Electron-Transfer Polymers. XXV. On "Hydrophobic Bonding." The Effect of Solvent on Quinhydrone

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An examination of the extent of quinhydrone formation between hydroquinone and p-benzoquinone in 20 different pure and aqueous solvents indicated a reasonable correlation between extent of quinhydrone formation, as judged by the magnitude of the association constant and of the related standard free energy, and the surface tension (surface free energy) of the solvent. This supported the hypothesis of Sinanoğlu and Abdulnur that the driving force of "hydrophobic bonding," e.g., in DNA double helix formation, is the decrease in free energy as the total area of solvent cage about the two dissociated entities is decreased in the process of complex formation. Thus the surface of contact between hydroquinone and quinone with solvent is decreased by the order of 20 Å. in quinhydrone formation. The energy change for water or a high surface tension solvent is large enough to drive complex formation in these solvents as compared with, e.g., tetrahydrofuran, glacial acetic acid, methanol, and n-butyl alcohol.

When a solution of polyvinylhydroquinone is oxidatively titrated there develops a pink-orange color which reaches maximum intensity at the midpoint of the titration and gives way then to the yellow color of the polyvinylquinone at complete oxidation.[1,2] The appearance of this new absorption band is due to a charge-transfer interaction of the quinhydrone type. Investigation of it[2] led to the findings reported here, wherein we have used the simplest model, quinhydrone. The molecular complex of hydroquinone and p-benzoquinone has been known for many years.[3] However, the nature of the binding force, the spectral properties, the geometrical conformations, and the extent of complex formation in solution have not been thoroughly investigated.

Quinhydrone complexes (A·B) in solution exist as an equilibrium mixture of free (A,B) and interacting (A·B) components. The association constant, K, is in-

$$A + B \underset{}{\overset{K}{\rightleftharpoons}} A \cdot B$$
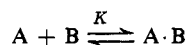
fluenced by all of the factors which normally affect chemical equilibria, *i.e.*, temperature, pressure, and solvent. The effects of temperature and pressure are generally predictable, in analogy to other systems, but very little is known about the effect of solvent on charge-transfer complexes.[4] Michaelis and Granick[5] had reported that increasing the amount of alcohol in an aqueous alcoholic solution of simple quinhydrone decreases the intensity of the observed complex absorption band. The suggestion was made that since there is little reason to expect molar absorption coefficients of molecular complexes of this type to vary appreciably according to solvent, decreases in optical density may be attributed to solvent effects on the association constant.

The peculiar behavior of water in promoting quinhydrone formation in solution is contrary to the usual effect of solvents of high cohesion[6,7] on bimolecular association reactions in which the products are of similar cohesion to, or lower cohesion than, the reactants[8]; in other words, the predicted behavior would be opposite to that observed. On the other hand, changes in the association constant with the composition of aqueous alcoholic solvent are in the direction that would be predicted if the complexed form is favored by solvents of high polarity or ionizing power. Such a correlation might be reasonable since complex formation involves a redistribution of electrons, with the development of a finite dipole moment.[9] Thus it appeared that Michaelis and Granick's assumption that the primary effect of water is upon the association constant (K), rather than upon the extinction coefficient of the absorption band of the complex, needed to be tested.

Molar extinction coefficients and association constants of molecular complexes in solution can be determined experimentally by the method of Benesi and Hildebrand[10] and by other techniques.[11] In order to facilitate comparison of experimental results with published data, the first method was chosen for use here. Tsubomura[12] has repeated the derivation of the Benesi–Hildebrand equation and applied it to quinhydrone. The maximum molar extinction coefficient of quinhydrone was found to be 890 at 440 mμ, with an association constant of 1.06 at 20° in 0.05 M aqueous hydrochloric acid solution.

Tsubomura's procedure has now been repeated using 50% aqueous tetrahydrofuran by volume, a solvent in which the observed absorption of quinhydrone is considerably lower than that in water. The results of this experiment support Michaelis and Granick's assumption that the effect of solvent is on the complex association constant.[5]

(1) A general review with complete literature references is to be found in H. G. Cassidy and K. A. Kun, "Oxidation-Reduction Polymers," Interscience Publishers, Inc., New York, N. Y., 1965.

