THE ELECTROCHEMISTRY OF LIGHT. III

BY WILDER D. BANCROFT

Halogen Carriers

Sunlight causes chlorine or bromine to react with toluene; ferric chloride has a similar effect; and substitution products are also obtained by the action of the current on a mixture of toluene and aqueous hydrochloric acid. Under the influence of sunlight ferric chloride reacts with alcohol, though slowly. Since some halogen carriers act in the same way as sunlight, while others act differently, it will simplify matters to consider the whole question of halogen carriers. The facts are not on record in any single book or article on organic chemistry, so far as I can learn. We will, therefore, take up the experimental data first and will afterwards consider whether any theory can be devised that will fit them all.

In the dark, benzene does not react with chlorine at any temperature up to the boiling point of the solution under atmospheric pressure.¹ It is usually stated that chlorine reacts with boiling benzene in the dark but the experiments of Slator² and of Goldberg³ prove that this is really a photochemical reaction and that it does not take place if no light reaches the boiling benzene. In bright sunlight benzene hexachloride⁴ is formed when benzene and chlorine are brought together even at 0°. With rising temperature the reaction takes place more readily until, at the boiling point, it takes place unless light is rigidly excluded. Benzene hexachloride is also obtained when chlorine is bubbled into a mixture of benzene with water or dilute caustic soda.⁵ Neither light nor

¹ Willgerodt: Jour. prakt. Chemie [2], 34, 264 (1886).

² Zeit. phys. Chem., 45, 513 (1903).

³ Zeit. wiss. Photographie, 4, 61 (1906).

⁴ In this paper it is not necessary to distinguish between the α - and the β -hexachlorides.

⁵ Matthews: Jour. Chem. Soc., 59, 165 (1891); 61, 103 (1892). Goldberg: Zeit. wiss. Photographie, 4, 63 (1904).

high temperature is necessary for this reaction. Chlorine reacts with benzene in presence of phosphorus pentachloride¹ producing the hexachloride. In this reaction the phosphorus pentachloride plays the part of a carrier. When benzene, chlorine and iodine monochloride are mixed in the dark, some hexachloride is formed,² though most of the chlorine reacts to form substitution products. In presence of ferric chloride,³ stannic chloride,⁴ aluminum chloride,⁵ antimony pentachloride,⁶ molybdenum pentachloride,⁷ sulphur,⁸ sulphuryl chloride,⁹ or sulphuric acid,¹⁰ chlorine and benzene react, forming substitution products only. With iodine monochloride alone the reaction takes place very slowly in the dark and yields substitution products exclusively in the light.¹¹

Benzene and bromine react slowly in the dark, forming brombenzene and hydrobromic acid. This reaction does not run to an end. When the benzene and the bromine are present in equivalent quantities, only fifty percent of the benzene is converted into brombenzene.¹² No experiments have been made to determine whether the brombenzene or the hydrobromic acid is the disturbing factor in this case, but Bruner's work¹³ makes it probable that the formation of HBr_3 is the cause of the phenomenon. The fact that bromine acts on benzene in the dark, while chlorine is said not to, is not due to the greater reacting power of ben-

¹ Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

² Müller: Jour. Chem. Soc., 15, 41 (1862); Slaton: Zeit. phys. Chem., 45, 524 (1903).

³ Page: Liebig's Ann., 225, 196 (1884).

⁴ Pétricot: Bull. Soc. chim. Paris [3], 3, 189 (1890).

⁵ Gustavson: Ber. chem. Ges. Berlin, 10, 911 (1877).

⁶ Beilstein and Kurbatow: Ber. chem. Ges. Berlin, 8, 1417 (1875).

⁷ Aronheim: Ibid., 8, 1400 (1875).

⁸ Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

⁹ Dubois: Zeit. Chemie [2], 2, 705.

¹⁰ Istrati and Pétricot: Bull. Soc. chim. Paris [3], 5, 165 (1891).

¹¹ Slaton: Zeit. phys. Chem., 45, 532 (1903).

¹² Schramm: Ber. chem. Ges. Berlin, 18, 350 (1885).

¹³ Zeit. phys. Chem., 41, 513 (1902).

zene but to its greater solubility in benzene. A dilute solution of bromine in benzene remains practically unchanged.¹

In sunlight, bromine and benzene form benzene hexabromide.² Hexabromide is also formed, together with some substitution products, when bromine is added to a mixture of benzene and water or dilute aqueous caustic soda solution,³ preferably in the sunlight though this is not absolutely necessary. In presence of iodine, ferric bromide, etc., bromine substitution products are obtained. Ferric chloride also acts as a bromine carrier,⁴ hydrochloric acid being evolved until the ferric chloride has been converted completely into ferric bromide.

Very little of an accurate nature is known in regard to the halogen addition products of toluene and we do not need to consider them. With toluene we have the contrast between substitution in the benzene ring and substitution in the methyl group or side chain instead of the contrast between the substitution products and the addition products in the case of benzene.

Substitution in the side chain takes place when chlorine and toluene at 0° are exposed to sunlight⁵ and when chlorine is led into boiling toluene.⁶ It is probable that the latter method of preparation is a photochemical one, but there is no direct evidence on the point. Phosphorus pentachloride acts as a chlorine carrier with toluene, forming benzyl chloride.⁷ Side-chain substitution occurs with nitrotoluene when sulphur is used as a carrier.⁸ I could not find any record of any one having bubbled chlorine through an emulsion of toluene and dilute aqueous caustic soda, as Matthews did

¹ Bruner: *Zeit. phys. Chem.*, **41**, 513 (1902).

² Mitscherlich: *Pogg. Ann.*, **35**, 374 (1835).

³ Matthews: *Jour. Chem. Soc.*, **59**, 165 (1891); **61**, 103 (1892); **73**, 243 (1898). Orndorff and Howells: *Am. Chem. Jour.*, **18**, 312 (1896).

⁴ Scheufelen: *Liebig's Ann.*, **231**, 152 (1885).

⁵ Schramm: *Ber. chem. Ges. Berlin*, **18**, 606 (1885).

⁶ Cannizzaro: *Comptes rendus*, **41**, 517 (1855).

⁷ Colson and Gautier: *Ann. Chim. Phys.* [6], **11**, 19 (1887).

⁸ Häussermann and Beck: *Ber. chem. Ges. Berlin*, **25**, 2445 (1892).

with benzene. Some experiments by Mr. Schluederberg in my laboratory have shown that the substitution takes place both in the ring and in the side chain.

