paper in this series, systems will be discussed in which an evaluation by the absolute method is essential. Even in those cases where similar results are obtained, our method has several advantages.

(1) Though in certain cases the B–H equation in conjunction with a least squares method provides results with as good a precision as our rigorous method, we feel the latter is simpler to employ.

(2) The method of Nagakura requires the solution of two simultaneous equations employing data collected under different experimental concentrations of the base. When several base concentrations are employed all combinations of pairs must be used and the equilibrium constant calculated in order to utilize all the measurements. In our method all possible combinations are obtained graphically. A poor set of data can be very easily noticed and eliminated from the final result.

(3) The results are presented graphically in our method and by inspection one can qualitatively determine the precision. The curves obtained can be used as a guide to indicate the best set of experimental conditions for obtaining lines with different enough slopes to make the results significant. Differentiation of equation 10 with respect to ϵ_c indicates that the slope of the K^{-1} *vs.* ϵ_c curves in the region used is largely determined by the term $C_DC_I/(A - A^0)$. Therefore, experimental conditions should be selected that give rise to different values for this term.

(4) This treatment will produce valid equilibrium constants for those acid–base reactions in which the reaction does not go to completion in the pure solvent. The assumption of completeness of reaction is inherent in the B–H extrapolation.

(5) In the Benesi–Hildebrand method it is necessary to assume that the extinction coefficient of the complex is a constant independent of base concentration and the bulk dielectric constant of the solvent. Trends in the values for ϵ_c and K^{-1} as a function of concentration are readily apparent in our treatment if they exist.

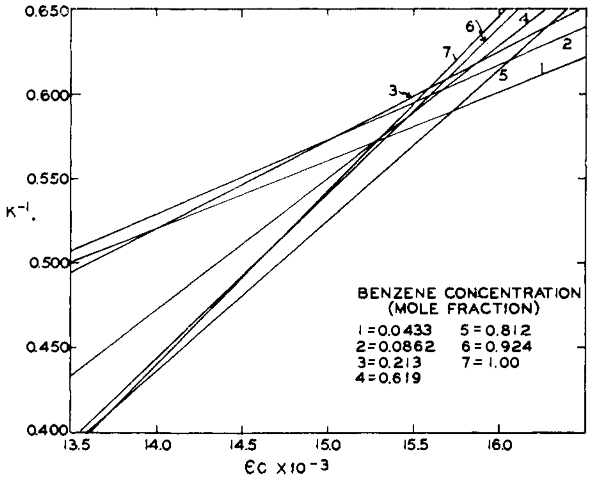

Fig. 1.

Use of our equation eliminates several objections reported in the literature[10,11] which cast doubt on the validity of thermodynamic data calculated by the method of Benesi and Hildebrand. The fact that the results obtained by a B–H calculation agree with those obtained by our more rigorous treatment gives added support to the B–H assumptions in the above cases.

Acknowledgments.—The authors wish to acknowledge helpful discussions with Dr. T. L. Brown and Mr. Larry Sacks on this problem.

[10] L. S. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[11] S. P. McGlynn, *ibid.*, **58**, 1113 (1958).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Molecular Addition Compounds of Iodine. II. Recalculation of Thermodynamic Data on Lewis Base–Iodine Systems Using an Absolute Equation

BY RUSSELL S. DRAGO AND NORMAN J. ROSE

RECEIVED APRIL 1, 1959

The general equation developed in the preceding paper in this series is applied to several sets of reported data. It can be shown that incorrect application of the Benesi–Hildebrand equation to the trimethylamine–iodine system has introduced error into calculated values of the equilibrium constant. A set of data is discussed in which the authors were able to calculate an equilibrium constant by the Benesi–Hildebrand method but which can be shown to be without any significance by our treatment. Finally, it will be demonstrated that in the dioxane–iodine system much more information can be obtained from the data by using our treatment instead of those previously employed.

