TABLE II

MOLAR HEATS OF SOLUTION OF SOME SILVER HALIDES AT −33.4°

Sample, g.	Moles NH_3 per mole salt	Molar heat of solution, cal.
Silver bromide		
2.6578	123.8	8931
1.1493	285.0	7044
0.8958	367.5	6370
.6260	525.7	5270
Silver iodide		
2.1615	156.2	6150
2.0618	199.6	6300
1.5235	268.7	6420
1.2294	332.8	6570
1.0004	411.0	6930
0.8493	484.2	7400

TABLE III

HEATS OF REACTION IN LIQUID AMMONIA

Subst. (1)	Wt. (1)	Subst. (2)	Wt. (2)	Heat of reaction, calories	Mean
$C_6H_5NH_3Cl$	1.0936	NH_3	Excess	12,336	12,383
$C_6H_5NH_3Cl$	1.1780	NH_3	Excess	12,431	
Aniline	1.4740	$NH_4Cl_{am.}$	Equiv.	3170	
Aniline	1.4743	NH_3	Excess	3220	
$AgI_{am.}$	3.0020	K	Equiv.	51,353	51,185
$AgI_{am.}$	1.4350	K	Equiv.	51,017	

The energies of the above reactions are represented by the equations

$$C_6H_5NH_3Cl + NH_3 \longrightarrow C_6H_5NH_2 + NH_4Cl + 12{,}383 \text{ cal.} \quad (1)$$

$$Ag^+ + I^- + K^+ + e^- = K^+ + I^- + Ag\text{ (solid)} + 51{,}185 \text{ cal.} \quad (2)$$

Combining the heat of mixing of the aniline with liquid ammonia (3221 cal.) (Table III) and the heat of solution of ammonium chloride[4] (6700 cal.) with the heat of reaction of equation 1, we obtain as a heat of solution and ammonolysis of aniline hydrochloride 2405 cal. This small heat effect indicates that phenylammonium ion is quite unstable and easily loses the proton to ammonia.

The net result of equation (2) would be

$$Ag^+\text{(solution)} + e^- = Ag\text{(solid)} + 51{,}185 \text{ cal.}$$

This heat represents the heat of reduction of the silver ion as it exists in liquid ammonia solution.

V. Summary

The heats of solution of the hydrochloride of methylamine, dimethylamine, ethylamine, silver bromide, and silver iodide have been determined over a range of concentrations in anhydrous liquid ammonia.

The heat of ammonolysis of aniline hydrochloride and the heat of reduction of the silver ion as it exists in liquid ammonia solution by the electron in liquid ammonia are reported.

[4] Schmidt, Sottysiak and Kluge, *ibid.*, **58**, 2509 (1936).

SCHENECTADY, N. Y. RECEIVED AUGUST 8, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Investigations. VIII. The Photolysis of Solutions of Ethylene Iodide[1]

BY ROBERT J. GRABENSTETTER[2] AND EDWIN O. WIIG

The thermal decomposition of ethylene iodide in carbon tetrachloride solution has been shown by Polissar[3] to proceed simultaneously by a unimolecular decomposition and an iodine catalyzed decomposition. Arnold and Kistiakowsky[4] found a similar behavior in the gas phase which Ogg[5] has shown can be explained by a chain mechanism similar to the one suggested by Schumacher[6] for the decomposition in carbon tetrachloride solution. Both Ogg and Schumacher suggested that such a chain mechanism would explain the addition of halogen to ethylenic linkages as well as the decomposition of such halogen compounds.

For the iodine photosensitized decomposition of ethylene iodide in carbon tetrachloride solution at 4360 and 4050 Å. a quantum yield of 25 was found,[7] in agreement with the suggested chain mechanism. At longer wave lengths Schumacher and Stieger[8] found a smaller quantum yield for this sensitized reaction. This was subsequently shown by Dickinson and Nies[9] to be due to the smaller absorption coefficient of iodine at the longer wave lengths. These workers also demonstrated that the regions of continuous absorption by iodine were only slightly more effective than the regions of discontinuous absorption. The direct photolysis and the iodine photosensitized decomposition of gaseous ethylene iodide also probably proceed by the same chain mechanism.[10]

In a previous investigation[11] of the photolysis of ethylene iodide in carbon tetrachloride solution, using light absorbed only by ethylene iodide, it

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[1] Presented at the Atlantic City, New Jersey, meeting of the American Chemical Society, September 10, 1941.

