Transient Intermediates in the Photo-Fries Isomerization of Phenyl Acetate via Spontaneous Raman Spectroscopy

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Received August 10, 1981

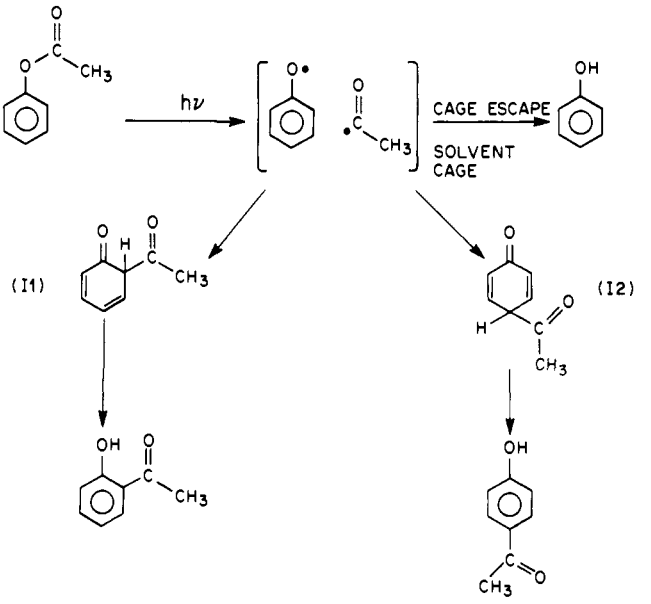
Abstract: Nanosecond-time-resolved 416- and 395-nm Raman spectroscopy is used to observe intermediate species in the solution-phase unimolecular isomerization and fragmentation of phenyl acetate. In aqueous solvent both fundamental and overtone vibrations are observed, while in CH_3OH, CCl_4, and ethylene glycol only overtones are investigated. The time evolution and solvent dependence of the spectra allow resolution of three species: phenoxy radical and (apparently) 6- and 4-acetylcyclohexadienones. These data support a caged radical photo-Fries mechanism; however, the relative yields do not correlate with bulk viscosity.

Transient spontaneous Raman spectroscopy potentially offers important chemical advantages over the technique of transient absorption spectroscopy in understanding the pathways of reactions in solution. These advantages stem from the fact that electronic transitions of molecular species in solution are often broad and featureless, offering little structural information and producing ambiguous kinetics if the spectra of several different species overlap. Transient Raman spectroscopy, however, is characterized in that (1) direct structural information is available from the spectra and (2) the specificity of a relatively sharp-lined Raman spectrum to a single species is high, and spectral changes due to subtle reactions and/or isotopic substitution are often resolved; reaction kinetics are more easily and uniquely determined.

The fundamental experimental problem of Raman spectroscopy is low sensitivity; nevertheless, it has been possible to apply the method to some transient species.[1] While most previous chemical applications have involved species with high resonant enhancement, it has been shown that chemically useful sensitivity in many cases of modest resonance Raman effect can be obtained by employing high power Nd:YAG lasers, extensive signal averaging with multichannel detection, and special techniques such as use of micelle hosts for suppressing solvent background in hydrocarbon-like environments.[2,3] The Raman technology of pulsed excitation with multichannel optical detection has been pioneered by Bridoux and Delhaye.[4]

The photo-Fries unimolecular isomerization and fragmentation of phenyl acetate has been extensively studied as an apparent prototype for geminate cage recombination and escape of large molecular radicals.[5-11] As shown in Scheme I, the final products are phenol and hydroxyacetophenones. A phenoxy radical intermediate has been detected by transient absorption spectroscopy,[10] and therefore at least some photolyzed phenyl acetate molecules initially dissociate into phenoxy and acetyl radicals. A fundamental question is whether the hydroxyacetophenones are

Scheme I



produced by geminate recombination of these same radicals or by a parallel concerted reaction of excited singlet phenyl acetate. In the gas phase it is clear that the radical mechanism dominates;[9] in solution the evidence is not conclusive, although recent workers favor the free radical pathway.[9-11] This isomerization is an interesting reaction for study via transient Raman spectroscopy, as a variety of intermediates produced by the intial photolysis can potentially be characterized.