(2) H. Kamogawa, Y. C. Giza, and H. G. Cassidy, *J. Polymer Sci.*, A2, 4647 (1964).

(3) R. Willstätter and J. Piccard, *Ber.*, 41, 1458 (1908).

(4) J. N. Murrell, *Quart. Rev.* (London), 15, 191 (1962).

(5) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, 66, 1023 (1944).

(6) M. Richardson and F. G. Soper, *J. Chem. Soc.*, 1873 (1929).

(7) S. Glasstone, *ibid.*, 723 (1936).

(8) A. Seidell, "Solubilities of Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1941.

(9) S. P. McGlynn, *Chem. Rev.*, 58, 1113 (1958).

(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949).

(11) K. Conrow, G. D. Johnson, and R. E. Bowen, *ibid.*, 86, 1025 (1964); R. S. Drago and N. J. Rose, *ibid.*, 81, 141 (1959); R. L. Scott, *Rec. Trav. Chim.*, 75, 787 (1956); J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit, and W. Dzcubas, *ibid.*, 71, 1104 (1952); J. A. A. Ketelaar, C. Van de Stolpe, and H. R. Gersmann, *ibid.*, 70, 499 (1951).

(12) H. Tsubomura, *Bull. Chem. Soc. Japan*, 26, 304 (1953).

In order to determine whether a qualitative relationship between the association constant for quinhydrone in solution and some property of the solvent exists, the complex was examined in a series of twenty different media. Since p-benzoquinone, but not hydroquinone, absorbs weakly in the visible region of the spectrum, optical densities of complex absorption bands were calculated by the formula

$$OD_{qh} = OD_{obsd} - OD_q$$

where OD_{qh} and OD_{obsd} are the optical densities of quinhydrone and that observed from a solution of hydroquinone and quinone of known concentrations, respectively, and OD_q is the optical density of quinone absorption at a concentration equal to that in the mixture. The long wave length band of quinone is known to be influenced strongly by the medium.[13,14] For this reason the same solvent was used for both solutions prepared for each calculation. A slight error may have been introduced by this procedure since all of the quinone present, rather than just that which was uncomplexed, was corrected for. However, the small extent of association reasonably permitted the approximation.[5,12]

Experimental

Materials. Hydroquinone was recrystallized several times from benzene–methanol and dried under vacuum (m.p. 172–73°). p-Benzoquinone was purified by repeated sublimation (m.p. 115–16°, sealed tube) and stored in an acid-rinsed amber bottle. Aqueous tetrahydrofuran (50%) was prepared by mixing equal volumes of deaerated water and the freshly dried and distilled ether.[15] Reagent grade methanol and n-butyl alcohol were distilled at atmospheric pressure, and glycol was distilled at reduced pressure from anhydrous sulfanilic acid.[16] Reagent grade glacial acetic acid was refluxed with chromic anhydride and distilled prior to use.[17] All solvents were deaerated with a stream of solvent-saturated nitrogen and were stored and transferred under an argon atmosphere. Ultraviolet absorption spectra of hydroquinone, p-benzoquinone, and quinhydrone, taken in aqueous or anhydrous solution in any of these solvents purified by these methods, remained unchanged for at least 24 hr.

Spectra. Solutions containing p-benzoquinone (0.00603 M) and hydroquinone (0 to 0.60834 M) in deaerated solvent were prepared under an inert atmosphere, and the spectra were recorded immediately over the range 300–600 mμ, at room temperature of 23 ± 1°. All maxima were observed at 440 mμ, and the required terms for the Benesi–Hildebrand equation[10,12] were calculated from these data.

The quinhydrone complex absorption spectrum was recorded in 0.05 M aqueous hydrochloric acid, anhydrous and aqueous tetrahydrofuran, glacial and aqueous acetic acid, anhydrous and aqueous methanol, anhydrous and aqueous glycol, and anhydrous n-

butyl alcohol. Approximately 10^{-2} M deaerated solutions of both hydroquinone and p-benzoquinone were prepared in each solvent under nitrogen or argon and the visible spectra were recorded at 28 ± 1°. Spectra of p-benzoquinone alone in each solvent at the same concentration as in the mixture were measured in order to correct for its absorption. The concentration of quinhydrone in each solvent was calculated from the observed optical density and the known molar extinction coefficient of the complex. Although it was shown to be reasonably valid only in one case, the molar extinction coefficient of quinhydrone was assumed to be invariant with solvent. This permitted the direct calculation of association constants (K) from the equilibrium expression

