and the resulting cloudy solution was extracted with four 100-ml. portions of ether. The ether extracts were dried with sodium sulfate and the solvent was removed to yield a bright yellow, oily solid. Crystallization from benzene–petroleum ether (b.p. 30–60°) gave 0.6 g. of a yellow solid, m.p. 97–101° (sintering). Two recrystallizations from cyclohexane, followed by one from ethanol–water (decolorized with Darco), gave an off-white solid having m.p. 108–109° (sintering), m.m.p. 109.5–110.5° (sintering) with authentic X as prepared above, and an infrared spectrum identical with that of X.

**3,6-Dimethylcatechol from IIb.**—A mixture of 30.8 g. (0.1 mole) of 3,6-bis(morpholinomethyl)catechol (IIb), 10 g. of 10% palladium on charcoal, and 200 ml. of ethanol was hydrogenated at 70° and 63 p.s.i. (initial pressure) in a Parr shaker. Reaction was complete in 7 hr., as indicated by a pressure drop equivalent to the consumption of 0.18 mole of hydrogen. Concentrated hydrochloric acid (20 ml.) was added to the reaction mixture which was then filtered. Removal of the solvent and addition of 300 ml. of water to the resulting oil gave a solid. The mixture was filtered and the solid washed with 100 ml. of water to yield, after drying, 4.6 g. of product, m.p. 99–100°. The combined filtrate and washings were extracted with three 100-ml. portions of ether. The ether extract, after it had been washed with 10 ml. of 5% sodium bicarbonate solution, was dried with sodium sulfate and stripped, to yield 7.4 g. (total yield 87%) of product, m.p. 95.5–99°. Recrystallization from benzene–ligroin (b.p. 66–75) gave pure material, m.p. 98.5–99.5° (lit.[17] m.p. 101°).

The **dibenzoate** was prepared and found to have m.p. 93–94.5° (lit.[17] m.p. 101°).

*Anal.* Calcd. for $C_{22}H_{18}O_4$: C, 76.3; H, 5.2. Found: C, 75.9; H, 5.3.

**3-Methylcatechol from IVa.**—A mixture of 133 g. (0.5 mole) of 3-acetoxymethylcatechol diacetate, 10 g. of 10% palladium on charcoal, and 100 ml. of ethanol was hydrogenated at 80° and 70 p.s.i. (initial pressure) in a Parr shaker for 5.5 hr. Filtration and removal of the solvent gave a light yellow oil. This was dissolved in 200 ml. of 5% methanolic hydrogen chloride which was then removed on a steam bath under reduced pressure. This was repeated using methanol and once again using methanol at atmospheric pressure. The resulting dark oil was distilled to give 43 g. of crude product, b.p. 120–134° (8 mm.). Seeding with authentic 3-methylcatechol gave a pasty solid which was recrystallized from benzene and then cyclohexane to give a white solid, m.p. 63–64.5°, whose infrared spectrum was superimposable on that of authentic 3-methylcatechol. The dibenzoate was prepared (m.p. 119–120.5°) and its infrared spectrum was found to be identical with that of an authentic sample (see below).

**3-Methylcatechol**[18] was purified by distillation, followed by recrystallization from benzene, and had m.p. 65–66.5° (lit.[19] m.p. 58–62°). The **dibenzoate** was prepared and had m.p. 120–122° (lit.[20] m.p. 122°).

*Anal.* Calcd. for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8. Found: C, 75.6; H, 5.0.

**4-Methylcatechol**[17] (m.p. 63.5–67°) was converted to the dibenzoate, m.p. 63–65°.

*Anal.* Calcd. for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8. Found: C, 75.5; H, 4.9.

**Acknowledgment.**—We gratefully acknowledge the assistance of Miss Jane O. Fournier, Dr. O. E. Schupp, Mrs. Irene H. S. So, and Mr. J. W. Westman.

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[17] W. Baker, H. F. Bondy, J. Gumb, and D. Miles, *J. Chem. Soc.*, 1615 (1953).

[18] Purchased from Aldrich Chemical Co.

[19] D. H. Rosenblatt, J. Epstein, and M. Levitch, *J. Am. Chem. Soc.*, **75**, 3277 (1953).

[20] L. Vargha and G. Ocskay, *Tetrahedron*, **2**, 151 (1958).

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# London Force Interactions in the Reactions of Benzyl Chlorides

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The rates of reaction of the nucleophiles $I^-$, $C_6H_4S^-$, and $CH_3O^-$ with substituted benzyl chlorides have been determined. Calculations of the magnitude of London forces operative in the transition state indicate that the changes in rate ratios may be attributed to these forces for *ortho* substituents.

