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Is There a Nitroalkane Anomaly?

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Abstract: The abnormal Brønsted slopes observed for nitroalkanes are interpreted as a variation in the work terms, which is caused by a variation in hydrogen bond strengths with the free energy for proton transfer, rather than as an anomaly in the proton-transfer stage itself.

I. Introduction

For most series of related proton-transfer reactions[1] the rate constant, k, is found to correlate with the equilibrium constant, K_{eq}. The Brønsted slope

$$\alpha \equiv d \ln k / d \ln K_{eq} \qquad (1)$$

varies in the range zero (for very exothermic reactions) to one (for very endothermic reactions). These findings motivated the postulates[2,3] that α is a measure of the position of the transition state along the reaction coordinate,[2] which is early for exothermic and late for endothermic reactions.[3] However, in some series of nitroalkanes α outside the range 0-1 was found,[4] and the validity of the Leffler-Hammond[2,3] postulates was questioned (at least for carbon acids). Before attempting to resolve this "nitroalkane anomaly", let us summarize experimental findings concerning proton transfer from nitroalkanes.

(a) Variation in the base (for a given nitroalkane) results in a normal Brønsted plot with $\alpha \approx 0.5$, over a considerable pK_{eq} range. Such are the results for arylnitromethane[5] shown in Figure 1a. This was taken to indicate[4] that either α is a bad measure for the location of the transition state or that its location does not change, in contrast to the Hammond-Leffler postulates.

(b) Variation in the nitroalkane (by substitution) results in Brønsted plots which are parallel to each other. Taking from each plot a point representing a reaction with a given base, one finds a correlation with an unusual slope:[4] for a strong base (e.g., OH^-) α may be larger than unity in the exothermic regime (or smaller than zero for the reverse, endothermic reactions). α has less extreme values for weaker bases. The abnormal behavior is not merely in the fact that $\alpha > 1$ or < 0, as sometimes stated, but, more generally, in the fact that α is large in the exothermic regime where it is expected to approach zero (at least α should be $\leqslant 0.5$), and $\alpha < 0.5$ in the endothermic regime, where it is expected to approach unity. In contrast to case (a), only a small pK_{eq} range is covered when the nitroalkane is varied.

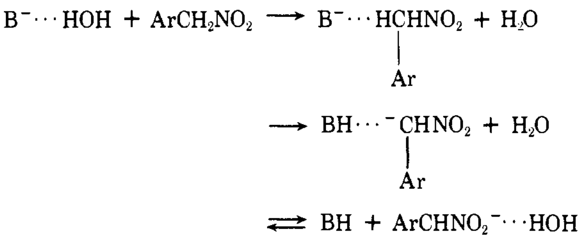
(c) Proton transfer from $ArCH_2NO_2$, when carried out in Me_2SO, instead of in aqueous solution, yields a normal Brønsted plot,[6] shown in Figure 1b. These results were interpreted in the original work[6] as "normal" because a straight line with a slope $\alpha = 0.92$ can be passed through the four most endothermic forward reaction points, plus a point for disubstitution ($k = 1930\ M^{-1}\ s^{-1}$, $K_{eq} = 174$), not shown in the figure. The magnitude of k in Me_2SO is considerably larger than in water.

(d) A normal Brønsted plot seems to be also the case for the ionization of substituted $ArCH(NO_2)_2$ in water,[7] as seen in Figure 1c. This point has been overlooked by most treatments: Why is the dinitro not more anomalous than the nitro compound?

Several explanations were given for the "nitroalkane anomaly", among which are the formation of an anionic intermediate,[4] the existence of several opposing interactions with different effects on the transition state than on reagents and products,[8] or the necessity for extensive nuclear rearrangement.[9]

It is not clear how (c) and (d) (above) are explained in this fashion. The finding of Keeffe et al.[6] clearly indicates that solvent effects are important. Therefore, these authors suggest that the NO_2^- moiety in the nitroate product is stabilized by hydrogen bonds in aqueous solutions, making it less sensitive to stabilization by substitution than the transition state. This explanation, as those mentioned above, is very qualitative. Which of the factors which determine the quantitative shape of the Brønsted plot is to be blamed for the anomaly?