[2] Abstract from part of a thesis submitted in 1941 to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy. Present address: Proctor and Gamble Co., Ivorydale, Ohio.

[3] Polissar, THIS JOURNAL, **52**, 956 (1930).

[4] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[5] Ogg, THIS JOURNAL, **58**, 607 (1936).

[6] Schumacher, *ibid.*, **52**, 3132 (1930).

[7] Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

[8] Schumacher and Stieger, *ibid.*, **12B**, 348 (1931).

[9] Dickinson and Nies, THIS JOURNAL, **57**, 2382 (1935).

[10] Janneck and Wiig, *ibid.*, **62**, 1877 (1940).

[11] DeRight and Wiig, *ibid.*, **57**, 2411 (1935).

was found that the rate of decomposition increased with time (or, which is the same, with the amount of iodine produced), reached a maximum and then slowly fell off. On the whole the reaction appeared in agreement with the chain mechanism mentioned above but no satisfactory explanation could be offered for the appearance of the maximum in the rate of decomposition, although it was tentatively suggested that possibly failure to exclude atmospheric oxygen from the reaction mixture might have been responsible. The work has been continued with the dual object of determining, if possible, the cause of the rate maximum and of testing further the atom mechanism previously suggested for the direct photolysis. That the primary process in the photodecomposition of ethylene iodide involves dissociation into C_2H_4I and an I atom is indicated in the present results by the chain character of the reaction observed at higher temperatures and by a study of the exchange reaction with radio-iodine during exposure to light.

Experimental Details

Preparation and Purification of Materials.—The carbon tetrachloride used was either J. T. Baker C. P. Analyzed Grade, redistilled before use with only the middle portion being retained, or technical grades purified by the method of Polissar[3] or of Schmitz-Dumont.[12] The other solvents used were of C. P. grade and carefully purified. Ethylene iodide and uranyl oxalate were prepared as previously.[11]

Apparatus and Procedure.—The decomposition of ethylene iodide was followed as a function of time of exposure by determining the concentration of the resulting iodine by means of a photoelectric colorimeter similar to one described in the literature.[13]

Three cylindrically shaped reaction cells with fused seams and optically plane windows were used during the course of the experiments. The cells were of different dimensions, two of quartz and one of Pyrex glass, but equivalent results were obtained in all three, except that the Pyrex cell gave a lower rate due to the decrease in the light transmitted.

The light source and monochromator were those used in the earlier work. The quartz mercury vapor lamp was allowed to run about four hours before starting an experiment, after which the light intensity remained constant. In some experiments a system of filters was used to isolate light of wave length in the region of 3100 Å. The filter system consisted of a Corning red-purple corex filter, a silver mirror on a quartz disk and a solution of cobalt and nickel sulfates.[14] Photographs of the light source taken with a spectrograph showed practically nothing but the 3100 Å. region.

In the determination of quantum yields the thermopile–uranyl oxalate actinometer system used previously was again employed. Due to the small temperature coefficient of the photochemical reaction it was unnecessary to use a thermostat at room temperature. For high temperature experiments the reaction cell, except for the windows, was immersed in a vapor-bath, water and ethanol being boiled to obtain temperatures of 100 and 78.5°. The temperature remained constant to within 0.2–0.3° during the entire experiment.

A weighed amount of ethylene iodide, freshly recrystallized from purified carbon tetrachloride, was dissolved in the desired volume of solvent and exposed in the cell to light of wave length 3100 Å. The cell was supported in such a manner that its position could always be duplicated. At intervals during an experiment the cell was removed from the holder, placed in the colorimeter and the iodine concentration determined. Exposure was continued until the iodine produced could no longer be accurately determined in the colorimeter. In the quantum yield experiments the energy absorbed by ethylene iodide was measured each time the iodine concentration was determined.

