

$$\phi_{\text{ox}}^{3300} = \frac{\text{no. of molecules reacted}}{\text{no. of photons absorbed}}$$

$$\begin{aligned} \text{No. of molecules reacted} &= \frac{\text{wt}}{\text{mol wt}} \times A \times \text{yield} \\ &= \frac{0.054}{208} \times 6.023 \times 10^{23} \times 0.13 \\ &= 2.03 \times 10^{19} \end{aligned}$$

$$\begin{aligned} \text{No. of photons absorbed in } 1500 \text{ s} &= 1.14 \times 10^{15} \times 1.5 \times 10^3 \\ &= 1.71 \times 10^{18} \end{aligned}$$

$$\phi_{\text{ox}}^{3300} = \frac{2.03 \times 10^{19}}{1.71 \times 10^{18}} = 11.9$$

Reaction of Bromohydroperoxide 5H (X = Br). A. With Lead Tetraacetate. Lead tetraacetate (66 mg, 0.15 mmol) (Matheson Coleman and Bell) was added to 32 mg (0.1 mmol) of bromohydroperoxide **5H** in 10 mL of benzene with 100 mg of sodium carbonate. The solution was stirred at room temperature for 5 min, purged with 10 mL of ether, and washed with three separate 10-mL portions of water. The organic layer was dried over magnesium sulfate, and solvent was removed at reduced pressure. The NMR spectrum of the residue indicated fluorenone as the major product. A small amount of a second, unidentified product was also observed. The crude product was purified on alumina with pentane-dichloromethane (4:1 v/v) as eluent. Fluorenone (9 mg, 50%) was isolated in this manner and was shown to be identical with an authentic sample (by comparison of NMR and IR spectra).

B. With Lead Tetraacetate in the Presence of 1. A solution of 208 mg (1.0 mmol) of **1**, 24 mg (0.075 mmol) of bromohydroperoxide **5H**, and 100 mg of sodium carbonate in 20 mL of benzene was continuously saturated with oxygen at room temperature. Lead tetraacetate (35 mg, 0.08 mmol) was added, and the resulting solution was stirred for 30 min. The reaction mixture was then purged with 20 mL of ether, washed with three separate 20-mL portions of water, and dried over magnesium sulfate. Solvent was removed at reduced pressure, and an NMR spectrum (CCl₄) of the residue (200 mg of a yellow oil) indicated the following product composition: 33% unreacted **1**, 32% **2**, and 35% fluorenone. Products were separated by low temperature (−78 °C) chromatography on alumina with dichloromethane as eluent

as previously described and were shown to be identical with authentic samples (by comparison of NMR and IR spectra).

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Gas-Phase Aromatic Substitution by Positive Bromine Ions from ^{80m}Br(IT)⁸⁰Br: A Study of Linear Free Energy Relationship

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Abstract: Mono- and disubstituted benzenes have been brominated by ⁸⁰Br⁺ in the gas phase following the isomeric transition ^{80m}Br(IT)⁸⁰Br. The ratios of rates, derived from product ratios, give linear $\sigma\rho$ plots using σ^+ parameters with $\rho^+ = -0.9$. Inductive and resonance effects were separated to obtain $\rho_1^m = -0.78$, $\rho_1^p = -0.80$, $\rho_R^m = -0.20$ and $\rho_R^p = -1.03$. An extension of these results led to a quantitative analysis of additive influences of the substituents in the *p*-dichlorobenzene molecule. Following the empirical formula $\log p_r^{\text{Me}} = c \log (p_r^{\text{Me}}/m_r^{\text{Me}})$ in the toluene system, a correlation between the experimental results and the theory is given by the expression $c = \sigma_p^+ / (\sigma_p^+ - \sigma_m^+)$. The fact that our results of the electrophilic substitution by ⁸⁰Br⁺ follow the "classical" reactivity-selectivity relationship seems to be a good proof for the validity of a linear free energy relationship even for extremely reactive electrophilic species like unsolvated ions in the gas phase. Obviously the naked ions follow a similar mechanism as solvated ions and there is no need for establishing a new reaction model for the gas-phase aromatic substitution.