Chlorine probably reacts slowly with toluene in the dark, substituting mostly in the ring; but Seelig's statements¹ are very vague and one does not know what to make of the remark that addition products are formed at 80°. Such carriers as FeCl_3 , MoCl_5 , SbCl_5 , and ICl substitute exclusively in the ring under ordinary circumstances. The statement is even made that with iodine and boiling toluene no benzyl chloride is formed.² In view of the results obtained for the action of bromine on boiling toluene in presence of IBr , it is safe to assume that this sweeping statement is true only so long as the iodine content of the solution does not fall below a certain minimum.

Bruner³ finds that toluene and bromine react in the dark with substitution both in the ring and in the side chain, while Schramm⁴ reports that only ring substitution takes place. This discrepancy is due chiefly to a difference in the conditions of the experiments. Schramm worked with toluene and bromine in equivalent quantities while Bruner studied the behavior of dilute solutions of bromine in toluene. The effect of concentration is shown in Table I, compiled from Bruner's data.

TABLE I
Temperature 25°

Concentration.	Percent $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	Concentration	Percent $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
$1\text{Br}_2 + 5\text{C}_7\text{H}_8$	2.7	$1\text{Br}_2 + 25\text{C}_7\text{H}_8$	36.3
$1\text{Br}_2 + 10\text{C}_7\text{H}_8$	10.4	$1\text{Br}_2 + 40\text{C}_7\text{H}_8$	45.6
$1\text{Br}_2 + 15\text{C}_7\text{H}_8$	24.4	$1\text{Br}_2 + 100\text{C}_7\text{H}_8$	42.4

¹ Liebig's Ann., 237, 169 (1887).

² Beilstein and Geitner: Liebig's Ann., 139, 331 (1866).

³ Bull. Acad. Sci. Cracovie, 1907, 693.

⁴ Schramm: Ber. chem. Ges. Berlin, 18, 350 (1885).

With rising temperature, relatively more benzyl bromide is formed as is shown in Table II, which is also compiled from Bruner's data.

TABLE II
 $\text{IBr}_2 + 4\text{OC}_7\text{H}_8$

Temp.	Percent $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	Temp.	Percent $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
0°	8.7	45°	87.0
10	18.0	58.5	94.1
25	45.6	74	99.5
35	974.0		

In these experiments the toluene and bromine were in sealed glass tubes enclosed in a metal casing. They were thus protected entirely from the light. In the experiments at the higher temperatures, some reaction undoubtedly took place while the tubes were heating and the percentages of benzyl bromide, as given in Table II, are undoubtedly a little low at the higher temperatures. Since these experiments were undertaken chiefly as a study in chemical kinetics, they were not carried through to an end and the data in the two tables refer to the percentages of benzyl bromide formed at the end of the run when 90–95 percent of the bromine had been used up. While the data do not therefore represent the percentages when the reaction has come to an end, the general relations remain the same.

Some experiments were made by Bruner with carbon tetrachloride as solvent. This solvent had no effect on the relative reaction velocities, the percentages of benzyl bromide being practically the same whether the reaction took place in presence or in absence of carbon tetrachloride. Very different results were obtained with nitrobenzene as solvent. A mixture was made up containing 75 parts nitrobenzene and 25 parts toluene by volume. One gram of bromine was added to 26.6 cc. of the mixture. The results are given in Table III. The effect of the nitrobenzene is very marked.

TABLE III
75 Vol Percent $C_6H_5NO_2$ + 25 Vol Percent C_7H_8
1 g Br_2 to 26.4 cc solution

Temp.	Percent $C_6H_5CH_2Br$	Temp.	Percent $C_6H_5CH_2Br$
25°	1.3	45°	11.4
35	2.9	74	18.9

Very little benzyl bromide is formed below 40° and even at 74° there is only 19 percent as against 100 percent when no nitrobenzene is present.

In sunlight, benzyl bromide is the sole product even at zero and in concentrated solutions.¹ With ferric bromide or ferric chloride as carrier, ring substitution is the only one. With iodine monobromide as carrier, ring substitution is usually the only reaction. Jackson and Field² have shown that at higher temperatures benzylbromide is formed even in presence of iodine, the relative amount of benzyl bromide increasing with decreasing concentration of iodine. This has been studied in more detail by Bruner.³ The results are tabulated in Table IV. The first column contains the molecular percentage of iodine to bromine. In the remaining columns are given the percentages of benzyl bromide at the different temperatures.

TABLE IV
1 Br_2 + 40 C_7H_8
Percent $C_6H_5CH_2Br$

Percent I/Br	0	25°	35°	45°
1.0	0.0	29.5	41.0	67.0
2.5	—	10.3	18.1	38.1
5.0	0.0	4.0		
10.0	0.0	1.2		

The reaction velocity experiments showed that the ring substitution and the chain substitution were independent

¹ Schramm: Ber., 18 (1885).

² Am. Chem. Jour., 2, 10 (1881).

³ Bull. Acad. Sci. Cracovie, 1907, 710.

reactions and that the iodine did not change the rate of the latter reaction. According to Schramm,¹ bromtoluene alone is formed when the solution containing iodine is exposed to direct sunlight. From Bruner's experiments it is safe to conclude that Schramm's statement applies only to the conditions under which he worked. With dilute solutions of bromine in benzene and with decreasing concentration of iodine the relative yield of benzyl bromide must increase. As Table IV shows, nearly thirty percent of benzyl bromide is formed at 25°. Since sunlight increases the rate of the chain substitution it is probable that even more benzyl bromide would have been formed if the tubes had been exposed to direct sunlight. This conclusion is confirmed by some experiments that Bruner made on photobromination in a nitrobenzene solution. From Table III we see that only 1.3 percent benzyl bromide is formed at 25° and only 18.9 percent at 74°. When this same solution was exposed to direct sunlight, the yield of benzyl bromide jumped up to seventy percent.

While bromine and toluene react in the dark, it is stated by Schramm² that bromine does not react at an appreciable rate with *p*-bromtoluene or ethyl benzene in the dark. In sunlight there are formed *p*-brombenzyl bromide and phenyl ethyl bromide.

The results of the preceding pages are given in a condensed form in Table V.

TABLE V

Benzene and Chlorine

No reaction in dark.
 Hexachloride in sunlight.
 Hexachloride in the dark with H₂O or dil. NaOH.
 Hexachloride with red phosphorus.
 Some hexachloride with ICl in the dark.
 Substitution with FeCl₃, SnCl₄, SbCl₅, MoCl₅, Al₂Cl₆ICl, S, SO₂Cl₂, H₂SO₄, etc.
 Substitution by electrolysis.
 Some substitution in the dark with H₂ or dil. NaOH.