Introduction

In the first article in this series[1] a general equation was developed to treat spectrophotometric data of acid–base equilibria and a method for solving the equation was presented. This paper will deal with acid–base equilibria to which the Benesi–Hildebrand and related treatments have been incorrectly applied resulting in errors of the order of magnitude of 10 to 15% in the value of the equilibrium constant.[2,3] In another instance, reported[3] data were calculated incorrectly and can be shown to be meaningless when interpreted on the basis of a 1:1 complex.

Discussion

There are several approaches which have been used to evaluate equilibrium constants from the

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[1] N. J. Rose and R. S. Drago, THIS JOURNAL, **81**, 6138 (1959).

[2] S. Nagakura, *ibid.*, **80**, 520 (1958)

[3] R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **24**, 1286 (1958).

ultraviolet spectra of iodine and Lewis bases in inert solvents.[4,5] Inherent in all of the derivations is the assumption that if $C_D >>> C_c$ (where C_D = initial concentration of the base and C_c = equilibrium concentration of the complex) then C_c can be neglected in the term $[C_D - C_c]$, in the denominator of the equilibrium constant expression

$$K = \frac{C_c}{[C_D - C_c][C_I - C_c]} \qquad (1)$$

This assumption inherent in all of the methods contained in the literature also has been stated openly by other investigators.[6] This is not always a valid assumption. The solution to the final equations obtained in all of the previous treatments depends upon differences in sets of experimental data for both K and ϵ_c are unknown. If the difference in $[C_D - C_c]$ and $[C_D' - C_c']$ (where the prime values correspond to a second set of base concentrations) is not very large the magnitude of C_c and C_c' may be important to the final solution even though $C_D >> C_c$.

The general equation that results when C_c is retained is derived in the first article in this series

$$K^{-1} = \frac{A - A^0}{\epsilon_c - \epsilon_I} - C_I - C_D + \frac{C_D C_I}{A - A^0}(\epsilon_c - \epsilon_I) \qquad (2)$$

All of these symbols are defined in Table I. For the case in which there is no overlapping of peaks, as is usually the case for the charge-transfer band (commonly around 290 mm.), equation 2 becomes

$$K^{-1} = \frac{A}{\epsilon_c} - C_I - C_D + \frac{C_D C_I}{A}(\epsilon_c) \qquad (3)$$

Rearranging the Benesi–Hildebrand equation (see Table I) produces

$$K^{-1} = -C_D + \frac{C_D C_I}{A}\epsilon_c \qquad (4)$$

The two terms A/ϵ_c and C_I are introduced by retaining C_c in the $[C_D - C_c]$ term of the denominator of the equilibrium constant expression. Only when experimental conditions are such that the term $(A/\epsilon_c) - C_I$ is insignificant compared to $[(C_D C_I)/A\epsilon_c] - C_D$ is the Benesi–Hildebrand or related treatments adequate.[7] It is not enough that these differences be small, they must be insignificant compared to experimental error to be without effect on the solution for the equilibrium constant.

TABLE I

C_I = initial iodine concn.
ϵ_I = molar absorptivity of iodine
ϵ_A = apparent molar absorptivity of iodine defined by $A = \epsilon_A C_I$
A^0 = absorbance due to initial iodine concn., *i.e.*, $C_D = 0$
$[I_2]$ = equilibrium concn. of free iodine
ϵ_c = molar absorptivity of complex
A = absorbance of system at a given wave length

Results and Conclusions

(A) **Trimethylamine.**—The data reported for the system trimethylamine–iodine require solution by the absolute method (*i.e.*, equation 3 for the charge-transfer band). Absorbance data for this system can be accurately obtained for the charge-transfer band from Fig. 4 of Nagakura's paper.[2] The values at 280 mm. were selected.

