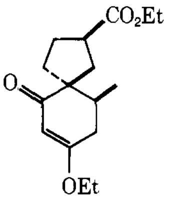
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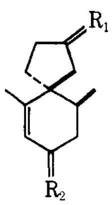
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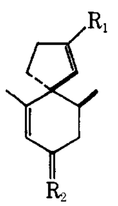
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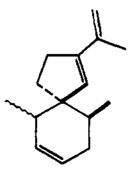
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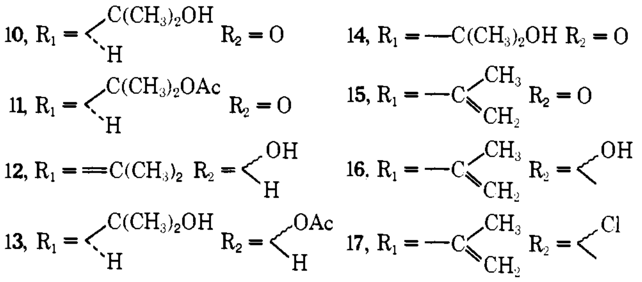

$10,\ R_1 = {<}^{C(CH_3)_2OH}_{H}\quad R_2 = O$; $14,\ R_1 = {-}C(CH_3)_2OH\quad R_2 = O$

$11,\ R_1 = {<}^{C(CH_3)_2OAc}_{H}\quad R_2 = O$; $15,\ R_1 = {-}C{<}^{CH_3}_{CH_2}\quad R_2 = O$

$12,\ R_1 = {=}C(CH_3)_2\quad R_2 = {<}^{OH}_{H}$; $16,\ R_1 = {-}C{<}^{CH_3}_{CH_2}\quad R_2 = {<}^{OH}$

$13,\ R_1 = {<}^{C(CH_3)_2OH}_{H}\quad R_2 = {<}^{OAc}_{H}$; $17,\ R_1 = {-}C{<}^{CH_3}_{CH_2}\quad R_2 = {<}^{Cl}$

afforded a 50% yield of (±)-β-vetivone (**1**), mp 43.5-47.0°. (lit. 43.5-46.0[3a]), spectrally and chromatographically identical with an authentic sample.[14] Lithium aluminum hydride reduction of **1** gave allylic alcohol **12**. Subsequent dehydration of **12** with 10-camphorsulfonic acid in benzene gave (±)-β-vetispirene (**3**), spectrally identical with (−)-β-vetispirene,[5a] in 86% overall yield.

Lithium aluminum hydride reduction of **10** followed by selective acetylation (acetic anhydride, pyridine) of the resulting diol produced a mixture of hydroxyacetates **13** in 81% yield (mp 45-55°; ir 3350, 1725, 1650, 1240 cm^{-1}; NMR (CCl_4) δ 0.97 (d, 3 H), 1.22 (s, 6 H), 1.3-2.1 (envelope with singlets at 1.75, 2.03, 17 H), 5.20 (m, 2 H)). Reduction of **13** with lithium in ethylamine[15] afforded a 75% yield of a 9:1 mixture of two compounds. The major component was shown to be (±)-hinesol (**2**), spectrally and chromatographically identical with an authentic sample.[14,16]

To make use of the C-1,2 double bond present in **6**, the following transformations were conducted. Successive treatment of **6** with methyllithium and 1.2 *N* HCl-ether (4:1) yielded ketol **14** which was dehydrated with 10-camphorsulfonic acid to trienone **15** in an overall yield of 78% (ir 1671, 892 cm^{-1}; NMR (CCl_4) δ 0.97 (d, 3 H), 1.83 (d, 3 H), 1.8-2.8 (envelope with singlet at 1.95, 10 H), 4.90 (broad s, 2 H), 5.58 (broad s, 1 H), 5.68 (q, 1 H)). Treatment of **15** with lithium aluminum hydride gave a mixture of solid isomeric alcohols **16** in quantitative yield (mp 51-62°). Conversion of **16** to the corresponding chlorides **17** with *N*-chlorosuccinimide-dimethyl sulfide complex[17] followed immediately by reduction with lithium aluminum hydride gave an 80% yield of a 37:63 mixture of trienes **18** and (±)-α-vetispirene (**5**),[18] separated and purified by preparative gas chromatography (10 ft × ¼ in. 10% SE-30, 190°, 60 ml He min^{-1}).