$$K = \frac{(C)}{(H-C)(Q-C)} \tag{1}$$

where (C), (H − C), and (Q − C) are the equilibrium concentrations of complex, hydroquinone, and quinone, respectively. Assuming ideal behavior, these were converted to reaction standard free energies by the usual expression (eq. 2). In all solvents, the ab-

$$\Delta F° = -RT \ln K \tag{2}$$

sorption maxima appeared at 440 ± 2 mμ. Table I summarizes the effects of solvent composition on the quinhydrone absorption spectrum.

Table I. Effect of Solvent on Quinhydrone at 28°

Solvent	Organic mole fraction	Surface tension,[a] dyne/cm.	$\Delta F°$, ergs/mole
Glacial acetic acid	1.000	26.5	6.11 × 10¹⁰
90.0% aqueous acetic acid	0.728	30.0	6.20 × 10¹⁰
63.0% aqueous acetic acid	0.338	35.6	4.60 × 10¹⁰
36.0% aqueous acetic acid	0.144	41.8	3.01 × 10¹⁰
10.0% aqueous acetic acid	0.033	54.6	1.13 × 10¹⁰
Anhydrous THF	1.000	27.0	6.60 × 10¹⁰
80.0% aqueous THF	0.500	28.0	6.40 × 10¹⁰
62.2% aqueous THF	0.291	28.4	5.94 × 10¹⁰
45.5% aqueous THF	0.172	29.0	4.90 × 10¹⁰
26.6% aqueous THF	0.083	30.0	3.60 × 10¹⁰
10.0% aqueous THF	0.027	33.6	1.34 × 10¹⁰
Anhydrous methanol	1.000	22.2	5.78 × 10¹⁰
84.3% aqueous methanol	0.751	25.1	5.16 × 10¹⁰
50.0% aqueous methanol	0.360	32.9	3.43 × 10¹⁰
10.0% aqueous methanol	0.059	54.6	1.17 × 10¹⁰
Anhydrous glycol	1.000	47.3	4.60 × 10¹⁰
82.0% aqueous glycol	0.569	50.0	3.65 × 10¹⁰
33.6% aqueous glycol	0.128	59.0	1.42 × 10¹⁰
Anhydrous n-butyl alcohol	1.000	24.2	5.53 × 10¹⁰
0.05 M aqueous HCl	0.000	71.5	0.13 × 10¹⁰

[a] See "Handbook of Chemistry and Physics," C. W. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1950; G. O. Curme, Jr., "Glycols," Reinhold Publishing Corp., New York, N. Y., 1952; J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1960.

Results and Discussion

The Benesi–Hildebrand equation and the method of least squares gave values of 1000 and 0.14, respectively, for the molar extinction coefficient and association constant of quinhydrone in 50% aqueous tetrahydrofuran. The experimentally determined extinction coefficient is essentially in agreement with Tsubomura's

(13) S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 4550 (1962).
(14) S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, **76**, 1003 (1954).
(15) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955.
(16) W. Herold and K. L. Wolf, *Z. physik. Chem.* (Frankfurt), **12**, 194 (1931).
(17) W. C. Eichelberger and V. K. Lamer, *J. Am. Chem. Soc.*, **55**, 3633 (1933).

value, but the association constant is considerably lower than that reported in water.[12] Thus, in agreement with Michaelis and Granick,[5] an inverse relationship exists between the association constant of quinhydrone and the amount of organic component in aqueous organic solvents. The effect cannot be due to a unique property of water. Table I shows that there is a significant change in association among the various anhydrous solvents. At the same time, the similarity of behavior of quinhydrone in all of the aqueous solvents, including acetic acid, cannot be attributed entirely to hydrogen ion concentration or to ionization properties of hydroquinone. Likewise, there is not a consistent relationship between the degree of association of quinhydrone in solution and the dielectric constants, dipole moments, or Winstein–Grunwald "Y values" of the corresponding solvents.[18]

Kosower[19] has suggested that the relative polarities of a series of solvents can be estimated from their effects upon the long wave length charge-transfer absorption band of 1-ethyl-4-carbomethoxypyridinium iodide. The energy of this transition (in kcal./mole, called the "Z value") is found to change markedly with solvent composition. In contrast to quinhydrone, the pyridinium iodide complex involves less charge separation in the excited state than in the ground state. This explains why solvents of high polarity shift the pyridinium iodide complex band to shorter wave lengths. The quinhydrone band might be expected to undergo a red shift in solvents with high Z values. Actually, the broad 440-mμ band of quinhydrone showed no detectable change in position in going from solvents of relatively low Z values (n-butyl alcohol) to those of high Z values (water).

