3. One of the compounds measured, *l*-sorbose, has been shown to possess a transition of the type displayed by ammonium chloride.

PITTSBURGH, PENNSYLVANIA RECEIVED MAY 5, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 825]

The Rate and Mechanism of the Hydrolysis of Hydroxylamine Disulfonate Ion

BY SAM NAIDITCH AND DON M. YOST

Neutral or dilute acid solutions of potassium hydroxylamine disulfonate hydrolyze at a measurable rate at room temperature to give potassium hydroxylamine monosulfonate and potassium bisulfate, the hydrolytic reaction being, in ionic form

$$HON(SO_3)_2^= + H_2O = HONHSO_3^- + H^+ + SO_4^= \tag{1}$$

The hydroxylamine monosulfonate ion is relatively stable and does not hydrolyze in dilute acid solution except at higher temperatures. Wagner[1] made a single measurement on the rate of hydrolysis of the disulfonate and found it to be proportional to the concentrations of $HON(SO_3)_2^=$ and H^+. The present paper describes the results of a detailed study of the rate and mechanism of this hydrolysis.

Preparation of the Materials. Experimental Procedure

Potassium hydroxylamine disulfonate was prepared according to the method described by Rollefson and Oldershaw[2] in which an ice-cold, acetate-buffered solution of potassium nitrite is treated with sulfur dioxide. The moist salt obtained was washed with ice-cold water and used directly, or it was washed repeatedly with absolute alcohol, and, after drying by evaporation, it was placed in a vacuum desiccator over concentrated sulfuric acid or phosphorus pentoxide and kept at about 5°. The anhydrous salt thus prepared, $K_2HON(SO_3)_2$, could be kept for more than a month without decomposition.

In the first 35 runs the freshly prepared, moist salt was washed repeatedly with ice-cold water, and then portions of it were dissolved rapidly in a thermostated volumetric flask nearly filled with a mixture of water and a measured quantity of hydrochloric acid; time was counted from solution of the salt upon shaking after filling the flask to the mark. For the remainder of the measurements the alcohol-washed salt was used, accurately weighed amounts being dissolved in water in a volumetric flask as before. For those experiments in which acid was added initially, hydrochloric acid was used.

The reaction was followed by determining the acid concentration of the reaction mixture at measured intervals. Samples of 25 or 50 ml. were pipetted into an excess of standard sodium hydroxide to stop the reaction, and the excess base was back-titrated with standard hydrochloric acid, using phenolphthalein as an indicator. Consistent results were not obtainable when the back-titration was postponed for more than about fifteen minutes.

All solutions used for the rate runs were carbonate-free, and all flasks were flushed free of carbon dioxide before use. The samples withdrawn from the reaction mixtures were pipetted by means of nitrogen under pressure. During the titration of the mechanically stirred samples, carbon dioxide-free air was passed into the flasks used.

That the alcohol-washed, anhydrous $K_2HON(SO_3)_2$ was pure is shown by the following experiments, in which accurately weighed amounts of the salt were dissolved in pure water and, after several days, the acid formed was determined by the same procedure as that used for the rate determinations.

$K_2HON(SO_3)_2$ taken, g.	Final acid concn. found, mole/l.	Final acid concn., calcd., mole/l.	Diff., %
0.6076	0.00453	0.00451	0.4
.5630	.00417	.00418	.2

It is believed that the present preparations of the pure, anhydrous potassium hydroxylamine disulfonate are the first that have been reported.

Results of the Rate Experiments

At ionic strengths from about 0.01 to 0.4 *m* the rate of hydrolysis in acid solution at 25° is adequately represented by the rate equation

$$-d(\Sigma Ds^=)/dt = k(\Sigma Ds^=)(\Sigma H^+) = k(a - x)(b + x) \tag{2}$$

where $(\Sigma Ds^=)$ is the total concentration of hydroxylamine disulfonate at the time t, and a is its initial concentration in mole/l.; b is the initial normality of acid, and x is the normality produced by the hydrolysis of the disulfonate during the time t. This equation may be integrated to give

$$\log \frac{b + x}{a - x} = \frac{a + b}{2.303}kt + \text{const.} \tag{3}$$

The specific reaction rate constants, k, were obtained from the slopes of the plots of $\log (b + x/a - x)$ against t. Apparently the acids H_3O^+, HSO_4^-, $HON(SO_3)_2H^-$, and $HONHSO_3H$, when present in appreciable concentrations, are equally

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(1) Wagner, *Z. physik. Chem.*, **19**, 678 (1896).

