balance of 94–100% of starting material. For ^1H NMR analysis, the reaction mixture was concentrated by fractional distillation and the products were separated and collected by preparative gas chromatography on a 4-m OV-17 column.

Spectral data for all compounds reported at summarized in Tables II and III.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Welch Foundation (Grant W-794), the Dow Chemical Company Foundation (for support of B.d.l.T.) and the National Science Foundation (Grant CHE-85-06038) for financial support of this work and (Grant CHE 86-1705) for partial assistance in the purchase of the Varian VXR-300 MHz nuclear magnetic resonance spectrometer. We also acknowledge helpful discussions with Professor Israel Agranat.

Gas-Phase Analogues of Solvolysis. The Conjugate Acid of *n*-Propyl Phenyl Ether

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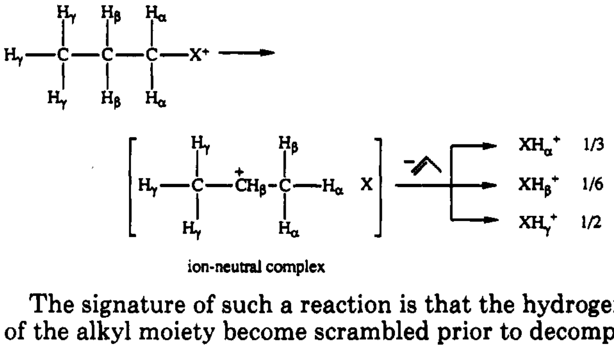
The analogy between first-order decomposition of gaseous ions via ion–neutral complexes and solvolytic elimination is explored using an MS/MS technique, chemical ionization-metastable ion kinetic energy spectroscopy (CI-MIKES). Expulsion of propene from M + 2 conjugate acid ions in the methane-d_4 CI-MIKES of *n*-propyl phenyl ethers shows isotopic exchange that is difficult to explain unless complexes containing propene and $PhOHD^+$ are formed reversibly. Comparison of the CD_4 CI-MIKES of $CH_3CD_2CH_2OPh$ (β-d_2), $CD_3CH_2CD_2OPh$ (α,γ-d_5), and $CH_3CH_2CH_2OPh$ (d_0) shows that further isotopic scrambling takes place, which is interpreted in terms of intermediates of the form [*i*-Pr^+ phenol]. Steady-state kinetic analysis of relative product yields shows that the ion–neutral complex [$CH_3CHCH_3^+$ PhOD] is at least 5 times more likely to yield free propene than to form a complex of the form [C_3H_6 $PhOHD^+$]. The complex [$CH_3CDCH_3^+$ PhOH] isomerizes to [$CDH_2CHCH_3^+$ PhOH] but is less than half as likely to do so as to yield free $CH_3CD{=}CH_2$. If the isotope effect for the proton transfer that yields free propene is assumed to be much larger than any other isotope effect in the reaction sequence, then its value is $k_H/k_D = 1.5$, which is consistent with proton transfer to the phenol ring.

In the gas phase, carbon–oxygen bonds of positive ions frequently heterolyze to produce ion–neutral complexes, as shown schematically by eq 1.[1-4] These contain electrically charged and uncharged fragments, which are not covalently bound but are held together by electrostatic attraction. Such heterolyses have been described as gas-phase analogues of solvolysis, since they represent the conversion of covalent to ionic bonds.[5] Transient electrostatically bound intermediates are frequently formed by gaseous cations derived from alkyl aryl ethers, as demonstrated by evidence from this laboratory ranging from photoionization studies[6,7] to analysis of the neutral alkenes formed by subsequent decomposition of the ion–neutral complexes.[2,8] The analogy to solvolytic elimination hinges on the intermediacy of [R^+ X], where at least one of the fragments in the complex enjoys virtually free rotation about axes perpendicular to the interfragment axis.[3,7] It is possible to draw other kinds of ion–neutral complexes as intermediates (such as the [alkene HX^+] complex that occurs downstream from [R^+ X] in the first-order decomposition of alkyl pyridyl ether radical cations[6]), but the comparison with solvolysis loses pertinence unless heterolysis to form [R^+ X] can be shown to intervene.

$$\underset{\text{molecular ion}}{RX^+} \rightarrow \underset{\text{ion–neutral complex}}{[R^+\ X]} \qquad (1)$$

The fragmentation pathway of an aryl alkyl ether is often independent of how charge is deposited. In 1976 Benoit and Harrison noted that *n*-propyl phenyl ether undergoes the same sort of decomposition process when it is protonated in the gas phase (chemical ionization or CI) as when an electron is removed from it by electron impact (EI).[9] CI produces the conjugate acid of the parent neutral, an even-electron ion that might have been expected to behave very differently from the odd-electron radical cation produced by EI. Yet both ions expel propene. Intermediacy of an ion–neutral complex in both cases accounts for the observed results, as eq 2 depicts. In EI the leaving group X is a phenoxy radical, while in CI X is phenol (a consequence of protonation on oxygen). Either can act as a Brønsted base, leading to the expulsion of propene, as the second step of eq 2 represents.



