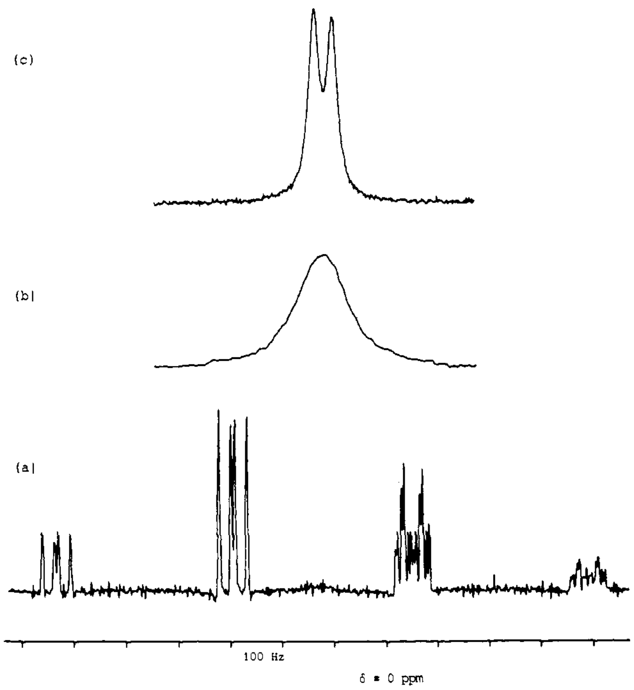

Figure 1. $^{31}P\{H\}$ NMR spectrum of $Ir(CO)ClF(PEt_3)_2SF_3$ recorded in CD_2Cl_2 at (a) 200, (b) 280, and (c) 325 K, with an operating frequency of 81 MHz. The centers of the resonances have been arranged to coincide, thus offsetting a small change in chemical shift with temperature.

only becoming slow enough to resolve distinct F environments at 130 K.

We have isolated B as a colorless solid, which is thermally stable, but it rapidly turns green if exposed to the atmosphere and is sensitive to moisture. The compound has been characterized by partial elemental analysis, by its infrared spectrum, and by single-crystal X-ray diffraction.[5] The determination of the crystal structure is not yet complete. Results so far confirm the geometry around iridium and show that fluoride is trans to carbonyl. We have been able to locate the fluorine atoms bound to sulfur, but we have not been able to refine them positionally; we are exploring various disorder models to try to overcome this difficulty. We have also prepared analogues of B from SF_4 and the corresponding iridium bromide or iodide.

Preliminary experiments show that B reacts with a small excess of BF_3 in CD_2Cl_2. The reaction is slow at 200 K but rapid at 270 K. The ^{19}F and ^{31}P NMR spectra of the product show it to be the novel complex $[Ir(CO)ClF(PEt_3)_2SF_2]^+[BF_4]^-$, formally analogous to $SF_3^+BF_4^-$ that is produced[6] from SF_4 and BF_3. The ^{19}F spectrum showed the resonance due to $[BF_4]^-$, together with two new resonances. One of these (δ −360.9) was in the region associated with Ir*F* and appeared as a triplet $[^2J(PF) = 33\ Hz]$ of triplets $[^3J(FF) = 17\ Hz]$. The other (δ −51.8) was in the region associated with main-group fluorides; it appeared as a doublet $[^3J(FF) = 17\ Hz]$ of triplets $[^3J(FP) = 15\ Hz]$. The P{H} resonance (δ 8.05) appeared as a doublet of triplets, with coupling constants corresponding to those observed in the ^{19}F spectrum. This complex decomposed slowly in solution at room temperature. We believe it to be the first reported example of a complex containing the SF_2^+ ligand, which is isoelectronic with PF_2.

We are studying the chemistry and structures of these and related complexes.

Acknowledgment. We thank Messrs Johnson Matthey for lending us chemicals.

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[5] Crystallographic parameters: space group $P2_1$; $Z = 2$; monoclinic; $a = 7.571$ (4), $b = 8.719$ (4), $c = 15.493$ (9) Å; $\beta = 100.92$ (4)°; $V = 1004$ Å; $T = 170$ K.

