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SOLVENT EFFECTS IN THE REACTIONS OF FREE RADICALS AND ATOMS—VI

SEPARATION OF POLAR AND RESONANCE EFFECTS IN THE REACTIONS OF CHLORINE ATOMS[1]

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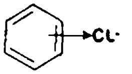
Abstract—Aromatic solvents have a large effect upon the reactivity of chlorine atoms toward carbon–hydrogen bonds having different bond dissociation energies. When the difference in reactivity of two carbon–hydrogen bonds is determined by polar effects, aromatic solvents have little effect upon the relative reactivities toward chlorine atoms. Two polar effects are important in the reactions of atoms and radicals with carbon–hydrogen bonds. When extensive bond rupture in the transition state occurs, a resonance contribution to the transition state involving charge separation is important (e.g. bromine atoms). For an atom as reactive as chlorine where little bond breaking occurs in the transition state, the polar effect is best considered in terms of a repulsion curve between the chlorine atom and the carbon–hydrogen bonds, repulsion being higher the lower the electron density of the carbon–hydrogen bond.

LARGE solvent effects have been observed in the competitive photochlorination of primary, secondary and tertiary carbon–hydrogen bonds.[2] Aromatic solvents have an effect proportional to their basicity suggesting the formation of a complexed chlorine atom which is more selective and less reactive than a free chlorine atom.



From a study of numerous chlorinations it was suggested that relative reactivities determined mainly by the availability of electrons in the carbon–hydrogen bonds (control by polar factors) are not particularly sensitive to solvent effects whereas relative reactivities determined mainly by the stabilities of the incipient free radicals (control by resonance factors) are very sensitive to changes in solvent. For example, the relative reactivities of the tertiary and primary hydrogen atoms of 2,3-dimethylbutane toward the chlorine atom at 25° increases from 4·2 : 1 in an aliphatic solvent to 20 : 1 in 4 M benzene to 225 : 1 in 12 M carbon disulfide.[2] Similarly, the relative reactivities of the secondary and primary hydrogens of n-pentane increase from 3·6 : 1 to 4·6 : 1 to 30 : 1. In both cases the strengths of the carbon–hydrogen bonds being ruptured are mainly responsible for the observed reactivities. On the other hand, when the relative reactivities of the hydrogen atoms of tetramethylsilane and trimethylchlorosilane are compared, the relative reactivity changes from 6·5 : 1 in an aliphatic solvent to 6·9 : 1 in 4 M t-butylbenzene to 5·1 in 12 M carbon disulfide. Although

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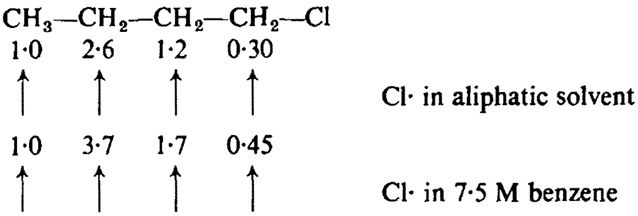
[1] Directive Effects in Aliphatic Substitutions—XIV.

[2] G. A. Russell, *J. Amer. Chem. Soc.* **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

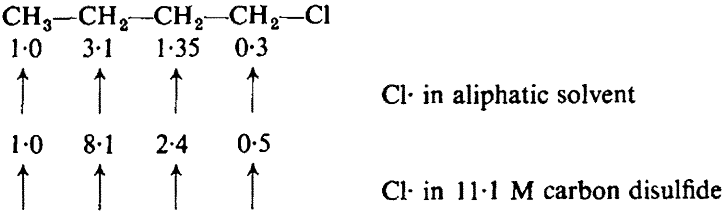
tetramethylsilane is considerably more reactive toward a chlorine atom than is trimethylchlorosilane, presumably because of the polar effect of the chlorine substituent, only a small effect of solvent upon relative reactivity was observed.