(2)

The signature of such a reaction is that the hydrogens of the alkyl moiety become scrambled prior to decompo-

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[1] Bowen, R. D.; Williams, D. H. *Int. J. Mass Spectrom Ion Phys.* **1979**, *29*, 47–55.

[2] Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596–1602.

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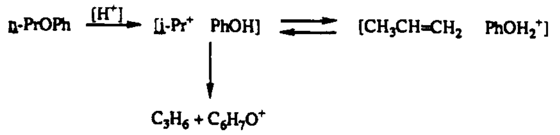
0022-3263/91/1956-0952$02.50/0

sition. A typical deuterium labeling experiment shows that, at the low energy limit, the *n*-propyl → isopropyl isomerization is irreversible, and one β-hydrogen, the two α-hydrogens, and the three γ-hydrogens become chemically equivalent. Equation 2 summarizes the resulting statistical proportions of products from elimination of propene. This has been reported in the CI of labeled phenyl propyl ethers using isobutane,[9] where the reagent ion is *tert*-butyl cation. The original α- and γ-positions of the alkyl chain are 4.9 times more likely to be the source of the proton that is transferred than is the original β-position, just as would be predicted from eq 2. When the conjugate acids are formed by more exothermic proton transfer (e.g. CI using methane, where CH_5^+ and $C_2H_5^+$ are the reagent ions) the α-, β-, and γ-hydrogens begin to randomize, and the ratio of $\alpha + \gamma$ to β transfer decreases. This is what one would anticipate: since *i*-Pr^+ has only a 70 kJ mol^{-1} barrier for intramolecular hydrogen interconversion in solution[10] (and a comparably low barrier in the gas phase[11]) further scrambling of alkyl hydrogens is to be expected with increasing internal energy. But, as will be discussed below, CI data reported to date do not uniquely implicate the mechanism shown in reaction 1.

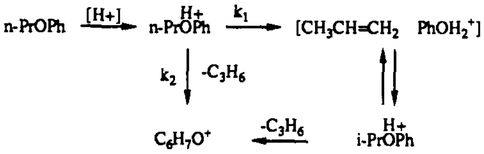


(3)

CI with methane also results in intramolecular exchange of the proton deposited by the reagent ion. This is exemplified by Benoit and Harrison's result for the conjugate acid of $CD_3CD_2CH_2OPh$, where, in addition to the ions representing loss of $C_3H_2D_4$ and loss of C_3HD_5, they report a fragment that corresponds to loss of $C_3H_3D_3$. Since there are only two hydrogens in the alkyl chain of the starting material, it is apparent that a transposition of D and H has occurred. A comparable result is reported for CI of undeuterated *n*-propyl phenyl ether with CD_4, whereby C_3H_5D is lost from the deuteronated parent ion. Clearly the exchange that is taking place must transpose the deuterium deposited by the CI reagent with a hydrogen in the alkyl chain. Mechanistically this means that an additional ion–neutral complex must also be invoked, as eq 3 portrays, which contains propene and the conjugate acid of phenol. From the available data it is not clear whether hydrogen exchange is limited to the alkyl chain or whether the phenyl ring also participates.

The present study describes CI of deuterated substrates with CD_4. Because proton transfer within ion–neutral complexes is often reversible[12] use of a D^+ donor allows us to ask the following questions: (1) Do the ring hydrogens participate in hydrogen exchange? (2) Can a mechanism simpler than eq 3 account for observed data?

As will be discussed below, the present experiments provide negative answers to both of these queries. Specifically, we inquire as to whether the complex that contains isopropyl cation, depicted in eq 3, is required in order to account for the partial randomization under conditions of methane CI. Could not a mechanism that invokes only one kind of ion–neutral complex, for instance eq 4, explain the results equally well? Such a mechanism cannot be considered as an analogue of solvolysis, since no simple heterolysis step is required. The ability to distinguish the mechanistic options represented by eqs 3 and 4 provides a test of the analogy between the gas phase and solution. The operational difference between these two mechanisms is that only six of the alkyl hydrogens can become scrambled in eq 4, while all seven can randomize in eq 3. For purposes of discussion we shall call eq 3 the "gas-phase solvolysis" mechanism and eq 4 the "elimination–readdition" mechanism. It turns out that formation of a single type of complex in the latter mechanism (the step represented by k_1) is not sufficient to account for the observed experimental results unless direct elimination (the step represented by k_2) operates in competition.



