# THE INDUCTION OF THE REACTION BETWEEN CHLORINE AND BENZENE BY ETHYLENE
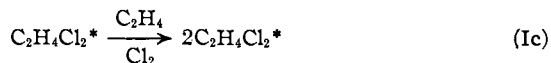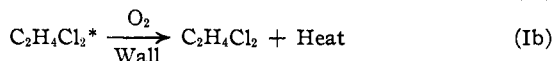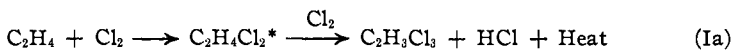
BY T. D. STEWART AND M. H. HANSON

In the reaction between ethylene and chlorine Stewart and Smith[1] postulated a chain mechanism of the type

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2{}^* \xrightarrow{Cl_2} C_2H_3Cl_3 + HCl + Heat \qquad (Ia)$$

$$C_2H_4Cl_2{}^* \xrightarrow[Wall]{O_2} C_2H_4Cl_2 + Heat \qquad (Ib)$$

$$C_2H_4Cl_2{}^* \xrightarrow[Cl_2]{C_2H_4} 2C_2H_4Cl_2{}^* \qquad (Ic)$$

in which the starred formulas represent an intermediate compound, presumably an activated ethylene dichloride.

The experiments described here were first designed to determine whether this intermediate would induce a reaction in other reacting systems, or itself undergo a reaction with other substances (than chlorine). For instance, in the presence of benzene, a Friedel–Crafts reaction is possible between the intermediate and benzene, or in the presence of both benzene and benzoyl chloride, benzophenone might be formed. Thorough search for these reactions has shown no indication of them. Oxidations of the reaction products by alkaline permanganate or chromic acid have yielded only traces of materials which could be considered aromatic carboxylic acids. Similarly, when the reaction between ethylene and chlorine was carried out in the presence of a mixture of benzoyl chloride and benzene, no trace of benzophenone could be found.[2]

However, when benzene is used as a solvent for the chlorine–ethylene reaction, considerable benzene hexachloride is always formed, usually a mixture of the stereoisomeric forms, with the $\alpha$-form (m. p. 157°) predominating.

$$C_6H_6 + 3Cl_2 \longrightarrow C_6H_6Cl_6$$
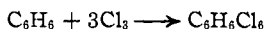
This reaction has long been known as one susceptible of induction by light,[3]

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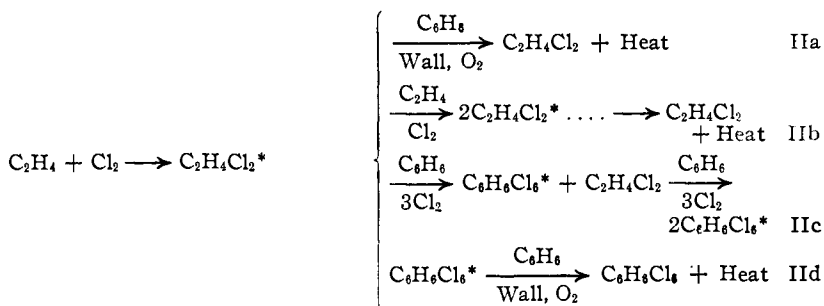[1] Stewart and Smith, THIS JOURNAL, 51, 3091 (1929); 52, 2869 (1930).

[2] The reaction mixture was distilled to remove ethylene dichloride and benzene, the residue completely hydrolyzed in dilute alkali, and the alkaline solution extracted with benzene. The residue from this extract, distilling above 100°, yielded no oxime soluble in dilute alkali but insoluble in neutral water solution (10 cc.).

[3] Faraday, Ann. Chem., [2] 4, 472 (1825); Slator, Z. physik. Chem., 45, 540 (1903). Luther and Goldberg, ibid., 56, 43 (1906), state that light is necessary even in boiling benzene. They studied the inhibiting effect of oxygen, from which Alyea (Ref. 6) estimates the quantum efficiency as about seventy-five moles per quanta.
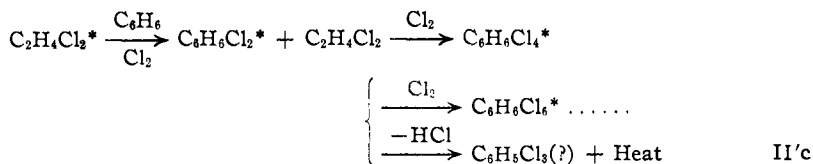
alkali,[4] iodine[5] and alpha particles.[6] The first and last of these have been shown to have a chain mechanism. The efficiency of the induction by ethylene is then of particular interest and the effect of the physical conditions of the experiments upon this efficiency of importance.

