somewhat less steep than the log k–log D curve in the region of the inflection point of the latter. Since we may write (16) as

$$k^{-1} = \frac{A}{D^3}\frac{1}{b^3}I(b)$$

where A represents universal constants, and since b^{-3} $I(b)$ is not very sensitive to the value of b in the inflection region of the log k–log D curve, we see that D^{-3} is the controlling factor in this region. This fact is probably the explanation of the empirical rule discovered by Walden, which states that the product D^3V is approximately constant, where V is the volume at which the minimum appears.

Summary

1. The hypothesis is made that a triple ion, formed from a neutral molecule and a simple ion by the action of electrostatic forces, will exist as a stable structure in solvents of low dielectric constant.
2. The presence of triple ions of the above type accounts in a large measure for the appearance of minima in conductance curves.
3. Dissociation constants for the triple ions computed theoretically agree with values obtained from conductance data.
4. The observed shift of the minimum of conductance toward higher concentrations with increasing dielectric constant of the solvent is given theoretical basis.

PROVIDENCE, RHODE ISLAND

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Polymorphism in the Substituted Thiazole, 3-Phenyl-2,4-thiazolidione

BY R. E. GIBSON AND K. S. MARKLEY[1]

Optical Crystallography of 3-Phenyl-2,4-thiazolidione

BY H. E. MERWIN

In the course of a study of the reaction between monochloroacetic acid and thiocarbanilide Markley and Reid[2] repeatedly prepared quantities of 3-phenyl-2,4-thiazolidione and recrystallized each preparation from hot glacial acetic acid. Thus obtained, the compound melted at 143–144°, as determined by the capillary tube method, in which a totally immersed thermometer and electrically heated melting apparatus[3] was used. Repeated crystallization from glacial acetic acid failed to effect a change in the melting point of the compound but after recrystallization from hot

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[1] Part III of the Ph.D. dissertation of K. S. Markley, June, 1929.

[2] Markley and Reid, THIS JOURNAL, **52**, 2137 (1930).

[3] Sando, *Ind. Eng. Chem., Anal. Ed.*, **3**, 65 (1931).

water it melted at 147–148°. Subsequent recrystallization from acetic acid caused a reversion of the melting point to 143–144°.

Lange,[4] the first to prepare 3-phenyl-2,4-thiazolidione, reported its melting point as 148°. Liebermann and Völtzkow[5] and later Meyer[6] reported the melting point of their preparations as 148° and Wheeler and Barnes[7] gave it as 147–148°. Evers,[8] however, reported 143° as the melting point of each of his three different preparations of 3-phenyl-2,4-thiazolidione. All of these authors mention several different solvents from which the compound can be crystallized but they do not state which solvent they used in crystallizing the preparation prior to determining the melting point.

Analyses of the preparations reported by Markley and Reid as well as additional ones made in the course of the present investigation indicated that the compound was pure and contained no solvent of crystallization. This was true also of a number of samples crystallized from 95% alcohol and melting at 147–148°, and of one sample crystallized from 50% alcohol and melting at 143–144°. When sublimed, the compound was found to melt at 143–144° or 147–148° and in some cases at intermediate temperatures, depending upon the conditions of sublimation.

It seemed probable that the differences in the melting temperatures of the samples were attributable to the fact that 3-phenyl-2,4-thiazolidione occurred in at least two different crystalline forms. From such partial optical data as could be obtained initially it was impossible to say definitely that the compound existed in different crystalline forms; later Dr. H. E. Merwin found slight but significant differences in the optical properties of the various samples which will be given in detail at the end of this paper.

In order to demonstrate the polymorphism of 3-phenyl-2,4-thiazolidione we resorted to thermal analysis—by heating and cooling curves—to dilatometer experiments, and to x-ray diffraction photographs which were kindly taken for us by Dr. Sterling B. Hendricks of the Fixed Nitrogen and Fertilizer Division of the United States Department of Agriculture. The results showed clearly that this compound does exist in two polymorphic modifications, the form which melts at 143–144° (usually obtained from glacial acetic acid solution) being stable at room temperature, whereas the form melting at 147–148° (obtained from aqueous solution) is stable at temperatures above *ca.* 100°.