(4)

We have prepared M + 2 conjugate acids (MD^+) of deuterated *n*-propyl phenyl ethers and examined their metastable decompositions in the mass spectrometer. This type of experiment selects for ions that decompose on the microsecond timescale and against those that decompose on shorter (as in the mass spectrometer source) or longer timescales. One advantage of studying metastable ions is that the precursor conjugate acid ions are separated first, which obviates the necessity of correcting the experimental data for ^{13}C natural abundance, contributions from $M^{\bullet+}$, and ions that are formed by alkylation of the parent neutral. Another advantage is that the internal energies associated with metastable decompositions are usually much lower than those of ions that decompose in the ion source, and we therefore feel safe in supposing that complexes of the form [cyclopropane $PhOHD^+$] can be dismissed at the outset. We also assume the MD^+ ions that expel propene under these conditions have a sufficiently narrow distribution of internal energies for analysis of relative rate constants to be appropriate.

Experimental Section

Deuterated *n*-propyl phenyl ethers, 1-phenoxy-1,1,3,3,3-pentadeuteriopropane (*n*-propyl-$\alpha,\alpha,\gamma,\gamma,\gamma$-$d_5$ phenyl ether) and 1-phenoxy-2,2-dideuteriopropane (*n*-propyl-β,β-d_2 phenyl ether), were prepared as previously described.[7] Chemical ionization-metastable ion kinetic energy spectroscopy (CI-MIKES) experiments were performed using CD_4 reagent gas (Cambridge Isotope Laboratories, 99 atom % D) on the VG ZAB 2F reverse Nier-Johnson double-focussing mass spectrometer in UCR's Analytical Chemistry Instrumentation Facility. CI-MIKES were recorded by standard techniques, with pressures in the second field-free region ranging from 1×10^{-8} to 1×10^{-7} Torr. The deuteronated propyl phenyl ether (M + 2 ion) from electron bombardment of a mixture with CD_4 was isolated using the magnetic sector at a resolution of 10^3. Metastable ions that decomposed in the field-free region between the two sectors of the instrument were energy analyzed using the electric sector. Profiles of the *m/z* 95–97 metastable fragments from the M + 2 ions were computer averaged for several hours, and independent replications of the d_0 and d_2 experiments were performed. The translational kinetic energy release calculated from the peak width of the *m/z* 96 ion from deuterated *n*-propyl phenyl ether is $T_{0.5} = 0.05$ V, a factor of 30 greater than $T_{0.5}$ reported for methane CI-MIKES of 1-propanol,[4] but only twice as large as the $T_{0.5}$ for the EI-MIKES of *n*-propyl phenyl ether radical cation.[7,9]

In principle, the M + 2 ions contain, in addition to deuteronated parent, a tiny amount of $M^{\bullet+}$ ion containing two ^{13}C atoms at natural abundance, whose contribution to the MIKES cannot be

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[10] (a) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53–59. (b) Koch, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479–3480.

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Table I. Proportions of m/z 95 ($C_6H_7O^+$), 96 ($C_6H_6DO^+$), and 97 ($C_6H_5D_2O^+$) from CI of Deuterated *n*-Propyl Phenyl Ethers

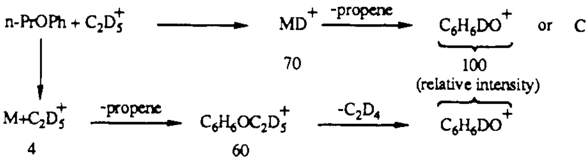
neutral	CI gas	m/z 95	m/z 96	m/z 97	ref
β,γ-d_5	CH_4[a]	0.41	0.52	0.07	*c*
d_0	CD_4[a]	0.07	0.93	–	*c*
d_0	CD_4[b]	0.11	0.89	<0.005	*d*
β-d_2	CD_4[b]	0.09	0.78	0.13	*d*
α,γ-d_5	CD_4[b]	<0.005	0.29	0.71	*d*

[a] Source CI. [b] CI-MIKES. [c] Reference 9. [d] This work (uncertainty ±0.03).

ruled out a priori. Statistically, half of these impurity ions would have one ^{13}C in the alkyl chain and one in the ring. Such an $M^{\bullet +}$ impurity could conceivably lead to m/z 95 fragments. Comparison of the m/z 95 intensity observed for β-d_2 with that for α,γ-d_5 shows that such a contribution must be negligible, for no m/z 94 (which would come from the one out of twelve $M^{\bullet +}$ ions with both ^{13}C atoms in the chain) is observed at all, nor is m/z 95 detectable above background in the MIKES of α,γ-d_5. Relative peak intensities in the CI-MIKES of deuterated substrates were determined by measuring relative peak areas, for which the uncertainty is ±0.01. Because the MIKES peaks are of low intensity, contribution of a small amount of collisionally activated decomposition leads to additional uncertainty in the CI-MIKES product ratios, and we gauge the uncertainties in the non-zero values reported in Table I to be ±0.03. Steady-state kinetic expressions were fitted to relative peak intensities using a nonlinear least-squares program,[13] and the accuracy of calculated relative rate constants was checked using the Runge–Kutta solution of the rate equations. The limits of detection are 2–3 times lower than the anticipated level of m/z 95 that would have been expected from a significant $M^{\bullet +}$ impurity in the conjugate acid ions from α,γ-d_5.