The above reaction is not the sole reaction. Considerable hydrogen chloride is often formed, indicating some substitution. In our experience phenyl chloride is not a product. When little or no hydrogen chloride is formed the product is cleanly crystalline, but otherwise it is contaminated by gummy higher chlorinated substitution products of benzene. There are thus two criteria as to the nature of the reaction itself. The substitution reaction is favored by low chlorine concentrations in the photochemical and presumably so in ethylene-induced reactions. No attempt is made here to formulate the actual products of substitution (see Equation II'c below).

**A Provisional Mechanism.**—The experimental results may be correlated by means of the following series of steps, in which chain mechanisms for both the ethylene–chlorine and benzene–chlorine reactions are assumed, but without precise specification of the mechanism of chain propagation.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2^*$$

$$\left\{
\begin{array}{l}
\dfrac{C_6H_8}{\text{Wall, } O_2} \longrightarrow C_2H_4Cl_2 + \text{Heat} \qquad\qquad \text{IIa} \\[2ex]
\dfrac{C_2H_4}{Cl_2} \longrightarrow 2C_2H_4Cl_2^* \ldots \longrightarrow \begin{array}{l} C_2H_4Cl_2 \\ + \text{Heat} \end{array} \quad \text{IIb} \\[2ex]
\dfrac{C_6H_6}{3Cl_2} \longrightarrow C_6H_6Cl_6^* + C_2H_4Cl_2 \dfrac{C_6H_6}{3Cl_2} \\ \qquad\qquad\qquad\qquad\qquad 2C_6H_6Cl_6^* \quad \text{IIc} \\[2ex]
C_6H_6Cl_6^* \dfrac{C_6H_6}{\text{Wall, } O_2} \longrightarrow C_6H_6Cl_4 + \text{Heat} \quad \text{IId}
\end{array}
\right.$$

Reaction IIc might better be written as follows

$$C_2H_4Cl_2^* \dfrac{C_6H_6}{Cl_2} \longrightarrow C_6H_6Cl_2^* + C_2H_4Cl_2 \dfrac{Cl_2}{} \longrightarrow C_6H_6Cl_4^*$$

$$\left\{
\begin{array}{l}
\dfrac{Cl_2}{} \longrightarrow C_6H_6Cl_6^* \ldots\ldots \\[2ex]
\dfrac{-HCl}{} \longrightarrow C_6H_5Cl_5(?) + \text{Heat} \qquad \text{II'c}
\end{array}
\right.$$

Other possibilities present themselves, such as reaction Ia, but in numerous fractional distillations, no fractions corresponding to the tri- and tetrachloroethanes have been observed. This reaction is believed to

[4] Matthews, Trans. Chem. Soc., **59**, 166 (1891). Luther and Goldberg (Ref. 3, p. 55) state that alkali serves as a catalyst even with the total exclusion of light.

[5] Müller, J. Chem. Soc., **15**, 41 (1862), states that the use of iodine as a catalyst results largely in substitution products.

[6] Alyea, THIS JOURNAL, **52**, 2743 (1930).

have been inhibited by the benzene.   Another type reaction, suggested to us by Professor G. N. Lewis, presumes no ethylene dichloride formed.

$$C_2H_4Cl_2{}^* + C_6H_6 + 2Cl_2 \longrightarrow C_6H_6Cl_6{}^* + C_2H_4 \ldots$$
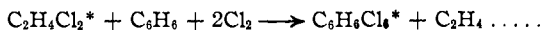
We have not observed conditions wherein little or no ethylene is used up. Moreover, when ethylene and chlorine react in the presence of ethylene dichloride (no benzene), the course of the substitution reaction approximates that of Equation Ia, since the hydrogen chloride produced never exceeds, in moles, the ethylene used up, which it might do if the hypothetical intermediate acted simply as a chlorinating reagent.   The appearance of ethylene dichloride as an isolable product would tend to eliminate this type of mechanism as a major step in the process.   The rupture of the benzene–chlorine chains by ethylene (or chlorine) is probable.