A number of kinetic and mechanistic studies of ionic gas-phase reactions in aliphatic and aromatic systems has been performed in the last years by various laboratories.¹⁻⁶ All ki-

netic results were obtained by mass spectrometric techniques, including ICR or by radiolytic methods. Little information, however, is known about kinetic studies using methods of

product identification other than mass spectrometry. Here, the nuclear method, based on the application of decay-induced reactions, represents an elegant and sensitive process for the determination of products by their radioactivity. In contrast to mass spectrometric techniques, where structural differences of the product ion can be distinguished only in special cases (for instance in the case of some ortho-substituted benzene compounds = ortho effect), the nuclear method allows a general determination of isomeric products. Extensive studies have been carried out by Cacace and co-workers on the gas-phase aromatic substitution by $^3\text{HeT}^+$, D_2T^+ , and R^+ resulting from the β^- decay of the corresponding tritiated precursors (for a review cf. ref 7). With these reactions, relative reactivities of the electrophilic attack of $^3\text{HeT}^+$ and D_2T^+ with some monosubstituted benzenes could be evaluated. Similarly, the alkylation by isopropyl and *tert*-butyl cations was carried out.^{8,9}

It has recently been shown by our laboratory¹⁰⁻¹³ that a nuclear technique can also be applied to the study of electrophilic halogenation reactions in the gas phase. Appropriate decay processes for the production of positive charged halogen ions are represented by the isomeric transition $^{80\text{m}}\text{Br}(\text{IT})^{80}\text{Br}$ and the electron capture decay $^{125}\text{Xe}(\text{EC})^{125}\text{I}$. Recently, we have also calculated the kinetic data for the isomerization of the *o*- and *p*-bromofluoroarenonium ion into the meta compound after the primary attack of the $^{80}\text{Br}^+$ ion at the aromatic fluorobenzene molecule using an inert gas dilution technique.¹³

The basic physical and chemical consequences of the isomeric transition of $^{80\text{m}}\text{Br}$ and the details of our specific technique have been described elsewhere (ref 11, 13, and the literature cited therein).

One of the oldest quantitative relationships in organic chemistry is the Hammett equation, correlating the structure of meta- and para-substituted benzene derivatives and the equilibrium and/or rate constants of their reactions:

$$\log(K/K_0) = \rho\sigma \quad \text{or} \quad \log(k/k_0) = \rho\sigma \quad (1)$$

After the first investigations,^{14,15} several modifications of the original equation had to be introduced considering the various types of reactions.¹⁶⁻²⁰ Further studies of aliphatic and aromatic reactivities by Taft, Roberts, and Moreland^{17,21,22} have led to an extended Hammett equation (dual-substituent-parameter correlation), separating the polar (I) and the π -delocalization (R) effect of the individual positions (*i*).²³⁻²⁸

$$\log(k/k_0) = I^i + R^i = \rho_I^i\sigma_I + \rho_R^i\sigma_R \quad (2)$$

According to the equation $\log(k/k_0) = \rho\Sigma\sigma_i^+$ for polysubstituted aromatic compounds,^{15,29-34} we have also attempted to investigate additive influences in molecules with more than one substituent for the gas-phase bromination via the isomeric transition of ^{80}Br with the symmetrical molecule *p*-dichlorobenzene.

Experimental Section

Materials. Benzene, fluorobenzene, chlorobenzene, bromobenzene, toluene, α,α,α -trifluorotoluene, anisole (methoxybenzene) and *p*-dichlorobenzene were obtained from Schuchardt GmbH (München), Merck (Darmstadt), and Fluka (Buchs, Switzerland) with a purity of >99% (*p*- $\text{C}_6\text{H}_4\text{Cl}_2$ >97%). They were further purified by preparative GLC or by distillation.

The preparation of the $^{80\text{m}}\text{Br}$ source ($^{80\text{m}}\text{Br}$ labeled CH_3Br), and of the reaction mixtures, the sample analysis, and the radioactivity determination have been described in our previous papers.^{11,13} Supplementary informations: (1) The competition experiments were carried out with an equimolar substrate-benzene mixture. (2) Gas chromatographic separations:^{35,36} The following columns were used (4-m glass column, 3.5-mm inner diameter, 100 mL He/min): (a) 6%

