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Neighboring Group Participation in Solvolysis. XIII. Kinetic Isotope Effects in Solvolysis of 2-Arylethyl *p*-Nitrobenzenesulfonates[1,2)]

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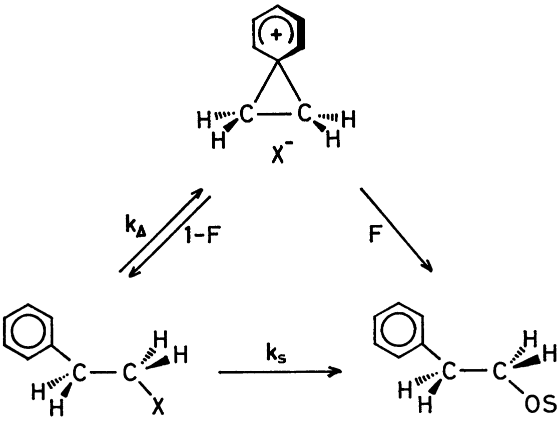
Carbon-14 kinetic isotope effects (k^{12}/k^{14}) were determined for the solvolysis of phenethyl (**1a**) and 2-(*p*-methoxyphenyl)ethyl (**1b**) *p*-nitrobenzenesulfonates in acetic, formic, and trifluoroacetic acids. Phenyl-1 carbon effects were all in the range of 1.02—1.04 except for the acetolysis of **1a** ($k^{12}/k^{14}=1.005$), which has been proved to proceed mainly *via* the aryl unassisted (k_s) pathway. In all other reactions, which proceed mainly *via* the aryl assisted (k_Δ) pathway, the phenyl-1 carbon apparently changes its bonding in the transition states. A large α-carbon effect (1.131) and a small β-carbon effect (1.013) as well as a medium phenyl-1 effect (1.022) were observed for the formolysis of **1b**, whose mechanism is thought to be exclusive k_Δ without troublesome ion-pair return. These observations, together with α- and β-deuterium effects reported already, enabled us to describe the qualitative nature of the bridged transition-state structure of the k_Δ pathway, *i.e.*, advanced C_α–O bond rupture, slight C_α–C_{Ph-1} bond formation, C_α–C_β double bond formation, slight C_β–C_{Ph-1} bond rupture, and breakdown of aromaticity at the phenyl-1 position. These characteristics are very similar to those of the phenonium ion.

After a long debate it has become a generally accepted idea that the solvolyses of all primary and most secondary 2-arylalkyl derivatives proceed through discrete aryl assisted (k_Δ) and/or aryl unassisted (k_s) pathways (Scheme 1).[3)] A great deal of attention has been focused on the k_Δ pathway, since it can be regarded as a prototype of intramolecular catalysis, an important phenomenon in enzyme reactions, and also because it leads to the so-called phenonium ion intermediate whose structure has been a subject of discussion.[3)] In 1969, we communicated the observation of normal carbon-14 kinetic isotope effects ($k^{12}/k^{14}>1.0$) of labeling at phenyl-1 in the solvolysis of 2-arylethyl *p*-nitrobenzenesulfonates (nosylates, **1**).[2)] It was the first definitive evidence for the bonding change of the phenyl-1 carbon in the transition state of the reaction. Details of the study are described in the first half of this paper.

In order to obtain further detailed information concerning the structure of the transition state of the k_Δ pathway, it is desirable to observe kinetic isotope effects of labeling at several different atoms of 2-arylethyl esters. This type of approach is referred to as the successive labeling technique.[4)] The first study along these lines has been carried out with 2-methyl-2-phenylpropyl (neophyl) esters (**2**).[5,6)]



Scheme 1.