¹ Ber. chem. Ges. Berlin, 18, 606 (1885).

² Ibid., 18, 350 (1885).

TABLE V—(Continued).

Benzene and Bromine

Up to 50% C_6H_5Br in the dark.
 Hexabromide in sunlight.
 Hexabromide in the dark with H_2O or dil. $NaOH$.
 Substitution with $FeBr_3$, $FeCl_3$, IBr , etc.
 Some substitution in the dark with H_2O or dil. $NaOH$.

Toluene and Chlorine

Ring and chain substitution in the dark, temperature effect.
 Chain substitution in sunlight.
 Chain substitution in the dark with H_2O or dil. $NaOH$.
 Chain substitution with phosphorus pentachloride.
 Chain substitution (nitrotoluene) with sulphur as carrier.
 Some chain substitution in the dark with H_2O or dil. $NaOH$.
 Ring substitution with $FeCl_3$, ICl , $SbCl_5$, etc.
 Ring substitution by electrolysis.
 Some ring substitution in the dark with H_2O or dil. $NaOH$.

Toluene and Bromine

Ring and chain substitution in the dark: concentration and temperature effect.
 Ring and chain substitution with bromine and water.
 Chain substitution in sunlight.
 Chiefly chain substitution in sunlight in presence of nitrobenzene.
 Chiefly ring substitution in the dark, in presence of nitrobenzene: temperature effect.
 Ring substitution with $FeBr_3$, $FeCl_3$, etc.: concentration effect.
 Ring (and chain) substitution with IBr : concentration and temperature effect.

Various explanations of the action of halogen carriers have been given. The following one is that of Page.¹

"No satisfactory explanation of the action of chlorine carriers seems yet to have been given. There are two hypotheses which are worthy of special consideration.

"According to the first the chlorine carrier first combines with chlorine and then gives up that chlorine to the substance which is to be chlorinated. This process of com-

¹ Liebig's Ann., 225, 203 (1884).

binning with chlorine and giving it up is then repeated. The following equations represent these reactions:

1. $\text{MoCl}_3 + \text{Cl}_2 = \text{MoCl}_5$.
2. $\text{C}_6\text{H}_6 + \text{MoCl}_5 = \text{C}_6\text{H}_5\text{Cl} + \text{HCl} + \text{MoCl}_3$.
3. $\text{MoCl}_3 + \text{Cl}_2 = \text{MoCl}_5$
and so on.

"In order to explain the process of chlorination by means of this hypothesis, one must assume that less energy is required to overcome the attraction by which the active chlorine is held to the molecule of the halogen carrier than is required to break the bond which holds the two atoms in the molecule of chlorine gas. The halogen carrier therefore converts the chlorine into a state similar to that of atomic chlorine, in which the reacting power of the halogen seems to be increased considerably. The following facts appear to be against this view:

"(a) *The difference in the action of chlorine on toluene, according to whether a halogen carrier is or is not present.*—If chlorine is led into boiling toluene, substitution takes place in the methyl group. This proves, what is also confirmed by other reactions, that substitution takes place more readily in the methyl group than in the benzene radical. We should therefore expect that, when either atomic or molecular chlorine acts on toluene, the hydrogen of the methyl group would first be replaced and that the hydrogen of the phenyl group, since it reacts less readily, would either not be replaced at all or only after the substitution in the methyl group was completed. Instead of this, the presence of a chlorine carrier causes a reversal of the behavior of toluene towards chlorine, substitution beginning in the phenyl group and ending in the methyl group. Such a reversal cannot be explained by any assumption in regard to a halogen carrier producing atomic chlorine.

"(b) Further, if the action of the halogen carrier consists in a simple giving off of chlorine, the halogen carrier must be reduced if it reacts in absence of chlorine with the substance to be chlorinated. To test this experimentally,

10 cc of benzene with 1.82 g of Fe_2Cl_6 were heated to 100° in a sealed tube. On opening the tube no pressure was noticeable and very little hydrochloric acid was evolved. Part of the benzene was charred and formed a black tarry mass with the ferric chloride. Neither in the liquid nor in the black residue could ferrous salt be detected. Therefore, the action of ferric chloride as a halogen carrier cannot consist in an alternate reduction to ferrous chloride and conversion back to ferric chloride. It still remained to determine whether dissolved ferric chloride might not take up chlorine as does lead chloride. When 60 g Fe_2Cl_6 were dissolved in 50 cc H_2O and the solution saturated with chlorine, no considerable increase in weight could be detected either at ordinary temperature or at higher temperatures.

"A second assumption seems to me to be more plausible, namely that *the halogen carrier and the substance to be chlorinated form a molecular compound* and that this compound is then decomposed by chlorine with formation of HCl and a chlorine substitution product. This reaction can be represented by the equations:

"This offers an explanation of the facts that the substitution occurs first in the phenyl group when a benzene derivative is chlorinated in presence of a halogen carrier and that the chlorination of a benzene compound is easier than that of a fatty compound because the ferric chloride adds on more readily to the benzene radical.

"This process of chlorination is perhaps analogous to the behavior of ferric chloride and water. Ferric chloride crystallizes with water. When this compound is heated in the air, a rearrangement takes place inside the molecule, in consequence of which hydrochloric acid passes off and not water, ferric oxide remaining behind. If, however, this compound, which contains water, is heated with hydrochloric acid gas, the $\text{Fe}_2(\text{OH})_6$, which one may assume to be

first formed, takes up Cl again. First, water distils over and then anhydrous ferric chloride.¹ Ferric chloride behaves in the same way towards alcohol as towards water.

"Perhaps a more appropriate example is the reaction between aluminum chloride and benzene, studied by Gustavson.² This forms a compound, $\text{Al}_2\text{Cl}_6 \cdot 6\text{C}_6\text{H}_6$ with benzene; aluminum bromide forms a corresponding compound. Bromine reacts violently with both compounds, forming C_6Br_6 . Aluminum chloride behaves similarly with toluene and other aromatic hydrocarbons. It may therefore be assumed that ferric chloride forms corresponding compounds."

Scheufelen³ has the following to say on the same subject.

"No thoroughly satisfactory explanation has yet been offered to account for the action of these bromine and chlorine carriers.

"Page⁴ believes that a molecular compound is formed from the halogen carrier and the substance to be chlorinated, and that this compound is then decomposed by chlorine with formation of hydrochloric acid and a chlorine substitution product. In agreement with this are also the observations of Gustavson,⁵ who has shown the existence of a compound of benzene and aluminum chloride or aluminum bromide, with both of which compounds bromine reacts violently, forming hexabrombenzene.