Results

The concentration of iodine produced at various times during any one run was plotted against the time and the slope of this curve at any chosen time gave the instantaneous rate of reaction at that time and that iodine concentration. These instantaneous rates were then plotted against the concentration of iodine produced in order to detect any change in rate during the experiment.

Experiments in which carefully purified pentane was used as the solvent showed the rate of photolysis to be constant until sufficient iodine had accumulated to result in retardation of the reaction (curve 3, Fig. 1). This leads one to suspect that perhaps the previously used carbon tetrachloride, purified by Polissar's method, contained impurities which were responsible for the rate maximum observed with it as solvent. As a result of a large number of experiments it has been shown that when the ethylene iodide is recrystallized shortly before use from redistilled Baker C. P. reagent grade carbon tetrachloride and when redistilled Baker C. P. carbon tetrachloride is used as the solvent in the photolysis, the rate of reaction is constant over the entire exposure until retardation sets in (curve 2, Fig. 1). When carbon tetrachloride purified by methods other than Polissar's was used a constant rate of decomposition was obtained, as with redistilled Baker C. P. reagent or with pentane.

Only those experiments in which carbon tetrachloride purified by Polissar's method was used as the solvent showed a maximum in the plot of rate *versus* iodine concentration (curve 1, Fig. 1). The three rate curves in Fig. 1, chosen to show on

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(12) Schmitz-Dumont, *Chem. Ztg.*, **21**, 511 (1897).

(13) Lebowich, Lebowich and Dinburg, *J. Lab. Clin. Med.*, **23**, 284 (1937).

(14) Bäckström, *Naturwissenschaften*, **21**, 251 (1933).

one plot the trend of rate with time, are representative of experiments at different light intensities. Carbon tetrachloride freshly purified by Polissar's method slowly turned pink on standing in light or more rapidly when exposed to ultraviolet light. From this it was surmised that a small amount of some iodine compound had remained in the carbon tetrachloride after the final distillation. The decomposition of this material caused the pink color on standing and perhaps was responsible for the rate maximum. Iodine monochloride was suspected as the impurity but when traces of iodine monochloride were added to the reaction mixture no rate maximum was observed, though the reaction rate was slightly increased and slowly continued to increase throughout the experiment.

In some experiments an ethylene iodide solution containing iodine from a previous exposure was re-exposed after removing the iodine by shaking with metallic silver or mercury and filtering or centrifuging. This treatment, used in the earlier study, had only a small effect on the reaction rate and hence is not the cause of the rate maximum. Saturating the carbon tetrachloride solution with oxygen caused a pronounced decrease in the rate of the photodecomposition of ethylene iodide. Freezing the carbon tetrachloride solution of ethylene iodide and then pumping to remove air before exposure of the solution to light in general had the effect of removing the maximum in the rate curve. These facts might seem to indicate that the presence of oxygen from the air is responsible for the appearance of the rate maximum found earlier. However, Baker C. P. carbon tetrachloride purified by distillation in air in the normal way must contain small amounts of dissolved air and yet, when used as the solvent, no increase is found in the rate of reaction during an experiment.

The results obtained in a large number of preliminary experiments in the present study thus lead to the following conclusions: (1) the photochemical decomposition of pure ethylene iodide in pure pentane or pure carbon tetrachloride proceeds at a constant rate under constant conditions. (2) When carbon tetrachloride purified by Polissar's method is used as the solvent a trace of some unknown impurity causes an increase in the rate of photodecomposition during the course of an experiment.

Quantum Yield Determination.—The light used during these experiments was that transmitted by the filter system. This corresponded to a weighted average of 3110 Å. Quantum yield determinations were carried out at room temperature, at 78.5° (the boiling point of ethanol) and at 100° (the boiling point of water). The reaction cell, optical system and thermopile were calibrated against the uranyl oxalate actinometer. In any one run the quantum yield was determined for various amounts of decomposition, that is, at various concentrations of iodine produced. This was possible due to the fact that the iodine concentration was determined colorimetrically without disrupting or ending an experiment.

