

187. *Free-radical Substitution in Aliphatic Compounds. Part I. Halogenation of n-Butane and isoButane in the Gas Phase.*¹

By P. C. ANSON, P. S. FREDRICKS (in part), and J. M. TEDDER.

Butane and *isobutane* have been fluorinated, chlorinated, and brominated in the gas phase over a range of temperature. The relative rates of substitution of the different hydrogen atoms is in the expected order tertiary > secondary > primary in each case, and the reaction selectivity decreases in the order bromination \gg chlorination > fluorination. The results permit a semiquantitative comparison.

THE principal reaction of aliphatic hydrocarbons is substitution by a free-radical process involving the initial formation of an alkyl radical by abstraction of hydrogen. This process is vastly different from the one-stage electrophilic substitution characteristic of aromatic compounds, and unlike the latter, very little is known about the effect of changes in the structure of the aliphatic compound on the reaction. Still less is known about the effect of changing the attacking radical. It is often suggested that because aliphatic substitution is a free-radical process it will be almost unaffected by polar groups in the substrate molecule, and that almost random attack may be expected. This is not borne out by available data, and probably authors are thinking solely about chlorination, where the activation energy of the all-important hydrogen-abstraction step is probably little over 1 kcal. mole⁻¹, whether primary, secondary, or tertiary hydrogen is removed,² so that near-random substitution is hardly surprising. With less reactive radicals aliphatic substitution

¹ Presented in part to the XV Congress of Pure and Applied Chemistry, Paris, 1957.

² Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629.

can become highly selective as is exemplified by the bromination of *isobutane*,³ and even with chlorination purely polar effects in the molecule can have a tremendous influence (cf. 1 : 1 : 1-trifluorobutane⁴). Some aspects of this problem have been discussed recently by Brown and his co-workers.⁵ In the work in the present Series it is planned to change the nature of the attacking free radical as well as the structure of the aliphatic compound so as to obtain a more detailed picture of aliphatic substitution. The reactivity of primary, secondary, and tertiary hydrogen atoms in simple aliphatic hydrocarbons as exemplified by *n*-butane and *isobutane* is now compared, fluorine, chlorine, and bromine atoms being the attacking radicals.

Previously no quantitative study of the gas-phase monofluorination of aliphatic hydrocarbons has been made although more extensive fluorination has received much attention, notably from Bigelow and his co-workers.⁶ Chlorination of aliphatic compounds has received considerable attention in the semitechnical literature, but for our purposes the most important work is the classical studies of Hass, McBee, and their co-workers.⁷ More recent work includes some from Russia⁸ and a careful study of the chlorination of propane by Knox.⁹ Bromination has received remarkably little quantitative study and the only significant papers are those by Kharasch and his co-workers,^{3, 10} Van Artsdalen and his co-workers,¹¹ and an earlier paper by Guyer and Rufer.¹² The present results and those previously reported will be compared below.

Initially we tried to start with the hydrocarbon in the liquid phase.¹³ Unfortunately fluorination under these conditions was heterogeneous and relatively uncontrolled, so after a preliminary study had been made liquid-phase work was abandoned. In the gas phase the great difficulty is the control of the temperature in the highly exothermic reactions. Control was achieved by using a continuous-flow apparatus and diluting the reactants with a vast excess of nitrogen.

EXPERIMENTAL

Two gaseous streams, one of butane and nitrogen, and the other of the halogen and nitrogen, were preheated separately to the intended reaction temperature and then brought together in a heated reaction chamber. When necessary the dissociation of the halogen was promoted by visible and/or ultraviolet light. After passing through the chamber the gas stream continued through two packed columns to remove the unchanged halogen and the hydrogen halide formed, then through a trap maintained at -70° in which the products and the unchanged butane condensed. Samples of liquid were then withdrawn from the trap for injection into a gas-phase chromatography column which was used for the separation and estimation of the components of the product.

Apparatus.—Two similar reaction vessels were constructed, one of glass surrounded by a vapour jacket and one of copper which fitted into an electric furnace. They consisted of two preheating coils (6 mm. O.D. tubing; total volume 25 c.c. each), a mixing vessel (75 c.c.), and a subsequent coil (25 c.c.). With flow rates of 170 c.c./min. as used for the fluorinations this gives a contact time of 0.59 min. All tubing subsequent to the reaction vessel was blacked-out.

