TABLE V

COMPOSITION OF Ni^{+2}–Ph–Y^{-4} SOLUTIONS, ANALYSES FOR FREE [Ph] AND $[Y^{-4}]$ AND VALUES FOR K_2 WHEN $K_1 = 0.12$

Soln. no.	$[Ni^{+2}]_{total}$ × 10^3	$[Y^{-4}]_{total}$ × 10^3	$[Ph]_{total}$ × 10^3	Free $[Y^{-4}]$ × 10^3	Free [Ph] × 10^3	$[Y^{-4}]_{bonded}$ × 10^3	$[Ph]_{bonded}$ × 10^3	K_2 × 10^4
1	7.14	2.86	21.42	1.53	1.19	1.33	20	..
2	5.56	4.44	16.68	3.01	1.65	1.43	15.03	6
3	5.00	5.00	15.00	3.31	1.62	1.69	13.38	5
4	4.54	5.46	13.62	3.84	1.61	1.62	12.01	4
5	4.16	5.84	12.48	4.17	1.59	1.67	10.89	..
6	1.12	4.51	3.09	3.6	0.69	0.9	2.40	6
7	1.12	2.25	3.09	1.4	.46	.9	2.63	4
8	1.12	1.13	3.09	0.4	.28	.7	2.81	2
9	1.12	1.13	2.06	.02	.10	1.11	1.96	3
10	1.12	1.13	1.03	.02	.03	1.11	1.00	..

still exists in our value of K' and the calculated value may be due to the 0.4 M NaOH. The proposed intermediates in every other way account for these data which were obtained from four different methods of analysis in solution. Attempts to crystallize the mixed complexes were unsuccessful.

Discussion

No effect on the dissociation rate of $NiPh_3^{+2}$ was observed with cyanide and azide ions. The effect from hydroxide ion is several orders of magnitude less than the effect with the $FePh_3^{+2}$ complex. Thus, the behavior of these three ions with the nickel(II) complex is in great contrast to their behavior with the iron(II) complex. A substitution mechanism based on the difference in the electronic configuration of nickel(II) and iron(II) is proposed to account for their behavior.[4,19]

The large increase in the rate of dissociation of $NiPh_2(OH)_2$ compared to $NiPh_2(H_2O)_2^{+2}$ is of interest and may be due to the effect of reduced charge on the ease of breaking the nickel(II)–1,10-phenanthroline bonds. The $NiPh_2(CN)_2$ system also is converted more rapidly to $Ni(CN)_4^{-2}$ than the dissociation rates of $NiPh_2(H_2O)_2^{+2}$ and $NiPh(H_2O)_4^{+2}$ would predict. Similarly, the $NiPh_2Y^{-2}$ complex must be more labile than $NiPh_2(H_2O)_2^{+2}$ because it is not observed as a reaction product in either the hydroxide ion or azide ion reactions with EDTA.

The mixed ligand complexes of Ni^{+2}–Ph–Y^{-4} are surprisingly stable considering the multidentate nature of both the chelate groups. There is no reason why this type of mixed complex would only occur for this system. The formation of mixed complexes of Y^{-4} and other mono or bidentate ligands may be a source of error in chelatometric analysis involving the use of masking agents or metallochromic indicators.

Acknowledgments.—The authors wish to express their thanks to the Research Corporation and to Purdue Research Foundation for their support of this work.

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(19) J. W. Richardson, D. W. Margerum and L. P. Morgenthaler, to be published.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZ., AND UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

Selenium Dioxide Oxidations. I. Studies on the Mechanism of Oxidation of 1,2-Dibenzoylethane[1]

BY JOHN P. SCHAEFER[2]

RECEIVED MAY 22, 1961

The oxidation of 1,2-dibenzoylethane in 80% acetic acid by selenious acid to *trans*-1,2-dibenzoylethylene follows the rate law $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3]^{1/2}$. The reaction is both acid and base catalyzed and the rate expression in the presence of an excess of strong acid is $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3][HA]$ and in the presence of an excess of base $-\,d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3][OAc^-]$. The large kinetic isotope effect observed when the α-methylene hydrogens are replaced with deuterium is consistent with a rate-determining attack of an oxidizing selenium species on the diketone to form an enol-selenite ester which decomposes to give the unsaturated 1,4-diketone. Alternate mechanisms are discussed and criticized.