Since good correlation between solvent Z and Y values is reported, it is not unexpected that the apparent intensity of pyridinium iodide complex bands vary with the choice of solvent.[19] The direction of intensity variation for the pyridinium complex with solvent differs markedly from that observed for quinhydrone. Water, which completely dissociates pyridinium iodide, promotes quinhydrone formation. This undoubtedly reflects the difference in the ground-state electron distribution of the two complexes, and suggests that other solvents with high Z values also should favor the complexed form of quinhydrone in solution. Actually, methanol ($Z = 83.6$) and acetic acid ($Z = 79.2$) both dissociate the complex relative to n-butyl alcohol ($Z = 77.7$). Glycol, with a Z value only slightly greater than that of methanol (85.1), gives a 50% greater association constant. Thus, the over-all effect of solvent on quinhydrone association cannot be directed entirely by electrical properties.

Surface tension of the solvent yields the best correlation between a physical property of the solvent and the effect of the solvent on quinhydrone association. This finding offers support to an hypothesis advanced by Sinanoğlu and Abdulnur[20] relative to the solvent denaturation of DNA.

The double helix of native deoxyribonucleic acids apparently results largely from its being a favorable conformation for adjacent base–base interaction.[21] The helical structure is favored in pure water, but is denatured to varying degrees in pure organic solvents,[22] and in aqueous organic mixtures.[21b,23] Many explanations have been advanced for the effect of water in promoting the helical conformation. Among these appears the concept of "apolar" or "hydrophobic" "bonding."[24] This is not bonding in a conventional sense, but "bonding" imposed from without by the effect of the solvent in conducing to the association of the "bonded" structures. This term has been applied to a variety of solvent effects shown by water.[21c,25] Sinanoğlu and Abdulnur[20] showed that the principal contributor to these solvent differences may be the energy gained in creating a solvent cavity around the helix relative to two cavities around the denatured coils.

As with the random-coil–double-helical coil reaction of deoxyribonucleic acids, the standard free energy of a hydroquinone–quinone complex reaction can be analyzed into four principal contributing terms (eq. 3).

$$\Delta F^\circ = \Delta F_{\text{vac}} + \Delta F_{\text{soln}} + \Delta F_{\text{solv}} + \Delta F_{\text{surface}} \quad (3)$$

ΔF_{vac}, the free energy change of the equilibrium reaction in a vacuum, by definition remains constant in all solvents. ΔF_{soln}, the reduction in free energy of a quinhydrone complex by the surrounding medium, is expected to change with solvent. Any change, if significant, however, would be accompanied by a shift in the wave length of the charge-transfer transition.[4] Simple quinhydrone absorbs with maximum intensity at approximately 440 mμ in all of the solvents considered. Consequently, changes in ΔF_{soln} probably contribute little to the over-all changes in the standard free energy. ΔF_{solv}, the net free energy of complex–solvent interactions minus the sum of component–solvent interactions, should also vary with changes in the solvent. $\Delta F_{\text{surface}}$, another term which may vary with solvent, equals the difference between the free energy (surface energy) required to create a solvent cavity around the complex and two cavities around the dissociated components. The latter term may be estimated by considering the surface tension of the solvent and the relative areas of the cavities around the solute molecules. This difference in the surface energy is nearly equal to $\sigma \Delta A$, where σ is the surface tension of the solvent and ΔA is the net change in surface area. Note that the use of an interfacial tension would have been inappropriate since a solute molecule cannot be considered macroscopic. In addition, there also may be a small contribution to $\Delta F_{\text{surface}}$ arising from secondary structures of the solvent around the solute molecules. This contribution probably is small relative to

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(19) E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958); E. M. Kosower and B. G. Ramsey, *ibid.*, **81**, 856 (1959).