(2) Rollefson and Oldershaw, THIS JOURNAL, **54**, 977 (1932).

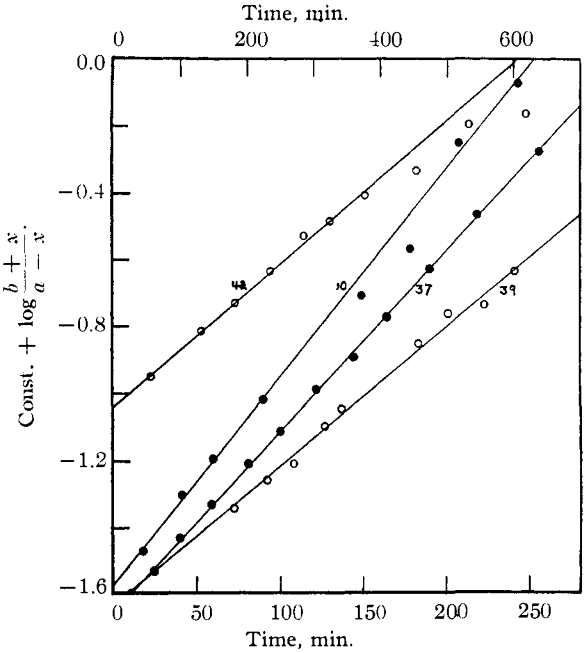

Fig. 1.—Curves for the evaluation of acid rate constants at 25.00°.

effective in catalyzing the reaction in this ionic strength range, since, as may be seen in Fig. 1, the curves show no systematic deviation from linearity.

TABLE I

REPRESENTATIVE TIME–CONCENTRATION DATA FOR RATE MEASUREMENTS AT 25.00°

Run 37	Run 10	Run 42	Run 39
$a = 0.0473$ mole/l.	$a = 0.0495$	$a = 0.00448$	$a = 0.00472$
$b =$ none[a]	$b = 0.00640$ N	$b = 0.000152$ N	$b =$ none[a]
$\mu = 0.142$	$\mu = 0.155$	$\mu = 0.0136$	$0 = 0.0142$
$k = 0.262$ l mole^{-1} min.$^{-1}$	$k = 0.257$	$k = 0.844$	$k = 0.837$

t, min.	$x \times 10^3$, mole/l.	t, min.	$x \times 10^2$, mole/l.	t, min.	$x \times 10^4$, mole/l.	t, min.	$x \times 10^4$, mole/l.
11	1.12	18	1.199	57	4.50	181	2.04
24	1.34	42	1.595	132	6.06	230	2.46
38	1.67	60	1.885	181	7.14	272	2.70
58	2.03	90	2.428	236	8.52	318	3.42
81	2.68	148	3.440	285	10.38	344	3.78
100	3.39	178	3.861	324	11.22	458	5.76
122	4.32	208	4.618	376	12.90	503	6.90
144	5.32	242	4.912	453	14.40	559	7.32
164	6.65			532	17.88	603	8.82
189	8.93			618	18.60		
218	12.08						
256	16.17						

[a] When the value *none* is given for the initial acid concentration, it means that no acid was added initially. The initial acid concentration is, therefore, only that obtaining in a solution of the disulfonate.

In Table I are presented the time–concentration data for four typical experiments made at moderate and at low ionic strengths; in two of these runs acid was added initially. Table II contains the rate constants found at 25.00° for a number of experiments. The significance of the constants shown in the last four columns of the table will appear later.