Assuming various values for ϵ_c in equation 3, one can calculate values of K^{-1} for a given set of experimental results. A plot of K^{-1} *vs.* ϵ_c then can be prepared as illustrated in Fig. 1. Each line in this figure represents a different experimental condition, in this case a different base concentration. The coördinates (K^{-1} and ϵ_c), of each intersection represent a common solution for K^{-1} and ϵ_c for two sets of experimental conditions.[8] The fact that all of the intersections occur in a very small area is indicative of: (1) a 1:1 complex; (2) extremely good precision; (3) no large change in solvation or ϵ_c in the base concentration range studied. The values of K^{-1} (*i.e.*, various intersections) are presented in Table II.

TABLE II

Two curves intersected	$\epsilon_c \times 10^4$	$K^{-1} \times 10^{-4}$
(1) and (5)	2.545	1.98
(2) and (1)	2.555	2.03
(2) and (5)	2.520	1.93
(3) and (2)	2.500	1.85
(3) and (1)	2.550	1.98
(3) and (5)	2.550	1.98
(4) and (2)	2.520	1.90
(4) and (3)	2.520	1.90
(4) and (1)	2.550	1.98
(4) and (5)	2.550	1.98
Av.	2.536 ± 0.016	1.95 ± 0.05

The value for the equilibrium constant K is 5,130 ± 130 and the extinction coefficient of the complex (ϵ_c) is 25,360 ± 160. These are to be compared with values of K = 4,710 and ϵ_c = 25,600 obtained by Nagakura. Thus the largest error in applying a Benesi–Hildebrand type treatment to this system is not in the intercept but in the slope of the line obtained by plotting C_I/A *vs.* $1/C_D$.

In order to demonstrate that the error did not arise in the Benesi–Hildebrand extrapolation, Nagakura's data were evaluated by plotting K^{-1} *vs.* ϵ_c as above but using equation 4 instead of equation 3. The results of these calculations are illustrated in Fig. 2. An equilibrium constant of 4,630 is derived in close agreement with the value obtained[2] by the Benesi–Hildebrand and the Nagakura methods. Thus the error in this study is not introduced by any of the other assumptions involved in the Benesi–Hildebrand treatment or in the extrapolation procedure but arises by dropping the C_c term from the $[C_D - C_c]$ quantity in the equilibrium constant expression. It is also possible that the ΔH value reported for the reaction is in error but data are not available in the article to permit a recalculation of this quantity.

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(4) J. A. A. Ketelaar, C. Van de Stolpe, *et al.*, *Rec. trav. chim.*, **71**, 1104 (1952).

(5) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

(6) C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

(7) It has been demonstrated [R. M. Keefer and T. L. Allen, *J. Chem. Phys.*, **25**, 1059 (1956)] that iodine absorbs in this region. In order for equation 2 to apply, it must be demonstrated that A^0 is insignificant compared to A and that $\epsilon_c >> \epsilon_I$.

(8) See paper I in the series for complete details of this procedure.

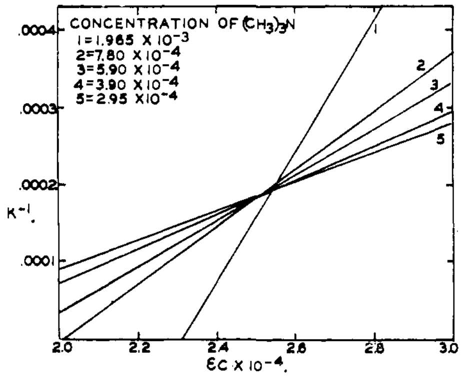

Fig. 1.

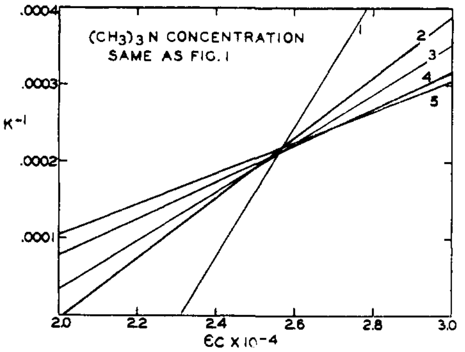

Fig. 2.

