The Nature of Solvent Participation in the Restriction of Rotation about Single Bonds

Sir:

In 1959 Leffler and coworkers published a series of papers on solvent effects in the racemization of optically active biphenyls.[1–4] Of particular interest was their study concerning solvent effects in the racemization of 2,2′-dimethoxy-6,6′-diphenamide (I).[4] In changing the reaction medium from acetone to acetic acid they observed a 2.6-fold increase in the rate constant, a decrease in the enthalpy of activation of 9.1 kcal/mol, and a decrease in the activation entropy of nearly 22 cal/(mol deg). For such a seemingly simple reaction to exhibit such a marked medium effect is very curious, and it would seem that a more complete understanding of this reaction would contribute significantly to the over-all understanding of solvent effects. In an effort to ascertain whether the 9.1-kcal/mol change in the activation enthalpy is due to a ground-state effect or a transition-state effect we have measured the partial molal heat of solution of I in acetone and in acetic acid. The observed heats of solution were 2.98 ± 0.74 and 1.98 ± 0.86 kcal/mol, respectively, giving an enthalpy of transfer from acetone to acetic acid of -1.0 ± 1.1 kcal/mol. Combining this with Graybill and Leffler's values for the activation enthalpies (30.6 ± 0.1 and 21.5 ± 0.2 kcal/mol for racemization in acetone and acetic acid, respectively) gives -10.1 ± 1.1 kcal/mol as the enthalpy of transfer from acetone to acetic acid for the transition state. Clearly the 9.1-kcal/mol decrease in the activation energy observed for this solvent change is due entirely to a medium effect on the transition state, the medium effect on the ground state being in the wrong direction to account for a decrease in ΔH^* for the change from acetone to acetic acid. The 9.1-kcal/mol change in activation energy observed for this change in medium is, to the knowledge of this author, the largest medium effect on the activation enthalpy which has been directly attributed to changes in the solvation of the transition state. This is in contrast with the solvolysis of *t*-butyl chloride[5] and benzyl chloride[6,7] in alcohol–water mixtures where variations in ΔH^* are attributed to changes in ground-state solvation. Likewise the increased reactivity of anions in dipolar aprotic solvents has been attributed to decreased solvation of the anions in the aprotic solvents.[8] However, it should also be noted that in the solvolysis of methyl benzenesulfonate in alcohol–water mixtures the initial and transition-state enthalpies show nearly the same solvent dependence.[6]

We are now in the process of measuring the heats of solution of I in various other solvents and are also engaged in the dissection of the activation parameters for other reactions involving rotation about single bonds. Also in progress is a study of the enthalpies of transfer for various substrates serving as models for the transition state of I. Any model of this transition state must reflect, to the extent that it resembles the transition state, the -10.1 kcal/mol calculated for the enthalpy of transfer for the transition state from acetone to acetic acid.

2-Amino-3-methoxybenzoic acid (II) was prepared by the method of Ruggli and Leonhardt.[9] Five grams of 2-nitro-3-methoxybenzoic acid (Aldrich Chemical Co.) was dissolved in 70 ml of H_2O and 30 ml of concentrated NH_4OH. A hot solution of 45 g of $FeSO_4 \cdot 5H_2O$ in 150 ml of H_2O was then added to the above solution with vigorous stirring. After 5 min the solution was filtered using a cellulose filter aid and a fritted-glass filter. The clear filtrate was evaporated down to 75 ml *via* a rotary evaporator and then made acid by the addition of 5 ml of concentrated HCl. The white precipitate which formed was recovered by suction filtration; 3.3 g of product melting at 171–172° was obtained.

2,2′-Dimethoxy-6,6′-diphenic acid (III) was prepared from II by the method of Leffler and Graybill.[3]

2,2′-Dimethoxy-6,6′-diphenamide (I) was prepared from III *via* the acid chloride as described by Adams.[10]

Calorimetry. The calorimeter used was similar to that already described by Arnett.[11] The errors reported above with the heats of solution are 95% confidence limits. The relatively large errors are due to the extremely small temperature change resulting from the solution of 100 mg of I in 175 ml of solvent. It was not practical to work with a larger sample size because of the slow rate of solution.

