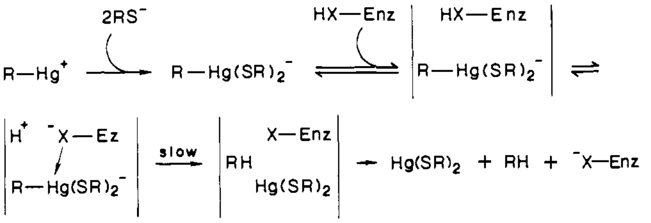
boxylate bases to be effective nucleophilic catalysts in protodemercuration when the mercury is bis-thiol ligated. Comparison of k_1 values shows HPO_4^{2-} is even better, while imidazole is found to be a much less effective catalyst.

Begley, Walts, and Walsh[2] have shown that the *E. coli* lyase does not possess an available sulfhydryl substituent at the active site (lack of reaction with ICH_2CONH_2). Bis ligation by thiol has been shown to be required to dissociate the Hg^{2+} product from the enzyme.[2] This study suggests that bis-thiol ligation is also required to create the actual substrate (eq 4). The mechanism



(4)

of eq 4 would predict activity to increase with pH until the pK_a of the functional group HX– is reached. Such behavior apparently pertains to the *E. coli* lyase.[2] If the proton dissociated from HX– is diffusable to solvent, a "bell-shaped" pH profile would be obtained as is apparently the case with the *Pseudomonas* enzyme and is seen in the present study.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

---

(10) Kreevoy, M. M., et al. *J. Am. Chem. Soc.* **1966**, *88*, 124.

Aromatic Hydrocarbon Dianions: Super Bases. Anthracene Anion Radical and Dianion Conjugate Acid pK_a Values

Vernon D. Parker,*[†] Mats Tilset,[†] and Ole Hammerich[‡]

Laboratory for Organic Chemistry, Norwegian
Institute of Technology, University of
Trondheim, 7034 Trondheim-NTH, Norway
Department of General and Organic Chemistry
The H. C. Ørsted Institute, University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen, Denmark

Received July 9, 1987

Although numerous mechanistic and product studies of the protonation reactions of anion radicals have been carried out,[1] information on the thermodynamic basicity of these reactive intermediates is still not available. Qualitatively, it is well known that the corresponding dianions react much more readily with proton donors.[2] Recently, detailed kinetic studies have shown that the mechanisms of these fundamentally important reactions, although complex, can be determined quantitatively.[3] Our goal to achieve a more complete understanding of these reactions led to the development of a method to evaluate pK_a values for the conjugate acids of anion radicals and the corresponding dianions.

We now report a simple method to determine (pK(DA) – pK(AR)), the difference in pK_a of the conjugate acids of the dianion (DA) and the anion radical (AR), involving the measurement of electrode potentials without the necessity to rely on theoretical or experimental data for any other equilibria. The experimental data necessary for the thermodynamic cycle[4] (Scheme I) consists of the reversible electrode potentials for the reduction of the anion radical (eq 1) and that for the oxidation of the carbanion (eq 2). The equilibrium constants for the reactions completing the thermodynamic cycle (eq 3 and 4) correspond to the relative values that we wish to determine.

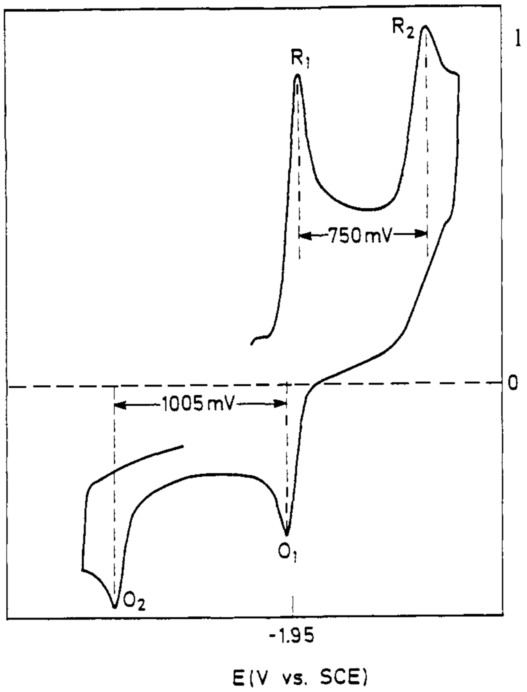


Figure 1. Cyclic voltammogram for the reduction of anthracene (1 mM) in $DMSO/Bu_4NBF_4$ (0.1 M) at 100 V/s and 20 °C.

