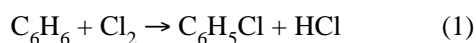# ARTHUR SLATOR AND THE CHLORINATION OF BENZENE

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Wilhelm Ostwald had a lifelong interest in catalysis. His receipt of the 1909 Nobel Prize for Chemistry was partly a result of his contributions to this topic. Following his appointment as professor of physical chemistry at the University of Leipzig in 1887, his interest was largely maintained through research assignments. The dissertations of about one-third of his English-speaking students were devoted to studies of catalysis or involved the use of catalytic effects.

Ostwald's decision that a thorough study of the chlorination of benzene should be made may have been based on the observation that, although many factors governing the results were well known, no quantitative measurements of the dynamics were available.

The choice of a catalyst can affect not only the rate of a chemical reaction but sometimes can also control the nature of the products. In the case of chlorine and a large excess of benzene, the rate of reaction in the dark is very slow. When a catalyst such as tin tetrachloride is added, chlorobenzene, a *substitution* product, is obtained:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \qquad (1)$$

Illumination accelerates the reaction between chlorine and benzene, but the result is an *addition* product, benzene hexachloride.
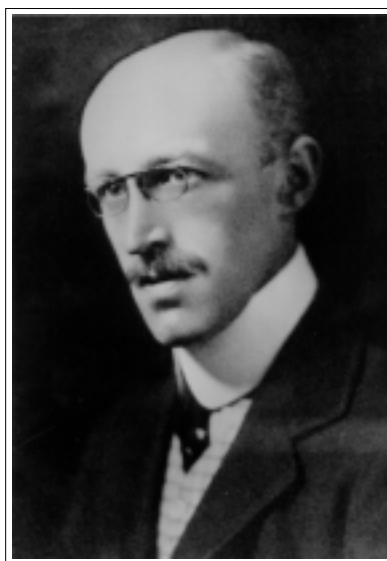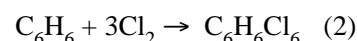

Figure 1. Arthur Slator

$$C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6 \quad (2)$$

The formation of hydrochloric acid in Reaction 1, but not in Reaction 2, is of obvious value in the analysis of mixed products that may result from the use of other catalysts.

As a student of Ostwald in Leipzig, Arthur Slator (Fig. 1) undertook a quantitative study of the chlorination of benzene. Slator was born in Burton-on-Trent, England, on April 21, 1879, the son of Henry Slator, head brewer at the Evershed brewery (1). He attended Burton Grammar School and Mason College, Birmingham, finally graduating with first-class honors from the University of London in 1899. The award of an 1851 Exhibition Scholarship enabled him to carry out research in Birmingham and, much more extensively, in Ostwald's laboratory in Leipzig. Here Slator thoroughly investigated the kinetics of the catalyzed action of chlorine on benzene (2). The symbols used by Slator are retained in the present account.

When Slator arrived in Leipzig, Ostwald had become strongly interested in philosophy. Although he retained the overall direction of chemical research, its immediate supervision passed increasingly to his very able assistants. Prominent among these was Robert Luther (1867-1945), who became sub-director of physical chemistry in 1901. It is clear that Luther became the

actual supervisor of the task that Slator was about to begin. Both in Slator's doctoral dissertation (1903) and the resulting publication (2), Luther received acknowledgment as mentor.

Slator repeatedly distilled commercial, thiophene-free benzene until the boiling point was constant to within a few tenths of a degree. Chlorine, prepared from HCl and $K_2Cr_2O_7$, was dried over H_2SO_4 and either immediately dissolved in benzene or stored for later dissolution. Dilution of the stock solution with benzene was used to prepare solutions for measurement of the velocities of reaction. With benzene present in large excess, its concentration could be regarded as remaining essentially constant.

Slator performed some reactions in sealed tubes, but when possible used the more convenient apparatus shown in Fig. 2. The capacity of the reaction vessel, A, was not stated; but, because the performance of an experiment involved a succession of samplings, it was probably not less than about 100 mL. The vessel, which was immersed in a thermostat set at 25° C, had an attached 3-mL pipet as shown. Measured samples of the solution could then be withdrawn for analysis. An unspecified red substance was used to color the bath liquid. According to Slator, the aim was to eliminate light (presumably of the spectral region that could bring about the chlorine-benzene addition) and thus to make the measurements in the dark.

