Reactions (9), (11), (13) and (15).—There does not seem to be any experimental evidence available for these reactions and in these cases also we have assigned values which are in agreement with the free radical mechanism.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MD.
RECEIVED NOVEMBER 29, 1933

Ammonolysis of Fluorenone and Fluorenone Anil

BY LOUIS A. PINCK AND GUIDO E. HILBERT

Strain[1] has shown that ketones, such as acetophenone, on heating with ammonia at 180° with aluminum chloride as a dehydrating agent, yield the corresponding ketimines. It has now been found that fluorenone imide can be prepared in excellent yield by the interaction of fluorenone and ammonia at room temperature. This method is superior to that of Kliegl[2] and is recommended for preparative purposes. Benzophenone, 9,9-dichlorofluorene and 1,2-dichlorodibiphenylene-ethane under similar conditions, however, do not react.

Additional information on the behavior of Schiff bases in liquid ammonia[3] was obtained in a study of the ammonolysis of fluorenone anil. This reaction leading to the formation of fluorenone imide and aniline was catalyzed by ammonium chloride and did not go to completion; apparently an equilibrium was attained. Fluorenone anil was readily prepared by heating fluorenone imide and aniline.

Experimental Procedure

Ammonolyis of Fluorenone.—Ten grams of fluorenone[4] was treated with 15 cc. of sodium-dried ammonia and allowed to stand at room temperature for several weeks. After the removal of ammonia the fluorenone imide was recrystallized from ligroin; m. p. 124°, yield practically quantitative.

Fluorenone Anil.—A mixture of 0.2 g. of fluorenone imide and 0.2 cc. of aniline was heated at 120° for ninety minutes; ammonia was evolved. The yellow sirupy reaction product solidified on cooling and was recrystallized from petroleum ether; m. p. 87°.[5]

Ammonolysis of Fluorenone Anil.—A solution of 0.5 g. of fluorenone anil and 0.25 g. of ammonium chloride in dry liquid ammonia was heated at 60° for four days. The ammonia was removed and the reaction product dissolved in boiling ligroin. On concentration of the solution 0.22 g. of fluorenone imide separated. From the mother liquor was isolated 0.15 g. of unchanged anil.

No fluorenone imide was isolated in an experiment in which a solution of fluorenone anil in dry ammonia was heated at 60° for twenty hours.

CONTRIBUTION FROM THE
BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
RECEIVED DECEMBER 8, 1933

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(1) Strain, THIS JOURNAL, **52**, 820 (1930).

(2) Kliegl, *Ber.*, **43**, 2488 (1910); see also Goldschmidt and Beuschel, *Ann.*, **447**, 203 (1926).

(3) Strain, THIS JOURNAL, **50**, 2218 (1928).

(4) This was prepared according to the method of Schmidt and Wagner, *Ber.*, **43**, 1796 (1910), (3 kilos of technical fluorene yielded 2450 g. of pure fluorenone), which is practically identical with that recently published by Huntress, Hershberg and Cliff, THIS JOURNAL, **53**, 2720 (1931).

(5) Reddelien, *Ber.*, **43**, 2479 (1910); Schlenk and Bergmann,, *Ann.*, **463**, 292 (1928).

COMMUNICATIONS TO THE EDITOR

TWO TYPES OF ACTIVATED ADSORPTION OF HYDROGEN ON THE SURFACE OF A PROMOTED IRON SYNTHETIC AMMONIA CATALYST

Sir:

By making adsorption measurements in conjunction with our study of the catalytic conversion of ortho to para hydrogen we have obtained data that seem to establish definitely the existence of two types [see Benton, *Trans. Faraday Soc.*, **28,** 202 (1932), and Langmuir, *Chem. Rev.*, **13,** 188 (1933)] of activated and one type of physical adsorption of hydrogen on the surface of an iron catalyst promoted with 1.3% Al_2O_3 and 1.59% K_2O. The characteristics of the three types of adsorption on the promoted iron catalyst are as follows.

