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Proton Affinities and the Methyl Inductive Effect¹

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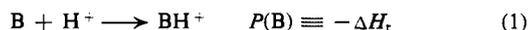
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The relative proton affinities or basicities of some polar hydrocarbon derivatives have been measured in the gas phase by observation in the source of a mass spectrometer of very rapid proton-transfer reactions from a protonated molecule to a neutral molecule of a different species. For the molecules studied, replacement of hydrogen by a methyl group increased the base strength of the molecule. Agreement between relative proton affinities from proton-transfer reaction and gas phase ion energetics is good. It was determined that $P(\text{H}_2\text{O}) < P(\text{CH}_3\text{OH}) < P(\text{CH}_3\text{OCH}_3)$; $P(\text{HCHO}) < P(\text{CH}_3\text{-CHO}) < P(\text{CH}_3\text{COCH}_3)$; $P(\text{CHOOH}) < P(\text{CH}_3\text{-COOH})$; $P(\text{NH}_3) < P(\text{CH}_3\text{NH}_2) < P[(\text{CH}_3)_2\text{NH}] < P[(\text{CH}_3)_3\text{N}]$.

Introduction

The relative acidities or basicities of a series of compounds can be determined readily in solution in a given solvent. However, theoretical predictions about variations in acidity or basicity with molecular structure are based on properties of isolated molecules. The observed variations in solution are the result of changes in solvation effects on molecular and ionic species as well as changes in acidity or basicity of the molecules. Separation of these two effects is virtually impossible, so that interpretation of differences in dissociation constants in terms of molecular models must be done with extreme caution.² Determination of the acidities or basicities of different solvents is even more complicated, and discussions of these differences in terms of molecular properties is fraught with pitfalls.^{2a} The basicities determined from solution studies are directly related to practical chemistry but, because of the unknown nature of the reactants, are virtually impossible to interpret. A determination of the base strengths of a series of molecules with a known acid under conditions which will give theoretically meaningful results would be valuable.

It is possible to determine directly in some cases the proton affinities of molecules in the gas phase



where the proton affinity, $P(\text{B}) = -[\Delta H_f(\text{BH}^+) -$

$\Delta H_f(\text{H}^+) - \Delta H_f(\text{B})]$. The proton affinity is, therefore, a direct measure of the Brønsted base strength of the molecule. Proton affinities can be determined in several ways. The proton affinity of NH_3 can be obtained from thermodynamic cycles of crystalline ammonium salts and $P(\text{H}_2\text{O})$ has been estimated from an analogy to this process.³

Several protonated species, H_3O^+ , CH_3OH_2^+ , RCOOH_2^+ , are formed as rearrangement ions in the mass spectra of many compounds so that it is possible to determine the heats of formation of some of these ions and, therefore, the proton affinities of the neutral molecules.⁴

It is generally considered that ionic reactions observed in mass spectrometric studies have essentially no activation energy and that the reactions which occur are, therefore, thermoneutral or exothermic.^{5,6} This criterion may be used to set an upper limit on heats of formation of ions and hence a lower limit for the proton affinities when the energies of the other species are known. Tal'roze and Frankevich suggested that reactions unobservable in the mass spectrometer could be considered as endothermic, and they calculated an upper limit for proton affinities of H_2O , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ as well.^{7,8} This second criterion can be readily demonstrated as false in many cases,^{9,10} but it is perhaps valid for the proton-transfer reactions which they were considering.

Recently, work has been done in these laboratories on ionic reactions in a mass spectrometer at pressures up to several tenths of a torr and it has been possible to observe reactions of secondary and even higher-order product ions at the highest pressures attainable.¹¹ At high pressures in the mass spectrometer source it is possible to make direct observation of proton-transfer reactions of several simple protonated organic compounds and therefore to determine the order of basicity

(3) J. Sherman, *Chem. Rev.*, **11**, 164 (1932).

(4) (a) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963); (b) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

(5) F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," Vol. I, Pergamon Press, Oxford, 1961.

(6) V. L. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962).

(7) V. L. Tal'roze and E. L. Frankevich, *Dokl. Akad. Nauk SSSR*, **111**, 376 (1956).

(8) E. L. Frankevich and V. L. Tal'roze, *Zh. Fiz. Khim.*, **33**, 1093 (1959).

(9) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

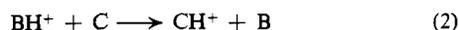
(10) J. L. Franklin and M. S. B. Munson, 10th International Combustion Symposium, Cambridge, England, 1964.