## Experimental Results

The main observation was the proportion of total chlorine used up which reacted with the benzene.   This was measured by weighing the non-volatile products formed and by noting the molal ratio of chlorine to ethylene reacting.   This ratio would be unity if the chlorine reacted solely with the ethylene, and only by addition (see above).   Any excess of chlorine used up, as shown by a value of this ratio greater than unity, is taken to mean reaction with benzene.

**The Homogeneous Reaction between Ethylene and Chlorine Dissolved in Benzene.**—The reagents were dissolved separately, and equal volumes of the solutions mixed and allowed to stand for two hours or more in the dark.   The results were very discordant, but a few conclusions may be drawn.   (1) The presence of glass wool or glass beads in the reaction mixture causes no difference in the molal ratio of total chlorine to ethylene used up, or in the nature or amount of the product.   (2) This molal ratio varied from 1.7 to 2.2 when the chlorine concentration lay between 0.3 and 0.42 $M$ and the ethylene concentration changed from 0.042 $M$ (initial) to zero.   In one experiment, with the chlorine within the above limits, but with the initial ethylene concentration at 0.013 $M$, this ratio was 10. When both were low (chlorine 0.036 $M$, ethylene 0.0043 $M$) the ratio was 1.26, very little of the chlorine reacting with benzene.   (3) In all cases the amount of non-volatile residue was close to that predicted on the assumption that it consisted of benzene hexachloride and was formed from that excess of chlorine over ethylene indicated by the above ratios (little or no phenyl chloride was formed).   But the product was always gummy in character, and the hydrogen chloride production was much higher than in experiments to be described later.   (4) In the absence of ethylene the disappearance of chlorine is represented by the following figures.

| Time (hours) | 0 | 16 | 40 | 68 |
|---|---|---|---|---|
| Chlorine concentrations (m./l.) | | | | |
| (a)  Dark | 0.431 | 0.447 | 0.444 | 0.431 |
| (b)  Diffused light | ... | .372 | .346 | .326 |
| (c)  Dark | .0347 | .0357 | .0364 | .0352 |

These solutions were all quiet; the reaction in diffused light is enormously hastened by constant shaking, but in the dark is unaffected (Expts. 2a and 2b, Table II). The variations above suggest analytical difficulties in part. Eventually these analyses could be reproduced to 1%. There is no evidence to indicate that diffused light affects the reaction induced by ethylene, since the ethylene-induced reaction was the same (in two hours) in the dark and in diffused light.

The homogeneous reaction is then attended by an undue amount of benzene substitution even at high chlorine concentrations, and a low efficiency of induction except in one case, which suggested that the efficiency of induction might be a function of the ethylene concentration, i. e., higher at lower ethylene concentrations. This would be expected on the basis of the competitive effect of Equations IIb and IIc.

**Experiments with Chlorine Dissolved in Benzene and the Ethylene Introduced into the Vapor Phase. I. Bubbler Experiment.**—In the first experiments dry ethylene gas was bubbled through the chlorine–benzene solution. The reaction vessel was essentially a glass tube, about 1 cm. in diameter and 25 cm. long, with smaller glass tube connections at each end. When filled with the solution and placed in a gently sloping position the bubbles of gas traveled the length of the tube, in contact with both the wall and the solution. The rate of flow varied from one to two cubic centimeters per minute, so that most of the gas entering was absorbed. The bubbles seemed to decrease to one-half or one-third their original volume, but the fraction of entering gas which was recovered was usually less than one-tenth  This seemed to indicate that a large proportion of the reaction took place at the entrance and exit. The point of interest is that in these experiments the ethylene partial pressure in the gas phase was high, and varied probably from two-tenths to five-tenths of an atmosphere. Table I gives a summary of the results. The average chlorine concentration varied in the different experiments. The hydrogen chloride formed should be considered a maximum, and of significance only as indicating very little substitution, for analytical reasons (see Experimental Part). The weight of product is not consistent with the amount of chlorine and ethylene used. This also involves an analytical difficulty (see footnote, Table II) and is not considered to alter the major conclusion that this method of introducing the ethylene leads to a definite reaction between the chlorine and benzene, to the extent of about half the total reacting chlorine, with comparatively little substitution.