Results

Under conditions of chemical ionization with methane-d_4 (CD_4CI) the reagent ions are CD_5^+ and $C_2D_5^+$. The latter ion can react with a neutral molecule M either as a Brønsted acid to yield the MD^+ conjugate acid or as a Lewis acid to yield the M + $C_2D_5^+$ alkylated parent ion. In the mass spectrum of the ions that are present in the CI source the products of both reactions can be observed.[9] The proportions vary according to operating conditions, but in this work we observe the relative proportions given in eq 5 for *n*-propyl phenyl ether.



$$\begin{tikzcd}
\text{n-PrOPh} + C_2D_5^+ \arrow[r] \arrow[d] & \underset{70}{MD^+} \arrow[r, "\text{-propene}"] & \underbrace{C_6H_6DO^+}_{\substack{100\\(\text{relative intensity})}} \text{ or } \underset{10}{C_6H_7O^+} \\
\underset{4}{M{+}C_2D_5^+} \arrow[r, "\text{-propene}"] & \underset{60}{C_6H_6OC_2D_5^+} \arrow[r, "-C_2D_4"] & \overbrace{C_6H_6DO^+}
\end{tikzcd} \qquad (5)$$

Use of an MS/MS technique such as MIKES obviates complications that arise because of this competition. The principal decomposition pathway for MD^+ from *n*-propyl phenyl ether is loss of propene to yield $C_6H_6D^+$ (m/z 96). The M + $C_2D_5^+$ ion also expels propene, and a portion of the $C_6H_6OC_2D_5^+$ daughter then expels C_2D_4 to yield $C_6H_6DO^+$, too (we detect no loss of partially deuterated ethylene in the MIKES of $C_6H_6OC_2D_5^+$). Equation 5 tabulates measured abundances (to one significant figure) of all of these ions relative to $C_6H_6DO^+$. Since both pathways can yield the same ultimate product, MIKES (which separates MD^+ from other ions before examination of its decomposition) gives potentially greater accuracy than a CI source experiment. As it happens, our measurement of the $C_6H_7O^+$:$C_6H_6DO^+$ ratio (m/z 95:m/z 96) from CI-MIKES is nearly the same as reported by Benoit and Harrison for their CI source experiment, as summarized in Table I.

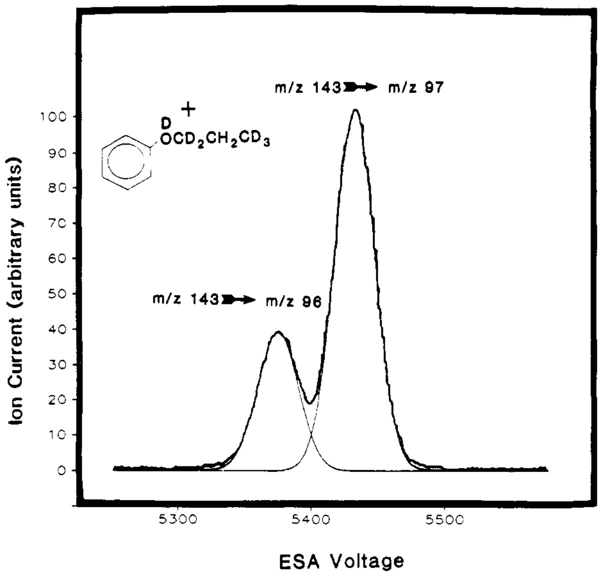


Figure 1. Metastable decompositions of M + 2 conjugate acid ions of $CD_3CH_2CD_2OPh$ (α,γ-d_5), monitored in a B–E two-sector instrument by scanning the electrostatic analyzer (ESA) with a fixed magnetic field (8 kV accelerating voltage). Least-squares fits of the observed peak profiles (using a standard Gaussian fitting routine in which individual peak widths, as well as peak heights, were permitted to vary independently) are superimposed on the experimental data in order to demonstrate that both peaks have the same width.

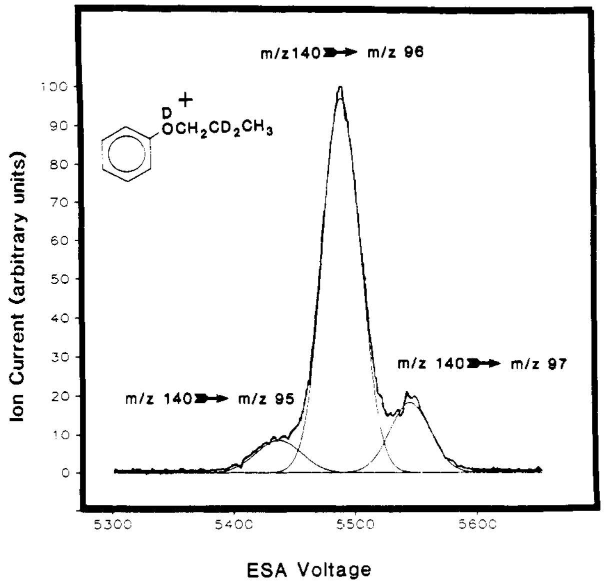


Figure 2. MIKES of M + 2 conugate acid ions of $CH_3CD_2CH_2OPh$ (β-d_2) recorded as in Figure 1. Least-squares fits of observed peak profiles, superimposed on the experimental data, show that all three metastable decompositions have the same peak width.