(11) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

(1) Supported in part by Project Squid under Contract Nonr-3623 (S-18).

(2) (a) For an excellent discussion on these topics, see R. P. Bell, "The Proton in Chemistry," Cornell University Press, New York, N. Y., 1959; (b) E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 223-403.

or proton affinities, since if a proton-transfer reaction



occurs, then $P(\text{C}) > P(\text{B})$.

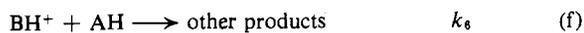
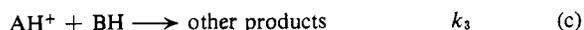
The series of compounds whose proton-transfer reactions are reported in this paper allow us to study the effect of substituting a methyl group for a hydrogen on the relative basicities of oxygen- and nitrogen-containing compounds.

Experimental

The mass spectrometer and experimental procedure for operating at these high source pressures (several tenths of a torr) have been thoroughly described^{11,12} and will not be discussed here. The chemicals were obtained from several sources and were purified by two distillations in the vacuum manifold. The purity of the different compounds is not known, but preliminary mass spectra indicated only small concentrations of impurities which did not interfere with the masses in question. The pressures within the source of the mass spectrometer are not accurately known; in some cases approximate calibrations were taken from those available for structurally similar compounds¹³ and for others ionization gauge readings for the pressure in the chamber surrounding the source were used. These readings are proportional to source pressure, but with a different proportionality constant for each compound. The source temperatures were 150–200°, but were held constant to within a few degrees in each experiment.

Pressure studies were made on mixtures of constant composition to study the proton-transfer reactions. These studies were made by admitting a known pressure of the mixture to the mass spectrometer source and scanning the mass spectrum. Additional amounts of the same mixture were added to increase the pressure within the mass spectrometer source and the mass spectrum was determined after each increase in pressure. The mixtures had been allowed to stand long enough to assure complete mixing. Typical data are shown in Figure 1 for mixtures of dimethyl ether and ammonia.

The kinetic equations necessary for the interpretation of the pressure studies and the establishment of the proton-transfer reactions are



If one assumes for the moment that only reactions 3a–c involve (AH^+) and (AH_2^+) , then the kinetic data equations are

$$\frac{d(\text{AH}^+)}{dt} = -k_1(\text{AH}^+)(\text{AH}) - (k_2 + k_3)(\text{AH}^+)(\text{BH}) \quad (4)$$

(12) F. H. Field, J. L. Franklin, and M. S. B. Munson, *J. Am. Chem. Soc.*, **85**, 3575 (1963).

(13) F. H. Field and M. S. B. Munson, paper presented at the 11th ASTM Conference on Mass Spectrometry, San Francisco, Calif., May 1963.

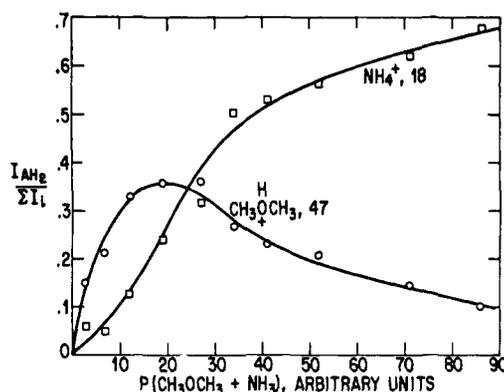


Figure 1. Proton-transfer reaction.

$$\frac{d(\text{AH}_2^+)}{dt} = k_1(\text{AH}^+)(\text{AH}) + k_2(\text{AH}^+)(\text{BH}) \quad (5)$$

Then, since $(\text{AH}^+) \ll (\text{AH})$ or (BH) , that is, the concentration of neutral molecules is much larger than that of the ions and remains constant

$$(\text{AH}^+) = (\text{AH}^+)_0 \exp\{-[k_1(\text{AH}) + (k_2 + k_3)(\text{BH})]t\} \quad (6)$$

$$\frac{(\text{AH}_2^+)}{(\text{AH}^+)_0} = \frac{k_1(\text{AH}) + k_2(\text{BH})}{k_1(\text{AH}) + (k_2 + k_3)(\text{BH})} \times (1 - \exp\{-[k_1(\text{AH}) + (k_2 + k_3)(\text{BH})]t\}) \quad (7)$$