The suggestion that the relative importance of polar effects and resonance effects in determining reactivity toward a chlorine atom could be separated by observations of the magnitude of the solvent effect has been discussed by Walling and Mayahi[3] and has been recently criticized by den Hertog and Smit.[4] However, at the present time the available data is in good agreement with the afore-mentioned suggestion. Estimates of the magnitudes of the solvent effects observed can be obtained from the data of Walling and Mayahi.[3] Thus, in the photochlorination of n-butyl chloride at 68° the following relative reactivities per hydrogen atom can be calculated.



$$\begin{array}{ccccl}
\mathrm{CH_3}\text{—} & \mathrm{CH_2}\text{—} & \mathrm{CH_2}\text{—} & \mathrm{CH_2}\text{—Cl} & \\
1{\cdot}0 & 2{\cdot}6 & 1{\cdot}2 & 0{\cdot}30 & \\
\uparrow & \uparrow & \uparrow & \uparrow & \text{Cl· in aliphatic solvent} \\
1{\cdot}0 & 3{\cdot}7 & 1{\cdot}7 & 0{\cdot}45 & \\
\uparrow & \uparrow & \uparrow & \uparrow & \text{Cl· in 7·5 M benzene}
\end{array}$$

In the 3- and 4-positions relative reactivities are determined by differences in bond dissociation energies and an increase from 2·6 to 3·7 (an increase of 40 per cent) is noted between an aliphatic solvent and 7·5 M benzene. In the 3- and 2-positions the large difference in reactivity may be connected with the polar effect of the chlorine substituent. Here, however, the relative reactivities change only from 2·1 : 1 in an aliphatic solvent to 2·25 : 1 in 7·5 M benzene (a change of 7 per cent). Little effect of solvent is noted for the relative reactivities of the hydrogen atoms at the 1- and 2-positions. In the presence of carbon disulfide at 0° the following relative reactivities were observed.



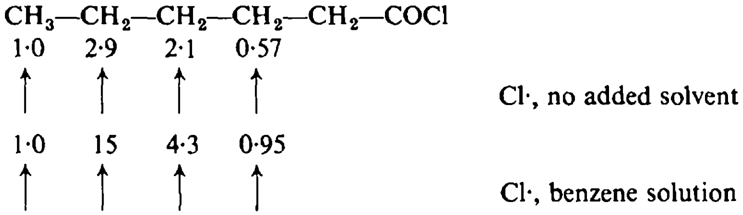
$$\begin{array}{ccccl}
\mathrm{CH_3}\text{—} & \mathrm{CH_2}\text{—} & \mathrm{CH_2}\text{—} & \mathrm{CH_2}\text{—Cl} & \\
1{\cdot}0 & 3{\cdot}1 & 1{\cdot}35 & 0{\cdot}3 & \\
\uparrow & \uparrow & \uparrow & \uparrow & \text{Cl· in aliphatic solvent} \\
1{\cdot}0 & 8{\cdot}1 & 2{\cdot}4 & 0{\cdot}5 & \\
\uparrow & \uparrow & \uparrow & \uparrow & \text{Cl· in 11·1 M carbon disulfide}
\end{array}$$

Again a large solvent effect upon the relative reactivities of the 3- and 4-hydrogen atoms was noted (an increase of 160 per cent). When the 3- and 2-positions are compared relative reactivity changes from 2·3 : 1 to 3·3 : 1 (a change of 45 per cent) while the relative reactivities at the 1- and 2-positions change only by 10 per cent. These results are in complete accord with one original suggestion.[2] The relative reactivities at the 1-, 2-, and possibly 3-positions are determined mainly by the polar effect of the chlorine substituent. The solvent effect upon the relative reactivities of the 3- and 4-hydrogens is 4–20 times as great as the solvent effect upon the relative reactivities of the 1-, 2- and 3-hydrogen atoms.

[3] C. Walling and M. F. Mayahi, *J. Amer. Chem. Soc.* **81**, 1485 (1959).

[4] H. J. den Hertog and P. Smit, *Proc. Chem. Soc.* 132 (1959).

The recent results of den Hertog and Smit[4] suggest a similar interpretation. They report that the relative reactivities of the α- and β-hydrogens of propionyl chloride (1 : 2·5) are relatively independent of solvent.[4] Here the relative reactivities are determined mainly by the polar effect since the primary hydrogen atom is considerably more reactive than the secondary hydrogen atom. We might expect aromatic solvents to increase the proportion of attack of the α-position (i.e., at the weakest carbon-hydrogen bond) and indications are that this is indeed the case.[5] From their reported products of the chlorination of hexanoyl chloride at 20° the following reactivities per hydrogen atom can be calculated.



