45.45, 45.26; N, 9.01, 9.18; ratio of C to N atoms, 5.88, 5.75.

F. Gabriel Synthesis.—The following procedure was adapted from that of Langenbeck,[10] who used 1,4-dibromo-2-butene. A mixture of 60 g. of phthalimide, 30 g. of potassium carbonate and 25 g. of dichlorobutene was heated for 6.5 hours at 175° under reflux. After cooling, the mixture was washed with hot water and hot alcohol to remove the by-products of the reaction, and the residue was recrystallized from chloroform, yielding 25 g. (32%) of 2-butene-1,4-diphthalimide. Six grams of the product was hydrolyzed by heating to 150° for 16 hours with 60 ml. of concentrated hydrochloric acid in a sealed tube. The phthalic acid was filtered off and the solution was evaporated to dryness, giving 2.5 g. (90%) of 2-butene-1,4-diamine hydrochloride, which was characterized by treatment with benzoyl chloride and aqueous sodium hydroxide, giving N,N'-dibenzoyl-2-butene-1,4-diamine shown by mixed melting points to be identical with that obtained from the product of the direct amination of 1,4-dichloro-2-butene.

G.—A solution of 0.2 mole of potassium thiocyanate and 0.1 mole of 1,4-dichloro-2-butene in 80 ml. of 75% ethanol when left in a refrigerator at −7° for three days precipitated yellow crystals of 2-butene-1,4-dithiocyanate; yield 75%, m.p. 82°. Muller and Freytag[11] report a melting point of 83.5° for this compound as obtained from thiocyanogen and butadiene. Distillation of these crystals yielded a yellow oil, possibly the isothiocyanate, but hydrolysis of the oil with hydrochloric acid produced only hydrogen sulfide and a heavy oil.

N,N'-Dibutylputrescine.—A solution of 25 g. (0.2 mole) of 1,4-dichloro-2-butene and 73 g. (1 mole) of butylamine in 200 ml. of benzene was allowed to stand for several days. Precipitated butylammonium chloride was removed periodically. When precipitation had ceased, the solution was extracted with dilute hydrochloric acid, the extract was made alkaline with sodium hydroxide and the amine layer was removed, dried and distilled. After the butylamine had been removed at atmospheric pressure, the pressure was reduced to less than 1 mm., but only 8.5 ml. of distillate could be removed from the residual tar. This distillate was hydrogenated at 3 atmospheres pressure and room temperature in alcohol solution; yield 4 g. (10%), m.p. 62–67°. *Anal.* Calcd. for $C_{12}H_{28}N_2$: N, 13.99. Found: N, 13.61, 13.75. The picrate of this product melted at 108–109°.

N,N-Diethyl-2-butene-1,4-diamine.—A mixture of 125 g. (1 mole) of 1,4-dichloro-2-butene, 146 g. (2 moles) of diethylamine and 1750 ml. of 95% ethanol was allowed to stand at room temperature. After 24 hours, 2.5 liters (40 moles) of 28% aqueous ammonia was added. When chloride ion determinations indicated that reaction was no longer proceeding at a significant rate, the solution was evaporated to half its volume, neutralized with concentrated hydrochloric acid, and evaporated to dryness. The residue was treated with 500 ml. of 50% sodium hydroxide solution, and the amine layer was separated, dried over sodium hydroxide, and rectified using a 120-cm. column packed with glass helices; yield 15.5 g. (11%), b.p. 89° (20 mm.) and 45 g. (23%), b.p. 113° (20 mm.). The second fraction was identified as N,N,N',N'-tetraethyl-2-butene-1,4-diamine. The first fraction, N,N-diethyl-2-butene-1,4-diamine, was converted to the picrate for analysis. (Calcd. for $C_{20}H_{24}N_8O_{14}$: C, 40.01; H, 4.02; N, 18.67. Found: C, 40.01, 39.89; H, 3.90, 3.81; N, 19.18, 19.05). The picrate, after recrystallization from 95% ethanol to constant melting point, melted at 152–154.5°. The N,N-diethyl-2-butene-1,4-diamine was hydrogenated at 3 atmospheres pressure in absolute alcohol with Raney nickel as a catalyst. The resulting N,N-diethylputrescine was converted to the picrate, which melted at 155–156° as reported by Whitmore and coworkers.[12]

Acknowledgment.—The authors wish to acknowledge their indebtedness to the University of Connecticut Research Fund for financial support and to Professor Ernest R. Kline for many helpful suggestions and for much skillful assistance in the construction of glass apparatus. The elementary analyses were made by Dr. Carl Tiedcke's Laboratory of Microchemistry, Teaneck, New Jersey.