References and Notes

(1) This work was supported by National Science Foundation Grant No. GP-8700.

(2) For a review on the spirovetivanes, see J. A. Marshall, S. F. Brady, and N. H. Anderson, *Fortschr. Chem. Org. Naturst.*, **31**, 283 (1974); for the most recent report of a spirovetivane see A. Stoessl, J. B. Stothers, and E. W. G. Ward, *J. Chem. Soc., Chem. Commun.*, 709 (1974).

(3) (a) For the structure and first total synthesis of this substance see J. A. Marshall and P. C. Johnson, *J. Org. Chem.*, **35**, 192 (1970); (b) for a recent efficient synthesis see G. Stork, R. L. Danheiser, and B. Ganem, *J. Am. Chem. Soc.*, **95**, 3414 (1973).

(4) For the structure and first total synthesis of this substance see J. A. Marshall and S. F. Brady, *J. Org. Chem.*, **35**, 4068 (1970).

(5) (a) For the structure of this substance see N. H. Anderson, M. S. Falcone, and D. D. Syrdal, *Tetrahedron Lett.*, 1759 (1970); (b) for the first total synthesis see P. M. McCurry and R. K. Singh, *ibid.*, 3325 (1973).

(6) (a) For the structure of this substance see D. T. Coxon, K. R. Price, and B. Howard, *Tetrahedron Lett.*, 2921 (1974); (b) for a relay synthesis from hinesol and β-rotunol see H. Hikino, K. Aota, D. Kuwano, and T. Takemoto, *Tetrahedron*, **27**, 4831 (1971); (c) for a relay synthesis from nootkatone see D. Caine and C. Chu, *Tetrahedron Lett.*, 703 (1974).

(7) For the first total synthesis of this substance see K. Yamada, H. Nagase, Y. Hayakawa, K. Aoki, and Y. Hirata, *Tetrahedron Lett.*, 4963, 4967 (1973); in this report, a 16-step synthesis of an intermediate suitable for conversion to **1-5** is described.

(8) P. L. Fuchs, *J. Am. Chem. Soc.*, **96**, 1607 (1974).

(9) For a recent review on the synthesis of spiro compounds see A. P. Krapcho, *Synthesis*, 383 (1974); for another method of preparing spiro compounds form 2-formylcycloalkanones see V. Dave and J. S. Whitehurst, *Tetrahedron*, **30**, 745 (1974), and references therein.

(10) The 2-formylcycloalkanones were those derived from the condensations of cyclooctanone, cycloheptanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-*tert*-butylcyclohexanone with ethyl formate.

(11) Prepared in 61.5% yield from 3-ethoxy-5-methylcyclohex-2-en-1-one and ethyl formate, bp 133-135° (1 mm).

(12) All new compounds reported herein were fully characterized. All yields refer to isolated materials.

(13) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492 (1965).

(14) We wish to thank Professor J. A. Marshall for kindly supplying us with samples of (±)-1, (±)-**2**, and (−)-**2**.

(15) A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, 1969 (1957).

(16) This material was also converted to hinesol acetate, spectrally and chromatographically identical with an authentic sample.

(17) E. J. Corey, C. V. Kim, and M. Takeda, *Tetrahedron Lett.*, 4339 (1972).

(18) Spectrally identical (ir, NMR, uv) to (+)-α-vetispirene (see ref 5a).

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Reactions of Transition Metal-Nitrogen σ-Bonds. II.[1] Pentakis(*N,N*-dimethylcarbamato)niobium(V) and Its Facile Exchange Reaction with Carbon Dioxide

Sir:

We wish to report the interesting structure and dynamic solution behavior of $Nb(O_2CNMe_2)_5$ (**1**) and to propose a mechanism which accounts for the observed facile carbon dioxide exchange reaction (eq 1).

