Free Radical Substitution in Aliphatic Compounds. Part XXX.[1] A Re-investigation of the Gas-phase Chlorination of Alkanes by t-Butyl Hypochlorite and a Study of the Chlorination of 1-Chloro-, 1-Fluoro-, and 1-Cyano-butane by the Same Reagent

By **Ian K. Stoddart** and **Antony Nechvatal,*** Department of Chemistry, The University, Dundee DD1 4HN
John M. Tedder, Chemistry Department, The University, St. Andrews KY16 9ST

The chlorination of hexane and 2,3-dimethylbutane using t-butyl hypochlorite in the gas phase has been studied using the method reported previously. However the relative selectivities [equations (ii) and (iii)] for the hydrogen abstraction (i) differ slightly from those reported previously ($RS^{T:P} = k^T{}_2/k^P{}_2$ where $k^T{}_2$ and $k^P{}_2$ are the rate constants per hydrogen for abstraction from the tertiary and primary positions; superscript S referring similarly to secondary hydrogen). The reasons for the small discrepancy with the earlier work is discussed. The absolute

$$R^PH(R^SH,R^TH) + Bu^tO\cdot \xrightarrow{k_2{}^{P(S,T)}} R^{P(S,T)\cdot} + Bu^tOH \qquad (i)$$

$$\log_{10} RS^{S:P} = -0{\cdot}05 \pm 0{\cdot}11 - (5{\cdot}68 \pm 0{\cdot}7\ \text{kJ})/2{\cdot}3RT \qquad (ii)$$

$$\log_{10} RS^{T:P} = -0{\cdot}2 \pm 0{\cdot}2 - (10{\cdot}0 \pm 1{\cdot}2\ \text{kJ})/2{\cdot}3RT \qquad (iii)$$

rates [equation (iv)] can be derived from the experimentally determined ratio $k^P{}_2/k_4$ using the recent literature value for k_4 (the decomposition of the t-butoxyl radical). The investigation was extended to a qualitative study of

$$\log k^P{}_2 = 8{\cdot}28 \pm 0{\cdot}7 - (34{\cdot}7 \pm 4{\cdot}4\ \text{kJ})/2{\cdot}3RT \qquad (iv)$$

the chlorination of 1-chloro-, 1-fluoro-, and 1-cyano-butane. The observed selectivities are discussed in terms of relative bond strengths and polarity.

We have previously reported an investigation of the chlorination of butane and 2-methylpropane by t-butyl hypochlorite in the gas phase.[2] The relative rates of chlorination of primary, secondary, and tertiary hydrogen atoms were determined and the absolute rates were estimated using the literature data on the decomposition of the t-butoxyl radical. One of the striking features of the previous work was that chlorination became more selective as the temperature rose. We attributed this to short chains and other chain-terminating processes involving the alkyl radicals ($R^{P}\cdot$, $R^{S}\cdot$, and $R^{T}\cdot$ where the superscript refers to primary, secondary, or tertiary, respectively) and we therefore included these steps in our rate expression. The present work suggests there is another explanation of the peculiar temperature coefficients of the relative selectivities (RS) [$RS^{T:P} = k^T{}_2/k^P{}_2$ where $k^T{}_2$ and $k^P{}_2$ are rate constants per hydrogen atom for the hydrogen abstraction (1)].

$$R^PH(R^SH,R^TH) + Bu^tO\cdot \xrightarrow{k_2} R^{P}\cdot(R^{S}\cdot,R^{T}\cdot) + Bu^tOH \qquad (1)$$

In attempting to extend the original studies to substituted alkanes, relative selectivities were observed which differed from these reported above and which were very close to those obtained in gas-phase studies with molecular chlorine. This suggested that the new batch of t-butyl hypochlorite might contain molecular chlorine. The commercial t-butyl hypochlorite was passed down a column packed with sodium hydroxide pellets. t-Butyl hypochlorite so treated showed much greater selectivity. In the previous work the purity of the t-butyl hypochlorite was checked by g.l.c. analysis. This would have detected t-butyl alcohol, but would not have detected dissolved molecular chlorine.

