data appears at this time to be the same as that of CsCP(FHF), but it has a significantly shorter Pt-Pt separation. In fact, the Pt-Pt distance of 2.798 (1) Å found in RbCP(FHF) is the shortest spacing yet observed in a POTCP salt. However, these findings do demonstrate that the anion content is not fixed at 0.30-0.33 as has been observed for KCP(Br,Cl).

Finally, room temperature resistance measurements of polycrystalline pellets of the family of compounds KCP(X), where X = $(FHF)^-$, Cl^-, and Br^-, has revealed that they all have high conductivity. Only four-probe single-crystal measurements (in progress) will determine the true conductivity ratios. It is very likely that, based on the shortened Pt-Pt separation, the Rb and Cs bifluoride complexes are better room temperature conductors than the prototype KCP(Br).

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(13) Midwest Microlabs, Indianapolis, Ind. This laboratory does not perform Cs and Pt analyses.
(14) Emission spectrographic analyses were performed by J. P. Faris, and iodine-thiosulfate analyses by E. Streets and K. Jensen, all of Argonne National Laboratory.
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An Isotope Effect Study of Triple Bond Participation during a Homopropargyl Rearrangement[1,2]

Sir:

The degree of rate acceleration owing to neighboring group participation[3] during the cyclization rearrangements[4] of homopropargyl esters has never been established, although all evidence points to involvement of the triple bond in the rate-determining formation of vinyl cation intermediates.

For example, in the trifluoroethanolysis of 1-pent-3-ynyl triflate[5] (**1**) (triflate = trifluoromethanesulfonate), homoallylic rearrangement has been ruled out: (1) by the demonstration[5] that trifluoroethanol does not add to the triple bond under the conditions of the reaction, and (2) by trapping[4] of the vinyl cation B as the ether **3**.[6]

We have now applied the isotope effect criterion[7] to the trifluoroethanolysis of **1**. Although an S_N1 reaction, the transition state (Figure 1) is surely S_N2-like, but not nearly so linear with respect to entering and leaving groups as for a typical S_N2 reaction. Consequently, a study of the ^{14}C-isotope effects (k/k^*) at C_1 and C_3, and the α-deuterium isotope effect at C_1 should provide us with estimates of the timing involved with respect to the incoming and departing groups about C_1.

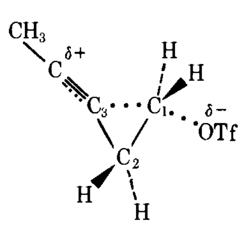


Figure 1. Presumed transition state for trifluoroethanolysis of 1-pent-3-ynyl triflate (**1**).

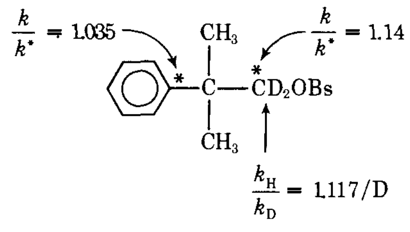
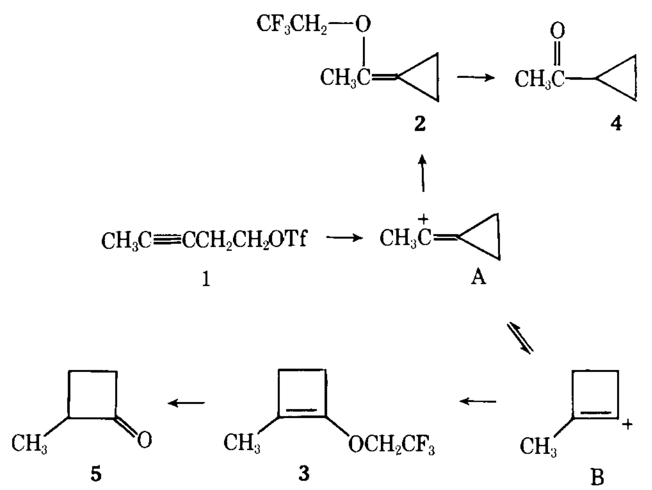


Figure 2. Isotope effects[9] in the trifluroacetolysis of neophyl brosylate.