Marcus[10a] sought an answer in the context of his electron-transfer theory[10b] as applied to photon-transfer reactions.[10c] The reaction is thought of as occurring in three consecutive steps.[10c,11] For the reaction of arylnitromethane with a base B^- one has



$$B^- \cdots HOH + ArCH_2NO_2 \longrightarrow B^- \cdots H\underset{\displaystyle Ar}{\underset{|}{C}}HNO_2 + H_2O \qquad (2a)$$

$$\longrightarrow BH \cdots {}^-\underset{\displaystyle Ar}{\underset{|}{C}}HNO_2 + H_2O \qquad (2b)$$

$$\rightleftarrows BH + ArCHNO_2^- \cdots HOH \qquad (2c)$$

Stage (a) is a replacement of a solvent molecule in the solvation shell of B^- by the nitroalkane. The free-energy change in this stage, conventionally called the "work term" and denoted by W_R, is composed of several effects:[12] solvent rearrangement, reagents rearrangement ("steric effects"), and a difference in hydrogen bond[13] strengths in reaction 2a. (The most significant is expected to be the replacement of the hydrogen bond between base and solvent by the (weak) hydrogen bond between base and carbon acid. Hydrogen bonds between the NO_2 and CH moieties and the solvent contribute less, because the acid is weak while the base is strong.) The reverse of stage (c) is similar to (a), with a "work term" W_P. Stage (b) is the proton-transfer step whose activation energy is G_a and standard free-energy change $\Delta G°$. Subsequently, one has for the observed equilibrium and (forward) rate constants[10]

$$K_{eq} = \exp[-(W_R + \Delta G° - W_P)/RT] \qquad (3a)$$

$$k = Z \exp[-(W_R + G_a)/RT] \qquad (3b)$$

Here Z is constant for the reaction series (usually in the range 10^{10}-$10^{11}\ M^{-1}\ s^{-1}$), and the reverse of (2a) is assumed to have a very small free-energy barrier, so that W_R can be simply added to G_a in (3b).

The dependence of G_a on $\Delta G°$ is given according to the Marcus theory[10] by

$$G_a = G_a°(1 + \Delta G°/4G_a°)^2 \qquad (4)$$

The "intrinsic barrier",[10] $G_a°$ ($G_a° = G_a(\Delta G° = 0)$) is ap-

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proximately the mean of the activation energies for the two symmetric reactions

$$B^- + HB \rightarrow BH + B^- \qquad (5a)$$

$$ArCH_2NO_2 + ArCHNO_2^- \rightarrow ArCHNO_2^- + ArCH_2NO_2 \qquad (5b)$$

If G_a° is constant for a reaction series one has normal behavior with

$$\alpha = \tfrac{1}{2}(1 + \Delta G^\circ/4G_a^\circ) \qquad (6)$$

in the range $|\Delta G^\circ| \leq 4G_a^\circ$. The abnormal α stems[10a] from a variation of G_a° with ΔG°. Because G_a° for (5b) is much larger than that of (5a), one expects a larger variation in G_a° of (2b) when the aryl group is varied, and would not expect such a large change when the base is varied. This reasoning explains why G_a° may vary with ΔG°, but not why this variation is systematic, nor why α is large in the exothermic regime and small in the endothermic regime. Also, from the above reasoning one may expect abnormal behavior also in aprotic solvents.

II. Varying Work Terms

All the explanations above search for the origin of the abnormal behavior in effects on the proton transfer stage (2b). It is the purpose of the present communication to raise the possibility that (2b) is in accord with the Hammond and Leffler postulates and that the assumption that does not hold is the constancy of W_R and W_P.[14] For a carbon acid in an aqueous solution, (2a) is expected to be endothermic, because a strong hydrogen bond is replaced by a very weak one. (At the same time the proton transfer stage (2b) is exothermic.) An electron-withdrawing substituent on the aryl group makes the carbon acid more acidic. It forms a stronger hydrogen bond, and the endothermicity of (2a) is lowered by δW_R, while the exothermicity of (2b) is increased by $\delta\Delta G^\circ$. Therefore, $\delta W_R = \gamma_R\delta\Delta G^\circ$ where $\gamma_R > 0$, and for a small ΔG° range γ_R is constant. Similarly $\delta W_P = \gamma_P\delta\Delta G^\circ$.