Physical Adsorption. The adsorption of hydrogen at 760 mm. pressure by a 10-cc. (about 22-g.) sample of catalyst that had been reduced by hydrogen at 450° and degassed at the same temperature, was 5.0, 2.8 and 0.25 cc. at −196, −183 and −144°, respectively. The heat of adsorption calculated from isotherms was about 2000 calories.

Type A Activated Adsorption.—Between −78 and 0° apparent equilibrium could be obtained in a few hours for a type of adsorption having all of the characteristics of activated adsorption [Taylor, THIS JOURNAL, **53**, 578 (1931)]. The energy of activation of the adsorption was about 9000 calories. The isobar at 760 mm. showed a gradual decrease from an adsorption of 7 to 8 cc. at $-78°$ to about 5 or 6 cc. at 0°.

Type B Activated Adsorption.—At 100° or higher an additional but much slower adsorption (type B) set in, the total adsorption (type A and type B) reaching at 100° a value of 8 to 9 cc. within two hours. At 212 and 450° the adsorptions were 5.5 and 3.5 cc., respectively, and reached an apparent equilibrium in less than an hour. Isotherms taken at 350 and 410° were reversible and indicated a heat of adsorption of about 8500 calories.

In a previous communication [Harkness and Emmett, THIS JOURNAL, **55**, 3496 (1933)] it was pointed out that the adsorption of hydrogen by the promoted iron catalyst at 100° and at 212° strongly inhibited the low temperature ($-190°$) catalytic conversion of ortho to para hydrogen. In continuing this study it has now been found that this inhibition produced by the adsorption of a given volume of hydrogen by the catalyst at 100° is about eight times as great as that produced by the same volume of hydrogen adsorbed at $-78°$.

From the combined adsorption data and measurements of the absolute and relative poisoning effects of types A and B adsorption on the low temperature ortho–para hydrogen conversion it therefore may be concluded (1) that both types A and B are primarily surface adsorptions and not solutions within the metal, and (2) that types A and B represent two distinctly different kinds of activated adsorption, the B type not being merely a slow continuation of type A.

BUREAU OF CHEMISTRY AND SOILS R. W. HARKNESS
WASHINGTON, D. C. P. H. EMMETT

RECEIVED DECEMBER 26, 1933

MOLECULAR REARRANGEMENTS OF OPTICALLY ACTIVE RADICALS

Sir:

Previous investigations in this Laboratory have shown that in certain molecular rearrangements involving optically active radicals, notably of the Hofmann, Curtius and Lossen types, the optically active group maintains an asymmetric configuration during the rearrangement. It has also been shown that such transformations are accompanied with little or no racemization. The optical stability of such radicals during rearrangement can be explained easily on the theory that the shift of the electron pair from the carbon atom to the nitrogen atom includes the group which it holds.

We have continued our studies of molecular rearrangements in order to determine more definitely whether the electronic nature of the migrating group is of great importance in maintaining the asymmetry of the radical during rearrangement. For this purpose a compound was chosen in which the group containing the asymmetric carbon atom is essentially of the nature of a positive group during rearrangement.

Accordingly we prepared *l*-2-methyl-2-phenylbutanol(1), $CH_3CH_2C(CH_3)(C_6H_5)CH_2OH$, $\alpha_D^{19} = -4.90°$ (homogeneous, 1-dm. tube), and studied its behavior when the hydroxyl group was replaced by chlorine. The chloride so produced was found to be a tertiary chloride, and not a primary chloride. This fact is to be expected on the basis of modern conceptions of molecular rearrangements. It was also found to be optically active. The rearrangement however is accompanied by an inversion in sign of the rotatory power. The *l*-alcohol yields a dextrorotatory rearrangement product. In conclusion it is to be pointed out that these facts have an important bearing on all investigations involving configurational relationships of optically active compounds.