In those runs in which no acid was added to the disulfonate, the intercepts of the curves with the ordinate at zero time (see Fig. 1) were larger than expected; for example, the intercept for run 37 corresponds to a value of $b = 1.06 \times 10^{-3}$ mole/l. whereas, since no acid was added initially, b is at most $10^{-6.8}$ (determined by use of a glass electrode about one minute after a test solution was made up). This indicates that the catalytic effect of water must be considered. This effect is included in the rate expression

$$-\mathrm{d}(\Sigma\mathrm{Ds}^{=})/\mathrm{d}t = [k'(\Sigma\mathrm{H}^+) + k'_{\mathrm{w}}(\mathrm{H_2O})]\,(\Sigma\mathrm{Ds})^{=} = [k'(b + x) + k'_{\mathrm{w}}](a - x) \quad (4)$$

where k'_{w} is the rate constant for water catalysis when the activity of water is taken as unity. This equation is readily integrated to give

$$\log\left[\frac{b + \frac{k'_{\mathrm{w}}}{k'} + x}{a - x}\right] = \frac{\left[a + b + \frac{k'_{\mathrm{w}}}{k'}\right]}{2.303} k't + \log\left[\frac{b + \frac{k'_{\mathrm{w}}}{k'}}{a}\right] \quad (5)$$

When it is assumed, as a first approximation, that the effect of the water catalysis is only important initially, then the rate constants of equation (5) may be obtained graphically from the slopes and intercepts at zero time of curves such as those shown in Fig. 1. This treatment was applied to the results for those runs in which no acid was added initially, and the values of k'_{w} so obtained are shown in Table II.

Because of the approximation involved in the above method for evaluating k'_{w}, the following second method was also used in some cases. The simplified rate equation

$$-\frac{\mathrm{d}(\Sigma\mathrm{Ds}^{=})}{\mathrm{d}t} = k''_{\mathrm{w}}(\mathrm{H_2O})(\Sigma\mathrm{Ds}^{=}) = k''_{\mathrm{w}}(a - x) \quad (6)$$

is applicable in the neighborhood of $t = 0$, providing no acid was added initially. On integration one obtains

$$\log(a - x) = -k''_{\mathrm{w}}t/2.30 + \log a \quad (7)$$

and by evaluating the slope of the log $(a - x)$ *versus* t curve at zero time (when practically all of

TABLE II

REPRESENTATIVE RATE MEASUREMENTS ON THE HYDROLYSIS OF POTASSIUM HYDROXYLAMINE DISULFONATE AT 25.00°

Expt.	Initial concn. of $K_2HON(SO_3)_2$, mole/l.	Initial acid concn., mole/l.	Initial ionic strength, μ	k, l., mole^{-1} min.$^{-1}$	$k'_W \times 10^4$, min.$^{-1}$	$k''_W \times 10^4$, min.$^{-1}$	k', l., mole^{-1} min.$^{-1}$	$k_B \times 10^2$ min.$^{-1}$
7, 8	0.127	0.00640	0.386	0.165			0.163	3.2
9	.0961	None[a]	.288	.202	1.2	2.3	.200	3.0
14	.0846	None	.254	.208	3.8	3.6	.206	2.8
13	.0762	.0104	.239	.229			.227	2.6
15	.0566	None	.169	.247	3.1	2.6	.243	2.4
10	.0495	.00640	.155	.257			.253	2.3
37	.0473	None	.142	.262	2.8	3.0	.258	2.3
29	.0263	None	.0789	.318	1.1	1.5	.310	1.7
38	.0230	None	.0689	.348	2.0	2.1	.339	1.8
30	.0191	None	.0573	.414	1.3	1.2	.403	1.9
40	.00842	None	.0253	.651	1.4	1.1	.626	1.8
39	.00472	None	.0142	.837	0.92		.792	1.7
42	.00448	.000152	.0136	.884			.798	1.5
41	.00273	.000152	.00835	.998			.926	1.5

[a] When the value *none* is given for the initial acid concentration, it means that no acid was added initially; the initial acid concentration is therefore only that resulting from a solution of the disulfonate.

the hydrolysis is caused by water), values of k''_w are found. These compare favorably with the k'_w, as may be seen in Table II. The average value found for k_w was 2.1×10^{-4} min.$^{-1}$, and it should be practically independent of the ionic strength.