"I shall now show that my experiments furnish, as I hope, an important contribution to the better understanding of these processes.

"If one lets bromine act on nitrobenzene and ferric chloride, there is formed bromnitrobenzene, ferric bromide, and hydrochloric acid. The reaction with benzene runs in the same way. Since the ferric chloride is converted almost completely into ferric bromide, it is not probable that hydro-

¹ Deville and Troost: *Comptes rendus*, 52, 920.

² *Ber. chem. Ges. Berlin*, 11, 2151 (1878).

³ *Liebig's Ann.*, 231, 191 (1885).

⁴ *Ibid.*, 225, 203 (1884).

⁵ *Ber. chem. Ges. Berlin*, 11, 2151 (1878).

chloric acid is a secondary product resulting from the action of hydrobromic acid on ferric chloride, although I assured myself by a special experiment that hydrobromic acid gas dried with phosphorus pentoxide, is able to set free hydrochloric acid in no inconsiderable amounts from ferric chloride which is partly dissolved in benzene and partly suspended in it.

"Page¹ made one experiment in which 10 cc of benzene and 1.82 g of ferric chloride were heated in a sealed tube to 100°; no ferrous salt could be detected among the reaction products. From this experiment it follows that ferric chloride alone cannot chlorinate benzene by giving off chlorine. If, now, bromine is also present, one atom of chlorine can tear itself loose from the iron and can combine with one atom of hydrogen from the benzene to form hydrochloric acid because at the same time the bromine molecule is split up and its atoms can saturate the free affinities of the iron and the benzene. If one looks upon the reaction as taking place in this way, it is easy to see that all the ferric chloride may be converted into ferric bromide.

"Chlorination in presence of ferric chloride probably takes place in the following way. The chlorine of the ferric chloride combines with the hydrogen of the benzene and at the same time the free chlorine molecules split into atoms, some of which combine with the benzene radical and the rest with the iron. The atoms of chlorine which have combined with the iron are now able to form hydrochloric acid again and to cause the same round. The chlorination can therefore be brought about by a much smaller amount of ferric chloride than corresponds to the hydrochloric acid formed.² The experimental results confirm this conclusion."

Willgerodt³ quotes the preceding paragraph from Scheu-

¹ Liebig's Ann., 225, 205 (1884).

² The whole process, being a reaction between *three* substances, is obviously analogous to the remarkable oxidations which have recently been studied thoroughly by Mr. Traube. Ber. chem. Ges. Berlin, 18, 1877 (1885). *Lothar Meyer*.

³ Jour. prakt. Chem. [2], 34, 290 (1886).

felen's paper, and then goes on: "Since benzene and the hydrocarbons derived from it cannot be chlorinated direct with ferric chloride at room temperatures, while chlorine and bromine even without a carrier form substitution products, I cannot adopt this view. For a long time I have held the view, expressed by Page, that the effectiveness of the halogen carriers is due to their forming molecular addition compounds with the aromatic substances, and to these molecular compounds being more easily attacked by the halogens than are the free organic substances themselves. This view of ours is supported by the fact that the halogen always substitutes in the aromatic ring when a halogen reacts in presence of a halogen carrier with an aromatic compound having aliphatic side chains. This view is also supported by the work of Gustavson¹ during which he succeeded in preparing the compounds $\text{Al}_2\text{Cl}_6 \cdot 6\text{C}_6\text{H}_6$ and $\text{Al}_2\text{Cl}_6 \cdot 6\text{C}_7\text{H}_8$. I suspect that the hydrocarbon molecules in these compounds do not all act exactly alike, which is quite conceivable. It is always quite probable that only one of them is united chemically with the aluminum chloride while the remaining five act as hydrocarbons of crystallization. The molecular compounds of benzene with Al_2Cl_6 or Fe_2Cl_6 (perhaps such oxychlorides as BiOCl may act similarly) must then be represented somewhat differently, depending on whether one starts with the benzene formulas of Kekulé, Claus, or Ladenburg. This is only conceivable, however, in case one assumes that one of the double or diagonal bonds of the benzene ring is broken and that the two valences set free thereby are neutralized by the inorganic halide, which can happen if the latter splits into a halogen atom and a univalent compound radical. If such an addition compound is brought in contact with the halogens, chlorine or bromine, a reaction takes place in such a way that a halide acid and an organic substitution product are formed while the inorganic halide is either regenerated or converted into another equivalent with respect to halogen. The halide acid is probably split

¹ Ber. chem. Ges. Berlin, **11**, 2151 (1878).

off from just one carbon atom, the organic and the inorganic halogen compounds by one halogen atom of the reacting molecule combining with this C atom while the other adds on to the compound inorganic radical. In this way it is possible to explain the forming again of the bond broken by the addition in the aromatic substance, and the substitution of hydrogen by the halogens. In violent reactions, it is conceivable that two halogen atoms might react simultaneously with the addition compound. In such cases the second molecule would substitute at the point to which the inorganic radical is attacked, and a di-substitution product would then be formed."

Since both Page and Scheufelen were pupils of Lothar Meyer, this expression of Willgerodt's views called forth an answer from Lothar Meyer. After commenting on Willgerodt's hypothesis that the ability of the elements to act as halogen carriers is a function of their atomic weights, Meyer¹ proceeds as follows:

"More important than these speculations according to my judgment is the question as to the real way in which halogen carriers act. At the end of the paper in question, Mr. Willgerodt says that he cannot agree with the view expressed by Scheufelen and that he is more in sympathy with the explanation offered by Page. There is, however, no conflict between these two views. Page considers it probable that the halogen carrier first forms a molecular compound with the hydrocarbon and that the free halogen decomposes this. Scheufelen showed that the reaction took place in such a way that the chlorine of the carrier combines with the hydrogen of the hydrocarbon, and the two are replaced each by one atom from the free halogen. This is no hypothetical opinion but an experimentally proved fact, for ferric chloride, bromine, and benzene form hydrochloric acid, ferric bromide, and brombenzene. Iodine acts similarly, though here, as one of my students, Mr. Schmidt, has recently

¹ Jour. prakt. Chem. [2], 34, 503 (1886).

noticed, the reaction soon ceases owing to a change having taken place represented by the equation:

In my opinion, these are very remarkable facts and I do not wish to see them ignored. For this reason I consider it advisable to emphasize them again here. Mr. Willgerodt remarks very truly that our knowledge in regard to halogen carriers cannot be considered as forming a closed chapter. The less this is the case, however, the more careful we must be to make certain of each step gained in our knowledge so as to be able to mount again from it."