Experimental Section

Our experimental techniques and apparatus have been described in detail recently.[4] A windowless, flowing solution stream is photolyzed with a 266-nm (~20 mJ) pulse from a Nd:YAG laser. After a time delay Δt, the Raman spectrum of the photolyzed region is taken with a 416- or 395-nm pulse from a second Nd:YAG laser. These latter wavelengths are generated by stimulated Raman scattering of a 355-nm third harmonic pulse in H_2 or CH_4 gas, respectively. The scattered light from the second pulse is dispersed with a small triple spectrograph and recorded with a gated, intensified reticon multichannel detector. The observed spectra are accumulated over several thousand laser pulse pairs. Time resolution is limited by the pulse widths to ~10 ns. Phenyl acetate (Aldrich) was vacuum distilled and analyzed by gas chromatography to be >99.9% pure. Phenol (Baker) was used without further purification.

Results

We have principally studied this reaction in water because the interfering background Raman spectrum of water is weak, and consequently there is increased sensitivity for the detection of

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(2) (a) S. M. Beck and L. E. Brus, *J. Am. Chem. Soc.*, **103**, 2495 (1981); (b) S. M. Beck and L. E. Brus, *J. Chem. Phys.*, **75**, 1031 (1981).
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(4) M. Bridoux and M. Delhaye, *Adv. Infrared Raman Spectrosc.*, **2**, 140 (1976).
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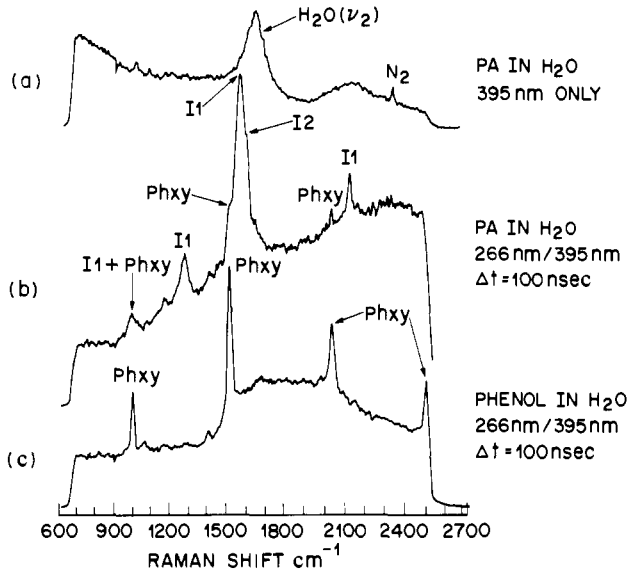

Figure 1. Spontaneous Raman spectra taken with 395-nm probe laser, 100 ns after photolysis with 266-nm pump laser pulse. Power of 395-nm laser ~10 MW/cm^2; 266-nm pump laser ~100 MW/cm^2. (a) Phenyl acetate (5×10^{-3} M) in H_2O. 266-nm pump laser blocked. (b) Phenyl acetate (5×10^{-3} M) in H_2O with 266-nm excitation. Peaks labeled "Phxy" are assigned to the phenoxy radical. Peaks labeled "I1" and "I2" are assigned to intermediate species described in text. (c) Phenol (5×10^{-3} M) in H_2O. All of the strong peaks are assigned to phenoxy radical.