Since Riley's[3] initial investigation, numerous examples describing selenium dioxide as an oxidant for organic molecules have been reported[4]; however, little detailed mechanistic information is available. To clarify the mechanism of oxidation of 1,4-diketones to 1,4-enediones, we have carried out a study of the oxidation of 1,2-dibenzoylethane (I) to *trans*-1,2-dibenzoylethylene (II).

$$2C_6H_5COCH_2CH_2COC_6H_5 + SeO_2 \longrightarrow 2C_6H_5COCH{=}CHCOC_6H_5 + Se + 2H_2O \quad (1)$$

In 80% acetic acid–20% water solvent, yields of 80–85% of II were obtained; no 1,4-diphenyl-1,2,4-butanetrione (III) could be detected. A kinetic study of the reaction is complicated slightly

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(3) H. L. Riley, J. F. Morley and N. A. Friend, *J. Chem. Soc.*, 1875 (1932).

(4) N. Rabjohn, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Chap. 8.

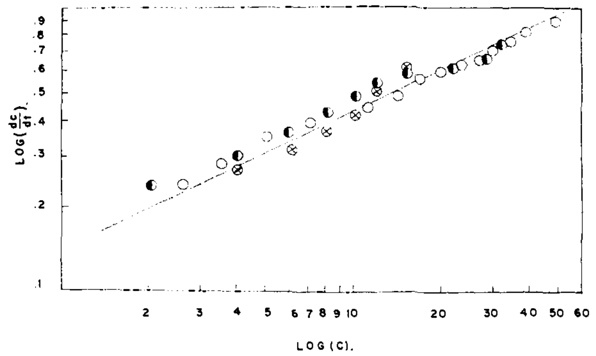

Fig. 1.—Oxidation of 1,2-dibenzoylethane at 90°: I = 0.100 *M;* H_2SeO_3 varied from 0.00209 to 0.00627 *M.*

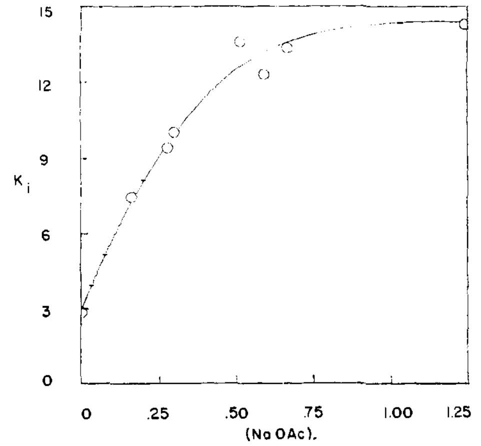

Fig. 2.—Oxidation of 1,2-dibenzoylethane at 90°: I = 0.0850 *M;* H_2SeO_3 = 0.0937 *M;* initial rate as a function of acetate concentration.

by the fact that II also reacts with selenious acid; however, the rate of oxidation of II is 30 times slower than that of I.

Figure 1 illustrates log (d*c*/d*t*) as a function of log *C* for three kinetic runs which varied in the initial concentration of selenious acid; a line of slope one-half is drawn through the data. The adequate correlation confirms the non-integral order of the reaction with respect to selenious acid. Individual correlations of $c^{1/2}_{SeO_2}$ as a function of time gave excellent and reproducible linear plots in the absence of acidic or basic catalysts.