Experimental MIKES profiles for CD_4 CI of deuterated *n*-propyl phenyl ethers are shown in Figures 1 and 2. When propyl-$\alpha,\alpha,\gamma,\gamma,\gamma$-$d_5$ phenyl ether is chemically ionized using CD_4, the metastable spectrum, reproduced in Figure 1, shows no $C_6H_6O^+$ (m/z 95). The proportions of m/z 96 and m/z 97 are given in Table I. The absence of any detectable level of m/z 95 from the propyl-$\alpha,\alpha,\gamma,\gamma,\gamma$-$d_5$ phenyl ether excludes exchange between the phenyl ring and the alkyl chain. It is likely that D^+ is initially deposited onto a ring carbon at least as often as onto the oxygen (since the oxygen of phenol and its ethers is much

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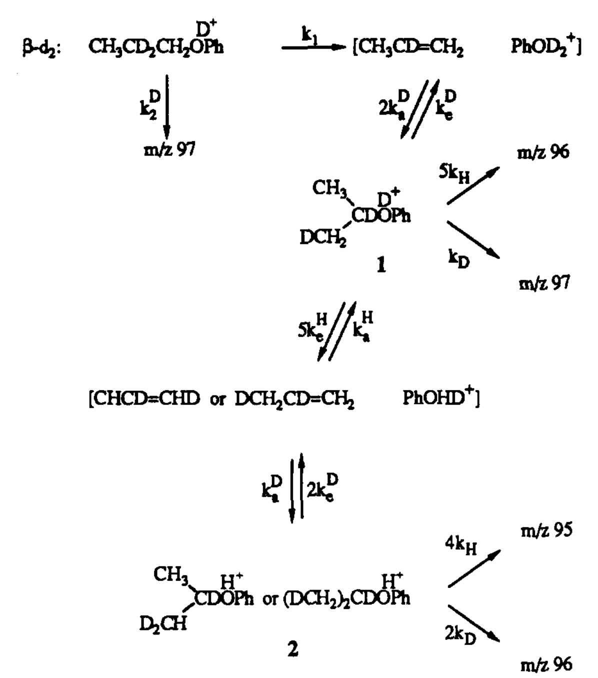
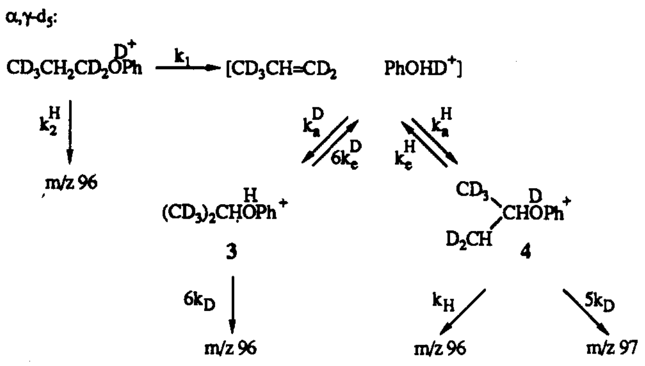
[13] Micromath, Inc., MINSQ (Version 2.3), 1988.

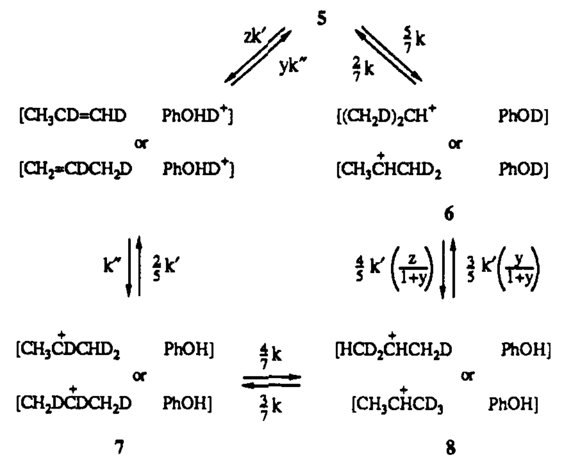
Scheme I



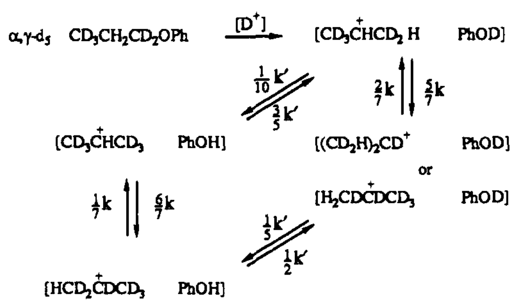
Scheme II



Scheme III



Scheme IV



less basic than the ring[14,15]), but the ion decomposes only in the latter case.