<div align="center">

TABLE I

EXPERIMENTS WITH BUBBLES

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Vol. of solution, 73 cc.; temp., 22–23°; semi-darkened room. Time: Expt. A, 45 min.; Expts. B, C, D, 4 hours. In Expts. A, B and C the reaction vessel was cleaned by solvents and air-dried at 100°; in Expt. D, by ignition in dry oxygen. Product was recovered as residue upon evaporation at room temperature and 3 mm. pressure.

| Expt. | Concn. of $Cl_2$ moles/liter Initial | Final | Moles of reactants $Cl_2$ | $C_2H_4$ | Ratio $Cl_2/C_2H_4$ | Moles HCl (at end) | Product, g. |
|-------|---------|--------|--------|---------|---------|---------|---------|
| A | 0.425 | 0.313 | 0.00814 | 0.00318 | 2.56 | 0.00137 | 0.411 |
| B | .853 | .406 | .0326 | .0149 | 2.19 | .00250 | 1.45 |
| C | 1.437 | .978 | .0335 | .0152 | 2.20 | .00715 | 2.36 |
| D | 1.297 | .782 | .0375 | .0158 | 2.37 | .... | 2.51 |

II. **Shaker Experiments.**—In these experiments, summarized in Table II, a large glass tube, sealed at both ends and provided with a side tube in the center, was the reaction flask. It was partly filled with the chlorine–benzene solution, connected to the ethylene supply through a three-way stopcock in the side tube, and placed on a rocker which caused the gas bubbles present to travel the length of the tube about once every second. The gas space could be varied at will and could be filled initially (by solution displacement) with ethylene, air or nitrogen. The ethylene supply was under constant pressure, and the gas flowed in as fast as the ethylene was used up. The initial partial pressure of the ethylene varied from about four-tenths of an atmosphere (Expts. 1, 3, 4) to about thirty centimeters of water (Expts. 5, 6), and varied greatly in single experiments, except in Expt. 6. This lack of constancy was due to decreasing vapor pressure of the solution, permitting more ethylene to enter, offset by the accumulation of any inert gas in the ethylene supply, and the production of hydrogen chloride. The difference in Expts. 3 and 4 could then be due to the difference in the volume of the gas phase in which the larger volume favored maintenance of a high ethylene partial pressure.

An attempt to hold this variable within narrow limits was made in subsequent experiments, by first filling the vapor phase with nitrogen to a total pressure of one atmosphere, and then allowing the ethylene to flow in at a pressure greater than this by 30 cm. of water. However, the rapidly decreasing chlorine partial pressure permitted the increase of the ethylene partial pressure, so that in Expt. 6 this was, in part, corrected for by closing the ethylene entrance periodically and opening the nitrogen entrance, thus allowing nitrogen to replace the accumulated ethylene in the gas phase. This was done six times during the experiment, and resulted in a marked increase in the proportion of chlorine reacting with the benzene. Any valid estimate of the ethylene partial pressure is impossible, but since the rate of solution of ethylene in benzene is low, and the rate of reaction is low, it may be assumed to be $30 \pm' 15$ cm. of water in Expt. 6.

In diffused daylight (Expt. 2a) benzene alone reacts with chlorine at an

appreciable rate (when shaken), but not in a darkened room (Expt. 2b). Experiment 1, then, cannot be compared strictly with subsequent experiments in which the reaction vessel as well as the room was darkened. The partial pressure of the ethylene appears to be an important factor in determining the proportion of chlorine reacting with benzene. Over 90% of the reacting chlorine reacts with benzene at low ethylene partial pressures. The effect of changing chlorine concentration upon this result has not yet been ascertained, but from the results given in Table I it would appear that at chlorine concentrations above 0.3 $M$ the ethylene partial pressure is the major variable. No induction period was looked for. From previous work, the presence of oxygen would tend to reduce the length of any benzene–chlorine chain for a photochemically induced reaction, but its effect upon the ethylene-induced reaction is as yet undetermined. The walls have some effect upon the reaction, as evidenced by the low induction ratio in the homogeneous reactions as compared to the heterogeneous, and by the faster photochemical reaction in diffused light brought about by shaking.[7] However, immersed glass beads or glass wool

