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# The Decomposition of Benzoyl Hypochlorite in the Presence of Metal Ions[1]

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The decomposition of benzoyl hypochlorite, the intermediate in the Hunsdiecker reaction between chlorine and silver benzoate, is accelerated by light and by azobisisobutyronitrile (AIBN), but not by transition metal ions. The molar yield of the chlorobenzene produced in the decomposition increases as the temperature of the reaction mixture is raised, but is independent of whether or not the reaction is promoted by light or AIBN. It is suggested that this variation in the yield is a result of the readier decarboxylation at higher temperatures of the benzoyloxy radicals which are believed to be intermediates in the decomposition process. No such pronounced effect of temperature on the yield of halides from aliphatic silver carboxylates has been observed, presumably because aliphatic acyloxy radicals decarboxylate readily even at low temperatures.

La décomposition de l'hypochlorite de benzoyle, l'intermédiaire dans la réaction de Hunsdiecker entre le chlore et le benzoate d'argent est accélérée par la lumière et l'azo bis isobutyronitrile mais non par les ions des métaux de transition. Le rendement molaire de chlorobenzène produit lors de la décomposition augmente proportionnellement avec la température du mélange réactionnel mais est indépendant des catalyseurs comme la lumière ou l'AIBN. Il est suggéré que ces variations dans le rendement sont le résultat d'une décomposition plus facile à haute température des radicaux benzoyloxy qui seraient les intermédiaires dans le processus de décomposition. Un effet aussi prononcé de la température sur les rendements de dérivés halogénés aliphatiques provenant des carboxylates d'argent correspondants n'a pas été observé probablement parce que les radicaux acyloxy aliphatiques se décarboxylent facilement même à basse température.

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The reaction between chloride ion and benzoyl peroxide has recently been investigated by several groups of workers (1–3). The first formed intermediate was found to display chemistry similar to that of the intermediate in the reaction between the halogens and silver carboxylates. The reactions compared included the decomposition to chlorobenzene and $CO_2$, addition to olefins, electrophilic chlorination of arenes, and free radical halogenation of alkanes. The reaction between halogens and silver carboxylates is the basis of the Hunsdiecker halodecarboxylation reaction (4, 5), which has been supposed to involve an acyl hypohalite as an intermediate. It was proposed therefore that the reaction of chloride ion with benzoyl peroxide also gives rise to such an intermediate, in this case benzoyl hypochlorite.

[1] $Cl^- + PhCO.OO.COPh \rightarrow PhCO_2Cl + PhCO_2^-$

[2] $Cl_2 + PhCO_2Ag \rightarrow PhCO_2Cl + AgCl$

In the Hunsdiecker reaction it is thought that the intermediate acyl hypohalite suffers homolytic fission (reaction 3) and that this initiates a free radical chain pathway for alkyl (or aryl) halide formation (reactions 4 and 5).

[3] $RCO_2X \rightarrow RCO_2^{\cdot} + X^{\cdot}$

[4] $RCO_2^{\cdot} \rightarrow R^{\cdot} + CO_2$

[5] $R^{\cdot} + RCO_2X \rightarrow RX + RCO_2^{\cdot}$

This homolytic fission of the O—X bond of the acyl hypohalite might be presumed to be a very facile process, for the Hunsdiecker reaction may often (5) be carried out successfully at temperatures below 0°. By contrast, however, the pre-

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sumed benzoyl hypochlorite of the previous work did not seem to suffer homolysis with great ease. For example (1, 2), at neither 60° nor 100° did it cause the polymerization of added styrene (addition is preferred), nor in the absence of excess benzoyl peroxide as a free radical initiator did it either cause free radical chlorination of an added alkane or decompose cleanly to chlorobenzene.

