Free Radical Substitution. Part 37.[1] The Effect of Solvent on the Atomic Chlorination of 1-Substituted Butanes and Related Compounds

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Experimental results reported in this paper show that the relative selectivity of atomic chlorination of 1-substituted butanes and related compounds is greatly influenced by the phase and by solvents. Solvents can be divided into three classes: (a) inert, (b) solvents which decrease the selectivity, and (c) solvents which increase the selectivity. The second group solvate the transition state and the third group solvate the chlorine atoms.

Part 35 [1] introduced the present study of solvent effects on atomic chlorination and in particular referred to the earlier studies of Hass,[2] Russell,[3] Walling,[4] and more recently Martens.[5] The present investigation was begun with the intention of investigating the possibility of using solvents to direct atomic chlorination of substituted alkanes towards a particular product. The present work is an attempt to elucidate the causes of changing selectivity in different solvents.

Experimental

The chlorination procedures have been described previously and similarly the identification of the various chlorinated products are described in earlier papers.

Discussion

The data in the Experimental section show the effect of temperature on the chlorination of 1-chlorobutane in the gas phase, in the liquid phase, neat and in benzene solution. There is too much scatter in the gas-phase results to attempt to estimate Arrhenius parameters and although approximate *A* factor ratios and activation energy differences have been calculated for the liquid phase experiments, the results reported in Part 35 [1] show that interpretation of the temperature dependent coefficient for liquid phase chlorination is difficult. The results also show the effect of a variety of solvents on the chlorination of 1-chlorobutane and the results can be fitted into the same three classes adopted for the chlorination of 2,2-dichloroethane.[1] The classes are unselective solvents (*i.e.* less selective than the gas phase), *e.g.* acetyl chloride, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane, and neat chlorobutane, moderately selective (*i.e.* similar selectivity to the gas phase) *e.g.* perfluoro-*N*-methylmorpholine, and finally the most selective, *e.g.* benzene and carbon disulphide. Nitrobenzene comes within the moderately selective group although it probably really belongs with benzene.

Table 1 lists the observed relative selectivity for the atomic chlorination of seven 1-substituted butanes collected from four earlier papers together with the present work. It is extremely important to remember that the figures are *relative*, and say nothing directly about the absolute rate of chlorination in the different media. For all the compounds studied Table 1 clearly shows that chlorination in the neat substrate or in the chloroalkane solvents (carbon tetrachloride and 1,1,2-trichlorotrifluoroethane) is the least selective process. Similarly, chlorination in carbon disulphide is much the most selective process.

Again adopting the four classes of reaction we developed in the previous paper [1] we can distinguish: chlorination in the gas phase; chlorination in inert fluorocarbon solvents; chlorination in polarisable solvents; and finally chlorination in complexing solvents.[1] The present work does not include fluorocarbon solvents but the two other types of solvent are clearly distinguished. Chlorination in the neat substituted butane or in the polarisable solvents (*e.g.* CCl_4) is much less selective than chlorination in the gas phase and following our earlier observations we attribute this to solvation of the polar activated-complex in the transition state. The polarity associated with the formation of hydrogen chloride is spread by the polarisable solvent, and the net effect is a levelling of the relative selectivities.

Chlorine atoms form complexes with benzene and carbon disulphide and this solvent shell has to be broken open before the hydrogen abstraction can occur. Notice that the relative selectivities for carbon disulphide are the largest at the γ-position and the smallest at the α-position, as we would expect for complexed atoms and electron attracting substituents.

These conclusions are supported by Table 2. In the gas-phase experiments it is quite clear that the substituent chlorocarbonyl group has virtually no effect beyond the β-position. In the solvating media (CCl_4, CH_3CN, and neat) the reaction is much less selective, but the effect of the substituent chlorocarbonyl group is now felt at least to the γ-position [in acetonitrile the effect of the chlorocarbonyl group appears to extend to the δ-position in heptanoyl chloride, but *all* the relative selectivities appear low for this compound; probably attack at the terminal (ς) position is over-estimated]. In the complexing solvents the effect of the chlorocarbonyl group is still manifest at the δ-position. In the chlorination of heptanoyl chloride the ε-positon is in most cases more reactive than the δ-position, but this is characteristic of penultimate position in the halogenation of alkanes in general. Indeed the exception in the literature is chlorination in carbon disulphide in which the methylene site one further down the chain is more reactive. Exactly the same is observed in the present work although the differences are almost within the limits of error.

The chlorination of 1,4-dichloro- and 1,4-difluoro-butane (see Experimental section) shows that in conformity with Table 1, hydrogen abstraction from a CH_2F group by chlorine atoms is faster than from a CH_2Cl group, in spite of the relative electronegativity of the halogens.