Gas-phase Chromatography.—This used apparatus essentially similar to that described previously.¹³ Two columns were used: a short one (3 ft.) of wide bore (12 mm.) and a longer

³ Kharasch, Hered, and Mayo, *J. Org. Chem.*, 1941, **6**, 818.

⁴ Henne and Hinkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 1197.

⁵ Ash and Brown, *Rec. Chem. Progr.*, 1948, **9**, 81; Brown and Ash, *J. Amer. Chem. Soc.*, 1955, **77**, 4019; Brown and Russell, *ibid.*, 1955, **77**, 4025.

⁶ Bigelow *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 198 and many succeeding papers.

⁷ Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190; 1936, **28**, 333.

⁸ Tischenko and Chibakov, *Zhur. obschei Khim.*, 1937, **7**, 658, 897; Tischenko and Zhokhovets, *ibid.*, 1948, **18**, 43; Krentsel and Pokotilo, *Zhur. priklad. Khim.*, 1951, **24**, 727; Nekrasova, *Doklady Akad. Nauk S.S.S.R.*, 1953, **88**, 73, 475.

⁹ Knox, *Chem. and Ind.*, 1955, 1631.

¹⁰ Kharasch, Yu Cheng Liu, and Nudenberg, *J. Org. Chem.*, 1955, **20**, 680.

¹¹ Eckstein, Scheraga, and Van Artsdalen, *J. Chem. Phys.*, 1954, **22**, 28.

¹² Guyer and Rufer, *Helv. Chim. Acta*, 1940, **23**, 533.

¹³ Anson and Tedder, *J.*, 1957, 4390.

one (12 ft.), somewhat narrower (6 mm.). Both were packed with "dinonyl phthalate" on Celite as before. The greatest difficulty was the separation of the fluorinated butanes from the vast excess of unchanged butane. To obtain peaks for the fluorobutanes of sufficient size for accurate estimation so much unchanged butane had to be introduced that the chromatography columns became overloaded, causing the butane peak to trail badly. This difficulty was partly overcome by using the two columns in series. The mixture of products was injected into the short, wide-bore column, the exit of which led through a trap cooled in liquid nitrogen and into the long column. The mixture was partially separated on the first column, and the unchanged butane, eluted first, was condensed in the trap and only the carrier nitrogen passed through into the second column. After most of the butane had been eluted from the first column, but before any of the fluorobutanes appeared, the trap was by-passed so that all subsequent material emerging from the short column now passed directly into the long narrow column. The second column was not now overloaded and satisfactory separation could be obtained even with the products from the fluorination of *isobutane*. Although the short column was originally intended solely for this purpose it was found suitable for the direct separation of the high-boiling bromides.

Fluorination.—A large number of preliminary runs were carried out with *n*-butane with different concentrations of reactants and both glass and copper vessels (the etching of the glass one was very slight). The products of the reaction was not altered by changing from one vessel to the other. Finally a series of runs was completed in the copper vessel at 25° (23 runs) and at 186° (24 runs) with the relative concentrations *n*-butane (5 parts), fluorine (0.75 parts, estimated from the current supplied to the generator, it being assumed to be 75% efficient), and nitrogen (180 parts). The total flow rate was 180 c.c./min. A similar series of runs was completed with *isobutane* at 25° (27 runs) and at 125° (24 runs). Temperatures above 186° were not attempted with *n*-butane because it was found that synthetic mixtures of 1-fluoro- and 2-fluoro-butane were decomposed. With *isobutane*, the reaction products when recycled through the vessel underwent thermal decomposition at much lower temperatures and for this reason the runs at 125° have little meaning. Hydrogen fluoride catalyses the decomposition of alkyl fluorides, but the high dilution and flow technique helped to minimise this effect.

Chlorination.—Chlorinations were carried out entirely in the glass vessel with two 100 w lamps for illumination. A series of runs with *n*-butane was made at -10° (12 runs), 10° (7 runs), 35° (19 runs), 80° (13 runs), and at 146° (20 runs). The relative concentrations were *n*-butane (15 parts), chlorine (1 part) and nitrogen (180 parts), with total flow rates of either 60 c.c./min. or 100 c.c./min. (these slight changes in flow had no effect on the reaction). Three runs were made at 35° with twice as much nitrogen and a total flow rate of 150 c.c./min. These again did not differ within experimental error from those at the higher concentration. *iso*-Butane was chlorinated under the same conditions at -10° (12 runs), 35° (16 runs), 80° (10 runs), and 146° (14 runs).

