Its infrared spectrum (neat between NaCl plates) is similar to that of dimer IVb. It shows absorptions at 1566 (m) ($\nu_{C=C}$), 709 (vs) (*cis*-olefinic C–H out-of-plane deformation), and 791 (vs), 799 (vs), 808 cm^{-1} (vs) (nortricyclene system).

Dimer IVb is a colorless, viscous liquid.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.43; H, 8.92; mol wt (mass spectrum), 184.

Its infrared spectrum (neat between NaCl plates) is similar to that of dimer IVa. It shows absorptions at 1570 (w) ($\nu_{C=C}$), 735 (vs) (*cis*-olefinic C–H out-of-plane deformation), and 779 (s), 786 (vs), 802 cm^{-1} (s) (nortricyclene system).

The pot residue from the distillation of the dimers solidified on cooling to room temperature. It was washed from the distillation flask with ethanol. Filtration and recrystallization from ethanol afforded 2.52 g (13% yield) of the trimer VI, white crystals, mp 176–178°. Recrystallization from ethanol failed to raise the melting point. The analytical sample was prepared by sublimation (130° at 5×10^{-3} mm).

Anal. Calcd for $C_{21}H_{24}$: C, 91.30; H, 8.70. Found: C, 91.52; H, 8.62; mol wt (mass spectrum), 276.

Its infrared spectrum (Nujol mull) showed absorptions at 800 (vs), 814 (vs), and 829 (s) (nortricyclene system), but no absorptions between 1500 and 1700 ($\nu_{C=C}$) and near 700 cm^{-1} (*cis*-olefinic C–H out-of-plane deformation).

In a subsequent similar experiment,[36] 20.5 g of norbornadiene and 3.0 g of the catalyst gave 13.6 g of dimers (66%) and 5.3 g of trimer (26%), a total yield of isolated product of 92%.

The reaction was also conducted on a larger scale without the use of much more catalyst. Thus 325 g of norbornadiene and 4.0 g of catalyst gave the same yield of dimer (218 g).[36]

Air was excluded from the reaction mixture in most experiments, but this precaution does not appear necessary.[36]

The dimerization could also be effected at room temperature. Norbornadiene (30 g) and 5% rhodium on charcoal (4.0 g) were shaken together in an evacuated sealed glass tube for 5 days. Addition of pentane, filtration, and distillation of the filtrate gave 2.3 g (8% yield) of a mixture of norbornadiene dimers, which vpc showed to be 20% I, 74% IVa, and 6% IVb.

Attempted Dimerization of Norbornadiene with Other Catalysts. (a) 30% Palladium on Carbon. Norbornadiene (23 g) and the catalyst (2.0 g) were refluxed in a nitrogen atmosphere for 2 days. Filtration, evaporation of excess norbornadiene, and chromatography on silicic acid (hexane eluent) gave 25 mg (0.1% yield) of I, identified by its nmr spectrum.

(b) 55% Platinum on Charcoal. Norbornadiene (20 g) and catalyst (3 g) were refluxed under argon for 1 day. Filtration with the aid of pentane and evaporation of solvent left no residue.

(c) Nickel. The catalyst, prepared using the procedure of Brown and Brown[19] from 1.0 g $NiCl_2 \cdot 6H_2O$, was stirred with norbornadiene at 80° for 2 days. Filtration and evaporation of solvent left no residue.

Attempted Dimerization of Norbornene with 5% Rhodium on Carbon. Norbornene (20 g) and catalyst (3 g) were stirred under argon in a bath at 90–95° for 5 days. Filtration and evaporation left no residue.

Attempted Addition of Norbornadiene to Norbornene. Norbornadiene (10 g, 0.11 mole), norbornene (40 g, 0.43 mole), and 5% Rh–C (4.4 g) were stirred under argon for 44 hr in a bath at 110°. Addition of pentane, filtration, and distillation gave 1.5 g (15%) of a mixture of norbornadiene dimers, identified by the nmr spectrum, and 0.6 g (6%) of the trimer VI after recrystallization of the pot residue.