(20) O. Sinanoğlu and S. Abdulnur, presented at the Symposium on Molecular Mechanisms in Photobiology, Wakulla Springs, Fla., Feb. 1964; *Federation Proc.*, in press.

(21) For review of the extensive literature see (a) S. Kit, *Ann. Rev. Biochem.*, **32**, 43 (1963); (b) S. J. Singer, *Advan. Protein Chem.*, **17**, 1 (1962); (c) B. H. Zimm and N. R. Kallenbach, *Ann. Rev. Phys. Chem.*, **13**, 171 (1962).

(22) L. Levine, J. A. Gordon, and W. P. Jencks, *Biochemistry*, **2**, 168 (1963).

(23) J. H. Coates and D. O. Jordan, *Biochim. Biophys. Acta*, **43**, 214 (1960); P. O. Ts'o, G. K. Helmkamp, and C. Sander, *ibid.*, **55**, 584 (1962); E. L. Duggan, *Biochem. Biophys. Res. Commun.*, **6**, 93 (1961); T. T. Herskovits, *Arch. Biochem. Biophys.*, **97**, 474 (1962).

(24) F. M. Richards, *Ann. Rev. Biochem.*, **32**, 269 (1963).

(25) I. M. Koltz, *Brookhaven Symp. Biol.*, **25**, (1960); W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).
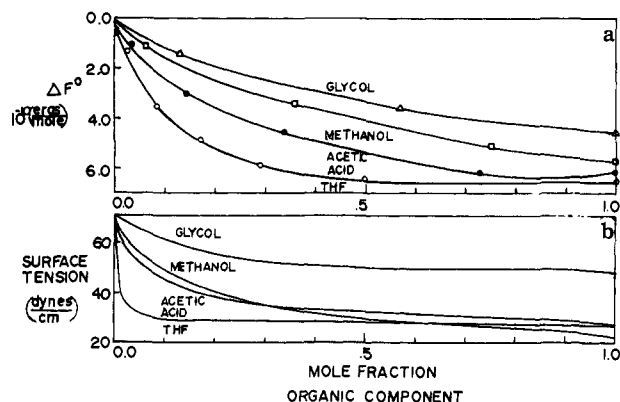
Figure 1. (a) Standard free energy of quinhydrone formation in aqueous organic solvents of different compositions. (b) Surface tensions of aqueous organic solvents of different compositions.

Figure 2. Standard free energy of quinhydrone formation in aqueous acetic acid, glycol, tetrahydrofuran, and methanol $vs.$ surface tension of the solvent mixture.

$\sigma \Delta A$, and eq. 3 reasonably may be approximated by the expression

$$\Delta F^{\circ} = \Delta F_{vac} + \Delta F_{soln} + \Delta F_{solv} + \sigma \Delta A \qquad (4)$$

Since ΔF_{vac} and ΔF_{soln} are constant with changes in solvent

$$\frac{d\Delta F^{\circ}}{dc} = \frac{d\Delta F_{solv}}{dc} + \Delta A \frac{d\sigma}{dc} + \sigma \frac{d\Delta A}{dc} \qquad (5)$$

where c is some quantity which is characteristic of the composition of the solvent system. Rearrangement of eq. 5 gives an expression for the change in solvent surface area accompanying quinhydrone formation. The relative significance of the last two terms of eq. 6

$$\Delta A = \frac{\dfrac{d\Delta F^{\circ}}{dc}}{\dfrac{d\sigma}{dc}} - \frac{\dfrac{d\Delta F_{solv}}{dc}}{\dfrac{d\sigma}{dc}} - \sigma \frac{\dfrac{d\Delta A}{dc}}{\dfrac{d\sigma}{dc}} \qquad (6)$$