bentone-38; 20% silicone oil DC 200 on Chromosorb W-AW-DMCS (60/80 mesh) at temperatures between 90 and 130 °C, for the separation of bromobenzene and the ortho, meta, and para isomers of α,α,α -trifluorotoluene, and at temperatures between 120 and 150 °C for the separation of the bromochlorobenzenes and 2-bromo-1,4-dichlorobenzene; (b) 20% Igepal CO-880 on Chromosorb W-AW-DMCS (60/80 mesh) at a temperature of 130 °C, for the separation of *o*-, *m*-, and *p*-bromoanisole; (c) 4-m glass column, 5-mm inner diameter, 100 mL He/min, 30% tetracyanoethylated pentaerythritol on Chromosorb P-AW (60/80 mesh) at a temperature of 140 °C, for the separation of bromobenzene and *p*-dichlorobenzene and for the separation of bromobenzene and anisole.

Results and Discussion

Linear Free Energy Relationship for the Gas-Phase Bromination. The applicability of the Hammett equation requires the calculation of the partial rate factors of the individual positions in the aromatic ring, thus yielding the equations:

$$\begin{aligned} \rho_f &= k_p/k_o = \frac{6k_{\text{para}}}{k_{\text{C}_6\text{H}_6}} \\ &= \frac{6(\text{yield } p\text{-C}_6\text{H}_4\text{XBr (from C}_6\text{H}_5\text{X}))}{\text{yield C}_6\text{H}_5\text{Br (from C}_6\text{H}_6)} \end{aligned} \quad (3)$$

$$\begin{aligned} m_f &= k_m/k_o = \frac{3k_{\text{meta}}}{k_{\text{C}_6\text{H}_6}} \\ &= \frac{3(\text{yield } m\text{-C}_6\text{H}_4\text{XBr (from C}_6\text{H}_5\text{X}))}{\text{yield C}_6\text{H}_5\text{Br (from C}_6\text{H}_6)} \end{aligned} \quad (4)$$

Some difficulties may arise when comparing yields with rate constants due to unknown competing processes, as can be seen by the small yields of the substitution products (cf., e.g., ref 11). However, an application of the relative rate constants seems reasonable, because it is possible to eliminate these competing processes mathematically by a direct comparison of the corresponding single and competition experiment. It can be seen from the single experiments that besides Br-for-H substitution, leading to ^{80}Br -labeled ortho, meta, and para products, a considerable amount of ^{80}Br -labeled bromobenzene is formed due to Br-for-X substitution. Thus, the yields of $\text{C}_6\text{H}_5^{80}\text{Br}$ from the competition experiments ($\text{C}_6\text{H}_5\text{X}/\text{C}_6\text{H}_6 = 1:1$) had to be corrected, and the reactivity of benzene was obtained by subtracting half the $\text{C}_6\text{H}_5^{80}\text{Br}$ yield as obtained from the single experiment from the total $\text{C}_6\text{H}_5^{80}\text{Br}$ yield of the competition experiment. This procedure seems to be justified because the Br-for-X substitution yield should be reduced to one-half under the conditions of the competition experiments provided no additional effects appear.

A plot of the $\log(k_p/k_o)$ and $\log(k_m/k_o)$ values, calculated from the experimental results in Tables I and II, vs. Brown's substituent constants,²⁰ is shown in Figure 1. It can be seen that a straight line results, covering the entire range with a slope of $\rho^+ = -0.9$. From the absolute value and the sign of the reaction constant, two conclusions can be drawn:

(i) Considering electrophilic aromatic substitution reactions, the value of -0.9 is the smallest known so far, thus showing a further continuation of the general reactivity-selectivity trend for solution chemistry. The consequences arising from the variation of the electrophilic species are an increasing isomer yield at the meta position on account of the ortho and para position with increasing reactivity, while a concomitant decrease of the ρ^+ values is observed.^{31,32,37-40} Consequently, for unsolvated $^{80}\text{Br}^+$ ions the greatest possible reactivity and the smallest inter- and intramolecular selectivity can be expected. The almost statistical isomer distribution and a ρ^+ value of -0.9 confirm this expectation.