Acknowledgments. We are grateful to James C. Carnahan, Jr., for his assistance, and to the National Science Foundation (GP-748 and GP-5537), the Alfred P. Sloan Foundation, and the National Institutes of Health for their support.

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[36] This experiment was performed by J. Carnahan.

Catalysis of Anhydride Formation in Aqueous Solutions of Dicarboxylic Acids[1]

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Contribution from the School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706. *Received May 12, 1966*

Abstract: The rate of anhydride formation in aqueous solutions of dicarboxylic acid is shown to be significantly increased by the presence of sulfite species. The catalytic effect determined directly on both succinic and methylsuccinic acid by the aniline method was expected on thermodynamic grounds.

There now seems to be ample evidence which suggests mediation of many hydrolytic reactions involving esters[3–5] and amides[6] by transient formation of corresponding acid anhydrides. In earlier publications,[7–9] we have shown also that formation of amides in aqueous solutions of certain polycarboxylic acids involves again, in all probability, intermediate formation of such acid anhydride species. The experimental data strongly suggested existence in the latter instance of relatively sluggish equilibria between the dicarboxylic acids and their corresponding cyclic anhydrides. The present report concerns evidence which apparently indicates that the rate of such anhydride formation can be significantly increased by certain catalytic species.

As has been previously shown, the rate of amide formation in solutions of amines and dicarboxylic acids exhibits a zero-order dependence with respect to the amines at higher free-amine concentration, the rate-limiting step apparently being the rate of conversion of carboxylic acid to its anhydride. It is evident that the catalytic activity of added species would be reflected by increase in the zero-order component. This somewhat tedious approach can and has, as a part of the present study, been used to measure the catalytic rate constants.

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[1] This work was supported in part by the National Institutes of Health under Grants AM-03437 and GM-05830 and by the Research Committee of the Graduate School from funds furnished by the Wisconsin Alumni Research Foundation.

[2] Author to whom reprint requests should be directed.

[3] M. L. Bender, F. Chloupek, and C. N. Maurice, *J. Am. Chem. Soc*, **80**, 5384 (1958).

[4] T. C. Bruice and U. K. Pandit, *ibid.*, **82**, 5858 (1960).

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[8] T. Higuchi, S. O. Erikson, H. Uno, and J. J. Windheuser, *J. Pharm. Sci.*, **53**, 280 (1964).

[9] T. Higuchi, H. Uno, and H. Shimada, *ibid.*, **54**, 302 (1965).

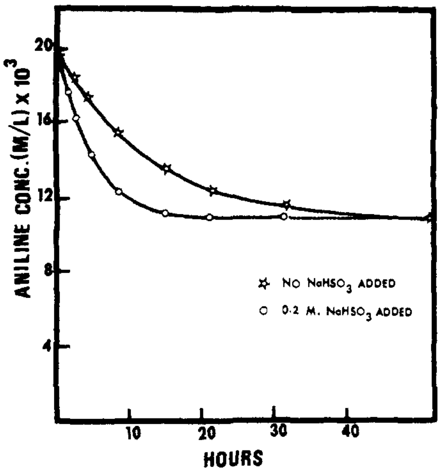

Figure 1. Residual aniline concentration in 0.5 *M* succinate pH 4.9 buffer at 95° as a function of time, both with and without addition of 0.2 *M* $NaHSO_3$.

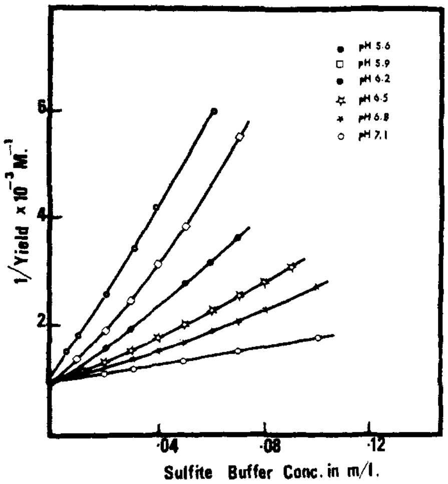

Figure 2. Yield of succinanilic acid plotted as a reciprocal function of sulfite buffer concentration at several pH values at 25°.

