[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL (CANADA)]

The Effect of Solvents on Tautomeric Equilibria

BY J. POWLING[1] AND H. J. BERNSTEIN

The heats of tautomerization of acetylacetone in dilute solutions in decalin, tetrachloroethylene and bromoform, and in the gas phase, were determined by use of an infrared analytical method. The gas value of the heat of tautomerization could also be obtained from the dilute solution data by application of the Onsager–Kirkwood theory of solvent interaction, interpreted in that the "cavity" is determined by the size of the solvent molecules. Similar treatment of the data from the literature on the free energies of tautomerization of several substances in a variety of solvents revealed extensive correlations.

In a recent paper[2] the effects of solvents upon the rotational isomerization energies of some halogen-substituted ethanes were discussed. It was shown in very dilute solution in non-polar solvents that the isomer with a permanent electric moment was stabilized with respect to the isomer of zero moment by an amount of energy proportional to

$$\left(\frac{\epsilon - 1}{2\epsilon + 1}\cdot\frac{1}{a^3}\right)\mu^2 \qquad (1)^{3,4}$$

where

ϵ = dielectric constant of solvent
μ = dipole moment of polar isomer
$a^3 \propto$ molecular volume of solvent

$$\propto \left(\frac{\text{molecular weight}}{\text{density}}\right)_{\text{solvent}} = \left(\frac{M}{\rho}\right)_{\text{solvent}}$$

In the original derivation,[3] a is the radius of a "cavity" in the medium of dielectric constant ϵ in which the dipole of moment μ is located. Usually a had been identified with the radius of the solute molecule.[5] There is nothing of a theoretical nature which compels this interpretation. Moreover, it has been found[2] that equilibrium data in dilute solution could only be interpreted with a^3 taken to be proportional to the molecular volume of the *solvent* molecule, and correlations disappeared when a^3 for solute molecule was chosen instead of a^3 for solvent.

In the gas phase the ratio of the concentration of the less stable isomer to the concentration of the more stable isomer is proportional to $e^{\frac{-\Delta H_{\text{gas}}}{RT}}$ It has been shown[2] that the heat of isomerization in the gas is related to that observed in dilute solution by the equation

$$\Delta H_{\text{gas}} = \Delta H_{\text{solution}} + \left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)_{\text{solvent}} \times \mu^2 \qquad (2)$$

If both isomers possess dipole moments then

$$\Delta H_{\text{gas}} = \Delta H_{\text{solution}} + \left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)_{\text{solvent}} (\mu_1^2 - \mu_2^2) \qquad (3)$$

where μ_1 is the electric moment of the less stable isomer and μ_2 that of the more stable isomer.

This simple relationship was found valuable for the determination of gas-phase heats of isomerization from the dilute solution values. Actual knowledge of the moments of the isomers was unnecessary since a plot of the observed $\Delta H_{\text{solution}}$ against the solvent property $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ gave a straight line with a slope equal to $-(\mu_1^2 - \mu_2^2)$ and an intercept on the ΔH axis equal to ΔH_{gas}.

Since this interaction energy of the polar molecule with its surrounding medium accounted for the changes in the isomerization energy of rotational isomers in different solvents, it was considered worthwhile to attempt to investigate the solvent effect on other simple equilibria. Well known examples of such equilibria are found in tautomeric systems. Although the equilibria of a number of tautomeric substances have been studied in some detail in solution[6,7,8] and in the vapor phase,[9,10] insufficient data are available for nonpolar solvents. The temperature coefficients of the equilibria in the gas phase, required for the true heat of tautomerization, are not readily determined chemically. Moreover, it is never quite certain that the equilibrium has not changed during the analytical process with chemical methods of analysis. In this paper an infrared analytical method has been used for the determination of the true heat of tautomerization of acetylacetone either directly in the gas phase or from dilute solution experiments. Some rough quantitative analytical work using infrared[11] and ultraviolet absorption[7] techniques has been reported on the equilibrium of the keto and enol forms of ethyl acetoacetate in solution.