$$\begin{array}{lllll} CH_3— & CH_2— & CH_2— & CH_2— & CH_2—COCl \\ 1{\cdot}0 & 2{\cdot}9 & 2{\cdot}1 & 0{\cdot}57 & \\ \uparrow & \uparrow & \uparrow & \uparrow & \text{Cl}\cdot\text{, no added solvent} \\ 1{\cdot}0 & 15 & 4{\cdot}3 & 0{\cdot}95 & \\ \uparrow & \uparrow & \uparrow & \uparrow & \text{Cl}\cdot\text{, benzene solution} \end{array}$$

Comparing the primary and secondary hydrogen atoms at the ε- and δ-positions indicates a solvent effect of 400 per cent upon the selectivity when the solvent is changed from the acid chloride itself to approximately 6·5 M benzene. When the relative reactivities of the β- and γ-hydrogens are compared only a small solvent effect is noted. Relative reactivities (γ : β) vary from 3·6 : 1 in an aliphatic solvent to 4·5 : 1 in benzene (a change of 25 per cent). This is consistent with our suggestion since den Hertog and Smit point out that the relative reactivities at the ε- and δ-positions are determined mainly by bond dissociation energies while the relative reactivities of the β- and γ-positions are determined mainly by polar effects.

The high reactivity of the δ-position in the presence of benzene (relative to the ε- or γ-positions) is surprising, and in view of the experimental uncertainties involved in the analysis of isomeric alkyl chlorides by distillation techniques, may be in error. By analogy with n-pentane,[2] n-butane[3] and n-butyl chloride[3] we might have expected the presence of 6·5 M benzene to increase the reactivity of the δ-hydrogen to about 6–7 times that of the ε-hydrogen rather than the 15-fold factor reported. The conclusion of den Hertog and Smit that solvents can have a pronounced effect on relative reactivities determined by the polar effect is based solely on the reactivity of the δ-position of hexanoyl chloride, and as mentioned earlier, is not supported when the β- and γ-positions are compared even though the difference in reactivity resulting from the polar effect is greater between the β- and γ-positions than between the γ- and δ-positions.

Variations in bond dissociations energies for the carbon hydrogen bonds in the 2- and 3-positions of n-butyl chloride and the γ- and δ-positions in n-hexanoyl chloride may be completely responsible for the solvent effects observed in the chlorination of these compounds. Fredericks and Tedder have recently reported rather compelling evidence that radicals with the structure $CH_3—\dot{C}H—CH_2—$ are more stable than radicals with the structure $—CH_2—\dot{C}H—CH_2—$, presumably because of hyperconjugative stabilization.[6] These workers were able to demonstrate that the chlorine atom of n-pentyl chloride has no deactivation effect upon hydrogen atoms in the 3-position.

[5] H. J. den Hertog, Private communication.

[6] P. J. Fredericks and J. M. Tedder, *Chem. & Ind.* 490 (1959).

However, because of the difference in bond dissociation energies the 4-position of n-pentyl chloride is 1·5 times as reactive as the 3-position toward a chlorine atom at 78° (vapor phase). Such behavior is consistent with the conclusion that in chlorination the relative reactivities of 2°- to 1°-hydrogen atoms decrease in the order propane > n-butane > n-pentane > n-hexane.[7]

Another factor that argues that solvent effects are not particularly important when the reactivities of the hydrogen atoms are determined by polar effects is that there is no consistency in the direction of the *small* effects observed. In the chlorination of n-hexanoyl chloride in benzene solution[4] or n-butyl chloride in carbon disulfide solution[3] the solvents appear to accentuate the polar effect whereas in the chlorination of n-butyl chloride at 68°,[3] the competitive chlorination of tetramethylsilane and trimethylchlorosilane,[2] and the competitive chlorination of toluene and *p*-chlorotoluene,[8] aromatic solvents decrease the importance of polar effects.* It is uncertain whether any significance can be attached to these small effects which fit no consistent pattern, particularly in view of the fact that the carbon–hydrogen bond dissociation energies involved are not known accurately.