$$\mathrm{ArCH_2CH_2OSO_2Ar'}$$

1a: $\mathrm{Ar=C_6H_5,\ Ar'}=p\text{-}\mathrm{NO_2C_6H_4}$
b: $\mathrm{Ar}=p\text{-}\mathrm{CH_3OC_6H_4},\ \mathrm{Ar'}=p\text{-}\mathrm{NO_2C_6H_4}$

$$\mathrm{ArC(CH_3)_2CH_2OSO_2Ar'}$$

2

Introduction of two methyl groups on the β-carbon of **1** not only causes the reaction to proceed *via* the k_Δ pathway almost exclusively but also inhibits scrambling of labels at α and β during the course of the reaction of **2**.[7,8)] Thus, kinetic isotope effects have been successfully measured for α-^{14}C, α-D_2, β-^{14}C as well as phenyl-1-^{14}C in the solvolysis of **2**,[5,6)] and the transition-state structure has been discussed both qualitatively and quantitatively using these data.[6)]

In the present study, the successive labeling technique was extended to the parent 2-arylethyl system. The transition-state structure of the k_Δ pathway of 2-arylethyl esters is discussed with the kinetic isotope effects measured for the formolysis of 2-(*p*-methoxyphenyl)ethyl nosylate (**1b**), and compared with that for the neophyl solvolysis.

Results

Labeling with carbon-14 at the specific carbons of phenethyl nosylate (**1a**) and 2-(*p*-methoxyphenyl)ethyl nosylate (**1b**) was performed by well-established procedures (see Experimental Section). The solvolyses of **1a** and **1b** in acetic, formic, and trifluoroacetic acids were followed by the gravimetric method, in which unreacted nosylates were recovered from the reaction solutions at various fractions of reaction, ranging from 0 to 70 or 80%. The recovery was quantitative for **1a** and almost so for **1b**; in the latter case the recovery factor was used in order to determine the fractions of reaction. The formolysis of **1b** was also followed by the spectrophotometric method. The rate con-

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TABLE 1. RATE CONSTANTS AND CARBON-14 KINETIC ISOTOPE EFFECTS IN SOLVOLYSIS OF PHENETHYL NOSYLATE (**1a**) AND 2-(p-METHOXYPHENYL)ETHYL NOSYLATE (**1b**)

Substrate	Label	Solvent	t/°C[a]	$k\times10^5$/s^{-1}	(r)[b]	k^{12}/k^{14}	n[c]	(r)[d]
1a	Phenyl-1[e]	CH_3CO_2H	100	4.65±0.04	(0.9997)	1.005±0.002	5	(0.76)
1a	Phenyl-1[e]	HCO_2H	60	6.67±0.07	(0.9997)	1.023±0.001	6	(0.994)
1a	Phenyl-1[e]	CF_3CO_2H	45	9.7±0.9	(0.97)	1.029±0.002	5	(0.991)
1a	Phenyl-1[e]	CF_3CO_2H[f]	30	5.96±0.12	(0.9992)	1.036±0.004	4	(0.991)
1b	Phenyl-1[g]	CH_3CO_2H	60	2.63±0.02	(0.9998)	1.028±0.002	5	(0.996)
1b	Phenyl-1[g]	HCO_2H	30	12.1±0.1	(0.9994)	1.022±0.002	5	(0.991)
1b	Phenyl-1[g]	CF_3CO_2H[f]	0[h]	3.24±0.04	(0.9996)	1.039±0.014	3	(0.94)
1b	α[i]	HCO_2H	30	12.2±0.1[j]	(0.998)	1.131±0.002	7	(0.998)
1b	β[i]	HCO_2H	30	12.2±0.1[j]	(0.998)	1.013±0.002	7	(0.96)

a) ±0.02 °C unless otherwise noted. b) Correlation coefficients of pseudo-first order rate plots. c) Number of radioassayed samples recovered at various fractions of reaction. See Ref. 10. d) Correlation coefficients for fit of radioactivities to Eq. 1. in the text. e) Substrate in 0.065 M (1M = 1 mol dm^{-3}). f) Sodium trifluoroacetate (0.1 M) was added. g) Substrate in 0.059 M. h) ±0.1 °C. i) Substrate in 0.05 M. j) Determined spectrophotometrically.

stants obtained by these two methods agreed very well with each other. The linearity of the first-order rate plot for the trifluoroacetolysis of **1a** was rather poor in the absence of sodium trifluoroacetate, but it was much improved when the sodium salt was added to the reaction medium.