Further interpretation of data taken from the literature on the heats of tautomerization in solution has been made on the basis of equation (3).

Experimental

The keto and enol tautomers of acetylacetone are shown in Fig. 1.

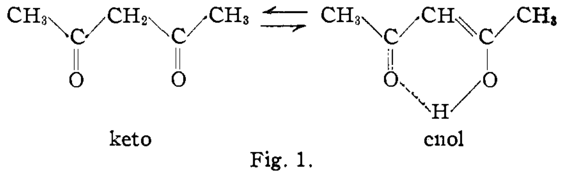

Fig. 1.

The infrared spectrum (obtained with a Perkin–Elmer model 12C infrared spectrometer) shows evidence of the presence of both forms under most experimental conditions. The band at 1725 cm.$^{-1}$ (vapor) associated with the C=O stretching vibration is characteristic of the unchelated ketone, and the strong band at about 1625 cm.$^{-1}$ (vapor) is due to the C=O stretching vibration in the enol where it is modified by hydrogen bonding and resonance in the

---

(1) National Research Laboratories Post-doctorate Fellow 1948–1950.

(2) J. Powling and H. J. Bernstein, THIS JOURNAL, **73**, 1815 (1951).

(3) L. Onsager, *ibid.*, **58**, 1486 (1936).

(4) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); *ibid.*, **7**, 911 (1939).

(5) K. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, **39**, 303 (1940).

(6) K. H. Meyer and P. Kappelmeier, *Ber.*, **44**, 2718 (1911); K. H. Meyer, *ibid.*, **45**, 2843 (1912); **47**, 826 (1914); K. H. Meyer and F. G. Wilson, *ibid.*, **47**, 832 (1914).

(7) P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924).

(8) A. B. Ness and S. M. McElvain, THIS JOURNAL, **60**, 2213 (1938).

(9) J. B. Conant and A. F. Thompson, Jr., *ibid.*, **54**, 4038 (1932).

(10) R. Schreck, *ibid.*, **71**, 1881 (1949).

(11) R. J. W. LeFevre and M. Welsh, *J. Chem. Soc.*, 2230 (1949).

ring.[12,13,13a] The OH band is also characteristic of the enol, but it is not useful for quantitative comparisons since it is very broad and has shifted from its usual region to around 2900 cm.$^{-1}$, where it overlaps the C–H stretching bands. The open chain enolic form is not expected to be present since it is found to be ~18 kcal./mole less stable than the diketone from bond energy considerations. Chelation involving hydrogen bonding, and resonance in the ring on the other hand, increase the stability of the chelated enol form to about that of the diketone.

The peak optical densities, d, of the two C=O bands at 1725 and 1625 cm.$^{-1}$ were used to measure the concentrations of the keto and enol forms, respectively. Beer's law was obeyed under the conditions employed. From the temperature dependence of the densities of these bands the heat of tautomerization ΔH was determined according to

$$\frac{d_{\text{enol}}}{d_{\text{keto}}} = \text{const}_1 \frac{[\text{enol}]}{[\text{keto}]} = \text{const}_2 e^{-\Delta H/RT} \qquad (4)$$

where ΔH is the heat of the reaction keto $\rightleftarrows$ enol. Determinations of ΔH were made in the gas phase at ~5 mm. pressure and in ~0.1 molar solution[14] in decalin, tetrachloroethylene and bromoform.[15] The determinations of ΔH_{gas} were made over the range of temperature 25–200°, and the solution values over the range 25–100°.

