tion 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 thereln.

(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.

M. H. Chisholm,* M. Extine

Frick Inorganic Chemical Laboratories
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received December 23, 1974

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.

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

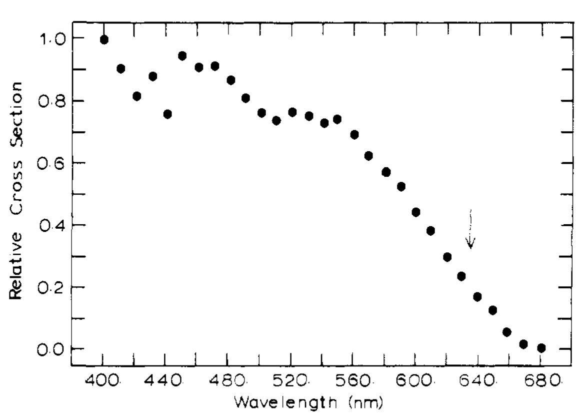

Figure 1. Relative photodetachment cross section for *tert*-butoxide anion in the energy range 1.82–3.0 eV. An average of three independently normalized runs is shown, resolution 23.8 nm (full width half maximum), maximum fractional signal decrease of 8% at 400 nm. The arrow indicates the threshold required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

$$A^- + h\nu \longrightarrow A + e^-$$

In this communication, we present results of photodetachment experiments for RO^- (R = CH_3, t-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).

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

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 ± 0.4) × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}); the corresponding reaction of *tert*-butyl alcohol + F^- (k = (0.9 ± 0.2) × 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($CH_3O\cdot$) ≤ 36.7 ± 0.9, EA(t-$C_4H_9O\cdot$) ≤ 43.1 ± 1.0, and EA(neo-$C_5H_{11}O\cdot$) ≤ 44.5 ± 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 by a straight line convoluted by a triangular slit function.[4] An error estimate of ±20 nm is based on uncertainties in threshold location, monochromator calibration, and convolution. For reasons similar to those outlined previously,[3-5] we think these thresholds correspond to good upper limit estimates of EA's.

Using McIver's $DH^\circ - EA$ values and our EA's, we calculate the RO-H bond energies for methanol, *tert*-butyl alcohol, and neopentyl alcohol as 101.2 ± 1.2, 102.2 ± 1.2, and 102.3 ± 1.5 kcal/mol, respectively. These numbers are within experimental error of the "best" gas kinetic values,[11] although they are systematically lower by about 2 kcal/mol.

Provided the anion is in its ground vibronic state, the photodetachment threshold represents an upper limit to the EA[3-5] and correspondingly an upper limit to DH°. However, vibrationally excited anions which photodetach with $\Delta\nu < 0$ would result in an apparent EA which was low. A number of factors suggest this is not happening in our experiments. First, the ions were formed by processes which are only slightly exothermic. In addition, hot bands have not previously been observed in ICR photodetachment experiments, presumably due to the long (≥ 1 sec) trapping times which allow radiative relaxation and thermalizing collisions to occur. Furthermore, although formed by different processes, each of the three anions studied has this same 2 kcal/mol discrepancy, and thus vibrational excitation would have to have been present to the same extent in each anion. Finally, Franck-Condon factors estimated from calculated geometries[13] suggest that diagonal transitions should be much stronger than nondiagonal transitions. Thus, even if the $\nu = 1$ state is appreciably populated, the $1 \rightarrow 0$ transition would be weak. Consistent with a $0 \rightarrow 0$ threshold we observe no shift for CD_3O^-.

Bond energies for aliphatic alcohols have been determined via pyrolyses of alkyl peroxides, nitrites, and nitrates,[7-11] with the usual assumption of zero barrier for radical recombination.[14] These results are internally consistent and have no obvious source of error. The systematic discrepancy (Figure 1) of 2 kcal/mol appears to be well outside of our experimental uncertainty and suggests that one of the more fundamental quantities used in the analyses may be in error.

In summary, we believe that the determination of DH° in complex molecules via these cycles is a viable alternative to other methods.[15] The apparent small discrepancy is more likely to be a result of errors in other basic data than a result of direct experimental error or unwarranted assumptions.