Experimental

Thermal Analysis.—With the apparatus shown diagrammatically in Fig. 1 thermal effects during the heating and cooling of the various samples were observed. The sample of 3-phenyl-2,4-thiazolidione was contained in the double jacketed vessel A and its tem-

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[4] Lange, *Ber.*, **12**, 595 (1879).

[5] Liebermann and Völtzkow, *ibid.*, **13**, 276 (1880); *Ann.*, **207**, 137 (1881).

[6] Meyer, *Ber.*, **14**, 1659 (1881).

[7] Wheeler and Barnes, *Am. Chem. J.*, **24**, 60 (1900).

[8] Evers, *Ber.*, **21**, 962–977 (1888).

perature was observed by the thermocouple B—a single junction of No. 30 constantan and No. 36 copper wires. The thermocouple was enclosed in a thin-walled glass tube just large enough to admit the wires. The melting tube A was immersed in oil contained in a Dewar flask. The oil was heated and stirred by the assembly S. A thermocouple D, immersed in the oil-bath, was connected in series with B so that the temperature difference between the junctions of B and D could be measured directly; this gave the "differential temperature," the criterion of latent-heat changes in the sample. In an experiment the current was adjusted so that the bath heated uniformly at a constant rate (0.5–1.5° per min.); readings of the temperature of the sample, the e. m. f. of the thermocouple B, and of the "differential temperature" were taken at half- or quarter-minute intervals. The "differential temperature" was plotted as ordinate against the temperature of the sample as abscissa, curves similar to those in Figs. 2 and 3 being obtained. As long as no reaction took place in the melting tube the curve was roughly parallel to the temperature axis, but heat absorption or emission accompanying a change of phase was manifested by a sharp increase or decrease in the "differential temperature." In all our experiments a positive "differential temperature" indicated that the sample was cooler than the bath—the normal state of affairs on heating.

Calibration of Thermocouples.—The thermocouples were standardized by comparison in a well-stirred bath with a special single junction element which had been calibrated at the U. S. Bureau of Standards. It was found that in the region between 0 and 200° the table of temperature as a function of e. m. f. given for copper-constantan elements in the "International Critical Tables"[9] could be used without any deviation curve for computing the temperature in degrees Centigrade from the observed reading in microvolts.

Heating Curves.—Curve I in Fig. 2 is the significant portion of the heating curve of a sample of 3-phenyl-2,4-thiazolidione crystallized from aqueous solution and melting in a capillary tube at 148°. It will be seen that there is only one break, around 6500 microvolts (146°), due in fact to the absorption of heat by the sample on melting. On the other hand, curve II, obtained with a sample recrystallized from glacial acetic acid (m. p. 143–144°), shows that a reaction takes place when the temperature is about 139°. Moreover, it was observed that the state of aggregation of the compound did not change during this absorption of heat. On being heated further the compound melted at 146° as did the sample crystallized from water. Curve II, which is one of many similar curves obtained with the lower melting samples, showed definitely that at 139–141° the samples of 3-phenyl-2,4-thiazolidione, melting at 143–144° in a capillary tube, which we shall now call Form II, undergo a rapid solid–solid transformation to the higher temperature modification, Form I. It may be remarked parenthetically that although Form II always appeared to melt at 143–144° in a capillary tube, it never melted at this temperature in the heating curve apparatus. The curves in Fig. 3 were obtained as follows. A sample recrystallized from glacial acetic acid was heated in the melting tube. After the usual heat effect around 139° (curve I) had taken place, the sample was withdrawn from the bath and allowed to cool in the air. The sample was replaced in the bath, kept at room temperature overnight, and the next day another heating curve, curve

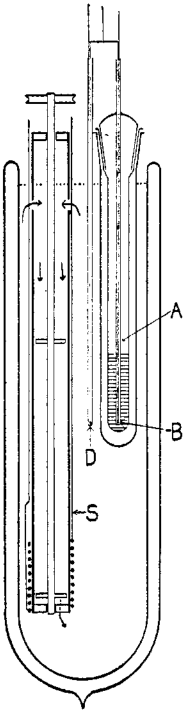

Fig. 1.—Apparatus for detection of phase changes by observation of thermal effects.