could not be estimated *a priori*. Sinanoğlu and Abdulnur[20] have shown, however, that $\Delta F_{surface}$ is of much greater importance than ΔF_{solv} in the denaturation reaction of deoxyribonucleic acids. If the latter two terms are small or cancel each other, the relationship between ΔF° and c should parallel that between σ and c. Figure 1a shows the relationship between the experimentally determined standard free energies of quinhydrone formation reactions in solution and the mole fraction of organic component in several aqueous organic solvents. In Figure 1b the surface tensions[26] of the corresponding solvents have been plotted against the mole fraction of organic component. Figures 1a and 1b illustrate the qualitative similarity between ΔF° and surface tension with respect to solvent composition. The conclusions of Sinanoğlu and Abdulnur[20] indicate that changes in ΔF° may be affected mostly by the surface tension of the solvent. Figure 2, in which ΔF° values for the reaction in the aqueous organic solvents have been plotted against surface tensions of the corresponding solvents, shows that this is not rigorously true. If ΔF° variations were dependent solely upon the surface energies of the solvent cages, straight lines would be obtained. Changes in the slopes of the curves can be attributed to changes in the solvation properties of the various solvents and
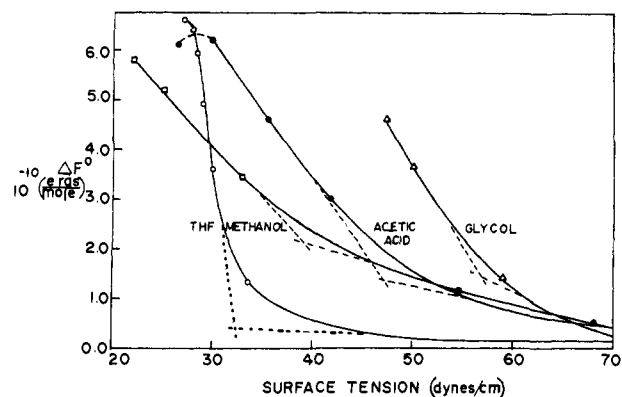
(26) See Table I, footnote a.

perhaps to variations in ΔA in each series. It would be unexpected for both of these terms to remain constant in progressing from an anhydrous alcohol, ether, or acid, to a corresponding highly aqueous solvent system. It is interesting to note, however, that each of the curves in Figure 2 can be approximated by two intersecting straight lines. If it is assumed that the sum of the last two terms of eq. 6 is equal to zero in each of the linear regions, the slopes of the lines equal ΔA. Table II shows estimated values for ΔA

Table II. ΔA per Molecule of Quinhydrone Formation in Aqueous Organic Solvents at 28°

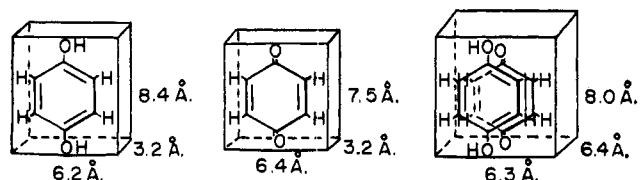| Aqueous solvent	Organic region, $\mathring{A}.^2$	Aqueous region, $\mathring{A}.^2$
Acetic acid	-46	-7.3
Tetrahydrofuran	-202	-0.78
Methanol	-37	-10.4
Glycol	-54	-15.8

for the highly aqueous and highly organic regions of each of the solvents, as determined from the curves in Figure 2.

Several empirical methods were available for determining which, if either, of the calculated values of ΔA in each series was more nearly correct. Comparison of corresponding curves in Figures 1a and 1b favors the values of ΔA calculated in highly aqueous solvents. Inclusion of 0.1 to 0.2 mole fraction of organic component in water caused a substantial decrease in the surface tension of the solvents. This decrease was accompanied by an increase in ΔF° in each of the solvents. Inclusion of proportionally more organic component caused less of a change in the surface tensions, but continued to effect considerable increases in ΔF°. This difference was particularly noticeable in aqueous tetrahydrofuran. On this basis, deviations from the straight lines obtained in *highly aqueous regions* of Figure 2 may be due to changes in ΔA and in the intrinsic solvating properties of the solvent.

A theoretical evaluation of the effects of solvation and of ΔA on this system would be complicated. Furthermore, the range of ΔF° values in the experimental data is approximately 7×10^{10} ergs/mole (2

kcal./mole). Extremely accurate calculations and a thorough knowledge of the specific interactions in each solvent would be required to make corrections within this narrow range.