$$Nb(O_2CNMe_2)_5 + x{*}CO_2 \rightleftharpoons Nb(O_2{*}CNMe_2)_n(O_2CNMe_2)_{5-n} + (x-n){*}CO_2 + nCO_2 \quad (1)$$

$$\text{where } n = 0\text{–}5$$

A benzene solution of $Nb(NMe_2)_5$ reacts with CO_2 (5 or more equiv) in a sealed tube at room temperature to give $Nb(O_2CNMe_2)_5$ (**1**). **1** is an air-sensitive, pale yellow crystalline solid, only very sparingly soluble in alkane solvents but appreciably soluble in benzene and toluene. A cryoscopic molecular weight determination shows that **1** is monomeric in benzene. The ^1H NMR spectrum of **1** in toluene-d_8 at 60 MHz shows a single resonance at 2.56 ppm from HMDS (hexamethyldisiloxane) at ambient temperatures. On cooling the sample this resonance splits into a 3:2 doublet at 2.28 and 2.50 ppm (rel HMDS), $T_c = -65°$. No further change in the spectrum is observed on cooling the sample to −90°. A methylene chloride-freon 11 solution of **1** shows similar ^1H NMR spectroscopic properties; the 3:2 doublet persists to −120° (100 MHz) which is the limit of our low temperature capability. The ^1H NMR spectroscopic properties of **1** are independent of the concentration of **1**. These observations alone, however, are singularly uninformative with regard to the coordination properties of the metal.

Early transition metal *N,N*-dimethylcarbamato compounds show strong infrared absorptions in the region 1690-1550 cm^{-1} attributable to a stretching mode of the NCO_2 moiety.[2] We have sought a distinction between bidentate and monodentate $Me_2NCO_2^-$ ligands from a comparison of the ir spectra of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O_2$

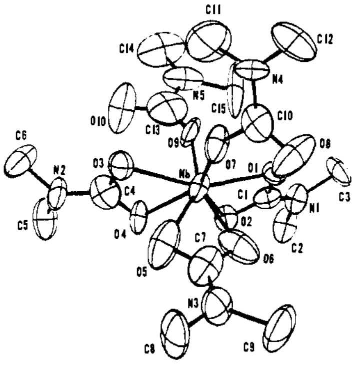

Figure 1. View of one molecule of $Nb(O_2CNMe_2)_5$ showing the atomic numbering scheme. Atom ellipsoids represent equiprobability surfaces of thermal displacement and contain 50% of the probability distribution. The sites and shapes of the atoms are determined by their final anisotropic thermal parameters and by their perspective view.

Table I. Infrared Absorption Maxima in the 1690–1550-cm^{-1} Region Characteristic of $\nu_{str}(NCO_2)$

Compound	$\nu_{str}(N^{12}C^{16}O_2)$	$\Delta^{13}C^a$	$\Delta^{18}O^b$
$Zr(O_2CNMe_2)_4$	1594	29	4
$W(NMe_2)_3(O_2CNMe_2)_3$	1640	43	23
$Nb(O_2CNMe_2)_5$	1616	24	0
	1685	40	25

[a] $\Delta^{13}C = \nu_{str}(N^{12}C^{16}O_2) - \nu_{str}(N^{13}C^{16}O_2)$. [b] $\Delta^{18}O = \nu_{str}(N^{12}C^{16}O_2) - \nu_{str}(N^{12}C^{18}O_2)$.

Table II. Bond Distances (Å), Bond Angles (deg), and Least-Squares Planes for the NbO_5 Moiety of $Nb(O_2CNMe_2)_5$[a]

Bond distances		Bond angles	
Nb–O1	2.17 (1)	O1–Nb–O2	61.5 (5)
Nb–O2	2.10 (1)	O1–Nb–O3	154.5 (5)
Nb–O3	2.20 (1)	O1–Nb–O4	134.7 (6)
Nb–O4	2.11 (1)	O1–Nb–O5	130.6 (6)
Nb–O5	2.20 (2)	O1–Nb–O6	74.8 (6)
Nb–O6	2.02 (2)	O1–Nb–O7	82.2 (6)
Nb–O7	1.91 (1)	O1–Nb–O9	80.8 (6)
Nb–O9	1.91 (2)	O2–Nb–O3	133.0 (6)
Bond angles		O2–Nb–O4	74.3 (6)
		O2–Nb–O5	112.9 (7)
O4–Nb–O6	106.2 (6)	O2–Nb–O6	78.1 (6)
O4–Nb–O7	141.8 (6)	O2–Nb–O7	143.6 (6)
O4–Nb–O9	87.2 (6)	O2–Nb–O9	85.8 (6)
O5–Nb–O6	56.9 (7)	O3–Nb–O4	60.6 (6)
O5–Nb–O7	88.6 (7)	O3–Nb–O5	68.2 (6)
O5–Nb–O9	148.0 (7)	O3–Nb–O6	124.8 (7)
O6–Nb–O7	91.4 (7)	O3–Nb–O7	81.4 (6)
O6–Nb–O9	155.1 (7)	O3–Nb–O9	80.0 (6)
O7–Nb–O9	90.5 (7)	O4–Nb–O5	74.2 (6)