Another and simpler method can be based on the assumption that the acids in aqueous environment are indeed in equilibrium with the anhydride although we would expect $k_1 << k_{-1}$ in most instances at room temperature.

$$\text{acid} \underset{\underset{H_2O}{k_{-1}}}{\overset{\overset{-H_2O}{k_1}}{\rightleftharpoons}} \text{anhydride} \qquad (1)$$

It is evident that any catalyst which would significantly influence k_{-1} will produce a proportional effect on k_1 on the basis of microscopic reversibility of these systems. Thus the extent of catalytic effect for formation of the anhydride can be determined by measuring the influence of the catalysts on the rate of the reverse reaction. Since the hydrolytic reaction can be followed readily and quickly at room temperature, this is certainly the easier approach.

Experimental Observations

Sulfite-Catalyzed Formation and Hydrolysis of Succinic Anhydride. The increased rate of production of anhydride species from free acid in the presence of sulfite ion is reflected in the rate of formation of succinanilic acid from aniline and succinic acid. The general behavior of the over-all reaction in the absence of catalysts has been previously discussed.[7] In Figure 1, the residual concentration of aniline in 0.5 *M* succinate buffer at pH 4.9 and 95° is shown over a 50-hr period both in the presence and absence of sulfite. It is evident that the initial rate of formation of amide is greatly increased in the former instance, the rate in this phase being largely independent of aniline concentration and being determined essentially by the rate of formation of the anhydride species. The equilibrium point corresponding to conditions under which succinanilic acid is hydrolyzed as rapidly as it is formed was found to be unaltered by the presence of sulfite. This, of course, is the situation to be expected for any true catalyst.

The catalytic effect of sulfite species on the reverse reaction was evaluated. The influence of sulfite on the rate of hydrolysis of anhydride was determined by measuring the yield of succinanilic acid produced when a small volume of a dioxane solution of succinic anhydride was added directly to a large volume of an aqueous solution of excess aniline and the catalytic agent. It can readily be shown in such a system that

$$1/Y = 1 + \frac{k_{-1}}{k_2 f_2(\text{An})} + \frac{k_{-1}'}{k_2 f_2(\text{An})}(\text{sulfite}) \qquad (2)$$

where Y = the fraction of anhydride converted to anilide, (An) = the total concentration of aniline species, f_2 = the fraction of An present as the free base, k_2 = the specific second-order rate constant for the reaction of free aniline with the anhydride, k_{-1} = the rate of hydrolysis of the acid anhydride in water alone, k_{-1}' = the catalytic hydrolytic rate constant for total sulfite species, and (sulfite) = the total concentration of sulfite species.

It is evident that if k_{-1}' was independent of sulfite concentration, a plot of $1/Y$ against sulfite concentration with all other factors held constant will be a straight line with an intercept of $1 + k_{-1}/k_2f_2(\text{An})$ and a slope of $k_{-1}'/k_2f_2(\text{An})$. In Figure 2 are shown a series of such plots based on experimentally determined yield values obtained in systems initially containing 0.01 *M* aniline and 0.001 *M* succinic anhydride. The reciprocal-yield values do not, however, show a strictly linear dependence on sulfite buffer concentration as would be expected from eq 2, the observed curvature becoming more evident at higher buffer concentration. A possible explanation may be offered based on the report of Golding[10] that the following equilibrium exists in aqueous solution for which $K_{eq} = 7 \times 10^{-2}$ mole^{-1}

$$2HSO_3^- \overset{K_{eq}}{\rightleftharpoons} S_2O_5^{2-} + H_2O$$

The value of the intercept predicted by eq 2 should show a pH dependency because of the presence of f_2 in the first term. The change in f_2 over the pH range studied is, however, relatively small, and the intercept should have a value of about 1.01. At higher pH values some contribution in the intercept value from attack on the anhydride may be expected, but at pH 7 or less this would be essentially negligible. The slopes of these plots at lower concentration of the catalytic species suggest that the active reactant is the doubly charged sulfite ion. Based on the pK_a values of

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[10] R. M. Golding, *J. Am. Chem. Soc.*, 82, 3711 (1960).