The values of k shown in Table II have been corrected for the catalytic effect of the water as follows. From equation 5, neglecting the effect of k'_w/k' in the logarithm term, the experimental slope, S, is $\left[a + b + \frac{k'_w}{k'}\right]\frac{k'}{2.30}$ hence, $k' = k - k'_w/(a + b)$. The values of k' so calculated are also presented in Table II.

Brönsted's equation as modified by Guggenheim,[3] namely

$$\log k = \log k_0 + \frac{Z_1Z_2\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \qquad (8)$$

was used to correlate k' with μ for $\mu < 0.1$. On using Fig. 2 and estimating k_0 analytically it was found that

$$\log k' = 0.167 - \frac{2\sqrt{\mu}}{1 + \sqrt{\mu}} - 3.4\,\mu \qquad (9)$$

The results of the experiments made at 45 and 55° are more difficult to treat than those at 25° because the hydrolytic reaction

$$HONHSO_3^- + H_2O = HONH_3^+ + SO_4^= \quad (10)$$

which may be expected to be catalyzed by acid, can no longer be neglected. A typical log $x/a - x)$, t curve at these temperatures is shown in Fig. 3. Features of the reaction to be noted are, (1) the high initial rate, caused by water catalysis; and (2) the upward concavity of the curve at a later time, caused by the hydrolysis of the monosulfonate to hydroxylamine. Since the concentrations of both the monosulfonate and acid increase with time, the hydrolysis of the former becomes important. The effect of water catalysis was estimated as before; the values obtained for k''_w (see Table III) are probably high and therefore the smallest are considered most acceptable.

$$k_w = 2.0 \times 10^{-3} \text{ min.}^{-1} \text{ at } 45°$$
$$k_w = 0.9 \times 10^{-2} \text{ min.}^{-1} \text{ at } 55°$$

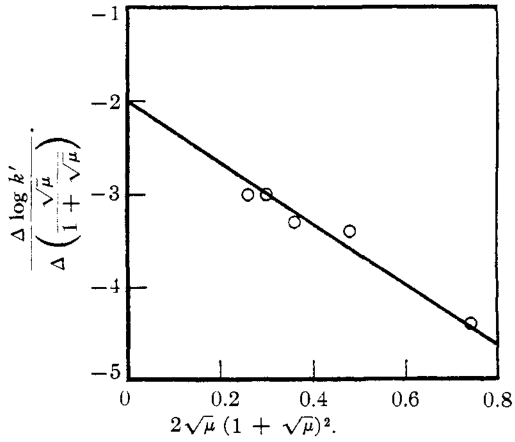

Fig. 2.—Curve for the determination of Z_1Z_2 and B at 25.00°.

Since no acid was added initially at 45 and 55°, the rate equation for the hydrolysis of the monosulfonate may be assumed to be

$$d(\Sigma HONH_2)/dt = k_2\,(\Sigma HONHSO_3^-)(\Sigma H^+) = k_2(x - y)(x + y) \quad (11)$$

where x is the amount of disulfonate hydrolyzed,

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(3) Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

TABLE III

RESULTS OF RATE MEASUREMENTS ON THE HYDROLYSIS OF POTASSIUM HYDROXYLAMINE DISULFONATE AT 45 AND 55°

No acid was added initially in these experiments.

Expt.	Initial concn. of $K_2HON(SO_3)_2$, mole/l.	Initial ionic strength, μ	k l. mole^{-1} min.$^{-1}$	k_P l. mole^{-1} min.$^{-1}$	k'_w min.$^{-1}$	k''_w min.$^{-1}$	k' l. mole^{-1} min.$^{-1}$	k'_P l. mole^{-1} min.$^{-1}$
				t = 45°				
50	0.00577	0.0173	5.18	4.59	3.2×10^{-3}	4.5×10^{-3}	4.83	
51	.04496	.0149	5.66	4.25	4.7	8.3	5.26	
45	.00467	.0141	5.67	5.72	1.8	4.5	5.24	5.29
52	.00342	.0103	6.32	6.22	3.1	4.0	5.74	5.64
47	.00321	.0097	6.33	6.41	2.2	2.7	5.71	5.79
				t = 55°				
54	.00457	.0137	14.5	14.0	1.9×10^{-2}	2.1×10^{-2}	12.5	12.0
55	.00423	.0127	14.8	17.7	3.4	1.5	12.7	
53	.00326	.0098	16.2	16.0	3.5	0.91	13.4	13.2

