Electrochemical Determination of the Basicities of Benzyl, Allyl, and Propargyl Anions, and a Study of Solvent and Electrolyte Effects

Sir:

We have reported[1] the use of electrochemical data, to determine the pK_a of isobutane (basicity of *tert*-butyl anion). The method uses a simple thermodynamic sequence:

$$\text{R-H} \xrightarrow{1} \text{R}\cdot + \text{H}\cdot \xrightarrow[+e]{2} \text{R}^- + \text{H}\cdot \xrightarrow[-e]{3} \text{R}^- + \text{H}^+$$

The first step involves the bond dissociation energy of the hydrocarbon; this is known in the gas phase, and we assume that it is not changed in solution. The second step has an energy which can be derived from the *reversible* electrochemical reduction potential of the alkyl radical in solution. The third step is common to all hydrocarbons. We cancel it, and mirror various solvation effects on the other steps, by running a standard hydrocarbon of known pK_a through the same sequence. For our standard we have used triphenylmethane, of known pK_a and bond dissociation energy.

Second-harmonic ac voltammetry was used to determine the radical reduction potentials reversibly.[2] A calibration of the method showed[1] that the known pK_a of cyclopentadiene, originally obtained by titration, could be obtained as well from our thermodynamic cycle. We found[1] the pK_a of isobutane to be 71, from electrochemical work in dimethoxyethane using tetrabutylammonium perchlorate electrolyte. Since this very

Table I. Reversible Potentials for the Reduction of Radicals to Anions, Using Second-Harmonic ac Voltammetry on Alkyl Iodides

Alkyl iodide	Electrode	Solvent[a]	Supporting electrolyte[b]	Radical reduction potential[c]
Allyl	Au	MeCN	TMAP	−1.55
Allyl	Au	MeCN	TBAP	−1.61
Allyl	Au	MeCN	THAP	−1.75
Allyl	Au	DME	TBAP	−1.61
Allyl	Pt	MeCN	TMAP	−1.60
Allyl	Pt	MeCN	TBAP	−1.61
Allyl	Pt	MeCN	THAP	−1.60
Allyl	Pt	DME	TBAP	−1.61
Benzyl	Au	MeCN	TMAP	−1.83
Benzyl	Au	MeCN	TBAP	−1.86
Benzyl	Au	MeCN	THAP	−1.87
Benzyl	Au	DME	TBAP	−1.86
Benzyl	Pt	MeCN	TMAP	−1.85
Benzyl	Pt	MeCN	TBAP	−1.88
Benzyl	Pt	MeCN	THAP	−1.88
Benzyl	Pt	DME	TBAP	−1.82
tert-Butyl	Au	MeCN	TBAP	−2.56
tert-Butyl	Au	MeCN	THAP	−2.44
tert-Butyl	Au	DME	TBAP	−2.24
tert-Butyl	Pt	MeCN	TBAP	−2.69
tert-Butyl	Pt	MeCN	THAP	−2.56
tert-Butyl	Pt	DME	TBAP	−2.19
Propargyl	Au	MeCN	TBAP	−1.95
Propargyl	Au	MeCN	THAP	−1.95
Propargyl	Au	DME	TBAP	−1.85
Propargyl	Pt	MeCN	THAP	−1.93
Propargyl	Pt	DME	TBAP	−1.90
Triphenylmethyl cation	Au	MeCN	TMAP	−1.00
Triphenylmethyl cation	Au	MeCN	TBAP	−0.97
Triphenylmethyl cation	Au	MeCN	THAP	−0.94
Triphenylmethyl cation	Au	DME	TBAP	−0.95
Triphenylmethyl cation	Pt	MeCN	TMAP	−0.99
Triphenylmethyl cation	Pt	MeCN	TBAP	−0.98
Triphenylmethyl cation	Pt	MeCN	THAP	−0.99
Triphenylmethyl cation	Pt	DME	TBAP	−0.99

[a] MeCN, acetonitrile; DME, 1,2-dimethoxyethane. [b] TMAP, tetramethylammonium perchlorate; TBAP, tetra-*n*-butylammonium perchlorate; THAP, tetra-*n*-heptylammonium perchlorate; all were used at 0.10 M. [c] The frequency-invariant crossing point for the second reduction wave of the substrate, obtained with full *iR* compensation. Values in volts vs. SCE.

Table II. pK_as of Hydrocarbons

Hydrocarbon (R-H)	Anion (R^-)	Bond dissociation energy of R-H[a]	Radical reduction potential[b]	pK_a[c]
Triphenylmethane	Triphenylmethyl	75	−0.97	31.5
Propene	Allyl	88.6	−1.61	53
Toluene	Benzyl	84.3	−1.86	54
Propyne	Propargyl	93.9	−1.95	63
Isobutane	*tert*-Butyl	91	−2.56	71

[a] From H. O'Neal and S. W/ Benson in "Free Radicals", Vol. I, J. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, pp 275–285. [b] Determined vs. SCE by the method of ref 1 and 2. The values listed are with TBAP electrolyte in CH_3CN solution. [c] Relative to triphenylmethane as standard, in CH_3CN solution 0.10 M in TBAP. It should be noted that the medium in which the carbanions are actually being generated, at the electrode, is very concentrated in electrolyte. However, the present work shows that the relative pK_as observed are *not* strongly dependent on the polarity of that electrolyte.

high pK_a was determined by use of a novel method, which had been calibrated only with cyclopentadiene, it was important to extend the method to other cases to see that a sensible consistent picture emerges. At the same time it was of interest to learn whether this thermodynamic pK_a was dependent on the exact solvent and electrolyte used. We now wish to report the results of such studies.