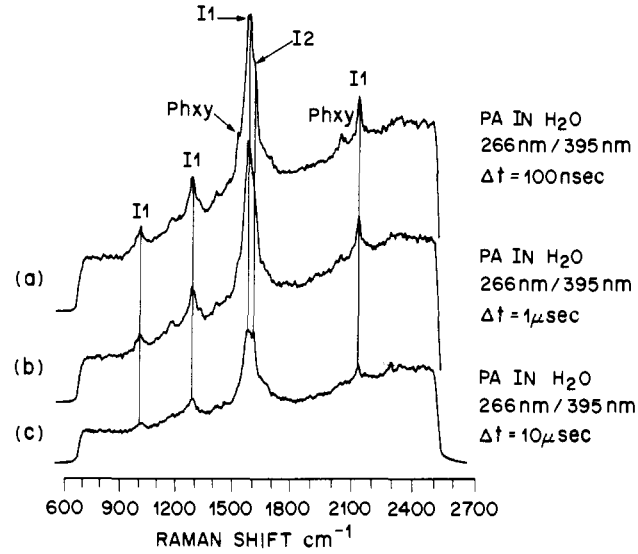

Figure 2. Spontaneous Raman spectrum of phenyl acetate (5×10^{-3} M) in H_2O following 266-nm laser photolysis at three different time delays, showing the time dependence of the various transients produced. Peaks labeled "Phxy" are assigned to the phenoxy radical and those labeled "I1" and "I2" are assigned to intermediates in the rearrangement of phenyl acetate to hydroxyacetophenone. The delays between the 266- and 395-nm pulses are (a) 100ns, (b) 1μs, (c) 10μs.

transients in low concentration.

Figure 1a shows the 700–2500-cm^{-1} Raman spectrum of ~5 $\times 10^{-3}$ M aqueous phenyl acetate (hereafter, PA) taken with a 395-nm probe laser *without* a prior photolyzing pulse. The continuous spectrum with a broad peak near 1700 cm^{-1} is the Raman spectrum of water. The small N_2 peak is scattering from air in front of the solution stream. Weak peaks near 1000 cm^{-1} represent unintensified Raman scattering of ground electronic state PA. Figure 1b shows the same spectrum when the 395-nm Raman probe pulse is preceded (Δt = 100 ns) by a 266-nm photolyzing pulse. Several new, strong Raman bands occur which must represent Raman scattering of species created by photolysis. This spectrum is unchanged at shorter delay times Δt. At this concentration and $\Delta t = 10^{-8}$ s, the species observed must represent the direct products of the unimolecular photolysis of PA; bimolecular reaction products (even at diffusion-controlled rates) could appear only on longer time scales. These Raman lines are underlain by a continuous luminescence background increasing toward higher cm^{-1} shifts. This luminescence background is more intense than the H_2O-solvent Raman in this particular case.

The transient Raman spectrum shows a broad feature near 1600 cm^{-1} as well as sharper and weaker transitions at higher and lower frequencies. Studies of the time evolution of this spectrum, as well as the variation with solvent, show that at least *three* different species contribute to this spectrum. None of the Raman lines in Figure 1b belong to the stable final reaction products phenol and (ortho and para) hydroxyacetophenone, whose aqueous Raman spectra we have independently generated. Therefore the new lines in Figure 1b all belong to intermediate species.

One species is the phenoxy radical, whose Raman spectrum we have generated via photolysis of aqueous phenol in Figure 1c. Phenol photolysis is known to produce phenoxy radical as the only molecular fragment, and in a separate work we describe the spectroscopic and structural implications of this spectrum.[12] Phenoxy radical has an electronic absorption near 400 nm, and with a 395-nm probe laser our ability to detect phenoxy is enhanced via the resonance Raman effect.[13] We note that in Figure 1b the phenoxy comes from photolysis of phenyl acetate and not

