methyl iodide. After 30 min water was added, the mixture was extracted with hexane, and the combined organic extracts were dried and concentrated. Material sufficiently pure for GC analysis was obtained by preparative TLC (0.5-mm Analtech silica gel plate, 5:1–10:1 hexane:ether). A liberal cut was taken to preclude enantiomeric fractionation.[10] Formation of the methyl ethers was confirmed by 300-MHz $^1$H NMR analysis.

**GC Analyses.** The columns, nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)camphorate] and nickel(II) bis[(1*R*,2*S*)-(heptafluorobutyryl)pinan-4-onate], both 10% in OV-1, 25 m × 0.25 mm, have been obtained from Chiral Complexation Capillary Columns (CC & CC), D7402 Kirchentellinsfurt, West Germany. The chromatograms were obtained with the use of a Hewlett-Packard HP5890 gas chromatograph configured for dual capillary columns with dual flame-ionizing detectors. A HP3392A recording integrator recorded the traces. The carrier gas was helium, and split ratios were set at 100:1.

**Acknowledgment.** This work was supported by the NIH (Grants GM 26782 and AI 20779). We thank C. Kwasigroch, Prof. R. L. Danheiser, and Prof. M. Midland for providing the acetylenic substrates and Professor V. Schurig for providing information on the use and handling of the chiral complexation capillary columns.

**Registry No.** (±)-**1**, 106756-91-6; (±)-**1** alcohol, 80735-94-0; (±)-**2**, 106650-72-0; (±)-**2** alcohol, 106756-92-7; (±)-**3**, 106650-73-1; (±)-**3** alcohol, 106650-97-9; (±)-**4**, 106680-47-1; (±)-**4** alcohol, 106650-98-0; (±)-**5**, 106650-74-2; (±)-**5** alcohol, 106756-93-8; (±)-**6**, 106650-75-3; (±)-**6** alcohol, 74851-31-3; (±)-**7**, 106650-76-4; (±)-**7** alcohol, 106756-94-9; (±)-**8**, 106680-33-5; (±)-**8** alcohol, 63553-62-8; (±)-**9**, 106650-77-5; (±)-**9** alcohol, 106650-99-1; (±)-**10**, 106650-78-6; (±)-**10** alcohol, 106680-36-8; (±)-**11**, 106650-79-7; (±)-**11** alcohol, 106651-00-7; (±)-**12**, 106650-80-0; (±)-**12** alcohol, 106651-01-8; (±)-**13**, 106650-81-1; (±)-**13** alcohol, 106651-02-9; (±)-**14**, 106650-82-2; (±)-**14** alcohol, 106756-95-0; (±)-**15**, 106650-83-3; (±)-**15** alcohol, 63553-63-9; (±)-**16**, 106650-84-4; (±)-**16** alcohol, 106651-03-0; (±)-**17**, 106650-85-5; (±)-**17** alcohol, 106651-04-1; (±)-**18**, 106680-34-6; (±)-**18** alcohol, 106651-05-2; (±)-**19a**, 106650-86-6; (±)-**19a** alcohol, 106680-48-2; (±)-**19b**, 106650-87-7; (±)-**19b** alcohol, 106651-06-3; (±)-**19c**, 106680-35-7; (±)-**19c** alcohol, 106680-37-9; (±)-**20a**, 106650-88-8; (±)-**20a** alcohol, 106651-07-4; (±)-**20b**, 106650-89-9; (±)-**20b** alcohol, 106651-08-5; (±)-**20c**, 106650-90-2; (±)-**20c** alcohol, 106651-09-6; (±)-**21a**, 106650-91-3; (±)-**21a** alcohol, 106756-96-1; (±)-**21b**, 106650-92-4; (±)-**21b** alcohol, 106756-97-2; (±)-**21c**, 106650-93-5; (±)-**21c** alcohol, 106651-10-9; (±)-**21d**, 106650-94-6; (±)-**21d** alcohol, 106756-98-3; (±)-**22**, 106650-95-7; (±)-**22** alcohol, 21632-18-8; (±)-**23**, 106650-96-8; (±)-**23** alcohol, 106756-99-4; Ni-R-cam, 68457-34-1; Ni-4-pin, 87306-50-1.

## Complexation Effects in the Photochlorination of 2,3-Dimethylbutane in the Presence of Fluorinated Benzenes

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*Received August 26, 1986*

The presence of benzene and other "complexing" solvents has long been known to increase the selectivity of attack of elemental chlorine on substrates such as 2,3-dimethylbutane.[1] This phenomenon was originally ascribed to the intervention of a second, more selective, hydrogen-abstracting agent which was proposed to be a benzene–chlorine atom $\pi$ complex. The $Cl_2$/benzene/2,3-dimethylbutane system recently received renewed attention[2,3] especially with regard to the number of hydrogen abstractors needed to explain observed concentration effects on selectivity and to the nature of the complexed abstracting agent(s). We argued[3] that the selectivity data in this system could be explained adequately in terms of a two abstractor model (Scheme I), in which the second abstractor $C_6H_6Cl$ was assigned to a chlorine atom–benzene $\pi$ complex, in conformity with Russell's original proposal.[1a] In Scheme I, 3°-R$^\bullet$ and 1°-R$^\bullet$ are $(CH_3)_2\dot{C}(CH_3)_2$ and $(CH_3)_2CHCH(CH_3)CH_2^\bullet$, and 3°-RCl and 1°-RCl are the corresponding alkyl chlorides.