Figure 2. Apparatus for catalytic studies.

After the introduction of a measured amount of catalyst, the stirred mixture was sampled at specified times. Each sample was shaken with KI solution, and the liberated I_2 was titrated with $Na_2S_2O_3$ solution, a technique known since the 1850s (3). This provided a measure of the remaining chlorine. To study the formation of HCl, the titration was continued with $Ba(OH)_2$ solution at 0° C. At this temperature hydrolysis of the $S_4O_6^{2-}$ formed in the first titration is slow and does not interfere.

According to Slator, the use of iodine as a halogenation catalyst had been known since 1862. However, applications of this catalyst in organic syntheses had been rare, because of possible attack on the reaction products or on other substances present. This restriction did not apply to Slator's work, because the addition of small

known concentrations of iodine to the chlorine-benzene solution generated iodine monochloride (ICl). He showed that ICl did not attack benzene but remained unchanged in the solution while catalyzing the chlorine-benzene reaction. In his studies with this catalyst, Slator was thus able to measure amounts of remaining chlorine by deducting the titer attributable to ICl from the total thiosulfate titer. He noted that, with this catalyst, both chlorobenzene and benzene hexachloride were produced. However, his first concern was to determine the rate of the consumption of chlorine, on the assumption that the data would fit the first-order equation:

$$K = \frac{1}{t} \log \frac{[Cl]_0}{[Cl]_t} \qquad (3)$$

In this equation, Slator used *K* to indicate the rate constant, $[Cl]_o$ the initial concentration of chlorine and $[Cl]_t$ the concentration after the elapse of *t* minutes. Slator found that *K*, which decreased as the ICl concentration was decreased, was inversely proportional to the square of this concentration. Additional experiments at 15° C indicated a temperature coefficient of about 1.07 for a 10° C rise.

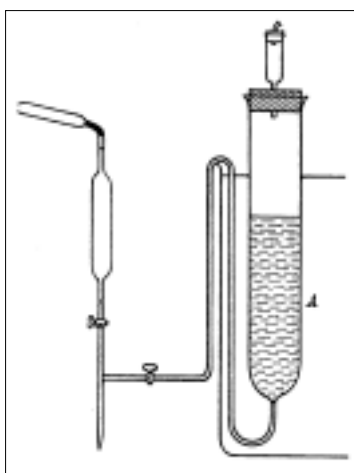Slator investigated the distribution of chlorine between the two products at temperatures of 20°, 25° and 80° C. Although he could not isolate the benzene hexachloride, he was able to determine it indirectly. An ICl-catalyzed chlorine-excess benzene reaction was run to completion, and the HCl thus formed was titrated with $Ba(OH)_2$ solution. This provided a measure of the total chlorine that had reacted. The benzene solution was then separated, washed with water, and dried over $CaCl_2$. A measured aliquot was heated with alcoholic NaOH (presumably standardized by acid titrimetry and in known amount) for 30 min. This treatment affects only the benzene hexachloride. From the decrease in titer, the amount of the hexachloride can be calculated. Then the corresponding amount of chlorobenzene can be obtained by difference. Slator found that the reaction temperature had almost no effect and that an average of 72.5% of the chlorine is converted into chlorobenzene.

Because carbon tetrachloride is not attacked by chlorine, Slator chose it as a solvent to examine the kinetic aspects of benzene itself. Numerous experiments

showed that the approximately 70% yield of chloroben-zene, found previously, was also observed when the concentration of benzene ranged from 10% to 60%. Because the value of $K / [ICl]^2$ for a 20% solution of benzene was approximately twice that for a 10% solution, Slator concluded that the rate of reaction was proportional to the concentration of benzene, despite some decreases in the value of the above ratio that could not be attributed to the low concentration of benzene alone. Slator thought that a solvent effect was involved but lacked the time to follow up this concept.