It seems likely that dissolved chlorine was the cause of the low selectivity and inverted temperature coefficient for the relative selectivities. In the experiments with the alkanes, chlorine would react very rapidly, but we found previously that the subsequent reaction between hydrogen chloride and t-butyl hypochlorite was slow in the gas phase, although very rapid in the liquid phase. The ' gas-phase ' reaction probably occurs at the walls. An exclusive chlorine atom chain (2)—(4) is therefore unlikely unless the concentration

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad (2)$$

$$Cl\cdot + RH \xrightarrow{\text{fast}} HCl + R\cdot \qquad (3)$$

$$HCl + Bu^tOCl \xrightarrow[\text{gas phase}]{\text{slow in}} Bu^tOH + Cl_2 \qquad (4)$$

of chlorine is very high. However, it means that when small amounts of chlorine are present, a proportion of the chloroalkane produced will be due to abstraction by chlorine. Because the activation energy of hydrogen abstraction by chlorine atoms is very low and the reaction between hydrogen chloride and t-butyl hypochlorite appears to occur largely at the reaction vessel surface, the rate of hydrogen abstraction by chlorine atoms will not vary much with temperature. On the other hand hydrogen abstraction by t-butoxyl radicals has an activation energy of the order of 25 kJ mol^{-1} so that the proportion of hydrogen abstraction by the more selective t-butoxyl radicals will increase with an increase in temperature. In the previous work the absolute rate was obtained by assuming a ' normal ' pre-exponential

---

[1] Part XXIX, D. A. Coates and J. M. Tedder, *J.C.S. Perkin II*, 1973, 1750.

[2] J. L. Brokenshire, A. Nechvatal, and J. M. Tedder, *Trans. Farday Soc.*, 1970, **66**, 2029.

factor and obtaining the activation energy from the known temperature coefficient for the decomposition of the t-butoxyl radical. The change in relative amounts of acetone and t-butyl alcohol with temperature should, to a first approximation, be independent of the chlorine atom reaction so that the absolute rate obtained originally should not be greatly affected. This paper reports a re-investigation of the chlorination of alkanes using t-butyl hypochlorite which had been purified to remove molecular chlorine.

The gas-phase chlorination of 1-substituted butanes using molecular chlorine has been extensively studied but there is no previous investigation of the gas-phase chlorination of these compounds using t-butyl hypochlorite. Walling [3] has investigated the chlorination of 1-chlorobutane in the solution phase, but comparison of these results with the gas-phase data would not be justified. The second part of this paper deals with an investigation in the directive effects of Cl, F, and CN on hydrogen abstraction by t-butoxyl radicals.

EXPERIMENTAL

Reagents.—Hexane. May and Baker material was redistilled on a Buchi spinning band fractionating column and the fraction boiling at 70·5° and 760 mmHg was found to be >99·5% pure by g.l.c.

2,3-*Dimethylbutane.* This was obtained from Koch–Light, and purified in a similar manner to afford a fraction, b.p. 59—61° at 762 mmHg, of >99·9% purity.

1-*Chlorobutane.* This was prepared from butan-1-ol and thionyl chloride [4] followed by purification on the spinning band column. A fraction, b.p. 77·5° at 755 mmHg, of >99·5% purity was obtained.

1-*Fluorobutane.* This was prepared from anhydrous potassium fluoride and 1-bromobutane in ethylene glycol.[5] Impurities present were but-1-ene and some 1-bromobutane. The olefin was removed by addition of bromine with stirring at solid carbon dioxide–acetone temperature. Distillation, on the vacuum line, at −2° through a 9 in tube of Carbosorb gave a product free from bromine and dibromobutane and with <0·5% 1-bromobutane.

1-*Cyanobutane.* Koch–Light material was purified on the spinning band column to give a fraction of >99·9% purity, b.p. 141—142° at 746 mmHg.

t-Butyl hypochlorite. The hypochlorite, prepared by the method of Lutz *et al.*,[6] was passed down a small column containing sodium hydroxide pellets, dried with calcium chloride, and stored in a blackened bottle. Re-purification was not necessary if the hypochlorite was kept cold and used within 2—3 weeks. I.r. and n.m.r. spectra indicated the absence of large proportions of t-butyl alcohol or acetone in the product. The passage down a sodium hydroxide column was vital. t-Butyl hypochlorite not treated in this way gave variable and always lower values for relative selectivities.