Results and Discussion

The values obtained for the heats of tautomerization in the vapor phase and in dilute solution with decalin, tetrachloroethylene and bromoform are shown in Fig. 2, where these values are plotted against the solvent quantity $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$. The low pressure gas phase is considered to be a medium in which this quantity is zero. The plot is a straight line and the solution values extrapolate to the experimentally determined value of $-\Delta H_{\text{gas}}$, *viz.*, 2.4 kcal./mole. The graph gives support to the original suggestion that the change in tautomeric equilibrium might be adequately accounted for by the different energies of dipole interaction of each tautomer with its surrounding medium, according to the model of Onsager.[2] Further evidence is supplied by similar treatment of some results of Grossmann[6] for the heat of tautomerization of ethyl acetoacetate in some non-polar or slightly polar solvents. The values for ΔH determined in hexane, carbon tetrachloride and ether were found to lie on a good straight line and indicate that $-\Delta H_{\text{gas}} =$ 2.0 kcal./mole (Fig. 3).[16] In view of these successful interpretations in the simpler cases of chemically inert solvents, one is encouraged to treat in the same manner the data available for tautomeric systems in other solvents, where perhaps more specific interactions with the solute (*e.g.*, hydroxy compounds) are involved.

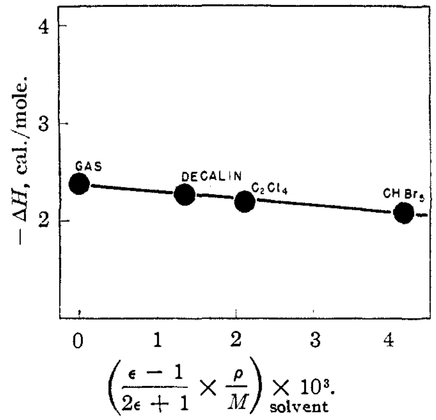

Fig. 2.—Acetylacetone.

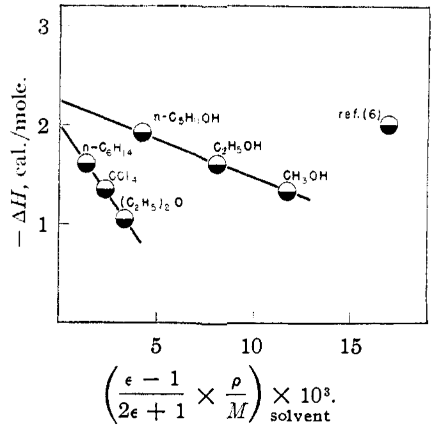

Fig. 3.—Ethyl acetoacetate.

Figure 3 includes Grossmann's ΔH values for ethyl acetoacetate in alcoholic solvents. These points also extrapolate to the same gas value to within ~0.2 kcal./mole but the slope of the line is considerably less than that for the non-polar solvents. It would seem that some additional specific influence of the OH group is operative. In Figs. 4 to 8 the data from the literature have been plotted. It is necessary to bear in mind that there is a lack of consistency in the same data obtained by different authors. The data from each source, however, are considered to be internally consistent to a higher degree of accuracy and have been treated separately. Although infinitely dilute solution data were not always available, the solute concentrations seemed small enough (~0.1 mole/l.) in most cases so that the solutions could be considered to be almost infinitely dilute.

In the following graphs the change in free energy, $-\Delta F$, for the tautomeric rearrangement of a number of compounds in dilute solution, has been plotted against the property $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ of the solvent in which they were determined. Most of the data reported by Meyer[6] have been plotted, except the determinations in toluene, alcohol and hexane for which the experimental error was very great.

In Figs. 4 and 5 some of the data for the tautomeric equilibrium of acetylacetone are given. A reasonable average error of ±100 cal./mole has been assumed. Figure 4 shows that the basic and acidic solvents give rise to different curves. The trend of the acid curve gives a good indication of the gas value of ΔF and the line for the bases extrapolates

---

(12) W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940).

(13) (a) R. S. Rassmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949); (b) D. N. Shigorin, *Zhur. Fiz. Khim.*, **23**, 506 (1949).

(14) In all cases 0.1 mole/l. was considered to be "infinitely dilute." See references (6) and (11).