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[10] Langenbeck, Waltersdorf and Blachnetski, *Ber.*, **72B**, 671 (1939).

[11] Muller and Freytag, *J. prakt. Chem.*, **146**, 58 (1936).

[12] Whitmore, Mosher, Adams, Taylor, Chapin, Weisel and Yanko, THIS JOURNAL, **66**, 725 (1944).

STORRS, CONN. RECEIVED AUGUST 11, 1949

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Reactions of Ethylenimines. II. With Thiophenol. A Rate Study

BY GARBIS MEGUERIAN[1] AND LEALLYN B. CLAPP

The rates of the reaction of 2-ethyl- and 2,2-dimethylethylenimines with thiophenol in carbon tetrachloride solutions were studied. The infrared spectroscopic method was used to follow the change in thiophenol concentration. It is proposed that an unstable intermediate is first formed which then reacts bimolecularly to yield the product, an α-amino sulfide. The intermediate may be a mixture of a hydrogen bonded molecular compound and an ion-pair of thiophenol and the ethylenimine.

Although ethylenimines are stable in the absence of electrophilic reagents, catalytic amounts of acids such as hydrochloric or boron trifluoride and even carbon dioxide[2] induce their polymerization. The three-membered ring is not opened in the presence of anhydrous amines[3] but in the presence of water,[3,4] aluminum chloride[5] or ammonium chloride,[6] the ethylenimines react with amines to yield products mainly of type II. Acidic hydrolysis[7] and alcoholysis[8] yield products of type III only. Tarbell and Noble suggest that the best explanation of the appearance of a type III product in an acid-catalyzed reaction is by way of a carbonium ion, stabilized by solvation. The results of the rate study with two ethylenimines and thiophenol reported here are compatible with an S_N2 mechanism; the only product isolated (92% in the case of 2-ethylethylenimine) was proved by an independent synthesis to be of type II (see Experimental part).

Quantitative chemical determination of the starting imine in the presence of the product (an amino sulfide) or *vice versa* could not be performed because of their similar chemical properties while

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[1] Taken from the thesis of G. Meguerian submitted in partial fulfillment of the requirements for the Ph.D. degree at Brown University, June, 1950; Jesse Metcalf Fellow 1948–1950; present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts.

[2] G. D. Jones, *J. Org. Chem.*, **9**, 125 (1944).

[3] G. I. Braz and V. A. Skorodumov, *Compt. rend. acad. sci. U. R. S. S.*, **55**, 315 (1947).

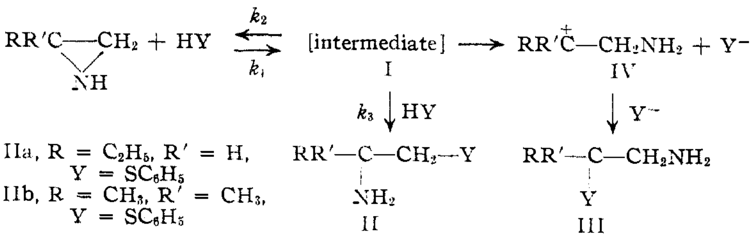
[4] A. L. Wilson, U. S. Patents 2,318,729, 2,318,730 (1943).

[5] G. H. Coleman and J. E. Callen, THIS JOURNAL, **69**, 2006 (1946).

[6] L. B. Clapp, *ibid.*, **70**, 184 (1948).

[7] T. Cairns, *ibid.*, **63**, 871 (1941).