In the study with trimethylamine and also in other studies involving strong electron pair donors the range of base concentrations employed is limited, for in concentrated base solution a secondary reaction leading to the formation of triiodide ion occurs. For these systems the data should be treated by our method to ensure that omission of any of the terms in the general equation is not significant.

(B) Condensed Benzene Aromatics.—The interaction between several condensed benzene donors and iodine has been investigated[3] and the measured values for the absorbance reported. In most of these studies only a twofold range of base concentrations was employed. We have recalculated the data for the systems pyrene, biphenyl, stilbene and anthracene. Comparison of the magnitude of the $(A/\epsilon_c) - C_I$ term with the $[(C_D C_I/A)\epsilon_c] - C_D$ term indicates that for the concentration ranges employed in this study, use of our equation is essential. The data for the system pyrene represent a poor set of values but it is the best of the systems we recalculated from this article. The results are contained in Table III.

TABLE III

Sets of base concn.	ϵ_c	K^{-1}
0.0279 and 0.0419	1295	0.0193
.0279 and .0699	1360	.0218
.0279 and .0559	1520	.0274
.0419 and .0699	1410	.0248
.0419 and .0559	Above 1750	Above 0.040
.0559 and .0699	1115	0.0076
Av. of first four values	1396	0.0233

Calculation of the standard deviation for the first four K^{-1} values in Table III gives a value of $K = 43 \pm 7$. This is to be compared with a reported value of 36.49. The reasons for the large deviation cannot be evaluated. The results lie far outside of the expected precision when compared with the reported results for benzene and substituted benzenes. This could be due to poor experimental technique or to complications arising from equilibria which are not represented by the formation of simple 1:1 complexes. In view of the discrepancy in the value for naphthalene reported by these investigators ($K = 0.62$) and the value reported[9] in the literature ($K = 0.25$) the accuracy of this set of data[3] is suspect.

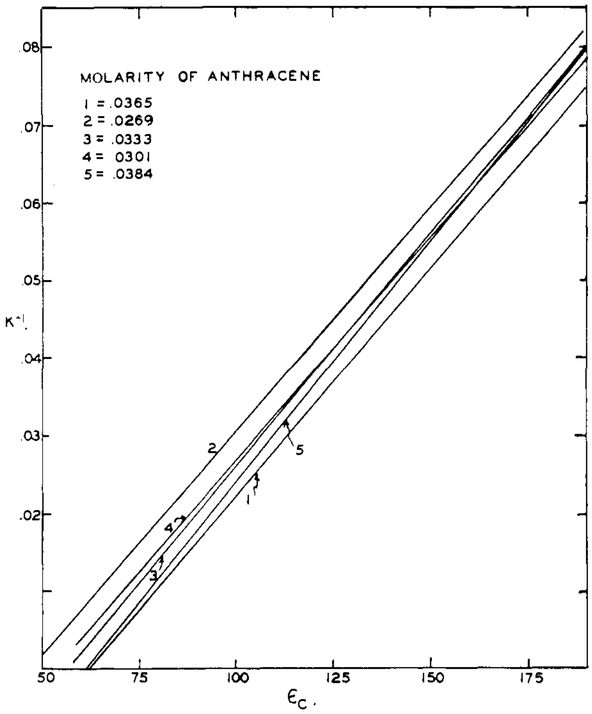

Fig. 3.

Data for the biphenyl–iodine system are reported in Table IV.

TABLE IV

Sets of base concns.	ϵ_c	K^{-1}
0.0432 and 0.1730	5500	3.36
.0432 and .1297	3000	1.98
.0432 and .0865	2200	1.47
.1730 and .1297	Far outside this range	
.1730 and .0865	Far outside this range	
.1297 and .0865	5000	3.38
Av.		2.55

The average value for $K = 0.39 \pm 0.15$. This is to be compared with a reported value of 0.37. However, close examination of the data in Table IV indicates a concentration dependence to the molar absorptivity and/or equilibrium constant value. However, in view of the questionable precision this trend may or may not be real.

