Chlorination by Sulfuryl Chloride. IV.1) The Effect of Substituents in the Radical Chlorination of Benzaldehydes

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In a previons peper of this series,1) the author has shown that the polar effect of reactant molecules exerts an influence on the reaction rate, an influence based on the relative reactivity of the C–H bond toward the radical chlorination by sulfuryl chloride.

In the present work, the author will investigate whether or not the chlorination of substituted benzaldehydes to the corresponding acid chlorides is governed by the Hammett equation; this will be done in order to estimate the polar effect of substituents. The study was extended to alkylbenzaldehydes with both alkyl and formyl groups on the same benzene-ring in order to establish the change in the reactivity of the groups compared with alkylbenzene or benzaldehyde.

Experimental

Materials and Reagents.—Toluene, of reagent grade, was purified in advance by fractional distillation, and the constantly boiling fraction was redistilled before use.

Substituted benzaldehydes, except *p*-isopropylbenzaldehyde and *p-t*-butylbenzaldehyde, all of reagent grade, were fractionated in an atmosphere of nitrogen; constantly boiling fraction was used.

Sulfuryl chloride, of first grade, was fractionally distilled, stored in a bottle wrapped with aluminum foil, and kept in a desiccator.

p-Isopropylbenzaldehyde was prepared by the chloromethylation of cumene, followed by heating with hexamethylenetetramine according to Blanc's method.2) The product was purified through a sodium hydrosulfite adduct, b. p. 91°C/7 mmHg. Semicarbazone, m. p. 210—211°C. Found: N, 20.72. Calcd. for $C_{11}H_{15}ON_3$: N, 20.47%

p-t-Butylbenzaldehyde was similarly prepapred by the chloromethylation of *t*-butylbenzene, followed by heating with formaldehyde and hexamethylenetetramine following Schaklett and Smith's method;3) b. p. 129—130°C/27 mmHg. 2,4-Dinitrophenylhydrazone, m. p. 250—251°C. Found: N, 16.25. Calcd. for $C_{17}H_{17}O_4N_4$: N, 16.37%.

General Procedure for Chlorination.—The materials to be chlorinated competitively were weighed in a 50 ml. round-bottomed flask equipped with a stirrer, a dropping funnel, and a reflux condenser with a calcium chloride tube on the top. After the air in the system had been replaced by dry nitrogen, benzoyl peroxide (0.1% of the weight of the sulfuryl chloride used) was added to the flask and the system was then heated to 80±1°C. Upon the gradual stirring in of sulfuryl chloride through the dropping funnel, the evolution of gas was observed after some induction period. Heating was continued until the gas evolution ceased. After cooling, the hydrogen chloride formed was driven off by passing nitrogen through.

Analytical Procedures. — The reaction mixture obtained by the method described above was weighed, and any loss of weight during the reaction was distributed among the starting materials according to the relative ratio of vapor pressure.

The total amount of chlorides was determined by the procedure described in Part III in the cases of all substituted benzaldehydes except chlorobenzaldehyde. In the case of chlorobenzaldehyde, since Rauscher's method could not be applied, 2 ml. of the reaction mixture was heated under reflux for 2 hr. with 10 ml. of 0.5 N sodium hydroxide in 30 ml. of ethanol, and the chloride liberated was determined by a silver nitrate solution (Mohr's method). Under these conditions, benzoyl chloride is also hydrolyzed quantitatively.

The amount of benzoyl chloride produced was also determined by the procedure described in Part III.

Chlorination Products of *p*-Tolualdehyde.—The reaction of 0.2349 mol. of *p*-tolualdehyde and 0.0481 mol. of sulfuryl chloride gave 4.75 g. of *p*-toluoyl chloride, b. p. 72—74°C/4 mmHg. Toluanilide, m. p. 140°C was derived quantitatively. Found: N, 6.80. Calcd. for $C_{14}H_3ON$: N, 6.81%. The residue of the above distillation (2.53 g.; positive in a Beilstein test) was boiled in water. Some needles, m. p. 82°C, were obtained. Found: C, 70.78, H, 6.10. Calcd. for $C_8H_8O_2$: C, 70.59; H, 5.88%

Results and Discussion

As it was experimentally difficult to determine each component in the acid chloride mixture as a result of the direct competitive reaction between benzaldehyde and substituted benzaldehydes, the substituent effect was derived indirectly as follows: the relative reactivity of substituted benzaldehydes was determined against toluene by competitive chlorination at 80°C, and then these values were compared with those obtained by the similar reaction of unsubstituted benzaldehyde and toluene.