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Infrared and Electron Spin Resonance Study of Hydrogen Tungsten Bronze

Sir:

Glemser and Naumann[1] have shown that the so-called "tungsten blues," obtained by reduction of tungsten trioxide or tungstates, are not simple compounds but are nonstoichiometric materials, frequently in combination with starting WO_3 or H_2WO_4. Further, they were able, on reduction of WO_3, to isolate cubic $H_{0.5}WO_3$, tetragonal $H_{0.33}WO_3$, and rhombic $H_{0.1}WO_3$ and show by X-ray analysis that these were indeed analog products to the well-known sodium tungsten bronzes, Na_xWO_3.[2] More recently, Dickens and Hurditch[3] have prepared an additional hydrogen tungsten bronze tetragonal phase in the range $0.21 < x < 0.25$. In an attempt to cast more light on the state of the hydrogen in these

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materials, we have examined their infrared and esr absorption, specifically to check whether the H in H_xWO_3 is bound to O as an OH, in which case the materials might better be formulated as $WO_{3-x}(OH)_x$.

Samples were prepared by suspending anhydrous WO_3 in 2 *N* HCl and reducing it for various times with zinc amalgam. After the zinc had been separated by filtration through a double thickness of 200-mesh silk screen, the aqueous phase was decanted and the reduction products pumped to dryness. To prevent air oxidation, samples were maintained under vacuum, under argon, or under mineral oil. For analysis, the bronzes were added to known volumes of boiling standardized potassium dichromate solution and back-titrated with ferrous ammonium sulfate, using diphenylsulfonic acid as indicator. Precision based on three or four samples of each preparation was ± 0.02 in the value of x, assuming all the reducing power was attributable to H_xWO_3. Powder diffraction data were also obtained, using a General Electric XRD-5 diffractometer with Ni-filtered Cu Kα radiation. Parameters were in agreement with those reported.

Infrared absorption spectra were measured in the range 200–4000 cm^{-1} using a Perkin-Elmer 521 double-beam recording spectrophotometer. Specimens were prepared both as Nujol mulls and pressed CsI pellets. Even at relatively high concentration the Nujol mulls showed only the spectral features of Nujol, probably because of insufficiently fine subdivision. Good spectra were obtained, however, with CsI as the dispersing agent. Runs were made with CsI pellets alone, with added stoichiometric anhydrous WO_3, and with addition of the various compositions ($0.03 < x < 0.50$) of hydrogen tungsten bronze. An argon atmosphere was maintained throughout in the preparation and handling of the various specimens. As for most transition-metal oxides, the transmittance spectrum of WO_3 is rather devoid of features, the most noteworthy being a rather broad double dip at about 800 cm^{-1}, two much smaller but also broad dips at 1600 and 3500 cm^{-1}, and three small but sharp dips at 1450, 1490, and 2920 cm^{-1}. All these features are retained for H_xWO_3 with the addition of a rather sharp spike at 690 cm^{-1}.

Esr spectra were examined at 77 and at 300°K using a standard homodyne system operating at 9.5 GHz with balanced crystal detection and 100-kHz field modulation. A rather broad, asymmetric absorption was observed for $H_{0.10}WO_3$ at $g = 1.97 \pm 0.03$. Neither the less concentrated nor the more concentrated specimens gave any detectable signal, the former probably because of too low a concentration of spins and the latter because of too high a conductivity. Specimens of H_xWO_3 with $x > 0.10$ "loaded" the resonance cavity severely.

The most striking finding of our study was the absence of any infrared absorption bands in the region 3400–3900 cm^{-1}, usually associated with constitutional hydroxyl groups,[4] and the appearance of the band at 690 cm^{-1}, in a region usually associated with metal–hydrogen deformation motions.[5] The 690-cm^{-1} band, although relatively weak, was moderately sharp and was clearly observed in H_xWO_3 preparations having $x = 0.10$, 0.21, 0.26, 0.31, and 0.50. The intensity of the band diminished if the sample were exposed to air oxidation, and it disappeared entirely on ignition of H_xWO_3 in air.