The effect of London forces on equilibria and reaction rates has been recognized by a number of authors. Pitzer and Donath[2] have refined the calculations of conformation and strain energy of hydrocarbons by including interactions of nonbonded atoms. Bunnett[3] suggested the operation of these forces in nucleophilic substitution reactions in a theoretical paper, and Reinheimer and Bunnett[4] and Lewis and Suhr[5] invoked London forces to explain reaction rate ratios and the order of halogen replacements in aromatic nucleophilic substitutions, respectively. Quantitative estimates of these forces in the transition states of halogen-exchange reactions of methyl halides were given by Spinner.[6] Bunnett and Reinheimer[7] have estimated these forces in the reactions of *ortho*-substituted benzyl chlorides with methoxide, thiophenoxide, and iodide ions. This paper reports the results of studies of the reactions of these nucleophiles with the isomeric *meta*- and *para*-substituted benzyl chlorides, and, by a new method of comparing the rates, a better correlation of theory and experiment is obtained.

## Results

The reaction rate constants and thermodynamic properties of the nucleophilic displacements of chloride from *meta*- and *para*-substituted benzyl chlorides are given in Tables I and II. The results of duplicate runs are given and indicate that the reproducibility is about ±2%. Comparison of the results with the literature shows moderate agreement. Extrapolated results of Bennett and Jones[8] give $k_2 = 144 \times 10^{-5}$ l./mole sec. for the reaction of KI with *p*-bromobenzyl chloride and $115 \times 10^{-5}$ for the reaction with the *m*-bromo compound at 25°. Our values of $108 \times 10^{-5}$ and $98 \times 10^{-5}$ l./mole sec. are somewhat lower. Charlton and Hughes[9] give $5.1 \times 10^{-5}$ and $5.46 \times 10^{-5}$ l./mole sec. for the same reaction with the *p*-methyl

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[1] Support of the National Science Foundation, Grant NSF-G3112, is gratefully acknowledged.

[2] K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1939).

[3] J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

[4] J. D. Reinheimer and J. F. Bunnett, *ibid.*, **81**, 315 (1959).

[5] E. S. Lewis and H. Suhr, *ibid.*, **82**, 862 (1960).

[6] E. Spinner, *Australian J. Chem.*, **13**, 218 (1960).

[7] J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

[8] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

[9] J. C. Charlton and E. D. Hughes, *ibid.*, 855 (1956).

TABLE I

RATE CONSTANTS FOR REACTIONS OF SUBSTITUTED BENZYL CHLORIDES

($k_2 \times 10^5$ l./mole sec.)

| Substituent | Reagent | Temp., °C. 0.0 | 25.00 | 46.25 | 49.35 |
|---|---|---|---|---|---|
| H | $LiOCH_3$ | | 2.47, 2.42 | 28.6, 27.7 | |
| | $LiSC_6H_5$ | | 2280, 2270 | 14900, 15500 | |
| | KI | | 58.0, 58.7 | | |
| | NaI | | 55.1 | | |
| | MeOH$^a$ | | 0.0062 | 0.077 | |
| $m$-$CH_3$ | $LiOCH_3$ | | 2.89, 2.86, 2.91 | | 52.1, 52.7 |
| | $LiSC_6H_5$ | 272, 295 | 3730, 3700 | | |
| | NaI | | 49.9, 48.7 | | 550, 557 |
| | MeOH$^a$ | | 0.0032, 0.0037 | | 0.0658, 0.0650, 0.0665 |
| $p$-$CH_3$ | $LiOCH_3$ | | 5.03, 4.88, 4.78 | | 76.9, 78.7 |
| | $LiSC_6H_5$ | 352, 338 | 4470, 4460 | | |
| | NaI | | 67.8, 65.5 | | 705, 722 |
| | MeOH$^a$ | | 0.0120, 0.0138 | 0.188, 0.175, 0.188 | |
| $m$-Br | $LiOCH_3$ | | 2.29, 2.42 | | 44.0, 43.0 |
| | $LiSC_6H_5$ | 354 | 4850, 4960 | | |
| | NaI | | 97.8, 98.4 | | 1050, 1040, 1041 |
| | MeOH$^a$ | | 0.0017$^b$ | | 0.021$^b$ |
| $p$-Br | $LiOCH_3$ | | 3.01, 3.10 | | 62.3, 61.7 |
| | $LiSC_6H_5$ | 402, 405 | 5640, 5440 | | |
| | NaI | | 108, 105, 110 | | 1190, 1240 |
| | MeOH$^a$ | | 0.0052$^b$ | | 0.065$^b$ |

[a] First-order rate constant, $k_1 \times 10^6$ in sec.$^{-1}$. [b] $k_1$ estimated (see text).