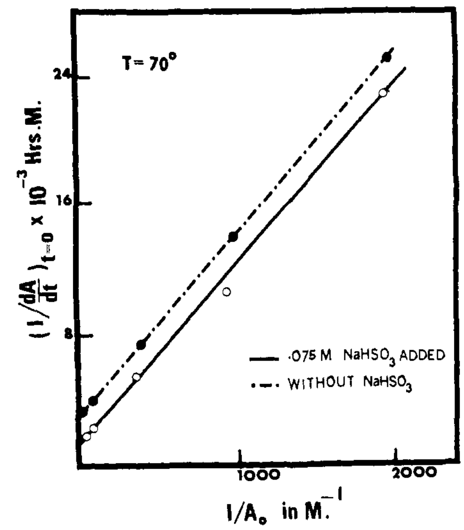


Figure 3. Reciprocal initial rate of aniline disappearance at 70° as a function of reciprocal initial aniline concentration in 0.6 M methylsuccinate buffer pH 5.0, both with and without addition of 0.075 M NaHSO$_3$.

4.7 for aniline and 6.6 for bisulfite, determined under present experimental conditions, the fraction of free aniline (f_2) and the fraction of doubly charged sulfite species were calculated. A k_2 value was experimentally determined to be 22.0 ± 0.5 M^{-1} sec^{-1} for the succinic anhydride–aniline reaction. Using these data, we have estimated from the limiting slopes in Figure 2 a sulfite ion catalytic rate constant (k_{-1}') of approximately 18 M^{-1} sec^{-1} at 25°.

Sulfite Catalysis in the Methylsuccinate System. Added evidence for sulfite catalysis of formation of cyclic anhydride is seen in its influence on the methylsuccinic acid system. The aniline method[7] of determining k_1 for methylsuccinic anhydride was used, and runs were conducted in 0.6 M methylsuccinate buffer at 70° and pH 5.0, both with and without addition of 0.075 M sodium sulfite. The reciprocal initial rates of aniline disappearance, $1/(dA/dt)_{t=0}$, observed in these measurements are shown in Figure 3 plotted as functions of the reciprocal initial aniline concentration ($1/A_0$). In the aniline method, such reciprocal functions are linearly related by the equation

$$-1/(dA/dt)_{t=0} = 1/k_1f_1(\mathrm{SH}) + \frac{k_{-1}}{k_1f_1(\mathrm{SH})k_2f_2}\,\frac{1}{A_0} \qquad (3)$$

Since f_1, the fraction of free methylsuccinic acid present, and (SH), the total methylsuccinic acid concentration, were essentially the same in both kinetic runs, the difference between the two intercept values indicates that the addition of sulfite had increased k_1 by a factor of about 2.6. A comparable catalytic effect by the added sodium sulfite on k_{-1}, the anhydride hydrolysis constant, can be inferred from the absence of an apparent difference in the slopes of the two sets of data. The slope is a function $(k_{-1}/k_1)(1/f_1(\mathrm{SH})k_2f_2)$. In the slope term, neither f_1 nor f_2 should be affected markedly, if at all, by the addition of bisulfite in the amount used, and (SH) is constant. Separate determinations showed k_2 to be unchanged by the addition of bisulfite. Thus it follows that if the slope remains unchanged when k_1 is catalytically increased by any species, then k_{-1} must experience a compensating catalysis by the same species.