The arguments in favor of the assumption of an intermediate compound and against any other explanation are apparently three:

(1) No hypothesis in regard to active chlorine can account for the reactions between chlorine and toluene.

(2) Ferric chloride alone does not react with benzene and ferric chloride does not take up chlorine.

(3) Aluminum chloride can form a crystalline compound with benzene or toluene.

The first argument falls to the ground if we succeed in framing a hypothesis which will account for the formation of chlortoluene in presence of a carrier and of benzyl chloride when no carrier is present. Since one object of this paper is to present such a hypothesis, it will be better to discuss the other two arguments first.

The second argument is that any explanation except that of the intermediate compound is impossible because ferric chloride alone does not react with benzene and because ferric chloride does not take up chlorine. The orthodox way of meeting a difficulty like this, is first to dispute the accuracy of the facts and then to point out that the facts do not prove anything even if they are as stated. I intend to avail myself of both of these methods of defense.

As regards the accuracy of the facts we have Seelig's

statement¹ that ferric chloride and toluene begin to react at about 60° and that ferrous chloride is formed. This evidence is not as satisfactory as I could wish it to be. Seelig apparently let the temperature run up so that some of the toluene charred and he does not state definitely that chlortoluene was formed though he implies it. Slator² found that benzene and iodine monochloride react in the sunlight forming monochlorbenzene, hydrochloric acid and iodine. Müller³ states that benzene and antimony pentachloride react. We thus have two cases in which the halogen carrier is reduced by the aromatic compound. It seems to me more than probable that this could be duplicated with molybdenum pentachloride, with antimony pentachloride and with phosphorus pentachloride. In fact, Page's own experiments are not conclusive. Some reaction took place because the benzene was charred, which certainly would not have happened at 100° if no ferric chloride had been present. It is quite possible that the reaction might have taken place smoothly at a somewhat lower temperature if the tubes had been exposed to bright sunlight.⁴ Slator found that the rate of reaction between benzene and iodine monochloride was practically negligible in the dark but that there was no difficulty about the reaction in bright sunlight. Considering the matter from the view-point of twenty-four years later, it is easy to see that the conditions of the experiment, which seemed best to Page (really to Lothar Meyer) in 1884, were admirably contrived so as not to throw any light on the subject at all. The most that anybody can claim for Page's conclusion is that it is not proved.

No valid conclusion can be drawn from Page's experiment in which he passed chlorine into a concentrated ferric chloride solution and found that no important increase of

¹ Seelig: *Liebig's Ann.*, **237**, 169 (1887).

² *Zeit. phys. Chem.*, **45**, 532 (1903).

³ *Jour. Chem. Soc.*, **15**, 43 (1862).

⁴ This prediction has since been realized experimentally by Mr. Schluederberg in my laboratory.

weight took place. If one is going to assume the existence of FeCl_5 , one is not obliged to assume the existence of a large amount of it. We may have a reversible equilibrium between FeCl_5 , FeCl_3 and Cl_2 without having anything more than the merest trace of FeCl_5 in the solution. This argument of Page's is, therefore, not sound. I do not care to lay very much stress on this point because I have no desire, myself, to assume the existence of FeCl_5 ; but it is only fair to point out that there is nothing in Page's work which prevents one from assuming the existence of such a compound if he so wishes.

Having thus shown that the facts are not necessarily as Page thought they were, we can now show that Page's argument does not hold even on his own statement of facts. For the sake of argument, we will grant that neither ferric chloride nor iodine monochloride will react either with benzene or toluene when there is no excess of chlorine. That does not prove in any way that ferric chloride will not react with benzene when an excess of chlorine is present. An illustration will make this clearer. Sunlight will not reduce ferric chloride in aqueous solution, because the reaction products would be ferrous chloride and chlorine (possibly some hypochlorous acid) which would give an electromotive force greater than that of light. In presence of alcohol, light can reduce ferric chloride, because the alcohol acts as a depolarizer for chlorine. Now, it might easily be that ferric chloride does not react with benzene because of the ferrous chloride that would then be formed. The reaction might, however, take place if we removed the ferrous chloride by means of a suitable depolarizer such as free chlorine. This suggests the possibility of making ferric chloride react with benzene by means of an oxidizing agent less powerful than chlorine. I have not been able to find any record of anybody having tried this experiment but I hope to have it tried before long. The important thing for the moment is to show that ferric chloride might conceivably react with benzene in presence of chlorine even though it did not in the absence of chlorine.

We can now consider Page's argument in favor of the reaction being due to the intermediate formation of an addition compound or molecular compound, so-called. At the time that Page put forward this hypothesis, it was unquestionably the one having the most evidence in its favor. In the last twenty years, however, there has been a good deal of new evidence, all of which tends against this explanation. Cohen¹ has shown that chlortoluene is formed when toluene and concentrated hydrochloric acid are electrolyzed between carbon electrodes. It is difficult to see what intermediate addition can be assumed here, and yet, if we can get substitution in the ring in some cases without assuming the existence of an intermediate compound, the burden of proof is on the man who tries to show that there are two fundamentally different ways of accomplishing ring substitution. Schramm's work with bromine and toluene is also disconcerting because bromtoluene is practically the only product when the solution is kept cold and out of the light. Under certain conditions of temperature and concentration, free halogen does substitute practically exclusively in the ring. With bromine and toluene we get ring substitution in three sets of cases:

- (1) With halogen alone, solution cold and dark.
- (2) With halogen and halogen carrier.
- (3) With electrolytically produced halogen.

Page said that the first case could not occur; he accounted for the second by the assumption of an intermediate compound; and the third case he did not know anything about. This in itself would be sufficient to show the inadequacy of Page's hypothesis, but this is not all. Within the last ten years, reaction velocity measurements have been made and these measurements do not confirm the hypothesis of Page. Bruner² finds that the rate of bromination of benzene and of toluene is proportional to the concentration of the hydro-

¹ Jour. Chem. Soc., 87, 1034 (1905).