A possible cause of this apparently different behavior might be that the Hunsdiecker reaction is carried out with silver carboxylates, whereas no transition metal ions were present in the reaction mixtures of chloride ion with benzoyl peroxide. Since transition metal ions are well known to catalyze the homolytic decomposition of organic peroxides (6, 7), peresters (8), *N*-chloroamines (9), and alkyl hypochlorites (10), it is possible that a similar catalytic decomposition of the acyl hypohalite to free radicals could account for the apparent ease of reaction of Hunsdiecker reaction mixtures and the lack of reactivity of the chloride ion/benzoyl peroxide reagent. Such reasoning is consistent with the observation that the Hunsdiecker decarboxylation reaction proceeds more readily with heavy metal salts than with the salts of the alkali or alkaline earth metals.

This study was therefore initiated to discover whether silver (or copper) salts are effective catalysts for the decomposition of benzoyl hypochlorite, with a view to enlarging our knowledge of the Hunsdiecker reaction mechanism. During the work we had occasion to examine the effect of temperature on the reaction, and these results are also included.

## Results and Discussion

The required metal-free solutions of benzoyl hypochlorite were prepared by filtration of silver benzoate – chlorine mixtures in carbon tetrachloride as solvent (11).[3, 4] Aliquots of these solutions were allowed to decompose at different temperatures under identical conditions except for the presence or absence of various initiators or reagents; after 1 h the solutions were analyzed for the extent of benzoyl hypochlorite decomposition and for chlorobenzene formation (Tables 1–4).[5]

From an examination of these Tables, the following points may be noted. First, light (at all temperatures) and AIBN (at 60°) accelerated the decomposition of the acyl hypochlorite, as would be expected since the reaction is known to be a free radical chain process (4, 5).

Second, neither cuprous ions nor silver ions cause any increase in the rate of decomposition, indicating that neither is a catalyst for the reaction. This is in contrast to the previously mentioned findings for peroxides, chloroamines, etc., but is consistent with the observation by Kochi *et al.* (3) that in the reaction of benzoyl hypochlorite (from benzoyl peroxide/lithium chloride) with toluene, the free radical chlorination of the side chain is not catalyzed but rather is suppressed by the addition of cupric ions to the reaction mixture. In a related system Jennings and Ziebarth (12) have found that the decomposition to 1-bromobutane of the intermediate in the reaction between bromine monoxide and valeric acid (presumed to be valeryl hypobromite) is not

TABLE 1. Decomposition[a] of 0.303 *M* benzoyl hypochlorite after 1 h at 0°

| Conditions[a] | $PhCO_2Cl$ remaining[b] in *M* | Chlorobenzene produced[c] *M* | % [d] |
|---|---|---|---|
| Dark | 0.259 | 0.013 | 29 |
| *h*v | 0.012 | 0.111 | 38 |
| Dark, $Ag^+$ | 0.273 | 0.013 | 43 |
| Dark, $Cu^+$ | 0.271 | 0.011 | 34 |

[a]For notes *a–d* see Table 3.

TABLE 2. Decomposition[a] of 0.255 *M* benzoyl hypochlorite after 1 h at 40°

| Conditions[a] | $PhCO_2Cl$ remaining[b] in *M* | Chlorobenzene produced[c] *M* | % [d] |
|---|---|---|---|
| Dark | 0.197 | 0.031 | 54 |
| *h*v | 0.054 | 0.137 | 68 |
| Dark, AIBN | 0.194 | 0.026 | 42 |
| Dark, $Ag^+$ | 0.181 | 0.025 | 34 |
| Dark, $Cu^+$ | 0.194 | 0.028 | 46 |

[a]For notes *a–d* see Table 3.

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[3] Other metal benzoates could not successfully be substituted for the silver salt, neither could acetonitrile be used as solvent instead of carbon tetrachloride. In acetonitrile there forms a red silver-containing substance whose chemistry is under investigation.

[4] The benzoyl peroxide – chloride ion route to benzoyl hypochlorite is inapplicable because reaction 1 is so slow that the hypochlorite decomposes at a rate comparable with its rate of production (2, 3).

[5] Tables 1 and 2 record the average of duplicate experiments; at 60° (Table 3) identical results were not obtained and both values are quoted.