FRICK CHEMICAL LABORATORY EVERETT S. WALLIS
PRINCETON, NEW JERSEY P. I. BOWMAN

RECEIVED JANUARY 2, 1934

THE INTRODUCTION OF DEUTERIUM ATOMS INTO ACETONE

Sir:

When a solution of acetone in water containing deuterium oxide and a small amount of potassium carbonate is warmed for a short time, an exchange of hydrogen atoms occurs, with the consequent introduction of deuterium into the acetone. We first studied the concomitant decrease in density of the water. For example, six solutions were prepared, each containing 30 cc. of water, 60 cc. of refractionated (0.1° range) "C. P. Analyzed" acetone, and about 0.1 g. of either phosphoric acid or potassium carbonate as indicated in the table. After warming from one to three hours on the steam-bath, the solutions were carefully fractionated, using a 90-cm. vacuum-jacketed column. The water in each case was collected in two fractions, and the density of the second was compared with that of the original water. The results are tabulated below. Those in the first column, with ordinary water, show the reliability of the method.

Substance added	K_2CO_3	H_3PO_4	None	K_2CO_3	K_2CO_3	K_2CO_3
Mole % D (init.)	0.02	0.73	0.73	0.73	1.08	4.07
Mole % D (final)	.02	.67	.68	.38	.64	1.93
Fr. D removed	0	.08	.07	.48	.41	0.52

The presence of deuterium in the acetone which had been treated with 4.07% heavy water was demonstrated by density measurements and by returning a part of the deuterium from this "heavy" acetone to a sample of ordinary water. The "heavy" acetone was dried for twenty hours with fused potassium hydroxide, then fractionated, and its density compared with that of similarly treated ordinary acetone, showing an increase of 1.4° in the temperature of equal density. It was then warmed with ordinary water and potassium carbonate and again fractionated. The first acetone fraction, dried as before, showed a density slightly greater (0.2°) than ordinary acetone, while the last aqueous fraction contained 0.94% deuterium, corresponding to a removal of 54% of the estimated deuterium content from the acetone. The mole fraction of acetone was 0.29 as compared with 0.33 in the earlier experiments. We may estimate the equilibrium constant for the formation of monodeuteroacetone and ordinary water from acetone and HH^2O as approximately 2, with equilibrium approached in both directions.

The effectiveness of an alkaline catalyst argues for a mechanism involving the postulated enol form of acetone, a possibility which led us initially to perform these experiments. The acidic hydrogen of the enol form should exchange rapidly with the hydrogens of water, and this, coupled with a mobile equilibrium between the keto and enol forms, should result in the formation of carbon–deuterium bonds. It is doubtful whether in an organic compound not susceptible to such a reaction mechanism, the replacement of protium by deuterium by direct contact with water will be realized.

We plan to continue the study of acetone along with other compounds for which enol forms are known or postulated. At present there is no reason to doubt that the treatment of acetone with successively heavier portions of water will result in the practically complete replacement of protium by deuterium. This opens interesting possibilities in synthesis.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

J. O. HALFORD
LEIGH C. ANDERSON
JOHN R. BATES

RECEIVED JANUARY 11, 1934

FRACTIONATION OF THE HYDROGEN ISOTOPES BY THE ADDITION OF SODIUM TO WATER

Sir:

Eyring[1] predicted, from zero point energy considerations, that isotopic separations will occur in the course of many reactions which do not involve electrolysis, through a difference in the reaction velocities of deuterium and of protium compounds. Such separations have been observed, and reported[2,3] for the reaction of iron with steam. We have recently made a quantitative study of the isotopic fractionation which we find to occur in the reaction of metallic sodium with water.

The reaction was carried out by adding small pieces of clean metallic sodium to a weighed quantity of water. Careful specific gravity determinations were made on the initial sample of water, on that collected by burning the evolved hydrogen and on the water distilled from the residue in the reaction flask (approximately 50% NaOH). Successive distillations with slightly alkaline permanganate yielded samples of constant density. Their specific gravities were determined by means of the buoyancy balance[4] equipped with a convenient thermostatic control which we have developed, and were reproducible to one part per million.

The quantitative results are given in the table. In the residue the hydrogen in NaOH is calculated as water.

Material		Wt., g.	ΔT, °C.	Δ sp. g. (p. p. m.)	Total Δm above ordinary water (p. p. m.)
Initial water		389.2	0.532	149	57,990
Final water	Heavy fraction	332.3	.601	168	55,820
	Light fraction	57.3	.179	50	2,860
	Totals	389.6			58,680

From these data we have derived the separation coefficient α, in the equation d ln $n_P = \alpha$d ln n_D where n_P and n_D are, respectively, the number of

[1] Eyring, *Proc. Nat. Acad. Sci.*, **19**, 78 (1933).