Dickens and Hurditch[3] have attempted to fix the positions of hydrogen atoms in tetragonal H_xWO_3 from neutron diffraction data by a comparison of the relative intensities of a hydrogen and a deuterium bronze of the same composition, $H_{0.25}WO_3$. Line broadening prohibited complete interpretation of the absolute intensities, but they concluded that H atoms were in special positions (*a*), 0, 0, 0 or $^1/_2$, $^1/_2$, 0, of the space group P4/nmm (No. 129). (Reference 3 gives the coordinates of two of the oxygen atoms incorrectly.) Using this space group and parameters $a_0 = 5.228$ Å and $c_0 = 3.881$ Å, we calculate 2.62 and 2.68 Å for the O-to-H distances, clearly much longer than any conventional OH group. Alternatively, the H could be considered as hydrogen bonding between oxygen atoms, but for the H positions postulated, the O-to-O distance is so great (approximately 5 Å) that it does not appear meaningful to invoke such a bond. If there were an OH group and it were involved in an $O—H \cdots O$ bond, the O–H stretching frequency would probably be only insignificantly lowered from its non-bonded position at about 3700 cm^{-1}. In crystals of TiO_2 grown by the Verneuil flame fusion technique, a nearly conventional OH vibration band was found[6] at 3300 cm^{-1}, corresponding to a frequency shift of 400 cm^{-1} for an O-to-O distance of 2.75 Å. Greater O-to-O distances generally correspond to smaller frequency shifts.[7]

Because the hydrogen-associated 690-cm^{-1} band falls in the region commonly assigned to metal–hydrogen bending motions, it is tempting to assign it to a W–H bending vibration. However, the W-to-H distance is 3.10 Å, considerably greater than M–H distances in hydride complexes and probably too great to be considered as a useful bond. Furthermore, the W 5d t_{2g} orbitals, which might be used to bond the H, are not properly oriented to give much orbital overlap with the hydrogen. Hence, the W–H bend is even less probable as an explanation than the O–H bend. It appears rather that the most likely mode of vibration is the motion of the H atoms in the [001] direction in and out of the roughly coplanar square of oxygens defined by special positions (*c*). Such a motion would resemble a trampoline motion and, given the large atom spacings, would probably have a small force constant and be of rather low frequency. Motions in the [100] or [010] directions would also be possible, but these would probably be of higher frequency.

The source of the esr line at $g = 1.97$ is not clear. Its appearance at $H_{0.10}WO_3$ and nonappearance in more concentrated bronzes is not significant since the high conductivity precludes penetration of the microwave power to a finite portion of the sample. The observed signal for $H_{0.10}WO_3$ was too broad to afford a precise estimate of the number of absorbing spins, but it appeared to be of the order of 10^{18}. There is the

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possibility that the line is due to an impurity in WO_3, but then it should have appeared also in the more dilute bronzes examined, $H_{0.03}WO_3$ and $H_{0.05}WO_3$. The line is probably not due to W^{5+}, which generally shows g factors in the range 1.4–1.7.

Since cavity loading was not a problem with $H_{0.10}WO_3$, it can be concluded that this composition is not highly conducting. Arguments have previously been given[8] for believing that the metallic bronzes should go over to semiconducting behavior when x in M_xWO_3 drops below approximately 0.25. The critical composition depends on the effective mass of the electron and may be smaller for H_xWO_3 than for M_xWO_3. In any case, there would be good reason for believing that electrons in dilute H_xWO_3 are localized enough to give esr absorption and semiconductivity. The closeness of the g value to 2 suggests localization at the H atoms. A detailed nmr study might be informative, but line broadening makes the problem a difficult one.