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1) Part III: M. Arai, This Bulletin, 37, 1280 (1964).

2) G. Blanc, *Bull. soc. chem. France*, [4] 33, 313 (1923).

3) C. D. Shacklett and H. A. Smith, *J. Am. Chem. Soc.*, 75, 2654 (1933).

The relative reactivity of the benzaldehydes to toluene was calculated by by the following equation:

$$\mathrm{ArCHO} + \cdot\mathrm{SO_2Cl} \xrightarrow{k} \mathrm{ArCO}\cdot + \mathrm{HCl} + \mathrm{SO_2}$$

$$\mathrm{C_6H_5CH_3} + \cdot\mathrm{SO_2Cl} \xrightarrow{k_T} \mathrm{C_6H_5CH_2}\cdot + \mathrm{HCl} + \mathrm{SO_2}$$

$$\frac{k}{k_T} = \frac{\log\ ([\mathrm{ArCHO}]_{\mathrm{int}}/[\mathrm{ArCHO}]_{\mathrm{fin}})}{\log\ ([\mathrm{C_6H_5CH_3}]_{\mathrm{int}}/[\mathrm{C_6H_5CH_3}]_{\mathrm{fin}})}$$

where $[\ ]_{\mathrm{int}}$ and $[\ ]_{\mathrm{fin}}$ denote the initial and final concentrations of ArCHO and $\mathrm{C_6H_5CH_3}$ respectively.

The value of 3.23 was used for k_O/k_T, in which k_O was the k value of unsubstituted benzaldehyde, as was shown in Part III of

TABLE I. COMPETITIVE CHLORINATION OF *p*-NITROBENZALDEHYDE AND TOLUENE AT 80°C a)

Reactant	mol.	mol.
p-Nitrobenzaldehyde	0.0662	0.0543
Toluene	0.1656	0.2494
Sulfuryl chloride	0.0247	0.0247
Product		
Total chlorides	0.0245	0.0248
p-Nitrobenzoyl chloride	0.0082	0.0059
Benzyl chloride b)	0.0163	0.0189
p-Nitrobenzaldehyde c)	0.0580	0.0484
Toluene c)	0.1493	0.2305
k/k_T	1.28	1.46
k/k_O	0.40	0.45
mean	0.43	

a) In the presence of benzoyl peroxide
b) Total chlorides minus *p*-nitrobenzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

TABLE II. COMPETITIVE CHLORINATION OF *m*-NITROBENZALDEHYDE AND TOLUENE AT 80°C a)

Reactant	mol.	mol.
m-Nitrobenzaldehyde	0.0687	0.0651
Toluene	0.1357	0.2583
Sulfuryl chloride	0.0247	0.0247
Product		
Total chlorides	0.0243	0.0241
m-Nitrobenzoyl chloride	0.0095	0.0059
Benzyl chloride b)	0.0148	0.0182
m-Nitrobenzaldehyde c)	0.0592	0.0592
Toluene c)	0.1209	0.2401
k/k_T	1.29	1.31
k/k_O	0.40	0.41
mean	0.41	

a) In the presence of benzoyl peroxide
b) Total chlorides minus *m*-nitrobenzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

TABLE III. COMPETITIVE CHLORINATION OF *p*-CHLOROBENZALDEHYDE AND TOLUENE AT 80°C a)

Reactant	mol.	mol.
p-Chlorobenzaldehyde	0.0698	0.0614
Toluene	0.1270	0.1526
Sulfuryl chloride	0.0247	0.0247
Product		
Total chlorides	0.0251	0.0248
p-Chlorobenzoyl chloride	0.0143	0.0121
Benzyl chloride b)	0.0108	0.0127
p-Chlorobenzaldehyde c)	0.0555	0.0493
Toluene c)	0.1162	0.1399
k/k_T	2.58	2.53
k/k_O	0.80	0.78
mean	0.79	

a) In the presence of benzoyl peroxide
b) Total chlorides minus *p*-chlorobenzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