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Transition Structures for Intramolecular Hydrogen Atom Transfers: The Energetic Advantage of Seven-Membered over Six-Membered Transition Structures

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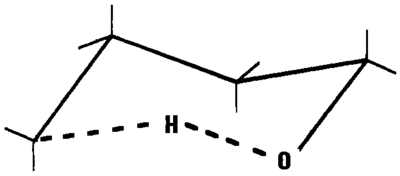
Intramolecular hydrogen abstractions by alkoxy radicals have been the subject of many mechanistic[1] and synthetic[2,3] investigations. In these systems, hydrogen transfer invariably takes place via a six-membered transition state. Reactions of substituted pentanols, hexanols, and octanols all give substituted tetrahydrofurans as the major products.[4–6] The preference for δ-hydrogen abstraction is usually rationalized by analogy: the carbocyclic six-membered cyclohexane ring is strain-free, while all other carbocyclic rings have some strain. However, as shown in **1**, a perfect analogy to cyclohexane requires a severely nonlinear geometry for hydrogen transfer.[7] By contrast, linearity is usually considered to be favored in hydrogen transfer.[8] Isotope effects and the stereoselectivity of hydrogen abstraction by the 2-hexyloxy radical have been interpreted as requiring a linear or nearly linear transition state.[9,10]



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We have carried out both ab initio molecular orbital calculations[11] and force-field modeling[12] which predict that abstraction of a δ-hydrogen atom is actually *disfavored* enthalpically with

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Table I. Energies of the Radicals and Transition States and Activation Parameters[a]

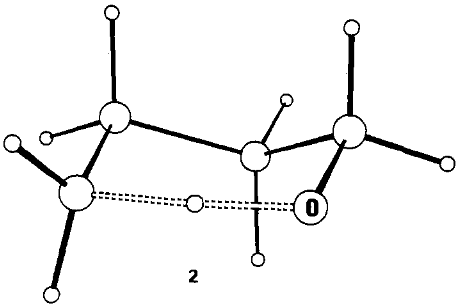
	total energy, au		E_{rel}, kcal/mol							
radical	UHF/3-21G	MP2/6-31 G*	UHF/3-21G	MP2/6-31G*	$\Delta H^{\ddagger}$	S, eu	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{300\mathrm{K}}$	$\Delta G^{\ddagger}_{200\mathrm{K}}$	$\Delta G^{\ddagger}_{80\mathrm{K}}$
butoxy										
reactant	−230.25690	−232.18555	0.0	0.0		82.5				
ts	−230.20173	−232.16181	34.6	14.9	18.8	78.9	−3.6	19.9	19.5	19.1
pentoxy										
reactant	−269.07603	−271.35104	0.0	0.0		92.0				
ts	−269.02185	−271.32859	34.0	14.1	18.1	80.1	−11.9	21.7	20.5	19.1

[a] Enthalpies were calculated from MP2 energies by correcting for zero-point energies and for the RT and C_pT terms (T = 298 K). The calculated activation enthalpies are estimated to be almost 14 kcal/mol above experimental values.[16] Entropies were derived from the calculated geometries and harmonic vibrational frequencies. Correction factors of R ln 9 and R ln 27 are added to the calculated entropies of the butoxy and pentoxy radicals, respectively, to account for the number of conformers available. A correction factor of R ln 2 is added to the entropy of each transition state (ts), to account for the existence of an enantiomeric ts. An additional factor of 4.4 eu is added to the six-membered ts to account for its low-frequency ring-puckering vibration (pseudorotation).[19]

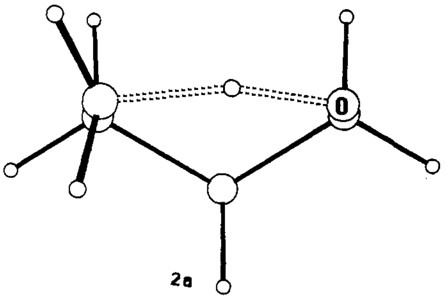
respect to the alternative ε-hydrogen abstraction. The experimental preference for a six-membered over a seven-membered transition state is predicted here to result from the more favorable *entropy* of activation of the six-membered transition state.[7c]

The structures of the butoxy and pentoxy radical were fully optimized, using the 3-21G[13] basis set and UHF theory. Single-point calculations were carried out on the pentoxy radical at the MP2/6-31G*[13,14] level. In both cases, the gauche conformation of the O–C–C–C atoms was favored by 0.7 kcal/mol over the anti conformation, just as in the corresponding alcohols.[15]

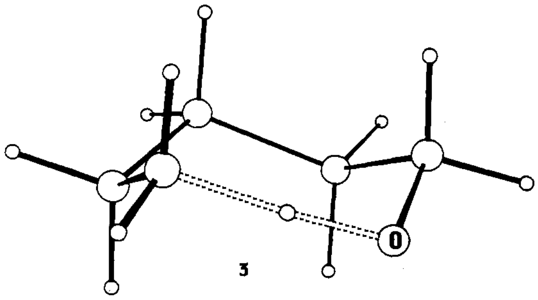
Transition structures for the δ-hydrogen abstraction in the butoxy radical (six-membered transition state, **2** and **2a**) and for ε-hydrogen abstraction in the pentoxy radical (seven-membered transition state, **3**) were located (HF/3-21G). The activation enthalpy calculated for the conversion of the butoxy radical to the 4-hydroxyl-1-butyl radical, via **2**, is 0.7 kcal/mol higher than that for the reaction of the pentoxy radical to form the 5-hydroxy-1-pentyl radical via **3** (see Table I).