Carbon-14 kinetic isotope effects were determined according to the procedures described previously.[6] Calculation of isotope effects was carried out by the linear regression method using

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

where x is the fraction of reaction, and A_0 and A_x are the molar radioactivities of the initial and recovered esters, respectively.[9,10] The results of kinetic isotope effects are summarized together with rate data in Table 1.

Discussion

Phenyl-1 carbon isotope effects were measured in seven cases for different substrates, solvents, and temperatures (Table 1). All the values were in the range of 1.02—1.04 except for the acetolysis of **1a**, for which a very small value close to unity (1.005) was obtained. Dissection of the rate constants (k_t) of the 2-arylalkyl solvolysis into the aryl assisted (Fk_Δ) and aryl unassisted (k_s) components has been carried out by a number of research groups.[3] They found that only the acetolysis of the phenethyl ester among all the systems studied here proceeds mainly *via* the k_s pathway,[11–14] although the dissection was usually studied not for nosylates but for tosylates or brosylates. The fraction of the k_Δ pathway (Fk_Δ/k_t) for the acetolysis of phenethyl tosylate was estimated to be 0.30—0.42 at 115 °C.[11–14] Because no bonding change for the phenyl-1 carbon is expected in the transition state of the k_s pathway, no isotope effect should be observed for this carbon. Thus, our observation of a small isotope effect in the acetolysis of **1a** is well in accord with the dissection studies by the tracer[11–13] or kinetic[14] method.

All the other values of the phenyl-1 carbon-14 isotope effects (1.02—1.04) definitely show that the bonding of the phenyl-1 carbon changes in the transition state of these reactions. Among these values, those for the trifluoroacetolysis (1.03—1.04) were slightly larger than those for the acetolysis or formolysis (1.02—1.03, Table 1). A similar phenomenon was also observed in the solvolysis of **2**; the phenyl-1 carbon-14 effect was 1.035 for the trifluoroacetolysis at 0 °C and 1.023 for the acetolysis at 75 °C.[5] Although the solvent effect on the isotope effects can not be completely neglected, since weaker solvation to the cationic moiety in a less nucleophilic solvent such as trifluoroacetic acid would result in decreased bonding and thus larger isotope effects, most of the difference in these isotope effects is likely to be attributable to the temperature dependence of the isotope effects. Trifluoroacetolysis was always carried out at a lower temperature than acetolysis and formolysis by 55—75 °C, and a definitive normal temperature dependence (a larger isotope effect at a lower temperature) was observed for this phenyl-1 carbon-14 effect in the acetolysis of **2**.[6] As a reported increase of the isotope effect was 0.003 for a decrease in temperature of 15 °C or 0.008 for 35 °C, the observed difference of 0.01 for **1** can be reasonably attributed to a difference in temperature of 55—75 °C.

In order to carry out the successive labeling study in the parent 2-arylethyl system, it is necessary to measure kinetic isotope effects in a solvolysis, in which the reaction not only proceeds exclusively *via* the k_Δ pathway, but is also free from an ion-pair return which is liable to cause scrambling of labels. The formolysis of **1b** is fitted for this purpose. According to the tracer study carried out with carbon-14 by Jenny and Winstein,[15] the formolysis of 2-(p-methoxyphenyl)ethyl tosylate proceeds exclusively *via* the k_Δ pathway (Fk_Δ/k_t=1.0) without any ion-pair return (F=1.00). The strong ionizing power and the considerable nucleophilicity of formic acid as well as the fairly strong nucleophilicity of the neighboring p-methoxyphenyl group may be the reasons for this unique situation. Taking advantage of this, Saunders and Glaser have already studied secondary α- and β-deuterium isotope effects in this formolysis;[16] we