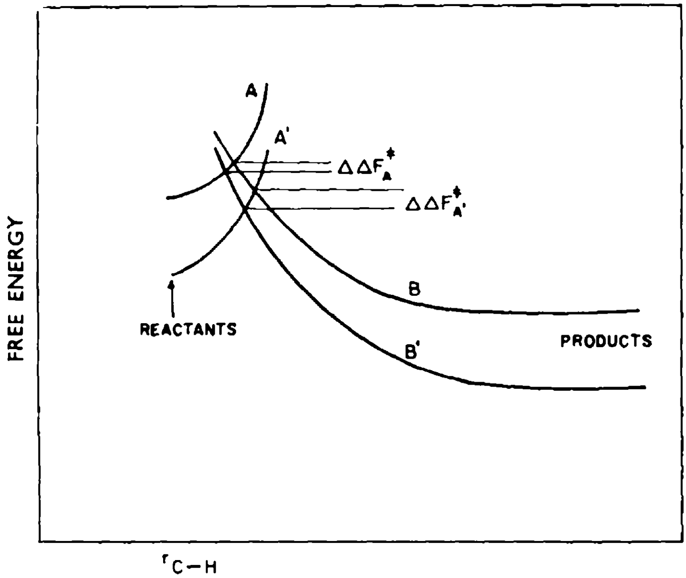


Fig. 1. Rationalization of solvent effect in reactions of chlorine atoms.

A rationalization of the effects of solvents upon the reactivity of carbon–hydrogen bonds can be made by use of energy diagrams. In Fig. 1 a possible diagram is given

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* *Note added in proof*, 1 *December* 1959:—A careful reinvestigation by Mr. Roger C. Williamson of the competitive chlorination of toluene and *p*-chlorotoluene has failed to reveal the solvent effect previously reported by Walling and Miller.[8] We find at 40° that the relative reactivities of the benzyl hydrogenatoms of toluene and *p*-chlorotoluene toward chlorine atoms are 1·26 ± 0·03 : 1 in carbon tetrachloride solution. At a constant toluene to *p*-chlorotoluene ratio of 1 : 2 this relative reactivity is independent of the total concentration of aromatic hydrocarbons between 0·05 and 1 M and of the percent reaction between 5 and 35 mole % chlorination. Chlorination of a 1 M solution of a 1 : 2 mole ratio of toluene and *p*-chlorotoluene in benzene at 40° gives a relative reactivity of 1·29 : 1, a value indistinguishable from the result observed in carbon tetrachloride solution.

[7] G. C. Chambers and A. R. Ubbelohde, *J. Chem. Soc.* 285 (1955); E. T. McBee, H. B. Hass and J. A. Pianfelli, *Industr. Engng. Chem.* **33**, 185 (1941).

[8] C. Walling and B. Miller, *J. Amer. Chem. Soc.* **79**, 4181 (1957).

for the attack of free (A) and complexed (A′) chlorine atoms upon two carbon-hydrogen bonds (B and B′) of different strengths but of the same electron density. Curve A is a repulsion curve between the free chlorine atom and either of the hydrogen atoms.[9] Curve A′ is the repulsion curve for the complexed chlorine atom and is displaced from A by the energy of complex formation. Curves B and B′ describe the repulsion between alkyl radical and hydrogen chloride as well as the differences in radical stabilization of the two alkyl radicals. Since $\Delta\Delta F^{\ddagger}_{A'} > \Delta\Delta F^{\ddagger}_{A}$, the complexed chlorine atom will be considerably more selective than the free chlorine atom and large solvent effects will be observed in the competitive chlorination of the two carbon-hydrogen bonds.

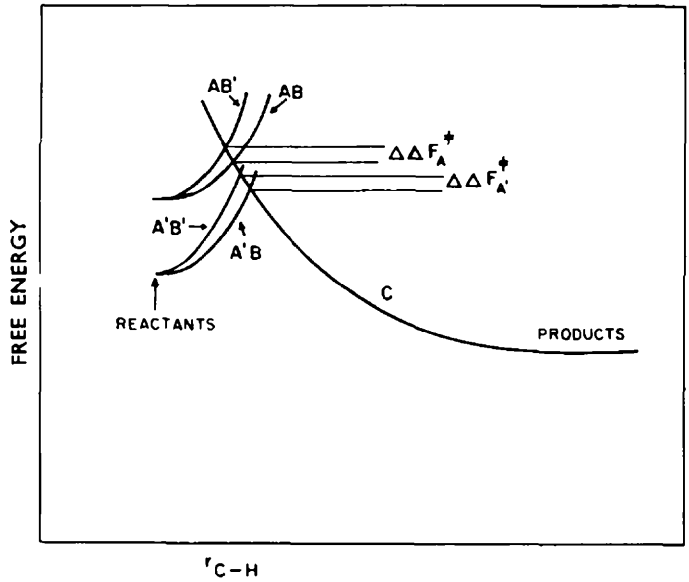

FIG. 2. Rationalization of polar effect in reactions of chlorine atoms.