Variation of the initial concentrations of diketone showed that the reaction is first order in diketone. We may therefore conclude that in 80% acetic acid rate law 2 holds.

$$-d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3]^{1/2} \quad (2)$$

Catalytic effects were evaluated by measuring the influence of added toluenesulfonic acid and sodium acetate on the reaction rate and order. It was found that the rate of oxidation of I is a linear function of added strong acid. Furthermore, the kinetic order of the reaction with respect to selenious acid is now unity and the oxidation obeys the rate law

$$-d[H_2SeO_3]/dt = k[C_6H_5COCH_2CH_2COC_6H_5][H_2SeO_3][HA] \quad (3)$$

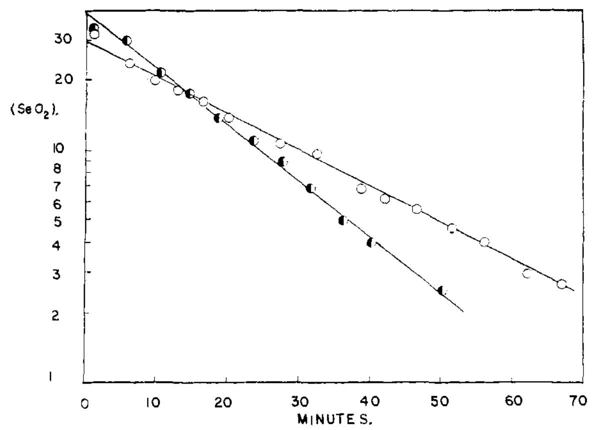

Fig. 3.—Oxidation of 1,2-dibenzoylethane; first-order of disappearance of selenious acid as a function of time: I = 0.100 *M;* H_2SeO_3 = 0.0044 *M;* ◐, toluenesulfonic acid = 0.10 *M;* ○, sodium acetate = 0.10 *M.*

Acetate catalysis was studied by measuring the initial rate of oxidation as a function of the concentration of added sodium acetate and was found to be complex (Fig. 2). A kinetic run at *low acetate concentration* (0.1*M*) indicated that the reaction was first order in selenious acid (Fig. 3). As is evident from Fig. 2, the order decreases at higher acetate concentrations.

From a consideration of the ionization constants involved (selenious acid,[5] $K_i = 2.4 \times 10^{-5}$; acetic acid,[6] $K_i = 1.75 \times 10^{-5}$), it appears that sodium acetate should be a sufficiently strong base to convert selenious acid to biselenite ion in aqueous solution. If we assume that this situation still obtains to a first approximation in 80% acetic acid, one might be tempted to interpret the acetate catalysis in terms of oxidation by biselenite.

To evaluate the effectiveness of biselenite ion as an oxidant the oxidation of acetone in water was studied. When a sufficient quantity of sodium acetate was added to assure half-neutralization of selenious acid,[5,6] *complete inhibition of oxidation occurred,* indicating that biselenite ion is not effective as an oxidizing agent for ketones. It appears that acetate catalysis is best interpreted as arising from simultaneous attack of selenious acid and acetate ion on the diketone. An additional point of significance is that the rate profile obtained for the oxidation of I (Fig. 2) is of the same form as that obtained for desoxybenzoin (in the concentration range studied). This suggests a similarity in mechanism.[7,8]

For isotope effect experiments 1,1,2,2-tetradeuterio-1,2-dibenzoylethane was prepared by the reduction of 1,2-dibenzoyl-1,2-dibromoethylene with zinc dust and deuterioacetic acid. At 90° the initial kinetic isotope effect (k_H/k_D) was 6.5. (This value decreased slowly due to a competing exchange reaction of deuterium with solvent protium through enolization.) This suggests that a

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(5) H. Hagisawa, *Bull. Inst. Phys. Chem. Res. Tokyo,* **18**, 648 (1939); *C. A.,* **34**, 4965 (1940).

(6) J. R. J. Dippy, *Chem. Revs.,* **25**, 151 (1939).

(7) The phenomena of acetate catalysis is discussed in greater detail in paper II of this series.[8]

(8) J. P. Schaefer, *J. Am. Chem. Soc.,* **84**, 717 (1962).

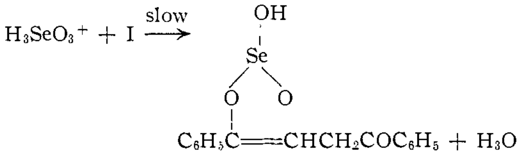
carbon–hydrogen bond is being broken in the rate-determining step.