[2] Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933).

[3] Horiuti and Polanyi, *Nature*, **132**, 819 (1933).

[4] Lewis and Macdonald, *J. Chem. Physics*, **1**, 341 (1933).

protium and of deuterium atoms in the undecomposed water, or solution.[5] We obtain[6] $\alpha = 2.5$, which compares with electrolytic separation coefficients[7] ranging from about 5 to about 7. By a similar calculation using the data given by Bleakney and Gould[2] we get the respective values 1.3 and 1.2 for the separation factor in the iron steam reaction.

These experiments were begun in the effort to seek a possible correlation between the electrolytic separation of isotopes and a secondary reaction between discharged alkali metal and the solution. That other factors are primarily responsible is shown clearly by the recent work of Topley and Eyring.[7] However, the experimental evidence now available does not preclude the possibility that a *fraction* of the effect may be separated from that of a purely electrode process.

We are continuing experiments with other metals.

We are indebted to Prof. Edward Mack, who suggested this experiment to one of us, and to the Capital City Products Company, of Columbus, who kindly placed at our disposal two thousand gallons of commercial electrolyte from which we are preparing "heavy water."

(5) This equation is similar to that for the separation efficiency in electrolysis. It is justified by consideration of the rate equation for the reaction of a metal with either isotopic water, which is

$$-\frac{dc}{dt} = k\sigma c f(\mu)$$

where σ, the available surface of the metal, is common to both waters and $f(\mu)$, which represents some function of the ionic environment, may reasonably be supposed to be the same function for both protium and deuterium ions. $\alpha = k_P/k_D$.

(6) Δ sp. g. for pure H^1H^1O was taken to be 21 p. p. m., which corresponds with the isotopic ratio of 1 in 5000 in ordinary water (Ref. 2).

(7) Topley and Eyring, THIS JOURNAL, **55**, 5058 (1933).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

CLYDE O. DAVIS
HERRICK L. JOHNSTON

RECEIVED JANUARY 22, 1934

SOME PROPERTIES OF PURE DEUTACETIC ACID

Sir:

Starting with 0.25 g. of pure $H^2{}_2O$ an equivalent amount of H^2Cl was prepared and studied (accompanying communication). This deutochloric acid was then introduced into a vessel containing silver acetate which had been thoroughly evacuated and kept dark. After twenty-four hours the system had undergone quantitatively the reaction, $H^2Cl + CH_3COOAg = AgCl + CH_3COOH^2$. After exhausting the system at $-40°$ the deutacetic acid was distilled from the reaction chamber. It showed a very sharp melting point at 13.3°, which is 3.3° below that of ordinary acetic acid.

In all cases so far investigated the vapor pressure has been lowered by the substitution of H^2 for H^1. In this case, however, we predicted that the deutacetic acid would have the higher vapor pressure. It is becoming evident that the great differences between the isotopic forms of such substances as water and ammonia [see Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933); Taylor and Junger, *ibid.*, **55**, 5057 (1933)] can be chiefly ascribed to the increase in strength of the H^2 bond over the H^1 bond. In such cases these bonds occur only in the liquid, but acetic acid is almost completely associated in the vapor state. Since this can be attributed to similar hydrogen bonds, it appeared likely that the association would be more complete in deutacetic acid. Preliminary measurements of the vapor density seemed to indicate that this is the case, but it must be investigated more carefully.

The increased association of the deutacetic acid in the vapor phase should lead to a higher vapor pressure and this we have established. The difference is 7.5% at 50° and 3% at 90°. Our measurements of p_2 and p_1, the vapor pressures of deutacetic acid and of ordinary acetic acid (prepared in precisely the same way and in the same apparatus) are given in the table. The values of $\log_{10} p$ are plotted against $1/T$ in the figure. Our values for ordinary acetic acid are, throughout the range, 5% higher than those of Ramsay and Young [*J. Chem. Soc.*, **49**, 805 (1886)].