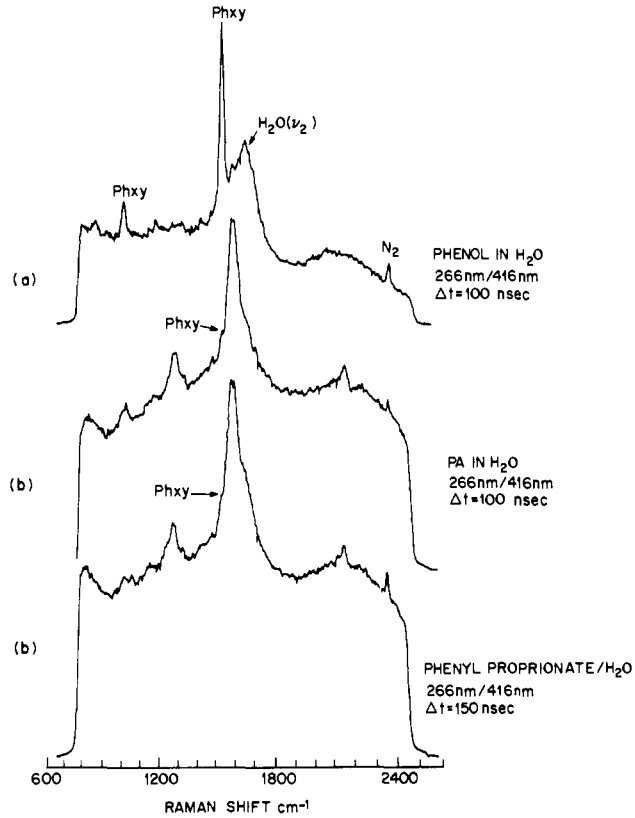

Figure 3. Spontaneous Raman spectra taken with 416-nm probe laser 100–150ns after photolysis with 266-nm pump laser. 416-nm probe laser power is ~10MW/cm^2 and that of the 266-nm pump laser ~50 MW/cm^2. All spectra are a sum of 2000 laser shots. Peaks labeled "Phxy" are assigned to phenoxy radical. (a) Phenol (5×10^{-3} M) in H_2O. The peak labeled N_2 is nitrogen from air in front of liquid sample stream. (b) Phenyl acetate (5×10^{-3} M) in H_2O. The largest peak is assigned to an intermediate species in the rearrangement of phenyl acetate. (c) Phenyl propionate (5×10^{-3} M) in H_2O.

from photolysis of the reaction product phenol, as the solution in the photolysis volume is replaced by the flowing stream between each pulse pair. As already noted, phenoxy has been previously detected on the 15-μs time scale via flash photolysis of PA in

(12) S. M. Beck and L. E. Brus, *J. Chem. Phys.*, accepted for publication.
(13) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1965).

Table I. Observed Frequencies (cm^{-1}) of Transient Species from Phenol, Phenyl Acetate, and Phenyl Propionate

phenol			phenyl acetate	phenyl propionate
H_2O	EtOH	CCl_4	H_2O	H_2O
2498	2490	2477	2128 (I1)	2130
2035	2031	2007	1608 (I2)	1608
1518			1573 (I1)	1573
1005			1274 (I1)	1265

Table II. Relative Intensity Ratios of I1 (2128 cm^{-1}) to Phenoxy (2498 cm^{-1}) for Different Solvents

solvent	ratio	viscosity,[a] cP at 20 °C
CCl_4	0.25	0.97
H_2O	5	1.0
EtOH	2	0.60
ethylene glycol	*b*	19.9

[a] Taken from "Handbook of Chemistry & Physics", 55th ed., CRC Press, Cleveland, OH, 1974-1975. [b] Phenoxy not detected.

ethanol, hexane, and freon solvents.[10]

In Figure 1b, the strongest phenoxy band is only a shoulder on the low cm^{-1} side of the 1600-cm^{-1} transient Raman feature. The major transient Raman bands belong to (one or more) species other than phenoxy.[14] Figure 2 shows the time evolution of this spectrum at delay times of 0.1, 1.0,, and 10.0 μs. The phenoxy bands decay on the ~1-μs time scale. The remaining bands divide into two groups I1 and I2 based upon their time dependence. The feature near 1600 cm^{-1} is actually an overlap of I1 and I2 bands; at 0.1 μs I1 is more intense than I2 while at 10 μs the two bands have equal intensity. I1 decays more rapidly than I2; both species decay more slowly than phenoxy. Table I gives the frequencies for all three species.