2



2a



3

The six-membered transition structure **2** strongly resembles a five-membered ring of heavy (non-hydrogen) atoms, having an "envelope" shape like that of cyclopentane, but with one long bond (2.5 Å) between C and O. Drawing **2a** demonstrates this most clearly. The seven-membered cyclic transition structure, **3**, has a "chair" form much like that of a chair cyclohexane, but with one long bond. In both cases the O–H–C angle is nonlinear (153° and 165°, respectively) but not nearly the 109.5° implied in **1**. Both the distortion of the C–H–O angle and partial eclipsing in **2** make it higher in energy than **3**.

Although these calculations were performed at a relatively low level, MP2/6-31G** calculations on hydroxyl radical plus methane[16] give about the same C–O distance.[17] No significant alteration in our conclusion is expected even when transition states are found by better methods.

What factors cause the δ-abstraction to be favored? The entropies of the reactants and transition structures were computed from the calculated geometries and frequencies at the 3-21G level. The entropies of the starting radicals can also be estimated from Benson's group equivalents (BGE).[18] In either case, the entropy of the favored *gauche* conformation of the radical must be corrected by the contribution of all other relatively low energy conformations in the molecule. The entropies of activation (Table I) are calculated to be −5.6 (−5.0 by BGE) eu for the six-membered δ-abstraction transition structure and −13.8 (−13.3) eu for the seven-membered ε-abstraction transition structure. The difference in activation entropies between six- and seven-membered transition states is therefore 8.2–8.3 eu, corresponding to 2.5 kcal/mol at room temperature. This is very close to the 9.1 eu more favorable entropy change for conversion of pentane to cyclopentane as compared to conversion of hexane to cyclohexane.[18] Thus, we estimate that the free energy of activation is 1.8 kcal/mol lower for the six-membered transition state than for the seven-membered at room temperature (see Table I).

We propose that the preference for the six-membered transition state for hydrogen abstraction observed experimentally originates

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(17) BEBO calculations[9] favor a "close to linear" (>150°) transition state, with O–H and C–H bond lengths of 1.32 and 1.20 Å.

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(19) The intrinsic entropy of a cyclic hydrocarbon is obtained from that of the corresponding acyclic species by the expression[18]

$$S^{\circ}_{\mathrm{c,int}} = S^{\circ}_{\mathrm{a,int}} - (n - 1)f$$

where n is the number of atoms in the ring. f = 4.7 for cyclohexane and for most cyclic hydrocarbons, but only 3.6 eu for cyclopentane. The low value of f in cyclopentane is due to pseudorotation.[18] Thus, the contribution of pseudorotation to the entropy of the five-membered ring is

$$[-(5 - 1)3.6] - [-(5 - 1)4.7] = 4.4 \text{ eu}$$

from the favorable entropy, not enthalpy, of activation. At low temperatures, $T\Delta S$ decreases, and we predict that the seven-membered ε-abstraction transition state will become favored at about −190 °C and below.

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Registry No. $CH_3(CH_2)_3O^\cdot$, 19062-98-7; $CH_3(CH_2)_4O^\cdot$, 26397-35-3.

Solid-State Microelectrochemistry: Electrical Characteristics of a Solid-State Microelectrochemical Transistor Based on Poly(3-methylthiophene)

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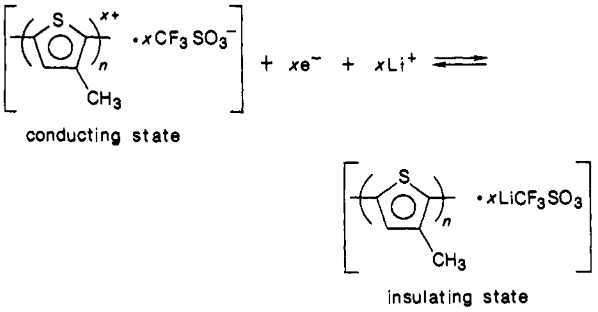
We wish to report fabrication and characterization of a "solid-state" microelectrochemical transistor on a chip with a crucial dimension (source–drain separation) of ~1 μm. The device is based on solid-state reduction and oxidation of poly(3-methylthiophene) (eq 1), connecting the source and drain of the transistor, Scheme I. The fundamentally significant finding is that ion transport occurs across the interface between the poly(3-methylthiophene) and the solid-state electrolyte. Work from this laboratory[1] and elsewhere[2] has demonstrated microelectrochemical devices that function when immersed in fluid electrolyte solution. Our new work is inspired by availability of ionic conducting polymers[3] and recent progress in solid-state electrochemistry of molecular materials.[4-6]