For different pressures at constant composition, $(\text{AH}) = b(\text{BH})$, and then

$$\frac{(\text{AH}_2^+)}{(\text{AH}^+)_0} = K\{1 - \exp[-k(\text{AH})t]\} \quad (8)$$

where

$$K = \frac{k_1 + k_2b}{k_1 + (k_2 + k_3)b}$$

$$k = k_1 + (k_2 + k_3)b$$

and (AH) is the concentration of AH . For these reactions one can see that $(\text{AH}_2^+)/(\text{AH}^+)_0$ or $I_{\text{AH}_2^+}/\Sigma I_i$, the relative concentration of AH_2^+ expressed as the ratio of ion current of AH_2^+ to the total current, increases to a constant value with increasing pressure. Reactions of other primary ions to give AH_2^+ will give equations of the same form which will increase the relative concentration of AH_2^+ . Reactions 3d–f for BH^+ and BH_2^+ will give equations identical in form with (6) and (7), but will have no effect on AH^+ or AH_2^+ .

Now, if we assume the existence of reactions 3g–h, then the relative concentration of AH_2^+ will pass through a maximum and then decrease as would be expected for an intermediate in sequential reactions. The kinetic equations will be complicated but, since these results are only qualitative, it will not be necessary to give an exact equation. This sequence is adequate to explain the data in Figure 1 for proton transfer from $\text{CH}_3\text{OHCH}_3^+$ to NH_3 to give NH_4^+ .

The equation for BH_2^+ will be too complicated to interpret since it is the sum of several reactions both second and third order. However, in the systems to be discussed the protonated species (the parent plus one ion) is the dominant second-order reaction product and the problems are simplified somewhat. It is possible to adjust the energy of the electrons so that the only secondary product ions of consequence are the pro-

tonated molecules, AH_2^+ and BH_2^+ , and then one may note that BH_2^+ is the only ion the growth of whose concentration is large enough to account for the decrease in concentration of AH_2^+ . These were the observations which were used to establish the relative basicities of the molecules: that AH_2^+ increased to a maximum and decreased (as in Figure 1) and that BH_2^+ was the only other product ion of large enough relative concentration to account for the decrease in AH_2^+ .

It is perhaps possible that at the low voltages of some of the experiments (within a few volts of the ionization potentials) the energy of the electrons might be lowered with increasing pressure. Since the cross sections for ionization are very sensitive functions of electron energy in this region, complications might be introduced. The same experiments were performed with 50-v. electrons; in this region the cross section for ionization of these molecules is insensitive to small changes in the electron energy. The same results were observed.

Since the pressure can be changed over a wider range than the residence time of the ions, the experiments were normally done by varying the pressure. However, as a further verification of the interpretation of these data, experiments were performed by changing the residence time of the ions in the source (by changing the applied repeller voltage) at constant pressure. For example, at a source pressure of roughly 0.2 torr for a mixture of CH_3NH_2 and NH_3 , the relative concentrations and absolute ion currents of the primary ions CH_3NH_2^+ and NH_3^+ decreased with increasing residence time. For the product ions, the ion current and relative concentration of NH_4^+ decreased with increasing time and the ion current and relative concentration of CH_3NH_3^+ increased with increasing time. These observations indicate that NH_4^+ is reacting with CH_3NH_2 to give CH_3NH_3^+ (CH_3NH_3^+ and NH_4^+ accounted for 80% of the total ionization).

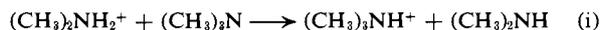
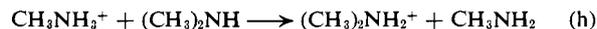
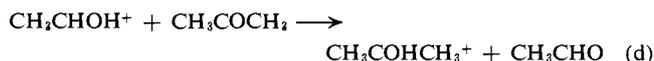
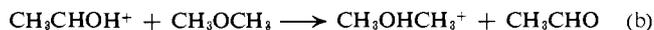
The observation that under these conditions in the mass spectrometer source the absolute intensity of mass 18 increases with increasing field strength (decreasing time) means that the mass 18 is not being lost by collision-induced decompositions in the source since this process should increase with increasing ion energy.

The proton-transfer reactions which are reverse to the ones reported in this paper should be endothermic by several kcal./mole, should have an activation energy at least this large, and should be notably slower than these reactions. No evidence was found for the occurrence of appreciable amounts of these reverse reactions; however, additional reactions to give more highly solvated protons, $\text{H}^+(\text{H}_2\text{O})_{1,2,3,4}$, $\text{H}^+(\text{CH}_3\text{OCH}_3)_{1,2}$, and $\text{H}^+(\text{NH}_3)_{1,2,3}$, occur in each system with increasing pressure, so any pseudo-equilibrium between these protonated molecule ions could not be observed easily. If in a sequence, AH_2^+ protonates BH and BH_2^+ protonates CH, then $P(\text{AH}) < P(\text{BH}) < P(\text{CH})$ and it is not necessary to study each pair of compounds.