(ii) The negative sign of the reaction constant indicates the formation of a transition state structure, which is stabilized by electron donating and destabilized by electron withdrawing substituents. This provides further evidence for the postulated

Table I. Absolute Radiochemical Yields^a from Gas-Phase^b ⁸⁰Br-for-H and ⁸⁰Br-for-X Substitution in Single^c and Competition^d Experiments

Product	C ₆ H ₅ F	C ₆ H ₅ Cl	C ₆ H ₅ Br	C ₆ H ₅ CH ₃	C ₆ H ₅ CF ₃	C ₆ H ₅ OCH ₃
Single Experiments						
<i>o</i> -C ₆ H ₄ XBr	1.02	0.84	0.36	1.90	0.08	1.48
<i>m</i> -C ₆ H ₄ XBr	1.10	0.79	0.27	1.45	0.69	0.63
<i>p</i> -C ₆ H ₄ XBr	1.11	0.85	0.28	1.19	0.26	2.97
C ₆ H ₅ Br	0.43	2.16	18.06	1.25	0.05	1.17
Competition Experiments						
<i>o</i> -C ₆ H ₄ XBr	0.62	0.49	0.39	1.40	?	0.90
<i>m</i> -C ₆ H ₄ XBr	0.95	0.49	0.32	0.86	0.34	0.41
<i>p</i> -C ₆ H ₄ XBr	0.46	0.38	0.31	0.84	0.17	1.49
C ₆ H ₅ Br	2.10	3.59	11.02	3.14	2.53	1.82

^a In percent of total ⁸⁰Br daughter ions formed; standard deviation about 10%. ^b The gaseous system was kept at 760 Torr at 70 °C. ^c Competition: 95 mol % of Ar, 2.5 mol % of C₆H₅X, and 2.5 mol % of ^{80m}Br-labeled CH₃Br as ⁸⁰Br⁺ source. ^d Composition: 95 mol % of Ar, 1.25 mol % of C₆H₅X, 1.25 mol % of C₆H₆, and 2.5 mol % of ^{80m}Br-labeled CH₃Br as ⁸⁰Br⁺ source.

Table II. Brown's Substituent Constants and Relative Reactivities in ⁸⁰Br-for-H Substitution

X	σ ⁺	k/k ₀	log(k/k ₀)
<i>p</i> -CH ₃	-0.311	2.00	0.3010
<i>m</i> -CH ₃	-0.066	1.02	0.0086
<i>p</i> -F	-0.073	1.46	0.1644
<i>p</i> -Cl	0.114	0.91	-0.0410
<i>m</i> -Cl	0.399	0.58	-0.2366
<i>p</i> -Br	0.150	0.93	-0.0315
<i>m</i> -Br	0.405	0.48	-0.3188
<i>p</i> -CF ₃	0.612	0.40	-0.3979
<i>m</i> -CF ₃	0.520	0.40	-0.3979
<i>p</i> -OCH ₃	-0.778	7.24	0.8597
<i>m</i> -OCH ₃	0.047	0.99	-0.0044
H	0	1.00	0.0000

and expected positive charge of the ⁸⁰Br species,^{10,11} as also indicated by the fact that Brown's σ⁺ substituent constants yield a better fit than Hammett's σ values. The transition state must therefore be stabilized by electron resonance donors like -OCH₃ and -CH₃ in the para position forming a chinoid structure.

For an extension of our investigations, we used the dual-parameter-relationship, described by Ehrenson, Brownlee, and Taft.²⁷ Since this equation cannot be solved by simple graphical linear evaluations, the data for a fit must be obtained by computer analysis. However, it is possible to derive an appropriate one-substituent-parameter calculation, thus being appropriate for the evaluation of the inductive and resonance constants ρ_I and ρ_R.²⁸

Starting from

$$\log(k/k_0) = \bar{\rho}\bar{\sigma} = \rho_I\sigma_I + \rho_R\sigma_R^+ \quad (5)$$

$$\lambda = \rho_R/\rho_I \quad (6)$$

$$\bar{\rho} = \rho_I + \rho_R \quad (7)$$

one obtains

$$\bar{\sigma} = (\sigma_I + \lambda\sigma_R^+)/ (1 + |\lambda|) \quad (8)$$

With these equations calculation of ρ_I and ρ_R is possible:

$$\rho_I = \bar{\rho}/(1 + |\lambda|) \quad (9)$$

$$\rho_R = \bar{\rho}\lambda/(1 + |\lambda|). \quad (10)$$

By multiple variation of λ and plotting the observed substituent effect vs. $\bar{\sigma}$, a set of $\bar{\sigma}$ values can be obtained with a given λ yielding the best fit for the data. From the slope $\bar{\rho}$ of the line with the best λ value, defining the $\bar{\sigma}$ set, ρ_I and ρ_R can be