Using standard procedures[4,8] we prepared the isotope position isomers **1**-*1*-^{14}C, **1**-*3*-^{14}C, and **1**-*1,1*-d_2-*3*-^{14}C and determined their isotope effects[8c]

$$\begin{array}{cc} CH_3C{\equiv}CCH_2\overset{*}{C}H_2OTf & CH_3C{\equiv}\overset{*}{C}CH_2CH_2OTf \\ \mathbf{1}\text{-}1\text{-}^{14}C & \mathbf{1}\text{-}3\text{-}^{14}C \\ k/k^* = 1.048 \pm 0.003 & k/k^* = 0.990 \pm 0.005 \end{array}$$

$$\begin{array}{c} CH_3C{\equiv}\overset{*}{C}CH_2CD_2OTf \\ \mathbf{1}\text{-}1,1\text{-}d_2\text{-}3\text{-}^{14}C \\ k_H/k_D = 1.098 \pm 0.004 \\ \text{(per deuterium)} \end{array}$$

for trifluoroethanolysis at 30.0 °C. Under the conditions used, the reactions proceeded quantitatively to ketone **5** with only a trace of **4**. The values for each isomer are shown under the appropriate structures. After solvolysis of **1**-*1,1*-d_2-*3*-^{14}C, the deuterium in the 2-methylcyclobutanone (**5**) produced was shown by NMR analysis to be distributed equally between positions 3 and 4.

Our isotope effect data can be compared with the results of Ando and co-workers[9] (Figure 2) in the trifluoroacetolysis of

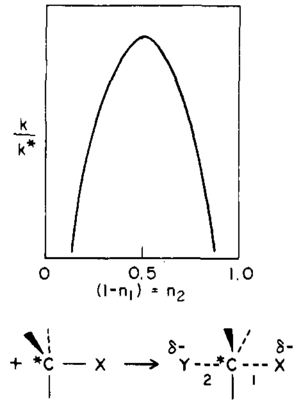


Figure 3. Representation of the Sims–Fry[13,14] relation between transition-state symmetry and heavy-atom isotope effect (k/k^*).

neophyl brosylate, and with the data of Shiner and Sieb,[10] who measured α-deuterium isotope effects for the solvolyses (25 °C) of a series of para-substituted neophyl methanesulfonates and triflates, the values (per deuterium) lying in the range 1.099–1.134. Our value (k_H/k_D = 1.098) for **1**-*1,1*-d_2 is clearly consistent with those reported[9,10] for the neophyl derivatives. Although slightly higher than expected for typical S_N2 reactions,[11] the out-of-plane bending in a nonlinear transition state such as illustrated in Figure 1 should be greater than in the typical S_N2 case. Thus the higher k_H/k_D ratios reported here and also by Ando[9] and Shiner[10] are consistent with the Streitwieser[12] explanation for α-deuterium isotope effects.

A possible explanation of the carbon-14 k/k^*'s is to be found in the treatment of Fry[13] and Sims, Fry, and co-workers,[14] who related the primary heavy atom isotope effects during S_N2 displacements to the bond orders (n_2 and n_1) for the developing and disappearing bonds, respectively, of the transition state. The results, for any given entering and leaving group are idealized as shown in Figure 3 (it is assumed that $n_1 + n_2 = 1$). Although Bron's treatment[15] shows no maximum in a similar plot, the Sims-Fry[13,14] calculations have been supported experimentally by Yamataka and Ando[16] in the Menschutkin reaction of para-substituted benzyl arylsulfonates with *N,N*-dimethyl-*p*-toluidine.

Thus, according to Fry,[13] Sims, and co-workers,[14] a maximum, primary heavy-atom isotope effect should be associated with an S_N2 or S_N2-like reaction only if the transition-state is nearly symmetrical. The observed value [k/k^* = 1.048] for **1**-*1*-^{14}C is smaller than that reported[9] for solvolysis of neophyl-*1*-^{14}C brosylate (Figure 2), but still much too large to imply a complete loss of S_N2 character. We therefore assume a reasonably unsymmetrical transition state ($n_1 \neq n_2$). The value k/k^* = 0.990 for solvolysis of **1**-*3*-^{14}C seems to indicate that the bond order (n_1) for the breaking C_1–O bond is greater than that (n_2) for the developing C_3–C_1 bond. This would imply that the vibrational stretching frequency and force constants for C_3–C_1 in the transition state are smaller than those for the C_1–O and that the activation energy for the solvolysis is lower than it would be in the event the transition state were symmetrical, meaning that anchimeric assistance by the triple bond must be considerable and probably much greater than for the neophyl[9,10] case.

References and Notes

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(2) The authors acknowledge, with thanks, travel funds generously provided through the Scientific Affairs Division of the North Atlantic Treaty Organization (Research Grant No. 814). Financial help of the "Fonds der Chemischen Industrie" is gratefully acknowledged.
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On the Aqueous Bromination of Maleate and Fumarate Ions

Sir:

In a classic paper by Roberts and Kimball,[1] the cyclic bromonium ion was first postulated in order to explain the stereospecific addition of bromine to the diethyl esters and the