Denote $\alpha_b \equiv dG_a/d\Delta G^\circ$ the Brønsted slope for (2b). The observed Brønsted slope is then given by (cf. eq 1 and 3)

$$\alpha \equiv \delta \ln k/\delta \ln K_{eq} = (\delta W_R + \alpha_b\delta\Delta G^\circ)/(\delta W_R + \delta\Delta G^\circ - \delta W_P) = (\gamma_R + \alpha_b)/(\gamma_R + 1 - \gamma_P) \qquad (7)$$

For "normal" acids it was found[15a] that the values of the γ's are small (0.1-0.2), which is an experimental justification for assuming constant W's for "normal" acids and bases. This may not be the case for nitroalkanes in aqueous solutions.

From (7) it is seen that $\alpha > 1$ is obtained: (a) if γ_P is considerably larger than γ_R, even if γ_R is negligible, and (b) if both are large, even when they are comparable in magnitude. Now γ_P may be large because, unlike γ_R, it correlates proton transfer and hydrogen bond on different sites. (The proton transfer is to carbon while the hydrogen bond is to the NO_2^- moiety.) This point can be made more strongly if one accepts Bordwell's postulate[4] of a tetrahedral carbanionic intermediate, because then the carbanion formed in stage 2b and the nitroate anion of stage 2c are even different chemical entities. These conclusions are also in agreement with those of Keeffe et al.,[6] who find the cause for the anomaly in hydrogen bonds in the nitroate anions, but it is proposed here that the effect is on W_P rather than on G_a°.

Another indication of a large γ_P value can be found in the results for neutralization of $C(NO_2)_3^-$ by solvated proton in a series of ROH solvents.[15b] The linear relation of ln k with the pK which is observed in this case is not a "normal" Brønsted plot, because it has a slope of 0.8 (i.e., >0.5), although these reactions are exothermic. In this case we have the same reaction carried out in different solvents, so it is natural to put the blame on the solvent, i.e., on the work terms. Because a neutralization reaction is the reverse of a deprotonation reaction of type (2) it is (in our notation) W_P which varies linearly with ΔG°.

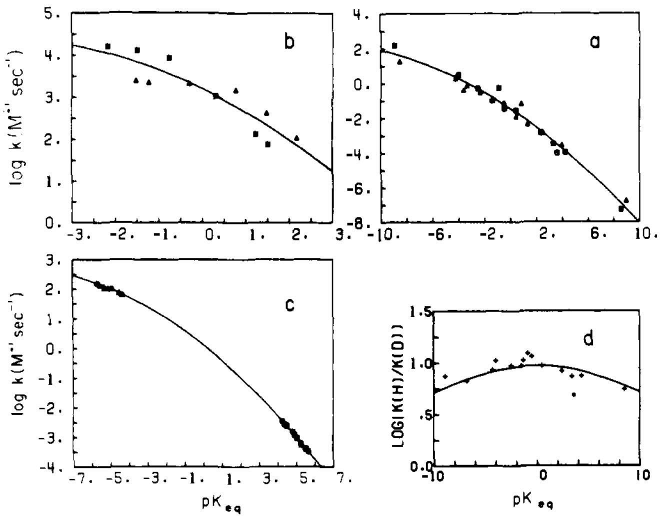

Figure 1. Brønsted plots and kinetic isotope effects for arylnitroalkanes. Rectangles and triangles represent points for forward and reverse reactions, respectively.

γ_R may be nonnegligible for very strong bases, such as OH^-, because then the proton is partially transferred already in the encounter complex, so that one may expect some influence of substitution on the Ar group, on the hydrogen bond shown on the right-hand side of (2a). This may account for the larger α values (up to 1.5) which are found for strong bases. The small rate constants observed in water are explained in this context by a large difference in hydrogen bond strength to base and nitroalkane, which results in a large W_R value.