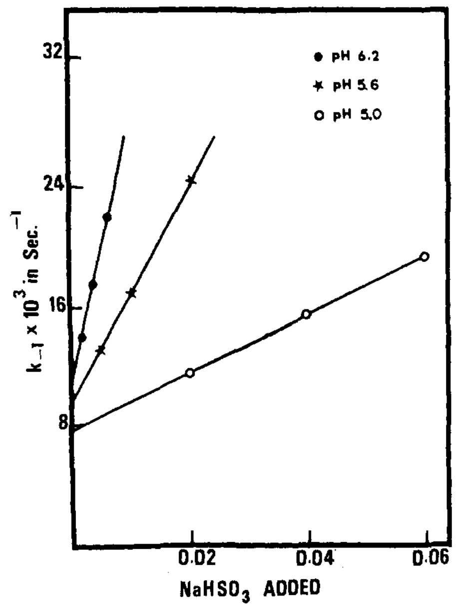


Figure 4. Observed hydrolysis constant, k_{-1}, for methylsuccinic anhydride at 25° as a function of added sodium bisulfite at pH 5.0, 5.6, and 6.2 in 0.6 M methylsuccinate buffers.

Direct studies on the rate of hydrolysis of the anhydride under the same conditions used in obtaining the data shown in Figure 3 were not performed because of the rapidity of hydrolysis at 70°. Studies of methylsuccinic anhydride hydrolysis were, however, made at 25° in the presence of 0.6 M methylsuccinate buffers at pH 5.00, 5.60, and 6.20. The results are shown in Figure 4 where it is evident that the catalytic effect from adding sodium bisulfite becomes much more pronounced as the pH of the solution increases. Calculations, based on the slopes of the curves in Figure 4 and the pK_a of HSO$_3^-$ as determined for these reaction conditions, indicated that the observed catalytic constant for methylsuccinic anhydride appears to be about 3.7 M^{-1} sec^{-1}. It is of some interest to note that 0.075 M NaHSO$_3$ produced about a 2.8 increase in the anhydride hydrolysis constant at 25° in pH 5.0 buffer, whereas the same sodium bisulfite concentration in the same buffer at 70° increased the anhydride formation constant by about a factor of 2.6.

The data shown in Figure 4 were obtained from observations of the rates of anhydride disappearance under the conditions indicated. At pH 5.0 and 5.6, the reactions appear to proceed in a strictly first-order manner with or without sodium bisulfite present in the buffers. In the absence of sodium bisulfite, anhydride hydrolysis in pH 6.2 buffer appeared to occur also at a first-order rate. With sodium bisulfite present in the pH 6.2 buffer, however, the apparent specific rate of anhydride disappearance appeared to decrease somewhat with time, suggesting perhaps an approach to equilibrium of some type. The increase with pH in the intercepts of the curves apparent in Figure 4 appears to be due to the catalytic effect of methylsuccinate ions on anhydride hydrolysis as discussed below.

Carboxylate Catalysis in the Methylsuccinate System. As noted above, methylsuccinate itself appears to catalyze the hydrolysis of methylsuccinic anhydride. In Figure 5 the catalytic behavior at 21.5° of 0.6 M buffer at different pH values is shown compared to the

