The Rearrangement of Molecules in Monomolecular Films: Polycyclic Compounds of the Five Ring Series

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LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Rearrangement of Molecules in Monomolecular Films: Polycyclic Compounds of the Five Ring Series

Monomolecular films of certain compounds whose molecules contain five benzene rings have been found to exhibit a remarkable phenomenon; that is, a rapid rearrangement of the molecules occurs in the film in such a way that the pressure almost entirely disappears. Thus with betuline the initial or immediate pressure at a molecular area of 24.5 sq. A is 17 dynes per cm while after this there is at this area an almost exponential fall of pressure with time to a practically constant value, in 30 seconds, of 1.0 dyne. Nevertheless a rapid compression to 33.5 sq. A, or by about 1/34 of the area, increases the pressure by 21 times to 21 dynes, or to 4 dynes more than the previous initial compression. At an area of 28 sq. A the initial pressure of 40 dynes falls to 5.5 dynes in 30 seconds, but on rapid compression to 26.2 sq. A rises to 50 dynes per cm.

At a pressure adjusted every 5 minutes to 16 dynes the area decreased in an hour by 18 percent, but by only about a fourth of this at 1.0 dyne. If the pressure is adjusted to constancy more frequently the area decreases more rapidly. Fig. 1 gives the values of the film pressures and surface potentials of betuline (polar groups Ring I at positions 2 and 3) and oleanolic acid (I, 3 and V, IV, 17), and Fig. 2 of the isomers sumaresinolic and siaresinolic acid (positions I, 2, 3 and V, IV, 17). The substances β-amyrine or vitamin E (position I, 2) and betuline diacelate (I, 2, 3) do not exhibit this rearrangement except at the highest pressures (Fig. 3).

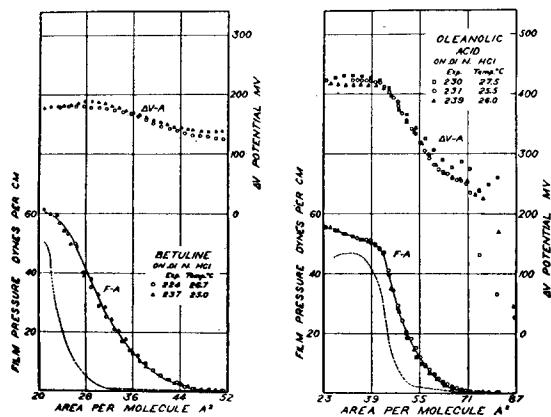In the figures the unbroken lines give the initial values and the dotted lines the values obtained after the rearrangement. The experimental points for these values lie very closely on the dotted lines. In order to show just how closely the initial values for different experiments lie on a single curve, the experimental values for these curves are represented by points. To obtain these points one worker compressed the film by a definite decrease of area which depended upon the slope of the curve, while the other, by turning the torsion head of the balance, kept the float and thus the beam of light in a constant position until just the moment when the compression was completed.

The molecular areas obtained for all of the substances are about what would be expected from their structure except in the case of betuline, which gives abnormally low areas, below 37 sq. A, not only for the final state but even for the initial state of the film at pressures above ten dynes. Mr. Robert T. Florence is beginning a study of this problem by various optical means, including the use of the ultramicroscope and the effects of the film on polarized light.

Of the relations exhibited by the surface potential (ΔV) the most remarkable is the difference shown by the two isomers. Thus sumaresinolic acid exhibits a maximum value of 400 mv while siaresinolic acid gives the very high value of 615 mv.

The values of $m = \Delta V/n$, where n is the number of molecules in the film per sq. cm are related to the dipole moments (u) of the molecules in the film in an unknown way; but in general m increases with u. The values of u for the

FIG. 1. Film pressures and potentials. The unbroken line gives the initial pressure, and the dotted line the pressure thirty seconds later.
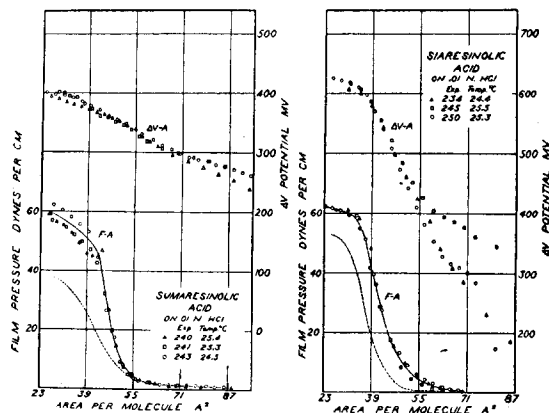