TABLE II

THERMODYNAMIC PROPERTIES OF REACTIONS OF SUBSTITUTED BENZYL CHLORIDES[a]

| Substituent | Reagent | $\Delta F^*$, kcal./mole | $\Delta H^*$, kcal./mole | $\Delta S^*$, e.u. |
|---|---|---|---|---|
| H | $LiOCH_3$ | 23.74 | 21.18 | −8.7 |
| | $LiSC_6H_5$ | 19.69 | 16.28 | −11.4 |
| | KI | 21.86 | 17.71 | −14.0 |
| $m$-$CH_3$ | $LiOCH_3$ | 23.64 | 22.18 | −4.9 |
| | $LiSC_6H_5$ | 19.41 | 16.09 | −11.1 |
| | KI | 21.96 | 18.44 | −11.8 |
| $p$-$CH_3$ | $LiOCH_3$ | 23.33 | 21.17 | −7.2 |
| | $LiSC_6H_5$ | 19.28 | 16.13 | −10.6 |
| | KI | 21.78 | 18.05 | −12.5 |
| $m$-Br | $LiOCH_3$ | 23.76 | 22.23 | −5.1 |
| | $LiSC_6H_5$ | 19.24 | 16.42 | −9.5 |
| | KI | 21.55 | 17.99 | −12.0 |
| $p$-Br | $LiOCH_3$ | 23.61 | 22.92 | −2.3 |
| | $LiSC_6H_5$ | 19.16 | 16.38 | −9.3 |
| | KI | 21.50 | 18.48 | −10.1 |

[a] At 25°.

compound at 0°. Their variation is due to varying initial concentrations. Extrapolation of our results to this temperature gives a value of $k_2 = 3.3 \times 10^{-5}$ l./mole sec.

We have considerable confidence in our results since the isomeric xylenes were carefully purified before chlorination by a sulfonation procedure given in Weissberger[10] and gas chromatographic analysis of the benzyl chlorides provided evidence that the materials were at least 99% pure. Before the kinetic experiments with the substituted compounds were performed, the reaction rate of the nucleophile with benzyl chloride was measured. When the rate constant was found to be in agreement with the literature value, it was judged that the analytical methods were accurate and the reagent concentrations correct. Isolation of the expected products from the reaction mixtures is reported in detail in the Experimental section.

## Discussion

**Calculation of London Forces between Nucleophiles and Substituents in the Transition State.**—London forces were evaluated using the approximate eq. 1 given by Pitzer[11] and others.[7]

$$W_{ab} \approx \frac{3\alpha_a\alpha_b}{2r^6}\left(\frac{I_aI_b}{I_a + I_b}\right) \times 2.1 \qquad (1)$$

$I_a$ and $I_b$ are the ionization potentials; $\alpha_a$ and $\alpha_b$ are the polarizabilities of the nucleophile and the substituent, respectively; and $r$ is the distance between the atomic centers. The values of $I$ and $\alpha$ used in the formula and the bond lengths used in the trigonometric calculation of $r$ are given in Table III.

TABLE III

Values of Constants Used in Eq. 1

| | Br | $CH_3$ | H | $O^{-1/2}$ | $S^{-1/2}$ | $I^{-1/2}$ |
|---|---|---|---|---|---|---|
| $\alpha$, Å.$^3$/mole | 3.34 | 2.19 | 0.42 | 1.44 | 3.36 | 6.34 |
| $I$, kcal./mole | 265 | 258 | 312 | 180 | 150 | 158 |

Bond Lengths Used in Calculation of $r$ in Eq. 1

| Bond | Length, Å. | Bond | Length, Å. |
|---|---|---|---|
| C—C (aromatic) | 1.39 | $C \cdots I^{-1/2}$ | 2.53 |
| C—C (benzylic) | 1.54 | $C \cdots S^{-1/2}$ | 2.34 |
| C—H | 1.10 | $C \cdots O^{-1/2}$ | 1.87 |
| C—Br | 1.89 | | |

The transition state that was assumed is given in Fig. 1. The entering and leaving groups are on a line through the benzylic carbon perpendicular to the

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(10) A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955, p. 321 ff.

(11) K. S. Pitzer, "Quantum Chemistry," Prentice Hall, Inc., New York, N. Y., 1953, pp. 198–201; K. S. Pitzer, "Advances in Chemical Physics," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1959, p. 59 ff.

plane of the benzene ring. The bond lengths are assumed to have their normal covalent values except the $N^{-1/2}\cdots\cdot C$ and $C\cdots\cdot Cl^{-1/2}$ bonds. The $N^{-1/2}\cdots\cdot C$ was taken to be the sum of the covalent radius of carbon and the average of the covalent and ionic radii of the $O^-$, $S^-$, or $I^-$ groups. The radii and the polarizabilities were taken from Rice[12] and Ingold.[13] The polarizability and ionization potential of the $N^{-1/2}$ in the transition state were taken as the average of those of the corresponding atom and ion.