(15) Bromoform is not a non-polar solvent but the change in $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)_{CHBr_3}$ is found to be within the experimental error over the limited range of temperature employed. Values determined in ether are used to the same approximation.

(16) The points obtained by each author are depicted in the same manner in all of the figures.

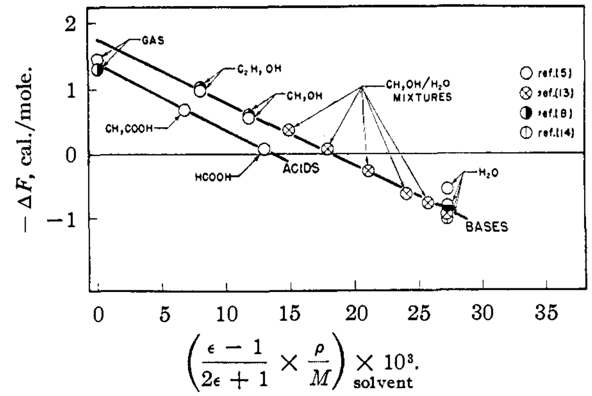

Fig. 4.—Acetylacetone.

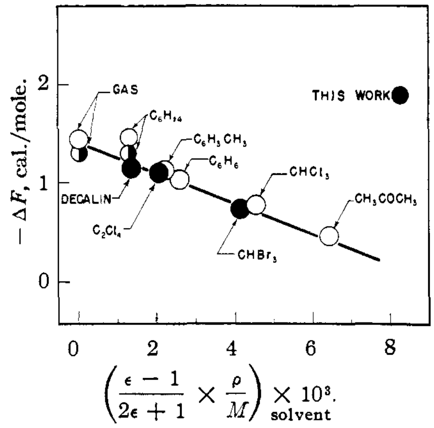

Fig. 5.—Acetylacetone.

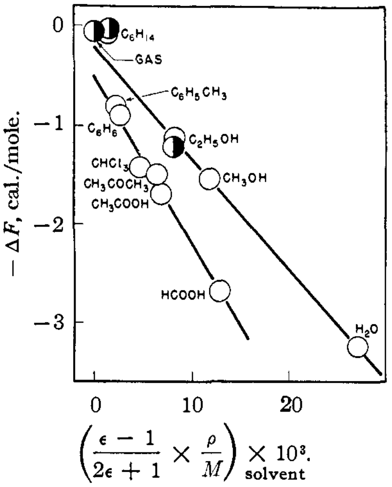

Fig. 6.—Ethyl acetoacetate.

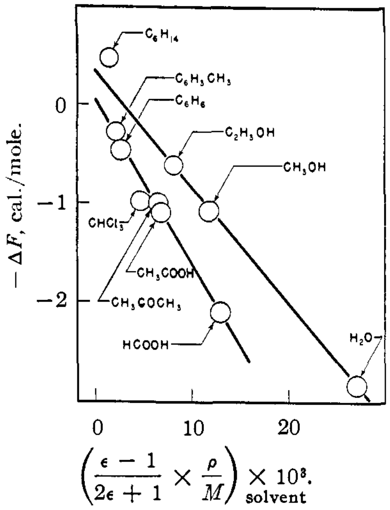

Fig. 7.—Methyl benzoylacetate.

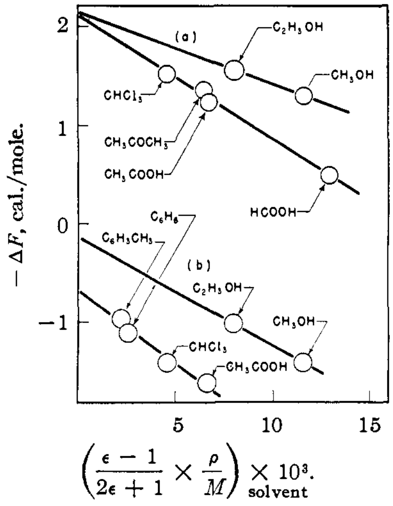

Fig. 8.—(a) Benzoylacetone, (b) acetoacetanilide.

