TABLE I

CLEAVAGE OF N-HETEROCYCLIC ETHERS BY ACIDS

| Ether | Acid | *p*Ka | Reaction temp., °C. | Time, hours | Products, % | Recovery of starting materials, % |
|---|---|---|---|---|---|---|
| 2-Ethoxyquinoline[a] | Thiophenol[b] | 7.78[c] | 170 | 48 | 2-Hydroxyquinoline,[d] 68<br>Ethyl phenyl sulfide,[e] 53 | |
| 2-Ethoxyquinoline[a] | β-Naphthol | 9.68[f] | 250 | 48 | | 2-Ethoxyquinoline,[g] 53 |
| 2-Ethoxyquinoline[a] | Phenol | 9.95[h] | 180 | 49 | | 2-Ethoxyquinoline,[g] 63 |
| 2-Ethoxybenzothiazole[i] | Barbituric acid | 4.0[j] | 100 | 28 | | Barbituric acid,[d] 95<br>2-Ethoxybenzothiazole,[k] 64 |
| 2-Ethoxybenzothiazole[i] | Benzoic acid | 4.2[j] | 170 | 24 | 2-Hydroxybenzothiazole,[d] 85<br>Ethyl benzoate,[l] 77 | |
| 2-Ethoxybenzothiazole[i] | Acetic acid | 4.76[m] | 118 | 24 | 2-Hydroxybenzothiazole,[d] 36<br>Ethyl acetate (trace) | |
| 2-Ethoxybenzothiazole[i] | *p*-Nitrophenol | 7.14[h] | 170 | 26 | | No recovery[n] |
| 2-Ethoxybenzothiazole[i] | β-Naphthol | 9.68[f] | 100 | 22 | | β-Naphthol,[d] 81<br>2-Ethoxybenzothiazole,[k] 81 |
| 2-Ethoxybenzothiazole[i] | Fluorene | 25[o] | 158 | 18.5 | | Fluorene,[d] 79<br>2-Ethoxybenzothiazole,[k] 51 |
| 2-Ethoxybenzothiazole[i] | 1,3-Diphenyl-1,3-propanedione | | 100 | 25 | | 1,3-Diphenyl-1,3-propanedione,[d] 89<br>2-Ethoxybenzothiazole,[k] 54 |
| 2-Benzyloxybenzothiazole[i] | Benzoic acid | 4.2[j] | 143 | 20 | 2-Hydroxybenzothiazole,[d] 64<br>Benzyl benzoate (trace) | |
| 2-Benzyloxybenzothiazole[i] | Acetic acid | 4.76[m] | 100 | 22 | 2-Hydroxybenzothiazole,[d] 26<br>Benzyl acetate,[p] 32 | |
| 2-Benzyloxybenzothiazole[i] | *p*-Nitrophenol | 7.14[h] | 100 | 24 | | 2-Benzyloxybenzothiazole,[d] 23<br>*p*-Nitrophenol,[d] 96 |
| 2-Benzyloxybenzothiazole[i] | *p*-Thiocresol | 8.07[c] | 105 | 15 | 2-Hydroxybenzothiazole,[d] 66<br>Benzyl *p*-tolyl sulfide,[d] 47 | |
| 2-Benzyloxybenzothiazole[i] | β-Naphthol | 9.68[f] | 100 | 72 | | No recovery |
| 2-Benzyloxybenzothiazole[i] | *p*-Cresol | 11.61[c] | 105 | 27 | | 2-Benzyloxybenzothiazole,[d] 93 |

[a] See ref. 5. [b] Included as a reference reaction. See Ref. 1. [c] Measured in 48.9% alcohol by G. Schwarzenback and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939). [d] Identified by mixed m.p. [e] B.p. 202–204° at 743 mm. [f] J. Eisenbrand, *Z. physik. Chem.*, **A144**, 441 (1929). [g] Identified by b.p. 264-266° at 745 mm. [h] C. M. Judson and M. Kilpatrick, THIS JOURNAL, **71**, 3110 (1949). [i] Preparation is given in experimental. [j] Calculated from value of $K_a$ given in Lange, "Handbook of Chemistry," 5th Ed., Handbook Publishers, Inc., Sandusky, O., 1944, p. 1396. [k] B.p. 88–89° at 0.5 mm. [l] Identified by saponification. [m] D. A. MacInnes and T. Shedlovksy, THIS JOURNAL, **54**, 1429 (1932). [n] A small amount of a viscous red liquid, which was not identified, was obtained. [o] W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936). [p] B.p. 211-212° at 745 mm. $n^{14}$D 1.5016 (lit. value, $n^{18}$D 1.5057).

by filtration, washed with ether or petroleum ether (b.p. 65–70°), and identified by the method of mixed m.p. The filtrate or the liquid reaction mixture was diluted with ether or petroleum ether (b.p. 65–70°) and extracted with 5% sodium hydroxide to remove unreacted acid. The alkali extraction was omitted in the acetic acid and fluorene reactions and was replaced by saturated sodium bicarbonate solution in the benzoic acid reactions. The ether-soluble fraction containing the cleavage products (alkyl derivatives of the acidic reagents) or unreacted heterocyclic ether was dried over calcium sulfate. After removal of the solvent, the liquid products and unreacted starting materials were vacuum distilled and identified by b.p. and refractive index. Solids remaining after removal of the solvent were identified by the method of mixed m.p. after recrystallization from a suitable solvent. In Table I we have listed the pertinent data for all experiments.