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TABLE 3. Decomposition of 0.245 $M$ benzoyl hypochlorite after 1 h at 60°

| Conditions[a] | $PhCO_2Cl$ remaining[b] in $M$ | Chlorobenzene produced[c] | |
|---|---|---|---|
| | | $M$ | %[d] |
| Dark | 0.142, 0.162 | 0.091, 0.074 | 88, 89 |
| $h\nu$ | 0.018, 0.020 | 0.160, 0.170 | 71, 75 |
| Dark, AIBN | 0.033, 0.012 | 0.168, 0.214 | 79, 92 |
| Dark, $Ag^+$ | 0.148, 0.063 | 0.067, 0.125 | 69, 69 |
| Dark, $Cu^+$ | 0.120, 0.080 | 0.095, 0.134 | 76, 81 |

[a] All added substances were added in 2.0–10.0 mg quantities. $Ag^+$ was silver benzoate; $Cu^+$ was cuprous oxide.
[b] By iodometric titration.
[c] By vapor phase chromatography.
[d] Moles of chlorobenzene produced per mol of benzoyl hypochlorite decomposed.

TABLE 4. Average yield of chlorobenzene from benzoyl hypochlorite at different temperatures

| Temperature (°C) | Chlorobenzene (%)[a] |
|---|---|
| 0 | 36 ± 7 |
| 40 | 49 ± 19 |
| 60 | 79 ± 13 |

[a] Average values of the data in Tables 1–3.

catalyzed by mercuric salts. Furthermore, in the reaction of silver carboxylates with iodine (reaction 6), the Simonini complex (4, 13) of constitution (1) may often be isolated, whereas it might be anticipated that if silver ions were active catalysts for acyl hypohalite decomposition, the silver ions in the complex would cause its ready destruction.

$$[6] \quad 2RCO_2Ag + I_2 \rightarrow AgI + \underset{(1)}{RCO_2I.RCO_2Ag}$$

A third point to note from Tables 1–3 is the effect of temperature on the decomposition. Apart from the rate of reaction increasing at higher temperatures, the yield of chlorobenzene (per mol of hypochlorite destroyed) is markedly greater at higher temperatures (Table 4) and is virtually independent of whether photoinitiation is employed. Since photoinitiation must increase the rate of reaction 3, we conclude that the temperature dependence of the yield is *not* caused by there being some other reaction competing with free radical decomposition. If that had been so, photoinitiation would have increased the yield by promoting reaction 3, the initiation step of the free radical chain reaction.

The temperature dependence of the yield of chlorobenzene is consistent with step 4 or step 5 having a large activation energy. This is unlikely for step 5 because of its analogy with one of the steps in free radical chlorinations by alkyl hypochlorites, which proceed readily even at −80° (14, 15). An appreciable activation energy for step 4 is consistent with the well-known stability of benzoate radicals towards decarboxylation, in particular, their ability to survive long enough to be intercepted by a variety of other reagents (16–20) to give products retaining the benzoate moiety intact. Of interest in the present connection are occasional observations of variations with temperature of the ratio of carboxyl-retaining to decarboxylated products (17, 21). Correspondingly in our studies, the decomposition of benzoyl hypochlorite in carbon tetrachloride at 0° gave benzoic acid as a major product, even when moisture was excluded from the system. It is not clear from where the hydroxyl hydrogen in the acid arises. Small quantities of chlorinated benzoic acid were also formed, presumably by electrophilic chlorination, since the *meta* isomer was produced in the largest amount (*cf.* the production of *m*-bromobenzoic acid from bromine and silver benzoate (5, 22)).