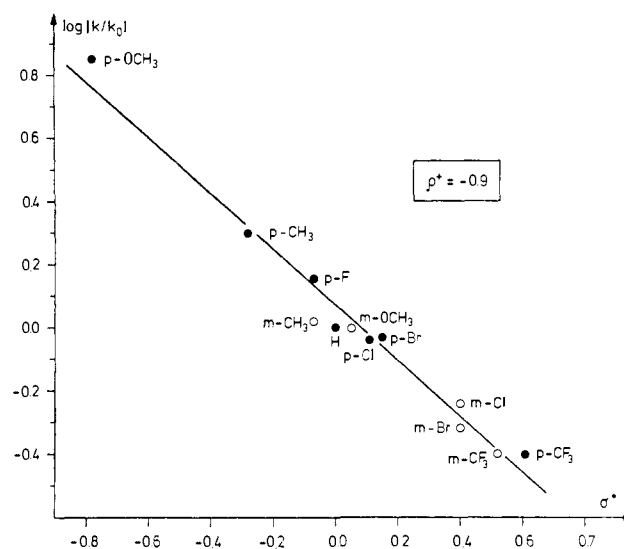


Figure 1. Comparison of relative reactivities of monosubstituted benzenes with Brown's σ⁺ values in the CH₅X/C₆H₆/CH₃^{80m}Br/Ar system; total pressure 760 Torr; temperature 70 °C; C₆H₅X and C₆H₆, 1.25 mol % each; ^{80m}Br-labeled CH₃Br, 2.5 mol %; Ar, 95 mol %.

evaluated following the eq 9 and 10. A computer fit of the experimental results following the above mentioned method is shown in Figure 2. For σ_I and σ_R⁺ the literature values were used.²⁷ It can be seen that an excellent fit of the theoretical line to the experimental data is possible, based upon the following reaction parameters:

$$\begin{aligned} \bar{\rho}_p &= -1.83 & \bar{\rho}_m &= -0.98 \\ \rho_I^p &= -0.80 & \rho_I^m &= -0.78 \\ \rho_R^p &= -1.03 & \rho_R^m &= -0.20 \\ \lambda_p &= 1.29 & \lambda_m &= 0.26 \end{aligned} \quad (11)$$

Following Ehrenson, Brownlee, and Taft²⁷ and Wells, Ehrenson, and Taft,²⁸ a good measure of precision is the dimension $f = \text{SD}/\text{RMS} \leq 0.1$:

$$\begin{aligned} \text{SD} &= (\sum(\Delta x)^2/n)^{1/2} \\ \text{RMS} &= (\sum(\log k/k_0)^2/n)^{1/2} \end{aligned} \quad (12)$$

where Δx = deviations of the experimental data from the theoretical log(k/k₀) values, and n = number of data. Based upon eq 12, the following f values were obtained:

$$\begin{aligned} f_{\text{para}} &= 0.07 \\ f_{\text{meta}} &= 0.18 \end{aligned} \quad (13)$$

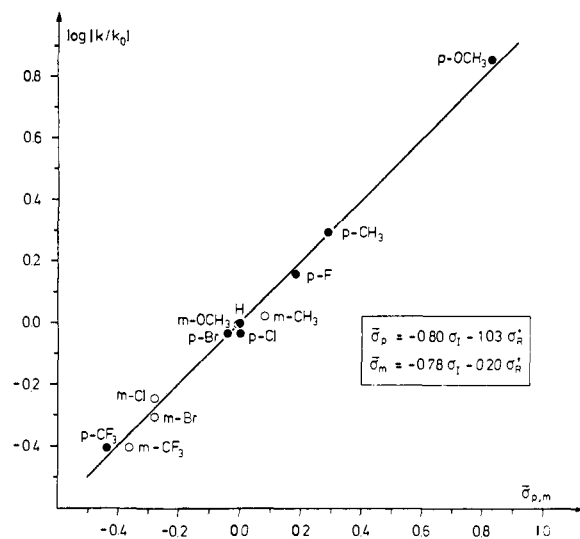


Figure 2. Comparison of relative reactivities of monosubstituted benzenes with the $\bar{\sigma}$ values.