Apparatus for Gas-phase Chlorination.—The apparatus was essentially the same as that described previously [2] except that Rotaflo Teflon taps replaced greased taps on the vacuum line. All reactions were carried out at a total initial pressure of 60 mmHg in a 274 ml reaction vessel. The temperature of the oven surrounding the vessel was held constant to within ±0·25° by a Fisons Fi-monitor temperature controller. The oven window was covered by Corning 7380 and 5860 filters which transmit 365 nm light, and irradiation was carried out by a Hanovia UVS 220 medium pressure mercury arc lamp.

Analysis.—G.l.c. analyses were carried out on a Pye 104 instrument using a flame ionization detector. The column was 1·5 m long and packed with 20% dinonyl phthalate on Embacel (60—100 mesh). The response of the flame ionization detector to the various reaction products was calibrated against that of a Griffin and George D6 gas density balance chromatograph. Peak areas were measured by a Honeywell Precision Integrator. All errors quoted are ' standard ' errors.

Identification of Reaction Products.—Methyl chloride, acetone, and t-butyl alcohol were all commercially available. 1- and 2-Chlorohexane were prepared from the respective alcohol and thionyl chloride.[7] 1- and 2-Chloro-2,3-dimethylbutane were identified by g.l.c.–mass spectral analysis of a reaction mixture. The primary chloride gave a strong peak at *m/e* 71 due to loss of a CH_2Cl fragment. Such a breakdown is not possible from 2-chloro-2,3-dimethylbutane.

The products from the chlorination of 1-chloro-, 1-fluoro-, and 1-cyano-butane have been fully identified previously.[8,9]

RESULTS

To confirm the absence of an appreciable thermal reaction, a mixture of chlorobutane (10 parts) and t-butyl hypochlorite (1 part) was left in the reaction vessel in the dark for 1·5 h at 373 K. G.l.c. analysis revealed only small traces of products plus considerable amounts of unchanged t-butyl hypochlorite.

Mixtures of hydrocarbon (10 parts) and t-butyl hypochlorite (1 part) were photolysed for 45 min at various temperatures. The relative amounts of monochlorinated products found is expressed as relative selectivity (RS) in Table 1. Mixtures of 2,3-dimethylbutane (10 parts) and t-butyl hypochlorite (1 part) were photolysed for 45 min at various incident light intensities; the relative selectivities are listed in Table 2. Mixtures of varying relative concentrations of 2,3-dimethylbutane and t-butyl hypochlorite were photolysed and again a variation in selectivity was

TABLE 1

Relative selectivities in the chlorination of hexane and 2,3-dimethylbutane together with the ratios $[Bu^tOH]_f : [(CH_3)_2CO]_f$ from the experiments with 2,3-dimethylbutane

T/K	$RS^{S:P}$	$RS^{T:P}$	$[Bu^tOH]_f : [(CH_3)_2CO]_f$
303	8·41 ± 1·08	36·29 ± 1·88	2·88
313	8·38 ± 0·44	28·71 ± 1·06	1·57
323	7·30 ± 0·80	29·54 ± 1·54	0·53
333	6·65 ± 0·42	27·72 ± 0·79	0·55
344	6·29 ± 1·35	23·47 ± 0·50	0·44
353	6·52 ± 0·42	18·70 ± 0·18	0·20

---

[3] C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6113.

[4] W. Gerrard, *J. Chem. Soc.*, 1939, 99.

[5] V. Desreux, *Bull. Soc. chim. belges*, 1935, **44**, 1.

[6] G. A. Lutz, A. E. Bearse, J. E. Leonard, and F. C. Croxton, *J. Amer. Chem. Soc.*, 1948, **70**, 4137.

[7] R. H. Clark and H. R. L. Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, 77.

[8] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1960, 144.

[9] D. S. Ashton, H. Singh, J. M. Tedder, J. C. Walton, and E. A. Watt, *J.C.S. Perkin II*, 1973, 125.

observed. Table 3 shows the results obtained. Mixtures of 1-chlorobutane (10 parts) and t-butyl hypochlorite (1 part) were photolysed for 45 min at various temperatures. The results are shown in Table 4. Mixtures of 1-fluorobutane (10 parts) and t-butyl hypochlorite (1 part) were photolysed for 45 min at various temperatures; the results are shown in Table 5. The reaction with 1-chlorobutane (10 parts) and t-butyl hypochlorite (1 part) was repeated at various light intensities at 362, 341, 326, and 309 K. Table 6 shows the results at 362 and 309 K; the figures obtained at 341 and 326 K are very similar. A further series of runs were carried out with 1-chlorobutane in which the t-butyl hypochlorite concentration was varied (I_0 100%). Table 7 shows the results. 1-Cyanobutane (10 parts) and t-butyl hypochlorite (1 part) was photolysed for 45 min at 346 K. Table 8 gives the observed selectivities.