The great hindrance to the complete interpretation of these chlorination results is the paucity of absolute rate data. Even competitive studies between similar monosubstituted butanes is very difficult because the isomeric chloro-products are very hard to separate. However, some comparison can be achieved by studying two monosubstituted butanes, $XCH_2CH_2CH_2CH_3$ and $YCH_2CH_2CH_2CH_3$, and then comparing the results with the chlorination of $XCH_2CH_2CH_2CH_2Y$. Table 4 shows the results of such a study. Unfortunately a similar study where

(a) Chlorination in the gas phase, results expressed as relative selectivities RS_4^x

Temp. (°C)	Cl-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
60	0.68 ± 0.04	2.19 ± 0.11	4.12 ± 0.04	1	2
90	0.53 ± 0.05	1.70 ± 0.06	4.04 ± 0.26	1	4
135	0.60 ± 0.10	1.90 ± 0.04	4.42 ± 0.21	1	3
170	0.77 ± 0.03	1.80 ± 0.09	3.93 ± 0.24	1	4

(b) Chlorination in the liquid phase (no solvent), expressed as RS_4^x

Temp. (°C)	Cl-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
5	0.36 ± 0.01	1.37 ± 0.04	3.09 ± 0.10	1	5
20	0.37 ± 0.03	1.38 ± 0.07	2.68 ± 0.11	1	4
33	0.39 ± 0.02	1.37 ± 0.06	2.69 ± 0.07	1	5
44	0.41 ± 0.03	1.33 ± 0.07	2.60 ± 0.12	1	5
52	0.47 ± 0.04	1.39 ± 0.05	2.58 ± 0.05	1	4

	$E_4 - E_x$/cal mol^{-1}	$\ln(A_x/A_4)$
$x = 1$	−760 ± 250	−0.06 ± 0.41
$x = 2$	−8 ± 90	−0.10 ± 0.16
$x = 3$	+590 ± 130	−0.39 ± 0.21

(c) Chlorination in benzene solution (5 parts C_6H_6 to 1 part C_4H_9Cl), expressed as RS_4^x

Temp. (°C)	Cl-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
5	0.42 ± 0.04	1.77 ± 0.09	5.29 ± 0.21	1	4
36	0.47 ± 0.03	1.84 ± 0.08	5.21 ± 0.17	1	5
43	0.48 ± 0.04	1.75 ± 0.12	4.92 ± 0.32	1	5
52	0.49 ± 0.02	1.72 ± 0.12	4.33 ± 0.23	1	5

	$E_4 - E_x$/cal mol^{-1}	$\ln(A_x/A_4)$
$x = 1$	−520 ± 8	−0.32 ± 0.01
$x = 2$	+72 ± 190	+0.05 ± 0.23
$x = 3$	+505 ± 360	+0.36 ± 0.59

(d) Chlorination of 1-chlorobutane in different solvents at ambient temperatures (*ca.* 20 °C), expressed as RS_4^x

Solvent	Cl-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Acetyl chloride (6 : 1)	0.29 ± 0.06	1.28 ± 0.15	2.76 ± 0.10	1	3
Carbon tetrachloride (4 : 1)	0.30 ± 0.02	1.20 ± 0.02	2.23 ± 0.07	1	3
Neat	0.36 ± 0.03	1.38 ± 0.07	2.68 ± 0.11	1	4
$CFCl_2CF_2Cl$ (3 : 4)	0.37 ± 0.03	1.42 ± 0.06	2.81 ± 0.13	1	3
Nitrobenzene (4 : 1)	0.25 ± 0.03	1.65 ± 0.22	3.47 ± 0.10	1	3
Carbon disulphide (6 : 1)	0.77 ± 0.08	2.90 ± 0.36	9.19 ± 0.82	1	3
PFNMM [a] (5.7 : 1)	0.60 ± 0.07	1.78 ± 0.10	3.19 ± 0.19	1	3

[a] Perfluoro-*N*-methylmorpholine.