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Negative Ion Mass Spectra of Benzene, Naphthalene, and Anthracene. A New Technique for Obtaining Relatively Intense and Reproducible Negative Ion Mass Spectra

Sir:

Negative ion mass spectra taken at low pressures and high electron energies are notoriously weak and nonreproducible.[1] As a consequence of these factors negative ion phenomena have received very little attention in the mass spectra of organic compounds. We herein report a new general technique for obtaining negative ion mass spectra in conventional mass spectrometers which substantially increases both the reproducibility and intensity of the spectra.

Negative ion mass spectra are the result of three ion-formation processes: (1) resonance capture; (2) dissociative resonance capture; and (3) heterolytic fission (ion-pair formation). The abundance of products from these processes depends on the sample pressure, electron current, and energy.

At high emission voltages (50–100 eV) process 3 depends on the transition probability for excitation and is independent of electron energy. Processes 1 and 2 are critically dependent on the energy of the impacting electron. Electrons in the appropriate energy region for resonance capture processes (0–10 eV) are generated as secondary electrons in the formation of positive ions. The magnitude of the secondary electron current is a function of sample pressure. Thus processes 1 and 2 may show a quadratic dependence on pressure.[1] At low pressures the intensities of resonance capture ions (process 1) often show a cubic dependence because of the need for collisional stabilization of the initial ion.[1] These three independent nonconcurrent modes of formation of negative ions by electron impact account for the nonreproducibility and in part the low intensity of negative ion mass spectra.

By use of high pressures of organic molecules intense negative ion mass spectra may be obtained.[2,3] These spectra are usually complicated by ion–molecule and ion–ion reactions,[3] and high pressures of organic molecules will soon destroy a general use analytical mass spectrometer.

Analytical mass spectrometers, particularly those with differential pumping like the MS-902, can be operated at high pressure of nonreactive gases. It should be possible to enhance the negative ion mass spectrum of a sample with such a gas. If the enhancing gas is at least an order of magnitude more abundant than the compound under investiagtion, three things should result. The abundance of secondary electrons should be increased. At relatively high pressures ($>10^{-5}$ torr) the secondary electron current can become almost as large as the primary current. Furthermore there will be a spectrum of electron energies due to secondary and degraded primary electrons that should cover the entire range of energies from zero to the primary electron energy. The energy spectrum of the secondary and degraded primary electrons should be relatively constant from sample to sample, and ion-forming processes 1, 2, and 3 should all be approximately first order in sample pressure. Processes 1 and 2 should be respectively second and first order in enhancing gas pressure.

Table I presents negative ion mass spectra of benzene, naphthalene, and anthracene which were obtained with an A.E.I. MS-902 under the following conditions: sample pressure,[4] 1×10^{-6} torr; nitrogen pressure,[4] 6×10^{-5} torr (under these conditions the analyzer pressure was $1.0 \pm 0.1 \times 10^{-6}$ torr); electron emission, 70 eV with 485 μA at the electron trap; ion repeller, 0.0 ± 0.05;[5] source housing, -8 kV; electron multiplier, 3000 V. The mass scale was determined by direct comparison with standard spectra[6] obtained for either positive or negative ions.

The second column in Table I presents the enhancement factors for benzene using nitrogen. This tech-

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[2] R. Tummler and G. Liebisch, *Chem. Tech.* (Berlin), **19**, 624 (1967).

[3] R. C. Dougherty, submitted for publication.

[4] Source pressure is measured just above the source liquid nitrogen trap on the MS-902. The actual pressure in the source chamber is certainly higher.

[5] The secondary electron energy spectrum critically depends on the repeller potential. If the repeller is adjusted to a modest negative value (~ -40 V) with respect to the source housing, the efficiency of ion drawout is increased; however, resonance capture processes are diminished because of the acceleration of the secondary electrons.

[6] The appropriate field reversals for negative ion studies were accomplished by using a Power Designs Pacific Model No. HV-1543 power supply for ± 8 kV and a Cohu Model 326 power supply of ± 270 V for the electrostatic analyzer. Using these supplies the low-resolution mass scale for a given scan rate and recorder speed shows virtually no variation over a period of 2 weeks, and we have successfully calibrated negative ion spectra by comparison with corresponding positive ion records with results that are entirely consistent with internal standard techniques.