TABLE 2

Effect of incident light intensity (I_0) on $RS^{T:P}$

I_0 (%)	$RS^{T:P}$ at 313 K	$RS^{T:P}$ at 343 K
100	28	23
80	38	39
42	48	37
23	55	47

TABLE 3

Effect of $[Bu^tOCl]_i$ on $RS^{T:P}$: photolysis time 45 min, I_0 100%, temperature 313 K

Parts $Me_2CHCHMe_2$: parts Bu^tOCl	$RS^{T:P}$
10 : 1	29 ± 1
5 : 1	23 ± 1
3 : 1	22 ± 1

TABLE 4

Relative selectivity ($RS^{X:1,3}$) for the chlorination of 1-chlorobutane

T/K	$RS^{1,1:1,3}$	$RS^{1,2:1,3}$	$RS^{1,3:1,3}$	$RS^{1,4:1,3}$
300	0·628 ± 0·061	0·427 ± 0·024	1	0·128 ± 0·014
311	0·590 ± 0·048	0·447 ± 0·014	1	0·127 ± 0·004
327	0·757 ± 0·016	0·446 ± 0·023	1	0·104 ± 0·015
341	0·819 ± 0·085	0·456 ± 0·031	1	0·126 ± 0·009
362	0·592 ± 0·099	0·487 ± 0·026	1	0·133 ± 0·017

TABLE 5

Relative selectivity ($RS^{X:1,3}$) for the chlorination of 1-fluorobutane

T/K	$RS^{1,1:1,3}$	$RS^{1,2:1,3}$	$RS^{1,3:1,3}$	$RS^{1,4:1,3}$
305	0·857 ± 0·027	0·362 ± 0·018	1	0·188 ± 0·003
314	0·868 ± 0·049	0·290 ± 0·025	1	0·122 ± 0·030
323	0·589 ± 0·023	0·379 ± 0·004	1	0·152 ± 0·020
334	0·519 ± 0·020	0·405 ± 0·011	1	0·206 ± 0·010
343	0·877 ± 0·083	0·415 ± 0·013	1	0·228 ± 0·008
354	0·931 ± 0·082	0·414 ± 0·023	1	0·178 ± 0·011

TABLE 6

Effect of incident light intensity (I_0) on relative selectivity ($RS^{X:1,3}$)

T/K	I_0 (%)	$RS^{1,1:1,3}$	$RS^{1,2:1,3}$	$RS^{1,4:1,3}$
362	100	0·592 ± 0·099	0·487 ± 0·026	0·133 ± 0·017
	57	0·678 ± 0·022	0·512 ± 0·011	0·157 ± 0·017
	41	0·709 ± 0·024	0·475 ± 0·011	0·147 ± 0·013
	23	0·623 ± 0·016	0·401 ± 0·014	0·101 ± 0·007
309	100	0·590 ± 0·049	0·447 ± 0·014	0·127 ± 0·004
	80	0·791 ± 0·058	0·472 ± 0·029	0·073 ± 0·009
	41	0·659 ± 0·114	0·397 ± 0·043	0·084 ± 0·009
	23	0·647 ± 0·026	0·414 ± 0·015	0·106 ± 0·006

TABLE 7

Variation of selectivity ($RS^{X:1,3}$) with $[Bu^tOCl]_i$

$\frac{[C_4H_9Cl]_i}{[Bu^tOCl]_i}$	$RS^{1,1:1,3}$	$RS^{1,2:1,3}$	$RS^{1,3:1,3}$	$RS^{1,4:1,3}$
10 : 1	0·819 ± 0·084	0·456 ± 0·031	1	0·126 ± 0·009
7 : 1	0·702 ± 0·011	0·457 ± 0·014	1	0·101 ± 0·017
5 : 1	0·816 ± 0·088	0·437 ± 0·031	1	0·078 ± 0·005
3 : 1	0·849 ± 0·068	0·405 ± 0·045	1	0·080 ± 0·008