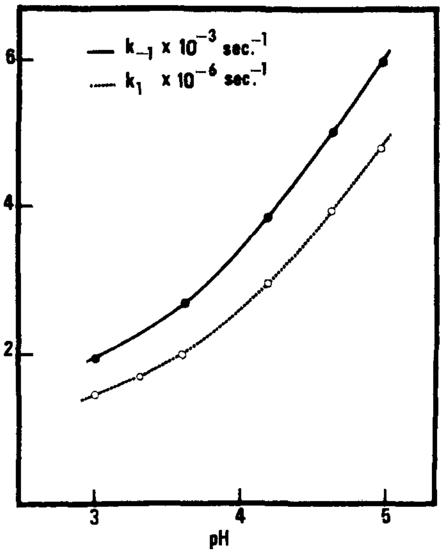


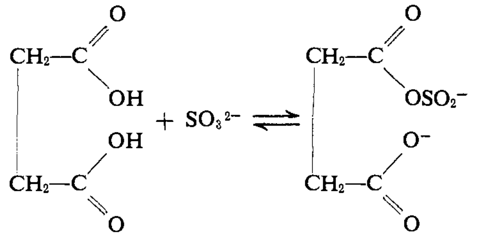
Figure 5. pH profile of methylsuccinic anhydride formation constant, k_1, at 70° and of methylsuccinic anhydride hydrolysis constant, k_{-1}, at 21.5° in 0.6 *M* methylsuccinate buffers.

rate of anhydride formation at 70° as determined by the aniline method. Although the temperatures of the systems are quite different, their pH dependencies seem to be approximately parallel and correspond closely to that which would be expected if the carboxylate groups were the responsible catalytic centers. Intramolecular carboxylate catalysis of anhydride formation was suggested in the report that the rate of anhydride formation from citric acid appears to have a maximum at the pH corresponding to the maximum concentration of singly charged citric acid.[8]

Discussion

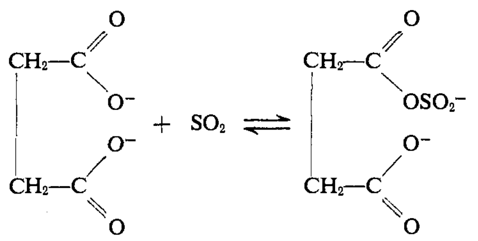
The data presented above appear to provide strong evidence supporting the proposed catalytic role of certain nucleophiles in promoting dehydration of sterically favored dicarboxylic and polycarboxylic acids to their corresponding anhydrides. We are, however, presently still uncertain as to the cause of this effect.

In the case of the sulfite–succinate system, for example, we can write



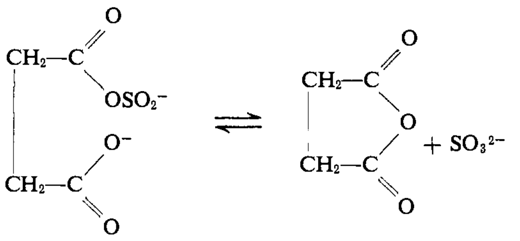
(4)

or



(5)

and



(6)

The last reaction in the series corresponding to reversible addition of SO_3^{2-} species to succinic anhydride appears to be well supported by the observed catalytic role of the doubly charged ion on the hydrolysis of the anhydride. The alternative reactions 4 and 5 are isoprotonic and difficult to distinguish kinetically. Although for convenience we calculated the catalytic constant of sulfite in terms of SO_3^{2-}, since the uncatalyzed reaction involves free succinic acid, we are more inclined to believe that (5) makes a larger contribution than (4).

Experimental Section

Equipment and Reagents. If available, reagent or analytical grade chemicals were used. Reagent grade aniline was freshly distilled prior to use and stored under nitrogen. Succinic anhydride was prepared by refluxing succinic acid with acetic anhydride as described by Vogel.[11] Methylsuccinic acid was obtained from Aldrich Chemical Co. and purified by recrystallization from a benzene–diethyl ether solvent system to obtain a product with mp 112–113° compared to the literature value of 112.5°. Methylsuccinic anhydride was obtained from Matheson Coleman and Bell and purified by recrystallization from diethyl ether to obtain a product with mp 34° compared to the literature value of 32–34°. Technical grade dioxane was purified[12] before use.

The determination and adjustments of pH were made with a Beckman Zeromatic pH meter. Mineral oil baths regulated to ±0.05° were used for kinetic runs to determine k_1, the anhydride formation constants. A thermostated Cary Model 11 MS spectrophotometer was used in the kinetic runs on anhydride hydrolysis.