(e) Chlorination of pentanoyl chloride in different solvents (20 °C) expressed as RS_4^x

Solvent	ClOC-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Neat	0.08 ± 0.03	1.22 ± 0.06	2.48 ± 0.17	1	4
Benzene (6 : 1)	0.04 ± 0.05	1.34 ± 0.07	6.09 ± 0.27	1	4
Carbon disulphide (4 : 1)	0.05 ± 0.01	1.48 ± 0.06	6.00 ± 0.16	1	5

(f) Chlorination of hexanoyl chloride in different solvents (20 °C) expressed as RS_5^x

Solvent	ClOC-CH$_2$—	CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Neat	0.02 ± 0.01	1.82 ± 0.13	1.70 ± 0.25	1.96 ± 0.28	1	5
Benzene (8 : 1)	0.00	1.25 ± 0.06	4.83 ± 0.53	6.39 ± 0.66	1	3
Carbon disulphide (5 : 1)	0.00	0.98 ± 0.06	5.86 ± 0.16	7.77 ± 0.32	1	5

(g) Chlorination of heptanoyl chloride in different solvents (20 °C), expressed as RS_6^x

Solvent	ClOC-CH—	CH$_2$—	CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Neat	0.03 ± 0.02	0.62 ± 0.04	1.58 ± 0.01	2.33 ± 0.05	2.58 ± 0.03	1	5
C_6H_6 (7 : 1)	0.00	0.75 ± 0.20	3.97 ± 0.10	7.67 ± 2.01	8.23 ± 2.05	1	5
CS_2 (5 : 1)	0.00	0.70 ± 0.09	4.51 ± 0.21	8.66 ± 0.45	8.63 ± 0.41	1	5

(h) Chlorination of valeronitrile in different solvents (20 °C) expressed as RS_4^x

Solvent	N≡C-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Neat	0.20 ± 0.03	0.82 ± 0.06	2.12 ± 0.12	1	3
C_6H_6 (5 : 1)	0.02 ± 0.03	0.91 ± 0.04	4.10 ± 0.23	1	3
CS_2 (11 : 1)	0.07 ± 0.05	1.28 ± 0.24	7.17 ± 0.98	1	7

(i) Chlorination of 1-fluorobutane in different solvents (20 °C) expressed as RS_4^x

Solvent	F-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
CCl_2FCClF_2 (2 : 1)	0.45 ± 0.01	0.89 ± 0.02	1.90 ± 0.05	1	3
C_6H_6 (5 : 1)	0.42 ± 0.0	*	4.51 ± 0.11	1	3
CS_2 (7 : 1)	0.49 ± 0.01	1.43 ± 0.28	5.55 ± 0.18	1	4

* 2-Chloro-1-fluorobutane had the same retention time as C_6H_6.

(j) Chlorination of 1,1,1-trifluoropentane in different solvents (20 °C) expressed as RS_4^x

Solvent	CF$_3$-CH$_2$—	CH$_2$—	CH$_2$—	CH$_3$	No. of runs
Neat	0.02 ± 0.01	0.83 ± 0.04	2.55 ± 0.09	1	5
C_6H_5Cl (7.5 : 1)	0.00	0.99 ± 0.10	4.85 ± 0.35	1	5
CS_2 (5 : 1)	0.00	1.59 ± 0.08	10.30 ± 0.82	1	5

Table (*continued*)

(k) Chlorination of 1,4-dichloro- and 1,4-difluoro-butane in different media (% yield of chlorinated product)

	$(ClCH_2\text{-}CH_2)_2$		$(FCH_2\text{-}CH_2)_2$	
Gas (120°)	34.0 ± 0.7	66.1 ± 0.7	42.8 ± 1.2	57.17 ± 1.2
Neat	29.3 ± 1.6	70.7 ± 1.6	38.7 ± 0.4	61.3 ± 0.4
C_6H_6 (4 : 1)	32.8 ± 0.5	67.2 ± 0.5	44.0 ± 1.8	56.0 ± 0.8

(l) Chlorination of 5-chloropentanoyl chloride (% yield of chlorinated products)

Media	$Cl\text{-}CH_2$—	—CH_2—	—CH_2—	—CH_2COCl	No. of runs
Gas	19.2 ± 2	38.3 ± 0.4	39.4 ± 1.7	3.2 ± 0.1	3
CCl_4 (7 : 1)	31.9 ± 2.0	44.5 ± 2.0	17.8 ± 1.0	5.8 ± 0.7	4
C_6H_6 (7 : 1)	21.2 ± 0.3	45.8 ± 1.5	32.0 ± 1.4	1.0 ± 0.2	4
CS_2 (11 : 1)	22.0 ± 0.3	46.4 ± 0.2	29.9 ± 0.4	7.1 ± 0.2	4

Table 1. Chlorination of 1-substituted butanes in the gas and different solvent phases. Relative selectivites