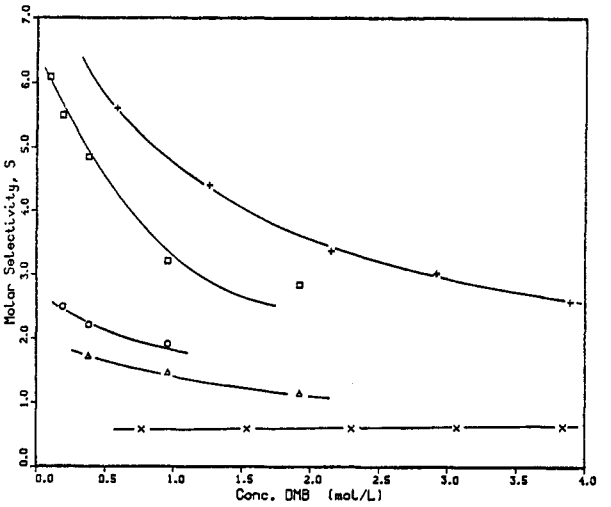


**Figure 1.** Variation in the molar selectivity $S$ with dimethylbutane concentration at constant concentrations of benzene derivatives: (+) benzene; (□) fluorobenzene; (○) difluorobenzene; (△) trifluorobenzene; (×) hexafluorobenzene. All benzene concentrations were 4.0 M except for hexafluorobenzene (3.0 M).

**Scheme I**

$$Cl^\bullet + DMB \xrightarrow{k_1} 3°\text{-}R^\bullet \rightarrow 3°\text{-}RCl$$

$$Cl^\bullet + DMB \xrightarrow{k_2} 1°\text{-}R^\bullet \rightarrow 1°\text{-}RCl$$

$$Cl^\bullet + ArH \xrightarrow{k_3} (ArHCl)^\bullet$$

$$(ArHCl)^\bullet \xrightarrow{k_4} Cl^\bullet + ArH$$

$$(ArHCl)^\bullet + DMB \xrightarrow{k_5} 3°\text{-}R^\bullet \rightarrow 3°\text{-}RCl$$

$$(ArHCl)^\bullet + DMB \xrightarrow{k_6} 1°\text{-}R^\bullet \rightarrow 1°\text{-}RCl$$

We now report the extension of our studies to the chlorination of 2,3-dimethylbutane in the presence of a series of fluorinated benzenes. The trends in selectivity as a function of reactant concentrations can be explained in terms of Scheme I, and we have been able to trace the effect of increasing fluorination of the benzene derivative upon the tertiary-to-primary (3°/1°) selectivity of the complexed chlorine atom.

### Results and Discussion

The selectivity for attack on 2,3-dimethylbutane was determined by monitoring the ratio of the two monochlorination products; i.e., the distribution of monochlorides was assumed to reflect the distribution of tertiary

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0022-3263/87/1952-1155$01.50/0 

Table I. Rate Constant Ratios and Derived Data for $Cl_2$/DMB/Fluorinated Benzenes[a]

| Ar | $k_4/k_6$, mol $L^{-1}$ | $k_5/k_6$ | $k_3/k_2$, mol $L^{-1}$ | $k_3$,[b] L $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| PhH | 19.6 ± 9.3 | 22.4 ± 6.6 | 2.7 ± 0.2 | $6.0 \times 10^9$ |
| PhF | 8.0 ± 4.4 | 11.8 ± 3.0 | 1.9 ± 0.4 | $3.8 \times 10^9$ |
| $PhF_2$ | 9.1 ± 3.9 | 7.8 ± 1.8 | 1.0 ± 0.2 | $2.0 \times 10^9$ |

[a] Uncertainties are 95% confidence intervals. [b] For benzene $k_3$ was taken from ref 3; for PhF and $PhF_2$, $k_3$ was calculated by using $k_2 = 2.0 \times 10^9$ L $mol^{-1}$ $s^{-1}$.[3]

and primary alkyl radicals. All experiments were done at dimethylbutane/$Cl_2$ ratios >10. The aromatic complexing solvents were fluorobenzene (PhF), 1,4-difluorobenzene ($PhF_2$), 1,3,5-trifluorobenzene ($PhF_3$), and hexafluorobenzene ($PhF_6$). The effect of the aromatic compound on the selectivity decreased in the order PhH > PhF > $PhF_2$ > $PhF_3$ and had disappeared completely in the case of $PhF_6$. Figure 1 shows the variation in molar selectivity [3°-Cl]/[1°-Cl] with dimethylbutane concentration.