The same type of labeling experiment using *n*-propyl-β,β-d_2 phenyl ether (Figure 2) helps differentiate between "gas-phase solvolysis" (eq 3) and the mechanistic alternative, elimination–readdition, shown in eq 4. The implications of elimination–readdition by itself are represented by Schemes I (for β-d_2) and II (for α,γ-d_5) for the case $k_2 = 0$. If the deuteronated parent of the β-d_2 propyl phenyl ether were to eliminate and readd in a Markownikoff sense, as depicted in Scheme I, then the net rearrangement would lead to two types of isopropyl phenyl ether conjugate acids, 1 and 2 (2 is a mixture of a pair of positional isomers that yield the same outcome). As the scheme shows, ions of three different masses should be observed from β-d_2, while α,γ-d_5 should yield ions of two different masses. The intensity ratios give three equations in three unknowns: the ratio of elimination rate constants, $k_e^H/k_H = k_e^D/k_D$, for ion–neutral complex formation versus fragmentation; the kinetic isotope effect, $k_H/k_D = k_e^H/k_e^D$, for elimination; and the kinetic isotope effect for readdition of protonated phenol to propene within the complex, k_a^H/k_a^D. We assume that the lifetimes of ion–neutral complexes are very brief compared to the microsecond timescale of MIKES (i.e. $k_H \gg k_1$), so steady-state analysis of relative product yields is valid. Algebraic solution gives $k_e^H/k_H = 0.82 \pm 0.03$, $k_H/k_D = 1.3 \pm 0.2$, and $k_a^D/k_a^D = 6 \pm 2$.

The "gas-phase solvolysis" mechanism offers a different analysis of the experimental data. Here we suppose that a complex is formed that contains isopropyl cation, which can transfer H^+ (or D^+) to either the ring or the oxygen of phenol. When transfer to the ring occurs, the complex breaks up and product ions are formed. When (less often) transfer to oxygen occurs, the complex between propene and O-protonated phenol (drawn in eq 3) persists long enough to transfer a proton back, ultimately leading to the *m/z* 95 seen in Figure 2. Such a proposal is thermodynamically reasonable, since the phenol ring has a proton affinity 65 kJ mol^{-1} greater than that of propene, while the oxygen has a basicity that is nearly the same as that of propene.[14]

Equation 3 can be extended to describe the effects of deuterium substitution in various ways. Schemes III and IV outline one of the most parsimonious versions. Scheme III portrays two ways that hydrogen randomizes: scrambling within the alkyl chain (e.g. 5 $\rightleftarrows$ 6) and exchange between the alkyl chain and deuteronated oxygen (e.g. 5 → 7) via an ion–neutral complex of propene with $PhOHD^+$. This model employs three parameters, as Scheme IV shows for α,γ-d_5: k_H/k_D for proton transfer from isopropyl cation to phenol; k, the rate constant for hydrogen scrambling of the isopropyl cation within the ion–neutral complex; and k', the rate constant for hydrogen exchange between carbon and oxygen, $[C_3H_7^+\ PhOD] \rightarrow [CH_3CHCH_2D^+\ PhOH]$. Both processes must be corrected for statistical effects. The simplest way to do so is to consider only the number of permutations of label for each isotopic analogue and to neglect isotope effects on scrambling and exchange (i.e. set

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[14] (a) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853–3854. (b) Mautner, M. *J. Phys. Chem.* **1980**, *84*, 2716–2723.

[15] Wood, K. V.; Burinsky, D. J.; Cameron, D.; Cooks, R. G. *J. Org. Chem.* **1983**, *48*, 5236–5242.

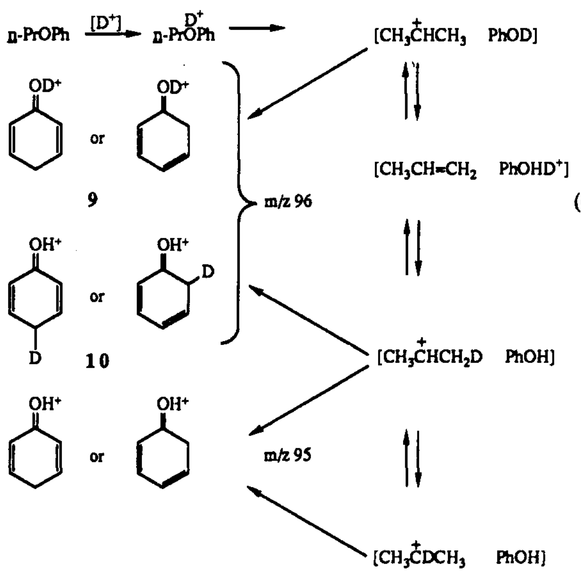
$y = z = 1$). The scrambling rate constants are adjusted so that the sum of forward and backward rate constants (e.g. **5** → **6** and **6** → **5**) is always equal to k.