The choice of an ionization potential for the methyl substituent was difficult. The ionization potential of the methyl radical has been given[14] as 230 kcal./mole, while those of the carbon and hydrogen atoms are 258 and 312 kcal./mole, respectively. Since the substituent is not a methyl *radical*, the value of 258 kcal./mole, the smaller value of the methyl group constituents, was used. Calculation of London forces with both values indicates that the choice of a value is not critical, for the above 11% change (from 230 to 258) gives less than half that per cent change in London forces. Other authors have made similar arbitrary assumptions concerning the value of ionization potentials. Brown[15] assigned a value of 100 to the factor $(I_aI_b)/(I_a + I_b)$, and Bunnett[7] used a value of 225 kcal./mole for the *o*-methyl substituent.

**Derivation of a Quantitative Relationship between London Forces and Rate Constants.**—Applying the theory of extrathermodynamic relationships as described recently by Leffler and Grunwald[16] to substituent effects may be (to a first approximation) considered a linear combination of independent effects. Equation 2 may be assumed, where the total relative activation energy is a sum of effects due to polar, steric,

$$\Delta\Delta F^* = \Delta\Delta F^*_{\text{pol}} + \Delta\Delta F^*_{\text{st}} + \Delta\Delta F^*_{\text{Lon}} \quad (2)$$

and London force interactions. The thermodynamic theory of the transition state relates the ratio of rates of reaction of a substituted and an unsubstituted substrate to the relative free energy of activation by eq. 3[17] where $k_X/k_H$ is the ratio of respective rates.

$$\Delta\Delta F^* = \Delta F^*_X - \Delta F^*_H = -2.3RT \log k_X/k_H \quad (3)$$

If we make the assumption that polar effects are equal in the *ortho* and *para* positions, that is, that $\Delta\Delta F^*_{\text{pol}(o\text{-X})} - \Delta\Delta F^*_{\text{pol}(p\text{-X})} = 0$, eq. 4 follows from subtraction of the correspondingly defined forms of eq. 2.

$$\begin{aligned}\Delta\Delta\Delta F^* &= \Delta\Delta F^*_{o\text{-X}} - \Delta\Delta F^*_{p\text{-X}} \\ &= [\Delta\Delta F^*_{\text{st}(o\text{-X})} - \Delta\Delta F^*_{\text{st}(p\text{-X})}] + \\ &\quad [\Delta\Delta F^*_{\text{Lon}(o\text{-X})} - \Delta\Delta F^*_{\text{Lon}(p\text{-X})}] \\ &= \Delta\Delta\Delta F^*_{\text{st}} + \Delta\Delta\Delta F^*_{\text{Lon}} \end{aligned} \quad (4)$$

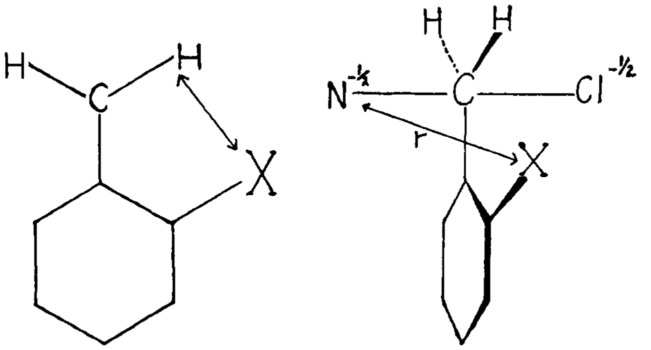

Figure 1.

Similarly, from eq. 3 follows eq. 5.

$$\begin{aligned}\Delta\Delta\Delta F^* &= -2.3RT\,[\log (k_{o\text{-X}}/k_H) - \log (k_{p\text{-X}}/k_H)] \\ &= -2.3RT \log (k_{o\text{-X}}/k_{p\text{-X}}) \end{aligned} \quad (5)$$

Partial justification of the assumption that $\Delta\Delta\Delta F^*_{\text{pol}} = 0$ has been given by Taft[18] in his derivation of polar substituent constants for *ortho* substituents, and numerous examples of limited demonstrations[19] and applications[20] of this principle exist.