Discussion

Table I presents a summary of data of recent proton affinity measurements from various sources and the sequence of relative basicities (or proton affinities) which it is possible to establish from these proton-transfer reactions. The notation in the column headed

(1) means that mixtures of X and the other compound were made and the proton-transfer reaction was observed from the protonated ion of the compound in (1)



to X or the proton affinity of X is greater than the proton affinity of the compound in column (1). That is, reactions 9a-i were observed. The observations of these reactions mean that the heats and free energies of reaction are exothermic in the direction written. Rate constants for these reactions have not yet been determined, but they are of the order of 10^{-10} to 10^{-9} cc./molecule sec. (or roughly 10^{11} l./mole sec.). The observation that these reactions are rapid also means that there is no steric inhibition of proton transfer for these molecules.

The reaction



was probably observed, since the appearance potential of mass 19 in a mixture of NH_3 and CD_4 was the same as that of mass 18 and 17. The occurrence of this reaction means that the proton affinity of NH_3 is greater than 181 kcal./mole; from proton-transfer reactions it must also be larger than this. Reactions of $\text{NH}_3 + \text{D}_2\text{O}$ mixtures were studied, but these were complicated by very rapid exchange reactions which made it essentially impossible to decide whether or not the desired reaction occurred.

The analogous reaction for each of the methylamines was not observed, even when the pressure of CD_4 was five to ten times that of the amine. When the ratio CD_4/NH_3 was about 6 the ion currents at masses 18 and 19 were about equal so that this deuterium-transfer reaction is relatively slow. If the failure to observe this reaction for the methylamines is the result of energetic considerations, then $P(\text{CH}_3\text{NH}_2) < 208$, $P[(\text{CH}_3)_2\text{NH}] < 225$, and $P[(\text{CH}_3)_3\text{N}] < 235$ kcal./mole. Since reaction 10 is slow and it is presumably vigorously exothermic, these upper limits for proton affinities probably should not be considered seriously.

An inspection of Table I shows that the methyl inductive effect is established without reservation for these compounds. For all four series (compounds containing $-\text{O}-$, $>\text{C}=\text{O}$, $-\text{COOH}$, and $>\text{N}-$) replacing each hydrogen by a methyl causes an increase in the proton affinity (or basicity) as one would expect on the basis that a methyl group increases the electron density at the oxygen or nitrogen.

The ionization potentials (recent photoionization measurements, all by the same workers) also show the expected trend with changes in structure. The electron is presumably removed from one of the nonbonding orbitals of the oxygen or nitrogen and an increase in

Table I. Proton Affinities and Ionization Potentials

X	$P(X)$, kcal./mole				$I(X)$, kcal./mole ^c
	(1) Proton transfer ^a	(2) Ionic reactions ^b	(3) Electron impact	(4) Other	
H ₂ O		163 ≤ P ≤ 172	151 ± 3 ^d	182 ^e ; 173 ^f	280
CH ₃ OH	>H ₂ O	177 ≤ P ≤ 183			250
CH ₃ OCH ₃	>CH ₃ CHO >CH ₃ OH				231
HCHO			163 ± 3 ^g		250
CH ₃ CHO	>CH ₃ OH		182 ^g		236
CH ₃ COCH	>CH ₃ CHO		190 ^h		224
HCOOH	>H ₂ O		166 ± 2 ^g		255
CH ₃ COOH			184 ± 3 ^g		239
NH ₃	>CH ₃ OCH ₃			202 ⁱ ; 239 ^f	234
CH ₃ NH ₂	>NH ₃				207
(CH ₃) ₂ NH	>CH ₃ NH ₂				190
(CH ₃) ₃ N	>(CH ₃) ₂ NH				180

^a These data. ^b References 7 and 8. ^c Photoionization values: K. Watanabe, T. Nakayama, and J. Mottl, Final Report on Ionization Potentials of Molecules by a Photoionization Method, Army Project No. 5B 99-01-004, Dec. 1959. ^d Reference 3; thermodynamic cycle. ^e F. W. Lampe and J. H. Futrell, *Trans. Faraday Soc.*, **59**, 1957 (1963); calculation. ^f Reference 4b; see also, E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962). ^g From appearance potential of mass 59 from *t*-butyl alcohol, 10.0 v., these data. ^h A. P. Altshuller, *J. Am. Chem. Soc.*, **77**, 3480 (1955); thermodynamic cycle.

the electron density caused by replacing a hydrogen atom with a methyl group should and does lower the ionization potential.