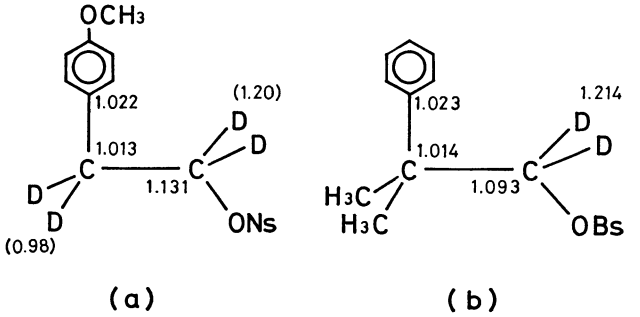

Fig. 1. Carbon-14 and deuterium isotope effects in the solvolysis of (a) 2-(*p*-methoxyphenyl)ethyl nosylate (**1b**) in formic acid at 30 °C, and (b) neophyl brosylate (**2**) in acetic acid at 75 °C. Deuterium effects in (a) are those reported by Saunders *et al.*[16] for the tosylate.

will use their results in our discussion.

Kinetic isotope effects observed in the formolysis of **1b** are summarized in Fig. 1, together with those reported for the acetolysis of **2** for comparison.[5]

It is obvious from Fig. 1 that the isotope effects for various atoms of **1b**, *i.e.*, a large α-^{14}C, medium α-D_2, small β-^{14}C, and medium phenyl-1-^{14}C effects, are almost the same as those for the corresponding atoms of **2**. These observations not only support the results of the dissection studies[7,8,15] that both the formolysis of **1b** and the acetolysis of **2** proceed *via* the k_Δ mechanism, but also indicate that the transition-state structures of both reactions are almost identical. This conclusion confirms the general assumption that neophyl solvolysis can be regarded as a model of the k_Δ process for phenethyl solvolysis.[13,17–19] Thus, the characteristics of the transition-state structure of **1b** can be discussed below in a similar manner to those of **2**[6] by use of the observed data of kinetic isotope effects.

The magnitude of the phenyl-1 carbon-14 effect, 1.022, is within the range (1.02—1.05) observed for the phenyl-1 carbon in a number of phenyl group rearrangements whose mechanisms have been proved to be concerted.[20–23] It is interesting that these medium carbon-14 effects show normal temperature dependence as mentioned above and as observed in the Beckmann rearrangement of acetophenone oxime.[23] When the bonding at the labeled position increases in the transition state, the isotope effect could be small normal, null, or even inverse, and the temperature dependence should be inverse. Thus, the total bonding of the phenyl-1 carbon should decrease, in spite of the hybridization change of this carbon from sp^2 to sp^3. In conclusion, the phenyl-1 carbon changes its bonding in the transition state of the k_Δ solvolysis as a result of C_{Ph-1}–C_α bond formation, breakdown of aromaticity in the benzene ring, and C_{Ph-1}–C_β bond rupture, among which the last two overwhelm the first one.

A large α-carbon-14 isotope effect comparable to those observed in S_N2[24] and a medium α-deuterium effect in contrast to large values for S_N1 and small ones for S_N2 are most characteristic of the k_Δ mechanism.[5,6,25] The importance of symmetry for a carbon isotope effect has been demonstrated in the S_N2 reaction,[26] in which the isotope effect of the central carbon atom becomes maximum when the two partial bonds are equal in strength. The magnitude of an α-deuterium effect is dependent on the vibrational frequencies of the bending motions including the C–H bond, and a larger effect is observed for a looser transition state.[27] Thus, the observed α-effects are compatible with a loose, pseudo-three-centered transition state composed of the phenyl-1 carbon, the α-carbon, and the oxygen of the leaving arenesulfonate.[5,6,25]

The difference between the α-carbon-14 effects for **1b** (1.131) and **2** (1.093), the only apparent difference in Fig. 1, is larger than that expected for the temperature dependence of this effect, since the reported increase in the effect is 0.004 for a decrease of 15 °C in the acetolysis temperature of **2**.[6] The difference in the solvent, formic acid *vs.* acetic acid, wolud not have much influence on the isotope effects. Therefore, the rest of the difference in the α-carbon-14 isotope effects may be attributed to the substituent effect of the phenyl group on the symmetry of the three-centered transition state.[6] The transition-state structure of **1b** may be more symmetric than that of **2** in terms of the breaking C_α–O bond and the forming C_α–C_{Ph-1} bond, resulting in a larger α-carbon isotope effect. Participation by the unsubstituted phenyl group in **2**, which is less nucleophilic than the *p*-methoxyphenyl group in **1b**, may lead to a later transition state with a stronger C_α–C_{Ph-1} bond and a weaker C_α–O bond, giving rise to a smaller isotope effect.[6,26]