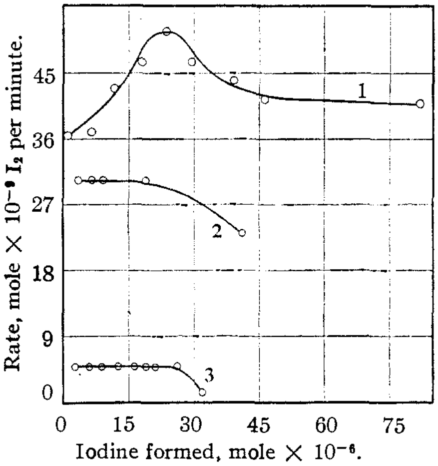

Fig. 1.—Rate of photolysis of ethylene iodide in solution: curve 1, in carbon tetrachloride purified by Polissar method; curve 2, in pure carbon tetrachloride; curve 3, in pentane.

The results of the quantum yield measurements at 25, 78.5 and 100° are summarized in Tables I, II and III, respectively. Since the purely thermal and iodine catalyzed reactions are not negligible at the higher temperatures, the thermal rates of these reactions were determined under conditions identical with those obtaining in the photochemical experiments and the necessary corrections applied. The average quantum yield obtained at room temperature is 0.96, that is, practically unity. This is slightly higher than the earlier average values of 0.76 over a whole experiment or of 0.86 in the region of maximum rate of photodecomposition. The increase in yield presumably results from the elimination of the traces of impurities in the earlier carbon tetrachloride. The effect of these impurities is to decrease the

TABLE I

QUANTUM YIELD OF THE PHOTOLYSIS OF ETHYLENE IODIDE IN CARBON TETRACHLORIDE AT 25°

Ethylene iodide = 0.07 molar

Time, min.	Total I_2 molar × 10^6	Quanta absorbed × 10^{-18}	Molecules decomposed × 10^{-18}	Quantum yield
883	3.6	2.2	1.93	0.89
1192	4.6	2.9	2.54	.88
2596	9.2	6.2	5.33	.86
4061	15.4	9.6	9.1	.95
5373	19.6	17.6	11.6	.92
1359	6.2	3.1	3.21	1.03
2621	10.7	6.0	5.93	0.98
575	3.8	1.66	1.58	0.95
2096	11.2	5.9	6.06	1.03
3540	17.6	9.7	9.9	1.02
5059	25.2	13.8	14.5	1.06
				Average 0.96

TABLE II

QUANTUM YIELD OF THE PHOTOLYSIS OF ETHYLENE IODIDE IN CARBON TETRACHLORIDE AT 78.5°

Ethylene iodide = 0.07 molar

Total I_2 molar × 10^6	I_2 Photochem. mole × 10^6	Molecules decomposed × 10^{-17}	Quanta absorbed × 10^{-17}	Quantum yield
1.20	1.05	6.36	1.39	4.6
2.2	1.8	10.7	2.9	3.6
3.2	2.5	15.4	4.3	3.6
5.1	4.2	25.4	6.2	4.1
5.8	4.7	28.5	7.6	3.7
7.0	5.6	33.9	9.9	3.4
7.4	5.8	35.1	11.3	3.1
8.2	6.7	37.6	14.5	2.6
10.9	8.7	52.7	16.5	3.2
14.4	11.7	70.9	20.2	3.5
				Average 3.5

TABLE III

QUANTUM YIELD OF THE PHOTOLYSIS OF ETHYLENE IODIDE IN CARBON TETRACHLORIDE AT 100°

Ethylene iodide = 0.07 molar

Total I_2 molar × 10^6	I_2 Photochem. mole × 10^6	Molecules decomposed × 10^{-17}	Quanta absorbed × 10^{-17}	Quantum yield
4.3	2.0	12.1	2.8	4.4
8.3	4.1	24.8	4.9	5.1
11.4	5.4	32.4	6.9	4.7
13.7	5.8	35.4	8.5	4.2
				Average 4.6

rate, the rate rising to a maximum as the impurities are destroyed. The net result would be a smaller total amount of decomposition, hence, a lower quantum yield. At 78.5 and 100° the quantum yields obtained are 3.5 and 4.6, respectively, indicating the chain character of the reaction at higher temperature.