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(9) "International Critical Tables," Vol. 1, p. 58 (1926).

II, was obtained. This time no heat effect was observed until melting began; the specimen behaved like the usual product from aqueous solution. Curves III and IV in Fig. 3 were obtained from observations on the same sample of 3-phenyl-2,4-thiazolidione that was used in the experiment which gave curve II, Fig. 2. This sample was melted, then chilled rapidly, and it was observed that Form II crystallized from the melt. Its behavior on reheating is illustrated by curve III which shows the two breaks at 139 and 146°, respectively. The melted material was then allowed to cool slowly and was seeded with Form I. On crystallization the temperature rose to 145° after which the whole was cooled slowly in the bath to room temperature. The heating curve of the sample so treated is curve IV in Fig. 3.

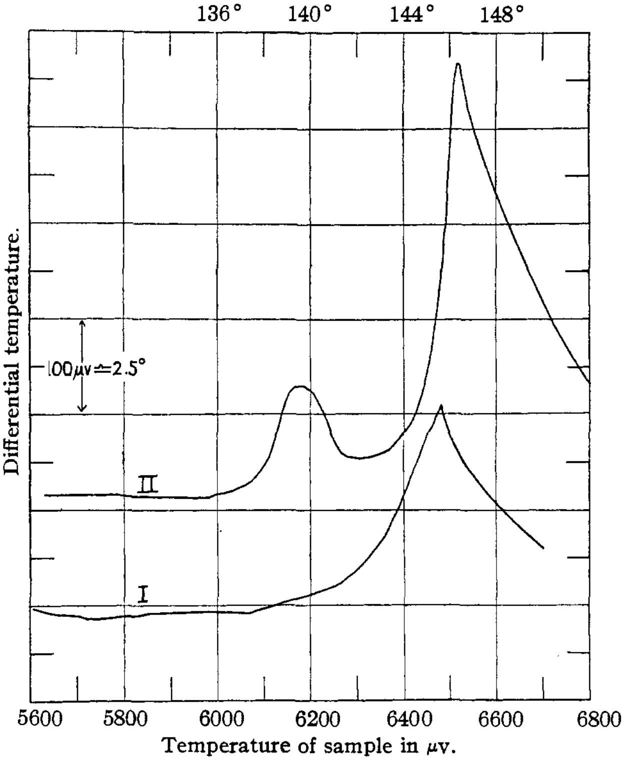

Fig. 2.—Heating curves for the two forms of 3-phenyl-2, 4-thiazolidione. Curve I represents compound crystallized from water and Curve II the same compound crystallized from glacial acetic acid. The ordinate represents the difference between the temperature of the bath and that of the sample and the abscissa gives the temperature of the sample in microvolts at the bottom of the diagram and degrees Centigrade at the top.

From the thermal analyses, therefore, it may be concluded first, that two modifications of 3-phenyl-2,4-thiazolidione exist, Form I which melts at 146° (in a capillary tube at 147–148°)[10] and Form II which inverts to Form I at about 139° when heated; second,

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[10] The difference between the temperatures at which the compound melted in the thermal analysis apparatus (146°) and at which it melted in a capillary tube placed in an electrically heated air-bath

that, as the results illustrated in Fig. 3 show, this inversion is not readily reversible; Form I does not change back to Form II when the temperature is lowered but may remain unchanged for a long time at room temperature; and third, that by suitable treatment either solid modification may be obtained from the same liquid phase. It should be remarked that in one case a sample, crystallized from water under special conditions, gave a heating curve which exhibited two heat effects.

