The Chlorination of Benzene with a Sodium Chloride-Ferric Chloride Melt

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(Received October 24, 1972)

The chlorination of C_6H_6 with a NaCl–$FeCl_3$ (52: 48 in mol) melt was studied in a batch reactor at 250 °C and at a constant pressure. The main chlorinated products were monochlorobenzene (MCB) and dichlorobenzene (DCB). The isomers in DCB were *ortho* and *para*, and did not include the *meta* form. The rate of chlorination was nearly proportional to the benzene pressure in the range from 0.5 to 2.0 atm. When O_2 was introduced into the reaction system, both the rate of chlorination and the selectivity of MCB increased with the increase in the partial pressure of O_2. These facts suggest that chlorination proceeds by the electrophilic substitution on the melt surface. It was indicated by an X-ray diffraction examination of the powder of the salts used, which lost the activity for chlorination after a prolonged experiment in the presence of O_2, that the source of Cl was $FeCl_3$ and not NaCl in this reaction.

Molten salts have relatively high thermal conductivities and heat capacities. These thermal characteristics are favorable to reaction-temperature control when the salts are used as chemical-reaction media, especially in highly exothermic reactions. Furthermore, the higher mobility of ions in fused salts seems to give an interesting difference from solid salts where the ion plays an important role as a component of the expected reaction. In view of these facts, studies have recently been done on the use of molten salts as organic reaction media, mainly as catalysts.[1] Only a few studies have, however, been made on the use of molten salts as reagents;[2] especially, little work has been reported on the reaction of aromatic hydrocarbons with molten chlorides. Therefore, we studied the chlorination of C_6H_6 with a NaCl–$FeCl_3$ melt, and examined the effect of O_2 on it; this effect is of interest in connection with oxychlorination.

Experimental

Scope of Experiment. The choice of the NaCl-$FeCl_3$ melt as a chlorinating agent was based on the following considerations. The chlorination of C_6H_6 with molten chlorides took place when their metallic cations, of a polyvalent type, were used in the form of a higher valence state.[3] NaCl–$FeCl_3$ (52: 48 in mol) melt has a low melting point (*ca.* 160 °C), and the vapor pressure is very small below 500 °C.[4] C_6H_6 was selected because the product distribution, especially the isomer distribution of DCB, suggests whether the reaction mechanism is radical or ionic. The benzene pressure was varied to see where the chlorination occurred—that is, in the gas phase, at the interface, or in the bulk molten phase. To examine the effect of O_2 on the chlorination, chlorination was done at various partial pressures of O_2—that is, at different ratios of O_2 to C_6H_6. Many runs were made repeatedly with the same melt charge. The purpose is to investigate the influence of the aging of the melt on the chlorination. The contact time was varied to see whether chlorination proceeded successively or simultaneously by examining the subsequent change in the ratio of MCB to DCB.

Materials. The anhydrous $FeCl_3$ was 98.5% pure, and the NaCl and C_6H_6 were guaranteed reagents from Wako Pure Chemicals Industries, Ltd. The oxygen was 99.8% pure and was obtained from the Miyagi Sanso Co. These materials were used without further purification.

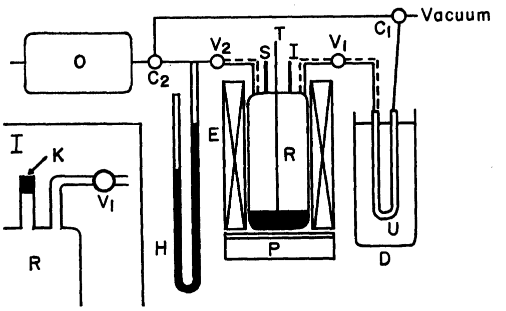

Fig. 1. Apparatus.
C: glass cock, D: dry-ice methanol trap, E: electric furnace, H: Hg-manometer, I: injection mouth of benzene, K: silicone rubber, O: oxygen reservoir, P: plate heater, R: reactor, S: charging mouth of salts, T: thermocouple, U: U-tube, V: teflon needle valve, - - -: electrically tracing.