III. The "Normal" Nitroalkanes

The cases where the variations in the work terms are small can be quantitatively analyzed. This may be achieved by a model for the free energy along the reaction coordinate,[16] which interpolates between the standard free energy of reactants, G_1°, and products, G_2° ($\Delta G^\circ \equiv G_2^\circ - G_1^\circ$). The interpolation is linear, with an additional "mixing" term M, which accounts for the existence of a barrier

$$G^\circ(n) = \sum_{i=1}^{2} n_i G_i^\circ + G_a^\circ M(n)/\ln 2 \qquad (8)$$

The bond orders, n_i, sum to unity along the reaction coordinate.[17] $n \equiv n_2$ is a measure for the extent of proton transfer. The functional form (8), even without specifying $M(n)$, suffices to show[16b-d,18] that the barrier's location $n^\ddagger$ (defined by $dG^\circ(n)/dn|_{n=n^\ddagger} = 0$) is equal to $\alpha \equiv dG^\circ(n^\ddagger)/d\Delta G^\circ$, which is the Leffler-Grunwald postulate.[2] The convexity of $M(n)$, which stems from the existence of a barrier, suffices to show[16b-d] that $dn^\ddagger/d\Delta G^\circ > 0$, which is a version of the Hammond postulate.[3] The Marcus dependence of G_a on ΔG°, eq 4, follows by choosing an inverted parabola for $M(n)$.[10c,18,19] However, better agreement with experiment[16c,d] is achieved by choosing $M(n)$ as the "mixing entropy" of the two bond orders

$$M(n) = -\sum_{i=1}^{2} n_i \ln n_i \qquad (9)$$

which gives (8) a "thermodynamic-like" form.[16a] This choice makes (8) equivalent in form to the expression derived by Marcus[10c] as an approximation to the BEBO potential profile.[17] With this choice one has

$$n^\ddagger = [1 + \exp(-\Delta G^\circ \ln 2/G_a^\circ)]^{-1} \qquad (10)$$

and

$$G_a \equiv G^\circ(n^\ddagger) - G_I^\circ = -G_a^\circ \ln(1 - n^\ddagger)/\ln 2 \quad (11)$$

The major difference between (11) and (4) is in the asymptotic region $|\Delta G^\circ| > 4G_a^\circ$, where by (10) $\alpha \rightarrow 0$ as $\Delta G^\circ \rightarrow -\infty$ and $\alpha \rightarrow 1$ as $\Delta G^\circ \rightarrow +\infty$. This behavior is in agreement with results for gas-phase Brønsted series[16c] and correlations of potential barrier heights,[16a,c] as well as for transfer reactions in solution (e.g., electron and proton transfers, nucleophilic substitutions).[16d] Agreement with (11) is so frequently observed that it well deserves the term "normal" behavior.

Figure 1a shows a fit by (11) and (3b) to the ionization of $PhCH_2NO_2$ by various bases in water[5] (excluding the deviating points for morpholine and piperidine). The points for the reverse reactions have been added to the correlation, because they should belong to the same reaction series (the reaction with $pK_{eq} = 0$ has the same rate in both directions, therefore the same intrinsic barrier, G_a°). Z is taken to be $10^{10.2}$ M^{-1} s^{-1} throughout. $W_R = 9.1$ kcal/mol. $G_a^\circ = 6.8$ kcal/mol is large (relative to the ΔG° range), therefore the curvature

$$d^2G_a/d\Delta G^{\circ 2} = dn^\ddagger/d\Delta G^\circ = n^\ddagger(1 - n^\ddagger) \ln 2/G_a^\circ \quad (12)$$

is small, and the plot appears nearly linear. This is not a failure[4] of the Leffler-Hammond postulates. The transition from $\alpha = 0$ to $\alpha = 1$ only takes place for a large ΔG° range. In fact, because G_a° is determined from the curvature, it is hard here to divide the overall activation energy into its two contributions, W_R and G_a°. In such a case, the kinetic isotope effects can help. On the assumption that W_R does not change by the isotopic substitution

$$k^H/k^D = \exp[-(G_a^H - G_a^D)/RT] \quad (13)$$

depends only on the two intrinsic barriers $G_a^{\circ H}$ and $G_a^{\circ D}$ (the superscripts H and D denote hydrogen and deuterium, respectively). Their magnitude again determines the curvature (which is smaller for larger G_a°), while their difference, $G_a^{\circ D} - G_a^{\circ H}$, determines the height at the maximum. This maximum is at the symmetric, $\Delta G^\circ = 0$, reaction, in accordance with Westheimer's prediction.[20] (In order that there is a maximum, the condition $G_a^{\circ D} > G_a^{\circ H}$ must hold, which is mostly the case because of the lower ZPE for deuterium.)