On the other hand, when a chlorine atom and a complexed chlorine atom attack carbon–hydrogen bonds of equal strength but different electron densities a different energy profile results. A possible situation is shown in Fig. 2. Curve AB′ is the repulsion curve for the attack of a free chloride atom on the carbon–hydrogen bond of lowest electron density and curve AB for attack on the bond of highest electron density. Curves A′B′ and A′B are the corresponding curves for the complexed chlorine atom. Curve C is again the repulsion curve between hydrogen chloride and either of the alkyl radicals. In this instance besides displacing the origin of A′B′ and A′B from the origin of AB′ and AB by the energy of complex formation, the curvature of A′B′ and A′B has been made greater than the curvature of AB′ and AB. This seems reasonable because complexing should decrease the electron deficiency of the

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[9] Previous arguments [G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* 77, 4031 (1955)] have indicated that the transition state for the attack of a chlorine atom upon carbon–hydrogen bonds involves very little bond breaking since differences in stabilities of transition states reflect only about 10 per cent of the energy differences between the products.

chlorine atom[8] and increase the repulsion between the chlorine atom and the carbon–hydrogen bond (similarly in Fig. 1 A′ has been drawn with more curvature than A).[10] As drawn, $\Delta\Delta F^{\ddagger}_{A}$ and $\Delta\Delta F^{\ddagger}_{A'}$ are not particularly different, in agreement with the observed facts.

The polar effect described in Fig. 2 might be termed the inductive polar effect. It is capable of explaining all the polar effects observed in chlorination, including the surprising result that toward chlorine atoms a cyclohexane hydrogen atom is considerably more reactive than a toluene hydrogen atom.[11] Another polar effect recognized in the reaction of atoms and radicals involves contributions to the transition state of structure I.[12]

$$R^{+}\dot{H}\;:\!\underset{\cdot\cdot}{\ddot{X}}\!:^{-}$$

This resonance polar effect would be shown in a free energy diagram as a rounding off of the curve intersections. A resonance polar effect of this type fails to explain the relative reactivities of toluene and cyclohexane toward the chlorine atom but may be partially responsible for the fact that toward the bromine atom, where the transition state involves much more bond breaking and resonance stabilization, a toluene hydrogen atom is 250 times as reactive as a cyclohexane hydrogen at 80°.[11]

Further support for the consideration of two polar effects in the reactions of atoms and radicals with carbon–hydrogen bonds results from the observation that toward *m*- and *p*-substituted toluene derivatives relative reactivities toward the bromine atom are proportional to the σ^{+}-constant of the substitutent while toward the chlorine atom σ-constants fit the data somewhat better than σ^{+}-constants.[13] The stabilities of I would be expected to be proportional to σ^{+} while the electron densities of the benzyl–hydrogen bonds and therefore the shapes of the repulsion curves toward chlorine atoms would be determined by the σ-constant of the substituent.[14]

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[10] The electron deficient chlorine atom is attracted by the electrons of the carbon–hydrogen bond. A reduction in the electron deficiency of the chlorine atom will decrease this attraction and increases the repulsion.

[11] G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.* **77**, 4578 (1955).

[12] F. R. Mayo and C. Walling, *Chem. Rev.* **46**, 191 (1950); G. A. Russell, *Tetrahedron* **5**, 101 (1959).

[13] G. A. Russell, *J. Org. Chem.* **23**, 1407 (1958).

[14] The relative rates of attack of bromine atoms, N-succinimdyl radicals [E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap, Proc.* **56B**, 75 (1953)], peroxy radicals [G. A. Russell, *J. Amer. Chem. Soc.* **78**, 1047 (1956)] and trichloromethyl radicals [E. Huyser, *Ibid.* In press] upon benzylic hydrogen atoms are correlated by σ^{+} whereas the attack of the more reactive chlorine atoms[8] or t-butoxy radicals [C. Walling, *Abstracts of Papers presented at the 16th National Organic Chemistry Symposium, Seattle,* 1959, p. 85] are better correlated by σ.