Least-Squares Planes

	Atoms	Equation of plane
I	Nb, O1, O2, O3, O4, O7	$-0.872x - 0.028y - 0.489z = -1.725$
II	Nb, O1, O3, O5, O6, O9	$0.141x - 0.958y - 0.250z = -3.441$

Distance of Atoms from Plane

I		II	
Nb	−0.16	Nb	0.11
O1	0.19	O1	−0.21
O2	−0.02	O3	−0.18
O3	0.22	O5	0.02
O4	−0.08	O6	0.09
O7	−0.15	O9	0.18
O5	−2.03	O2	1.78
O6	−1.99	O4	1.79
O9	1.75	O7	−1.81

[a] For complete details see supplementary data.

labeled compounds. A comparison of the ir spectra of **1** with those of the presumed[3] eight-coordinate $Zr(O_2CNMe_2)_4$ and the known[1] six-coordinate $W(NMe_2)_3(O_2CNMe_2)_3$ led us to believe that **1** has both monodentate and bidentate $Me_2NCO_2^-$ ligands.[4] See Table I. Thus the low temperature limiting ^1H NMR spectrum[5] and vibrational spectra could readily be interpreted in terms of either seven- or eight-coordinate niobium. Because of the uncertainty of this prediction and the intriguing structural possibilities which both seven- and eight-coordination offer for **1**, we resorted to a single-crystal X-ray determination.[6] See paragraph at end of paper regarding supplementary material.

Crystal data: $Nb(O_2CNMe_2)_5$; M = 533.34; triclinic; a = 9.437 (4), b = 9.710 (3), c = 13.746 (5) Å; α = 88.08 (3), β = 95.68 (3), γ = 114.42 (3)°; $Z = 2$; d_{calcd} = 1.552 g/cm^2; space group $P\bar{1}$. Intensity data were collected on a Syntex $P\bar{1}$ computer controlled diffractometer using Mo Kα radiation. In the refinement of the structure, 1577 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. Niobium and the other 30 non-hydrogen atoms were refined anisotropically to give the final agreement factors $R_1 = 0.092$ and $R_2 = 0.106$. An ORTEP view of the molecular structure of **1** is shown in Figure 1 and the pertinent bond distances and bond angles for the immediate coordination geometry of niobium are given in Table II. Niobium is eight-coordinate having three bidentate and two monodentate $Me_2NCO_2^-$ ligands. The NbO_8 moiety does not correspond to any idealized ML_8 polyhedra.[7,8] This is clearly evident from the fact that two almost mutually perpendicular planes contain Nb and *five* of the NbO_8 oxygens. See Table II. Of course, for a $ML_2(L-L)_3$ structure a departure from an idealized ML_8 geometry is expected due to the constraints imposed by the chelating ligands. In this context it is interesting to compare **1** with eight-coordinate uranium(VI) compounds $UL_2(L-6)_3$.[8] The latter adopt a trans L-U-L geometry whereas **1** shows a cis L-Nb-L geometry; the O(7)-Nb-O(9) angle is 90.5 (7)°. Note also that the Nb-O(7) and Nb-O(9) bond distances, 1.91 (1) and 1.91 (2) Å are much shorter than the W-O bond distances, 2.041 (6) Å, in $W(NMe_2)_3(O_2CNMe_2)_3$.[1] Oxygen to niobium π-bonding may be important in **1** since niobium attains only 16 valence shell electrons via NbO_8 σ-bonding; cf.[1] $W(NMe_2)_3(O_2CNMe_2)_3$ where N to W π-bonding (i) allows tungsten to attain 18 valence shell electrons and (ii) exerts a high trans influence,[9] thus lengthening the trans W-O bonds in the *fac*-WN_3O_3 octahedron.

