sulfate–water and silver sulfate–cesium sulfate–water have been studied at 25°. The only solid phases observed were the pure salts.

2. The isothermally invariant solutions saturated with the two salts have the compositions:

| T, °C. | $Ag_2SO_4$, % | Alkali sulfate, % | Density |
|---|---|---|---|
| I 25 | 1.38 | 33.63 ($Rb_2SO_4$) | 1.372 |
| II 25 | 1.57 | 63.76 ($Cs_2SO_4$) | 2.049 |
| III 35 | 1.80 | 64.27 ($Cs_2SO_4$) | 2.058 |

NEW BRUNSWICK, N. J. RECEIVED JULY 24, 1950

# NOTES

## The Interaction of Chlorine with Benzene and *m*-Xylene[1,2]

BY L. J. ANDREWS AND R. M. KEEFER

By employing the same ultraviolet absorption techniques used to demonstrate 1:1 complex formation between iodine,[3] bromine[4] and iodine monochloride[5] and a variety of benzene derivatives it has now been shown that chlorine also undergoes interaction with aromatic substances. The chlorine complexes, like those of the other halogens, display high intensity absorption maxima at wave lengths in the vicinity of 290 mμ. In the present study the spectra of solutions of chlorine in solvent mixtures of carbon tetrachloride and benzene or *m*-xylene have been investigated. Typical spectrophotometric data for these solutions at the absorption maxima of the complexes are given in Table I.

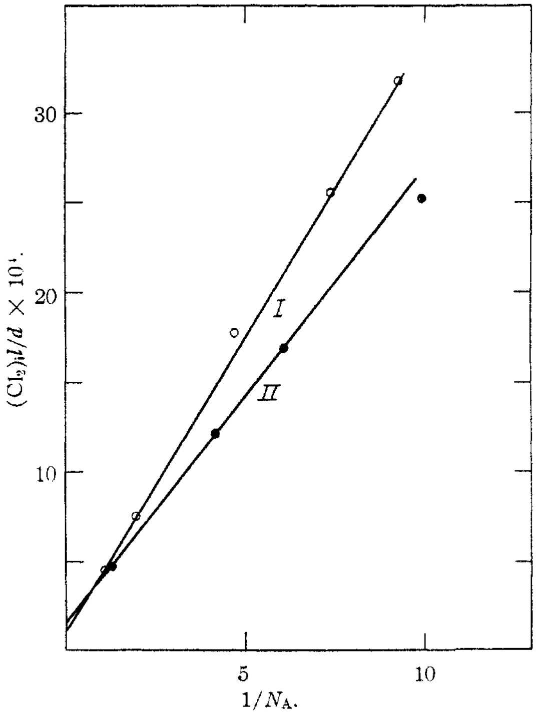

Fig. 1.—The evaluation of $\epsilon_c$ and *K*: I, data for benzene; II, data for *m*-xylene.

TABLE I

THE EXTINCTION COEFFICIENT OF CHLORINE IN CARBON TETRACHLORIDE SOLUTIONS OF BENZENE OR *m*-XYLENE

| Aromatic substance | $N_A$ mole fractn. | $\lambda_{max}$, mμ | $\epsilon_{max}{}^a$ |
|---|---|---|---|
| Benzene | 0.915 | $278^b$ | 2220 |
| *m*-Xylene | .845 | $290^b$ | 2180 |

[a] Based on total chlorine present in the solution as free halogen and in complex form. [b] The extinction coefficient of chlorine in carbon tetrachloride is 6.1 at 278 mμ and 19.5 at 290 mμ.