Scheme I

$$\begin{array}{llr} & \Delta G^\circ & \\ A^{\bullet-} + e^- \rightleftarrows A^{2-} & -FE_1^\circ & (1) \\ AH^- \rightleftarrows AH^\bullet + e^- & FE_2^\circ & (2) \\ A^{2-} + H^+ \rightleftarrows AH^- & RT \ln K(DA) & (3) \\ AH^\bullet \rightleftarrows A^{\bullet-} + H^+ & -RT \ln K(AR) & (4) \end{array}$$

$$pK(DA) - pK(AR) = F(E_2^\circ - E_1^\circ)/2.303RT \qquad (5)$$

Scheme II

$$\begin{array}{llr} & \Delta G^\circ & \\ A + H_2 \rightleftarrows AH_2 & -RT \ln K_6 & (6) \\ AH_2 \rightleftarrows AH^- + H^+ & -RT \ln K(AH_2) & (7) \\ A^{\bullet-} \rightleftarrows A + e^- & FE_8^\circ & (8) \\ AH^- \rightleftarrows AH^\bullet + e^- & FE_9^\circ & (9) \\ 2H^+ + 2e^- \rightleftarrows H_2 & 0 & (10) \\ AH^\bullet \rightleftarrows A^{\bullet-} + H^+ & -RT \ln K(AR) & (11) \end{array}$$

$$pK(AR) = -pK(AH_2) - pK(6) - F(E_8^\circ + E_9^\circ)/2.303RT \qquad (12)$$

Table I. Thermodynamic and Electrode Potential Data for the Determination of pK(AR) of Anthracene Anion Radical

reaction	data	remarks
$AH_2 \rightleftarrows AH^- + H^+$	$pK(AH_2) = 27$	*a*
$AH^- \rightleftarrows AH^\bullet + e^-$	$-E_2 = 730$ mV	*b*
$A^{\bullet-} \rightleftarrows A + e^-$	$-E_8 = 1730$ mV	*b*
$A + H_2 \rightleftarrows AH_2$	$\Delta G^\circ = -11$ kcal/mol	*c*
$AH^\bullet \rightleftarrows A^{\bullet-} + H^+$	$pK(AR) = 23$	

[a] The difference in pK_a for triphenylmethane and 9,10-dihydroanthracene is 1 pK_a unit in cyclohexylamine and in dimethoxyethane and is assumed to be the same in DMSO. The pK_a of triphenylmethane is 28 in DMSO.[15] [b] The reversible electrode potential vs the standard hydrogen electrode. [c] From data in ref 16.

[†] University of Trondheim.

[‡] University of Copenhagen.

(1) Nielsen, M. F.; Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1986**, *40B*, 101 and references cited.

(2) Parker, V. D. *Pure Appl. Chem.* **1979**, *51*, 1021.

(3) Nielsen, M. F.; Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1987**, *41B*, 50.

(4) Thermodynamic cycles using electrode potential data give access to thermodynamic quantities such as pK_a values for hydrocarbons[5] and pK_a values for cation radicals.[6,7]

0002-7863/87/1509-7905$01.50/0

A second thermodynamic cycle (Scheme II), which requires thermodynamic data for hydrogenation of the aromatic compound (eq 6) and the pK_a of the dihydroaromatic (eq 7) in addition to the electrode potential data (eq 8 and 9) results in an expression (eq 12) to estimate the pK_a of the conjugate acid of the anion radical, i.e., pK(AR).

The direct determination of pK(DA) - pK(AR) from a single cyclic voltammogram (Scheme I) is illustrated in Figure 1. The reversible couple, R_1/O_1, corresponds to electrode reaction 8 where A represents anthracene. The reversible reduction of the anion radical to the dianion (eq 1) takes place at R_2.[8] On the return scan the process at O_2 involves the oxidation of AH^- (eq 2). The reversible potential estimated for reaction 2 is in error by the kinetic shift due to the irreversible reaction of $AH^\bullet$. The magnitude of the error can be estimated by using well-known theoretical relationships.[10]

The data in Table I illustrate the determination of pK(AR) for the conjugate acid of the anthracene anion radical in DMSO making use of Scheme II and literature data for equilibria 6 and 7. The value obtained, pK(AR) = 23, indicates that the anion radical is significantly less basic than AH^-, the monoanion of 9,10-dihydroanthracene (pK(AH_2) = 27). Electrode potential data taken from Figure 1 indicate that pK(DA) - pK(AR) (Scheme I) is equal to 30 which results in a value of 53 for pK(AH^-). These values appear to be consistent with previous observations. Reversible cyclic voltammograms for formation of dianions can only be observed when water and other protic impurities are rigorously excluded.[11] On the other hand, reversible formation of anion radicals can be observed even in the presence of significant concentrations of water. The oxidation peak for the carbanion is only observed when the water concentration is quite low.[12] This would appear to be at least qualitatively in line with the pK_a values that we have determined by using the two thermodynamic cycles.

A value of pK(AH^-) has been reported previously by Streitwieser.[13] Only 4 pK units difference were observed for the first and second ionization constants of dihydroanthracene in cyclohexylamine. This was attributed to the relative inherent stability of the dianion derived from delocalization energy and, more importantly, to triple ion formation with two cesium ions. The large discrepancy in this pK_a difference with what we observe could arise from the fact that the dianion is not expected to associate strongly with tetrabutylammonium ions used in this study in DMSO as solvent.