Allyl iodide, benzyl iodide, propargyl iodide, *tert*-butyl iodide and triphenylmethyl fluoborate were examined electrochemically using second-harmonic ac voltammetry as previously described.[1,2] All showed two reduction waves, the second being that for reduction of allyl radical, benzyl radical, etc., to the corresponding anion. Good reversible behavior was observed, with a well-defined crossing point. The results are listed in Table I.

The data in Table I show that there are minor but real medium effects on the reduction potentials. Considering only the data at a gold electrode, which we have shown[2] to be the most reliable, we see that the change of solvent from acetonitrile to dimethoxyethane has essentially no effect on the reduction potential of the allyl, benzyl, or triphenylmethyl radicals, but does change that of *tert*-butyl radical by 300 mV (corresponding to 5 pK_a units). Since the radical is reduced to a carbanion in the presence of a high local concentration of the supporting electrolyte cation,[3] one might expect ion-pairing stabilization differences as one goes from the small tetramethylammonium ion to the almost insulated tetraheptylammonium ion. However, significant effects are seen only with the allyl and *tert*-butyl systems, while benzyl and triphenylmethyl are almost unaffected by the change in electrolyte. The small relatively localized *tert*-butyl and allyl anions should be particularly subject to solvation and ion-pairing effects, but pK_a changes of only $\sim$2 units are involved.

Our value for the allyl radical reduction potential agrees well with that of -1.57 V vs. SCE reported by Baizer[4] using polarography in dimethyl sulfoxide with TBAP electrolyte. Furthermore, our data for the benzyl system confirm values from -1.82 to -1.88 V reported from polarography.[5,6] Carbon dioxide trapping[6] has shown that the benzyl anion is the product of this reduction. Thus our data can be used with confidence, together with bond dissociation energies, to derive pK_as for ionization of a methyl hydrogen in toluene, propene, and propyne. The results are listed in Table II.

The pK_as observed are sensible and consistent. With toluene and propene having pK_as in the mid-50s, our value of 71 for isobutane seems reasonable. Methane should have a pK_a higher than that of propyne,[7] and probably less than that of isobutane;[8] so an estimate of 68–70 for methane seems right. Assuming this value, the substitution of one phenyl to produce the benzyl anion is almost as acidifying as is the substitution of the next two to form triphenylmethyl anion. Such a saturation effect of substituents is well precedented.

It is apparent that our thermodynamic pK_a scale is affected somewhat by the exact medium used. For instance, assuming that triphenylmethane always has a pK_a of 31.5, the pK_a of isobutane ranges from 66 to 71 over the extreme of our data on changing solvent from dimethoxyethane to acetonitrile. However, the general consistency of the picture is such that these pK_as should now be considered the most likely thermodynamic values for the otherwise inaccessible high pK_a region.

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References and Notes

(1) R. Breslow and R. Goodin, *J. Am. Chem. Soc.*, **98**, 6077 (1976).
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(5) L. W. Marple, L. E. Hummelstadt, and L. B. Rogers, *J. Electrochem. Soc.*, **107**, 437 (1960).
(6) R. C. Duty and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964).

(7) Our estimate makes the resonance stabilization of propargyl anion slightly less than that, from bond dissociation energies, for propargyl radical. Rehydridization and solvation effects could explain this.

(8) Although this might well reverse in the gas phase when the methyl groups act as an internal solvent. In solution they exclude more polar solvent molecules.

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Book Reviews

Thermodynamics of Nonequilibrium Processes. By S. WISENIEWSKI, B. STANISZEWSKI, and R. SZYMANIK. D. Reidel Publishing Co., Dordrecht-Holland/Boston. 1976. xiii + 274 pp. $36.00.

This book is a translation from Polish of a textbook for technical universities. Thus the symbols and units are those commonly used by engineers and not SI.

The first half of the book presents a development of general nonequilibrium thermodynamics according to a format similar to that in other texts. The second half is devoted to a section on more specialized applied topics: thermoelectric generators and refrigerators, thermionic generators, and magnetohydrodynamic generators. These chapters include discussions of the potentials and problems inherent in practical application of these effects.

There are a number of worked-out examples in the book (31 in all). However, there are no references to specific articles of interest, only a listing of general references to classical and nonequilibrium thermodynamics. It can most probably be used successfully as a guide for study of nonequilibrium thermodynamics in general, but its main contribution is its thorough and application-oriented discussion of heat to electricity conversion devices.

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Biochemical Analysis of Membranes. Edited by A. H. MADDY (University of Edinburgh). Halsted Press/John Wiley & Sons, New York, N.Y. 1976. ix + 513 pp. $37.50.

The first half of this compilation covers methods for isolation of various types of membranes. These include the cell surface membrane, with special emphasis on the liver plasma membrane, and the membranes of subcellular organelles (separate chapters on mitochondria, endoplasmic reticulum, and nucleus). The first chapter presents a discussion of the cultivation of mycoplasmas and the isolation of their membranes. These microorganisms are particularly useful because their only membrane constituent is the plasma membrane and because its composition is determined by the relative concentrations of lipids in the growth media. These natural membranes are, thus, being used as alternatives to artificial lipid bilayers for studies of the effect of lipid composition on membrane structure and function.

The second section of the book deals with the isolation, purification, and analysis of membrane components. There are separate chapters on solubilization of membrane proteins, analysis of membrane proteins, analysis of lipids, and analysis of carbohydrates. The special problems associated with the handling of membrane proteins are especially well highlighted. A separate chapter describes immuno-