The order of basicities of the methylamines and ammonia has been extensively, but inconclusively, studied in the condensed phase. Trimethylamine is apparently a weaker base than dimethylamine in several solvents^{14,15} and, despite observations that the order of basicities of these compounds is different for different types of measurements,^{2a} it is still sometimes considered that this order (that in water) is determined by a property of the isolated amine molecules.¹⁴ The intrinsic base strengths of the alkylamines, as estimated by Wynne-Jones¹⁶ from extrapolation to infinite dielectric constant (which is presumed to eliminate dielectric effects), showed an increase with increasing number of alkyl substituents for ethyl, propyl, and isobutyl, but not for methyl groups, even though in water the trialkylamines are weaker bases than the dialkylamines.

The "B-strain" theory was proposed to account for the apparent lower basicity of the trimethylamine¹⁷ and has been used as an explanation of the apparent low basicities of some oxygenated compounds in solution.¹⁸ However, calculations have been made¹⁹ which indicated that the magnitude of this strain in the "back" of the molecule was too small to account for this effect. Since the present work shows that in the gas phase trimethylamine is the strongest of the methylamines with respect to a proton as an acid, this theory is unnecessary. The irregular order observed in condensed phase is the result of solvation effects or F-strain due to the bulky acid group.

Table I shows that the increase in proton affinity caused by replacing a hydrogen with a methyl group is 15–20 kcal./mole. The decrease in ionization potential

caused by the same substitution is about the same. There is apparently a larger change in ionization potential caused by replacing the first hydrogen in water or ammonia than is caused by the second or third replacement. This effect is perhaps indicated for the sequence HCHO, CH₃CHO, CH₃COCH₃, but the absolute values of the proton affinities are not known well enough to make reliable comments about the effect of the second methyl substitution.

The disagreement between the electron impact determination (151 ± 3) and the values from ionic reactions (168 ± 4) for $P(\text{H}_2\text{O})$ is somewhat disconcerting. This new value¹⁴ from electron impact measurements supersedes previous estimates by this method and is in much closer agreement with Tal'roze's value than the earlier values. Calculated values for $P(\text{H}_2\text{O})$ have ranged from 180–200 kcal./mole.^{2a} Recent calculations, however, give values of 170 kcal./mole if allowances are made for hydrogen bonding in the crystals.²⁰ If the absolute value for $P(\text{HCOOH})$ is correct, then $P(\text{H}_2\text{O})$ is less than 166 kcal./mole, since H_3O^+ gives a proton-transfer reaction to HCOOH. The value for $P(\text{CH}_3\text{OH})$ from gas phase ionic reactions (180 ± 3 kcal./mole) is consistent with the observation that $P(\text{CH}_3\text{OH}) < P(\text{CH}_3\text{CHO}) = 182$ kcal./mole.

The increase in base strength in the sequence $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{CH}_3\text{OCH}_3$ indicated by the present data is what would be predicted from the methyl inductive effect in a manner analogous to ammonia and the methylamines. The generally accepted order of base strengths of these compounds in condensed phase is probably the reverse.² The data are hardly conclusive, however. Estimates of proton solvation energies have been made by Izmailov²¹ which are also in reverse to the sequence presented here. It should be mentioned that the heat of solvation and proton affinity are not directly related since the former involves an interaction of several molecules with a proton.

The differences in ionic solvation may be illustrated by two cases: water and dimethyl ether. For water there is evidence that in dilute solution the proton is

- (14) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).
 (15) D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 2387 (1964).
 (16) W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A140**, 440 (1933).
 (17) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).
 (18) (a) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952); (b) P. D. Bartlett and J. D. McCullom, *ibid.*, **78**, 1441 (1956).
 (19) R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948).

- (20) See ref. 6 for a discussion and references.
 (21) N. A. Izmailov, *Proc. Acad. Sci. USSR*, **150**, 120 (1963).