To eliminate steric effects on the rate ratios and further limit the London-force interactions included in the total free-energy difference, a final comparison is made, that of values of $\Delta\Delta\Delta F^*$ for various nucleophiles (eq. 6 and 7).

$$-2.3RT \log (k_o/k_p)N'',X/(k_o/k_p)N',X = \Delta\Delta\Delta F^*_{N''} - \Delta\Delta\Delta F^*_{N'} = \Delta\Delta\Delta\Delta F^* \quad (6)$$

Also

$$\begin{aligned}\Delta\Delta\Delta\Delta F^* &= (\Delta\Delta\Delta F^*_{\text{Lon}\,N''} - \Delta\Delta\Delta F^*_{\text{Lon}\,N'}) + \\ &\quad (\Delta\Delta\Delta F^*_{\text{st}\,N''} - \Delta\Delta\Delta F^*_{\text{st}\,N'}) \\ &= \Delta\Delta\Delta\Delta F^*_{\text{Lon}} \end{aligned} \quad (7)$$

if $\Delta\Delta\Delta\Delta F^*_{\text{st}} = 0$

This assumption is similar to that made by Taft[18] in his evaluation of polar substituent constants if one assumes that the steric interaction is between the *ortho* substituent and the nearest benzylic hydrogen in the transition state, a distance of approximately 2.5 Å. (Fig. 1b).

A further important result of this last comparison is the elimination (assumed) of London force effects due to interaction between the substituent and the leaving chloride, as well as ground-state interactions of this type. Thus, comparison need only be made of London forces between the nucleophile and the substituent in the transition state to evaluate $\Delta\Delta\Delta\Delta F^*_{\text{Lon}}$ in eq. 7. Values of $F_{\text{Lon}}$ from eq. 1 are given in Table IV. Values of $\Delta\Delta\Delta\Delta F^*_{\text{Lon}}$ calculated as defined in equations above are given in Table V along with the corresponding values of $\Delta\Delta\Delta\Delta F^*$ calculated by eq. 6 and Table VI. N′ is taken as $CH_3O^-$ and N″ as $I^-$ and $C_6H_5S^-$.

As seen in Table VI and in Fig. 2, which is a graph of Table VI, there is a linear relationship between $\Delta\Delta\Delta\Delta F^*$ and $\Delta\Delta\Delta\Delta F^*_{\text{Lon}}$, although the two *ortho* substituents give different slopes to the lines through the three nucleophiles. This is not unexpected as eq.

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(12) O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 178, 259.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 121.

(14) F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1490 (1954).

(15) T. L. Brown, *J. Am. Chem. Soc.*, **81**, 3229 (1959).

(16) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 135–147; see also R. E. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 559–659.

(17) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 566.

(18) R. W. Taft, *J. Am. Chem. Soc.*, **75**, 4231 (1953), and references therein.

(19) See for examples (a) H. C. Brown and X. R. Mihm, *ibid.*, **77**, 1724 (1955); (b) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 247 (1961).

(20) See for examples (a) K. U. Ingold, *Can. J. Chem.*, **40**, 111 (1962); (b) K. Yates and B. F. Scott, *ibid.*, **41**, 2320 (1963).

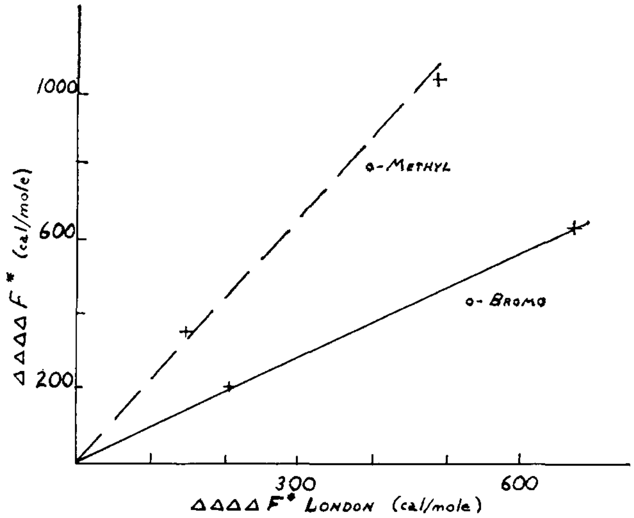

Fig. 2.—Comparison of $\Delta\Delta\Delta\Delta F^*$ (from rates) and $\Delta\Delta\Delta\Delta F^*$ London (calculated) for the reactions of substituted benzyl halides with $OCH_3^-$, $PhS^-$, and $I^-$.

TABLE IV

ENERGY OF TRANSITION-STATE LONDON FORCES BETWEEN SUBSTITUENT AND NUCLEOPHILE[a]

| Substituent | Nucleophile | | | |
|---|---|---|---|---|
| | $CH_3O^-$ | $C_6H_5S^-$ | $I^-$ | $Cl^-$ |
| o-H | 163 | 207 | 318 | |
| m-H | 13 | 21 | 34 | |
| p-H | 6 | 11 | 22 | |
| o-Me | 598 | 801 | 1264 | |
| p-Me | 22 | 35 | 63 | |
| o-Br | 701 | 963 | 1565 | |
| m-Br | 52 | 83 | 148 | |
| p-Br | 22 | 40 | 72 | |

[a] Values in cal./mole.

