Unusual Solvent Effects on the *ortho*:*para* Ratio in the Chlorination of Anisole*[1]

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In the uncatalyzed molecular chlorination of aromatic compounds, no relationship has been observed between the *ortho*:*para* ratio and the dielectric constants of the media.[1] However, the present authors wish to report an interesting correlation between the dielectric constants of the solvents and the *ortho*:*para* ratios in the chlorination of anisole. Anisole was chlorinated[2] in a series of solvents; the logarithms of the *ortho*:*para* ratios are plotted against $1/\varepsilon$ in Fig. 1.

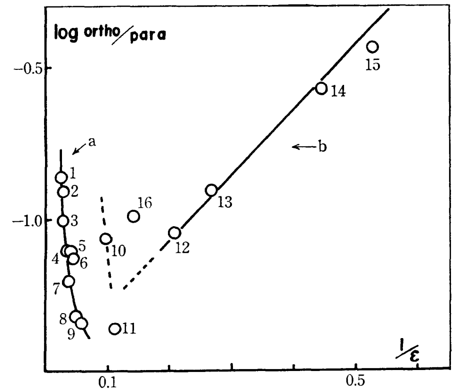
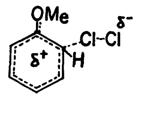


Fig. 1. Plot of log *o*/*p* against $1/\varepsilon$.
a: in alkyl cyanides and nitroalkanes; 1, $MeNO_2$; 2, MeCN; 3, DMF; 4, $EtNO_2$; 5, *iso*-$PrNO_2$; 6, *n*-$PrNO_2$; 7, EtCN; 8, *n*-PrCN; 9, *n*-BuCN.
b: in halogenated hydrocarbons; 10, $(CH_2Cl)_2$; 11, CH_2Cl_2; 12, $CHCl_3$; 13, $CHCl_2CCl_3$; 14, CCl_4; 15, *n*-C_6H_{14}; 16, *s*-BuCl.



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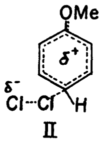
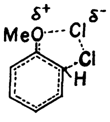


II



I'

The results show that: (1) in the aprotic media with relatively high dielectric constants, the *ortho*:*para* ratio decreases with a decrease in the dielectric constant, and (2) in the aprotic media with relatively low dielectric constants, the ratio increases unexpectedly with a decrease in the dielectric constant. These results can be interpreted qualitatively in terms of the following two factors; that is, (a) the difference in the solvation of the cationic moiety, $Ar^{\delta+}$, in I and II, and (b) the interaction of $\cdots Cl^{\delta-}$ with $\cdots O^{\delta+}{-}CH_3$ in the *ortho*-transition state, as in I′. In the chlorination of anisole, the positive charge generated during the activation process will delocalize more extensively in the transition state II than in I. Accordingly, I will be solvated more strongly than II, and the difference in solvation in these two species will become larger with an increase in the polarity of the medium. The observed increase in the *ortho*:*para* ratio with increase in the dielectric constant (curve a) may be mainly ascribable to this difference in solvation between I and II. The effect of pressure on the *ortho*:*para* ratio in aprotic solvents supports this suggestion.[3] The *ortho*:*para* ratios increase with an increase in the pressure in acetonitrile and DMF.[4] This means that the activation volume in *ortho* substitution is smaller than that in *para* substitution ($\delta\Delta V^{\neq} = -1.6$—$-2.4$ m*l*/mol[5]). This difference in the activation volumes must result from the difference in solvation between I and II.[6]

On the other hand, the *ortho*:*para* ratio decreases with an increase in the dielectric constants of media in halogenated hydrocarbons (curve b). This fact suggests that, in less polar solvents in this series, an additional stabilization of the *ortho*-transition state arises from an interaction between positively and negatively charged atoms in the molecule (I′). Such stabilization will become less important in more polar solvents. In the medium with a dielectric constant of about 9, the two effects, the difference in the solvation of $Ar^{\delta+}$ and the stabilization by the interaction between $\cdots Cl^{\delta-}$ and $\cdots O^{\delta+} - CH_3$ are balanced and the *ortho*: *para* ratio reaches its minimum value.[7]

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*1 Organic Reactions under High Pressure. V.

[1] L. M. Stock and A. Himoe, *Tetrahedron Lett.*, No. 13, 9 (1960).

[2] The molar ratio of anisole to chlorine was kept at *ca.* 2 in order to prevent disubstitution.

[3] Unpublished results.

[4] Iodobenzene dichloride was employed as a chlorine source; *cf.* R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **80**, 277 (1958).

[5] $\delta\Delta V^{\neq} = \Delta V^{\neq}_{(ortho)} - \Delta V^{\neq}_{(para)}$, at 1 atom.

[6] See T. Asano, This Bulletin, **42**, 2005 (1969).

[7] Such a minimum was not observed in the chlorination of toluene in halogenated hydrocarbons.[3]