Apparatus. The apparatus is illustrated in Fig. 1. The reactor (R) consisted of a Pyrex vessel 60 mm in diameter and 130 mm long. It was equipped with two open stems: one (S) was to charge salts, and the other (I), to introduce C_6H_6. As is shown in the detailed figure, at the top of (I) a plug of silicone rubber (K) was attached, through which C_6H_6 was injected. (R) was heated by a surrounding electric furnace (E) and by a plate heater (P) at the bottom. The reaction temperature was measured with a chromel-alumel thermocouple (T) located in a well embedded in the melt, and was controlled within ±5 °C. (R) was connected to the oxygen reservoir (O) and a U-tube (U) in a dry-ice methanol trap (D; *ca.* −75 °C) through two separate Pyrex tubings. Each tubing had a Teflon needle valve (V), by which the influence of grease contamination was avoided, to close or open the line. The Pyrex lines were electrically heated to prevent chlorination products from condensing.

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[1] a) W. Sundermeyer, *Angew. Chem.*, **77**, 241 (1965), (Review). b) R. T. Struck, W. E. Clark, P. J. Dudt, W. A. Rosenhoover, C. W. Zielke, and E. Gorin, *Ind. Eng. Chem. Process Res. Develop.*, **8**, 546 (1969). c) S. Kikkawa, T. Hayashi, T. Tani, and H. Osima, *Kogyo Kagaku Zasshi*, **73**, 964 (1970). d) C. N. Kenney and R. Takahashi, *J. Catal.*, **22**, 16 (1971).

[2] a) R. B. Temple, C. Fay, and J. Williamson, *Chem. Commun.*, **1967**, 966. b) T. Kunugi, H. Tominaga, A. Sawanobori, and M. Nushi, *Kogyo Kagaku Zasshi*, **72**, 2385 (1969).

[3] Y. Ohtsuka, K. Saegusa, and Y. Tamai, Preprint, the 26th Annual Meeting of the Chemical Society of Japan, Tokyo, 1972.

[4] C. M. Cook, Jr., and W. E. Dunn, Jr., *J. Phys. Chem.*, **65**, 1505 (1961).

Procedure. The salts were ground separately and mixed together by weight (15.2 g of NaCl and 38.9 g of $FeCl_3$) in a dry box of flowing nitrogen. The mixed salts were charged quickly through (S) into (R) in laboratory air. After charging, (S) was sealed off. Then, the salts were heated to melt and then further continuously up to the reaction temperature under a vacuum produced by a rotary pump. After 30–60 mins' preheating under a vacuum, (V_1) and (V_2) were closed, and a given amount of C_6H_6 was injected through (I) into (R) with a syringe. In the following discussion, this time of injection was taken as the time of initiation of the reaction.

In this reactor, the gas volume above the melt was 250 cm^3, and the contact area was 23.7 cm^2.

After a definite contact time, (V_1) was opened to introduce the products into (U), which was then evacuated with special care so as to condense the products perfectly. To make sure that all the contents of (R) were taken out, (V_2) was opened to measure the residual pressure by means of a Hg-manometer (H). When the condensation was finished, (V_1) was closed and (U), containing the condensed materials, was removed into a Dewar vessel for storage.

The next run was usually conducted immediately after the foregoing run without changing the melt used. The procedure was repeated in the exactly same way and the melt was under a vacuum all the time between the runs.

To study the effect of O_2, the following procedures were employed. At first, the melt was preheated under a vacuum in the way described above, and then (V_1) was closed and the three-way cock (C_2) was opened to let the oxygen gas in (O) flow into the reactor until the scheduled pressure was reached (this pressure could be read with (H)). After this introduction of O_2, (V_2) was closed and a calculated amount of C_6H_6 was injected so that the total pressure could reach the atmospheric level.

Conditions of Chlorination. *General Conditions*: Unless otherwise stated, the chlorination was studied under the following conditions; amount of salts, 15.2 g of NaCl and 38.9 g of $FeCl_3$; reaction temperature, 250 °C; contact time, 50 min; total pressure, 1.0 atm. The melt was newly-prepared prior to every run in all the examinations, except when the effect of the aging of the melt was studied. The variables were as follows.

Partial Pressure of O_2: 0–0.33 atm at a constant total pressure of 1.0 atm.

Benzene Pressure: 0.5–2.0 atm in the absence of O_2.

Number of Runs: 6–9 runs with the same melt charge at constant partial pressures of O_2, 0–0.33 atm.

Contact Time: 20–120 min at a constant partial pressure of O_2, 0.33 atm.