TABLE V

EXPERIMENTAL $\Delta\Delta\Delta\Delta F^*$ AND CALCULATED LONDON FORCES

| Substituent | Nucleophile (N'') | $\Delta\Delta\Delta\Delta F^*$, cal./mole | $\Delta\Delta\Delta\Delta F^*_{Lon}$, cal./mole |
|---|---|---|---|
| o-Me | $CH_3O^-$ | 0 | 0 |
| o-Me | $C_6H_5S^-$ | 354 | 151 |
| o-Me | $I^-$ | 1025 | 485 |
| o-Br | $CH_3O^-$ | 0 | 0 |
| o-Br | $C_6H_5S^-$ | 200 | 205 |
| o-Br | $I^-$ | 634 | 675 |

TABLE VI

RATE CONSTANT RATIOS FOR VARIOUS COMBINATIONS OF NUCLEOPHILE AND SUBSTITUENT AND CORRESPONDING $\Delta\Delta\Delta F^*$ VALUES IN EQ. 5

| Substituent | Nucleophile | $k_o/k_p$ | $\Delta\Delta\Delta F^*$, cal. |
|---|---|---|---|
| H | All | 1.00 | 0 |
| $CH_3$ | $CH_3O^-$ | 1.43 | −212 |
| | $C_6H_5S^-$ | 2.61 | −566 |
| | $I^-$ | 8.16 | −1267 |
| Br | $CH_3O^-$ | 0.84 | +103 |
| | $C_6H_5S^-$ | 1.18 | −97 |
| | $I^-$ | 2.45 | −531 |

1 is only approximate and errors resulting from its use have been noted before.[11] As an example, a factor of 2.1 has been introduced as a correction.[11b,7]

Another possible cause of these deviations from equality lies in the assumptions made in calculating the values of constants given in Table III and used in eq. 1. $F_{Lon}^*$ is particularly dependent upon values of $r$ assumed.

The only previous analysis of this system[7] was based on the assumption of equal values of $\rho$ for the reactions of benzyl chlorides with various nucleophiles. As has been demonstrated by Klopman and Hudson,[21] this is almost certainly not the case; in fact, in most cases a value of $\rho$ cannot be determined owing to a pronounced curvature in the Hammett plot. The present derivation assumes either the equivalence of $\sigma_p$ and $\sigma^*$ or $\rho$ and $\rho^*$, properties which have been substantiated by Taft.[16b]

That the observed trend is not due to a steric effect is supported by the fact that the substituents used are of nearly equal size.[22] Further, it has been shown[9] that the reaction studied is retarded by the steric effects of *ortho* substituents.

One problem with this analysis is the omission of the London forces of solvation. These forces are not negligible in either the ground state or in the transition state. Since the $I^-$ rates were determined in acetone and those for $PhS^-$ and $^-OCH_3$ in MeOH, gross differences in London forces of solvation are expected. These forces must be eliminated, otherwise those points in Fig. 2 for the $I^-$ rates should deviate greatly from the linear relationship. A tentative explanation of this cancellation lies in the process of taking ratios for a given nucleophile. This process eliminates the London forces of solvation due to the nucleophile. If we write $\Delta\Delta\Delta L$ solvation $= (L_{\text{trans-}o} - L_{\text{ground-}o}) - (L_{\text{trans-}p} - L_{\text{ground-}p})$, then $\Delta\Delta\Delta L$ solvation will be zero if (a) $L_{\text{t-}o}$, $L_{\text{g-}p}$, etc. are each equal to zero; or (b) if the first term equals the second; or (c) if $L_{\text{t-}o} = L_{\text{t-}p}$ and $L_{\text{g-}o} = L_{\text{g-}p}$. Of these possibilities, (a) is trivial and unreasonable in that it denies the existence of solvation; (c) seems unlikely, for the number of molecules of solvation should not be the same for both *ortho* and *para* isomers; (b) is the most reasonable of the three. It states that the change in solvation for the *ortho* isomer is the same as the change in solvation for the *para* isomer for these reactions.

The results of this study have also an advantage over the previous analysis[3] that London-force interactions are not required in the *para* and *meta* positions. In fact, it is shown that they are so small in these positions (5–10% of the *ortho* effect) as to be nearly negligible.