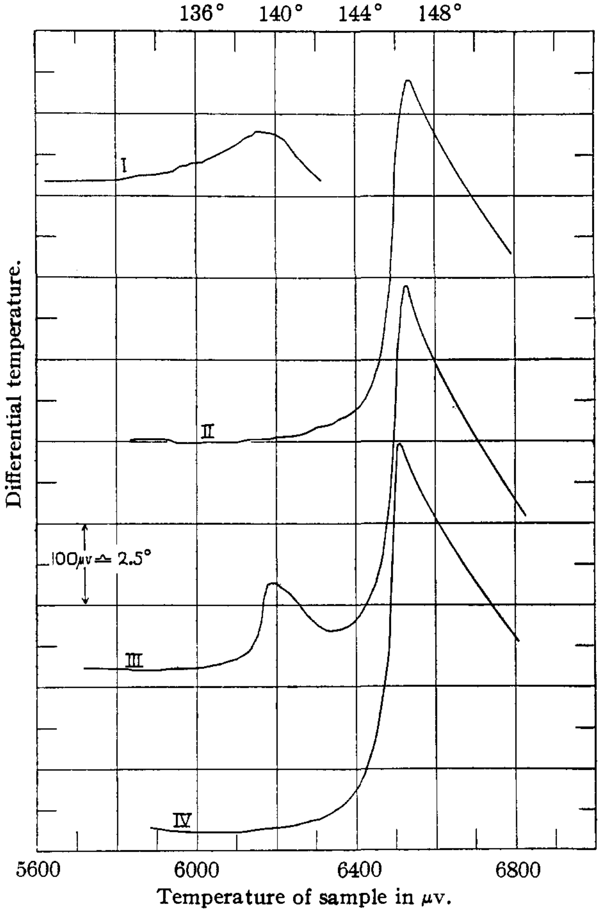

Fig. 3.—Heating curves of 3-phenyl-2,4-thiazolidione treated in different ways.

Dilatometer Experiments.—A sample of 3-phenyl-2,4-thiazolidione was enclosed in the liquid state over mercury in a glass dilatometer. In this way air bubbles were excluded. On account of the impossibility of

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(147–148°) has been partially accounted for by the fact that the latter apparatus gives results which are too high. In a capillary tube immersed in a stirred oil-bath whose temperature was read by thermocouple A, Form I melted between 146 and 147°, a melting temperature definitely higher than 146° as observed in the thermal analysis apparatus. We are unable at present to give a satisfactory explanation of this slight discrepancy.

ensuring that only one form of the solid was present no quantitative measurements could be made. It was found, however, that an anomalous expansion of the solid occurred rapidly in the neighborhood of 136°. This corresponded to the first break in the heating curve of Form II. In addition it was found that this anomalous expansion could be observed to take place slowly at temperatures around 100°. When the sample was held for hours at 100° a small but perceptible expansion, which showed no signs of stopping, could be observed. These qualitative observations led to the conclusion that the first break on the heating curve of Form II merely represents the temperature at which the inversion proceeds rapidly enough to be detected thermally and that the temperature above which Form II ceases to be stable is certainly below 100°.

x-Ray Diffraction Experiments.—Powder diffraction photographs were made with unfiltered Cu K radiation. The samples of 3-phenyl-2,4-thiazolidione were mounted on hairs in the centers of cylindrical cameras with a radius of about 3.50 cm. From the various samples of the substituted diketone which were examined two different x-ray diffraction patterns were obtained, as is evident from an examination of those reproduced in Fig. 4. Fig. 4-A shows the diffraction pattern given by a sample which had been recrystallized from water. The pattern in Fig. 4-C was obtained from a sample crystallized from glacial acetic acid, a sample which showed the thermal effect at 139°. Patterns A and C are significantly different and correspond respectively to the polymorphic Forms I and II. A portion of the specimen from which Pattern C was obtained was melted, cooled to 140°, seeded with the form crystallized from water, and examined in the x-ray spectrograph. The result was Fig. 4-B which is identical with Fig. 4-A. A sample known definitely to be Form I was heated until it was completely melted and then plunged into ice water. The x-ray diffraction pattern of the resultant solid, Fig. 4-D, was the same as that of Form II, Fig. 4-C. The experiments establish quite definitely the fact that 3-phenyl-2,4-thiazolidione exists in at least two solid modifications.