Analytical Method. *Benzene Derivatives*: The liquid products, collected in a dry-ice methanol trap, were analyzed by the gas-chromatography method with 5% Bentone 34 and 5% DIDP on 60–80 mesh Celite 545 as the partitioning agent.[5)]

Cl_2 and HCl: The Cl_2 evolved from the melt in the absence of C_6H_6 was detected by iodometry. The HCl formed by chlorination was identified by the use of an aqueous solution of ammonia.

Salts Used: To analyze the salts used, the following special experiment was conducted. That is, the chlorination of C_6H_6 in the presence of O_2 was run as follows; many runs were made with an unchanged melt charge of a rather small amount, that is, 3.0 g of NaCl and 7.8 g of $FeCl_3$ (52 : 48 in mol), using the same procedure as has been described before, until the melt did not react with C_6H_6. At that time the reaction conditions were slightly modified; temperatures, 250–450 °C; contact time, 50 min; partial pressure of O_2, 0.33 atm; total pressure, 1.0 atm. Then, the melt was solidified in the vessel under a vacuum and taken out to be ground. The ground powder was analyzed by means of a standard X-ray diffraction unit, cobalt $K\alpha$ radiation being used.

Results and Discussion

The main chlorinated products were monochlorobenzene (MCB) and dichlorobenzene (DCB). A small amount of trichlorobenzene (TCB) was also formed. HCl was evolved as a by-product. The isomers in DCB were *ortho* and *para*, and did not include the *meta* form. Most of the TCB was the 1,2,4-isomer. These results were common findings throughout the experiments whether O_2 existed in the reaction system or not. In addition, the chlorination of MCB under the same conditions as in this work gave the same isomer distributions of DCB and TCB as do the present results on C_6H_6.[6)]

It has been reported that, in the gas-phase chlorination of C_6H_6 with Cl_2 in the absence of the catalyst above 400 °C, the orientation is reversed and the products containing *m*-DCB and 1,3,5-TCB are obtained.[7)] With the chlorination of MCB at 275 to 500 °C, all three DCBs are formed, with the *meta*-isomer predominating.[8)] These gas-phase chlorinations in the absence of the catalyst proceed by the radical substitution, the initiation of which is the formation of a Cl radical by the thermal activation.

The present isomer distributions of DCB and TCB differ markedly from these, suggesting that the chlorination of C_6H_6 with the NaCl–$FeCl_3$ melt proceeds by the electrophilic substitution.

The chlorination of C_6H_6 in the presence of O_2 gave the same isomer distributions of DCB and TCB as in the absence of O_2. The formation of phenol as an oxidation product was expected, but not found. Carbon, CO, CO_2, and H_2O, all of which may be formed by the combustion of C_6H_6, were not identified. A very small amount of a liquid material was obtained; it was immiscible with C_6H_6 and chlorinated benzenes and was soluble in acetone and H_2O. This material may be H_2O. Furthermore, a carbon-like material was observed on the reactor wall. This material was insoluble in hot water and hydrochloric acid. These materials may be combustion products. Their amounts, however, are negligible, because, according to the observed mass balance, the charged benzene is almost completely converted to chlorinated benzenes. The formation of a compound like H_2O may also suggest the chlorination of C_6H_6 by the HCl formed and O_2 introduced, that is, oxychlorination. To elucidate its process, a quantitative analysis of HCl and H_2O should be made.

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5) S. Abe, A. Hongo, and E. Shirakawa, *Bunseki Kagaku*, **16**, 399 (1967).

6) Y. Tamai and Y. Ohtsuka, unpublished.

7) J. P. Wibaut, L. M. F. van der Lande, and G. W. A. Wallagh, U.S. 2123857 (1938).

8) J. W. Engelsma, E. C. Kooyman, and J. R. van der Bij, *Rec. Trav. Chim.*, **76**, 325 (1957).

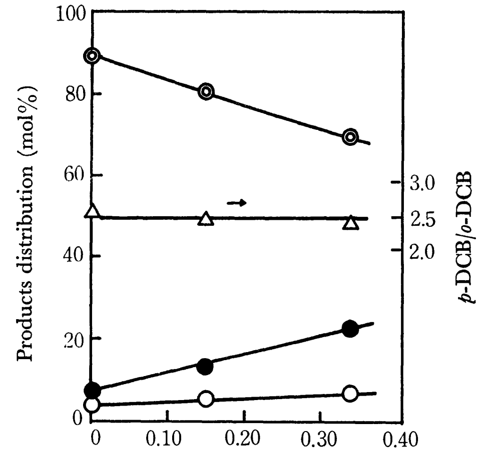

Fig. 2. Effect of partial pressure of O_2 on products distribution. ◎ unreacted C_6H_6, △: p/o, ●: MCB, ○: DCB.