TABLE 8

Relative selectivity ($RS^{X:1,3}$) for the chlorination of 1-cyanobutane

NC——CH_2	——CH_2	——CH_2	——CH_3
0·352 ± 0·070	0·318 ± 0·039	1	0·151 ± 0·038

DISCUSSION

The full mechanism was discussed in detail previously [2] and need not be described again here. We shall adopt the same simplified mechanism (5)—(10) we used previously.

$$Bu^tOCl \xrightarrow{h\nu} Bu^tO\cdot + Cl\cdot \qquad (5)$$

$$Bu^tO\cdot + R^PH(R^SH,R^TH) \xrightarrow{k^P{}_2(k^S{}_2,k^T{}_2)} Bu^tOH + R^P\cdot(R^S\cdot,R^T\cdot) \qquad (6)$$

$$Bu^tOCl + R^P\cdot(R^S\cdot,R^T\cdot) \xrightarrow{k^P{}_3(k^S{}_3,k^T{}_3)} Bu^tO\cdot + R^PCl(R^SCl,R^TCl) \qquad (7)$$

$$Bu^tO\cdot \xrightarrow{k_4} (CH_3)_2CO + CH_3\cdot \qquad (8)$$

$$CH_3\cdot + Bu^tOCl \xrightarrow{k_5} CH_3Cl + Bu^tO\cdot \qquad (9)$$

$$2Bu^tO\cdot \xrightarrow{k_t} Bu^tOOBu^t \qquad (10)$$

Table 1 shows that, in contrast to our previous investigation, the relative selectivities decrease with increasing temperature. Previously we had attributed an unexpected increase in selectivity with temperature in terms of short chains and the loss of alkyl radicals in chain-terminating steps leading to the other products. From the present results it appears that no such assumption is necessary. The other important difference between the new work and that reported previously is that the reaction is more selective ($RS^{S:P} = 8$; $RS^{T:P} = 28$ at 313 K) compared with the previous values ($RS^{S:P} = 6$; $RS^{T:P} = 10$ at 303 K). In the introduction we have discussed the possibility that in the earlier work the hypochlorite contained small amounts of dissolved molecular chlorine. Throughout this work the t-butyl hypochlorite was pretreated with sodium hydroxide. The new results are consistent with the suggestion that chlorine atom chains were indeed present in the earlier study. Such a decrease in selectivity of the reaction of t-butyl hypochlorite by deliberate generation of competing chlorine atom chains has been observed by Davies.[10] Even in the complete absence of molecular chlorine, chlorine atoms are formed in the initiation reaction and if the chains are only of a moderate

---

[10] A. G. Davies, T. Maki, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 744.

length we might expect reduction of the light intensity to result in longer chains and hence increased selectivity, *in other words*, a smaller contribution from chlorine atoms. Evidence that this occurs in the chlorination of 2,3-dimethylbutane is shown in Table 2. However, no change in selectivity was observed in the chlorination of 1-chlorobutane (Table 6). This is probably because the observed $RS^{T:P}$ is much larger than that observed for chlorine atoms and a small contribution from chlorine atoms would not have an appreciable effect. Correctly, therefore, we should extrapolate $RS^{T:P}$ to zero light intensity in which case we get values of 65 at 40 °C and of 53 at 70 °C. These values are more consistent with solution values given by Walling and Jacknow[11] ($RS^{T:P} = 44$ at 40 °C) than those of Williams and his co-workers[12] ($RS^{T:P} = 28$ at 40 °C); however, exact agreement between liquid phase and gas phase results is not to be expected.

If this explanation for the change in selectivity is correct we would expect that an increase in hypochlorite concentration would cause a decrease in selectivity. Evidence of this is shown in Tables 3 and 7.