(1)

The device in Scheme I has been fabricated by beginning with ~3 mm × 3 mm chips having eight, individually addressable, Pt microelectrodes (~2 μm wide, ~50 μm long, and ~0.1 μm high) separated from each other by ~1.2 μm.[1,7] Six adjacent microelectrodes, numbered 1–6, are coated with poly(3-methylthiophene) by anodic polymerization of 3-methylthiophene[7,8] using the minimum amount of poly(3-methylthiophene) necessary to connect 1–6. Two adjacent microelectrodes, 7 and 8, comprise the counter electrode, and a small spot of Ag epoxy on the chip is used as a quasi-reference. Optical microscopy shows that the poly(3-methylthiophene) is confined to microelectrodes 1–6, and cyclic voltammetry shows that each electrode allows access to the same amount (~7 × 10^{-12} mol of monomer units) of polymer, Figure 1. The solid-state device is completed by (1) removing the poly(3-methylthiophene)-coated chip from CH_3CN/0.1 M $LiCF_3SO_3$ at +0.65 V vs. SCE where the polymer is partially oxidized and contains $CF_3SO_3^-$ ions and (2) coating with poly(ethylene oxide) (PEO) containing one $LiCF_3SO_3$ for every 16 PEO units ($PEO_{16}\cdot LiCF_3SO_3$) by evaporation of solvent from 1 μM PEO (MW = 5 × 10^6), 7.1 mM $LiCF_3SO_3$ 9/1 CH_3CN/MeOH (v/v).

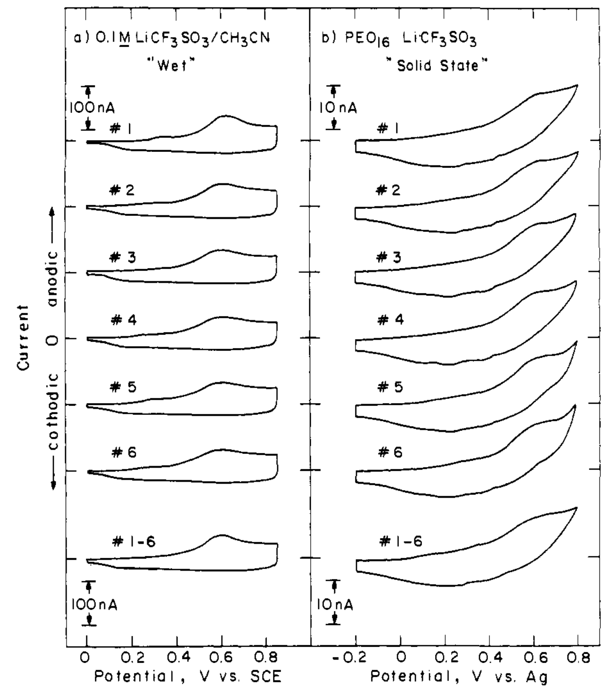


Figure 1. Comparison of cyclic voltammetry in solution (a) (100 mV/s, 25 °C, CH_3CN/0.1 M $LiCF_3SO_3$, volts vs. SCE) and solid state (b) (50 mV/s, 95 °C under N_2 $PEO_{16}\cdot LiCF_3SO_3$, volts vs. Ag) for microelectrodes 1–6 coated with poly(3-methylthiophene) scanned individually and scanned together. Note that for either solution or solid-state cyclic voltammograms the data show the same amount of polymer accessed by one electrode as with all six, but the solution scans show more electroactive polymer.

Figure 1 includes cyclic voltammetry of microelectrodes 1–6 for the solid-state device operated at 95 °C in a N_2 atmosphere. At 25 °C under N_2 the solid-state oxidation/reduction of the poly(3-methylthiophene) is not well-defined, consistent with low ionic conductivity of PEO or poly(3-methylthiophene). Data shown in Figure 1 for the solution (CH_3CN/0.1 M $LiCF_3SO_3$ at 25 °C) and the solid state (N_2, 95 °C) are for the same device. For several independently prepared devices the amount of charge associated with cyclic oxidation/reduction of poly(3-methylthiophene) is less for the solid-state measurement than for that of the solution. This suggests that not all poly(3-methylthiophene)

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* Author to whom correspondence should be addressed.

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