A small β-carbon-14 isotope effect, 1.013, is consistent with small but distinct bonding changes at this carbon, which may include C_{Ph-1}–C_β bond rupture and C_α–C_β double bond formation.[28] It is interesting that this change has not been detected by the β-deuterium effect.[16] Quite recently, we observed negative CD_3 effects in the solvolysis of [γ-D_6]-**2** (0.959 per D_6 in acetic acid at 75 °C), which were attributed to the inductive effect by these non-migrating methyl groups.[1] Nevertheless, the β-carbon-14 isotope effects of **1b** and **2** did not show any appreciable difference. The fact suggests that the inductive effect exerted on the β-carbon by the methyl groups may not greatly alter the structure of the transition state in this solvolytic rearrangement, although the rate of the reaction itself is enhanced to a great extent in the presence of these methyl groups.[29]

All of the above enable us to describe the qualitative nature of the transition-state structure of the k_Δ pathway in the phenethyl solvolysis as follows: (1) C_α–O bond rupture is well advanced, (2) the neighboring phenyl group behaves as an intramolecular nucleophile but C_α–C_{Ph-1} bond formation is not advanced, (3) the aromatic π-electron system of the phenyl group has broken down as a result of the participation, and (4) geometrical changes at C_β are small but may include partial C_β–C_{Ph-1} bond rupture and C_α–C_β double bond formation. Although a bridged ion intermediate does not necessarily follow this bridged transition state of the k_Δ solvolysis, as exemplified in the case of the neophyl solvolysis, in which the rearranged tertiary cation is believed to be the first intermediate, it is important to point out that the phenonium ion, whose structure was estimated by molecular orbital calculations,[30,31] can be attained with the least structural changes from this transition state.

Experimental

Materials. [*phenyl*-1-^{14}C]Phenethyl alcohol was prepared from [*phenyl*-1-^{14}C]benzoic acid *via* benzoyl chloride, α-diazoacetophenone, and methyl phenylacetate; the last step made use of the Wolff rearrangement in methanol.[32] Esterification of the phenethyl alcohol with *p*-nitrobenzenesulfonyl chloride in pyridine gave [*phenyl*-1-^{14}C]-**1a.** The multistep synthesis of 2-(*p*-methoxy[*phenyl*-1-^{14}C]phenyl)ethyl nosylate ([*phenyl*-1-^{14}C]-**1b**) from [*phenyl*-1-^{14}C]toluene has already been reported.[33] 2-(*p*-Methoxyphenyl)ethyl nosylates labeled with carbon-14 at the α- and β-carbons ([α-^{14}C]- and [β-^{14}C]-**1b**, respectively) were prepared from *p*-methoxybenzyl cyanide (**3**) labeled at the cyanide- and benzyl-carbons, respectively, *via* acid hydrolysis, esterification with methanol, reduction with lithium aluminum hydride, and esterification with *p*-nitrobenzenesulfonyl chloride, successively. One of the precursors, [*cyanide*-^{14}C]-**3**, was synthesized from the reaction of *p*-methoxybenzyl chloride with sodium [^{14}C]cyanide.[34] The other, [*benzyl*-^{14}C]-**3**, was prepared by cyanation of *p*-methoxyphenyl bromide with copper(I) [^{14}C]cyanide[35,36] followed by hydrolysis, esterification, reduction, chlorination, and cyanation.[34] The chemical purity of the labeled compounds was verified by comparison of their physical constants and spectroscopic data with those for the unlabeled compounds. All ^{14}C labeled compounds had molar radioactivities of about 1.3—2.7 mCi/mol. The final arenesulfonates were carefully purified by repeated recrystallization until the molar activities remained constant. Phenethyl nosylate (**1a**): mp 102—103 °C (from hexane–carbon tetrachloride). 2-(*p*-Methoxyphenyl)ethyl nosylate (**1b**): mp 100.0—100.5 °C (from hexane–carbon tetrachloride or hexane–benzene).