Treatment by our method indicates that the data[3] for the anthracene–iodine system are extremely bad for a 1:1 complex (see Fig. 3). The choice of experimental conditions was such

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[9] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952).

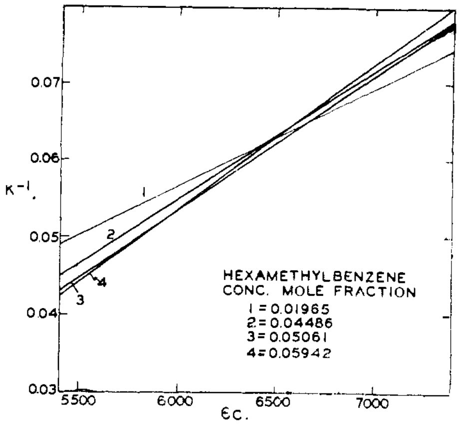

Fig. 4.

that the lines obtained for the plot of K *vs.* ϵ_c all had nearly the same slope. Instead of ten intersections only four were obtained in the range of $K^{-1} = 0$ to 0.12 (curves 5 and 2 of Fig. 3 intersect at around 0.12 and are not illustrated). If values for all ten intersections were obtained, a tremendous range of K^{-1} values would result. Thus even though the authors could justify a value of $K = 52.35$ application of our method to the data indicates that no significance can be given to the reported value. A similar result is obtained for the stilbene–iodine system.[3]

C. Dioxane.—The ultraviolet absorption at 451.5 mm. has been reported[4,10] for mixtures of dioxane and iodine in carbon tetrachloride at 17°. In the initial report[10] an equilibrium constant ($K = 1.08$) and a molar absorptivity ($\epsilon_c = 937$) were reported for dilute solutions of dioxane which were 0.000716 *M* in iodine. These values were calculated without taking into consideration absorption under the complex band due to overlap with the free iodine. The measured molar absorptivity was used to calculate values for the equilibrium constant. It was found that the constant was concentration dependent changing from 1.2 to 1.9 with increasing base concentration. It was proposed that in concentrated dioxane solution the species $I_2 \cdot 2C_4H_8O_2$ existed and the equilibria were more complex than that of a simple 1:1 complex.

In a second paper by Ketelaar a modified Benesi–Hildebrand type extrapolation correcting for overlap was presented. A molar absorptivity ($\epsilon_c = 988$) was now obtained. Using this value for ϵ_c, the equilibrium constants were calculated and found to be independent of the base concentration. In concentrated dioxane solution the value for K is very much dependent on the value for the molar absorptivity. A realistic evaluation of the error in ϵ_c indicates that one cannot distinguish between a constant value for K or a changing one.

In order to obtain a valid constant, our method of calculation requires a value for ϵ_c that is independent of base concentration. If such a requirement is not satisfied it will be readily apparent when the various values of K and ϵ_c are compared. Previous treatments would average out such an effect. Therefore, it was decided to recalculate the data on the dioxane–iodine system. Equation 2 was used to calculate the equilibrium constant. In this study $[(A - A^0)/(\epsilon_c - \epsilon_I)] - C_I$ is insignificant and can be ignored. The results for comparison of the intersections (*i.e.*, K and ϵ_c values) in concentrated solution with those in dilute solution are presented in Table V.