Since the final plot of experimental *vs.* theoretical relative free energies shows reasonable correlation, it seems reasonable that London forces may be operable as a significant effect for *ortho* substituents.

## Experimental

**Preparation and Purification of Materials.**—The *m*- and *p*-methylbenzyl chlorides were prepared by the method of Kharasch and Brown,[23] and were purified by fractionation through a spinning-band column: *m*-methylbenzyl chloride, b.p. 67.0–67.5° (5.5 mm.), $n^{25}D$ 1.5320 [lit.[24] b.p. 79.5° (11 mm.), $n^{25}D$ 1.5333]; *p*-

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[21] G. Klopman and R. F. Hudson, *Helv. Chim. Acta*, **44**, 1914 (1961).

[22] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 189.

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methylbenzyl chloride, b.p. 68.5–69° (6 mm.), $n^{25}\text{D}$ 1.5311 [lit.[25] b.p. 76° (9.5 mm.), $n^{25}\text{D}$ 1.5320].

The *p*-bromobenzyl chloride was prepared by the method of Goerner and Nametz.[26] The melting point of the white crystals obtained after repeated recrystallizations from petroleum ether was 38–39°, lit.[26] m.p. 40–41°.

The *m*-bromobenzyl chloride was prepared by the method given by Swain.[27] The product was vacuum distilled as above: b.p. 95.9–96.5° (7 mm.), $n^{25}\text{D}$ –1.5815; lit.[28] b.p. 111–120° (15 mm.). Each of the benzyl chlorides was tested for purity by vapor phase chromatography. No impurities were detected in either of the methyl benzyl chlorides or in the *m*-bromobenzyl chloride. Approximately 1% impurity was noted in the *p*-bromobenzyl chloride. The thiophenol, reagent grade, was distilled through a 24-in. packed, silvered, vacuum-jacketed column: b.p. 168–169°, lit.[29] b.p. 169.5°. The solvents, methanol and acetone, were dried over Drierite for at least 24 hr. and distilled from fresh Drierite. Lithium methoxide was prepared in solution by adding clean lithium metal to methanol.

**Rate Measurements. With Sodium Iodide.**—Runs at 25° were carried out in glass-stoppered volumetric flasks in a water bath regulated to ±0.1°. The benzyl chloride was weighed into the flask and dissolved in acetone. Ten milliliters of a standardized solution of sodium iodide in acetone was added, and the mixture was diluted to the mark. Ten-milliliter samples were taken at intervals and released into beakers containing 10 ml. of water and 15 ml. of ethyl ether. The aqueous layer was separated and titrated potentiometrically for iodide ion content with $AgNO_3$. Runs at 50° were carried out in sealed Pyrex test tubes each containing 10 ml. of reaction mixture. The concentrations of the reactants were equal and this concentration was 0.035 to 0.040 *M* for most experiments.

**With Lithium Methoxide.**—All runs were carried out in glass-stoppered volumetric flasks in a constant-temperature water bath. The benzyl chloride was weighed into the volumetric flask and dissolved in methanol. Ten milliliters of a standardized concentrated lithium methoxide solution was added and the mixture was diluted to the mark. Ten-milliliter samples were taken and released into beakers containing 10 ml. of 0.1 *N* $HNO_3$ and 15 ml. of ether. The aqueous layer was separated and titrated potentiometrically for chloride ion content with $AgNO_3$. The concentrations of the reagents were equal and this concentration was 0.033 to 0.039 *M* for most experiments.

**With Lithium Thiophenoxide.**—Runs at 25° were carried out in 100-ml. round-bottom flasks. Twenty milliliters of standardized solution of lithium methoxide was added to a slight (10%) excess of thiophenol in the flask, 25 ml. of methanol was added to dilute the solution, and finally 5 ml. of a solution of the benzyl chloride in methanol was added. Five-milliliter samples were taken with a constant-delivery syringe and were discharged into beakers containing 20 ml. of 1.0 *N* $H_2SO_4$ and 15 ml. of ether. The aqueous layer was separated and titrated potentiometrically for chloride ion. Runs at 0° were carried out in glass-stoppered volumetric flasks and sampling was done with a 5-ml. pipet. The concentrations of the reagents were equal and the concentration was 0.036 *M* for most experiments.