TABLE IV. COMPETITIVE CHLORINATION OF *m*-CHLOROBENZALDEHYDE AND TOLUENE AT 80°C a)

Reactant	mol.
m-Chlorobenzaldehyde	0.0826
Toluene	0.1012
Sulfuryl chloride	0.0247
Product	
Total chlorides	0.0243
m-Chlorobenzoyl chloride	0.0155
Benzyl chloride b)	0.0088
m-Chlorobenzaldehyde c)	0.0671
Toluene c)	0.0924
k/k_T	2.29
k/k_O	0.71

a) In the presence of benzoyl peroxide
b) Total chloride minus *m*-chlorobenzoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

TABLE V. COMPETITIVE CHLORINATION OF ANISALDEHYDE AND TOLUENE AT 80°C a)

Reactant	mol.	mol.
Anisaldehyde	0.0543	0.0819
Toluene	0.1914	0.1112
Sulfuryl chloride	0.0247	0.0247
Product		
Total chlorides	0.0245	0.0232
Anisoyl chloride	0.0110	0.0153
Benzyl chloride b)	0.0135	0.0079
Anisaldehyde c)	0.0433	0.0666
Toluene c)	0.1779	0.1033
k/k_T	3.10	2.80
k/k_O	0.96	0.87
mean	0.92	

a) In the presence of benzoyl peroxide
b) Total chloride minus anisoyl chloride
c) Initial quantity minus the amount substituted and the amount vaporized

this series.[1] The results obtained in the cases of *m*- and *p*-nitrobenzaldehydes, *m*- and *p*-chlorobenzaldehydes, and anisaldehyde are listed in Tables I—V.

A linear relation was found between log k/k_O and Hammett's σ values,[4] as is shown in Fig. 1, where $\rho=-0.48$, excepting for anisaldehyde.

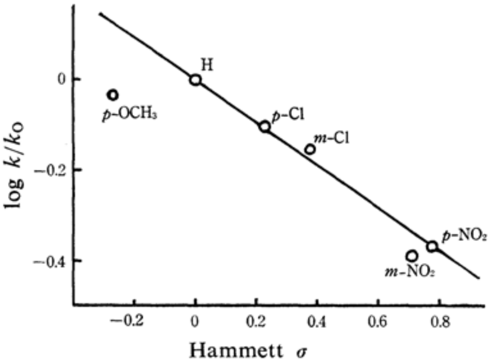
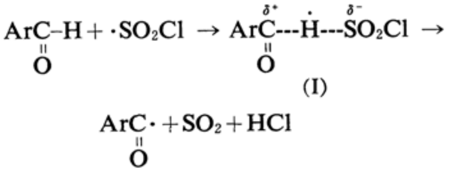


Fig. 1. Correlation of relative reactivities of substituted benzaldehydes with Hammett σ values.

As reasons for the deviation of the value for the *p*-methoxy group, (1) the inadequacy of using the σ value (the application of the σ^+ value, etc. should also be considered) and (2) the occurrence of a considerable side-reaction are both conceivable. As for the first factor, it is stated the σ^+ value is better than the σ value when the reactivity of the electron-releasing group is greater than the value expected from the log $k/k_O-\sigma$ line determined by the other substituents. The experimental results show the smaller log k/k_O value for the *p*-methoxy group. Although the application of Yukawa's modified Hammett relationship[5] can also be considered, no conclusion can be drawn before more experimental results are available regarding other electron-releasing groups. As the second factor, there is a possibility of chlorination at the methoxy group, since the methylenedioxy group suffers from radical chlorination, as has been shown in Part II of this series.[6]

The chlorination reaction of benzaldehyde by sulfuryl chloride is, by nature, a radical reaction.[7] However, since the reaction follows Hammett rule, the polar effect of substituents is also recognized in the reaction. This effect can easily be understood on the assumption of the following activated complex I:



$$\underset{\displaystyle O}{\underset{\|}{\mathrm{ArC}}}\text{–H}+\cdot\mathrm{SO_2Cl}\rightarrow \underset{\displaystyle O}{\underset{\|}{\overset{\delta^+}{\mathrm{ArC}}}}\text{---}\dot{\mathrm{H}}\text{---}\overset{\delta^-}{\mathrm{S}}\mathrm{O_2Cl}\rightarrow$$

(I)

$$\underset{\displaystyle O}{\underset{\|}{\mathrm{ArC}}}\cdot+\mathrm{SO_2}+\mathrm{HCl}$$

I would be more easily formed in the case of the formyl group has more electrons around it, and then, the reaction would be accelerated.