Provided the reaction time remains the same, the contribution to the overall reaction from chlorine atoms will stay virtually constant when the temperature is changed because the activation energy for hydrogen abstraction by chlorine atoms is so small. It is not necessary therefore to extrapolate to zero light intensity in order to determine the difference in activation energy for hydrogen abstraction from primary, secondary, and tertiary positions by t-butoxyl radicals. Provided the chains are reasonably long we have equation (11) from

$$\log_{10} RS^{S:P} = \log_{10} (k^S{}_2/k^P{}_2) = -0{\cdot}05 \pm 0{\cdot}11 + (5{\cdot}68 \pm 0{\cdot}7 \text{ kJ})/2{\cdot}3RT \quad (11)$$

the hexane results (Table 1) and equation (12) from the

$$\log_{10} RS^{T:P} = \log_{10} (k^T{}_2/k^P{}_2) = -0{\cdot}17 \pm 0{\cdot}20 + (10{\cdot}00 \pm 1{\cdot}26 \text{ kJ})/2{\cdot}3RT \quad (12)$$

2,3-dimethylbutane results (Table 1).

The activation energy differences are somewhat greater than reported previously, in agreement with the hypothesis that in the previous work dissolved chlorine was present in the t-butyl hypochlorite used.

Using the data from the 2,3-dimethylbutane experiments the rate constants $k^P{}_2$ and $k^T{}_2$ can be related to the rate constant for the decomposition of the t-butoxyl radical (k_4) {equation (13) where $[RH]_i$ = initial con-

$$\frac{[Bu^tOH]_f}{[(CH_3)_2CO]_f} = \frac{12k^P{}_2[RH]_i}{k_4} + \frac{2k^T{}_2[RH]_i}{k_4} \quad (13)$$

centration of hydrocarbon, $[Bu^tOH]_f$ and $[(CH_3)_2CO]_f$ = final concentrations of t-butyl alcohol and acetone respectively}. Since the measured $RS^{T:P}$ is equivalent to $k^T{}_2/k^P{}_2$ equations (14) follows. A plot of the

$$\frac{k^P{}_2}{k_4} = \frac{[Bu^tOH]_f}{2[(CH_3)_2CO]_f[RH]_i}\left(\frac{1}{6 + RS^{T:P}}\right) \text{l mol}^{-1} \quad (14)$$

logarithm of the right hand side of this expression against T^{-1} should give a straight line of slope $(E_4 - E_2{}^P)/2{\cdot}3R$ and intercept $\log_{10} A^P{}_2/A_4$. Values for the right hand side of the equation can be computed from Table 1 where $[RH]_i = 2{\cdot}84 \times 10^{-3}$M and give equation (15). The activation energy difference is, within experimental error, the same as that obtained previously.

$$\log_{10} k_2{}^P/k_4 = -5{\cdot}08 \pm 0{\cdot}70 - (35{\cdot}5 \pm 4{\cdot}3 \text{ kJ})/2{\cdot}3RT \quad (15)$$

In the earlier work there was an arithmetical error in the ratio of A factors which should have read $\log A^P{}_2/A_4 = -5{\cdot}57 \pm 1{\cdot}1$ (which also agrees with the present results). Recently the value of k_4 in the high pressure region has been surveyed[13] and also a new determination of k_4 has been made[14] which is within the limits of the preferred value suggested by Benson and O'Neal.[13] Using this value ($\log_{10} k_4 = 13{\cdot}4 - (70{\cdot}2 \text{ kJ})/2{\cdot}3RT$) we derive from equation (14) $E^P{}_2 = 34{\cdot}7 \pm 4{\cdot}3$ kJ mol^{-1} and $A^P{}_2 = 10^{8\cdot3 \pm 0\cdot7}$ l mol s^{-1}. This leads to values for secondary and tertiary hydrogen atoms: $E^S{}_2 = 29{\cdot}0 \pm 0{\cdot}7$ kJ mol^{-1} and $A^S{}_2 = 10^{8\cdot2 \pm 0\cdot1}$ l mol^{-1} s^{-1}; $E^T{}_2 = 23{\cdot}8 \pm 1{\cdot}3$ kJ mol^{-1} and $A^T{}_2 = 10^{8\cdot1 \pm 0\cdot2}$ l mol^{-1} s^{-1}. The activation energies are each *ca.* 5—6 kJ higher than those reported for methoxyl radicals. Such a difference seems reasonable although the difference is little more than experimental error.[15]