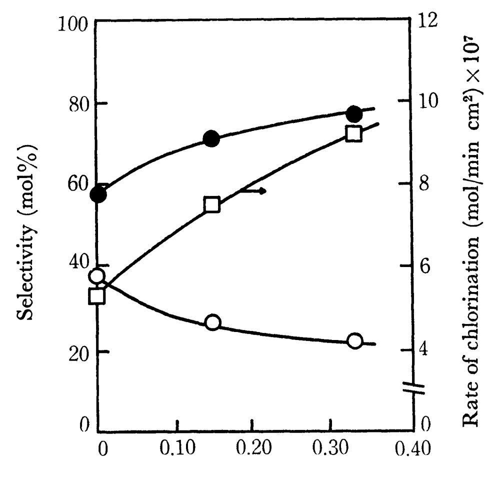

Fig. 3. Dependence of rate of chlorination and selectivity of MCB and DCB on partial pressure of O_2.
●: MCB, ○: DCB, □: rate of chlorination.

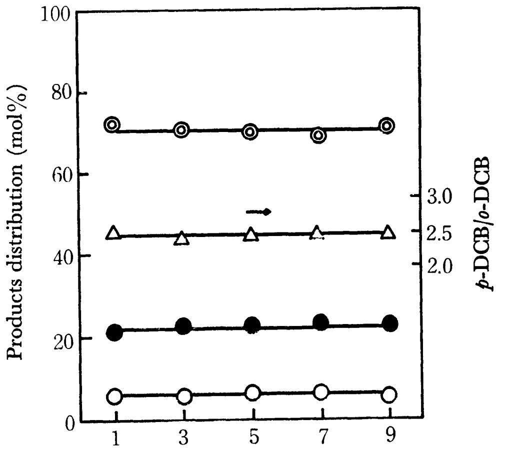

Fig. 4. Influence of benzene pressure on products distribution.
◎: unreacted C_6H_6, △: p/o, ●: MCB, ○: DCB.

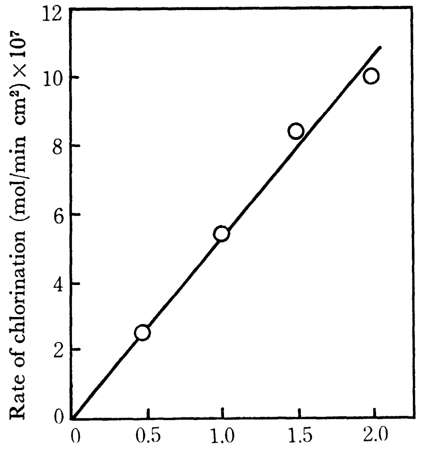

Fig. 5. Dependence of rate of chlorination on benzene pressure.

The effect of the O_2 introduced into the reaction system on the chlorination is shown in Figs. 2 and 3. Figure 2 shows that the conversion of C_6H_6 increases with the increase in the partial pressure of O_2, that is, the decrease in the partial pressure of C_6H_6. It is shown in Fig. 3 that the O_2 introduced raises both the rate of chlorination, which is expressed as moles of chlorinated benzenes formed per unit of contact time per unit of contact area, and the selectivity of MCB. In other words, O_2 promotes the chlorination and favors the formation of MCB.

The fact that the O_2 introduced raises the rate of chlorination seems to support the above suggestion of the electrophilic substitution, for, the O_2 molecule generally behaves as an inhibitor in the radical reaction because of its easy bonding to a radical. Therefore, if the radical mechanism were predominant in this chlorination, the effect of O_2 described above would not be observed.

The influence of the benzene pressure on the chlorination is shown in Figs. 4 and 5. Figure 4 shows that the products distribution is independent of the benzene pressure. The rate of chlorination is nearly proportional to the benzene pressure in the range from 0.5 to 2.0 atm, as is shown in Fig. 5. A very small amount of free Cl_2 was evolved from the melt in the absence of C_6H_6. The pressure of Cl_2 on the NaCl–$FeCl_3$ (54: 46 in mol) melt at 250 °C was estimated to be about 10^{-5} mmHg. This estimation was made by using the pressure of the $FeCl_3$ vapor, which existed almost entirely in the form of Fe_2Cl_6 at 250 °C, about 10^{-4} mmHg,[4)] and the equilibrium constant between Cl_2 and Fe_2Cl_6.[9)] The gas-phase chlorination by free Cl_2, however, is not considerable, because it proceeds by the radical mechanism, which gives isomer distributions of DCB and TCB different from the present results.