The changes in the optical density at the complex absorption maximum for these chlorine solutions, as influenced by changes in the mole fraction of aromatic hydrocarbon in the solvent, have been determined. The resultant data have been used to evaluate the equilibrium constants *K* for the reaction between the halogen ($X_2$) and the aromatic substance (A). As is required for a 1:1 complex[3b]

$$X_2 + A = X_2{\cdot}A,\ K = \frac{(X_2)(A)}{(X_2{\cdot}A)} \qquad (1)$$

These data were found to fit equation (2)

$$\frac{(Cl_2)_i l}{d} = \frac{1}{K\epsilon_c} \times \frac{1}{N_A} + \frac{1}{\epsilon_c} \qquad (2)$$

in which

$(Cl_2)_i$ = total molar chlorine concentration
*d* = maximum optical density of the solution at the complex absorption peak
*l* = light path length = 1 cm.
$\epsilon_c$ = molecular extinction coefficient of the complex at the absorption maximum

That is, a plot of $(Cl_2)_i l/d$ values against $1/N_A$ for both the benzene and *m*-xylene solutions produced straight lines (see Fig. 1 for a plot of data for solutions at 25°). The $\epsilon_c$ and *K* values calculated using the ordinate intercepts and slopes of these lines along with corresponding data for the other halogens studied previously are given in Table II. The $(Cl_2)_i l/d$ values as represented in Fig. 1 were corrected for the slight absorption of the free halogen in the manner described in previous papers.[4,5]

In the studies with chlorine, both the degree of complex formation and the $\epsilon_c$ values were small. Appreciable error therefore entered into the reading of $1/\epsilon_c$ values from the ordinate intercepts (Fig. 1) which seriously limited the accuracy of reported

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[1] This investigation has been supported by a grant-in-aid from Research Corporation.

[2] Reported in the Symposium on Generalized Acids and Bases before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Illinois, September, 1950.

[3] (a) Benesi and Hildebrand, THIS JOURNAL, **70**, 3978 (1948); (b) *ibid.*, **71**, 2703 (1949).

[4] Keefer and Andrews, *ibid.*, **72**, 4677 (1950).

[5] Keefer and Andrews, *ibid.*, **72**, 5170 (1950).

TABLE II

EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS AT 25° FOR HALOGEN COMPLEXES OF BENZENE AND *m*-XYLENE

| Benzene | $Cl_2$ | $Br_2$[a] | $I_2$[b, c] | $ICl$[d] |
|---|---|---|---|---|
| $\epsilon_c$ | 9090 | 13400 | 15400 | 9900 |
| $K$ | 0.33 | 1.04 | 1.72 | 4.76 |
| *m*-Xylene | | | | |
| $\epsilon_c$ | 6340 | 10100 | ...... | 9000 |
| $K$ | 0.62 | 2.16 | ...... | 16.0 |

[a] Ref. 4. [b] Ref. 3(b). Data taken at room temperature. [c] Cromwell and Scott, THIS JOURNAL, 72, 3825(1950), report a refinement in the mathematical treatment of the spectrophotometric data for iodine–benzene systems which leads to somewhat different values than those listed here. [d] Ref. 5.

$K$ values. For this reason plans to investigate an extended series of aromatic–chlorine complexes by this method were abandoned.

While no uniform trends in $\epsilon_c$ values with changes in the halogen were observed for the benzene and *m*-xylene complexes, the $K$ values increased in the order $Cl_2 < Br_2 < I_2 < ICl$. This series is regarded as representative of the relative acid strengths of the halogens since the role of the aromatic nucleus in forming the complex seems best represented as that of an electron donor.[3,4,5]

The authors have postulated[5] a tentative structure for these complexes in which the axis of the halogen molecule has been located on the sixfold symmetry axis of the ring. The proposed electronic structure is based on the many resonance structures corresponding to $C_6H_6^+\ \overset{-}{:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$ In the case of the chlorine complexes an ion pair structure $C_6H_6^+:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\ \ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^-$ may be preferable since it avoids a central chlorine atom with ten electrons in its valence shell.[6] Since however the complexes form even at high dilution in the nonpolar carbon tetrachloride medium the expanded halogen valence shell picture seems attractive. The magnitude of the $K$ values for the chlorine complexes is indeed considerably smaller than those for the iodine containing complexes for which the octet rule restrictions very likely do not apply.[7]

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(6) *Cf.* (a) Buckles, Hausmann and Wheeler, *ibid.*, **72**, 2494 (1950). (b) Williams, *Trans. Faraday Soc.*, **37**, 761 (1941).

(7) See, for example, Luder and Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 32.