back to a fair measure of the experimental gas phase value (to within 0.2–0.3 kcal./mole). The relationship appears to hold well over the complete range of methanol–water mixtures representing a wide range of dielectric constant. A third straight line given in Fig. 5 is obtained with solvents which might be considered inert. The ΔF values from this work, which are the basis of the line in Fig. 5, were obtained from the optical densities ratio $\frac{d_{\text{enol}}}{d_{\text{keto}}} = \text{const}_1 \frac{[\text{enol}]}{[\text{keto}]}$, determined in the gas phase by evaluating the const_1 from the true equilibrium constant in the gas phase, taken from Meyer.[6] The dilute solution equilibrium constants, and hence the ΔF values, were then obtained from the optical density ratios assuming the same factor. On this straight line (Fig. 5) obtained from the plot of $-\Delta F$ against $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ are found to lie several other values of ΔF obtained from the data in the literature. In the examples treated (Figs. 6, 7, 8), except perhaps for acetylacetone (Fig. 5) the line obtained from plotting ΔF *vs.* $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ for the solvents in Fig. 5 cannot be distinguished from the line for the acidic solvents. Whether the grouping of such a variety of solvents is justified must await more precise results over a wider range of dielectric constant and molecular volume but within the accuracy so far available it would seem permissible. A similar relation between ΔF and the solvent property $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ is shown for some other tautomeric systems, ethyl acetoacetate, methyl benzoylacetate and benzoic acetone and acetoacetanilide, in Figs. 6, 7 and 8, respectively. Meyer's data for ether and carbon disulfide are not quantitatively explained in terms of this solvent property, but since their behavior is not consistent in the several examples he investigated[6] they have not been included. It does not seem very likely that these two solvents should have any specific associations with the solute, especially since Grossmann's[7] data for ether are in line with those for hexane and carbon tetrachloride. However, the values for ΔF obtained in hexane are consistently too high and are usually the same as the gas values[9] although the values in decalin are lower (see Fig. 5).

Conclusions

The changes in the heats of tautomerization of acetylacetone in decalin, tetrachloroethylene and bromoform may be interpreted in terms of the Onsager–Kirkwood model of electrostatic interaction, using the volume of the solvent molecule for the "cavity." The gas value of the heat of tautomerization may be obtained to a fair degree of accuracy from the dilute solution values. The value for acetylacetone arrived at in this way (2.4 kcal./mole) is the same as the experimentally determined gas value. Similar treatment of Grossmann's data for ethyl acetoacetate in hexane, carbon tetrachloride and ether leads to a value of $-\Delta H_{\text{gas}} = 2.0$ kcal./mole for this tautomeric change. Application of the Onsager model as described would appear to account for the behavior of such equilibria in most non-polar or slightly polar solvents, provided no other specific interaction occurs between the solvent and either tautomer. Even where specific associations of the solvent with the tautomeric forms would be expected, namely, in alcohol and methanol–water mixtures, a separate straight line relation between $-\Delta F$ and solvent property $\left(\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}\right)$ has been obtained. Extrapolation of this line gave also a fair approximation to the gas value of ΔF, but the slope of the line differed from that with non-polar solvents and acidic solvents. The correspondence between the dipole moments of the tautomers (according to Equation 3) and the slope of the line is obviously affected. As far as the data available at present can indicate, acidic solvents will also give a straight line relationship, and so will polar solvents provided no specific associations are visualized. These lines also extrapolate to a reasonably good approximation of the gas value of ΔF.

OTTAWA, CANADA RECEIVED JANUARY 11, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Absorption Spectra of Some Phenyl Sulfides, Sulfoxides and Sulfones Containing Nitro and Amino Groups

BY H. HARRY SZMANT AND J. J. McINTOSH

The ultraviolet absorption spectra of phenyl sulfides, sulfoxides and sulfones containing amino- and nitro-substituents are reported and discussed in terms of the electronic structures.