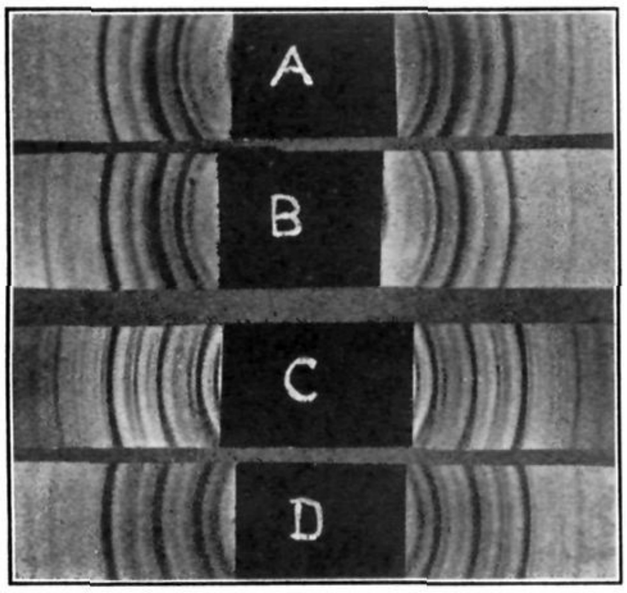

Fig. 4.—x-Ray diffraction patterns of 3-phenyl-2,4-thiazolidione.

It is noteworthy that the two forms have optical properties which are so closely alike that it was impossible to state confidently from results of a casual examination under a polarizing microscope that there was an actual difference in crystal form.

Stability Relations.—The fact that heat is absorbed when Form II transforms to Form I excludes the possibility of monotropy and shows that this change is an enantiotropic one, that is to say, Form II is the stable phase at lower temperatures while Form I is stable at higher temperatures. This was checked by an experiment in which the two forms were enclosed in a tensimeter and it was found that at room temperature Form I had a greater vapor pressure than Form II. As further confirmation, a sample known definitely to be Form I was placed in contact with a saturated solution of the compound in glacial acetic acid and a trace of Form II was added. In another vessel a sample of Form II and a trace of Form I were left in contact with the saturated solution in acetic acid. The mixtures were allowed to stand at room temperature for several months, being agitated at intervals. In each case the resulting solid phase was found by x-ray powder photographs to consist of Form II.

The inversion of Form II to Form I is of a type which is quite common. With rising temperature the change proceeds only very slowly until the temperature is considerably above the equilibrium value at atmospheric pressure, while with falling temperature Form II shows such reluctance to appear that Form I may remain metastable for a long time even at room temperature.

When a compound exists in two or more solid forms, it is of interest to inquire whether the phenomenon is due to polymorphism, that is to say, whether molecules of the same structure are built up in different crystal arrays; or whether it is a result of tautomerism in which case differences in molecular structure would in general appear in other phases than the solid ones. N. V. Sidgwick[11] suggested a convenient method of distinguishing between the two phenomena in cases where the velocity of transformation of tautomers is small. In the case of two solid forms the method consists of determining the following eutectic temperatures: *a*, Form I- Solid Solvent–Solution of I; *b*, Form II- Solid Solvent–Solution of II; and *c*, Form I-Form II-, Solid Solvent–Solution of I and II. If the phenomenon is one of polymorphism the temperature of eutectic *c* will be not less than the temperature of the eutectic of the more soluble (metastable) solid form, the solution and the solid solvent, as both solid forms contribute the same molecular species to the solution. On the other hand, if the solid forms consist of tautomers, each will contribute its own type of molecules to the solution and hence, unless the tautomeric equilibrium in the solution is very rapid, the temperature of the eutectic *c* will be lower than the temperature of eutectics *a* or *b*.

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(11) Sidgwick, *J. Chem. Soc.*, **107**, 672 (1915).

Table I summarizes the results of experiments to determine the invariant temperatures at which the two solid forms of 3-phenyl-2,4-thiazolidione are in equilibrium with solid and liquid benzene. It will be seen that the experiment indicates, either that the case is one of true polymorphism, or that the velocity of the attainment of tautomeric equilibrium in the solution is extremely high.