TABLE II

EXPERIMENTS WITH CHLORINE–BENZENE SOLUTIONS IN A SHAKER

Temp., 19–20°; concentration in moles per liter, volume of container, 116 cc. Conditions: Expts. 1, 2a in diffused daylight, others in the dark. In Expts. 1, 3 and 4 ethylene was alone in the gas phase; Expts. 2a and 2b, air present; Expt. 5, 36 cc. of $N_2$ present; Expt. 6, 31 cc. of $N_2$ present at start, 43.7 cc. at end. Time in minutes, Expts. 1, 120; 2a, 450; 2b, 210; 3, 240; 4, 24; 5, 180; 6, —.

| Expt. | Concn. of chlorine Initial | Final | Volumes (cc.) Solution, g. | | Moles of reactants $Cl_2$ | $C_2H_4$ | Ratio $Cl_2/C_2H_4$ | Product, g. | Moles HCl at end |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.075 | 0.000 | 90 | 26 | 0.0968 | 0.0137 | 7.0 | 9.03 | 0.0138 |
| 2a | 0.914 | .187 | 88 | 28 | .064 | None | .. | 7.17 | .0113 |
| 2b | 1.242 | 1.228 | .. | .. | ... | None | .. | .. | ... |
| 3 | 1.250 | 0.337 | 104 | 12 | .0950 | .0145 | 6.65 | 7.3 | .0161 |
| 4 | 1.42 | .000 | 51 | 65 | .0725 | .0258 | 2.81 | 6.64 | .0058 |
| 5 | 1.295 | .151 | 48 | 68 | .0550 | .0077 | 7.14 | 3.01[a] | .0201[a] |
| 6 | 1.295 | .347 | 44 | 72 | .0417 | .00356 | 11.7 | 4.88 | .0058 |

[a] In Expt. 5 the reaction mixture as a whole, instead of an aliquot portion, was treated with standard bisulfite and the excess bisulfite titrated with standard iodine as usual. The mixture then stood overnight before titrating the acid present. By morning this unusually large proportion of acid was present, and the yield of solid products, although cleanly crystalline, was lower than usual. It is thought that this may possibly be a function of the time of standing of the reaction mixture with water. Since the isolated products do not yield acid in contact with water, the experiment suggests either an unknown variable in the original reaction or possibly an unstable product first formed which reacts slowly with water to yield acid and water-soluble or volatile products, but which might change to water-stable products on standing. The isolated product did not appear to differ from that derived from other experiments, except that it was crystalline, whereas the presence of much acid is usually accompanied by gummy residues upon evaporation.

[7] The effect of boiling the solution, mentioned by Luther and Goldberg (Ref. 3) may be related to an agitation factor.

have little or no effect, hence the gas–wall interface, if any, would appear to be the important one.

**Preparation of Materials.**—The ethylene was generated from ethylene dibromide and zinc, washed with alcohol and stored over water. A drying train including phosphorus pentoxide was interposed between the reservoir and the reaction flask. When necessary for accuracy in measuring the gas volumes, a nitrometer was used as a reservoir. Analysis showed up to 1% of air or other inert gas.

A tank of chlorine containing less than one mole per cent. of hydrogen chloride was used. Blackened bottles contained the benzene, into which the chlorine was passed slowly, usually overnight.

The benzene was distilled from chromic acid and sulfuric acid mixture, washed and distilled from solid potassium hydroxide and finally from sodium wire.

**Analysis.**—Benzene was saturated with ethylene in a bubbler and the ethylene pressure used to force the solution up into a pipet. The measured solution was then delivered below a bromine solution in carbon tetrachloride at $-20°$. After standing tightly stoppered in the dark for six hours (in two hours the reaction was 75% complete) the excess bromine was titrated, using aqueous potassium iodide and thiosulfate. Appropriate blanks showed no conflicting reactions with the benzene. At 22° the saturated solution was 0.084 $M$, and this value agreed closely with a direct measurement of the volume of gas dissolved. In the homogeneous reaction experiments the containers had a small gas phase to minimize volatilization. More dilute solutions were prepared by diluting the saturated stock solutions.