It is considered that the chlorination in the bulk of the melt is not appreciable because of the poor solubility of organic compounds in molten salts.[1a)] By the way, the solubility of Cl_2 in molten chlorides, which is larger than those of other inorganic gases, is 3.65×10^{-7}

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9) L. E. Wilson and N. W. Gregory, *J. Phys. Chem.*, **62**, 433 (1958).

mol per cm^3 of the NaCl–KCl (50: 50 in mol) melt at 750 °C.[10]

These discussions suggest that the chlorination of C_6H_6 with the NaCl–$FeCl_3$ melt takes place mainly on the melt surface. Accordingly, the rate of chlorination may be represented as the product of the rate constant, the concentration of the adsorbed benzene on the melt surface, and that of the active species. Therefore, the fact that the rate of chlorination is nearly proportional to the benzene pressure suggests that the adsorption of C_6H_6 is of a Henry-type in the pressure range from 0.5 to 2.0 atm.

The effect of the aging of the melt on the chlorination is shown in Figs. 6 and 7. The decrease in reactivity is not observed within the conducted runs whether O_2 exists in the reaction system or not, as is shown in these figures. These results may throw some doubt on the above suggestion that chlorination occurs mainly on the melt surface, for, as the numbers of runs increase, that is, as the reaction time gets longer, the composition of the melt surface should change because of the consumption of Cl. Therefore, the reactivity should decrease if the surface reaction is predominant. However, the fact that the reactivity does not decrease does not necessarily conflict with the surface-composition change resulting from the consumption of Cl. The color of the surface layer of the solidified salts used turned dark-green after many runs in the absence of O_2 and red-brown in the presence of O_2. Such changes suggest the formation of $FeCl_2$ and Fe_2O_3 respectively; Fe_2O_3 was identified by X-ray diffraction, as will be shown later. However, in the working state, the $FeCl_2$ and Fe_2O_3 formed do not stay on the melt surface as a solid, but dissolve or are suspended in the bulk of the melt. In other words, the active species of chlorination easily diffuses from the bulk to the interface. To elucidate further the suggestion that chlorination takes place predominantly on the melt surface, the effect of changes in the contact area on the chlorination, the determination of the surface tension of the melt during chlorination, and so on should be studied in the future.

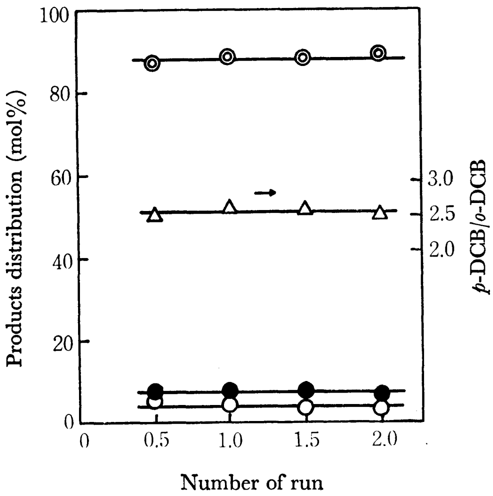

Fig. 6. Products distribution as a function of number of run in the absence of O_2.
◎: unreacted C_6H_6, △: *p*/*o*, ●: MCB, ○: DCB.

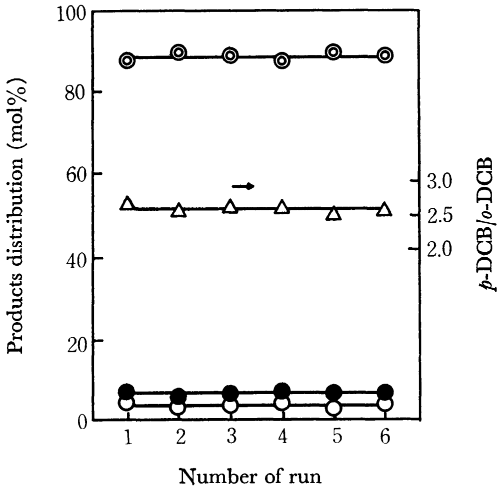

Fig. 7. Products distribution as a function of number of run in the presence of O_2.
◎: unreacted C_6H_6, △: *p*/*o*, ●: MCB, ○: DCB.