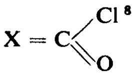
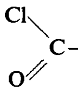
	α XCH_2—	β —CH_2—	γ —CH_2—	δ —CH_3	
X = H	1	3.9	3.9	1	Gas
	1	3.0	3.0	1	Liquid CCl_4
	1	5.1	5.1	1	Liquid C_6H_6
	1	9.3	9.3	1	Liquid CS_2
X = F[6]	0.9	1.7	3.7	1	Gas
	0.5	0.9	1.9	1	Liquid $C_2F_3Cl_3$
	0.4	—	4.5	1	Liquid C_6H_6
	0.5	1.4	5.6	1	Liquid CS_2
X = Cl[6]	0.7	2.2	4.1	1	Gas
	0.4	1.4	2.7	1	Liquid CCl_4
	0.5	1.8	5.2	1	Liquid C_6H_6
	0.8	2.9	9.2	1	Liquid CS_2
X = CN[7]	0.2	1.7	3.9	1	Gas
	0.2	0.8	2.1	1	Liquid neat
	0.02	0.9	4.1	1	Liquid C_6H_6
	0.02	1.3	7.2	1	Liquid CS_2
 $X = C(Cl){=}O$ [8]	0.08	1.6	4.2	1	Gas
	0.08	1.2	2.5	1	Liquid neat
	0.04	1.3	6.1	1	Liquid C_6H_6
	0.05	1.5	6.0	1	Liquid CS_2
X = CF_3[9]	0.04	1.2	4.3	1	Gas
	0.02	0.8	2.6	1	Liquid neat
	0.00	1.0	4.9	1	Liquid C_6H_5Cl
	0.00	1.6	10.3	1	Liquid CS_2
X = NO_2[10]	—	—	3.8	1	Gas
	0.01	0.4	2.3	1	Liquid CCl_4
	0.00	0.4	4.8	1	Liquid C_6H_6

Table 2. The chlorination of pentanoyl, hexanoyl, and heptanoyl chlorides in different media at 20 °C. Relative selectivities [8,11]

Solvent	 $ClC(=O)$— α —CH_2—	β —CH_2—	γ —CH_2—	δ —CH_2—	ε —CH_2—	ς —CH_3
Gas * phase	0.08	1.6	4.2	1		
	0.17	1.5	4.0	4.5	1	
	0.21	1.8	4.1	4.1	4.5	1
CCl_4	0.19	0.8	2.1	1		
	0.15	0.6	1.6	2.0	1	
CH_3CN	0.15	0.9	2.3	1		
	0.16	0.5	1.6	2.2	1	
	0.06	0.4	0.9	1.1	1.4	1
Neat	0.08	1.2	2.5	1		
	0.02	0.8	1.7	2.0	1	
	0.03	0.6	1.6	2.3	2.6	1
C_6H_6	0.04	1.3	6.1	1		
	0.00	1.3	4.8	6.4	1	
	0.00	0.8	4.0	7.7	8.2	1
CS_2	0.05	1.5	6.0	1		
	0.00	1.0	5.9	7.8	1	
	0.00	0.7	4.5	8.7	8.6	1

* Gas-phase results relate to acid fluorides at 60 °C.

Table 3. Relative selectivities in the chlorination of n-heptane at 20 °C

	CH_3—	—CH_2—	—CH_2—	—C_4H_9	Ref.
Cl_2 neat	1	3.0	2.9		12
Cl_2 in SC_2	1	27	35		12

Table 4. The relative rates of chlorination at different sites in 4-chloropentanoyl chloride taking the attack on the primary position on n-butane as unity (20 °C)

Solvent	Cl-CH_2—	—CH_2—	—CH_2—	—CH_2—	—COCl
(Gas phase)	0.7	1.4	1.4	0.12	
CCl_4	0.4	0.6	0.2	0.07	
C_6H_6	0.5	1.0	0.7	0.03	
CS_2	0.7	1.5	0.9	0.06	

$X = Cl$ and $Y = F$ had to be abandoned because isomers from the chlorination of 1-chloro-4-fluorobutane could not be separated.

Table 4 was constructed as follows. (i) The average relative selectivities $R^3{}_4$ for all seven compounds in Table 1 were taken as standard. (ii) The $RS^2{}_4$ and $RS^1{}_4$ values for 1-chlorobutane was then calculated using the ' average ' values for $RS^3{}_4$. (iii) The $RS^1{}_4$ value so obtained was equated with the 4-position in 4-chloropentanoyl chloride and the relative selectivities calculated accordingly. The validity of this method of inter-relating the results for different substituents is shown by the relative rates so obtained for the 1-position in 4-chloropentanoyl chloride.

The results show that the selectivity of atomic chlorination can be very substantially varied by carrying out the reaction in a solvent. Whether the changes in selectivity are sufficient to counterbalance the complications involved in separating the products in a solution phase reaction is more open to question.

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