An alternative fate of a benzoyloxy radical is free radical substitution of a suitable aromatic substrate to give the aryl benzoate (23). Because of this reaction, benzene has been noted to be a poor solvent for carrying out Hunsdiecker reactions (4, 24). In our studies we found that the decomposition of silver-free solutions of benzoyl hypochlorite in benzene gave virtually no phenyl benzoate, and that even at 0°, electrophilic chlorination of the solvent occurred almost exclusively. Benzoyl hypobromite was found to be a much less active halogenating agent, and on decomposition in benzene at 3° afforded a moderate yield of phenyl benzoate, though little

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TABLE 5. Effects of silver salts as halogen carriers for the electrophilic chlorination of benzene at 0°

| Chlorinating agent ($M$) | Silver salt (mmol/ml) | Time (h) | ($Cl^+$) remaining, ($M$) | PhCl | |
|---|---|---|---|---|---|
| | | | | $M$ | %[a] |
| $Cl_2$ (0.60) | None (—) | 140 | 0.29 | 0.21 | 68 |
| $Cl_2$ (0.60) | $Ag_2O$ (0.11) | 140 | 0.23 | 0.32 | 88 |
| $Cl_2$ (0.60) | AgCl (0.35) | 140 | 0.23 | 0.35 | 95 |
| $PhCO_2Cl$ (0.31) | None (—)[b] | 120 | ~0.01 | 0.22 | 71 |
| $PhCO_2Cl$ (0.30) | AgCl (0.30)[c] | 70 | ~0.01 | 0.25 | 85 |

[a] Estimated by v.p.c.; % yields based on the chlorinating agent destroyed.
[b] Hunsdiecker reaction mixture, filtered after 5 min at 0°.
[c] As *b*, only not filtered.

of this product was formed at reflux. It was noted that silver salts have a slight catalytic effect as halogen carriers for both benzoyl hypochlorite and elemental chlorine, and that benzoyl hypochlorite is the more reactive halogenating agent (Table 5). Acetyl hypohalites are likewise more reactive electrophilic reagents than the elemental halogens (25–27).

The dependence of the yield of aryl halide on the temperature of decomposition is not peculiar to benzoyl hypochlorite. Benzoyl hypobromite and substituted benzoyl hypobromites behave similarly. The polar solvent acetonitrile gave results similar to those obtained in the non-polar carbon tetrachloride (Table 6).

In Table 6 we have also collected literature values for the yields of aliphatic halides from Hunsdiecker reactions that have been conducted at different temperatures, for comparison with our own data. Aliphatic substrates do not exhibit the same marked depression of the yield on lowering the temperature; indeed halides derived from *secondary* alkyl groups R are produced in better yield at lower temperatures. On the limited data at hand we propose the following explanation. Aryl halides form with difficulty at low temperatures because of the less facile decarboxylation of the resonance-stabilized aroyloxy radicals; by contrast alkanoy oxy radicals decarboxylate readily even at low temperatures (28). There is thus less tendency for alkanoyloxy radicals to be diverted to other products before decarboxylation occurs. Readier formation of halide in aliphatic compared with aromatic systems has also been observed in diacyl peroxide/chloride ion systems (3, 29), again indicating the importance of the nature of the R group in decarboxylations. In the valeryl peroxide reaction (29), a faster reaction in the presence of copper salts was attributed to copper catalyzed decomposition of the peroxide rather than of an intermediate valeryl hypochlorite.

The increased yield of secondary halides at low temperatures probably results from less of the product being destroyed after formation: tertiary halides cannot be synthesized by the Hunsdiecker method (4, 5) because the silver salts present in solution destroy them as they are formed by assisted ionization (eq. 7).[6]

$$[7] \qquad RX + Ag^+ \rightarrow AgX + R^+ \rightarrow \text{products}$$

Silver salts attack secondary halides less rapidly, and this reaction may be suppressed by low temperature operation, so that a better yield of halide is obtained.

To conclude, these experiments show that neither silver nor cuprous ions are catalysts for the decomposition of benzoyl hypochlorite. The only reservation we have to this conclusion is that while we were unable to detect any silver salts in the carbon tetrachloride solutions used in our experiments, there remains the possibility that a small but undetected quantity was present and that this was sufficient to catalyze the decomposition even when no further quantity was added. To try to resolve this problem, we are currently trying to prepare acyl hypohalites by routes not involving metallic precursors. Concerning the effect of temperature on the yield of aryl halides from the Hunsdiecker reaction, we suggest that this is simply a reflection of the readier decomposition of benzoate radicals at elevated temperatures.