The number of mechanisms which are consistent with these findings are limited. We suggest:

$$H_2SeO_3 \rightleftarrows H^+ + HSeO_3^- \quad (5)$$

$$H_2SeO_3 + OAc \rightleftarrows HSeO_3^- + HOAc \quad (6)$$

$$H_2SeO_3 + H^- \rightleftarrows H_3SeO_3^+ \quad (7)$$



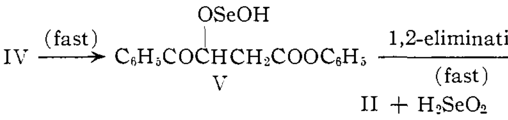
(8)

IV

or

$$H_2SeO_3 + I + OAc^- \xrightarrow{slow} IV + H_2O + OAc^- \quad (9)$$

or



$$IV \xrightarrow{(fast)} C_6H_5CO\overset{OSeOH}{\overset{|}{C}}HCH_2COOC_6H_5 \xrightarrow[(fast)]{1,2\text{-elimination}} II + H_2SeO_2 \quad (10)$$

V

$$IV \xrightarrow[(fast)]{1,4\text{-elimination}} II + H_2SeO_2 \quad (11)$$

$$H_2SeO_2 \xrightarrow{fast} {}^1/_2H_2SeO_3 + {}^1/_2Se + {}^1/_2H_2O \quad (12)$$

In the absence of catalysts, selenious acid will be partially dissociated into biselenite ion and hydrogen ion (eq. 5). Addition of acid will repress this ionization and favor equilibrium 7, which produces the $H_3SeO_3^+$ ion which would then react with I in the rate-determining step to form the enolselenite ester IV.

Addition of acetate will favor the formation of biselenite ion (eq. 6). Since the biselenite ion is not an effective oxidant, there will be a tendency toward decreasing the rate of oxidation brought about by a lowering of the concentration of oxidizing selenium species. Opposing this will be a rate-enhancing effect due to the presence of a more effective nucleophile to catalyze the formation of an enol-selenite ester (*e.g.*, eq. 9). What is measured kinetically is the sum of these two opposing effects.[8]

Rate-determining attack of the appropriate selenium species on the ketone to produce IV is consistent with the isotope effects found previously[9] as well as in the present investigation. The similarity of this step, from the electronic viewpoint, to the acid-catalyzed enolization of ketones also accounts for the parallel found by Barton and his group[10,11] between the rates of enolization and selenium dioxide oxidation of the eleven 1,4-diketones which they studied.

Either a direct 1,4-elimination from IV or a rearrangement of IV to V followed by a rapid elimination of the elements of H_2SeO_2 would account for the formation of the observed organic product. Little can be said about the reality of hyposelenious acid. There is no precedent for this species and, if it forms, it must be much less stable than selenious acid since the rate of oxidation does not decrease with time. A more plausible formulation of this compound may be as a hydrate of Se_2O_3 which could be formed through reaction of either hyposelenious acid or one of its precursors (IV or V) with selenious acid.

The most difficult results to explain are the half-order kinetics which were observed in the absence of an acidic or basic catalyst. Half-order kinetics are usually obtained in only two types of rate processes: (a) chain reactions which involve a second-order chain-terminating step; and (b) an equilibrium which involves the dissociation of a single species into two components, one of which influences the rate-determining step.

Previous studies[9] indicated that the selenium dioxide oxidation of ketones is insensitive to the presence of free radical initiators and inhibitors. Since the present reaction is not subject to light catalysis and did not show an induction period, a free radical chain mechanism does not seem plausible. Furthermore, in view of the contribution of the acetic acid (14*M*) to the acidity of the solvent medium, we have not been able to write a mechanism which involves a simple dissociation of selenious acid to explain the half-order kinetics. For these reasons we feel that the probable source of half-order kinetics stems from a series of equilibria which occur prior to the rate-determining step and which are presently not fully understood.