The only source of significant error in our estimate of pK(DA) - pK(AR) derives from equating the potential measured for the oxidation of AH^- to the reversible value. The possibility of a kinetic shift contribution to this potential makes the measured potential difference, $E_2° - E_1°$, a minimum value. Thus our estimate of pK(DA) - pK(AR) is minimal, subject to a possible correction of +2 pK_a units. The major assumption in our treatment is the value of the pK_a of AH_2 in DMSO. We estimate that this assumption could give rise to an error as much as 2 pK_a units. Therefore, the value of pK(DA) - pK(AH_2) in DMSO is 27 ± 3. The value reported for the cyclohexylamine/cesium$^+$ system then differs from ours by about 23 pK_a units. Since ion pair $AH^-(Cs^+)$ and triple ion $A^{2-}(Cs^+)_2$ formation are expected to affect pK(AH_2) and pK(DA) in the same direction, we find a difference of 23 for ΔpK_a, free ions vs complexed ions, somewhat more than expected. The resolution of this problem requires further work. Our method should be applicable to the cyclohexylamine/cesium$^+$ system and provides a more direct comparison between free and complexes ions.

The two thermodynamic cycles (Schemes I and II) are readily applied to a variety of other anion radicals, dianions, and the corresponding dihydroaromatic compounds. When experimental data for reaction 6 are not available, it may be possible to obtain satisfactory results by using theoretical data from molecular mechanics calculations.[14] The quantity of most interest with regard to the reactivity of anion radicals toward proton donors is pK(DA) - pK(AR) and this can be determined to a high degree of precision by using only electrode potential measurements.

Acknowledgment. We gratefully acknowledge support from the Norwegian Research Council for Science and the Humanities.

---

(5) Jaun, B.; Schwarts, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(6) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(7) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473.

(8) To obtain the reversible potential it was necessary to carry out a separate experiment in the presence of neutral alumina to remove protic impurities.[9]

(9) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

(10) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 11.

(11) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

(12) Dietz, R.; Peover, M. *Trans. Faraday Soc.* **1966**, *62*, 3535.

(13) Streitwieser, A., Jr.; Berke, C. M.; Robbers, K. *J. Am. Chem. Soc.* **1978**, *100*, 8271.

(14) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177, American Chemical Society, Washington, DC, 1982.

(15) Streitwieser, A., Jr.; Jauristi, E.; Nebenzahl, L. L. *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Chapter 7.

(16) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 1716.

Transition-Metal Compounds with Bridging Nitride Ligands. Synthesis and Structure of *cis*-$(Me_3SiO)_3V{\equiv}N{-}Pt(Me)(PEt_3)_2$

Nancy M. Doherty* and Susan C. Critchlow

Department of Chemistry, University of Washington
Seattle, Washington 98195

Received July 24, 1987

Inorganic and organometallic polymers have recently become the subject of intense interest and study because of their unusual properties[1] and their potential for applications in the areas of electronics[2] and ceramics.[3] In comparison to organic polymers, however, general and versatile methods for the synthesis of inorganic and organometallic polymers are not readily available.[4] In particular, the preparation of polymers which (1) contain transition-metal atoms and (2) have these metal centers incorporated into the polymer backbone has received very little attention.[1,5] This may be, in part, because known reactions that couple two ligated metal centers, by formation of either direct metal–metal bonds or bonds to a bridging ligand, have a strong tendency to produce cluster compounds on addition of subsequent metal centers.[6] We are examining the synthesis of molecules in which two metal centers are linked by a single, bare nitrogen atom, the μ_2-nitride ligand. Our approach utilizes condensation of a trimethylsilylimido complex with a metal halide derivative to

---

(1) (a) *Metal-Containing Polymeric Systems*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds.; Plenum: New York, 1985. (b) *Rings, Clusters, and Polymers of the Main Group Elements*; Cowley, A. H., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1983. (c) *Advances in Organometallic and Inorganic Polymer Science*; Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Marcel Dekker: New York, 1982. (d) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vols. 1-3. (e) *Inorganic Polymers*; Ray, N. H., Ed.; Academic: London, 1978.

(2) (a) *Electrical Properties of Polymers*; Seanor, D. A., Ed.; Academic: New York, 1982. (b) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. (c) *Molecular Metals*; Hatfield, W. E., Ed.; Plenum: New York, 1979.

(3) *Ultrastructure Processing of Ceramics, Glasses, and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984.

(4) Allock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22-36.

(5) For examples of polymers containing transition-metal atoms incorporated into the polymer backbone, see: (a) Williams, J. M. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 235-268. (b) Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103-107. (c) Hiller, W.; Strähle, J.; Datz, A.; Hanack, M.; Hatfield, W. E.; ter Haar, L. W.; Gütlich, P. *J. Am. Chem. Soc.* **1984**, *106*, 329-335.

(6) See, for example: Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Permagon: Oxford, 1982; Vol. 6, Chapter 40.

0002-7863/87/1509-7906$01.50/0