Next, in order to compare the reactivity of the formyl group with that of various alkyl groups at the *p*-position, the reaction was carried out with *p*-tolualdehyde, cuminaldehyde and *p*-*t*-butylbenzaldehyde, using about 1/5 mol. of sulfuryl chloride. The results are smmarized in Tables VI—VIII.

TABLE VI. ISOMER DISTRIBUTION IN THE CHLORINATION OF *p*-TOLUALDEHYDE AT 80°C[a)]

Reactant	mol.	mol.
p-Tolualdehyde	0.2349	0.2496
Sulfuryl chloride	0.0481	0.0506
Product		
Total chlorides	0.0478	0.0502
p-Toluoyl chloride	0.0345	0.0375
p-Chloromethylbenzaldehyde[b)]	0.0133	0.0127
Reactivity of -CH_3 group[c)]	0.39	0.34
mean	0.37	

a) In the presence of benzoyl peroxide
b) Total chlorides minus *p*-toluoyl chloride
c) Reactivity of -CHO group assumed to be 1.00

TABLE VII. ISOMER DISTRIBUTION IN THE CHLORINATION OF CUMINALDEHYDE AT 80°C[a)]

Reactant	mol.
Cuminaldeyde	0.1301
Sulfuryl chloride	0.0247
Product	
Total chlorides	0.0250
(HCl)[b)]	0.0233
β-Chloride of -$CH(CH_3)_2$ group[c)]	0.0017
α-Chloride of -$CH(CH_3)_2$ group[d)]	0.0115
p-Isopropylbenzoyl chloride[e)]	0.0118
Reactivity of -$CH(CH_3)_2$ group[f)]	1.11

a) In the presence of benzoyl peroxide
b) The amount of HCl by hydrolyzed with 80% EtOH — *p*-isopropylbenzoyl chloride and α-chloride of -$CH(CH_3)_2$ group
c) Total chlorides minus (HCl)
d) 6.80 times β-chlride[1)]
e) (HCl) minus α-chloride
f) Reactivity of -CHO group assumed to be 1.00

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[4] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[5] Y. Tsuno, T. Ibata and Y. Yukawa, This Bulletin, **32**, 960 (1959); Y. Yukawa and Y. Tsuno, ibid., **32**, 965, 971 (1959).

[6] M. Arai, This Bulletin, **35**, 1272 (1962).

[7] M. Arai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1450 (1960).

TABLE VIII. ISOMER DISTRIBUTION IN THE CHLORINATION OF *p-t*-BUTYLBENZALDEHYDE AT 80°C[a]

	mol.
Reactant	
p-t-Butylbenzaldehyde	0.1558
Sulfury chloride	0.0408
Product	
Total chlorides	0.0406
p-t-Butylbenzoyl chloride	0.0298
Chloride of $-C(CH_3)_3$ group[b]	0.0108
Reactivity of $-C(CH_3)_3$ group[c]	0.36

a) In the presence of benzoyl peroxide

b) Total chlorides minus *p-t*-butylbenzoyl chloride

c) Reactivity of -CHO group assumed to be 1.00.

Furthermore, two kinds of chlorination products, *p*-toluoyl chloride and *p*-chloromethylbenzaldehydes, were obtained in the reaction of *p*-tolualdehyde. The results are listed in Table VI.

As is shown in Tables VI—VIII, the relative reactivities of the methyl, isopropyl and *t*-butyl groups toward the formyl group are 0.37, 1.11 and 0.36 respectively. These values are close enough to those (0.31, 1.37 and 0.25) resuling from the reaction of toluene, cumene and *t*-butylbenzene toward benzaldehyde.[1] In the reaction of alkylbenzaldehydes, it is considered that the reactivity of the formyl group is increased by the presence of the alkyl group, while the reactivity of the alkyl group is decreased by the presence of the formyl group. Therefore, the reactions in this series show that the modified reactivity of groups is due to mutual electronic interaction.

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