In continuation of our studies[1] of the spectroscopic behavior of the sulfur group at its various oxidation states we wish to report in this paper the results obtained with a series of mono- and disubstituted phenyl sulfides, sulfoxides, and sulfones. In order to intensify any spectroscopic results which could be attributed to the electron transmitting capacity of the sulfur-containing group, we have chosen to investigate the *p*-nitro-, *p*-amino- and, finally, the *p*-nitro-*p'*-amino substituents. The latter represent a system in which the electron push and pull, if it is to be coöperative, must be exerted *via* the sulfur group.

Experimental[2]

The physical properties, the spectrophotometric data and other pertinent information concerning the compounds used in this study are summarized in Table I. The absorption spectra reproduced in Figs. 1–4 were obtained by using solutions in 95% ethanol and a Beckman DU spectrophotometer.

Preparation of Compounds.—***p*-Nitrophenyl phenyl sulfoxide** was prepared by the oxidation of the sulfide with 30% hydrogen peroxide in glacial acetic acid.

Anal. Calcd. for $C_{12}H_9O_3NS$: C, 58.29; H, 3.63. Found: C, 58.54; H, 3.79.

Phenyl *p*-aminophenyl sulfoxide was prepared by the hydrolysis of the acetanilide obtained by the Schmidt reaction of *p*-phenylthionylacetophenone. The anilide had a m.p. 137–137.5°.

Anal. Calcd. for $C_{14}H_{13}O_2NS$: C, 64.84; H, 5.05. Found: C, 64.93; H, 5.20.

The identical product was obtained by the oxidation of *p*-phenylmercaptoacetanilide by means of hydrogen peroxide.

The hydrolysis of the acetanilide yielded the desired amine of m.p. 151°.[3]

***p,p'*-Dinitrophenyl sulfoxide** was prepared by Mr. Howard Corey of this Laboratory. The corresponding sulfide was dissolved in a large volume of warm glacial acetic acid and to the stirred solution there was added dropwise an equimolar amount of hydrogen peroxide dissolved in acetic acid. The product was crystallized from isopropyl alcohol to remove traces of sulfone and unreacted sulfide.

Anal. Calcd. for $C_{12}H_8N_2O_5S$: C, 49.31; H, 2.76. Found: C, 49.42; H, 2.76.

***p,p'*-Dinitrophenyl sulfone** has been reported in the literature to melt at 282°,[4] 254°[5] and 245°.[6] Our sample was prepared by a vigorous chromic acid oxidation of the corresponding sulfide, and repeated oxidations and crystallizations did not raise the melting point above 250–251°.

Anal. Calcd. for $C_{12}H_8N_2O_6S$: C, 46.75; H, 2.62. Found: C, 47.03; H, 2.91.

***p*-Nitro-*p'*-aminophenyl Sulfide.**—The reduction of *p,p'*-dinitrophenyl sulfide[7] was improved in the following way. The dinitro compound, 0.2 mole, was dissolved in approxi-

---

[1] H. H. Szmant and H. J. Planinsek (a) THIS JOURNAL, **72**, 4042 (1950); (b) **72**, 4981 (1950).

[2] All melting points are uncorrected. Microanalyses by the Microanalytical Laboratory, University of Pittsburgh.

[3] E. H. Northey, "Sulfonamides and Allied Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, pp. 364, 381, 385.

[4] E. Fromm and J. Wittmann, *Ber.*, **41**, 2267 (1908).

[5] A. A. M. Witte, *Rec. trav. chim.*, **51**, 299 (1932).

[6] B. Ciocca and L. Canonica, *Gazz. chim. ital.*, **76**, 113 (1946).

[7] R. C. Fuson and S. Melamed, *J. Org. Chem.*, **13**, 690 (1948).