Free Radical Substitution. Part 35.[1] A Study of the Effect of Solvent on Atomic Chlorination of 1,1-Dichloroethane

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A study has been made of the changes in selectivity observed when atomic chlorination of 1,1-dichloroethane is performed in the gas phase and in the liquid phase in various solvents. In the liquid phase, selectivity is affected by the polarisability of the solvent. Chlorination in fluorocarbons or their derivatives shows a selectivity similar to the gas phase; chlorination in unreactive polarisable solvents is much less selective whereas chlorination in aromatic solvents is as selective as the gas phase and in carbon disulphide is much more selective, probably due to the formation of a π-complex and an adduct radical ($CS_2Cl\cdot$) respectively.

HASS *et al.* were the first to report that atomic chlorination of alkanes was less selective in the liquid phase than in the gas phase.[2] Twenty years later Russell described a more pronounced solvent effect; he observed that when aromatic compounds are used as solvents the selectivity was increased.[3] Shortly afterwards Walling and Mayahi found that when carbon disulphide was used as solvent, chlorination was more selective than with benzene or in the gas phase.[4] The work of Russell and Walling can be explained in terms of the formation of ' complexes ' between the chlorine atoms and the solvent molecules, but no such explanation can account for the original observation that in the liquid phase without a complexing solvent the reaction is less selective.

In 1966 in an attempt to put these observations on a more quantitative basis we confirmed that the chlorination of n-hexane in carbon tetrachloride solution was less selective than in the gas phase.[5] The reaction was studied over a range of temperatures and the results showed that the greater selectivity in the gas phase was due to the pre-exponential term in the rate expression which at room temperature over-rode the greater activation energy.

The problem of changing selectivity of chlorination in going from the gas phase to solution has been most thoroughly studied by Martens and his co-workers. They have confirmed that both the pre-exponential term and the activation energy seem to be involved.[6]

The present study is an attempt to throw further light on the factors which cause the changes in selectivity of atomic chlorination.

EXPERIMENTAL

The experimental details were similar to those described previously. The gas-phase chlorination was performed in a conventional vacuum line and the analysis was carried out using a g.l.c. apparatus in which the detector was a density balance. The technique employed for the liquid phase has been described; the biggest difficulty was the tendency of some solutions to separate into two layers (*i.e.* the neutral solubility of CCl_2HCH_3 and the fluorocarbon solvents was sometimes low).

The results are tabulated, each rate constant ratio is the mean value from five or six individual chromatograms.

TABLE 1

Chlorination of 1,1-dichloroethane in the gas phase. Subscripts denote carbon atom

T/K	10^3T^{-1}/K^{-1}	k_1/k_2	ln(k_1/k_2)
296	3.38	13.72	2.62
304	3.29	9.03	2.20
328	3.05	8.97	2.19
361	2.77	6.68	1.90
379	2.64	6.50	1.87
404	2.48	5.45	1.70
463	2.16	5.52	1.71
508	1.97	5.22	1.65

A plot of ln(k_1/k_2) against the inverse of temperature gives a straight line of slope $E_2 - E_1 = 1\,190$ (± 220) cal mol^{-1} and an intercept ln(A_1/A_2) = 0.35 (± 0.30). 1 cal = 4·184 J.

TABLE 2

Chlorination of 1,1-dichloroethane in the liquid phase (neat). Subscripts denote carbon atom

T/K	10^3T^{-1}/K^{-1}	k_1/k_2	ln(k_1/k_2)
273.5	3.66	3.06	1.12
277	3.61	3.01	1.10
286	3.49	2.83	1.04
293	3.41	2.73	1.00
300	3.33	2.94	1.08
306	3.27	2.73	1.00
311	3.22	2.71	0.99
315	3.17	2.59	0.95
321	3.12	2.24	0.81
327	3.06	2.26	0.82

A plot of ln(k_1/k_2) against the inverse of temperature gives a straight line of slope $E_2 - E_1 = 910$ (± 180) cal mol^{-1} and intercept ln(A_1/A_2) = -0.530 (± 0.300).