Figure 3 shows the spectra for a 416-nm Raman probe wavelength. Figure 3a gives phenoxy spectra from phenol photolysis, while 3b gives the phenyl acetate transient spectra. Both spectra are weaker in absolute magnitude at 416 nm than at 395 nm. The phenoxy spectrum is simpler at 416 nm, with the high frequency overtones near 2000 and 2500 cm^{-1} absent. At 416 nm, the phenoxy contribution is still small with respect to the overlapping I1 and I2 ~1600-cm^{-1} peaks. The fact that the I1 and I2 spectra are stronger at 395 nm suggests that the I1 and I2 transient absorptions lie further blue in the ultraviolet region. Also, the fact that the same fundamental vibrations appear in both 416- and 395-nm spectra implies that these weak scattering features actually are Raman lines and not luminescence.

Figure 3c shows the $\Delta t = 0.1$ μs spectrum for phenyl propionate. The I1 and I2 lines are virtually identical, at out experimental resolution of ~7 cm^{-1}, with those of phenyl acetate. If one assumes for the moment that I1 and I2 are transient isomers of phenyl acetate, such as I1 and I2 in Scheme I, then the insensitivity to propionate substitution suggests that the strong lines near 1600 cm^{-1} are not unconjugated carbonyl modes next to propionate and acetate moieties.

As previously mentioned, water is a preferred solvent for transient Raman spectroscopy, with a low background throughout the energy range in Figures 1 and 3. Other solvents generally have intense, structured bands which effectively block parts of this range. Nevertheless, we find in Figure 4 that we are able to observe the 1800–2700-cm^{-1} range in the series of solvents CCl_4, methanol, and ethylene glycol. This region contains the (395-nm probe laser) overtone lines of phenoxy and the I1 intermediate species. By observing both species, we can monitor the relative variation in yield as a function of solvent. For example, I1 dominates in H_2O, while in CCl_4 phenoxy is stronger than I1.

(14) Note, however, that we cannot state that phenoxy has a lower concentration than the other species as the various Raman cross sections are not known.

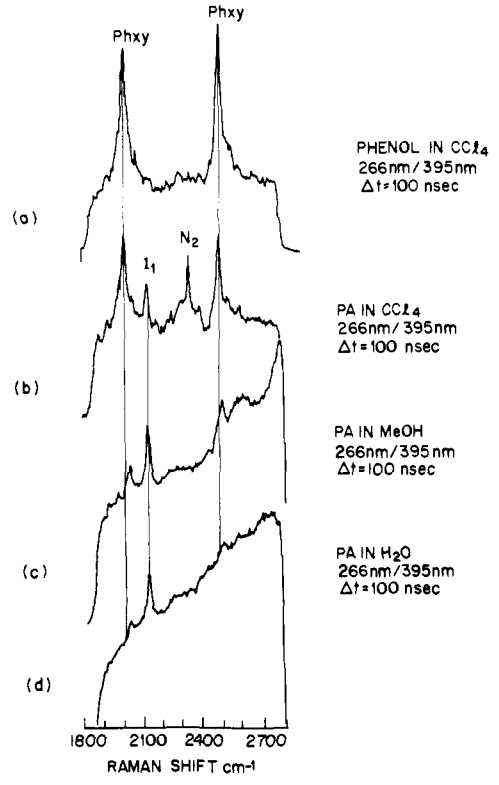

Figure 4. 395-nm Raman spectra taken 100 ns after photolysis with 266-nm laser pulse, showing how the relative production of phenoxy vs. I1 is affected by solvent. All spectra are sum of 600 laser shots. (a) Phenol (5×10^{-3} M) in CCl_4. Peaks labeled "Phxy" are assigned to phenoxy radical. (b) Phenyl acetate (5×10^{-3} M) in CCl_4. Peak labeled I1 is assigned as 6-acetylcyclohexadienone. The N_2 peak is from nitrogen in air in front of sample stream. (c) Phenyl acetate (5×10^{-3} M) in MeOH. The phenoxy peaks have shifted to higher frequency in the more polar solvent; however, I1 peak has remained constant in frequency. (d) Phenyl acetate (5×10^{-3} M) in H_2O. A large fluorescence background is produced by 395-nm excitation of transient species.