[8] D. S. Tarbell and P. Noble, Jr., *ibid.*, **72**, 2657 (1950).



preliminary determinations of thiophenol concentrations by the iodine method[9] in the presence of the ethylenimine and the aminosulfide gave erratic results. Search for a physical method revealed the efficacy of an infrared spectroscopic analysis. The S–H stretching band of thiophenol appearing at 2575 cm.$^{-1}$ is not overlapped by any band belonging to the other components of the reaction mixture and the determination of its change in intensity presented a convenient method of following the change in thiophenol concentration.

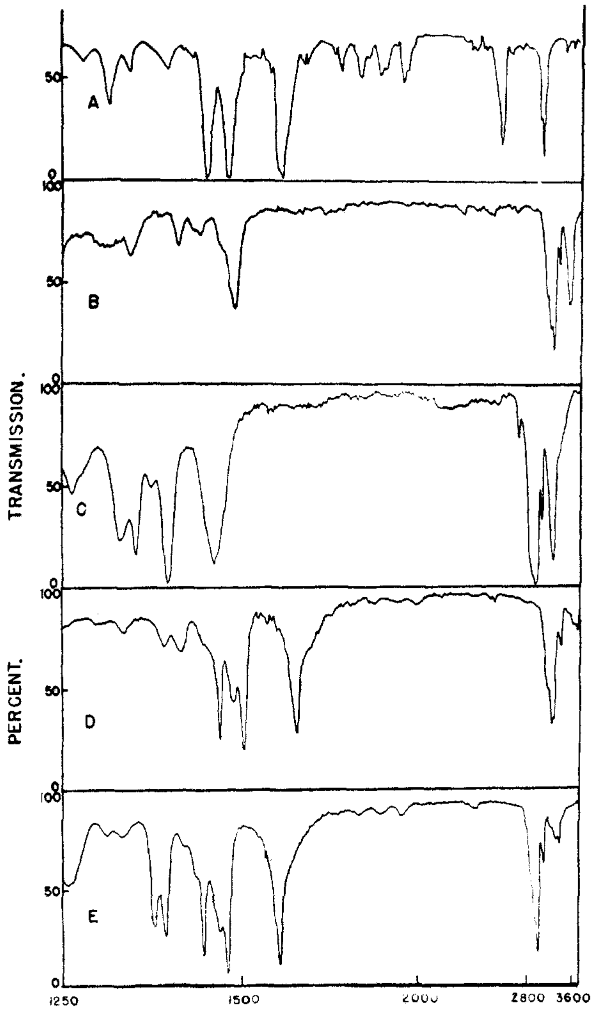


Fig. 1.—Infrared absorption spectra of: A, thiophenol; B, 2-ethylethylenimine; C, 2,2-dimethylethylenimine; D, 2-aminobutyl phenyl sulfide; E, 2-amino-2-methylpropyl phenyl sulfide.

Instrumentation and Technique

Apparatus.—The infrared spectrometer used was a modified Perkin-Elmer Model 12B in which a double-beam arrangement replaced the original single-beam optical system.[10] The electrical signals from the two beams are amplified, "sorted" and rectified by synchronous switches, compared potentiometrically and their ratio recorded, thus giving the percentage transmission of radiation through the sample. The slit opening was controlled by means of a servo slit-width control. With this instrument the "base-line" absorption densities were reproduced to the third decimal place (deviation from the average, ±0.0004) and the signal to-noise ratio (the ratio of the average signal intensity to the root mean square deviation) was 610 at 2680 cm.$^{-1}$ with a slit opening of 0.125 mm. and an output of 1 volt. A calcium fluoride prism was used.

A Colthup[11] type fixed cell with calcium fluoride windows and 0.040" thick "Teflon" spacer was employed. Calcium fluoride windows, whose transmission in the 3.8 μ region of the S–H absorption band is very good, were preferred because of their chemical inertness to the reactants.

The reaction vessel consisted of a 250-ml. erlenmeyer flask provided with a ground glass stopper and a small side arm. During the runs the side-arm was closed with a rubber stopper (a rubber cap of a serum vial) and the flask was kept in a constant temperature bath with a variation of ±0.2°. A magnetic stirrer provided thorough mixing of the reactants.