TABLE 3

Chlorination of 1,1-dichloroethane in benzene solution (5 : 1). Subscripts denote carbon atom

T/K	10^3T^{-1}/K^{-1}	k_1/k_2	ln(k_1/k_2)
273.5	3.66	10.61	2.36
285	3.51	9.63	2.26
297	3.37	8.68	2.16
307	3.26	8.07	2.09
317	3.16	6.35	1.85
328	3.05	5.28	1.66

A plot of ln(k_1/k_2) against the inverse of temperature gives a straight line of slope ($E_2 - E_1$) = 2 220 (± 350) cal mol^{-1} and intercept ln(A_1/A_2) = -1.660 (± 0.548).

DISCUSSION

Table 5 shows that the solvents can be divided into three classes, unselective aliphatic compounds (RS_2^1 6.3—9.9), moderately selective fluorocarbon derivatives

TABLE 4

Chlorination of 1,1-dichloroethane in benzene and deuteriobenzene at different concentrations at 298 K

Solvent	[Dichloroethane]/M	RS_2^1
C_6H_6	0.91	14.1 ± 0.6
C_6D_6	0.98	15.6 ± 2.5
C_6H_6	1.88	20.6 ± 2.5
C_6D_6	2.07	18.0 ± 1.6
C_6H_6	2.37	20.7 ± 1.3
C_6D_6	3.63	20.3 ± 1.7
C_6H_6	4.90	20.6 ± 1.3
C_6D_6	6.11	20.2 ± 2.2
C_6H_6	8.7	21.4 ± 2.3
C_6D_6	14.1	25.7 ± 2.4

(RS_2^1 14.6—29.9), and very selective carbon disulphide (RS_2^1 45.5). Benzene and chlorobenzene have been separated from the fluorocarbon solvents because they promote a much more selective reaction than the fluorocarbons when used as solvents for the chlorination of aliphatic hydrocarbons and monosubstituted butanes.[7] Benzene is therefore to be grouped with carbon disulphide, not with the fluorocarbon derivatives.

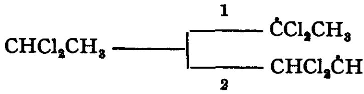
TABLE 5

Chlorination of 1,1-dichloroethane in various solvents (298 K). Relative selectivities (*i.e.* rate per type of hydrogen)

Solvent	Solvent: $C_2H_4Cl_2$	RS_2^1
CH_3COCl	5 : 1	6.3 ± 0.5
CH_2Cl_2	5 : 1	7.9 ± 0.4
Neat		8.8 ± 0.4
CF_3CO_2H	4 : 1	9.5 ± 1.0
CH_3CN	6 : 1	9.9 ± 2.1
$C_{10}F_{20}O$	8 : 1	14.6 ± 2.0
C_6F_{14}	6 : 1	15.7 ± 1.7
C_8F_{18}	9 : 1	18.3 ± 1.7
$C_5F_{11}NO$	4 : 1	20.1 ± 0.6
$(n\text{-}C_4F_9)_3N$	8 : 1	29.9 ± 3.3
C_6H_5Cl	3 : 1	17.2 ± 1.4
C_6H_6	5 : 1	20.6
CS_2	6 : 1	45.5 ± 5.8
Gas phase		30.9 (from Table 1)

TABLE 6

Chlorination of 1,1-dichloroethane



$$CHCl_2CH_3 \longrightarrow \begin{cases} \xrightarrow{1} \dot{C}Cl_2CH_3 \\ \xrightarrow[2]{} CHCl_2\dot{C}H_2 \end{cases}$$

Phase	k_1/k_2	RS_2^1 at 323 K	Ref.
Gas	1.42 ± 0.43 exp (1 200 ± 200/*RT*)	27.3	This work
Gas	0.89 ± 0.13 exp (1 500 ± 150/*RT*)	27.3	6
Neat liquid	0.59 ± 0.18 exp (900 ± 200/*RT*)	7.2	This work
Neat liquid	1.82 ± 0.13 exp (120 ± 100/*RT*)	6.9	6
C_6H_6 solution	0.19 ± 0.13 exp (2 200 ± 300/*RT*)	17.1	This work
CS_2 solution	10.5 ± 0.13 exp (150 ± 100/*RT*)	39.5	6

R in cal mol^{-1} K^{-1}.