Procedure for Kinetic Runs to Determine k_1 and k_2. The aniline method[7] detailed in a previous publication for determining the anhydride formation constants, k_1, was followed in the current study. The rate constant, k_2, for the succinic anhydride–aniline reaction was determined spectrophotometrically.

Procedure for Determination of k_{-1} and the Sulfite Catalysis Constant for Methylsuccinic Anhydride. These were determined in a conventional fashion in a thermostated Cary Model 11 spectrophotometer. The reactions were permitted to occur directly in the photometer cell to which varying amounts of the anhydride were added in a dioxane solution followed by methylsuccinate buffer. The resulting rate constants were extrapolated to zero dioxane concentration. When the catalytic effect of added sodium bisulfite on anhydride hydrolysis was studied, it was freshly dissolved in water and then immediately combined with methylsuccinate buffer and placed in the photometer cell with the dioxane solution of anhydride.

Procedure for Determination of the Sulfite Catalysis Constant for Succinic Anhydride Hydrolysis. A series of sulfite buffer solutions at different sulfite concentrations, each containing 0.01 *M* aniline, was prepared in 100-ml volumetric flasks. By adding an appropriate amount of sodium chloride to each of these solutions, ionic strength 0.5 was maintained in each of these solutions. The solutions were adjusted to the desired pH value and then equilibrated to 25° in a thermostated water bath. One milliliter of 0.1 *M* succinic anhydride in dioxane solution was added to each buffer solution with constant stirring. The solutions were allowed to stand for about 30 min at 25° and then brought to about pH 9.0 by addition of sodium hydroxide. The yield of anilic acid formed was determined spectrophotometrically at 240 mμ, after chloroform

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(11) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1962.

(12) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948.

extraction of the residual aniline and decomposition of sulfite by addition of a small amount of hydrogen peroxide.

Procedure for Determination of the Dissociation Constant. The dissociation constants of the carboxylic acids and bisulfite were determined potentiometrically on systems comparable to those used in the study. For methylsuccinic acid pK_{a_1} and pK_{a_2} were determined to be 3.73 and 5.15, respectively; for succinic acid the previously reported values of 4.4 and 4.8 for pK_{a_1} and pK_{a_2} were used.[5] The dissociation constant for aniline was determined spectrophotometrically in a 0.05 *M* succinate buffer.

Hydrogen Bonding of Phenol to π Electrons of Aromatics, Polyolefins, Heteroaromatics, Fulvenes, and Azulenes[1]

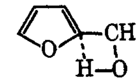
Zen-ichi Yoshida and Eiji Ōsawa

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan. *Received March 29, 1966*

Abstract: Hydrogen-bond shifts and equilibrium constants of phenol–aromatic and phenol–olefin complexes in CCl_4 solution have been determined by the use of a grating infrared spectrophotometer. In a large excess of π base, the composition of the complexes has been confirmed to be 1:1. In the series of methyl-substituted benzenes as the proton acceptor, steric inhibition of complex formation by the methyl groups does not appear until durene. It is shown from the $-\Delta F$ *vs.* $\Delta\nu$ plot that complex stability increases as the π base is changed from monoolefins to conjugated diolefins, alkylbenzenes, and polycondensed aromatics. The meaning of the $-\Delta F$ *vs.* $\Delta\nu$ plot is discussed. From the comparison of the $-\Delta F$ *vs.* $\Delta\nu$ plots for furans and thiophenes with those for benzenoid hydrocarbons, it is concluded that the heteroaromatics act as π donors in the hydrogen-bonding interaction. The polar nonbenzenoid aromatic hydrocarbons, fulvenes, and azulenes have been found to be stronger proton acceptors than the less polar aromatic π bases. 4,6,8-Trialkylazulenes proved to be the strongest π bases ever studied. From the $-\Delta F$ *vs.* $\Delta\nu$ plots it is deduced that the importance of the 6π-electron cyclic conjugation structure is enhanced in fulvenes and azulenes in the hydrogen-bonded state.