Figure 1d is a fit to the kinetic isotope effects[5] for the reaction series of Figure 1a, subject to the approximation that ΔG° is the same for hydrogen and deuterium. $G_a^{\circ H} = 6.4$ kcal/mol is similar to its value from Figure 1a, and $G_a^{\circ D} = 7.7$ kcal/mol. (The uncertainty in the parameters cited here is 0.2-1.0 kcal/mol.) A fit for the kinetic isotope effects in ionization of various arylnitroalkanes[4b] gave[16a] $G_a^{\circ H} = 6.3$ and $G_a^{\circ D} = 7.6$ kcal/mol, in agreement with the values cited above.

Figure 1b shows a fit for the ionization of arylnitromethanes in Me_2SO.[6] If the results are interpreted as in the original paper,[6] by a straight line with a slope $\alpha = 0.92$, they are certainly not a normal Brønsted plot, because the ΔG° range extends from the $\Delta G^\circ > 0$ into the $\Delta G^\circ < 0$ regime, where $\alpha > 0.5$ is expected. This interpretation, however, is based on a single point for the 3,5-dinitro compound, while two points (p-CN and p-NO_2) show negative deviations. It is possible to suggest an alternative interpretation by omitting the 3,5-dinitro compound,[21] and passing a curved plot through all other points, as done in Figure 1b. This yields $W_R = 7.7$ kcal/mol (the difference of 1.4 kcal/mol from the value in aqueous solution may be attributed to the difference in the hydrogen bond strength[22]) and $G_a^\circ = 2.2$ kcal/mol (a value more typical for "normal" oxygen and nitrogen acids in water). This agrees with other results showing that proton transfers from carbon acids to oxygen bases are faster in Me_2SO than in methanol and their Bronsted plot is more curved.[23]

It can be seen from Figure 1b that the forward and reverse rate constants do not form one smooth curve,[24] indicating perhaps that one is still not witnessing an elementary reaction step, and that also in nonaqueous solutions there are complications from the solvent (e.g., $W_R \neq W_P$).

Figure 1c shows a fit to the Brønsted plot of ionization of $ArCH(NO_2)_2$ in water[7] (except for ortho and disubstitutions, which deviate; the disubstitutions deviated also from the curve shown in Figure 1b). As mentioned above, the seemingly "normal" behavior in this case is in contrast with that discussed in section II. This may be rationalized in terms of (the lack of) hydrogen bonds to NO_2^-. The additional NO_2 either helps to disperse the negative charge effectively enough, or its steric hindrance with the other nitro group prevents these groups from being in a fully coplanar configuration with the central carbon atom, so that their resonance interaction with the negative charge is not fully developed.[25] In both cases hydrogen bond to the NO_2^- groups is not expected to be as important in stabilizing the negative charge as in the case of $ArCH_2NO_2$, so that γ_P should be smaller. The best values for the parameters in the fit are $W_R = 9.0$ and $G_a^\circ = 4.5$ kcal/mol. This is in some contrast to our expectation of a smaller W_R value in this case where hydrogen bonds are less important. However, the small pK_{eq} region for the experimental results does not allow us to determine these parameters with great certainty. It may be that G_a° is larger (e.g., the same as for $ArCH_2NO_2$) while W_R is indeed smaller.

IV. Summary

Relatively "normal" Brønsted plots for nitroalkanes are observed in cases where variations in hydrogen bond strength are not expected to play a major role: when the reactions are carried out in H_2O, but only the base is varied; when the nitroalkane is varied, but the reaction is carried out in nonaqueous solutions; for $ArCH(NO_2)_2$. These "normal" Brønsted plots fit the quantitative structure-reactivity relation (11). The abnormal Brønsted plots are observed in cases where the variations in hydrogen bonds are expected to be significant (varying the nitroalkane in aqueous solutions). It is proposed that in these cases the work terms may change with ΔG°, and that this accounts for the abnormal Brønsted slopes, while the elementary proton transfer event itself is "normal". There still remains to check experimentally the values of γ_R and γ_P for nitroalkanes, to see whether the abnormal slopes can be quantitatively calculated from (7).