Slator attempted to use cryoscopy to ascertain the nature of the solutes in the solutions. Because chlorine and benzene react very slowly in the dark, he was able to obtain six closely agreeing values for the apparent molecular weight of chlorine. However, the average value was only 88% of that expected for the molecule Cl_2. In the examination of ICl, the freezing point of a sample of benzene was first measured. Iodine was then added and both its concentration and the resulting freezing point were determined. Chlorine, in quantity insufficient to destroy all the iodine, was then introduced and the freezing point was again determined. From this, the depression due to iodine was calculated and subtracted from the total depression. Slator gave no example of the calculation used to obtain the apparent molecular weight of ICl, which, from the average of three experiments, he found to be 85% of that for the molecule ICl.

It is not clear whether Slator performed any experiments concerning iodine. He mentioned an earlier report that gave an apparent molecular weight 1.40 times that required for the molecule I_2 (4). Slator commented (2):

> …but when corrected for the solid solution, gives 0.90 I_2. Consequently, it appears that chlorine, iodine and iodine monochloride in benzene solution are present as Cl_2, I_2 and ICl, but in all of these cases we find the values approximately 15% too small.

No explanation was given for the cause of this apparent peculiarity.

In summarizing the reactions with ICl as catalyst, Slator stated that the velocity of the entire consumption of chlorine can be expressed by

Figure 3. Decrease of light intensity in a colored (i.e., light-absorbing) solution

$$- \frac{d[Cl]}{dt} = K[Cl_2] [C_6H_6] [ICl]^2 \qquad (4)$$

and the overall reaction can be approximated as:

$$8 \, C_6H_6 + 10 \, Cl_2 \rightarrow 7 \, C_6H_5Cl + 7 \, HCl + C_6H_6Cl_6$$
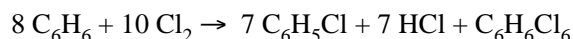
In experiments with $SnCl_4$ as catalyst, a measured volume of its solution in benzene was added to benzene in the reaction vessel and chlorine was then introduced. Samples of the mixture were withdrawn and analyzed as indicated earlier. Only the substitution reaction occurred, with a temperature coefficient of 1.5 per 10° C and a rate expressed by:

$$- \frac{d[Cl]}{dt} = K[Cl_2] [SnCl_4] \qquad (5)$$

Experiments with four different concentrations of $SnCl_4$ led to values of from 34.8 to 35.5 for the ratio (K x 10^4) / [$SnCl_4$]. In experiments with $FeCl_3$ as catalyst, every trace of water had to be excluded and the apparatus was modified because the solutions were hygroscopic. The K values varied with time and also changed when additional chlorine was introduced. Despite these results, Slator concluded that the rate of reaction appeared to be proportional to the $FeCl_3$ concentration. Notably, the temperature coefficient, 2.5, was larger than that found for $SnCl_4$.

Because ICl and $SnCl_4$ had shown very different catalytic effects, Slator experimented with mixtures of the two. He concluded that, with such mixtures, chlorine is consumed at a rate almost equal to that calculated for the sum of the rates for the individual catalysts.