**Evaluation of Rate Constants.**—For reactions with sodium iodide, the rate constants were determined from the slopes of plots of $1/[I^-]$ *vs.* time. Linear plots to 40% reaction were obtained and precision in duplicate runs was 2–3%. Beyond 40% reaction the observed rate generally decreased, and infinity titrations after 20 half-lives indicated the establishment of an equilibrium; *e.g.*, with *p*-methylbenzyl chloride at 50°, reaction gives 86% products. The corresponding equilibrium constant is 6.8 × $10^{-2}$. The solubility of NaCl in acetone was determined to be 6.1 × $10^{-5}$ *N* at 50°, lit.[30] 6.4 × $10^{-5}$ *M*. For the reactions with lithium methoxide and thiophenoxide, the quantity $([\text{RCl}]_0 - [\text{Cl}^-])^{-1}$ was plotted *vs.* time, the slope being equal to the rate constant. For the solvolysis in methanol, rate constants were either calculated from the slopes of plots of log $([\text{RCl}]_0 - [\text{Cl}^-])$ *vs.* time or estimated from corresponding data on these and similar compounds (see Table III). Rate constants observed for lithium methoxide runs are composites of the methoxide and solvolysis reactions. To correct the observed rate constant for solvolysis, the quantity $k_1/[\text{RCl}]_0$ is subtracted from each, where $k_1$ is the pseudo-first-order rate constant for the solvolysis.[7] Rate constants observed for sodium iodide runs at 50° were corrected for solvent expansion and the resulting concentration decrease since the volumes were apportioned at room temperature. This correction factor, 1.037, is the ratio of the densities of the solvent at the two temperatures.[31] The concentration of the RCl was varied so that $[\text{RCl}] = 0.5[\text{I}^-]$. The rate constants for these experiments compared within experimental error with those in which $[\text{RCl}] = [\text{I}^-]$. A similar set of experiments with the nucleophile $LiOCH_3$ gave a similar satisfactory result. Since the $PhS^-$ was made from the standard $LiOCH_3$ solution, no experiments were made in which RCl was varied.

**Isolation of Products. From Iodide Runs.**—The products of the reactions of the bromobenzyl chlorides with iodide ion in acetone were isolated from the ether layer of the extraction of the reaction mixture. The products were white crystals after recrystallization from ether: *m*-bromobenzyl iodide, m.p. 40–41°, lit.[32] m.p. 42°; *p*-bromobenzyl iodide, m.p. 68–69°, lit.[32] m.p. 73°.

**From Methoxide Runs.**—The products were isolated for each benzyl halide reaction with methoxide ion in methanol: *m*-methylbenzyl methyl ether, b.p. 190° (738 mm.), $n^{25}\text{D}$ 1.5042; *p*-methylbenzyl methyl ether, b.p. 190–191° (738 mm.), $n^{25}\text{D}$ 1.5018 (lit.[33] b.p. 196°, $n^{25}\text{D}$ 1.4990[34]); *m*-bromobenzyl methyl ether, b.p. 227° (738 mm.), $n^{25}\text{D}$ 1.5468 (no literature values at atmospheric pressure); *p*-bromobenzyl methyl ether, b.p. 228° (738 mm.), $n^{25}\text{D}$ 1.5478 (lit.[35] b.p. 235°).

**From Thiophenoxide Runs.**—The products of the reactions of the *para*-substituted benzyl chlorides with thiophenoxide ion were isolated directly from the reaction mixture as solids: *p*-methylbenzyl phenyl sulfide, white crystals from methanol, m.p. 69–70°; *p*-bromobenzyl phenyl sulfide, shiny white flakes from methanol, m.p. 78–79°. The *m*-methylbenzyl phenyl sulfide was isolated as an impure liquid from an ether extract of its reaction mixture. Approximately 1 g. of the *p*-bromobenzyl phenyl sulfide and 0.7 gm. of each of the methylbenzyl phenyl sulfides were treated with 5 ml. of 30% $H_2O_2$ in 10 ml. of glacial acetic acid at 100° for 1 hr. Solid products precipitated from each of the oxidation reaction mixtures. The following products were filtered out and recrystallized from ethanol.

*p*-Methylbenzyl phenyl sulfone had m.p. 151–152°; infrared absorbtion at 1080 and 1140 cm.$^{-1}$ (lit.[36,37] m.p. 145°; infrared absorption[37] of benzyl phenyl sulfone at 1080, 1128, and 1155 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.72; S, 13.02. Found: C, 67.97; H, 5.62; S, 12.95.

*m*-Methylbenzyl phenyl sulfone had m.p. 120–121°; infrared at 1080, 1130, and 1155 cm.$^{-1}$ (lit.[36,37] m.p. 104–105°; infrared at 1080, 1128, and 1155 cm.$^{-1}$).

*Anal.* Calcd. for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.72, S, 13.02. Found: C, 67.90; H, 5.82; S, 13.05.

*p*-Bromobenzyl phenyl sulfone had m.p. 191–193°.

*Anal.* Calcd. for $C_{13}H_{11}BrSO_2$: C, 50.17; H, 3.56; S, 10.30. Found: C 50.16; H, 3.41; S, 10.42.

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