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## Lanthionine in Subtilin

BY GORDON ALDERTON AND H. L. FEVOLD[1]

Subtilin,[2] a peptide with antibiotic activity produced by a particular strain of *Bacillus subtilis*, contains 4.2% sulfur but no disulfide or sulfhydryl groups as judged by nitroprusside test with and without NaCN treatment. Analyses of subtilin hydrolyzates for cystine and for methionine were negative.

Subtilin gives a strong and rapid plumbite test for labile sulfur. Heating subtilin with concentrated sulfuric acid at 100° converts approximately 40% of the sulfur-bearing constituents to cystine as measured by the Sullivan[3] method.

*meso*-Lanthionine was isolated from subtilin hydrolyzates by fractionation with phosphotungstic acid and later by the method of Horn, Jones and Ringel,[4] in a yield accounting for approximately 10% of the sulfur. It was identified through the benzoyl and carbobenzoxy derivatives, degradation of the benzoyl derivative with Raney nickel, and X-ray powder photographs. The literature contains divergent reports of the melting points of the benzoyl derivatives of both *dl*- and *meso*-lanthionine. The melting points of benzoyl derivatives of our preparations, both from alkali-treated hair and from subtilin, have been found to vary widely with the rate of heating and to exhibit a previously unreported preliminary melting and resolidification at 110–115°. Refluxing of dibenzoyl-*meso*-lanthionine in 80% alcohol with Raney nickel as described by Mozingo, Wolf, Harris and Folkers[5] for general catalytic desulfurization caused a reduction of the benzenoid ring to give cyclohexylformyl-*dl*-alanine rather than the expected benzoyl-*dl*-alanine. Similar treatment of lanthionine isolated from subtilin hydrolyzates gave the same product. Benzoyl-*dl*-alanine was also reduced to cyclohexylformylalanine under the same conditions. A short digestion at low temperature was used in the preparation of the nickel catalyst.

Lanthionine has been isolated from alkali-treated hair and several other proteins after alkali treatment[4] and has also been found in small amounts in the tips of virgin wool by paper chromatography.[6] However, demonstration of its presence as a major constituent of protein material not previously conditioned with alkali is uncommon. The *p*H of the *B. subtilis* cultures from which subtilin was recovered remained below 7 during both incubation and isolation.

### Experimental

**Analyses for Cystine, Methionine and Sulfhydryl.**—Concentrated solutions of subtilin gave negative nitroprusside tests for SH before and after reduction with sodium cyanide and with and without urea as a denaturing agent. Subtilin was hydrolyzed by refluxing overnight as a 20% solution in 6 *N* HCl. Analysis for cystine by the Sullivan[3] method and for methionine by the Sullivan–McCarthy[7] method showed zero or trace amounts of these amino acids, while recoveries of cystine and methionine added to the hydrolyzates were satisfactory. Heating a solution of 200 mg. of subtilin in 1 ml. of concentrated sulfuric acid for 15 hours on a steam-bath formed 5.8% cystine (equivalent to 38% of the sulfur of the peptide) as measured by the Sullivan method. Van Veen and Hyman[8] have reported that djenkolic acid is cleaved to cysteine and formaldehyde by similar treatment. Later trials with *meso*-lanthionine indicated that it may be converted almost quantitatively to cystine (as measured

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(1) Quartermaster Food and Container Institute, Chicago, Illinois.

(2) Dimick, Alderton, Lewis, Lightbody and Fevold, *Arch. Biochem.*, **15**, 1 (1947).

(3) Sullivan, Hess and Howard, *J. Biol. Chem.*, **145**, 621 (1942).

(4) Horn, Jones and Ringel, *ibid.*, **144**, 87 (1942).

(5) Mozingo, Wolf, Harris and Folkers, THIS JOURNAL, **65**, 1013 (1943).

(6) Consden, Gordon and Martin, *Biochem. J.*, **40**, 580 (1946).

(7) McCarthy and Sullivan, *J. Biol. Chem.*, **141**, 871 (1941).

(8) Van Veen and Hyman, *Rec. trav. chim.*, **54**, 493 (1935).