Table 6 compares the present work with the previous study of Martens and his co-workers [6] on the chlorination of 1,1-dichloroethane. The gas-phase data are in very good agreement. The relative selectivities are identical over the range studied, but the small differences in slope (ΔE) make the ratio of the pre-exponential factors appear to differ slightly. The liquid-phase data agree less well. The relative selectivities are identical at the lower end of the temperature range, but the present work implies there is a small activation energy difference, not apparent in the Belgian work which also reports k_1/k_2 1.44 ± 0.1 exp(320 ± 10/*RT*) for chlorination in $CHCl_3$ solution.[8] Trying to establish very small activation energies is notoriously difficult but certainly the two sets of results confirm that the liquid-phase reaction is less affected by temperature than the gas-phase reaction. The two solvent-phase reactions appear very different. The greater selectivity of the reaction in carbon disulphide solution is entirely due to a very large *A* factor ratio, whereas the relatively high selectivity of the reaction in benzene solution is attributable to an activation energy difference. This is contrary to expectation, as the increased selectivity of the reactions in carbon disulphide and in benzene compared with no solvent is usually attributed to the formation of a 'complex' between the chlorine atom and the solvent. The complex with benzene is believed to be a 'π-complex' and that with carbon disulphide a 'σ-complex'. We can represent the reaction sequences as reactions (1)—(3). If reactions (2) and (3) are rate-

$$\text{Cl}^\bullet + S \overset{K}{\rightleftharpoons} \text{Cl}S^\bullet \qquad (1)$$

$$S = \text{solvent}$$

$$\text{Cl}^\bullet + \text{RH} \xrightarrow{k_2} \text{R}^\bullet + \text{HCl} \qquad (2)$$

$$K = \frac{[\text{Cl}S^\bullet]}{[\text{Cl}^\bullet][S]}$$

$$\text{Cl}^\bullet + \text{R'H} \xrightarrow{k'_2} \text{R'}^\bullet + \text{HCl} \qquad (2')$$

$$S\text{Cl}^\bullet + \text{RH} \xrightarrow{k_3} \text{R}^\bullet + \text{HCl} + S \qquad (3)$$

$$S\text{Cl}^\bullet + \text{R'H} \xrightarrow{k'_3} \text{R'}^\bullet + \text{HCl} + S \qquad (3')$$

determining and the only fate of $\text{R}^\bullet$ (or $\text{R'}^\bullet$) is to react with molecular chlorine we have equations (4)—(7) and therefore (8).

$$\text{Rate [RCl]} = k_2[\text{Cl}^\bullet][\text{RH}] + k_3[S\text{Cl}^\bullet][\text{RH}] \qquad (4)$$

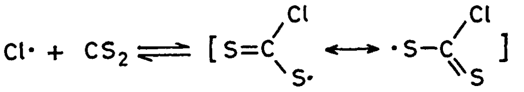
$$\text{Rate [R'Cl]} = k'_2[\text{Cl}^\bullet][\text{R'H}] + k'_3[S\text{Cl}^\bullet][\text{R'H}] \qquad (5)$$

$$[\text{RCl}]_f/[\text{R'Cl}]_f = \frac{k_2[\text{RH}][\text{Cl}^\bullet] + k_3[\text{RH}][S\text{Cl}^\bullet]}{k'_2[\text{R'H}][\text{Cl}^\bullet] + k'_3[\text{R'H}][S\text{Cl}^\bullet]} \qquad (6)$$

$$[\text{Cl}^\bullet] = [S\text{Cl}^\bullet]/K[S] \qquad (7)$$

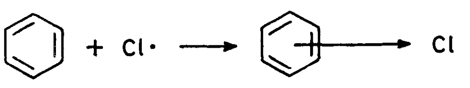
$$\therefore \quad \frac{[\text{RCl}]_f}{[\text{R'Cl}]_f} = \frac{[\text{RH}](k_2/K[S] + k_3]}{[\text{R'H}](k'_2/K[S] + k'_3)} \qquad (8)$$

We expect the 'complex' $S\text{Cl}^\bullet$ to be more selective and less reactive than free chlorine atoms. This is because we anticipate the activation energies for hydrogen abstraction by $S\text{Cl}^\bullet$ will be greater than $\text{Cl}^\bullet$. However the situation is more complicated than this. If the 'complex' involves a σ-bond the pre-exponential term for hydrogen abstraction by complex (3a) will be between two and a half and three orders of magnitude smaller than for hydrogen abstraction (2a) by chlorine atoms.