Several alternate mechanisms merit discussion. Banerji, Barton and Cookson[11] have suggested on the basis of their studies on the oxidation of 1,4-diketones that oxidation may proceed through the enol. If the formation of the enol were rate determining, the reaction would be zero order in selenious acid, particularly in the presence of added acid. This is not observed. If the mechanism involves a rapid and reversible enolization, no kinetic isotope effect for oxidation would be observed since all the α-deuterium atoms would rapidly be exchanged with the solvent. Since reaction can involve neither a rate-determining enolization or a rapid and reversible enolization, the formation of an enol as an important intermediate is prohibited.

A second mechanism postulated by these workers is a molecular mechanism whereby selenium dioxide is visualized as removing two hydrogens by direct attack upon the diketone. Data are presented which show that if the configuration of the hydrogens in the diketone is *cis*, oxidation occurs more rapidly than when the configuration is *trans*. We have assessed the plausibility of this reaction path by means of deuterium-labeling experiments.

Partially deuteriated 1,2-dibenzoylethane was prepared by the reduction of 1,2-dibenzoylethylene with tin amalgam in the presence of deuterioethanol and deuterium chloride. Assuming that the C–H bonds in the dideuteriated compound break with the same ease as the C–H bonds in the undeuteriated compound and that the C–D bonds break with the same ease as those in the tetradeuteriated compound, we can calculate that the rela-

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[9] E. J. Corey and J. P. Schaefer, *J. Am. Chem. So.c*, **82**, 918 (1960).

[10] C. S. Barnes and D. H. R. Barton, *J. Chem. Soc.*, 1419 (1953).

[11] J. C. Banerji, D. H. R. Barton and R. C. Cookson, *ibid.*, 5041 (1957).

tive rate of oxidation for the dideuteriated compound (see Experimental) compared to the un-

$$C_6H_5COCH{=}CHCOC_6H_5 \xrightarrow[\substack{C_2H_5OD \\ DCl}]{Sn(Hg)} C_6H_5COCHDCHDCOC_6H_5 \quad (13)$$

deuteriated compound should be *2.02*. This compares well with the observed value of *1.96* and substantiates the validity of our assumption.

If the reaction proceeds by a reaction path which includes the simultaneous removal of two hydrogens by the oxidant, the isotope effect measured kinetically for the partially deuteriated compound should be equal to that calculated from a comparison of the deuterium analysis of the starting material and the product, care being taken to avoid exchange due to enolization.

If the reaction proceeds through a sequence which involves a rate-determining removal of a second hydrogen later in the oxidative sequence, we would expect to find that the isotope effect calculated from a product analysis would be considerably less than that measured kinetically. This follows since the second elimination of hydrogen would occur from a high energy intermediate and the nucleophile removing the second hydrogen in question would therefore be less discriminating. The isotope effect calculated from product analysis is 5.4. Since this is substantially lower than that observed kinetically (6.5) we can conclude that carbon–hydrogen bonds are being broken in two discrete steps and thereby eliminate the molecular mechanisms postulated by the previous workers.

Experimental

Kinetic Measurements.—An oil-bath which was stirred by a Lightnin mixer and insulated with vermiculite was regulated to ±0.01° by means of a thermostat. Temperatures were measured with the Bureau of Standards thermometers. In all kinetic runs 80% acetic acid was used as the solvent, prepared by diluting four volumes of distilled glacial acetic acid with one volume of distilled water.

In the kinetic runs a weighed amount of diketone was placed in a 100-ml. two-necked flask fitted with a condenser and a tip-flask containing 20 ml. of standardized selenium dioxide solution in 80% acetic acid. To the diketone was added 80 ml. of solvent, and the entire apparatus was then placed in the oil-bath. After the solutions had equilibrated, the reaction was started by tipping the flask containing the selenious acid, thereby mixing the two solutions.

Aliquots were withdrawn at measured time intervals in a pipet which was heated to the bath temperature and the reaction quenched by allowing the solution to run into a mixture of 20 ml. of 10% potassium iodide and 80 ml. of 12% hydrochloric acid. The solution was then filtered into a 500-ml. suction filter flask through a cotton plug which was then washed thoroughly with distilled water until no more iodine appeared in the wash water. The liberated iodine was titrated with standardized sodium thiosulfate to the starch end-point. Using the above analytical procedure, known amounts of selenium dioxide could be determined to within 1% of the total present.