Spectral Scanning and Determination of "Base-line" Absorption Constants.—The spectra of thiophenol, 2-ethylethylenimine, 2,2-dimethylethylenimine, 2-aminobutyl phenyl sulfide and 2-amino-2-methylpropyl phenyl sulfide between 2.7 and 8.1 μ are shown in Fig. 1. The cell used for the recording of these spectra had rocksalt windows separated by means of an aluminum foil 0.002" thick in the case of thiophenol and 0.001" thick for the remainder.

Solutions of known concentrations of the above five compounds in carbon tetrachloride were prepared and their "base-line" optical densities[12] at 2575 cm.$^{-1}$ determined, using 1578 (2618 cm.$^{-1}$) and 1553 (2538 cm.$^{-1}$) micrometer readings as base points. To record the entire S–H band region 1.3 minutes was required. For each compound "base-line" optical density was plotted as a function of concentration. The resulting linear relationship is given in Fig. 2. The "base-line" optical densities for 2-aminobutyl phenyl sulfide and 2-amino-2-methylpropyl phenyl sulfide up to 1 M concentrations were within the noise level of the instrument and that for carbon tetrachloride was zero. The slopes of these straight lines gave the "base-line" absorption constants, defined as $k'_b = d_b/m$: thiophenol, 0.310; 2-ethylethylenimine, −0.045; 2,2-dimethylethylenimine, −0.013 and zero for the remainder.

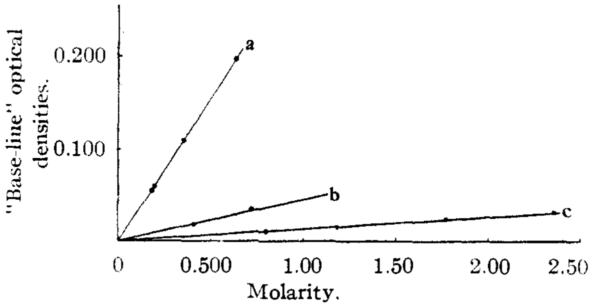


Fig. 2.—a, thiophenol; b, 2-ethylethylenimine; c, 2,2-dimethylethylenimine.

Procedure for Rate Study.—Required amounts of stock solutions were transferred into the reaction vessel by means of calibrated pipets which were filled by the use of compressed dry nitrogen. Immediately before every run the

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[9] D. S. Tarbell and D. P. Harnish, *Anal. Chem.*, **21**, 968 (1949).

[10] D. F. Hornig, G. E. Hyde and W. A. Adcock, *J. Optical Soc. Am.*, **40**, 497 (1950).

[11] N. B. Colthup, *Rev. Sci. Instruments*, **18**, 64 (1947).

[12] J. J. Heigl, H. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

vessel was dried at 110° and cooled while flushing it with dry nitrogen. Samples from the reaction vessel were taken at intervals through the rubber cap of the side arm by means of a hypodermic needle and a syringe and introduced into the cell. Then the "base-line" optical densities at 2575 cm.$^{-1}$ for the reaction mixture were determined. From the optical densities of the samples and the "base-line" absorption constants of the components of the reaction mixture the concentrations of thiophenol at given intervals were calculated. Table I gives the results for a typical run.

TABLE I

CONCENTRATIONS OF THIOPHENOL IN RUN 1

Time in minutes	"Base-line" opt. density	Thiophenol per mole per liter	1/thiophenol
0		0.315	3.18
13	0.074	.279	3.58
34	.065	.245	4.08
47	.063	.238	4.20
68	.059	.222	4.50
94	.055	.208	4.81
120	.054	.204	4.90
156	.050	.189	5.28
190	.048	.181	5.52
220	.047	.177	5.65
315	.041	.154	6.46
395	.036	.136	7.38
457	.034	.128	7.82
509	.031	.117	8.55

Accuracy of the Method.—The "base-line" optical method[12] was chosen for three reasons: it eliminates errors due to scattering on the surface of the cell, it is self-calibrating and does not require 100% transmission calibration during the runs, and, finally, the "base-line" constants of the products of the reactions studied were zero. The average deviation from the average value for the "base-line" constants was ±0.002, which in the case of thiophenol corresponds to ±0.4% error based on total sample in 100 ml. of a 0.348 molar solution of thiophenol.