**2-Ethoxybenzothiazole.**—Since the only published preparative method for this compound[5] lacks experimental detail, our procedure will be described.

A solution of sodium ethoxide in ethanol was prepared from 11.5 g. (0.5 g. atom)[6] of sodium and 500 ml. of absolute ethanol and cooled in an ice–salt-bath at 0°. To this 84.6 g. (0.5 mole) of 2-chlorobenzothiazole was added dropwise over a period of ten minutes. After the addition was complete, the resulting yellow suspension was refluxed 30 minutes, during which the color turned white. The excess ethanol was removed at room temperature under reduced pressure. Sufficient water and ether were added to dissolve the solid residue and to obtain distinct phase separation. The ether layer was removed, and the aqueous layer was extracted with several portions of ether. After removal of the ether from the combined extracts under reduced pressure the residue was distilled under vacuum to give 79.1 g. (93%) of a liquid (b.p. 80–81° at 0.2 mm.).

**2-Benzyloxybenzothiazole.**—A solution of sodium benzyloxide was prepared from 4.6 g. (0.2 g. atom)[7] of sodium and 150 ml. of benzyl alcohol and cooled in an ice–salt-bath to 0°. To this vigorously stirred solution was added dropwise 33.9 g. (0.2 mole) of 2-chlorobenzothiazole. At the end of the addition the mixture was allowed to warm to room temperature, and the stirring was continued for two hours longer. At the end of this period the reaction flask was heated to 30° under a pressure of 0.5 micron in order to remove the excess benzyl alcohol. The white residue was then dissolved in 250 ml. of ether and 150 ml. of water. The aqueous layer was extracted with ether, and the combined ether extracts were dried over calcium sulfate. Removal of the ether under vacuum at room temperature yielded 43.8 g. (91%) of a white solid which melted sharply at 64.5–65°, unchanged after two recrystallizations from petroleum ether (b.p. 68–75°).

*Anal.* Calcd. for $C_{14}H_{11}ONS$: S, 13.28. Found: S, 13.23.

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(5) A. W. Hofmann, *Ber.*, **13**, 8 (1880).

(6) With equimolar quantities of sodium ethoxide and 2-chlorobenzothiazole yields of 90% or more were consistently obtained; with 50% excess sodium ethoxide, the yields dropped to 55–60%.

(7) The use of equimolar quantities of sodium benzyloxide and the 2-chloro compound and the avoidance of temperatures greater than 50° are essential. When the preparation was attempted with a 10% excess of sodium benzyloxide at 120° described for the preparation of 2-benzyloxyquinoline (ref. 1) only side reaction products (to be reported later) were obtained.

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## On Multilayer Adsorption

BY G. D. HALSEY, JR.

The empirical isotherm

$$p/p_0 = \exp. a/RT\Theta^r \qquad (1)$$

where $\Theta$ is coverage in monolayers, $p$ is pressure and

$p_0$ saturation pressure, is remarkably successful if $r = 2.5$. In a recent paper[1] the author showed that with appropriate assumptions, van der Waals' forces decaying with the third power of distance result in the value of $r = 2.5$ in equation (1), from $\Theta = 1$ to 10. As W. K. Hall[2] has pointed out, one of these assumptions implies that surface heterogeneity extends indefinitely into the bulk of the adsorbent.

If heterogeneity is confined to the surface layer of the adsorbent, the leading term in the London forces from this layer declines with the fourth power of distance. It would appear at first sight that equation 13 of reference (1) would be replaced by the isotherm

$$\Theta = \exp\{+\Delta E_0/\Delta E_\mathrm{m}\} \sum_{n=1}^{\infty} z^{n4} \qquad (2)$$

where

$$z = (p/p_0)^{RT/\Delta E_\mathrm{m}}$$

However, this is not the case. The influence of the London forces from inside, considered now as homogeneous and decaying with the third power of distance, will be added to a heterogeneous contribution from the surface which decays with the fourth power of distance. Thus the condensation pressure is given by

$$-RT \ln (p/p_0) = \Delta E_\mathrm{B}/n^3 + \Delta E/n^4 \qquad (3)$$

where $n$ is the distance in adsorbate diameters from the surface, $\Delta E_\mathrm{B}/n^3$ the bulk term and $\Delta E/n^4$ the (variable) surface term.