The structure of **1** provides no insight into the mechanism of the CO_2 exchange reaction (eq 1). The lability of **1** toward CO_2 exchange is seen in the following. When $Nb(O_2{}^{13}CNMe_2)_5$, 0.01 mmol, was dissolved in toluene-d_8, 0.40 ml, in an NMR tube, volume 3 ml, and allowed to react with $^{12}CO_2$, 0.20 mmol, at −40°, the half-life of $Nb(O_2{}^{13}CNMe_2)_5$ was about 24 min.[10]

A plausible mechanism for the exchange reaction (eq 1) involves the initial deinsertion of CO_2 and formation of $Nb(O_2CNMe_2)_4(NMe_2)$. Direct evidence for the existence of significant concentrations of $Nb(O_2CNMe_2)_4(NMe_2)$ in solutions of **1** is seen in the following. **1** dissolved in toluene-d_8 yields a pale yellow solution, and, in the ^1H NMR spectrum, in addition to the single resonance at 2.56 ppm (HMDS), there are small peaks at 4.00 and 2.53 ppm (HMDS). In the ^1H NMR spectrum of $Nb(O_2{}^{13}CNMe_2)_5$ only the high field resonances show $^3J_{^{13}C-H}$ = 3 Hz. However, toluene-d_8 solutions of **1** sealed under a positive pressure of CO_2 are colorless and show *only* the single resonance at 2.56 ppm (HMDS). When **1** is kept under a high vacuum for a prolonged time or solutions of **1** are degassed repeatedly, the relative concentration of the resonances assigned to $Nb(O_2CNMe_2)_4(NMe_2)$ increases.

The existence of a significant concentration of $Nb(O_2CNMe_2)_4(NMe_2)$ and its concentration dependence on CO_2 pressure imply that it is an intermediate in the reaction leading to the rapid CO_2 exchange (eq 1). If this is indeed the case[11] the facile reversible formation and cleavage of M-N, M-O, and C-N bonds in eq 1 is truly remarkable and has an obvious parallel in the facile reversible formation and rupture of M-H, M-C, and C-H bonds which forms the basis for most catalytic processes involving transition metals and hydrocarbons.[12]

The generality of CO_2 exchange reactions involving $M(O_2CNMe_2)_n$, where M = an early transition metal, has now been established,[2] and kinetic studies of these reactions are currently in progress.

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Supplementary Material Available. A listing of bond distances, bond angles, and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-1623.

References and Notes

(1) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **96**, 6214 (1974).
(2) M. H. Chisholm and M. Extine, results to be submitted for publication.
(3) $Zr(O_2CNMe_2)_4$ is monomeric in benzene, shows a single band in the ir spectrum due to $\nu_{str}(NCO_2)$ (see Table I), and a single methyl resonance in the 60 MHz ^1H NMR spectrum in the temperature range +90 to −120°. These properties are analogous to the presumed eight-coordinate $Zr(S_2CNR_2)_4$; e.g., see E. L. Muetterties, *Inorg. Chem.*, **12**, 1963 (1973), and references therein.
(4) $\Delta^{18}O$ is very small (0–5 cm^{-1}) for compounds believed to contain only bidentate $^-O_2CNMe_2$ ligands. Cf. $\Delta^{18}O = 23\ cm^{-1}$ for $W(NMe_2)_3(O_2CNMe_2)_3$.
(5) This may be viewed as the freezing out of monodentate–bidentate ligand interconversions.
(6) This was carried out by Molecular Structure Corporation, College Station, Texas 77840.
(7) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
(8) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967).
(9) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(10) This reaction may be followed by ^1H NMR spectroscopy since the $Me_2N^{13}CO_2$ ligand shows $J_{^{13}C-H} = 3$ Hz.
(11) That is, if CO_2 exchange occurs via rapid reversible insertion of CO_2 into $Nb-NMe_2$ bonds.
(12) F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, N.Y., 1972, Chapter 24.