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[6] In the case where R = cyclobutyl, products derived by rearrangement of $R^+$ are observed.

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TABLE 6. Percentage yields of halides from several silver carboxylates at different temperatures[a]

| R— of $RCO_2Ag$ | Halogen | RX% (Upper temperature) | RX% (Lower temperature) |
|---|---|---|---|
| *Aryl R*[b] | | | |
| $C_6H_5$ | Br[c] | 46 (reflux) | 5 (3°) |
| $C_6H_5$ | Br[d] | 53 (reflux) | 16 (3°) |
| $C_6H_5$ | Br[e] | 36 (reflux) | 22 (3°) |
| $C_6H_5$ | Cl | 65 (reflux) | 3 (3°) |
| $C_6H_5$ | Cl[d] | 36 (reflux) | 16 (0°) |
| *p*-$NO_2C_6H_4$ | Br[f] | 76 (reflux) | 2 (3°) |
| *p*-$ClC_6H_4$ | Br | 31 (reflux) | 8 (3°) |
| *p*-$CH_3C_6H_4$ | Br | 17[g] (reflux) | < 1 (3°) |
| *Primary R* | | | |
| *n*-$C_5H_{11}$— | Br | 92 (reflux)[h] | 67 (cold)[i] |
| $(CH_3)_3CCH_2$— | Br | 83 (reflux)[h] | 53 (cold)[i] |
| *n*-$C_{15}H_{31}$— | Cl | 55 (reflux)[j] | 31 (cold)[j] |
| —$CH_2$—$CH_2$— | Br | 32 (reflux)[k] | 37 (15°)[k] |
| $C_6H_5CH_2$— | Br | 37 (reflux)[l] | 20 (cold)[l] |
| *Secondary R* | | | |
| 3-Heptyl- | Br | 35, 29 (reflux)[m] | 40–60 (cold)[l] |
| cyclo-$C_4H_7$— | Br | 44 (12°)[n] | 53 (−25°)[o] |
| cyclo-$C_6H_{11}$— | Br | 58 (reflux)[h] | 73–80 (cold)[p] |
| *cis*-4-*t*-Butyl-cyclo-$C_6H_{11}$— | Br | 38 (reflux)[q] | 62 (−15°)[q] |
| *Tertiary R* | | | |
| 7,7-Dimethyl-bicyclo[2,2,1]-hept-1-yl | Br | 58 (reflux)[r] | 60 (−10°)[r] |

[a] In $CCl_4$ except as noted otherwise.
[b] This work except as noted otherwise.
[c] For other values, see ref. 5.
[d] In acetonitrile.
[e] In benzene; includes electrophilic halogenation of the solvent; at 3° phenyl benzoate (28%) was also formed.
[f] Barnes and Prochaska, ref. 31, quote a 79% yield at reflux and no reaction at room temperature.
[g] Reference 31.
[h] Reference 34.
[i] Reference 35, quoted in ref. 5.
[j] Reference 36, quoted in ref. 5.
[k] Reference 37.
[l] Reference 38, quoted in ref. 5.
[m] Reference 39.
[n] Reference 40.
[o] Reference 41.
[p] Reference 42, quoted in ref. 5.
[q] Reference 43.
[r] Reference 44.

## Experimental

Solvents were reagent grade materials, dried with activated molecular sieve. Silver benzoate was supplied by Eastman Organic Chemicals or alternatively by British Drug Houses Ltd. Substituted silver benzoates were prepared by the method of Dauben and Tilles (32). Lithium benzoate (m.p. > 360°) was prepared by the action of lithium hydroxide on benzoic acid. Cupric benzoate was prepared by reacting cupric sulfate solution with aqueous sodium benzoate; the product was recrystallized from acetonitrile. Lead benzoate (m.p. 90–95°) was prepared from lead acetate and hot aqueous benzoic acid; mercuric benzoate (dec. > 156°) from mercuric nitrate/nitric acid solution and hot aqueous benzoic acid. All the metal benzoates were dried at 70° (120° for the alkali metal salts) for several days before use.