Chlorine in benzene cannot be analyzed for by adding aqueous potassium iodide and titrating the iodine. Errors as high as 30% are involved. The analysis was made by delivering pipetted samples below the surface of a known volume of standard 0.1 $N$ sodium acid sulfite solution (standardized against iodine solution) and back-titrating the excess. The hydrogen chloride formed was estimated from the same sample by subsequently titrating the total acid present with standard alkali, using phenolphthalein, and subtracting from this total the acid found in the reaction

$$HSO_3^- + Cl_2(or\ I_2) + H_2O \longrightarrow SO_4^- + 2Cl^- (or\ I^-) + 3H^+$$
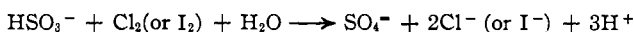
By suitable blanks the ratio (in equivalents) of acid formed to bisulfite used up was determined. It was usually very close to the theoretical value of 1.5, and constant. However, any error in this ratio caused a very large error in the acid calculated as formed in the reaction studied, and this, together with slight (1%) uncertainties in the analysis for chlorine, made the estimate of the amount of substitution very uncertain. The values given in the text are probably high.

The normality of a bisulfite solution is reasonably constant if the volume of solution is large, if air admitted to the solution is drawn through a similar solution, and if the buret and reservoir do not form a closed system. This last proviso eliminated some anomalous changes in normality, that is, each time the buret was emptied air from the room (not from the reservoir) was admitted to the buret. The difficulty seemed real and is probably connected with the auto-oxidation problem of sulfites.

The benzene hexachloride was purified and analyzed for chlorine; no evidence of the presence of $C_6H_5Cl_7$, which has similar properties and could have been formed, was observed.

## Summary

Benzene hexachloride, together with substitution products, is formed when ethylene gas is passed into a benzene solution of chlorine in the dark. A mixture of the various stereoisomers is obtained, with the $\alpha$-form (m. p.

157°) predominating.   The molal ratio of total chlorine reacting to ethylene reacting varies from two to eleven in the present experiments, and is greater the lower the partial pressure of ethylene. . This is explained on the basis of chain mechanisms for both the ethylene–chlorine and benzene–chlorine reactions, the latter being induced by and acting as an inhibitor of the former.

In homogeneous solution the above ratio, with chlorine in large excess, is approximately two.   A higher proportion of the chlorine is used in substitution than in the heterogeneous reactions.

No evidence of a Friedel–Crafts type of reaction between the ethylene chloride formed and benzene could be found.   In a mixture of benzene, benzoyl chloride and chlorine no benzophenone was formed with introduction of ethylene.

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## THE REDUCTION POTENTIALS OF SOME HIGHER BENZOLOGUES OF THE QUINONES

BY LOUIS F. FIESER AND EMMA M. DIETZ

With the view of applying certain new tests to the theories of the structure of anthracene, we have prepared three angular dibenz-anthraquinones,[1] and determined their reduction potentials.   It seemed appropriate to include in this study other quinones derived from tetra- or pentacyclic hydrocarbons, and we have thus examined potentiometrically most of the known compounds of this type.

We were fortunate in securing a sample of picenequinone through the kindness of Professor Frederick D. Chattaway of Oxford University, while the chrysene used in the preparation of the 5,6-quinone was furnished by the Gesellschaft für Teerverwertung through the courtesy of the late Dr. R. Weissgerber.   The other derivatives of 5,6-chrysenequinone, as well as the 6,12-isomer, were prepared by the synthesis of Beschke and Diehm.[2]

The results of the electrometric titrations are summarized in the accompanying table.   The nature of the titrating reagent indicates the method of titration employed; in most cases it was found expedient to reduce the quinone catalytically and to titrate the reductant with an oxidizing agent.   While satisfactory results were easily obtained with the tetracyclic quinones, the very sparing solubility of the pentacyclic compounds presented a serious obstacle.   With the very dilute solutions slight sources of error have a magnified effect upon the potentials.   It

[1] Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

[2] Beschke and Diehm, *Ann.*, **384**, 143 (1911).