TABLE I

EUTECTIC TEMPERATURES IN THE SYSTEM, 3-PHENYL-2,4-THIAZOLIDIONE–BENZENE

Phases in system at equilibrium	Equil. temp., °C.
Liquid benzene–solid benzene	5.34
Solution–solid benzene–Form I	4.98
Solution–solid benzene–Form II	5.09
Solution–solid benzene–Form I–Form II	5.00

Summary

The observation that different samples of 3-phenyl-2,4-thiazolidione melt either at 143–144° or 147–148° in a capillary tube is accounted for by the fact that this compound exists in two solid modifications, Form II which is stable at room temperature and Form I which, although stable only at higher temperatures, is capable of existing indefinitely in a metastable state at room temperature. The transformation of Form II to Form I goes so reluctantly that when the compound is heated rapidly, as in a capillary tube, Form II may actually melt metastably before the inversion to the stable phase occurs.

OPTICAL CRYSTALLOGRAPHY OF 3-PHENYL-2,4-THIAZOLIDIONE

The faintly yellow crystals of 3-phenyl-2,4-thiazolidione were studied by means of the petrographic microscope and the goniometer. For nomenclature see Part I of this paper.

Form I (higher temperature). Needles with refractive index β parallel to their length; optic axes, showing indistinctly curved bars, without apparent dispersion, and representing $-2V$ about 80°, emerge from the sides of the needles.

$\alpha = 1.570$, $\beta = 1.696$, $\gamma = 1.779$. The preparation examined was crystallized from water.

Form II (lower temperature). Rectangular, monoclinic blades, with refractive index β and crystallographic axis b parallel to their length, flattened parallel to the front pinacoid; cleavage on the base (angle $\beta = 78.5°$) perfect, and on the side pinacoid poor. An optic axis showing a straight bar, without apparent dispersion, is directed within the crystal 3.5° toward axis a from normal to the plane of flattening. $\alpha \wedge c = 41 \pm 2°$ in obtuse angle β. $\alpha = 1.575$, $\beta = 1.693$, $\gamma = 1.805$, from which $-2V =$ about 83°. The preparation was crystallized from glacial acetic acid.

The orientation, the optic axial angle, and the refractive indices α and β are so similar in the two forms that measurements of γ were required to establish the essential optical difference. Even then a knowledge that the fine-grained preparations contained no disturbing contaminant was necessary. One preparation from water contained both needles and blades. Refractive index β of the needles was definitely the higher. The immersion liquids used between 1.74 and 1.79 were saturated solutions of sulfur in mixtures of methylene iodide and iodobenzene.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photochemical Reaction between Quinine and Dichromic Acid. III. Quinine Derivatives and Utilization of Absorbed Quanta

BY GEORGE S. FORBES AND LAWRENCE J. HEIDT

Two recent papers[1,2] from this Laboratory support the view previously advanced[3] that quinine activated by light is oxidized by non-activated chromic acid. One activated quinine molecule appears to react with one of chromic, as distinguished from dichromic acid. Hydrogen ion in excess has little effect upon the kinetic pattern.

The present study indicates that ten quinine derivatives conform to this same reaction scheme. In all cases the quinoline group can be held chiefly responsible for the absorption of light, and the secondary hydroxyl on carbon atom 4 of Fig. 2 for the reduction of chromic acid. There follows an attempt to correlate structural variations with the efficiency of energy transmission from the absorbing group to the reactive group, also with the purely steric factors of the oxidation reaction.

Our experimental methods have been described.[1,2] The mixtures were irradiated by monochromatic light of several wave lengths in the same trapezoidal quartz cell, capacity 11.5 cc. Radiometric and analytical precautions were not relaxed. Extinctions, to be discussed more in detail in a later paper, were here measured by spectroradiometer with thermopile. These absorptions were approximately 50%. Light absorbed by solutions photolyzed was properly apportioned between each quinine derivative and the chromate which acted as an inner light filter. The quantum yield, ϕ_q, represents half the (oxidation) equivalents of chromate reduced per Einstein absorbed by the quinine *derivative*, after correction for the dark reaction which was always measured separately in a parallel experiment.

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(1) Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).

(2) Forbes, Heidt and Brackett, *ibid.*, **55**, 588 (1933).

(3) Luther and Forbes, *ibid.*, **31**, 770 (1909).