Energy of Activation.—The slopes of the curves obtained by plotting the concentration of iodine produced against the time of reaction give the instantaneous rates. Such rates, corrected for the thermal reaction, were obtained for the photodecomposition at the two higher temperatures investigated. Comparing the rates of the photochemical reaction at corresponding amounts of decomposition at the two temperatures the average energy of activation for the over-all photochemical reaction is found to be 13800 calories. The data are shown in Table IV.

TABLE IV

ENERGY OF ACTIVATION OF THE OVER-ALL PHOTOLYSIS OF ETHYLENE IODIDE IN CARBON TETRACHLORIDE

Ethylene iodide = 0.07 molar

I_2 concn. molar × 10^6	Photochem. rate at 78.5° Mole × 10^6 per min.	Photochem. rate at 100° Mole × 10^8 per min.	E, kcal.
3.2	0.80	2.24	12.5
5.8	1.04	2.98	12.7
9.0	1.21	4.28	15.2
13.3	1.81	6.29	15.0
16.3	1.88	5.72	13.4
			Average 13.8

Exchange with Radioactive Iodine.—The addition of iodine containing radioactive iodine to a carbon tetrachloride solution of ethylene iodide may be used to test for the presence of iodine atoms. The exchange of radio-iodine with ethylene iodide to give radioactive ethylene iodide is slow. If the photodecomposition of ethylene iodide proceeds in a single step into ethylene and iodine, then in the presence of radioactive iodine little or no radioactivity should appear in the ethylene iodide. On the other hand, if the photolysis proceeds through C_2H_4I and iodine atoms as suggested later, then there will be an opportunity for exchange to occur and radioactivity will appear in the ethylene iodide.

Radio-iodine was obtained by bombardment of tellurium with protons in the cyclotron of the Physics Department. Sodium iodide was added as a carrier and the radio-iodine was separated from the tellurium. The exchange occurring in a carbon tetrachloride solution of radio-iodine and ethylene iodide was then observed under various conditions. To determine the radioactivity of the ethylene iodide the free iodine was removed from the solution with metallic mercury or silver, filtered off and the radioactivity of the ethylene iodide solution determined on a Geiger–Müller counter of the type described by Bale.[15]

The radioactivity in the ethylene iodide in a solution kept in the dark could be compared with that of a solution subjected to photodecomposition. As mentioned previously, practically no exchange should occur between $C_2H_4I_2$ and II* (where I* indicates radio-iodine) in carbon tetrachloride solution in the dark. Actually 5.7% exchange was observed. This is probably due to the presence of traces of water introduced into the carbon tetrachloride in the process of obtaining a radioactive iodine solution. Iodide and bromide ions in solution have been shown to exchange with organic iodides and bromides.[16] As can be seen from the data in Table V the exchange in a solution exposed to ultraviolet light is double that obtained in the dark. The thermal or dark exchange is seen to increase with temperature. This is to be expected since increasing the temperature

TABLE V

EXCHANGE BETWEEN ETHYLENE IODIDE AND RADIO-IODINE IN CARBON TETRACHLORIDE

Expt.	Temp., °C.	Time, min.	I_2 molar × 10^3	$C_2H_4I_2$ molar	% Exchange
Thermal	25	1660	0.88	0.07	5.7
	100	1660	2.64	.07	15
Photo[a]	25	920	3.3	.04	43
Photo[b]	25	1135	5.11	.07	11
	100	1080	1.98	.07	36
	100	1480	2.64	.07	39

[a] Light of an incandescent lamp. [b] Light of 3130 Å.

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[15] Bale, *Radiology*, **35**, 184 (1940).

[16] le Roux and Sugden, *J. Chem. Soc.*, 1279 (1939); McKay, THIS JOURNAL, **65**, 702 (1943).

increases the dissociation of iodine molecules into atoms. However, the exchange in ultraviolet light is again much greater than the thermal exchange at the higher temperature. When the solution at room temperature is exposed to visible light which dissociates iodine into atoms a large increase in the exchange is observed. This is further evidence for an atom mechanism for the exchange and points to the presence of atoms during the photolysis of ethylene iodide itself.