Alternatively, an "average value" of ΔA can be determined by considering a series of *pure* single component solvents. In Figure 3, $\Delta F°$ values for quinhydrone in solution have been plotted against the surface tension of the corresponding solvents. The best line connecting these points, by the method of least squares, has been drawn. The slope of this line, -0.129×10^{10} cm.^{2}/mole, corresponds to a value of -21.4 Å.^{2} per molecule for ΔA. This value, which lies between those calculated for each aqueous solvent system, suggests that solvation effects may vary throughout the ranges of aqueous composition.
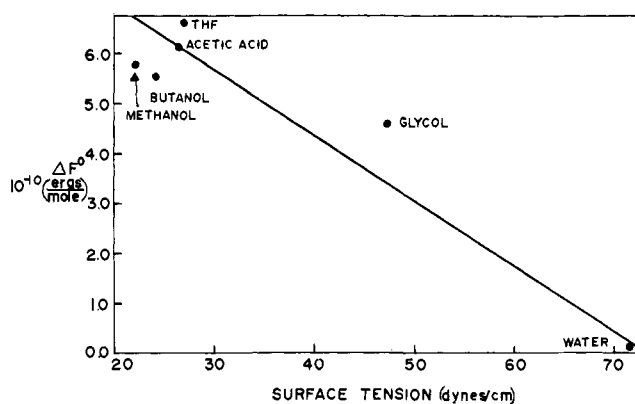

Figure 3. Standard free energy of quinhydrone formation in pure organic solvents vs. surface tension of the solvent; line fitted by the method of least squares.

Another value for ΔA may be estimated from the dimensions of "solvent cages" around molecular models of quinhydrone and its components assuming no specific solvent-solute interactions. For the purpose of these calculations, the solvent cages were estimated to be rectangular boxes with dimensions determined from van der Waals radii. The predicted loss in surface area in going from isolated components to the complex is 89 Å.^{2}. (Note that the volume is assumed not to change.)

Studies in Phosphinemethylene Chemistry. XI. The Reaction of Alkyllithium Reagents with Tetraphenylphosphonium Bromide[1]

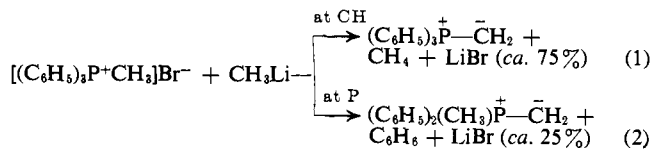Dietmar Seyferth,[2a] William B. Hughes, and James K. Heeren[2b]

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The reaction of methyllithium with tetraphenylphosphonium bromide in THF–ether medium has been studied in some detail. The principal attack occurs at phosphorus and results in formation of triphenylphosphinemethylene, benzene, and lithium bromide. A portion (<20%) of the attack by the lithium reagent involves abstraction of an ortho proton and leads to formation of 9-phenyl-9-phosphafluorene. Triphenylphosphineethylidene and triphenylphosphine-n-butylidene were prepared by the action of ethyllithium and n-butyllithium, respectively, on tetraphenylphosphonium bromide, again via RLi attack at phosphorus.

(1) (a) Part X: D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, in press. (b) Preliminary communication: D. Seyferth, J. K. Heeren, and W. B. Hughes, *ibid.*, **84**, 1764 (1962). (c) Presented in part at the symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 12–15, 1963.

(2) (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) Fellow of the M. I. T. School for Advanced Study, 1961–1962.

In the previous paper of this series[1a] we showed that methyl-, ethyl-, and *n*-butyllithium attacked methyltriphenylphosphonium halides at phosphorus as well as at the methyl protons (eq. 1 and 2). This observation led to the prediction that the reaction of an alkyllithium compound with tetraphenylphosphonium bromide, in which there are no aliphatic C–H bonds adjacent to phosphorus, should result in formation of a triphenylphosphinealkylidene *via* attack at phosphorus (eq. 3). It was the purpose of this study to test this prediction.

$$[(C_6H_5)_3P^+CH_3]Br^- + CH_3Li \longrightarrow \begin{cases} \xrightarrow{\text{at } CH} (C_6H_5)_3P^+-\bar{C}H_2 + CH_4 + LiBr \ (ca.\ 75\%) & (1) \\ \xrightarrow{\text{at } P} (C_6H_5)_2(CH_3)P^+-\bar{C}H_2 + C_6H_6 + LiBr \ (ca.\ 25\%) & (2) \end{cases}$$