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References and Notes

(1) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 6561 (1968); (b) *ibid.*, **92**, 5986 (1970); (c) *ibid.*, **93**, 4315 (1971).
(2) K. J. Reed, A. H. Zimmerman, and J. I. Brauman, manuscript in preparation.
(3) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Chem. Phys.*, **59** 5068 (1973).
(4) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 1132 (1972).
(5) K. J. Reed and J. I. Brauman, *J. Chem. Phys.*, **61**, 4830 (1974).
(6) R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 4323 (1974). The value for CH_3OH is actually 1.3 kcal/mol less acidic than reported (R. T. McIver, personal communication); our DH° is based on the corrected value.
(7) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).
(8) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(9) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
(10) P. Gray, R. Shaw, and J. C. J. Thynne, *Prog. React. Kinet.*, **4**, 63 (1967).
(11) S. W. Benson and R. Shaw, *Adv. Chem. Ser.*, **No. 75**, 288 (1968).
(12) These results are consistent with EA estimates of other alkoxy radicals obtained by appearance potential measurements, see J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968).
(13) D. R. Yarkony, H. F. Schaefer III, and S. Rothenberg, *J. Am. Chem. Soc.*, **96**, 656 (1974).
(14) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).
(15) See, for instance, D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, *J. Chem. Phys.*, **59**, 77 (1973). The NH_3 bond energy calculated here is 107.4 ± 1.1 kcal/mol as opposed to the previous value of 110 ± 2.

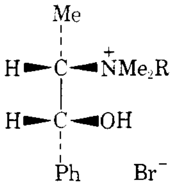
Kenneth J. Reed, John I. Brauman*
Department of Chemistry, Stanford University
Stanford, California 94305
Received December 5, 1974

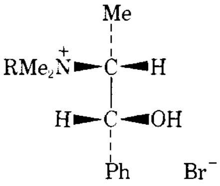
Enantioselective Oxirane Synthesis by Means of Dimethylsulfonium Methylide and Chiral Phase-Transfer Catalysts

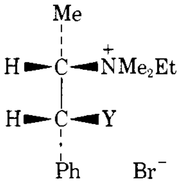
Sir:

We wish to report a novel type of asymmetric synthesis[1] of 2-phenyloxirane from benzaldehyde and the achiral Corey's ylide in the presence of an optically active, β-oxido quarternary ammonium zwitterion, V, as a catalyst.[2,3]

In a standard experiment benzaldehyde (283 mg, 2.68 mmol) dissolved in dichloromethane (1.5 ml) was added dropwise with stirring to a mixture of trimethylsulfonium iodide (612 mg, 3.00 mmol), 50% aqueous sodium hydroxide (1.8 g of NaOH in 1.8 ml of water) and (−)-*N*,*N*-dimethylephedrinium bromide (Ia)[4] (41.1 mg, 0.15 mmol) at 38° under nitrogen atmosphere. After 48 hr at this temperature[5] work-up and preparative TLC (silica gel, *n*-hexane: ether 10:1, R_f 0.5) gave a single product, 2-phenyloxirane (240 mg, 77%), $[\alpha]^{25}\mathrm{D}$ +4.36° (*c* 5.28, acetone),[6] 67% enantiomeric excess (*R* predominating).[6b] Use of the higher homologous R groups in I resulted in a slight increase of the chemical yield and a less effective asymmetric induction (the added quaternary ammonium salt,[7] chemical yield (%), $[\alpha]^{25}\mathrm{D}$ (*c*), enantiomeric excess (%)): Ib, 81, +4.15° (10.1), 52;[6a] Ic, 66, +4.87° (8.21), 61;[6a] Id, 83, +3.91° (3.86), 47.[6b] In the presence of the (−) quaternary ammonium salts of ψ-ephedrine[4,9] (II) the opposite direction of the asymmetric induction (*S* predominating) has been observed (ammonium salt, chemical yield (%), $[\alpha]^{25}\mathrm{D}$ (*c*), enantiomeric excess (%)): IIa, 71, −2.64° (3.63), 40;[6b] IIb, 65, −1.64° (3.29), 25.[6b] Thus the configuration of the carbon atom bearing the ammonium group is apparently responsible for the direction. The role of the hydroxyl group in I and II, however, cannot be overlooked, as the following experiments show. The catalysis of the chiral ammonium salts, III and IV,[10] gave 2-phenyloxirane in 67 and 72% yields, respectively, without any trace of optical rotation.


Ia, R = Me
b, R = Et
c, R = *n*-Pr
d, R = *n*-Bu


IIa, R = Me
b, R = Et


III, Y = H
IV, Y = OMe

These observations suggest that zwitterionic species such as V and VI in the organic phase should account for the induction, which originates from the dipole-dipole interaction