Exchange of hydrogen between carbon and oxygen is statistically weighted in the same way, again neglecting isotope effects. The coefficients are adjusted so that the sum of forward and backward rate constants is always equal to $0.7k'$. Analysis of the CI-MIKES data in Table I using Schemes III and IV gives $k_H/k_D = 1.53 \pm 0.15$; $k'/k_D = 2.0 \pm 0.3$, and $k/k_D = 2.7 \pm 1.3$. Unlike Scheme II, Scheme IV predicts that some m/z 95 should be formed from α,γ-d_5, but the expected ratio of m/z 95 to m/z 96 is ≤ 0.015, which is below the detection limit of our experiments.

Two mechanistic models, represented by eqs 3 and 4, are contrasted. Either model can be used to fit the CD_4 CI-MIKES data for β-d_2 and α,γ-d_5 in terms of three relative rate constants. The results for each model exhibit one relative rate constant (k_a^H/k_a^D for eq 4; k/k_D for eq 3) that is more affected by the uncertainty in the data than the others. In the discussion below the predictions of each model will be compared to experiment.

Discussion

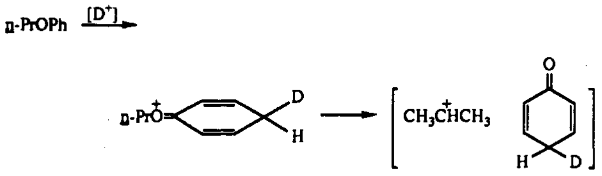
As first reported by Benoit and Harrison,[9] the hydron[16] deposited by the CI reagent exchanges with the alkyl chain of propyl phenyl ether. The labeling experiments in the present study extend our knowledge of this exchange, and metastable ion decompositions of the M + 2 conjugate acid of n-propyl phenyl ether under conditions of CD_4 CI can be interpreted in terms of the sequence of steps shown in eq 6. Our approach for testing alternative mechanisms is to fit the experimental data for β-d_2 and α,γ-d_5 to a model and then to compare the prediction of that model for the CD_4 CI-MIKES of undeuterated n-propyl phenyl ether with experiment.



(6)

The absence of detectable levels of m/z 95 from the M + 2 conjugate acid of $CD_3CH_2CD_2OPh$ rules out participation of phenyl ring protons in the isotopic exchange process. To discuss kinetic models that are consistent with the experimental data, first consider the implications of the elimination–readdition mechanism. It turns out that no more than a small fraction of the conjugate acid ions decompose directly by the pathway corresponding to k_2 in eq 4, since the observed fragment ion ratios from β-d_2 and α,γ-d_5 do not permit values for $k_2/k_1 > 0.03$ (if k_2^H is constrained to be equal to k_2^D). Analysis of the β-d_2 and α,γ-d_5 data predicts the value for the m/z 95:m/z 96 ratio to be expected from CD_4CI of undeuterated n-propyl phenyl ether, which ranges from 0.25 ± 0.06 if k_2 is assumed to be zero) to 0.16 ± 0.10 (if k_2 is assumed to have its largest possible value realtive to k_1). A normal primary isotope would make k_2 smaller for α,γ-d_5 than for d_0 or β-d_2. It turns our that this consideration further reduces the predicted value for m/z 95:m/z 96 (to 0.14 ± 0.08 if k_2^H is allowed to have its maximum permissible value, 0.35, when $k_2^D = 0$). The uncertainty of the predicted values is large enough that, for some values of k_2, the uncertainty in the predicted values overlaps the error bars on the experimental value.

The experimental m/z 95:m/z 96 ratio for CD_4 CI-MIKES on n-propyl phenyl ether is 0.12. Using the relative rate constants for "gas-phase solvolysis" extracted from Schemes III and IV to predict the m/z 95:m/z 96 ratio for eq 6, we get a value of 0.11 ± 0.04 (assuming $k_2 = 0$). Our experimental results are therefore consistent with "gas-phase solvolysis" without having to invoke any competition with direct elimination. The elimination–readdition mechanism can be made to fit the experimental results only if an additional parameter is added, i.e. if direct elimination is presumed to compete with ion–neutral complex formation: k_2/k_1 in the range 0.01–0.03 at the limit $k_2^H = k_2^D$ or k_2^H/k_1 in the range 0.1–0.35 at the limit $k_2^H \gg k_2^D$.



(7)

The data clearly rule out ring protonation as the first step in fragmentation under CI conditions. This would have led to ion–neutral complexes containing cyclohexadienones, as exemplified by eq 7. If such an intermediate were able to exchange hydrogens with the alkyl cation, then exchange should have been seen in the α,γ-d_5 ether. Since no m/z 95 (the expected product of such an exchange) is seen in that instance, eq 7 can be excluded. Furthermore, the decomposition of a cyclohexadienone-containing complex would involve a proton transfer from an alkyl cation to oxygen. This would be expected to exhibit a primary kinetic isotope effect that is comparable to the value from EI-MIKES of n-propyl ethers[7] (eq 1 where X = PhO•), $k_H/k_D = 1.2$. The value of k_H/k_D from Schemes III and IV, 1.5, is larger and is consistent with hydron transfer to carbon.