Solvolysis Media. Acetic acid was refluxed over 2.0 wt% potassium permanganate, fractionally distilled, and the middle cut was refluxed with 1% pure acetic anhydride followed by fractional distillation (bp 119.1—119.3 °C).[37] Formic acid was purified according to the procedure described by Winstein and Marshall (bp 28.0—29.0 °C/6.60 kPa).[38] Trifluoroacetic acid was distilled through a 1 m, vacuum-jacketed column packed with glass helices. To the middle cut (bp 72.2—72.4 °C) was added 1 wt% freshly distilled trifluoroacetic anhydride.[39] Buffered medium (1.0 dm^3) was prepared by dissolving 0.1 mol of sodium trifluoroacetate in the above trifluoroacetic acid.

*Quantitative Recovery of Nosylates **1a** and **1b**.* About 100 mg of **1a** or **1b** was weighed in a flask and dissolved in 11—30 cm^3 of solvolysis media. Cold distilled water (5 to 20 times the volume of the media used) was added to the solution, and the mixture was left overnight in a refrigerator. Precipitates of **1a** or **1b** were filtered with a weighed glass filtering crucible, washed thoroughly with cold distilled water, dried overnight in an oven at 70 °C (for **1a**) or in a vacuum desiccator over phosphorus pentaoxide (for **1b**), and weighed. The recovery of **1a** was 99.3±0.5% (acetic acid), 99.7±0.3% (formic acid), and 99.1±0.9% (trifluoroacetic acid), and that of **1b** was 97.6±0.1% (acetic acid), 98.4±0.1% (formic acid), and 95.9±1.4% (trifluoroacetic acid).

Kinetic Procedures. Samples of starting material large enough to yield about 100 mg unreacted esters after preselected fractions of reaction, ranging from 0 to 80% completion, were delivered to individual ampoules, dissolved in suitable volumes of the reaction media, and the ampoules were sealed. The reaction was started by placing the ampoules in a constant temperature bath, and quenched by cooling them in an ice bath or a Dry Ice–acetone mixture. After breaking the seal, the contents and the washings of the ampoules (5 cm^3 of the reaction media) were poured into cold water (5 to 20 times the combined volume of the reaction solution and the washing). After standing overnight in a refrigerator, the precipitates (unreacted esters) were filtered with a glass filtering crucible, and then treated as described above. The fractions of reaction were determined from the quantities of the samples used and recovered. For **1b** the recovery factors of 1.025 (acetic acid), 1.016 (formic acid), and 1.043 (trifluoroacetic acid) were used. Data points measured were usually seven.

The rate of formolysis of **1b** was also determined by a spectrophotometric method similar to that used for trifluoroacetolysis by Peterson,[40] in which the increase in the absorbance at 275 nm was followed. The rate constant determined by this method agreed very well with that determined by the gravimetric method (Table 1).

Radioactivity Measurement. The recovered precipitates of unreacted esters were recrystallized repeatedly, usually four times. The purified esters (5—10 mg) were oxidized in a modified Pregl micro combustion furnace,[41] and the ionization current of the radioactive carbon dioxide gas thus generated was measured in an ionization chamber (250 cm^3 capacity, Nuclear-Chicago) with a vibrating-reed electrometer (Nuclear-Chicago Model 6000 Dynacon electrometer system). The rate-of-charge method using a Model T4 interval timer was applied.[41] For the formolysis of [α-^{14}C]- and [β-^{14}C]-**1b**, the ionization current was measured with a Takeda Riken TR-84M vibrating-reed electrometer connected with a digital voltmeter and a computer.[6] It was confirmed that further recrystallization did not change the radioactivities beyond experimental errors.

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