Having demonstrated the effect of light on the chlorine-benzene reaction, Slator decided to study its kinetics. Parallel experiments were designed with pairs of solutions of chlorine of differing concentrations. The solutions were sealed in separate thin-walled glass tubes, which were then exposed either to diffused daylight or to sunlight. The apparent order, n, of the reaction was then calculated from the following equation, where A_1 and A_2 are the chlorine concentrations at the beginning of the experiments and E_1, E_2 are the concentrations at the end:
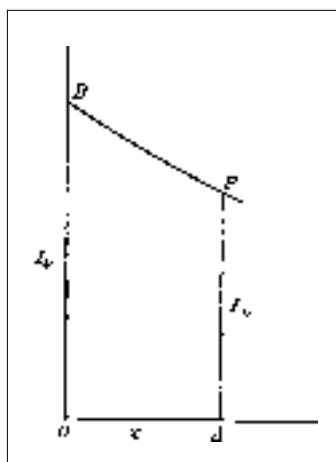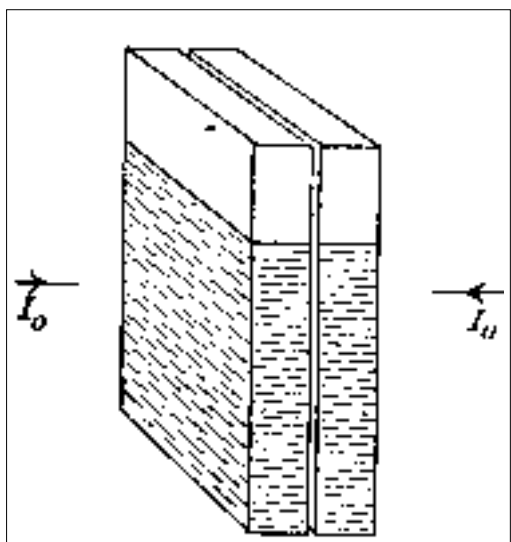
Figure 4. Double-cell system

$$\frac{A_1 - E_1}{A_2 - E_2} = \left(\frac{A_1 + E_1}{A_2 + E_2}\right)^n \qquad (6)$$

Three pairs of experiments gave 1.25, 1.55, and 1.15 as the values for *n*. The difficulty here arises from the fact that one of the reactants, chlorine, absorbs light and thus interferes with the obtaining of a correct reaction order. In other words, the intensity of the light, I_0, at the surface of the solution is greater than at any distance within the solution. The intensity becomes smaller as the light travels farther into the interior of the solution, as illustrated qualitatively in Fig. 3. Here I_x represents the intensity at a plane distant *x* from the surface.

In an attempt to compensate for this effect, Slator used a solution of chlorine in CCl_4 as a light filter. He found that the filter considerably decreased the rate of reaction, but concluded that the apparent order of reaction was 2. To obtain this number, a large correction would have to be applied to 1.3, the average of the results given above.

Luther drew Slator's attention to the possibility of estimating the correction by the measurement of the influence of the light filter on differing concentrations of chlorine. Slator decided to seek an approach by which the influence of the absorptive action was eliminated. In order to compare the absorption in two solutions, he needed to ensure that each solution received illumination of the same intensity. To satisfy this requirement, Slator constructed two thin plate-glass cells placed face

to face, as shown in Fig. 4. The narrow edges of the assembly were covered with strips of black paper, and cells were exchanged to compensate for any differences. The assembly was placed vertically on a turntable and adjusted so that an essentially parallel beam of sunlight fell squarely aand exclusively on the outer face of cell 1. When the table was turned through 180º, cell 2 received the same illumination. In his experiments, the table was turned about 20 times. By considering the relationships between light intensity, extinction coefficients, and concentrations, Slator proved theoretically that, when the cell pair was equally illuminated from both sides, the light strengths in the two solutions must be approximately equal. The greater diminution of light in the solution 2 is offset by the smaller effect in the solution in 1, and vice versa.

Slator carried out five experiments in which the chlorine concentrations in the respective cells were in an exact 2:1 ratio. For example, for the initial chlorine titers of 21.20 and 42.40, the final titers were 14.30 and 22.25, respectively. The calculated second order constants were 23 and 21.5, respectively, leading to 1.9 as the apparent order of reaction. The results of all experiments gave 1.95 ± 0.15, as close to 2 as could be expected. The reaction with respect to benzene had been shown to be of the first order, so that the rate of reaction could be expressed by the equation:

$$-\frac{d[Cl]}{dt} = K[Cl_2]^2 \cdot [C_6H_6] \qquad (7)$$

The temperature coefficient, 1.5 for a 10º C interval, was larger than any reported for light reactions at that time.