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Electron Affinities of Alkoxy Radicals and the Bond Dissociation Energies in Aliphatic Alcohols

Sir:

One of the fundamental properties of a gas phase radical is its adiabatic electron affinity. EA values are important because of their utility in structure-stability correlations,[1-3] and their knowledge is required[1b] for thermodynamic cycles, e.g.

$$\mathrm{ROH} \longrightarrow \mathrm{RO^-} + \mathrm{H^+}$$
$$\Delta H^\circ = \mathrm{DH^\circ(RO{-}H)} - \mathrm{EA(RO\cdot)} + \mathrm{IP(H\cdot)} \qquad (1)$$

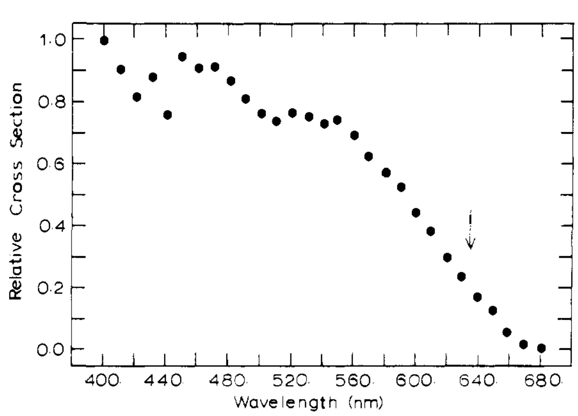

Figure 1. Relative photodetachment cross section for *tert*-butoxide anion in the energy range 1.82–3.0 eV. An average of three independently normalized runs is shown, resolution 23.8 nm (full width half maximum), maximum fractional signal decrease of 8% at 400 nm. The arrow indicates the threshold required to yield a hydroxyl bond strength for *tert*-butyl alcohol of 104 kcal/mol.

Recently, photodetachment experiments on small polyatomic anions have been shown to provide reliable limiting EA estimates[3-5] through the determination of the thresholds for

$$\mathrm{A^-} + h\nu \longrightarrow \mathrm{A} + \mathrm{e^-}$$

In this communication, we present results of photodetachment experiments for RO^- (R = CH_3, $t\text{-}C_4H_9$, neo-C_5H_{11}). These results are particularly important in that they establish the applicability of the technique to larger and more complex ions. We draw attention here to the implications of these data to O-H bond energies in aliphatic alcohols. This is accomplished by utilizing the ionic equilibria measurements of McIver and Miller,[6] eq 2 (AH =HF, R′OH, RC≡CH).

$$\mathrm{ROH} + \mathrm{A^-} \rightleftharpoons \mathrm{RO^-} + \mathrm{AH}$$
$$\Delta H^\circ = \mathrm{DH^\circ(RO{-}H)} + \mathrm{EA(A\cdot)} - \mathrm{DH^\circ(AH)} - \mathrm{EA(A\cdot)} \qquad (2)$$

Application of such cycles would provide an important alternative to other methods, particularly thermochemical kinetics.[7-11]

Alkoxide anions were generated in a Varian V-5900 ICR spectrometer by 1 eV electron impact on dimethyl (and dimethyl-d_6) peroxide; 8 or 12 eV electron impact on *tert*-butyl alcohol and its deuterated analog. Neopentoxide anions were produced via proton transfer from the alcohol to fluoride ion (from NF_3). Ion ejection and kinetic experiments showed that this reaction is practically encounter controlled and thus cannot be appreciably endothermic ($k = (2.2 \pm 0.4) \times 10^{-10}\ cm^3\ molecule^{-1}\ sec^{-1}$); the corresponding reaction of *tert*-butyl alcohol + F^- ($k = (0.9 \pm 0.2) \times 10^{-10}\ cm^3\ molecule^{-1}\ sec^{-1}$) could be driven by reactant irradiation to produce additional *tert*-butoxide anion. This independently establishes the relative acidity order, neopentyl alcohol ≥ HF > *tert*-butyl alcohol, observed by McIver.[6] This order is critical to the discussion that follows.

Relative photodetachment cross sections and threshold energies were determined by methods previously described.[4,5] Extrapolation of the linearly rising portion of the curve to zero cross section (Figure 1) gives[12] $EA(CH_3O\cdot) \leq 36.7 \pm 0.9$, $EA(t\text{-}C_4H_9O\cdot) \leq 43.1 \pm 1.0$, and $EA(\text{neo-}C_5H_{11}O\cdot) \leq 44.5 \pm 1.4$ kcal/mol (thresholds at 779.6, 663.0, and 640.5 nm). Alternative onset values obtained by subtracting the band width (23.8 nm) from the apparent threshold gave 776.2, 657.0, and 637.0 nm respectively, indicating that the data are adequately represented