.005$, *i.e.*, 0.979 per CD_3.

As a conclusion, the kinetic isotope effect study confirmed definitely that acetolysis of neopentyl derivatives proceeds in a concerted fashion.

References.   1) Part V: H. Yamataka, S.-G. Kim, T. Ando, and Y. Yukawa, *Tetrahedron Lett.*, 4767 (1973).   2) For a recent review of this subject, see J. M. Harris in "Progress in Physical Organic Chemistry," Vol. 11, A. Streitwieser and R. W. Taft, Ed., John Wiley & Sons, New York, N. Y., 1974, p. 89.   3) M. J. Blandamer and R. E. Robertson, *Can. J. Chem.*, **42**, 2137 (1964). 4) W. M. Schubert and W. L. Henson, *J. Amer. Chem. Soc.*, **93**, 6299 (1971). 5) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions," Vol. 2, M. Szwarc, Ed., John Wiley & Sons, New York, N. Y., 1974, p. 247.   6) S. H. Liggero, R. Sustmann, P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4571 (1969).   7) 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.