Bromination.—Bromination required slightly different techniques. Bromine was introduced into the gas stream by passing nitrogen through a bubbler, containing the bromine, and surrounded by a constant-temperature bath. The concentration of bromine in the gas stream was controlled by the temperature in the bath, and estimated from the known values of its vapour pressure. Because of the selective nature of the reaction it was not possible to estimate directly the relative areas of the peaks of *n*- and *iso*-butane on the same chromatogram (the actual ratio was about 1 : 60). Two different methods were employed. In the first, two chromatograms were made for each run, one with sufficient product to give a good secondary peak and the other with ten times as much material from which the primary peak could be estimated. In the second method a single chromatogram was made for each run but as soon as the *sec.*-butyl bromide had been eluted the sensitivity of the detecting recorder was increased by removing a shunt of known resistance. The ratios obtained by the two methods were, within experimental error, the same. All brominations were performed in the glass vessel illuminated by two 100 w lamps (in some runs these were supplemented by an ultraviolet lamp and in one run replaced by two 50 w lamps without affecting the ratio of the products). Runs were made at 146° (9 runs by each method). At higher temperatures there was some breakdown of products and at lower temperatures the reaction became too selective even for the above techniques. The relative concentrations of the reactants were butane (5 parts), bromine (0.5—1 part), nitrogen (80 parts), and a total gas flow of 85 c.c./min. Bromination of *isobutane* was too selective for either of the above techniques, the ratio of *isobutyl* bromide to *tert.*-butyl bromide being of the order of 1 : 200. To have sufficient material to give a measurable peak for

isobutyl bromide on the chromatogram meant that the column was overloaded with *tert.*-butyl bromide which, being eluted first, then trailed, making accurate estimation of the *isobutyl* bromide impossible. Butane and *isobutane* were therefore brominated competitively, and rates of formation of *tert.*-butyl bromide and of *sec.*-butyl bromide compared. Since the relative rates of bromination of primary and secondary hydrogen atoms were already known from the experiments with *n*-butane, it was possible to calculate the difference in rate of formation of *iso*- and *tert.*-butyl bromide by assuming the hydrogen atoms in *n*-butane and *isobutane* to react similarly. Six competitive runs were made at 160° with the relative concentrations *n*-butane (3 parts), *isobutane* (3 parts), bromine (1 part), nitrogen (120 parts), and a total flow of 125 c.c./min.

DISCUSSION

The three types of halogenation may be considered to proceed by an identical process.



However the thermochemistry of these steps is vastly different. Assuming $D(R-H)$ to be approximately 100 kcal. mole⁻¹, and taking the best values for the other relevant bond dissociation energies,¹⁴ we obtain the heats of reaction in Table 1. The importance of the

TABLE 1. Approximate heats of reaction (kcal. mole⁻¹) for aliphatic halogenation.

X = F	$\Delta H_2 \approx -34.0$	$\Delta H_3 \approx -68.0$
X = Cl	$\Delta H_2 \approx -3.0$	$\Delta H_3 \approx -23.0$
X = Br	$\Delta H_2 \approx +12.5$	$\Delta H_3 \approx -23.0$

enormous overall heat of reaction (*ca.* 100 kcal. mole⁻¹) in the case of fluorine, compared with *ca.* 25 kcal. mole⁻¹ for chlorine and 10 for bromine, when attempting controlled fluorination has been discussed previously.¹⁵ These figures also show that reaction (2) may be expected to be reversible in bromination and possibly also in chlorination, but is unlikely to be in fluorination.