Table V

No. of mixture	Concn., moles/l.	No. of mixture	Concn., moles/l.
2	0.0936	9	1.005
3	.1905	13	2.683
5	.3742	14	3.613
7	.6136	15	5.786
		16	7.000

Set of base concn., moles/l.	K^{-1}	$\epsilon_c - \epsilon_I$	Set of base concn., moles/l.	K^{-1}	$\epsilon_c - \epsilon_I$
2 and 5	0.830	772	15 and 2	0.882	817
5 and 3	.908	819	15 and 3	.905	820
7 and 2	.850	789	15 and 5	.905	820
7 and 5	.893	812	15 and 7	.905	820
7 and 3	.902	817	15 and 13	.970	827
9 and 5	.822	767	15 and 9	.970	827
9 and 2	.826	770	16 and 2	.868	805
9 and 3	.850	780	16 and 13	.880	807
13 and 2	.868	805	16 and 7	.882	807
13 and 5	.883	807	16 and 5	.884	807
13 and 7	.885	807	16 and 3	.888	807
13 and 3	.892	809	16 and 9	.930	812
13 and 9	.970	824	16 and 14	.980	807
14 and 9	.916	806			

An average and an average deviation were calculated for the data in Table V producing values of $K = 1.14 \pm 0.03$ and $\epsilon_c = 979 \pm 10$ ($E_I = 168$). These are to be compared with the values reported by Ketelaar, $K = 1.05$ and $\epsilon_c = 991$.

The results in concentrated solution produce a series of K *vs.* ϵ_c lines with similar slopes. If the best values are selected (*i.e.*, intersections 16–13, 16–14, 16–19, 15–13, 15–9, 14–9, 13–9) a value of $K = 1.06 \pm 0.05$ and $\epsilon_c = 970 \pm 17$ is obtained. The results in the most dilute solution (*i.e.*, intersections 5–2, 5–3, 7–2, 7–3, 7–5) produced a value of $K = 1.14 \pm 0.03$ and $\epsilon_c = 979 \pm 10$. There appears to be a slight difference in the equilibrium constants obtained under different conditions. The absorption spectra for these data, presented in Fig. 1 of Ketelaar's paper,[10] indicate that the conditions in concentrated solutions are complex. In dilute dioxane solutions (1.26 *M* or less) the absorption spectra for the blue shift and iodine band have an isosbestic point indicating that there are only two species present. In the more concentrated solutions the curves do not intersect, indicating that more species are present. This could be due to higher order complexes or to the presence of triiodide ion in these systems. The data presented do not allow a decision. It does appear, however, that in solutions up to a 1 *M* dioxane concentration the system is best described by a 1:1 complex and an equilibrium constant $K = 1.14 \pm 0.03$ and $\epsilon_c = 979 \pm 10$. Data were not presented to allow a recalculation of ΔH.

D. Hexamethyl- and Hexaethylbenzene–Iodine.—Equilibrium constants for a series of poly-

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(10) J. A. A. Ketelaar, *Rec. trav. chim.*, **71**, 1104 (1952).

alkylated benzenes have been reported.[11] The absorbance values[12] for the charge-transfer band of hexamethylbenzene were recalculated by our method and plotted in Fig. 4. Values of K_x = 15.3 ± 0.3 and ϵ_c = 6,600 ± 400 were obtained as compared with values of K_x = 15.24 and ϵ_c = 6,690 reported by Tamres, *et al.*

The equilibrium between hexaethylbenzene and iodine was re-examined and the data are plotted in Fig. 3. The data show extremely good precision. However, the conditions chosen were such that the slopes of the K *vs.* ϵ_c lines were all very much alike. If one evaluates the accuracy of the results considering the reported reproducibility of the absorption values (*i.e.*, 0.01), intersections in the region K = 3 to 7 are possible (Fig. 5). The equilibrium constant is lower than that for hexamethylbenzene but is not accurately known. This problem was also investigated by Keefer and Andrews but neither absorbance values nor base concentrations were reported so the data could not be evaluated. A re-evaluation of the accuracy of the ΔH measurement by Keefer and Andrews is desirable to establish the cause of the difference between hexaethyl- and hexamethylbenzene.