and y is the amount of hydroxylamine formed, in mole/l. On using this equation in conjunction with (2) there results for $x < a$

$$d(\Sigma H^+)/dt = k_P(\Sigma H^+)[a - (1 - P)(\Sigma H^+)]$$

which integrates to

$$\log\left[\frac{(\Sigma H^+)}{a - (1 - P)(\Sigma H)}\right] = \frac{ak_P}{2.303}t + \text{const.} \quad (12)$$

where $P = k_2/k$.

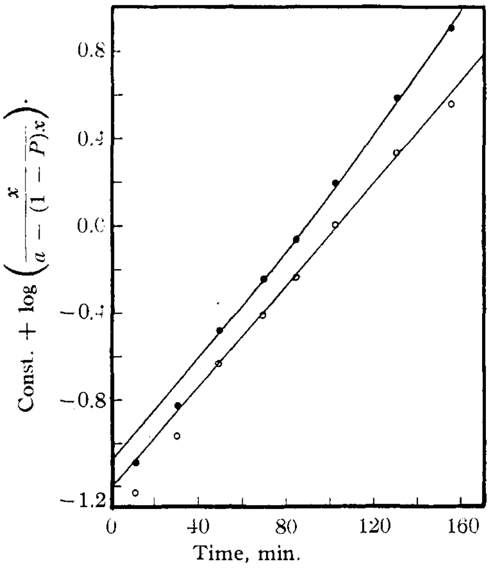

Fig. 3.—Curves showing the effect of the hydrolysis of hydroxylmonosulfonate ion: P = 0, ●; P = 0.1, ○.

The value of P is not known, but the assumption that an upper limit is P = 0.1 leads, except for the initial period in which water catalysis is important, to the straight line shown in Fig. 3. Since P = 0.10 is probably too large, and since the P's are different for different ionic strengths, the resulting curves, although more nearly linear than those obtained previously, will yield only approximate values of k_P. The values of the acid rate constant k_P obtained using P = 0.10 are tabulated in Table III. The water catalysis corrections to the rate constants were made as before.

The Arrhenius equations for the acid and water catalyzed hydrolysis of hydroxylamine disulfonate were derived for solutions of zero ionic strength and are shown in Table IV which also contains the limiting values of k' and k_w.

TABLE IV

THE LIMITING VALUES OF k' AND k_w FOR SOLUTIONS OF ZERO IONIC STRENGTH

Temp., °C.	k'_0 l. mole^{-1} min.$^{-1}$	k^0_w min.$^{-1}$
25.00	1.47	2.1×10^{-4}
45.00	10.4	2.0×10^{-3}
55.00	22.0	0.9×10^{-2}

$$k'_0 = 10^{13.1} e^{-17,600/RT} \text{ l. mole}^{-1} \text{ min.}^{-1}$$
$$k^0_w = 10^{13} e^{-23,000/RT} \text{ min.}^{-1}$$

The Reaction Mechanism

The simplest mechanism suggested by the results for the hydrolysis catalyzed by acid assumes that the ion $HON(SO_3)_2H^-$ forms a reactive complex with water. The over-all rate is determined by the rate at which the complex is converted into the hydrolytic products. It is evident that the concentration of $HON(SO_3)_2H^-$ will be determined by that of H^+.

$$H^+ + HON(SO_3)_2^= \rightleftarrows HON(SO_3)_2H^-$$
$$HON(SO_3)_2H^- + H_2O \rightleftarrows HON(SO_3)_2H_3O^-$$
$$HON(SO_3)_2H_3O^- \longrightarrow HONHSO_3H + HSO_4^-$$