Discussion

The photochemical decomposition of ethylene iodide in carbon tetrachloride solution is accounted for by the following mechanism

$$C_2H_4I_2 + h\nu \longrightarrow C_2H_4I + I \quad (1)$$
$$C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2 \quad (2)$$
$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I \quad (3)$$
$$C_2H_4I \longrightarrow C_2H_4 + I \quad (4)$$
$$C_2H_4 + I \longrightarrow C_2H_4I \quad (5)$$
$$I + I \longrightarrow I_2 \quad (6)$$

Of these reactions all except one have been suggested previously in connection with the formation,[6] thermal decomposition[4] and iodine photosensitized decomposition of ethylene iodide.[7] Reaction (1) was suggested by DeRight and Wiig.[11] Light of wave length 3110 Å. contains more than enough energy to dissociate ethylene iodide. Reaction (3) is needed to account for inhibition by added iodine.[11] These reactions may be combined in the usual way to give a rate expression which is in agreement with all the experimental facts observed in both this and the earlier work.

The present work presents three pieces of evidence which support the above mechanism.

As mentioned previously the over-all temperature coefficient of the photochemical reaction determined from experiments at 78 and 100° corresponds to an energy of activation of 13.8 kcal. Sherman and Sun[17] give 1.8 kcal. as the energy of activation for reaction (3) while the values for reactions (4) and (5) would be negligible.[6] Schumacher[6] calculated the energy of activation for reaction (2) from thermal data to be 11.5 ± 2 kcal. while Schumacher and Wiig[7] found 11.8 kcal. from a study of the iodine photosensitized reaction. The Hirschfelder rule gives for reaction (2) a value of $E = 11.0$ or 15.2 kcal. depending on whether the carbon–iodine bond is taken as 44 kcal.[17] or 48 kcal.[6] Thus the energy of activation of 13.8 kcal. found for the photochemical reaction in this study is due to reaction (2) and is in good agreement with the above values.

The increase in the quantum yield observed with increase in temperature points toward a chain mechanism rather than a one step decomposition as suggested by Emschwiller.[18] Reaction (2) would be negligibly slow at room temperatures since E is equal to about 13 kcal. This is in agreement with the quantum yield of approximately unity. As the temperature is increased to 78 and 100°, however, reaction (2) will become important. Under these conditions reactions (2) and (4) furnish a chain mechanism for the decomposition of ethylene iodide and the quantum yield would be expected to rise, as actually observed. These same reactions account for the quantum yield of 25 and the chain character of the iodine photosensitized reaction.[7]

Finally, the study of the exchange reaction of iodine and ethylene iodide points to an atom mechanism. The exchange between iodine and ethylene iodide dissolved in carbon tetrachloride is small in the dark at room temperatures. If the solution is exposed to visible light absorbed by iodine considerable exchange (43%) is observed. Since this is known to cause dissociation of iodine into atoms, the exchange involves atoms, proceeding by reactions (2) and (3). Similarly, when the solution is exposed to light absorbed only by the ethylene iodide an increase in the extent of the exchange is observed. This points to reaction (1) as the primary process.

With the elimination of the previously reported increase in rate in any one experiment, the photochemical decomposition of ethylene iodide seems to be rather well understood. The mechanism would appear to be that suggested above, which is in agreement with all the known facts.

Summary

The photochemical decomposition of pentane and carbon tetrachloride solutions of ethylene iodide by light of wave length 3110 Å. proceeds at a constant rate rather than at an increasing rate up to a maximum as found previously. The earlier results were apparently due to an impurity introduced into the carbon tetrachloride in one method of purification. The quantum yield has been found to be 1, 3.5 and 4.6 molecules of iodine produced at room temperature, 78 and 100°, respectively. These data point to a chain reaction such as is involved in the mechanism previously suggested. Additional evidence for this mechanism is found in the observed exchange of radioiodine with ethylene iodide undergoing photolysis. The over-all energy of activation for the photodecomposition is found to be 13.8 kcal. in good agreement with that to be expected.

ROCHESTER, N. Y. RECEIVED DECEMBER 23, 1946

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[17] Sherman and Sun, THIS JOURNAL, **56**, 1096 (1934).

[18] Emschwiller, *Compt. rend.*, **199**, 854 (1934).