We have previously demonstrated that two types of ion–neutral complexes can occur sequentially in a radical cation fragmentation.[6] We interpret the present experiments as demonstrating that two types of complexes can interconvert in the first-order decomposition of even electron ions, as portrayed in reaction 6. This mechanism predicts that isomeric m/z 96 products, **9** and **10** should form in the CD_4 CI-MIKES of n-propyl phenyl ether. While our current apparatus does not permit us to test this, the relative rate constants calculated from Schemes III and IV predict a **9**:**10** ratio ≥50.

Conclusion

Isotopic exchange between deuterium deposited by a chemical ionization reagent and the alkyl chain of n-propyl phenyl ether requires reversible formation of ion–neutral

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[16] According to IUPAC nomenclature, the term "hydron" designates a hydrogen ion irrespective of its isotopic identity, *Chem. Int.* 1986, *8*, 21.

complexes of the form [propene $PhOHD^+$]. While such a mechanism might conceivably account for additional randomization within the alkyl chain of deuterated *n*-propyl phenyl ethers all by itself, the observed proportions of scrambling are more easily fit by a pathway that includes complexes of the form [iPr^+ phenol] (which scramble all seven of the alkyl hydrogens) as intermediates. Ring hydrogens do not participate in the scrambling. Our analyses of the experiments presented here contrast two mechanisms, both of which invoke gas-phase ion–neutral complexes that resemble ion–molecule pairs formed in S_N1 reactions.[17] One mechanism involves a heterolysis corresponding to reaction 1, whose similarity to the first step of solvolytic elimination has been discussed for more than a decade. The alternative, elimination–readdition, does not bear a formal resemblance to solvolysis; this mechanism is ruled out unless direct elimination is presumed to occur concurrently in competition with ion–neutral complex formation. The quantitative data at hand are well fit as a "gas-phase solvolysis" using a reasonable kinetic scheme with three relative rate constants. While the elimination–readdition mechanism alternative represents a plausible sequence of steps, it can be made to fit the experimental observations only if four relative rate constants are used as parameters (since the ion neutral complexes in eq 4 scramble only six of the alkyl hydrogens). We conclude that parallels between the gas phase and solution are aptly drawn and that studies of cation chemistry in one regime will continue to illumine the other.

Acknowledgment. Support of this work by NSF grant CHE8802086b is gratefully acknowledged.

Supplementary Material Available: Algebraic derivations of steady state expressions for Schemes I–IV and expressions for m/z 95:m/z 96 predicted for M + 2 ions of d_0 (4 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Some Properties of 2,5,7,10-Tetraiodo-1,6-methano[10]annulene

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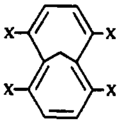
The title compound (**1a**) was prepared by a two-step procedure via an organomercurial. Both **1a** and its 11,11-difluoro analogue are crystalline solids that were fully characterized. The tetraiodide **1a** is unusual in that the aromatic character of the π periphery is almost destroyed as determined from ring current effects on the 11,11 hydrogen atoms. The crystal structure of **1a** is reported and it bears out the "localization" of the π electrons with a concomitant opening of the transannular bridge angle.

Introduction

The subtle interplay between structural parameters and electronic character at the molecular level is a subject of ongoing interest in organic chemistry.[1] The 1,6-methano[10]annulene is a particularly interesting molecule from the point of view of the effect of structural parameters on the electronic delocalization of its 10 π electrons. Sterically demanding substituents in the 2,5,7,10-positions are expected to have a deleterious effect on cyclic delocalization in this bicycle. Trimethylsilyl substituents, indeed, distort the ring sufficiently to cause electronic localization.[2]

In this paper we describe the preparation and full characterization of the previously unknown title compound **1a**, prepared by a route not previously applied to the methano[10]annulenes and described below. The reactivity of the "peri" positions toward coupling reactions was expected to be enhanced in the title compound. By comparison with the parent and tetrakis(trimethylsilyl) derivative, we find that the tetraiodo derivative shows bond localization but the bond alteration is not as severe as in the case of the tetrakis(trimethylsilyl) derivative. This "intermediate localization" is also substantiated in the ^{1}H NMR chemical shift of the methano bridge.



1a, X = I
1b, X = Br
1c, X = TMS

Experimental Section

General. All reactions were performed under an inert atmosphere. Commercial solvents were dried by using standard conditions, e.g. CaH_2 for acetonitrile, etc. IR spectra were recorded with a Perkin-Elmer Model 1300 spectrophotometer under a nitrogen flow as KBr disks (unless stated otherwise) and are reported in ν (cm^{-1}). NMR spectra were recorded with a General Electric GN500, 500-MHz instrument. Data are reported in δ relative to TMS (internal) in d_8-THF, unless stated otherwise. Melting points were obtained with a Büchi oil bath apparatus and are reported uncorrected.

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