In discussing possible mechanisms for the chlorine-benzene reaction, Slator pointed out that these might proceed through the formation of intermediate compounds, as in the electrolytic reduction of nitrobenzene to aniline (5). Concerning the effect of light, Max Bodenstein (1871-1942) had found that the decomposition of hydrogen iodide was a reaction of the first order, governed by the dissociation $HI \rightarrow H + I$. However, a reaction of the second order, attributed to $2HI \rightarrow H_2 + I_2$, occurred in the dark (6). An explanation as simple as this was not possible in Slator's work. He did, however, suggest that a more "active" form of chlorine might arise from the action of light.

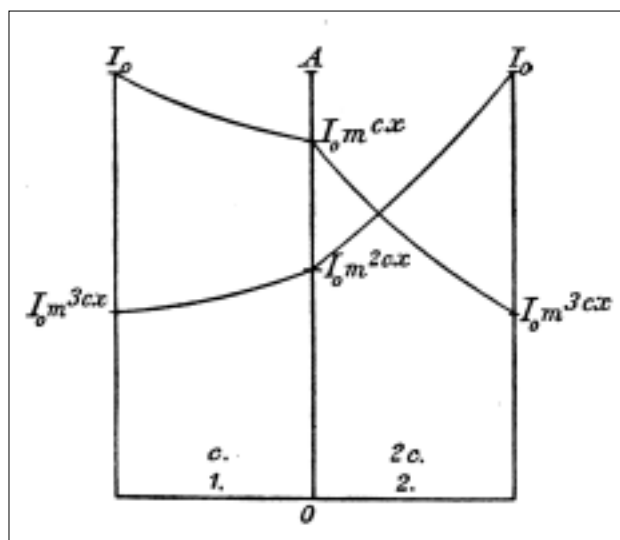In addition to the full account of his study (2), Slator published a shorter account in English (7). After com-

Figure 5. Light intensity in a pair of solutions with concentrations in the ratio 1 : 2

pleting his Ph.D. in 1903, he returned to England, to become lecturer in chemistry at University College, Nottingham. He described the iodide-induced decomposition of ethylene iodide (8) and wrote three papers on the dynamics of the reactions between sodium thiosulfate and halogenated organic compounds (9). His next paper, dealing with fermentation, indicated a considerable change in field (10). Deciding to follow his father's profession, Slator moved back to the town of his birth. In 1905 he was appointed brewing research chemist to Bass, Ratcliffe & Gretton in Burton, where he spent the rest of his active career. He rapidly acquired an appreciation of microbiology and fermentation and wrote numerous papers, especially on various aspects for fermentation (10). Grounded in kinetics while at Leipzig, Slator became very interested in their applications in fermentation, including the growth rates of yeasts and bacteria. His work was recognized by the awarding doctorates from the University of Birmingham and the University of London. After 42 years of service, Slator retired in 1947. He died on July 30, 1953, at his son's home in Berkhamsted.

Apparently, Slator had not continued his work on the chlorination of benzene after he left Leipzig, but Luther decided to expand Slator's studies on the photochemical aspects of the reaction (11). He found that the frequent irregularities observed were due to the retarding effect of small quantities of dissolved oxygen. If freed from air by vaporization under reduced pressure, a solution of chlorine in benzene became 20 times as sensitive to light as one that had been in contact with air. In the chlorination of air-containing benzene, the oxygen is gradually removed as the reaction attains its maximum velocity. Subsequent introduction of traces of oxygen through such sources as the interaction of chlorine with water from leaking stopcocks can cause a subsequent decrease in velocity.

As is obvious from a scrutiny of *Chemical Abstracts*, the realization of the insecticidal properties of the γ isomer of benzene hexachloride has led to many patents. Typical is a process in which the chlorination of benzene is carried out in illuminated glacial acetic acid (12). This medium has been used for various fundamental studies of benzene chlorination. Slator's work on the catalytic effects of iodine and of iodine monochloride has been greatly extended. Further, he had found that the ferric chloride-catalyzed chlorination of benzene was of first order with respect to chlorine and to this catalyst. Half a century after his discovery, a study of this reaction in carbon tetrachloride medium yielded the same conclusion (13). In a 1933 report of the photochemical gaseous-phase chlorination of benzene (14), the earliest reference cited on the liquid-phase aspects of the reaction is that of Slator (2).

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