TABLE

T, °C.	p_1, mm.	p_2, mm.
49.7		63.2
52.2	66.1	
64.4		120.4
65.3	117.8	
73.4		171.0
74.4	172.7	
86.0		271.5
86.9	272.9	
94.2		366.4

Finally, it was necessary to ascertain whether our deutacetic acid had remained CH_3COOH^2 or whether the deutons had become distributed between the carboxyl and the methyl groups. A part of our deutacetic acid was treated with anhydrous sodium carbonate and again with calcium carbonate until all of the acid was gone.

The water thus produced, 0.06 g., was freed from carbon dioxide and carefully distilled. If all of the deutacetic acid had remained in the form CH_3COOH^2 and if no ordinary hydrogen had been picked up in the long series of manipulations the specific gravity at 25° should be 1.106. If the H^2 had been randomly distributed between carboxyl and methyl groups the specific gravity should be 1.026. The specific gravity found was 1.096. Considering the difficulty of a density determination with so small a sample, and the many opportunities for contamination with ordinary water, this result indicates that there had been no interchange with the hydrogen of the methyl group.

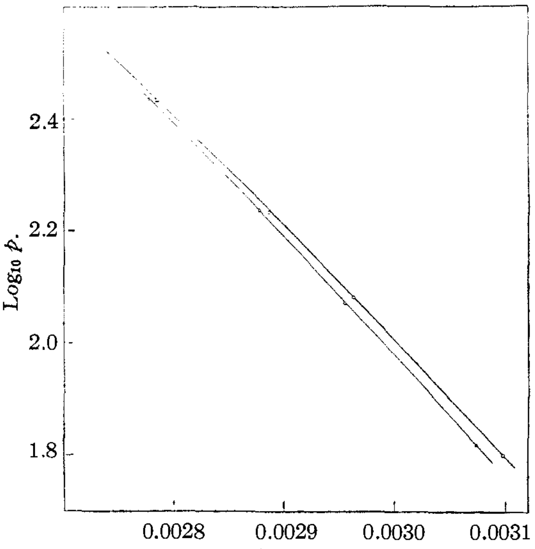

Fig. 1.—○, H^2Ac; □, H^1Ac.

DEPARTMENT OF CHEMISTRY
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BERKELEY, CALIFORNIA

GILBERT N. LEWIS
PHILIP W. SCHUTZ

RECEIVED JANUARY 23, 1934

THE VAPOR PRESSURE OF LIQUID AND SOLID DEUTOCHLORIC ACID

Sir:

Some time ago we attempted to measure the vapor pressure of pure deutochloric acid, H^2Cl. The values obtained were almost identical with those found for ordinary hydrochloric acid except that there was no pronounced break in the curve at the freezing point. The work was not altogether satisfactory owing to uncertainty regarding the purity of the H^2Cl and to some difficulty in maintaining and measuring the temperatures. It seemed worth while to repeat the experiments using the utmost care in these particulars.

After trying many chlorides it was found that the best H^2Cl was obtained by allowing pure $H^2{}_2O$ to react with anhydrous magnesium chloride at 600°, the system being so designed that, after removing H^2Cl, the excess water could be returned to react further with the magnesium chloride. From the vessel containing magnesium chloride the H^2Cl was finally distilled at −130° into the measuring apparatus, to remove water and any other impurities of relatively low volatility. The thermostat consisted of a Dewar tube filled with pentane which was kept at a desired temperature by external cooling and stirred by a stream of cold air. The thermocouple was calibrated by determining in the same apparatus the vapor pressure of ordinary HCl for which we have the extremely accurate and concordant data of Henning and Stock and Giauque and Wiebe [*Z. Physik*, **4**, 226 (1921); THIS JOURNAL, **50**, 101 (1928)]. Our results are given in the table. The triple point of H^2Cl was determined visually as 158.2°K.