Table II lists the ratio of Raman intensities, along with solvent viscosities from the literature.

Discussion

In ethanol, hexane, and freon solvents, Kalmus and Hercules previously observed transients via flash photolysis on the 10^{-5}-s time scale.[10] They reported a phenoxy radical near 400 nm, and another species near 315 nm (in hexane), reasonably suggested to be a cyclohexadienone precursor of the hydroxyacetophenone (hereafter, HoA) products in Scheme I. In ethanol, HoAs are the major photoproducts; several workers have shown that the ratio of HoA to phenol final products varies strongly with solvent. The relative yields of our phenoxy and I1 + I2 intermediates on the ~10^{-8}-s time also vary strongly with solvent. We cannot directly compare our relative Raman intensities with the reported relative yields of final HoA and phenol photoproducts, as we do not know the relative resonance Raman cross sections of the phenoxy and I1 + I2 species.

We tentatively assign our I1 and I2 intermediates as the acetylcyclohexadienones shown in Scheme I. We have experimentally shown that I1 and I2 are formed in unimolecular photolysis of phenyl acetate, and these assignments are logical structural precursors of the known, dominate HoA final products. Formation of cyclohexadienone intermdiates via geminate recombination as in Scheme I was first proposed by Kobsa in 1962.[6] These specific molecules (6-acetyl-2,4 cyclohexadien-1-one and 4-acetyl-2,5 cyclohexadien-1-one) have, to our knowledge, not been independently prepared and/or characterized, and we lack an alternative way of generating their Raman spectra in order to confirm these assignments. Quinkert has reported the UV absorption spectra of various substituted cyclohexadienones; the absorption typically maximizes near 300 nm, with a weak tail extending

through the 400-nm region.[15] This expected absorption at 395 and 415 nm will yield the resonance Raman effect necessary for detection. Strong lines near 1600 cm^{-1} would be expected for the system of a ring carbonyl conjugated with two carbon–carbon double bonds.[12,16] As previously mentioned, we do not think these strong lines represent the acetyl carbonyl modes.

The kinetic and structural usefulness of the transient Raman technique is shown by the following facts: (a) We actually resolve two additional intermediates I1 and I2, whereas the transient absorption in ethanol (figure 1 of reference 10) barely indicates a weak, broad spectrum near 315 nm on top of the phenoxy absorption. (b) An *intense* resonance Raman effect is not required to detect these species, as our probe laser wavelengths lie only in the weak tail of the apparent transient absorption. On the other hand, detection at these concentration levels does require at least a modest resonance Raman effect.

We speculate that I1 is the ortho, and I2 is the para, compound. I1 is the dominate intermediate and decays faster; ortho HoA is the dominante photoproduct. One might logically expect the ortho compound to unimolecularly decay into ortho HoA faster at neutral pH.

In the Table II the relative yields of I1 and I2 vs. phenoxy vary strongly with solvent. This result is as expected if the cyclohexadienones and free phenoxy radicals are competing products for caged radicals as in Scheme I. This result is consistent with the previously reported variation in final products, which has been used to support the solution phase, cage effect photo-Fries mechanism.[9,10]

Table II shows that the relative yields are not simply correlated with bulk solvent viscosity; the chemical and physical nature of the solvent molecules clearly affect the reaction. A specific comparison of the chemically similar molecules methanol and ethylene glycol shows that high viscosity strongly favors the recombination products I1 and I2. This is the expected cage effect behavior. However, CCl_4 has about the same viscosity as H_2O, and yet phenoxy is strongly favored in CCl_4. This may reflect the fact that acetyl radicals can abstract Cl atoms from CCl_4.[17] If Cl abstraction competes with caged radical recombination, then the I1 and I2 yields will be decreased. This mechanism, if correct, would provide direct experimental evidence against a concerted mechanism of I1 and I2 production.