Obviously, because of the reactivity of thiophenol with ethylenimines, the additivity of optical densities of the individual compounds in the reaction mixture could not be tested. However, a carbon tetrachloride solution, 0.176 molar in thiophenol and 0.307 molar in 2-aminobutyl phenyl sulfide, gave a "base-line" optical density of 0.054; calcd., 0.054. This result demonstrates also that hydrogen bonding between thiophenol and the amino-sulfide in dilute solutions is not detectable. A test of the accuracy of this method was provided by the comparison of runs 4 and 6 where the concentrations of thiophenol and 2-ethylethylenimine were different but equimolecular. The second order rate constants given by the slopes of the straight portions of the curves were 4.7 and 4.8 × 10^{-2} liters per mole-min., respectively.

Preparation of Compounds[13]

Thiophenol obtained from Eastman Kodak Co. was found to be of high purity[9]; distillation did not change the "base-line" constant. Care was taken, however, to keep it out of contact with air. Baker and Adamson reagent grade carbon tetrachloride was used as solvent. The ethylenimines were dried over metallic sodium and distilled from sodium until no hydrogen was released in contact with freshly cut sodium. All three compounds gave the accepted values for the index of refraction before they were used for the rate determinations.

2-Aminobutyl Phenyl Sulfide (IIa).—To a solution of 8.7 g. (0.08 mole) of thiophenol in 60 ml. of carbon tetrachloride, 5.5 g. (0.08 mole) of 2-ethylethylenimine[2] was added dropwise with stirring over a period of 20 minutes at room temperature. After standing overnight the solvent was removed at normal pressure, and the residue distilled under reduced pressure; yield 13 g. (92%); colorless liquid, n^{20}_D 1.5647, b.p. 130–131° (8 mm.).

Anal. Calcd. for $C_{10}H_{16}NS$: N, 7.70; S, 17.69. Found: N, 7.63; S, 17.42.

The phenylthiourea derivative melted at 103–104° after three recrystallizations from 95% ethanol.

Anal. Calcd. for $C_{17}H_{21}N_2S_2$: N, 8.85. Found: N, 8.77.

2-Amino-2-methylpropyl Phenyl Sulfide (IIb).—This compound was prepared from 2,2-dimethylethylenimine[7] (7.1 g., 0.1 mole) and thiophenol (13 g., 0.12 mole) in the manner just described for its isomer. The product was a colorless liquid, n^{20}_D 1.5606, b.p. 104–104.5° (4 mm.); yield 15.5 g. (86%).

Anal. Calcd. for $C_{10}H_{16}NS$: N, 7.70; S, 17.69. Found: N, 7.65; S, 17.45.

The phenylthiourea derivative, recrystallized from 95% ethanol, melted at 125–126°.

Anal. Calcd. for $C_{17}H_{21}N_2S_2$: N, 8.85. Found: N, 8.54.

Proof of Structure

2-Phthalimido-1-chlorobutane (V).—To 72.5 g. (0.35 mole) of phosphorus pentachloride, 77 g. (0.35 mole) of 2-phthalimido-1-hydroxybutane, prepared by the method of Cope, *et al.*,[14] was added dropwise. After the addition, the mixture was heated on the steam-bath until no more hydrogen chloride was evolved, cooled and washed several times with water. The product was extracted with ether, dried and distilled to give 39 g. (46%) of a viscous oil, b.p. 160–161° (4 mm.), which crystallized upon standing; after five recrystallizations from petroleum ether (b.p. 60–68°), m.p. 51.5–52°.

Anal. Calcd. for $C_{12}H_{12}O_2NCl$: C, 60.64; H, 5.09; N, 5.89. Found: C, 61.05; H, 5.25; N, 5.84.