Solutions of chlorine or of benzoyl hypochlorite were estimated iodometrically. The color of iodine was used as its own indicator.

Vapor phase chromatography (v.p.c.) analyses were carried out on a Varian Aerograph Model 90-P3 instrument using helium as the carrier gas. Where quantitative determinations were to be made a weighed quantity of a standard substance was added to the reaction mixture, and the product in question quantitated by measuring the area of the product relative to the area of the standard. All such analyses were carried out in triplicate, and the reported values are the average. In the present study, chlorocyclohexane or bromobenzene were used as standards for chlorobenzene, and chlorobenzene or chlorocyclohexane as standards for bromobenzene. The response of the gas chromatograph was shown to be approximately equal towards these three compounds.

### *Attempts to Prepare Benzoyl Hypochlorite*

#### *(i) Reaction of Chlorine with Silver Benzoate and Addition of the Product to Cyclohexene*

A 0.37 *M* solution of chlorine in carbon tetrachloride (18 ml) cooled to 0° was allowed to react in the dark with dry silver benzoate (3.0 g, 13.1 mmol) for 5 min and then filtered. To the filtrate was added cyclohexene (5 ml), after which the solution was washed twice with 0.1 *M* sodium bicarbonate (50 ml), with water (50 ml), and dried over calcium chloride. The solvent was removed,

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and the residue was redissolved in carbon tetrachloride and examined by nuclear magnetic resonance (n.m.r.) ($\tau$ 1.8–3.0, 5H; $\tau$ 4.8–5.3, 1H; $\tau$ 5.7–6.3, 1H; $\tau$ 7.0–9.1, 8H; all multiplets). The n.m.r. was identical to that previously reported for 2-chlorocyclohexyl benzoate (1) and the compound was essentially free of 1,2-dichlorocyclohexane, which would change the spectrum by increasing the relative intensities of the resonances at $\tau$ 5.7–6.3 and $\tau$ 7.0–9.1.

### *(ii) Reaction of the Halogens with Other Metal Benzoates*

Chlorine (occasionally bromine) was allowed to interact with various metal benzoates in different solvents (carbon tetrachloride, acetonitrile, *N*,*N*-dimethylformamide (*cf.* ref. 2), and water (*cf.* ref. 33), at temperatures in the range 0–100°. There was no evident reaction when the lithium, sodium, cupric, or lead salts were used. Both the mercuric and silver salts reacted with the halogens, but only the latter was used because the reactions with the mercuric salt were very slow and, furthermore, did not subsequently yield any aryl halide (possibly because the mercuric salt is hydrated).

### *Decomposition of Benzoyl Hypochlorite at Different Temperatures*

A solution (approximately 0.3 *M*) of chlorine in carbon tetrachloride was cooled to 0° and allowed to react at 0° with silver benzoate (5.0 g), so that the latter was in at least two fold excess. After 5 min the solution was filtered, and 2 ml portions of the solution were placed in Pyrex ampoules, some of which already contained added reagents. (At this point two 2 ml portions were allowed to react with acidified potassium iodide solution and shown by v.p.c. *not* to have decomposed to chlorobenzene in the procedure.) The ampoules were cooled to 77 °K and evacuated to a pressure of 1 mm, after which they were sealed and placed in a constant temperature bath. Those samples to be irradiated were placed a few inches from two 100 W tungsten lamps; the other samples were protected from the light by means of aluminum foil. After 1 h the reaction ampoules were cooled to 77 °K, opened, their contents poured into acidified potassium iodide solution, and the liberated iodine was estimated volumetrically. The carbon tetrachloride solution from each such analysis was recovered; to a 1 ml portion was added bromobenzene as a standard and the chlorobenzene produced was estimated by v.p.c. The results of this study are given in Tables 1–4.