Concerning the behavior of aromatics and olefins as the proton acceptor in hydrogen bonding,[2,3] serious discrepancies have appeared in the literature. Krueger and Mettee[4] reported that the association constants between methanol and methylbenzenes in CCl_4, as determined by the infrared spectroscopic method, go through a minimum value for *m*-xylene with the highest value for benzene. On this basis, they suggested the importance of steric hindrance of the methyl groups when the methanol molecule approaches the benzene ring. On the other hand, Basila, Saier, and Cousins[5] have stated that with an excess of benzene, ethylbenzene, or mesitylene in CCl_4 solution, *t*-butyl alcohol forms 1:2 as well as 1:1 complexes. Both these results differ from our findings. We found a linear relationship between log *K* and $\Delta\nu_{OH}$ for phenol–methylbenzene complexes on the assumption that all complexes are 1:1.[2] The first purpose of this paper is to discuss these discrepancies by a careful redetermination of $\Delta\nu_{OH}$ and *K* for phenol–π-base complexes.

This paper includes the results of the $\Delta\nu_{OH}$ and *K* determinations for various phenol–π-base complexes with azulene, fulvene, furan, thiophene, and their derivatives acting as proton acceptors. From their high reactivity in electrophilic substitution reactions,[6,7] the first two nonbenzenoid aromatics are expected to be very strong acceptors. Furan and thiophene are of particular interest, since there is some confusion in the literature on the donor character of these heteroaromatic hydrocarbons. Several authors favor a single donor ability, either π[8] or n,[9,10] while Pajak[11] proposes



a bifunctional donor character of furan from nmr measurements.

Experimental Section

Materials. Most of the chemicals were commercially available and were purified by the usual methods. Pyrene was purified according to the procedure of Clar.[12] Isopropylcyclopentadiene,[13]

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(1) (a) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 7, 1965. (b) Part IV, "Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor."

(2) For pertinent literature see references cited in a previous paper of this series: part II, Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965).

(3) (a) R. J. Abraham, *Mol. Phys.*, **4**, 367 (1961); (b) D. L. Powell and R. West, *Spectrochim. Acta*, 20, 983 (1964); (c) H. Dunken and H. Fritzsche, *Z. Chem.*, **2**, 345 (1962); (d) B. Ghosh and S. Basu, *Trans. Faraday Soc.*, 61, 2097 (1965).

(4) P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, **42**, 288 (1964).

(5) M. R. Basila, E. L. Saier, and L. R. Cousins, *J. Am. Chem. Soc.*, 87, 1665 (1965).

(6) W. Keller-Schierlein and E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y. 1959, p 277.

(7) K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *Angew. Chem.*, **75**, 35 (1963).

(8) I. P. Gol'dshtein, E. N. Gur'yanova, and K A. Kocheshkov, *Z. Obshch. Khim.*, **32**, 317 (1962); *Chem. Abstr.*, **57**, 15933*c* (1962).

(9) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963).

(10) From infrared data, V. N. Novikov (*Materialy 4-oi* [*Chetvertoi*] *Nauchn. Konf. Aspirantov* (*Rostov-on-Don-Rostovsky. Univ.*) *Sb.*, 112 (1962): *Chem. Abstr.*, 60, 10518*a* (1964)) claimed that the hybrid orbital of oxygen in furan is trigonal and that in furfuryl alcohol the unshared electrons in this orbital form an intramolecular hydrogen bond with the OH group. This hydrogen bonding, however, could be due to an intramolecular O–H···π interaction as seen in benzyl alcohol (*cf.* M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 950 (1959)).

(11) (a) Z. Pajak and F. Pellan, *Compt. Rend.*, **251**, 79 (1960); (b) Z. Pajak, *Arch. Sci.* (Geneva), **13**, 527 (1960); *Chem. Abstr.*, **57**, 16521*i* (1962).

(12) E. Clar, *Ber.*, **69**, 1683 (1936).

(13) K. Hafner, *Ann.*, **606**, 79 (1957).