2-Phthalimidobutyl Phenyl Sulfide (VI).—Thiophenol (16.2 g., 0.15 mole) was added in portions to a cold solution of 10.5 g. of sodium ethoxide in 60 ml. of absolute ethanol. After the addition of 35 g. (0.15 mole) of V, the mixture was refluxed for 3 hours, and the alcohol distilled under reduced pressure. The residue was taken up with water, neutralized with dilute acetic acid and extracted with ether. The dried ether extract was distilled to give 26 g. (57%) of a viscous, pale yellow liquid, b.p. 234–235° (4 mm.), n^{26}_D 1.6020.

Anal. Calcd. for $C_{18}H_{17}O_2NS$: N, 4.50; S, 10.29. Found: N, 4.53; S, 9.91.

2-Aminobutyl Phenyl Sulfide (IIa).—The oily product resulting from the hydrolysis of 19 g. of VI with hydrazine hydrate[15] was extracted with ether. The dried ether extract was distilled to yield 4.5 g. (44%) of a colorless liquid having the same refractive index and giving the same phenylthiourea derivative as IIa, the product of the reaction of 2-ethylethylenimine with thiophenol.

Discussion

The change in intensity of the spectral peak at 2575 cm.$^{-1}$ gave the change in the concentration of free thiophenol. Even in dilute solutions the existence of hydrogen bonding between the nitrogen of the imine and hydrogen of the thiophenol can not be excluded; however, the bond due to S–H–N appears, in general, about 100 cm.$^{-1}$ lower than that for free S–H,[16] and hydrogen bonding to the extent it existed did not distort the shape of the free S–H band, whose width (from base point to base point) at dilutions used was only 75 cm.$^{-1}$; furthermore, the peak was reproduced always at 2575 cm.$^{-1}$.

From Fig. 3, which gives second order plots for four runs, it is to be observed that the initial rate of disappearance of thiophenol was fast but in about 70 to 100 minutes subsided to the regular second order rate. Since thiophenol with its acidic hydrogen may function both as a mild acidic catalyst and as a reactant, these experimental observations are interpreted as demonstrating the formation of an intermediate containing bonded

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[13] All melting points are corrected. Analyses were done by Mr. S. M. Nagy of the Microanalytical Lab., M. I. T.

[14] A. C. Cope, H. R. Nace, W. R. Hatchard, W. H. Jones, M. A. Stahmann and R. B. Turner, THIS JOURNAL, **71**, 554 (1949).

[15] H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2348 (1926).

[16] W. Gordy and S. C. Stanford, THIS JOURNAL, **62**, 497 (1940).

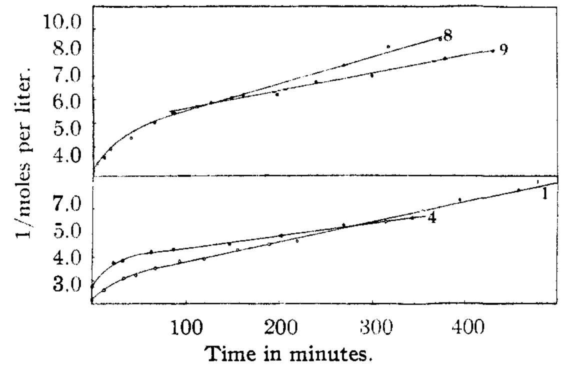


Fig. 3.—Second order rate curves: 1 and 4, thiophenol and 2-ethylethylenimine at 26° and 17°, respectively; 8 and 9, thiophenol and 2,2-dimethylethylenimine at 25° and 15°, respectively.

thiophenol whose concentration increases gradually until a "steady state" is reached. Thereafter, the reaction is a regular bimolecular reaction, thiophenol reacting with the intermediate. The use of the "method of the unstable intermediate"[17] gives the rate equation

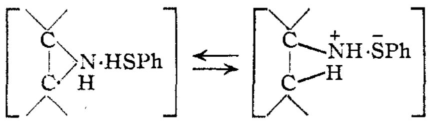
$$-\frac{d(T)}{dt} = \frac{k_1k_3(E)(T)^2}{k_2 + k_3(T)}$$

where (T) = concn. of thiophenol, (E) = concn. of imine and k_1, k_2 and k_3 are defined in the diagram above.