The rate equation for the hydrolysis will be

$$-\ d(\Sigma HON(SO_3)_2^=)/dt = k_B(H_2O)(HON(SO_3)_2H^-) \quad (13)$$

and this may be integrated readily on the assumption that the ionization constants of the acids HSO_4^-, $HONHSO_3H$ and $HON(SO_3)_2H^-$ are all equal. After lumping several very insensitive terms (terms which vary little with time) into the integration constant, the following integral is obtained for equation (13) for the cases in which no acid was added initially

$$\log \frac{x}{a - x} + C \log (a - x) = \frac{k_B a}{2.303\,(a + K)}\, t + \text{const.} \qquad (14)$$

where K is the acid ionization constant for HSO_4^-, $HON(SO_3)_2H^-$ and $HONHSO_3H$; C is a constant, less than unity in most cases, and affects the linearity of the log $x/a - x$, t curves only slightly. Equation (14) differs little from equation (3), and it is for this reason that straight lines were obtained in Fig. 1.

As a first approximation

$$k_B(a + b)/(a - b + K) = k'(a + b) \qquad (15)$$

and therefore, $k_B = k'(a + K)$ for those runs in which no acid was added initially. In order to obtain values of k_B which may be subjected to inspection, the values of K for HSO_4^- calculated by Pedersen[4] were used, those for the other acids not being known.

The values obtained for k_B are tabulated in the last column of Table II; for zero ionic strength $k_B = 1.5 \times 10^{-2}$ min.$^{-1}$ at 25°, and should be nearly independent of μ. When $\mu < 0.1$, k_B is effectively constant as may be seen in the table.

That the mechanism assumed provides a satisfactory explanation for the experimental results is shown by their accord with the experimentally found rate equation and by the fact that the rate constant k_B varies but little with the ionic strength.

Summary

Anhydrous potassium hydroxylamine disulfonate, $K_2HON(SO_3)_2$, has been prepared and kept more than a month without appreciable decomposition.

The rate of the hydrolysis

$$HON(SO_3)_2^{=} + H_2O = HONHSO_3^- + H^+SO_4^{=}$$

has been measured. For acid solutions the rate equation was found to be

$$-d(\Sigma HON(SO_3)_2^{=}(/dt = k(\Sigma H^+)(\Sigma HON(SO_3)_2^{=})$$

where the sigmas refer to the total concentration of all ions containing the group indicated. Water also catalyzes the hydrolysis, but its effect is much less than that of acid. The effect of temperature on k corresponds to an energy of activation of 17,600 cal./mole.

A mechanism which explains the observations satisfactorily assumes that $HON(SO_3)_2H{\cdot}H_2O^-$ is the intermediate whose rate of decomposition into the final products determines the over-all rate of the hydrolysis.

PASADENA, CALIFORNIA RECEIVED MAY 2, 1941

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[4] Pedersen, *J. Phys. Chem.*, **38**, 601 (1934).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Dielectric Behavior of Solutions of the Protein Gliadin[1]

BY P. P. ENTRIKIN[2]

In the first sedimentation study of gliadin, the prolamine of wheat, Krejci and Svedberg[3] found the protein to be inhomogeneous, a result to be expected in view of the earlier careful and detailed analysis of the material by Haugaard and Johnson.[4] In the sedimentations both whole and fractionated gliadins were used. A sedimentation equilibrium experiment with an approximately homogeneous gliadin fraction which had the same specific sedimentation velocity or sedimentation constant, $s_{20} = 2 \times 10^{-13}$ cm./sec./dyne, as that of the main constituent of purified gliadin gave a value of 27,000 for the molecular weight of the substance. Measurable differences in sedimentation constant of the several gliadin fractions were not observed. Later on the diffusion constants of three gliadin fractions were determined by Lamm and Polson,[5] making it possible to calculate the molecular weight of the predominant constituent. For this fraction the diffusion constant was reported to be $D_{20} = 6.7 \times 10^{-7}$ so that

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[1] More complete details of this work are to be found in the thesis of Paul P. Entrikin submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree in June, 1940.

[2] Present address: Technical Division, Standard Oil Company of Louisiana, Baton Rouge, Louisiana.

[3] Krejci and Svedberg, THIS JOURNAL, **57**, 946 (1935).

[4] Haugaard and Johnson, *Compt. rend. trav. Lab. Carlsberg*, **18**, No. 2 (1930).

[5] Lamm and Polson, *Biochem. J.*, **30**, 528 (1936).