Tables 4, 5, and 8 show the relative selectivities for the chlorination of 1-fluoro-, 1-chloro-, and 1-cyanobutane with t-butyl hypochlorite. The results are expressed relative to the 3-position because the rate of attack at the 4-position is small and hence the estimation of the amount of attack at this site is liable to error. The reactivity pattern is somewhat different to that observed in chlorination by elemental chlorine, confirming that chlorine atoms are not major contributors under the present conditions. It has been suggested that reaction (7) rather than reaction (6) is rate determining,[16] however, no cross-termination products were detected. Furthermore if reaction (7) is slow it would be possible for the radicals to scramble (reaction (16)]. If this process was important an increase in t-butyl hypochlorite concentration would *reduce* the selectivity. In fact the exact opposite is observed (Table 7) and we have already attributed this to a very small contribution from chlorine atoms formed in the initiation process. We

$$XCH_2CH_2CH_2\dot{C}H_2 + XCH_2CH_2CH_2CH_3 \longrightarrow XCH_2CH_2CH_2CH_3 + XCH_2CH_2\dot{C}HCH_3 \quad (16)$$

---

[11] C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6108.

[12] A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Amer. Chem. Soc.*, 1956, **78**, 1190.

[13] S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions,' NSRDS-NBS 21, Washington, 1970, p. 597.

[14] P. Cadman, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc.* (*A*), 1971, 2296.

[15] T. Bercés and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 348.

[16] A. A. Zavitsas and J. D. Blank, *J. Amer. Chem. Soc.*, 1972, **94**, 4603

have already commented on the absence of a change in selectivity when the light intensity is altered (Table 6).

The results for 1-fluoro- (Table 5) and 1-chloro-butane (Table 4) are reported over a range of temperatures. The changes in selectivity are very small compared with the small difference in activation energy reported above for attack at primary and secondary positions. The trends which can be detected, are consistent with the idea that the differences in reactivity of different sites are due, at least in part, to small changes in activation energy. However the results are too scattered to justify calculating the Arrhenius parameters.

TABLE 9

Relative selectivities for the attack by Cl•, Bu^{t}O•, and Br• on butane, 1-fluoro-, 1-chloro-, and 1-cyano-butane at *ca.* 90 °C in the gas phase

		Cl•				Bu^{t}O•				Br•			
	X =	H	F	Cl	CN	H	F	Cl	CN	H	F	Cl	CN
α	CH_2	1	0·9	0·8	0·2	1	6·8	6·4	2·8	1	10	34	25
β	CH_2	3·8	1·7	2·1	1·7	8·0	3·3	3·6	2·5	82	9	32	8
γ	CH_2	3·8	3·7	3·7	3·9	8·0	8·0	8·0	8·0	82	82	82	80
δ	CH_3	1	1	1	1	1	1	1	1	1	1	1	1
Reference		8	8	8	9	This work				8	8	8	9

Table 9 shows the relative selectivities exhibited by chlorine atoms, t-butoxyl radicals, and by bromine atoms. The first feature to notice is that none of the substituents (X = F, Cl, or CN) have any effect on attack by these species beyond the second carbon atom. The β-position is deactivated to all three radicals, the fluorine atom and the cyano-group showing a greater effect than the chlorine atom. This result is consistent with the idea that these substituents exert their influence through polar forces in the transition state. The α-position is more reactive than the δ-position to attack by t-butoxyl radicals and bromine atoms, but less reactive to attack by chlorine atoms.

The marked difference in selectivity of t-butoxyl radicals and chlorine atoms can be explained if $D(\mathrm{Bu^tO{-}H})$ is less than $D(\mathrm{Cl{-}H})$. The literature values are similar, but the present results suggest that the oxygen–hydrogen bond in t-butyl alcohol is weaker. Walling concluded that the polar properties of t-butoxyl radicals and chlorine atoms were about equal. The present results while showing they are similar, indicate that t-butoxyl radicals are less affected by polar forces. In fact the reactivity of t-butoxyl radicals lies between that of bromine atoms and that of chlorine atoms, although it approaches much more closely to the latter. Hydrogen abstraction by bromine atoms is endothermic and although polar influences are important, bond strength considerations predominate. Hydrogen abstraction by t-butoxyl radicals is probably slightly exothermic and the reaction is much less selective but bond strength considerations still predominate. Hydrogen abstraction by chlorine atoms is exothermic and here polar effects predominate in a very unselective process.

We thank the S.R.C. for financial support for purchase of a gas chromatograph and an integrator, and for a maintenance award to I. K. S.

[3/2055 *Received, 5th October*, 1973]