In order that the reaction be of second order after the "steady state" is reached, the expression

$$k_{bi} = \frac{k_1k_3(T)}{k_2 + k_3(T)}$$

must be constant, where k_{bi} = bimolecular rate constant. This means that the rate of the reaction of the intermediate with thiophenol must be much greater than the rate at which it reverts to the starting compounds, and that the rate-determining step is the formation of the intermediate. In view of this argument then, the intermediate is not likely a simple hydrogen-bonded molecular compound, since hydrogen bonding (with its small activation energy[18]) should be a fast reaction. However, it is possible that the intermediate is a mixture of two forms, namely, a hydrogen bonded molecular compound and an ion-pair, which differ only in the position of the proton.[19] In the case of thiophenol and the imines this can be represented as



It is proposed that this ion-pair, in which the C–N bonds are weakened due to a positive charge on the nitrogen,[20] is the reacting species. Such an equilibrium between ion-pair and molecular compound should be measurably slow in the non-polar solvent, carbon tetrachloride, and may be the rate-determining step. In polar solvents such as alcohol and water (in which the reactions yield products of type III) and in the presence of strong acid catalysts, the ion-pair may more easily separate into an anion and a free immonium cation, thus increasing the probability of carbonium ion (IV) formation.

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[17] A. Skrabal, *Monatsh.*, **64**, 289 (1934).

[18] Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 284.

[19] R. M. Fuoss, D. Edelson and B. I. Spinrad, THIS JOURNAL, **72**, 327 (1950).

[20] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 303.

PROVIDENCE, RHODE ISLAND RECEIVED NOVEMBER 1, 1950

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Sorption of Water Vapor by Proteins and Polymers. IV[1,2]

BY BERNARD KATCHMAN AND A. D. MCLAREN

The water vapor sorption isotherms of a number of polymers and proteins have been acquired in the continuing effort to determine the relative efficiency of site adsorption by polar groups. Unlike many proteins, the first sorbed water apparently does not penetrate the tobacco mosaic virus particles. Crystalline insulin and soya-bean trypsin inhibitor sorb more water than the corresponding amorphous samples. The sorption capacity of polar groups (ether, hydroxyl) can depend on the structure of the polymer. Ester linkages have very little affinity for water vapor. The carboxyl group, like the hydroxyl group, has a strong affinity for water. The over-all results indicate that a one-to-one correlation of polar groups and sorbed water molecules in proteins and polymers is generally not observed as structural relationships tend to limit sorption.

In line with the stoichiometric views of water vapor sorption by polar groups in proteins[3] and nylon,[4] we have examined a few polymeric materials in order to further examine this hypothesis.[5]

Comparative studies have been made with polymethacrylic acid, polyvinyl benzoate, polyisobutyl methacrylate, polyethylene, polyvinylisobutyl ether, methoxypolyglycol, polyacrylonitrile, polyvinyl acetate, ethylene-vinyl alcohol, polyglycine-DL-alanine and polymethyl vinyl ketone. Water vapor uptake by crystalline and amorphous trypsin-inhibitor (STI) protein from the soya bean and insulin have been examined. Tobacco mosaic virus has also been exposed to water vapor with results differing markedly from those found for simple proteins.

Experimental Procedure and Results

The sorption measurements with water vapor were carried

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[1] For previous paper see J. A. Cutler and A. D. McLaren, *J. Polymer Sci.*, **3**, 792 (1948).

[2] From Part I of the Ph.D. thesis of B. Katchman, Polytechnic Institute of Brooklyn, 1950. Work done under contract with the Technical Command, Chemical Corps, U. S. Army.

[3] L. Pauling, THIS JOURNAL, **67**, 555 (1945).

[4] M. Dole and A. D. McLaren, *ibid.*, **69**, 651 (1947).

[5] Previous references in this field have been summarized by M. Dole and I. L. Faller, *ibid.*, **72**, 414 (1950).