Conclusions

(1) Transient spontaneous Raman spectroscopy shows the existence of three intermediate species formed via unimolecular photolysis of phenyl acetate. One species is the phenoxy radical, and the other two appear to be 6- and 4-acetylcyclohexadienones. (2) A strong solvent dependence in the relative yields of phenoxy vs. (apparently) cyclohexadienone intermediates supports the caged radical photo-Fries mechanism. The competitive yields of geminate recombination vs. radical escape do not correlate with bulk viscosity.

Acknowledgment. We thank H. Roth and M. Kaplan for useful discussions. We also thank T. Wolf for gas chromatography analyses.

Registry No. I1, 80753-89-5; **I2**, 80753-90-8; phenyl acetate, 122-79-2; phenol, 108-95-2; phenyl propionate, 637-27-4; phenoxy radical, 2122-46-5.

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(16) For example, see Y. Nishimura and M. Tsuboi, "Proceedings of the International Conference on Raman Spectroscopy, 7th"; North Holland: Amsterdam, 1980, p 568.
(17) We thank Heinz Roth for this suggestion.

Model Calculations of Kinetic Isotope Effects for the Solvolysis of Neopentyl Arenesulfonates

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Abstract: Model calculations of α-^{14}C, β-^{14}C, γ-^{14}C, α-D_2, and γ-D_3 kinetic isotope effects in the acetolysis of neopentyl arenesulfonate were carried out for two possible pathways, concerted (k_Δ) and stepwise (k_c). In the k_Δ transition state (TS), four bond orders, $n_{\alpha-O}$, $n_{\alpha-\beta}$, $n_{\beta-\gamma}$, and $n_{\alpha-\gamma}$, were taken as independent parameters which define the model, whereas in the k_c model, $n_{\alpha-O}$, $n_{\alpha-\beta}$, $n_{\beta-\gamma}$, and $n_{\gamma-H}$ were taken as the parameters; other geometrical parameters and diagonal force constants were related to these four parameters by empirical expressions. One or more off-diagonal force constants were used to generate the reaction-coordinate frequency. The calculations suggested that the reaction proceeds via the k_Δ pathway whose TS has a weak but significant α–γ interaction; the alternative k_c pathway was shown to be less probable. The k_Δ TS structure determined was then compared with that of the 2-methyl-2-phenylpropyl (neophyl) solvolysis. The calculated k_Δ TS of the neopentyl solvolysis has (1) a stronger C_α–O bond, (2) a stronger C_α–C_β bond, (3) a weaker C_β–C_γ bond, and (4) a weaker C_α–C_γ bond than the TS of the neophyl solvolysis has. The results were interpreted in terms of the difference in the migrating group, methyl vs. phenyl, and it was concluded that the major mode of neighboring group participation by the phenyl is bridging whereas that by the methyl is hyperconjugation.

The mechanism of the neopentyl solvolysis (Scheme I) has been a subject of discussion for a long time, and various approaches have been tried in order to determine whether the mechanism is concerted (k_Δ) or stepwise (k_c).[1]

Quite recently, two groups reported the results of kinetic isotope-effect studies which provided strong support for the k_Δ mechanism.[2,3] Observations of normal carbon-14 isotope effects at the α-, β-, and γ-positions in the acetolysis of neopentyl nosylate (**1**, X = *p*-nitrobenzenesulfonate) indicated that the bondings at the three positions change in the transition state (TS). The results are consistent with the k_Δ pathway. Furthermore, the magnitudes

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(2) Ando, T.; Yamataka, H.; Morisaki, H.; Yamawaki, J.; Kuramochi, J.; Yukawa, Y. *J. Am. Chem. Soc.* **1981**, *103*, 430-436.
(3) Shiner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436-442.

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