### *Decomposition of Benzoyl Hypochlorite at 0°*

To silver benzoate (2.5 g) was added 15 ml of a 0.33 *M* solution of chlorine in carbon tetrachloride. After 5 min the reaction mixture was filtered and the filtrate was stored at 3° in a corked ampoule for 16 days, at which time the "positive chlorine" content of the sample was 0.06 *M*. Vapor phase chromatographic analysis of the carbon tetrachloride phase gave an estimated yield of chlorobenzene at 0.116 *M* (34%). A 5 ml portion of the solution was extracted with aqueous sodium bicarbonate; the aqueous phase was acidified and after extraction into ether, drying and evaporation of the solvent, yielded 107 mg of a white solid, m.p. 105–109°. The solid was esterified with methanol/sulfuric acid and analyzed by v.p.c. (10% diisodecyl phthalate on acid-washed 60/80 Chromosorb W). The esters of benzoic acid and of *o*-, *m*-, and *p*-chlorobenzoic acids were present in the ratio of 80:1.2:6.1:1.0.

### *Reaction of Halogens with Silver Benzoate at 80 and 0°*

#### *(i) Bromine at 80°*

The following procedure is typical: To duplicate samples of dry silver benzoate (5.8 g, 25 mmol) and dry acetonitrile (40 ml) in 100 ml flasks equipped with reflux condensers and calcium chloride drying tubes was added in small portions a mixture of bromine (4.0 g, 25 mmol) and acetonitrile (total volume 10 ml). After 9.5 (9.5) ml of this mixture had been added, the solution assumed the red color of molecular bromine, and this color was not discharged by refluxing for a further 0.5 h. Heating now continued for 3 h more, after which weighed quantities of chlorobenzene were added to two aliquots of each solution. The bromobenzene produced was estimated by v.p.c. (Carbowax 20 *M*, 130°) and a sample of bromobenzene was isolated and its identity checked by infrared (i.r.) (this was not done in subsequent experiments).

#### *(ii) Bromine at 0°*

To a solution of bromine in the appropriate solvent cooled to 0° was added an equimolar quantity of silver benzoate. The reaction mixture was stirred at 0° with a magnetic stirrer for 4 h, then analyzed by v.p.c. as described above.

#### *(iii) Chlorine at 0°*

A solution of chlorine in the appropriate solvent was cooled to 0° and estimated iodometrically. Sufficient of this solution to contain 12.5 mmol of chlorine was added to silver benzoate (12.5 mmol) and the mixture was stirred at 0° for 4 h, then analyzed by v.p.c. as described previously.

#### *(iv) Chlorine at 80°*

Silver benzoate (12.5 mmol) and the appropriate solvent (40 ml) were placed in a two-necked flask equipped with reflux condenser and the mixture was brought to reflux. Through the second neck of the flask was introduced a slow stream of chlorine gas, which was maintained for 0.5 h. The mixture was refluxed for 1 h more, then analyzed by v.p.c. as described above.

### *Reaction of Bromine with Substituted Silver Benzoates*

The following procedure is typical. To duplicate reaction mixtures of silver *p*-nitrobenzoate (2.7 g, 10 mmol) and carbon tetrachloride (40 ml) at reflux was added bromine (1.6 g, 10 mmol) and the solution was refluxed for 2 h. After the reaction bromine (0.050, 0.052 *M*) was estimated by iodometric titration of aliquots of the solution. To other aliquots was added bromobenzene as a v.p.c. standard (SE30, 200°), when the *p*-bromonitrobenzene produced was estimated at 0.20, 0.18 *M*. The solutions remaining were combined and filtered, yielding 52 ml of filtrates. Evaporation of the solvent followed by chromatography of the residue on silica gel (50 g) eluted *p*-bromonitrobenzene (1.6 g, 61%) as pale yellow needles, m.p. 126–126½°, undepressed by admixture with authentic material made from *p*-nitroaniline by the Sandmeyer reaction.

The experiment at 3° was also carried out in duplicate as follows. To the mixture of carbon tetrachloride and

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the silver salt cooled to 0° was added bromine, after which the mixture was allowed to stand in a refrigerator (3 ± 2°) for 140 h. Analysis of the solutions was as described above but there was too little product to be isolated.

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