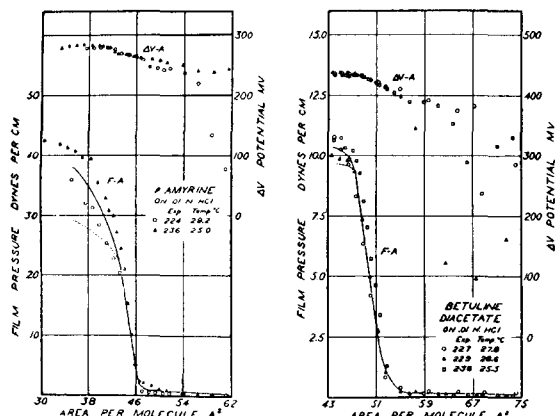FIG. 2. Film pressures and potential for two isomers.

FIG. 3. Film pressures and potentials for vitamin E and betuline diacetate.

film as given by investigators in England are not dipole moments at all, but only values of $m/4\pi$. In units of 10^{-18} e.s.u. per molecule the maximum values of m are approximately 2.2 for betuline, 2.1 for amyrine, 6.0 for oleanic acid, 6.8 for sumaresinolic acid, 7.5 for betuline diaceto and 7.8 for siaresinolic acid. These values are much higher than those given by films of fatty acids, alcohols, etc., which lie in general between 2 and 3 when the number of carbon atoms is between 12 and 18.

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        February 11, 1936.

The Infrared Absorption Spectrum of HDS and D_2S

The infrared absorption spectrum of the molecules HDS and D_2S has been investigated between 1.5μ and 12.0μ, by using a prism spectrometer of the Wadsworth type, with the result that several vibration-rotation bands characteristic of each were found. The two samples of gas studied were prepared with D_2O of two different purities. The HDS was made by dropping 55 percent D_2O on chemically pure aluminum sulfide, and the D_2S was made by dropping 99.2 percent D_2O on aluminum sulfide, in each case being very careful to trap out any "heavy water" vapor. The purity of the samples was thus assured. The cell of HDS contained, of course, some H_2S, and some D_2S also, and all the previously known bands of H_2S [1] were found in its spectrum in addition to the new ones. The purity of the D_2S could not be doubted and the bands found were attributed to it alone.

The positions of the bands found in D_2S are as follows: 3.65μ, 4.55μ, and 10.8μ. Two of these regions have been studied with a prism-grating spectrometer with the result that their rotational structure has been very completely resolved. The band at 3.65μ appears to be of the P, Q, R type with a very broad and partially resolved Q branch.

The band at 10.8μ has also been resolved, but it does not have a Q branch and is probably more nearly the doublet type.

In HDS none of the bands have as yet been studied with the grating and resolved. The positions of the bands given by the prism data are: 2.1μ, 3.15μ, 4.1μ, 9.0μ. By combining these new bands with the ones already known in H_2S in a table it can be seen how the bands corresponding in HDS, and D_2S are shifted toward longer wave-lengths in the anticipated manner.

TABLE I.

H_2S	HDS	D_2S
1.9μ	2.1μ	—
2.65	3.15	3.65μ
3.70	4.1	4.55
7.9	9.0	10.8

The grating measurements on the remaining bands have been begun and will be reported in this journal in the near future. We wish to express our appreciation to Professor H. L. Johnston of the Chemistry Department of Ohio State University, for his kind cooperation in furnishing us with the quantities of "heavy water" used in making the samples of gas.

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        January 22, 1936.

[1] Rollefsen, Phys. Rev. **34**, 604 (1929); Nielsen, ibid. **37**, 727 (1931).
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On Some Gas-Kinetic Properties of Light and Heavy Hydrogen

The knowledge of certain gas-kinetic quantities as the coefficients of viscosity, of thermal conductivity and diffusion which are mutually interrelated has become of considerable importance, particularly since their measurement has been used for the determination of the concentration of the *ortho* and *para* modifications in the case of the two hydrogens. We have therefore closely investigated the influence of the statistical weights of the various molecules on these coefficients. It thereby turned out for example, that in the neighborhood of $70°K$, the coefficient of viscosity of pure parahydrogen should be approximately six percent smaller than that of ordinary hydrogen. This difference decreases at lower and higher temperatures, but is expected to increase again when the temperature becomes extremely low. A corresponding effect for deuterium should be vanishingly small. The calculations have been made on the basis of the rigid sphere model and the numbers given might therefore still depend on the actual force of interaction between the molecules. We shall later on report in more detail on the application of the theory to other gas-kinetic quantities and to other gases.

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        February 3, 1936.