eventually become linear. A long oxidation at 170° is shown in Fig. 4. The initially parabolic oxidation became more rapid than parabolic after 100 minutes.

Thus there is some evidence in favor of the film-cracking hypothesis. Further investigation should be made to test it.

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On Halsey's New Multilayer Adsorption Equation

BY W. KEITH HALL

In a recent paper,[1] Halsey derived a multilayer isotherm involving the following assumptions: (1) The source of the van der Waals energy, ΔE, has its origin one adsorbate diameter below the center of the first adsorbed layer. (2) ΔE decays with the third power of the distance from the surface. (3) Regions of equal ΔE are localized into large enough patches so that edge effects may be neglected.

The first two of these assumptions are incompatible. The r^{-3} law for van der Waals attractive energy near a surface arises from the r^{-6} law for two isolated atoms or molecules by integrating over the entire volume of the solid, treating it as a continuous medium.[2] In surface chemistry it is usually assumed that the surface "sites" have considerably greater attractive energy than the underlying layers and, if this is the case, the attractive energy could be closely approximated by integration over the surface layer only. This, however, leads to an r^{-4} law. Halsey's use of the r^{-3} law implies that each layer of atoms in the solid has the same attractive power as the surface layer, *i.e.*, the patches of constant energy are piers extending into the solid to a considerable depth. This is in contradiction to assumption (1).

Use of the r^{-4} law would make very little difference in the derivation of Halsey's equation (13), which will become

$$\theta = \exp\{+\Delta E_0/\Delta E_m\} \sum_{n=1}^{\infty} Z^{n^4} \qquad (13')$$

The series will converge more rapidly, and so the shape of the calculated isotherms, for a given set of parameters, will be somewhat changed in the direction of greater steepness as the liquefaction pressure is approached. The flat portions will become visible at the same relative pressures, but will extend over a greater pressure range and appear at higher values of $\exp\{-\Delta E_0/\Delta E_m\}$.

Alternatively, use of the r^{-3} law requires that one have an exponential distribution of *three* dimensional patches of different adsorption energies, severely restricting the concept of a "site."

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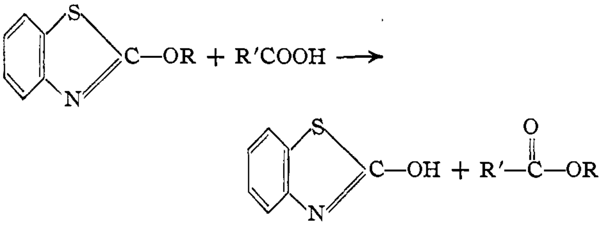
[1] Halsey, THIS JOURNAL, **73**, 2693 (1951).

[2] Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, N. J., 1945, p. 205.

The Effect of Some Organic Acids on Alkyl Heterocyclic Ethers

BY HENRY GILMAN, KENNETH E. LENTZ AND JOHN A. BEEL

The cleavage of 2-alkoxyquinoline and 2-alkoxybenzothiazole compounds by aryl thiols at 170° to form 2-hydroxy derivatives of the heterocycles and alkyl aryl sulfides has recently been reported.[1] We have now carried out further investigations of this reaction in order to determine the effect of varying strengths of acids. In this study the only acids which effected a cleavage similar to that of the thiols[1] were carboxylic acids. Thus, acetic and benzoic acids reacted with 2-ethoxybenzothiazole (I) and 2-benzyloxybenzothiazole (II) to form 32 to 85% yields of 2-hydroxybenzothiazole (III) and the corresponding esters. Oxalic acid has been shown to react similarly with alkyl aryl ethers.[2]



III, R = C_2H_5–, $C_6H_5CH_2$–
R' = CH_3–, C_6H_5–

Phenolic analogs of the thiols, phenol, *p*-cresol and *β*-naphthol, did not cleave I or II, and in most instances the recovery of starting material was high. However, no II was recovered in the reaction with *β*-naphthol even though no cleavage products were isolated. Following the discovery that these phenols were unreactive, experiments were conducted employing the more strongly acidic *p*-nitrophenol. Again the expected alkyl aryl ethers were not obtained though the recovery of starting material was significantly low. *p*-Nitrophenol has been found to react with piperidinomethyl ethyl ether to give an ortho-substituted phenol.[3]

From our results the *pK*a values of the reagents were not significant. Barbituric acid with a *pK*a value less than that of benzoic or acetic acid (see Table I) was almost completely recovered from the reaction with I. The weakly acidic sulfhydryl compounds exhibited an especial reactivity which has been shown previously in reactions with triethylbismuth and tetraethyllead.[4] Two other compounds, 1,3-diphenyl-1,3-propanedione (*β*-hydroxychalcone) and fluorene were found to be unreactive.

Experimental

Cleavage Reactions.—The heterocyclic ether was mixed in a molar ratio 1:1 to 1:3 with the acidic reagent and heated with vigorous stirring in a dry nitrogen atmosphere for 15 to 48 hours. The 2-hydroxy derivative separated from the reaction mixture on cooling, if cleavage had occurred. Frequently the acidic reagent would separate when there had been little or no reaction. Any solid material was isolated

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[1] G. Illuminati and H. Gilman, THIS JOURNAL, **71**, 3349 (1949).

[2] E. Waser and K. Sander, *Helv. Chim. Acta*, **8**, 106 (1925).

[3] C. Yang, *J. Org. Chem.*, **10**, 67 (1945).

[4] H. Gilman and J. F. Nelson, THIS JOURNAL, **59**, 935 (1937).

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 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 2-Ethoxybenzothiazole,[k] 64
2-Ethoxybenzothiazole[i]	Benzoic acid	4.2[j]	170	24	2-Hydroxybenzothiazole,[d] 85 Ethyl benzoate,[l] 77	
2-Ethoxybenzothiazole[i]	Acetic acid	4.76[m]	118	24	2-Hydroxybenzothiazole,[d] 36 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 2-Ethoxybenzothiazole,[k] 81
2-Ethoxybenzothiazole[i]	Fluorene	25[o]	158	18.5		Fluorene,[d] 79 2-Ethoxybenzothiazole,[k] 51
2-Ethoxybenzothiazole[i]	1,3-Diphenyl-1,3-propanedione		100	25		1,3-Diphenyl-1,3-propanedione,[d] 89 2-Ethoxybenzothiazole,[k] 54
2-Benzyloxybenzothiazole[i]	Benzoic acid	4.2[j]	143	20	2-Hydroxybenzothiazole,[d] 64 Benzyl benzoate (trace)	
2-Benzyloxybenzothiazole[i]	Acetic acid	4.76[m]	100	22	2-Hydroxybenzothiazole,[d] 26 Benzyl acetate,[p] 32	
2-Benzyloxybenzothiazole[i]	*p*-Nitrophenol	7.14[h]	100	24		2-Benzyloxybenzothiazole,[d] 23 *p*-Nitrophenol,[d] 96
2-Benzyloxybenzothiazole[i]	*p*-Thiocresol	8.07[c]	105	15	2-Hydroxybenzothiazole,[d] 66 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. $n^{14}\text{D}$ 1.5016 (lit. value, $n^{18}\text{D}$ 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.

On Multilayer Adsorption

BY G. D. HALSEY, JR.

The empirical isotherm

$$p/p_0 = \exp. a/RT\Theta^r \tag{1}$$

where Θ is coverage in monolayers, p is pressure and