TABLE

T,°K.	p, mm.	
152.6	54.5	Solid
154.7	67.5	Solid
157.1	84.5	Solid
157.6	88.0	Solid
159.5	104.0	Liquid
168.2	205.5	Liquid
175.0	329.0	Liquid
181.0	486.5	Liquid
188.3	757.5	Liquid
195.9	1131.5	Liquid
200.9	1474.5	Liquid

Comparing the vapor pressure of H^2Cl, p_2, with that of H^1Cl, p_1, we find that the data for the two liquids agree accurately with the equation

$$\log_{10}\frac{p_1}{p_2} = \frac{15.4}{T} - 0.075 \qquad (1)$$

while those for the two solids are in rougher agreement with the equation

$$\log_{10}\frac{p_1}{p_2} = -\frac{57.7}{T} + 0.387 \qquad (2)$$

It is interesting that the ratio of the two vapor pressures reaches a maximum of 1.05 at the triple point, below which they approach each other as the temperature is lowered. Assuming that the molal volumes for gas, liquid and solid are approximately the same for H^1Cl and H^2Cl

under similar conditions, we may calculate accurately from Equations (1) and (2) the difference in their heats of vaporization; that of liquid H^2Cl being greater than that of H^1Cl by 70 ± 1 calories per mole, while in the case of the solids, there is a difference of 265 ± 20 in the other direction. Thus, from the work of Giauque and Wiebe, the heat of vaporization of liquid, the heat of vaporization of solid, and the heat of fusion, are, respectively, for H^1Cl at its triple point, 4081, 4557 and 476 calories per mole. Our corresponding values for H^2Cl are 4151, 4292, and 141. Our low value for the heat of fusion is very striking and accounts for our earlier failure to detect a break in the vapor pressure curve at the freezing point.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
GILBERT N. LEWIS
RONALD T. MACDONALD
PHILIP W. SCHUTZ

RECEIVED JANUARY 23, 1934

MONOMOLECULAR FILMS OF FATTY ACIDS ON GLASS

Sir:

Langmuir showed in 1919 that a monomolecular oil film could be deposited on a solid surface by dipping the solid beneath a water surface covered with a monomolecular film, and withdrawing the solid slowly. After the water peeled away from the solid surface, or evaporated, the oil film was left on the solid, the molecules in the film retaining the orientation which they had on water.

This method has been developed further for depositing fatty acids on glass. The nicest experimental procedure is that in which water peels completely off the glass as the glass is withdrawn from the water-bath. This occurs when molecules of the fatty acid, which are spread on the water surface, leave the water and attach themselves to the edges of the glass slide as soon as one end of the slide emerges from the bath. Water then peels away from this coated area, and, as the water retreats, the oil film coats new areas until all the water is displaced.

Films which attach themselves to glass in the manner just described, called glass-adhering films, are formed only under special conditions. Fatty acids form these films, provided the film on the water surface is under surface pressure, and provided the glass is wet with alkaline water ($^1/_{1000}$ N NaOH). Stearic acid gives excellent results, used at a surface pressure of 20 dynes per cm. on an alkaline water-bath. Some fatty acid films, however, collapse when compressed on alkaline water, though they will withstand pressure on acid water. One can spread substances of this type on acid water, rinse the slide in alkaline water, touch only the tip of the slide to the oil film, and the film spreads instantly over the wet slide to form a glass-adhering film.

Stearic acid may be deposited in successive layers, the layers of odd number being oriented with the CH_3-groups away from the glass, the layers of even number with these groups toward the glass. The former occur when glass is raised through an oil film spread on water, the latter when glass coated with a glass-adhering layer is lowered slowly through a similar film. As the glass is lowered, the film on the water surface attaches itself tightly to the slide, but, since water makes a contact angle of approximately 90° with a coated slide, the film is turned upside down as the slide carries it down into the water. The phenomenon is striking when the motion of the film is observed by means of scattered talc particles.

Films deposited on glass with the molecules oriented so that only CH_3-groups are exposed at the upper surface, form a surface which oil and benzene will not wet. A drop of pure mineral oil, or tetradecane, or benzene, placed on a layer that is 1, or 3, or 5, . . . molecules deep, rolls about on the surface leaving no trace of its path, although stearic acid is soluble in these liquids. Water rolls about on a layer 3, or 5, . . . molecules deep. Films oriented in the opposite direction, with all COOH-groups on the outer surface, are completely wet by clean water.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.
KATHARINE B. BLODGETT

RECEIVED JANUARY 24, 1934