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References and Notes

(1) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Chapman and Hall: London, 1973. Caldin, E., Gold V., Eds. "Proton Transfer Reactions"; Chapman and Hall: London, 1975. Bamford, C. H., Tipper, C. F. H., Eds. "Comprehensive Chemical Kinetics", Vol. 8; Elsevier: Amsterdam, 1977. Kresge, A. J. *Chem. Soc. Rev.* **1973,** *2*, 475–503.

(2) Leffler, J. E. *Science* **1953,** *117*, 340–341. Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963.

(3) Hammond, G. S. *J. Am. Chem. Soc.* **1955,** *77*, 334–338.

(4) (a) Bordwell, F. G.; Boyle, W. J., Jr.; Hautala, J. A.; Yee, K. C. *J. Am. Chem. Soc.* **1969,** *91*, 4002–4003. Bordwell, F. G.; Boyle, W. J., Jr.; Yee, K. C. *Ibid.* **1970,** *92*, 5926–5932. Bordwell, F. G.; Boyle, W. J., Jr. *Ibid.* **1972,** *94*, 3907–3911. Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978,** *43*, 3107–3113. (b) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1975,** *97*, 3447–3452.

(5) Keeffe, J. R.; Munderloh, N. H. *J. Chem. Soc., Chem. Commun.* **1974,** 17–18.

(6) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979,** *101*, 1295–1297.

(7) Dronov, V. N.; Tselinskii, I. V.; Shokhor, I. N. *Org. React.* (*Engl. Transl.*) **1969,** *6*, 408–412.

(8) Kresge, A. J. *J. Am. Chem. Soc.* **1970,** *92*, 3210–3211. *Can. J. Chem.* **1974,** *52*, 1897–1903.

(9) Okuyama, T.; Ikenouchi, Y.; Fueno, T. *J. Am. Chem. Soc.* **1978,** *100*, 6162–6166.

(10) (a) Marcus, R. A. *J. Am. Chem. Soc.* **1969,** *91*, 7224–7225. (b) In "Special

Topics in Electrochemistry", Rock, P. A., Ed.; Elsevier: Amsterdam, 1977; pp 161-224, and references cited therein. (c) *J. Phys. Chem.* **1968**, *72*, 891-899; *Faraday Symp. Chem. Soc.* **1975**, *10*, 60-68. Cohen, A. O.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249-4254.

(11) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1963**, *3*, 1-19.

(12) Kreevoy, M. M.; Konasewich, D. E. *Adv. Chem. Phys.* **1971**, *21*, 243-252. Hassid, A. I.; Kreevoy, M. M.; Liang, T. M. *Faraday Symp. Chem. Soc.* **1975**, *10*, 69-77.

(13) Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1961. Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974. Shuster, P., Zundel, G., Sandorfy, C., Eds. "The Hydrogen Bond"; North-Holland Publishing Co.: Amsterdam, 1976.

(14) Some implications of nonconstant work terms are discussed: Albery, W. J.; Campbell-Crawford, A. N.; Curran, J. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2206-2214.

(15) (a) Arnett, E. M.; Mitchell, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 4052-4053. Taft, R. W.; Gurka, D.; Joris, P.; Schleyer, P. von R.; Rakshys, J. W. *Ibid.* **1969**, *91*, 4801-4808. (b) Chaudhri, S. A.; Asmus, K. D. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 385-392, 1010-1016.

(16) (a) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197-201. (b) Levine, R. D. *J. Phys. Chem.* **1979**, *83*, 159-170. (c) Agmon, N.; Levine, R. D., *Isr. J. Chem.*, in press. (d) Agmon, N. In "Lectures on Biological and Chemical Physics, a Symposium in Honour of S. Lifson, July 1979".

(17) (a) Johnston, H. S. *Adv. Chem. Phys.* **1960**, *3*, 131-170. Johnston, H. S.; Parr, C. A. *J. Am. Chem. Soc.* **1963**, *85*, 2544-2551. (b) Johnston, H. S. "Gas Phase Reaction Rate Theory"; Ronald Press: New York, 1966.