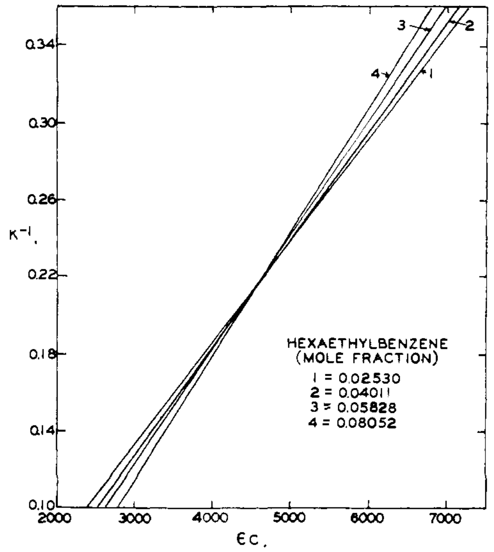

Fig. 5.

URBANA, ILLINOIS

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[11] M. Tamres, D. R. Virzi and S. Searles, THIS JOURNAL, **75**, 4359 (1953).

[12] D. R. Virzi, B.S. Thesis, University of Illinois, 1952.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogen Bonding Studies. II.[1] The Acidity and Basicity of Silanols Compared to Alcohols[2]

BY ROBERT WEST AND RONALD H. BANEY

RECEIVED MAY 18, 1959

The hydrogen bonding acidity and basicity of some silanols and carbinols has been determined by the measurement of O–H stretching infrared band shifts[3] upon admixture with the bases ether and mesitylene, and the acid phenol, respectively. The silanols studied are much more strongly acidic, but only slightly less basic, than the carbinols with analogous structure. The results for the silanols are discussed in terms of a model with strong π-bonding from oxygen to silicon involving only one of the two unshared electron pairs on the silanol oxygen. Intermolecular association of silanols also was studied by infrared spectroscopy. Trimethyl- and triethylsilanol are somewhat more associated than the corresponding carbinols, and the hydrogen bonds formed between silanol molecules appear to be decidedly stronger than those involving alcohols.

Organosilicon hydroxides (silanols) have been known since the first preparation of triethylsilanol by Ladenburg in 1871,[4] but only in recent years has any attempt been made to compare the properties of silanols with those of their purely organic analogs, the carbinols, in any direct or quantitative manner. In 1946 Sommer, Pietrusza and Whitmore showed that trimethylsilanol is converted to its sodium salt by 12 N NaOH and commented on the increased reactivity of the hydroxyl proton in silanols compared to alcohols.[5] More recently Allred, Rochow and Stone have examined the n.m.r. spectrum of trimethylsilanol and found that the hydroxyl hydrogen is less shielded (more protonic) than that in *t*-butyl alcohol.[6] The reverse would be expected on the basis of the electronegativity and inductive effect of silicon[7] and these workers attributed the decreased shielding in the silanol to π-bonding involving p-electrons of oxygen and vacant 3d orbitals of silicon.[8]

The boiling points of silanols indicate that, like alcohols, they are associated by intermolecular hydrogen bonding. The apparent molecular weights of some silanols in cyclohexane solution have been determined by Grubb and Osthoff and found to be similar to those for the corresponding carbinols.[9] The infrared spectra of several sil-

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[1] R. West, THIS JOURNAL, **81**, 1614 (1959), will be regarded as the first paper in this series.

[2] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

[4] A. Ladenburg, *Ber.*, **4**, 901 (1871); *Ann.*, **164**, 300 (1872).

[5] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946); L. H. Sommer, L. Q. Green and F. C. Whitmore, *ibid.*, **71**, 3253 (1949).

[6] L. Allred, E. G. Rochow and F. G. A. Stone, *J. Inorg. and Nuclear Chem.*, **2**, 416 (1956).

[7] R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953); L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951); C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954).

[8] F. G. A. Stone and D. Seyferth, *J. Inorg. and Nuclear Chem.*, **1**, 112 (1955).

[9] W. T. Grubb and R. C. Osthoff, THIS JOURNAL, **75**, 2230 (1953).