According to Scheme I, the overall molar selectivity for dimethylbutane is given by eq 1.

$$S^m = \frac{k_1[Cl^\bullet] + k_5[ArHCl^\bullet]}{k_2[Cl^\bullet] + k_6[ArHCl^\bullet]} \quad (1)$$

When the nonobservable concentrations of $Cl^\bullet$ and $(ArHCl)^\bullet$ are eliminated, eq 2 is obtained. When [ArH]

$$S^m = \frac{k_1(k_4 + (k_5 + k_6)[DMB]) + k_3k_5[ArH]}{k_2(k_4 + (k_5 + k_6)[DMB]) + k_3k_6[ArH]} \quad (2)$$

= 0 (absence of complexing solvent) then $S^m = k_1/k_2$, i.e., the selectivity in noncomplexing solvents. However as [DMB] → 0, eq 2 does not reduce to the selectivity of the complex ($k_5/k_6$) but instead to a more complicated function. Rearranging eq 2 somewhat, we obtain eq 3 in which $S^m$ is expressed in terms of the two reactant concentrations [ArH] and [DMB] and four combinations of rate constants.

$$S^m = \{(k_1/k_2)((k_4/k_6) + (1 + (k_5/k_6)) \times [DMB]) + (k_5/k_6)(k_3/k_2)[ArH]\}/\{((k_4/k_6) + (1 + (k_5/k_6))[DMB]) + (k_3/k_2)[ArH]\} \quad (3)$$

We obtained values $k_5/k_6$ (the selectivity of the complex), $k_3/k_2$, and $k_4/k_6$ by a multiple regression procedure (Table I) in which $k_1/k_2$ (the selectivity of uncomplexed $Cl^\bullet$) was set equal to 0.66.[3] For benzene, the results are in good agreement with those we reported previously.[3] Convergence of the regression analysis was obtained for PhF and $PhF_2$, but not for $PhF_3$. The data for $PhF_3$ show similar trends to those obtained with the less fluorinated benzenes, but the quality of the data is poor; at low [$PhF_3$] the molar selectivity changes very little, while at high [$PhF_3$] a minor impurity in the $PhF_3$ interfered with the analysis of the alkyl chlorides. Consequently, we were not able to quantitate the trend of decreasing selectivity of the complex ($k_5/k_6$) beyond difluorobenzene.

The trend that the overall selectivity falls in the series PhH > PhF .... $PhF_6$ can be interpreted to result from the combination of several factors. Both the rate constant for forming the complex ($k_3$) and the intrinsic selectivity ($k_5/k_6$) decrease in this series. These effects may be ascribed to the electron-attracting tendency of the fluorine substituents. Complex formation ($k_3$) becomes increasingly less competitive with the attack of $Cl^\bullet$ on DMB because $Cl^\bullet$ is a rather electrophilic species. Correspondingly, the stabilization of the complexes is reduced by fluorine substitution, and this makes the complex less selective; i.e. the activation energy for hydrogen abstraction by the complex is reduced as originally argued by Walling.[1b] It may thus be presumed that both $k_5$ and $k_6$ increase with increasing fluorination of the aromatic component. Finally, if $k_6$ increases, it must follow that $k_4$, the dissociation of the complex, grows rapidly with increasing fluorination. None of these effects should be the result of steric hindrance, given the similar covalent radii of fluorine and hydrogen. To summarize, the lower selectivity for chlorination of 2,3-dimethylbutane in the presence of increasingly fluorinated benzenes results from a combination of three factors: lower rate of complex formation; higher rate of complex dissociation; and lower intrinsic selectivity of the complex.

## Experimental Section

Procedures for sample preparation and VPC analysis were described recently.[4] The fluorinated benzenes were available commercially (Aldrich); they were used as received, after first checking their purities by VPC Only 1,3,5-trifluorobenzene had purity <99.5%; its purity was between 98% and 99% (two different lots). A list of the reactant concentrations and observed selectivities (Table II) is available from N.J.B.

The multiple regression analysis was based on a group of subroutines (MLREGR) written by R. A. LaBudde and modified by R. J. LeRoy and J. E. Grabenstetter. A driver program written by C. L. Forber of our laboratory was used to convert the observed quantities [DMB], [ArH], and S into the form required by MLREGR. This involved obtaining the analytical forms of the partial derivatives $\delta S^m/\delta(k_4/k_6)$, $\delta S^m/\delta(k_5/k_6)$, and $\delta S^m/\delta(k_3/k_2)$. Values of these partial derivatives were obtained from trial values of the rate constant ratios. The program was run iteratively so that the "best" values of the rate constant ratios were those that minimized the partial derivatives.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial support and C. L. Forber for assistance with the multiple regression analysis.

**Registry No.** 2,4-Dimethylbutane, 79-29-8; fluorobenzene, 462-06-6; 1,4-diflurobenzene, 540-36-3; 1,3,5-trifluorobenzene, 372-38-3; hexafluorobenzene, 392-56-3.

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# Studies on the Reactivity of Carbon Monosulfide toward Amines and Thiols[1]

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*Received September 19, 1986*

Carbon monosulfide, CS, is a highly reactive gaseous species which in the absence of reaction partners rapidly polymerizes to a brown-black polymer.[3,4] CS has been known for almost a century, but due to the transient nature of CS it has mainly been subjected only to spectroscopic

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0022-3263/87/1952-1156$01.50/0 