(18) Kurz, J. L. *Chem. Phys. Lett.* **1978**, *57*, 243-246.

(19) Agmon, N. *J. Chem. Soc., Faraday Trans. 2*, **1978**, *74*, 388-404.

(20) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265-273.

(21) It is strange that this compound has the same pK_a as the *p*-NO$_2$ compound. A Hammett σ^- or σ correlation would suggest a pK_a value 1-2 units smaller. The disubstituted compound deviates also for ArCH(NO$_2$)$_2$.[7]

(22) This may not be exactly so, because other factors in W_R may vary with the solvent.

(23) Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 3415-3418.

(24) Yet, on the average, the curved correlation is better than the linear one also when points for reverse reactions are added.

(25) Remark made by the referee.

Studies on Monolayers. 1. Surface Tension and Absorption Spectroscopic Measurements of Monolayers of Surface-Active Azo and Stilbene Dyes

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Abstract: In order to develop new molecules as functional components of monolayer assemblies a series of nine surface-active azo and stilbene compounds are synthesized. Their monolayer properties at the air-water interface are studied by surface pressure-surface area measurements and spectroscopic techniques. The results show that small changes in the molecular structure of the surfactants (such as, e.g., length of the fatty acid chain, type of the chromophore) have an immense influence on the monolayer properties. For monolayers of compounds I and III-VIII, van der Waals-like isotherms are obtained, which show a liquid expanded state, a phase transition region, and a condensed state. From monolayer absorbance spectra it is found that in the liquid expanded state at 100-110 Å^2/molecule the chromophores lie flatly on the water surface, forming monomers. As concluded from surface absorbance-surface area isotherms the phase transition region of the isotherms can be assigned to a change of orientation of the chromophore axis (horizontal → vertical) and an aggregation process of the chromophores (monomers → H aggregates). High dichroic and narrow absorbance bands are observed for condensed films of dyes VI and IX, which are assigned to H aggregates (planar pincushion-like arrangement of the chromophores). By means of molecular CPK models several molecular arrangements are discussed which are consistent with the experimental results.

Introduction

In the last few years there has been an increasing interest in the use of surface-active dyes to study properties of biological and artificial membranes and to construct monomolecular systems by self-organization.[1-6] The majority of dye molecules used for this field consists of hydrophilic chromophores, which are convalently bound to long-chain paraffins. When these dyes are incorporated into lamellar systems, it is found that the paraffin chains stand perpendicularly on the plane of the layer while the chromophores lie flat near the hydrophilic interface. It would be desirable to realize monolayer assemblies with chromophores of which the molecular long axis is oriented perpendicular to the plane of the layer. Chromophores in this arrangement should be useful as dye probes for biomembrane research, e.g., as transmembrane electric field indicators and as functional components of monolayer assemblies. For this reason the surface-active dyes I-IX were synthesized and their surface-active behavior at the air-water interface was studied by determining surface pressure-area isotherms and linearly polarized absorption spectra. Several points which lead to the design of these molecules should be mentioned.

(1) In order to possess lipid properties, the chromophore should be attached to a lipid, e.g., fatty acid or monoglyceride.

(2) The chromophore must be sufficiently hydrophobic in order to be lifted up easily from the water surface at relatively low surface pressures.

(3) The chromophore must be almost as long as the lipid backbone to reduce environmental perturbation in the lamellar system.

(4) The absorption and the emission spectra of the chromophores should depend on the polarity of their environment.

(5) In the visible region of light there should be a strong π-π transition, the polarization of which, in relation to the geometry of the molecule, must be known.

The azo and stilbene chromophores, described here, satisfy these criteria.[7]

Experimental Section

General. Melting points were obtained on a Mettler FP2 apparatus and are uncorrected. Elemental analyses were performed by Microlab. Beller, Göttingen. For column chromatography silica gel 60 (Merck, Darmstadt) was used. Mass spectra were recorded on a Varian MAT 311. NMR spectra were determined in CDCl$_3$ solutions with tetramethylsilane as a reference on a Bruker WH 270. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; br, broad and no line separation, respectively.

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