Table III. Isomer Distribution and Absolute Radiochemical Yields^a of Br-for-H and Br-for-Cl Substitution in the p - $C_6H_4Cl_2/C_6H_6$ System Following the Isomeric Transition of ^{80}mBr

Isomer distribution	Absolute radiochemical yields of Br-for-Cl and Br-for-H substitution	
	o - C_6H_4BrCl	0.11%
	m - C_6H_4BrCl	0.11%
	p - C_6H_4BrCl	0.35%
	2-bromo-1,4-dichlorobenzene	0.33%
	C_6H_5Br	2.46%

^a In percent of the produced ^{80}Br atoms. Conditions: 1.25 mol % p - $C_6H_4Cl_2$, 1.25 mol % C_6H_6 , 2.5 mol % CH_3^*Br , and 95 mol % Ar; total pressure, 760 Torr; reaction time, 30 min; temperature, 70 °C.

A calculation with the $\sigma_{R(BA)}$ values instead of the σ_R^+ values yields f values with less precision.

The dual-substituent-parameter correlation seems to be a method to discuss transition states, for instance in the course of electrophilic aromatic substitution reactions. By its means some features can be deduced from the results, which can be summarized as follows:

(a) The application of the σ_R^+ values, yielding a better correlation than the $\sigma_{R(BA)}$ values, indicates a transition state with a strong direct resonance participation of the reaction center for electron-donating substituents in para position.

(b) The ρ_I values, measuring the sensitivity of the reaction to polar changes of the substituents, are nearly equal for the meta and the para position ($\rho_I^m \approx \rho_I^p$), a finding which is in good agreement with Taft's postulate.²³⁻²⁶ The low value indicates little influence of the electronic properties of the substituents on the bromination. The negative sign reflects a stabilization of the transition state by electron releasing and destabilization by electron withdrawing substituents (more cationic than anionic character). Probably, reaction types with negative ρ_I values occur by an approach of the positive charge to the substituent when moving toward the transition state.

(c) Presumably, the ρ_R values are in close connection with the π -electron demand. Increasing demand increases the ρ_R value being compensated by direct resonance stabilization with an electron-releasing substituent.

(d) The λ values definitely reflect the transmission of π -delocalization effects. Due to direct resonance these effects are more effective in the para than in the meta position, demonstrated by their different sizes of magnitude ($\lambda_p = 1.29$; $\lambda_m = 0.26$). Reactions in the liquid phase have λ_m values of about

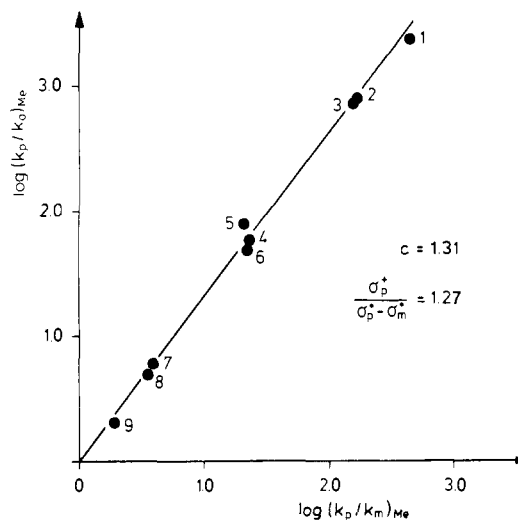


Figure 3. Comparison of selectivity factors $\log(k_p/k_m)_{Me}$ with the partial rate constants $\log(k_p/k_0)_{Me}$ in some electrophilic substitution reactions of toluene. Reactions: 1, bromination, Br_2 , $HOAc-H_2O$, 25 °C;³¹ 2, chlorination, Cl_2 , $HOAc$, 25 °C;³² 3, acetylation, CH_3COCl , $AlCl_3$, dichloroethane, 25 °C;³⁷ 4, bromination, $HOBr$, $HClO_4$, dioxane, 25 °C;³⁸ 5, chlorination, $HOCl$, $HClO_4$, H_2O , 25 °C;⁴⁴ 6, nitration, $AcONO_2$, Ac_2O , 25 °C;⁴⁵ 7, ethylation, C_2H_5Br , $GaBr_3$, 25 °C;³⁹ 8, isopropylation, $(CH_3)_2CHBr$, $GaBr_3$, 25 °C;⁴⁰ 9, gas-phase bromination, $^{80}Br^+$, 70 °C (this work).