In any layer $n$ the sites are covered up to the value of $\Delta E$ satisfying eq. 3. If $N_1(\Delta E)$ is the distribution function for $\Delta E$ in the first layer the distribution function in layer $n$ is $N_1(\Delta E/n^3)$. Therefore the coverage in the $n$th layer is

$$\Theta_{(\mathrm{n})} = \int_{\Delta E}^{\infty} N_1(\Delta E)\mathrm{d}\Delta E \qquad (4)$$

Substitution of $\Delta E$ from (3) as the lower limit in (4) yields

$$\Theta_{(\mathrm{n})} = \int_{-n^4 RT \ln (p/p_0) - n\Delta E_\mathrm{B}}^{\infty} N_1(\Delta E)\mathrm{d}\Delta E \qquad (5)$$

Insertion of the exponential distribution

$$N_1(\Delta E) = (1/\Delta E_\mathrm{m}) \exp\{-\Delta E/\Delta E_\mathrm{m}\} \qquad (6)$$

and integration gives

$$\Theta_{(\mathrm{n})} = \exp\{n\Delta E_\mathrm{B}/\Delta E_m\} z^{n4} = (A z^{n3})^n \qquad (7)$$

when $A$ is a constant.

This expression reaches unity before $z = 1$, reflecting the fact that the bulk force $\Delta E_\mathrm{B}$ does not vary over the surface. Thus

$$\Theta = \sum \Theta_{(\mathrm{n})} = \sum_{n=1}^{\infty} (A z^{n3})^n \qquad (8)$$

with the condition that unity is substituted for any term greater than unity in the sum.

With a value of $\Delta E_\mathrm{B}/\Delta E_\mathrm{m}$ of between $^1/_4$ and 1, (8) gives good isotherms with a "point B" at $\Theta = 1$. Larger values of this ratio give steps and smaller values cause "point B" to vary with temperature. If $\Delta E_\mathrm{B}/\Delta E_\mathrm{m} = 0$ (8) reduces to (2). However such an eventuality is prevented by the definite theoretical estimate of London forces, from the bulk of the crystal, which are roughly adequate to explain adsorption by themselves.[3]

When plotted according to equation (1) these isotherms yield $r = 3.0$ from $\Theta = 1$ to 10. Equation (2) gives $r = 3.3$. Therefore, neither of these treatments removes the difficulty of smaller experimental values of $r$.

We thus clarify assumption 1 of reference (1); the heterogeneity persists to a depth comparable with $\Theta$; however, the (mathematical) origin of van der Waals forces remains at one diameter below the first layer, making the treatment correct as it stands. Hall's observation makes it clear, however, that the type of heterogeneity postulated is not that of "active points" in the surface layer. Rather than that, it is suggested that different faces of polycrystalline nature combine in various ways to produce heterogeneity.[4]

If we follow the suggestion of Hill,[5] and introduce a repulsive term $-\Delta E_\mathrm{R}/n^s$ that is constant over the surface, equation (3) becomes

$$-RT \ln p/p_0 = \Delta E_\mathrm{B}/n^3 - \Delta E_\mathrm{R}/n^s + \Delta E/n^4 \qquad (9)$$

We then find

$$\Theta_{(\mathrm{n})} = \{\exp -\Delta E_\mathrm{R}/n^{s-4}\Delta E_\mathrm{m}\}(A z^{n3})^n \qquad (10)$$

which in the case $s = 4$ differs from (7) only by a normalization factor.

If the repulsive term is included in the treatment of ref. (1) we have

$$-RT \ln p/p_0 = -\Delta E_\mathrm{R}/n^s + \Delta E/n^3 \qquad (11)$$

leading to

$$\Theta_{(\mathrm{n})} = \text{const.} \times \exp\{-\Delta E_\mathrm{R}/n^{s-3}\,\Delta E_\mathrm{m}\} z^{n3} \qquad (12)$$

The value of $s$ is presumably greater than 4; even with this value the effect of $\Delta E_\mathrm{R}$ dies out rapidly without affecting $r$ except over one or two layers. An increase in $\Delta E_\mathrm{R}$ causes "point B" to shift to $\Theta = n > 1$. This behavior has been suggested to explain the "anomalous" density of helium films,[6] with "point B" at $\Theta = 2$ or 3.

We may point out that the isotherm of reference (1) must eventually approach a value of $r = 3$ as $\Theta$ increases indefinitely. Thus for large $\Theta$

$$\Theta = \sum_{n=1}^{\infty} z^{n3} \approx \int_0^{\infty} z^{n3}\,\mathrm{d}n = \frac{1}{3}\frac{\Gamma(^1/_3)}{(-\log z)^{1/3}} \qquad (13)$$

giving $r = 3$ in equation (1). The same is true of equation (12) when summed for all $n$.

This result is generally true of any isotherm that takes proper account of the leading term in the London expansion at large distances. It is not true of equation (2) which approaches $r = 4$, and thus is incorrect.

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[1] G. D. Halsey, THIS JOURNAL, **73**, 2693 (1951).

[2] W. K. Hall, *ibid.*, **74**, 1081 (1952)

[3] R. H. Fowler, "Statistical Mechanics," Cambridge University Press, 1936, p. 335.

[4] G. D. Halsey, "Advances in Catalysis," Volume IV, in press.

[5] T. L. Hill, *J. Chem. Phys.*, **17**, 590 (1949).

[6] J. G. Aston and S. V. R. Mastrangelo, *ibid.*, **19**, 1067 (1951).