$Cl\cdot + CS_2 \rightleftharpoons [S{=}C(Cl){-}S\cdot \longleftrightarrow \cdot S{-}C(Cl){=}S]$ (1a)

$CS_2Cl\cdot + RH \longrightarrow R\cdot + HCl + CS_2$ (3a)



(1b)

$(C_6H_6 \longrightarrow Cl)^\cdot + RH \longrightarrow R\cdot + HCl + C_6H_6$ (3b)

On the other hand if the ' complex ' is the π-type there will be less loss of degrees of freedom when the transition state is formed in step (3b) and there will be much less difference between the pre-exponential term for reaction (3b) and the pre-exponential term for hydrogen abstraction by chlorine atoms (2b). Evidence that the complex of chlorine atoms with benzene is of the π-type comes from Table 4. Table 4 shows no isotope effect. If the complex had been of the σ-type a kinetic isotope effect would be expected.

We can distinguish two extreme possibilities for the reaction in carbon disulphide solution, first when K is very large and secondly when K is very small. When K is large the selectivity of the reaction will depend on the ratio k_3/k'_3, *i.e.* on hydrogen abstraction by $CS_2Cl^\cdot$ radicals. When K is small the selectivity of the reaction will depend on the ratio k_2/k'_2, *i.e.* on hydrogen abstraction by chlorine atoms. The bond formed between a chlorine atom and a carbon disulphide molecule is likely to be a normal σ-bond and therefore ΔH will be substantial and negative (*i.e.* K will decrease appreciably with increasing temperature). At low temperatures the concentration of chlorine atoms will be small and that of $CS_2Cl^\cdot$ radicals large, but the rate of hydrogen abstraction by these selective radicals will be low because reactions (3) and (3′) have considerable activation energies. As the temperature rises the concentration of $CS_2Cl^\cdot$ radicals decreases but the rate at which these radicals abstract hydrogen will increase. Thus there are two opposing effects, at low temperatures the selective $CS_2Cl^\cdot$ radicals are in high concentration but are unreactive, while at higher temperatures the radicals are in lower concentration but are much more reactive. The reactivity of the chlorine atoms will change little because the activation energies of reactions (2) and (2′) are small, but the concentration of chlorine atoms will increase with temperature. On top of these enthalpy effects there are the much larger pre-exponential terms for reactions (2) and (2′) where even when the concentration of chlorine atoms is two orders of magnitude less than the $CS_2Cl^\cdot$ radicals, their reactivity will be similar to the radicals. The combined effect of these conflicting factors is that over the temperature range we have studied there is a large ' apparent ' A factor ratio and a negligible ' apparent ' activation energy difference.

In complete contrast the π-bond formed between a chlorine atom and a benzene molecule is weak, ΔH is small and in benzene solution temperature will have little effect on K. The concentration of the $C_6H_6Cl^\cdot$ (π-complex) radicals will not vary much with temperature and the greater activation energy of reactions (3) and (3′) will contribute to the ' apparent ' (or overall) activation energy.

Table 5 shows that there are three types of solvent. First there are those which lead to a selectivity approximately the same as the neat liquid dichloroethane. Secondly there are those which lead to a greatly increased selectivity, *i.e.* those we have just discussed (benzene and carbon disulphide), and thirdly there are the fluorocarbon solvents. These last are most unlikely to ' complex ' and indeed it is probably more reasonable to compare the reactions in the fluorocarbon solvents with the gas-phase reaction. This means that we should regard the first group of solvents as reducing selectivity rather than fluorocarbon solvents as increasing selectivity. The first group of solvents are relatively polarisable and are thus able to ' solvate ' the activated complex in the transition state. This will lower the activation energy and tend to have a levelling effect. In contrast the fluorocarbon solvents will have no tendency to solvate the transition state so that chlorination in such solvents will have a selectivity approaching that of the gas-phase reaction.

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