² Zeit. phys. Chem., 41, 513 (1902). Bull. Acad. Sci. Cracovie, 1907, 691.

carbon, to the concentration of the bromine and to the square of the concentration of the iodine monobromide. Slator¹ studied the rate of chlorination of benzene in presence of different catalytic agents and found that the rate was proportional to the concentration of the benzene, to the concentration of the chlorine, and to the concentration of the ferric chloride or stannic chloride when these were used as catalytic agents. When iodine monochloride was used as a catalytic agent, the rate was proportional to the square of its concentration and not to the first power of it. Now, of course, an experiment in reaction velocity is not an absolutely safe guide because there may easily be several ways of accounting for a given result, as indeed Slator² points out in this very case. On the other hand, a hypothesis which is not compatible with the kinetic measurements cannot be right. It is difficult to see how the rate can be proportional to the first power of the benzene concentration and the first power of the ferric chloride concentration if we postulate the intermediate formation of a compound of the type $\text{Fe}_2\text{Cl}_6 \cdot 6\text{C}_6\text{H}_6$. Even if this difficulty were surmounted, we should still have to account for the rate being proportional to the square of the concentration in the case of the iodine monochloride and monobromide. I do not mean to say that both these difficulties might not be overcome by some ingenious man; but he would still be confronted by the three facts that bromine substitutes in the ring without a carrier, that electrolytic chlorine substitutes in the ring, and that phosphorus pentachloride is a carrier substituting in the chain. For the present, at any rate, we are justified in concluding that the arguments in favor of an intermediate compound and against any other explanation are not valid and that we are ready for an entirely fresh start.

Bruner³ has offered an explanation of some of the reaction velocity relations when bromine reacts with toluene forming

¹ Zeit. phys. Chem., 45, 513 (1903).

² Ibid., 45, 553 (1903).

³ Bull. Acad. Sci. Cracovie, 1907, 718.

bromtoluene under one set of conditions and benzyl bromide under other conditions.

"The chief difference between the two reactions is, after all, the difference in the temperature coefficient, which determines the distribution at different temperatures. If we examine, for instance, the list given by van't Hoff of the temperature coefficients of different reactions so far as determined, it is distinctly noticeable that these are in general higher, the more complicated the substances that enter into the reaction, the highest values, 6-7, being observed with enzymes. The smallest on the other hand (1.2-1.3) are for the dissociation of arsine and phosphine (determined at higher temperatures, it is true) where we are compelled by the reaction being monomolecular, to assume that the first decomposition is into free atoms.¹

"If one takes this into account, together with the fact that electrolytic halogen, which we usually consider as *in statu nascendi*, forms only substitutions in the ring even with boiling toluene, it seems very probable that the ring substitution is effected by other chemical individuals than those concerned in the chain substitution. The extraordinary photochemical sensitiveness of the chain substitution and the lack of sensitiveness to light of the ring substitution are to be cited as evidence in favor of the hypothesis. The simplest explanation would be to assume that the chain substitution was due to the bromine molecule, present in relatively large amounts, and the ring substitution to the free Br atoms² which, though present in relatively very small amounts, are much more ready to react. The formulation of the two reactions would then be as follows:

¹ It may be mentioned here that subatomic (radio-active) changes are entirely unaffected by temperature changes.

² Cf. Bruner: Bull. Acad. Sci. Cracovie, 1902, 181; Zeit. phys. Chem., 41, 524 (1902).

"The two equations give the same monomolecular reaction with respect to the change of the bromine concentration with the time, provided one assumes, what has often been proved by molecular weight determinations, that most of the bromine is present as Br_2 and that the bromine is only very slightly dissociated into atoms.¹

"Then according to the relation

we have $(\text{Br})_2$ proportional to (Br_2) which is the concentration of the bromine as determined by titration or by weighing.

"This formulation is in harmony with the recognized fact that the reaction is monomolecular in the absence of a catalytic agent. If iodine (iodine bromide) is added, the concentration of the Br atoms is determined both by the equilibrium

and also by the dissociation of the iodine bromide

and the (Br) concentration is therefore proportional to the concentration of the (IBr) . The equilibrium of the bromine atoms must be satisfied both with reference to equation 3 and equation 4; consequently the rate of consumption of the bromine atoms will be, according to equation 2 and in agreement with the experimental data previously given:²

$$-\frac{d[\text{Bromine}]}{dt} = k_1 [\text{Br}]^2 = k_1 [\text{Br}_2]$$

and on addition of iodine

$$-\frac{d[\text{Bromine}]}{dt} = k_1 [\text{Br}_2] + k'_1 [\text{Br}_2][\text{IBr}]^2.$$

¹ Cf. Bruner: *Zeit. phys. Chem.*, 41, 524 (1902). Slaton: *Ibid.*, 45, 553 (1903).

² In the paper so often referred to, Slaton remarks quite truly, in connection with Prof. R. Luther's exposition, that different formulations of a reaction may be compatible with the kinetic equations. It would however be unwise not to make some attempt at an explanation and formulation of the reactions, especially if there are also other reasons which may serve to support a given formulation.

"From this point of view, the variation from the quadratic law at higher temperatures must be only a superficial one caused by the unknown and therefore unheeded dissociation relations of the iodine bromide.

"The experiments to be described give some information as to the nature of the bromine atoms, which we assume to be formed by the dissociation of the bromine and the iodine bromide. It seems probable that we must consider them as ions."¹

In some experiments with bromine, toluene and nitrobenzene, the reaction velocity constant was not satisfactory. Bruner attributes this disturbance to the action of hydrobromic acid, which is somewhat soluble in nitrobenzene. He then proceeds.²

"Next to the disturbed course of the reaction we have *the strongly marked preponderance of the ring substitution products* as a peculiarity of the reaction in nitrobenzene. This phenomenon is certainly connected with the fact that bromine and a *portion* of the acid of the polybromides is dissociated into ions in nitrobenzene as solvent.³ Even though the strong, mutually influenced ions, such as the chlorine or bromine anions of hydrochloric or hydrobromic acid, have no direct chlorinating action, it is however very plausible that the free halogen atoms, resulting from the neutralization of the electrical charges, might cause ring substitution by preference. Attention may also be called to the important fact noticed by J. B. Cohen⁴ and his co-workers, that chlorine set free electrolytically at a carbon anode causes ring substitution exclusively, even in boiling toluene. The halogen atoms, thus formed, are incapable of substituting in the chain."

In the main I agree with this explanation of Bruner's.

¹ L. Bruner: "On the Electrolytic Conductivity of Bromine and Iodine." Bull. Acad. Sci. Cracovie, 1907, 731.

² Bruner: Bull. Acad. Sci. Cracovie, 1907, 726.

³ Ibid., p. 731.

⁴ Jour. Chem. Soc., 87, 1034 (1905).

It is good as far as it goes; but it seems to me that the theory does not take cognizance of the following three items:

- (1) The electrochemical action of light.
- (2) The formation of benzyl chloride with water as a carrier.
- (3) The formation of benzyl chloride with phosphorus pentachloride as a carrier.