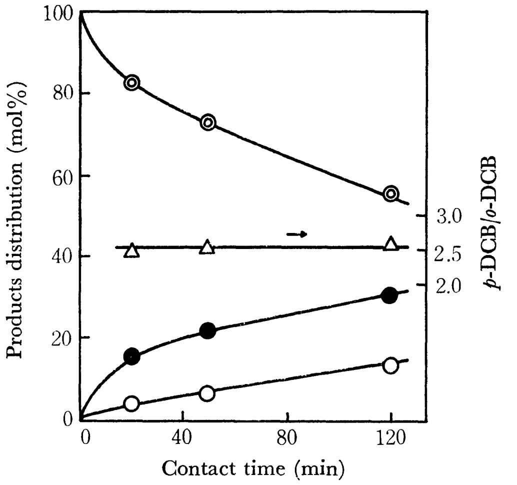

Fig. 8. Dependence of products distribution on contact time.
◎: unreacted C_6H_6, △: *p*/*o*, ●: MCB, ○: DCB.

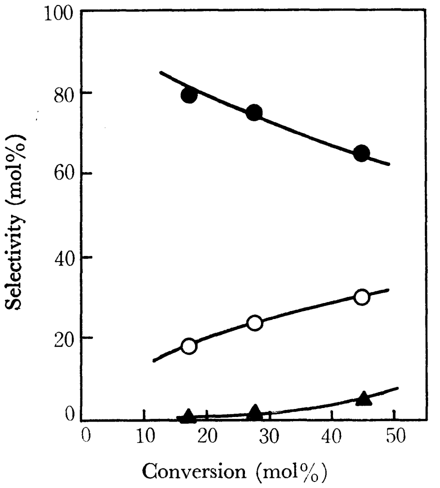

Fig. 9. Selectivity of chlorinated benzenes as a function of conversion of benzene.
●: MCB ○: DCB ▲: TCB

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[10] N. R. Thompson and B. Tittle, "Halogen Chemistry," Vol. 2, ed. by V. Gutmann, Academic Press, New York (1967), p. 387.

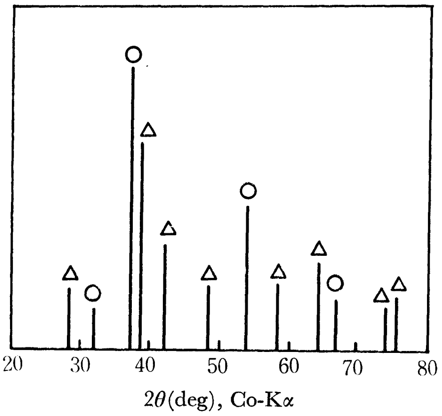

Fig. 10. X-ray diffraction pattern of used salts.
○: NaCl △: α-Fe_2O_3

The dependence of the chlorination on the contact time is shown in Figs. 8 and 9. It is shown in Fig. 9 that the selectivities of poly-substituted DCB and TCB get higher as the conversion of C_6H_6 higher. This tendency was observed whether O_2 existed in the reaction system or not. It suggests the possibility that chlorination proceeds consecutively; to confirm this mechanism, runs at shorter or longer contact times should be examined.

Figure 10 shows the X-ray diffraction pattern of the salts used, which became inactive to chlorination in the presence of O_2. The observed peaks were assigned to NaCl and α-Fe_2O_3. These results indicate that the source of Cl was $FeCl_3$ and not NaCl in this reaction. This indication gives the impression that only $FeCl_3$ participated in the chlorination. The following result, however, suggests that NaCl also participates in the chlorination. That is, when KCl was used in place of NaCl and when the chlorination of C_6H_6 with the KCl–$FeCl_3$ (52: 48 in mol; mp *ca.* 230 °C) was conducted under the same conditions as in this work, the reactivity decreased.⁶⁾ Cook *et al.* showed the existence of $NaFeCl_4$ by examinations of the vapor pressure above the NaCl–$FeCl_3$ melts and by the X-ray diffraction of their powder,⁴⁾ and Gruen *et al.* indicated the existence of $FeCl_4^-$ by studying the absorption spectra of $FeCl_3$ in a LiCl–KCl eutectic.¹¹⁾ These reports also suggest that NaCl participates in this reaction.

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11) G. Harrington and B. R. Sundheim, *Ann. N. Y. Acad. Sci.*, **79**, 950 (1960).