H_9O_4^+ or at least it is highly hydrated.²² In experiments related to these, ions of mass as high as H_9O_4^+ have been observed as products of ionic reactions in water at pressures up to several tenths of a torr at about 200°, but in dimethyl ether the highest protonated

(22) See the article by M. Eigen and L. DeMayer in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959.

species observed was $(\text{CH}_3\text{OCH}_3)_2\text{H}^+$. These are preliminary results which will be studied further, but they indicate the marked differences in solvation of ions by different solvents.

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Electrolytic Reduction of Cyclooctatetraene¹

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Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912. Received December 28, 1964

The reduction of cyclooctatetraene has been studied in *N,N*-dimethylformamide and dimethyl sulfoxide by the techniques of d.c. polarography, triangular wave oscillopolarography, and a.c. polarography. It was found that cyclooctatetraene is reduced in two one-electron steps. Previous experiments in which the anion radical was found to disproportionate have been explained on the basis of reactions of the cyclooctatetraene dianion with alkali metal ions to form tightly bound complexes or with water to form cyclooctatrienes. The electron spin resonance spectrum of cyclooctatetraene anion radicals, produced by controlled-potential electrolysis in DMF, was virtually identical with previous results. The first electron transfer to cyclooctatetraene was found to be slow and to proceed through a transition state which resembles planar cyclooctatetraene. The cathodic transfer coefficient was found to be significantly less than 0.5, and a suggestion is made regarding its interpretation. Rapid electron transfer to the anion radical was observed, and the significance discussed. The difference between the two half-wave potentials of the hypothetical planar conformer was estimated to be about 0.80 v.

Introduction

Cyclooctatetraene, the mechanism of its reduction, and the nature of its reduction products have attracted considerable interest in recent years.³⁻¹¹ It has been shown polarographically that cyclooctatetraene in 50% aqueous ethanol^{3,5} or 96% dioxane-water⁹ undergoes a two-electron reduction. In tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) cyclooctatetraene is reduced by alkali metals primarily to the dianion.

(1) Supported in part by a grant from the National Science Foundation and by the ARPA program at Brown University.

(2) Du Pont Teaching Fellow, 1964-1965.

(3) R. M. Eloffsen, *Anal. Chem.*, **21**, 917 (1949).

(4) A. C. Cope, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

(5) J. H. Glover and H. W. Hodgson, *Analyst*, **77**, 473 (1952).

(6) L. E. Craig, R. M. Eloffsen, and I. J. Ressa, *J. Am. Chem. Soc.*, **75**, 480 (1953).

(7) T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

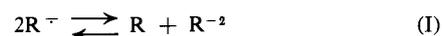
(8) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

(9) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

(10) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).

(11) A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 1525 (1964).

Under these conditions, the equilibrium



lies very far to the right with $\Delta F_d = -0.48$ e.v. although the anion radical of cyclooctatetraene was detected by electron spin resonance (e.s.r.) spectroscopy.^{8,10} Evidence for the planarity of both anions has been presented.^{7,8,10,11}

The position of the disproportionation equilibrium, reaction I, for aromatic hydrocarbons has been found, in general, to lie far to the left,^{12,13} primarily because of electron repulsion in the doubly filled molecular orbital of the dianion.¹⁴ Katz^{9,10} has pointed out that if the compression energy required to flatten the cyclooctatetraene ring exceeds the electron repulsion energy, attenuated by solvation, then the disproportionation equilibrium may lie to the right. For most aromatic hydrocarbons, the free energy of reaction I is on the order of $\Delta F_d = +0.4$ e.v.^{9,12,13}; thus, assuming the same value for hypothetical planar aromatic cyclooctatetraene, the compression energy must be approximately 21 kcal./mole to account for the observed results.¹⁰

In the present work, we have investigated the reduction of cyclooctatetraene by a number of polarographic techniques as well as by e.s.r. spectroscopy. The polar aprotic solvents *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used to avoid the effects of water or alkali metal ions.

In the following, we shall show that: (1) the monoanion is stable to disproportionation in DMF or DMSO in the absence of alkali metal ions; (2) the e.s.r. spectrum of the monoanion radical in DMF is virtually identical with those obtained previously in THF or DME; (3) the electron-transfer reaction, $\text{R} + \text{e}^- \rightleftharpoons \text{R}^-$, is slow with an activation free energy comparable with the energy estimated to be required to flatten the cyclooctatetraene ring; (4) electron transfer to the monoanion to form the dianion is very rapid; (5) in the presence of water, both anions are rapidly protonated, thus coalescing the two polarographic

(12) G. J. Hoijtink, *Rec. trav. chim.*, **74**, 1525 (1955).

(13) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *ibid.*, **75**, 487 (1956).

(14) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).