We know that light of a proper wave-length increases the conductivity of most gases, apparently by forming ions. We must therefore find some difference other than that between the bromine molecule and the bromine atom so-called if we are going to account for the two different ways in which bromine and toluene react. If sunlight forms atoms or ions or anything else out of bromine or chlorine, we shall probably get products, one-half of which may be called positive and the other half negative. No assumption is made as to what we mean by positive and negative. If the dissociation products are ions, the words have their usual meaning. If the dissociation products are not ions, the words have another meaning. It will simplify matters, perhaps, if we speak of the hypothetical dissociation products as gaseous ions though this is not an essential part of the explanation. In an aqueous solution of chlorides or bromides we have negative chlorine anions or bromine anions but no chlorine cations or bromine cations. When these ions are discharged electrolytically, we have at first solely negative hypothetical chlorine or bromine gaseous ions. If there is nothing with which these hypothetical substances can react, there will necessarily be a re-arrangement of some sort and the formation of chlorine or bromine gas. If there is some substance present with which they can react, they will react so far as possible, as negative ions. With this as a starting point, I make the following assumptions in order to account for the reactions between bromine and toluene for instance.

- (1) There is a slight reversible dissociation of bromine into positive and negative particles or gaseous ions.

(2) There is a slight reversible reaction between bromine and the positive gaseous ion.

(3) Substitution takes place in the ring when the negative gaseous ions are present in excess; otherwise it takes place in the side chain.

(4) The addition products of benzene are to be considered as analogous to the chain substitution products of toluene.

(5) There is a reversible dissociation of the halogen carriers with formation of so-called gaseous halogen ions. Whether these ions are positive or negative depends on the nature of the carrier.

Of these assumptions the first and fourth are not new; the first half of the fifth has been made implicitly by everybody who has tried to account for halogen carriers without postulating the formation of an intermediate compound. It was made explicitly by Bruner. The second half of the fifth assumption is new but is a necessary consequence of the first part of the assumption.

The second assumption is new, so far as I know, and is made because I cannot get along without it. The third assumption is also new but is a necessary consequence of the first two assumptions.

I will now show how these assumptions apply to the cases which we have to account for. At low temperatures and in the dark, there will be a formation of $\text{Br}_2 \cdot \text{Br}^+$ and consequently an excess of Br^- . The relative excess will be greater, the greater the concentration of the bromine. We should therefore expect ring substitution in concentrated solutions with an increasing percentage of substitution in the side chain as we start with a more and more dilute bromine solution. This is exactly what was found by Bruner and some data illustrating the point were given in Table I. With rising temperature we get increasing dissociation of $\text{Br}_2 \cdot \text{Br}^+$, the ratio of Br^+ to Br^- increases, and consequently we should

get an increasing percentage of benzyl bromide among the reaction products. This was also found experimentally by Bruner and some data were given in Table II. Sunlight will increase the dissociation of Br_2 and $\text{Br}_2\cdot\text{Br}^+$ and will therefore bring the ratio of Br^+ to Br^- up very close to unity and consequently under the third assumption we shall get side chain substitution only, provided the intensity of the light is sufficient. In diffused light we shall of course get a state of things intermediate between the results for darkness and for bright light. Both of these predictions have been confirmed experimentally.

With a carrier such as ferric chloride our fifth assumption calls for a reversible dissociation into gaseous halogen ions and ferrous chloride. With iron we can, of course, only have negative gaseous halogen ions and the equilibrium will be represented by the equation

Under these conditions there will be enough negative gaseous ions from the ferric chloride to overbalance any positive ions which might come from the chlorine gas and we should expect to get ring substitution even in boiling toluene and even when the system is exposed to bright sunlight. This is exactly what happens.

With the chlorides of iron, antimony, molybdenum and aluminum, there can be no question but that chlorine is the negative radical. With iodine monochloride, however, the matter is more open to doubt. Since chlorine is a more powerful oxidizing agent than iodine, we might reasonably expect that iodine would be the positive radical and chlorine the negative radical. The margin of safety is not large however and the experimental results are just what we should expect under these circumstances. Iodine monochloride as carrier does substitute in the ring; but the dissociation is not sufficient to prevent substitution in the side chain in boiling toluene, especially if the concentration of iodine monochloride or monobromide be low. Of course, if one were to decrease

sufficiently the concentration of ferric chloride as carrier there would come a point at which chain substitution would also occur in boiling toluene in spite of the iron; but no such point has been determined experimentally.

According to Slator's¹ experiments iodine monochloride is so near on the line that both addition and substitution products are formed when chlorine, iodine monochloride and benzene are brought together in the dark. With benzene and iodine monochloride alone practically no reaction takes place in the dark, presumably because the chemical potential is not sufficiently high to set free iodine. The action of sunlight so increases the dissociation of the iodine monochloride that the reaction can now take place. As was to be expected only negative gaseous chlorine ions are set free and chlorobenzene is the sole product. This is an especially interesting case because we have here a photochemical ring substitution, the existence of which is denied by Bruner. Corresponding experiments with toluene and iodine monochloride or monobromide in sunlight have not been made; but such experiments, when made, will undoubtedly confirm the theory. In some cases iodine monochloride can be used to prepare iodine substitution products.²

While iodine monochloride is on the line, phosphorus pentachloride is apparently over it and either forms positive gaseous chlorine ions only or an equal quantity of positive and negative gaseous chlorine ions. It makes no difference which reaction we postulate,

or

Either one will account for the formation of benzyl chloride by the action of chlorine and phosphorus pentachloride on toluene.³ Since the phosphorus pentachloride accelerates

¹ Zeit. phys. Chem., 45, 521 (1903).

² Lassar-Cohn: Arbeitsmethoden, 3rd Ed., 409.

³ Colson and Gautier: Ann. chim. Phys. [6], 11, 19 (1887); Erdmann: Liebig's Ann., 272, 150 (1893).

the rate, we must look upon it as a halogen carrier. This differs from the case of the iodine monochloride because chain substitution takes place with phosphorus pentachloride and chlorine in sunshine. Willgerodt has shown that phosphorus pentachloride, chlorine and benzene form benzene hexachloride, so that its behavior with benzene corresponds to the behavior with toluene.