1,2-Dibenzoylethane was prepared according to the procedure previously described.[12] Recrystallization from 95% ethanol containing a little chloroform gave white needles, m.p. 143.0–143.5°.

1,2-Dideuterio-1,2-dibenzoylethane.—The reduction of *trans*-1,2-dibenzoylethylene was carried out with amalgamated tin and deuterioethanol in the presence of deuterium chloride, generated by adding a small amount of acetyl chloride to the reaction mixture. The deuterium content of the product was determined by combustion analysis.[13] Oxidation of a sample containing 16.93 atom per cent. deuterium was slower than an undeuteriated sample by a factor of 1.96.

Oxidation of 1.0 g. of I containing 9.06 atom per cent. deuterium with 9.0 g. of selenium dioxide in 100 ml. of 80% acetic acid for 3 hours gave *trans*-1,2-dibenzoylethylene which contained 9.98 atom per cent. of deuterium. This corresponds to an isotope effect of 5.4.

1,1,2,2-Tetradeuterio-1,2-dibenzoylethane, prepared using the procedure of Conant and Lutz[14] by the reduction of 1,2-dibromo-1,2-dibenzoylethylene with zinc dust and deuterioacetic acid, showed m.p. 143.0–143.5°; Compound I oxidized 6.5 times faster at 90°.

Selenium Dioxide Oxidation of the Ketones.—In a preparative oxidation 2.38 g. of 1,2-dibenzoylethane was dissolved in 100 ml. of 75% aqueous acetic acid and heated to 90°. To this was added 1.93 g. of selenium dioxide and the mixture allowed to stand at this temperature for 21 hours. The solution was poured into water, extracted with ether, neutralized with saturated potassium carbonate, dried and crystallized to give 1.06 g. of 1,2-dibenzoylethylene in the first crop of crystals (40%), m.p. 111°. Further concentration gave an additional 0.70 g. of product (total yield 75%) plus some red, oily, material which resisted purification efforts.

Precise studies on yields were carried out by carefully weighing out a known amount of selenium dioxide and treating it with a large excess of diketone. After the reaction had gone to completion the amount of olefin was determined by titration with standardized bromine solution. Yields determined by this method were 82, 85 and 83% for three different runs. This procedure on a known mixture of 1,2-dibenzoylethane was found to be accurate to within 2%. Attempts to detect the presence of 1,4-diphenyl-1,2,4-butanetrione by formation of the copper chelate gave negative results.

Acid Catalysis.—The acid-catalyzed oxidation of I was studied using solutions which were 0.1 M in I, 0.00875 M in selenious acid and from 0 to 0.08 M in toluenesulfonic acid at 70°. A plot of the initial first-order rate constant *versus* the concentration of added acid gave an excellent linear plot.

Base Catalysis.—Base catalysis was studied using various concentrations of sodium acetate dissolved in the reaction mixture at 90°. The rate profile obtained (Fig. 2) represents initial rate as a function of acetate concentrations.

Oxidation of Acetone.—A kinetic run in aqueous solution which was 0.0740 M in selenious acid and 1.60 M in acetone gave a rate constant of 2.08×10^{-6}sec.$^{-1}$ at 50°. When an identical solution was made 0.1 M in sodium acetate no oxidation was observed for 3 days.

Oxidation of 1,2-Dibenzoylethylene.—A kinetic run in 80% acetic acid at 90° with a solution which was 0.2 M in II and 0.0850 M in selenious acid showed that the half-life for oxidation was about 900 minutes. At identical conditions the half-life for the oxidation of I was 32 minutes. This corresponds to a relative rate factor of about 30. The product of oxidation was not determined.

Acknowledgment.—The author wishes to thank the Research Corporation for a generous grant.

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[12] J. P. Schaefer, *J. Org. Chem.*, **25**, 2027 (1960).

[13] Deuterium analyses were performed by Mr. J. Nemeth and associates, Microanalytical Laboratory, The University of Illinois.

[14] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 881 (1925).