0.4 and λ_p values of 1.²⁷ Thus, the decreasing λ_p values indicate the decreasing importance of para-quinoid structures.

(e) The same sign for ρ_I and ρ_R demonstrates that both the polar and the π -delocalization effect electronically show the same direction in the transition state.

Additive Influences of Substituents. Intramolecular competition experiments of the gas-phase bromination of p - $C_6H_4F_2$ have already been reported by our laboratory.¹¹ As the products resulting from Br-for-H and Br-for-F substitution are not well separable by gas chromatography due to their similar boiling points, we now chose the disubstituted chloro compound. The results are shown in Table III. It can be seen that the main product is p - C_6H_4BrCl formed by Br-for-Cl substitution, while the ortho and meta compound show lower yields. Br-for-H substitution leads to 2-bromo-1,4-dichlorobenzene. Since the experiment was performed as a competition experiment in the presence of an equimolar quantity of benzene, ^{80}Br -labeled bromobenzene was found with high yields.

The postulated mechanism of the Br-for-X substitution has been described in an earlier paper.¹¹ Here, we shall only discuss the kinetics of the Br-for-H substitution. The partial rate constant for the formation of 2-bromo-1,4-dichlorobenzene can be evaluated to

$$(k_2/k_0)_{\text{expt}} = 0.20 \pm 0.04 \quad (14)$$

The theoretical value is based upon the calculations of additive influences by the substituents:

$$\begin{aligned} \log(k_2/k_0) &= \rho(\sigma_{o-Cl}^+ + \sigma_{m-Cl}^+) \\ &= \log o_f^{Cl} + \log m_f^{Cl} \\ k_2/k_0 &= o_f^{Cl} m_f^{Cl} \end{aligned} \quad (15)$$

The partial rate constant o_f^{Cl} for the ortho position is evaluated from the experimental results in Table I:

$$o_f^{Cl} = 0.58 \quad (16)$$

The partial rate constant m_f^{Cl} for the meta position was taken from the straight line in Figure 1:

$$m_f^{Cl} = 0.50 \quad (17)$$

With these values, the partial rate constant of the Br-for-H substitution in position 2 can be evaluated to

$$(k_2/k_0)_{\text{calcd}} = 0.29 \quad (18)$$

Considering the experimental errors, a good agreement between experiment and the theoretical calculation is achieved, thus confirming the additivity of the influences caused by the substituents in polysubstituted benzene derivatives even for unsolvated reactive species in the gas phase.

Electrophilic Aromatic Substitution of Toluene. A correlation between reactivity and selectivity of electrophilic aromatic substitution reactions in solution is well established as a result of numerous experiments.⁴¹ Thus, data for the substitution of toluene confirm a close connection between the product ratio para/meta and the relative reactivity $k_{\text{toluene}}/k_{\text{benzene}}$. The results have been described by the empirical formula⁴²

$$\log p_f^{\text{Me}} = c \log (p_f^{\text{Me}}/m_f^{\text{Me}}) \quad (19)$$

This equation can also be obtained by simple calculations from the Hammett equation⁴³ and one obtains:

$$\log p_f = (\sigma_p/(\sigma_p - \sigma_m)) \log (p_f/m_f) \quad (20)$$

Following this equation, a plot of the $(\log p_f)$ values for a number of substitution reactions of toluene vs. $\log (p_f/m_f)$ should give a straight line with the slope $c = \sigma_p/(\sigma_p - \sigma_m)$. The results are shown in Figure 3. By the application of the Hammett values σ_{BA} , a line with the slope 1.68 should be obtained instead of the empirical value 1.310. However, using Brown's substituent constants σ^+ , a good approach to the experiment can be achieved [$\sigma_p^+ / (\sigma_p^+ - \sigma_m^+) = 1.27$]. Further, it can be shown that the experimental value for the gas-phase bromination of toluene by $^{80}\text{Br}^+$ is in very good agreement with the trend observed in the "classical" substitution reactions of toluene in solution.

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