With the two non-metallic halides, iodine monochloride and phosphorus pentachloride, we have evidence of more or less well-marked tendency to form positive gaseous chlorine ions. This same tendency is also shown by sulphur chloride. Willgerodt¹ states that sulphur acts as a halogen carrier with benzene, forming chlorine substitution products. On the other hand Häussermann and Beck² have prepared *o*-nitrobenzyl chloride by letting chlorine act on *o*-nitrotoluene in presence of sulphur as a carrier. In this case it looks as though we had the formation of positive gaseous chlorine ions.³

A still more interesting case from the theoretical point of view is Matthews' synthesis of benzene hexachloride by passing chlorine through a mixture of benzene and water or dilute caustic soda. Goldberg⁴ says that at present we can only make guesses at the mechanism of this reaction. It does not seem to me that matters are quite so bad as that. If we pass chlorine into water we get a reversible equilibrium represented by the equation

Since this is a reversible reaction, there is a continuous formation and consumption of chlorine. As a preliminary step to the formation of Cl_2 we have the setting free of Cl^- from the hydrochloric acid and of Cl^+ from the hypochlorous

¹ Willgerodt: Jour. prakt. Chem. [2], 34, 264 (1886).

² Ber. chem. Ges. Berlin, 25, 2445 (1892).

³ Chlorination by means of sulphuric acid appears to depend on the formation and decomposition of a sulphuric acid compound, and sulphuric acid is therefore not a halogen carrier of the same type as the others.

⁴ Zeit. wiss. Photochemie, 4, 63 (1906).

acid. If benzene is present, these intermediate products of course react with it forming benzene hexachloride. This synthesis is therefore a necessary consequence of our third assumption and is an additional justification of it. If the chlorine gas combines to a certain extent with the positive gaseous ion, we shall get ring substitution to a greater or lesser extent.

The explanation of the action of halogen carriers is in accord with the reaction velocity measurements. It has already been pointed out that the rate is proportional to the first power of the concentration of the ferric chloride or the stannic chloride; but to the second power of the concentration of the iodine monochloride. This is a necessary consequence of the following equations:

Bruner's reasoning in regard to iodine monochloride is applicable without change to ferric chloride and stannic chloride. Since we have the relation

the rate of chain substitution with toluene will be proportional to the concentration of the chlorine. The rate of formation of benzene hexachloride will be of the first, second, or third order with respect to chlorine, depending on which of the following reactions is the one actually measured:

It would strengthen the argument if it were possible to show why negative chlorine substitutes in the ring and positive chlorine in the side chain; but I do not see any explanation which can be carried through. We might assume that the hydrogen of the chain was positive and was therefore re-

placed by the positive chlorine and combined with the negative chlorine to form hydrochloric acid. In that case we should call the ring hydrogen negative. This hydrogen would be displaced by the negative chlorine, would change to positive in some unknown way and would form hydrochloric acid with the negative chlorine. This is not an unreasonable way of looking at things; but it does not account for the fact that ferric chloride is a bromine carrier. Lothar Meyer's contention seems to be sound, that the first step in the reaction is the formation of hydrochloric acid. Until some way is found of getting round this difficulty, we cannot do anything more than say that the assumption in regard to ring substitution is an assumption *ad hoc*, and that we cannot deduce it from anything else.

To a certain extent the chlorination or bromination of the aliphatic compounds follows the same general rules that have been laid down for the aromatic compounds; but this is by no means always the case. Hell and Gantter¹ have brominated the fatty acids with red phosphorus as a carrier and Volhard² has used the same method. Béhal and Anger³ have chlorinated acetic acid with S or S₂Cl₂ as carrier. Mel-sens⁴ has found that chloracetic acid is formed when sulphur dioxide and chlorine are passed into glacial acetic acid; but there is some question whether this is anything more than a coupled reaction. These cases are all in keeping with the assumption that we have positive gaseous chlorine ions with these carriers. The fact that iodine monochloride in boiling acetic acid acts as a chlorine carrier⁵ might possibly pass, though it is rather stretching a point. Page⁶ found that molybdenum pentachloride was not a carrier for aliphatic compounds and that ferric chloride in acetic acid was not a

¹ Ber. chem. Ges. Berlin, 14, 891 (1881).

² Liebig's Ann., 242, 141 (1887).

³ Bull. Soc. chim. Paris [3], 3, 144 (189).

⁴ Comptes rendus, 76, 92 (1873).

⁵ Müller: Jour. Chem. Soc., 15, 41 (1862).

⁶ Liebig's Ann., 225, 196 (1884).

chlorine carrier. This is all as it should be; but any premature rejoicing is checked by the fact that ferric chloride is a chlorine carrier in alcohol. It is not difficult to find other cases of the same sort.¹ All that can be said at present is that those substances which ought to be halogen carriers for aliphatic compounds are halogen carriers; but that the converse is only occasionally true.

It may be asked what substances are halogen carriers for aromatic compounds. According to the explanation given in this paper, the other element in a halogen carrier must lose chlorine under the conditions of the experiment. It must either have two effective valences in regard to the halogen or must reduce readily to the element as in the case of iodine monochloride. Of course, the converse is not necessarily true, that every substance forming two chlorine compounds is necessarily a chlorine carrier. An apparent weak point in the argument is the behavior of aluminum. From the experiments of Goldschmidt and Larsen² we know that aluminum chloride behaves exactly like tin tetrachloride as a carrier. We must therefore have the following reactions taking place:

Unfortunately no such substance as aluminous chloride is known at present. It was therefore necessary to demonstrate the possibility of such a compound. This was done by making aluminum anode in a chloride solution. When a heavy current density is used, aluminum dissolves with a lower effective valence as is shown by the instable salt breaking down and evolving hydrogen at the anode.³ Though the aluminous chloride has not yet been isolated, its existence as an instable salt has been demonstrated sufficiently to account for the behavior of aluminum chloride as a halogen carrier.

¹ Lassar-Cohn: *Arbeitsmethoden*, 3rd Ed., 305.

² *Zeit. phys. Chem.*, 48, 424 (1904).

³ Turrentine: *Jour. phys. Chem.*, 12, 455 (1908).

The general conclusions are as follows:

(1) The action of halogen carriers is not due to the intermediate formation of addition compounds.

(2) Under suitable experimental conditions the halogen carriers react with benzene or toluene even when no free halogen is present.

(3) A theory of halogen carriers has been developed on the assumption of positive and negative dissociation products of the halogens.

(4) This theory is a development or amplification of Bruner's theory.

(5) The theory accounts for the catalytic action of ferric chloride, aluminum chloride, stannic chloride, iodine monochloride, phosphorus pentachloride, water and sunlight.

(6) The theory accounts for the reaction velocity relations with ferric chloride, stannic chloride, aluminum chloride, iodine monochloride and water.

(7) There is strong experimental evidence of the existence of aluminous compounds.

(8) The theory of Grotthuss has proved serviceable in explaining the action of halogen carriers.

Cornell University.