In our investigation the total extent of halogenation was never allowed to exceed 15%, so the formation of polyhalogenation products can be neglected and the ratio of the two products, *e.g.*, *sec.*-butyl chloride : *n*-butyl chloride, can be equated with the rates of substitution at the primary and secondary hydrogen atoms. Steady-state conditions being assumed, and provided that recombination of the halogen atoms is the only important chain-termination step,* then the ratio of these rates multiplied by the inverse ratio of the number of hydrogen atoms of each type (Relative Selection, RS), is equal to the ratio of the rate constants k_2 for the different types of hydrogen atom (*p*, *s*, *t* = primary, secondary, tertiary):

$$\frac{[\text{Bu}^s\text{X}]}{[\text{Bu}^p\text{X}]} \times \frac{3}{2} = \text{RS}_p^s = \frac{k_2^s}{k_2^p}$$

Combining all the individual readings by the usual "least squares" procedure, we obtain $k_2^s/k_2^p = 1.8 \exp(480 \pm 70 \text{ cal./RT})$ for chlorination and a very tentative $k_2^s/k_2^p = 1.1 \exp(97 \pm 20 \text{ cal./RT})$ for fluorination.

At 398° K fluorination of *isobutane* appears to have an RS value less than unity. This

* The essential assumption here is that $k_3 \gg k_2$. Then $[R\cdot] \ll [X\cdot]$ and if k_5 and k_6 are not too large compared with k_4 , only reaction 4 will be important:

$$d[\text{RX}]/dt = k_3[\text{R}\cdot][\text{X}_2]$$

By the usual steady-state assumption this becomes

$$d[\text{RX}]/dt = k_2[\text{RH}]\sqrt{(k_1/k_4[\text{M}]})$$

Thus for competitive halogenation of RH and R'H

$$[\text{RX}]/[\text{R}'\text{X}] = (k_2/k_2')/([\text{RH}]/[\text{R}'\text{H}])$$

¹⁴ Cottrell, "Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1954.

¹⁵ Tedder, *Chem. and Ind.*, 1955, 508.

TABLE 2. RS_p^s (mean) for halogenation of *n*-butane.

Temp. (°K)	F	Cl	Br
263		4.29 ± 0.12	
283		4.07 ± 0.17	
298	1.25 ± 0.19		
308		3.89 ± 0.30	
353		3.63 ± 0.15	
398			82 ± 15
419		3.34 ± 0.21	
459	1.18 ± 0.14		

TABLE 3. RS_p^t (mean) for halogenation of isobutane.

	F	Cl	Br
		5.84 ± 0.13	
	1.39 ± 0.16		
		5.16 ± 0.31	
		4.51 ± 0.18	
(0.98)		3.93 ± 0.09	1640 ± 300

is not so: at 398° K the products of the reaction are unstable. Combining the individual chlorination readings we obtain $k_2^t/k_2^p = 2.1 \exp(540 \pm 70 \text{ cal./RT})$.

Qualitatively the results are as expected and agree well with previous work. Quantitatively the chlorination results are very close to those of Knox who chlorinated propane by a static method. They differ slightly from the original work of Hass and McBee⁶ presumably for the reasons discussed by Knox. Kharasch³ and Van Artsdalen,¹¹ using far less sensitive analytical techniques, only detected *tert.*-butyl bromide as monobromination product of isobutane, which is hardly surprising in view of our results. Two recent papers report the attack of CH_3 and CD_3 radicals on propane, isobutane, and *n*-butane;^{16, 17} the results fit in well with ours.

TABLE 4. Selectivity of different radicals $X\cdot$ for primary, secondary, and tertiary hydrogen atoms.

	RS at 300° K			Differences (cal. mole ⁻¹) in activation energy		
	$-CH_3$	$>CH_2$	$\geq CH$	$E_2^p - E_2^s$	$E_2^p - E_2^t$	$E_2^p^*$
X = F	1	1.2	1.4	90	—	?
X = Cl	1	3.9	5.1	480	540	1000
X = CD_3	1	35	—	2100	—	11,000
X = CH_3	1	—	—	2300	2900	11,400
X = Br	1	82 †	1600 †	—	—	14,000

* Except for CD_3 radicals where E_2^p for butane was determined directly, these values are those reported for the corresponding reaction with ethane [$Cl\cdot + C_2H_6$ (ref. 2); $CH_3\cdot + C_2H_6$ (Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Phys.*, 1951, **19**, 161); $Br\cdot + C_2H_6$ (Andersen and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 478)]. † RS values for bromination at 400° K.

Table 4 shows how the different radicals form a very consistent overall picture, and it suggests that E_2^p for fluorination is about 0.5 kcal. mole⁻¹ or less. The only anomaly occurs in the ratios of the frequency factors A_2^s/A_2^p . For chlorination our work and that of Knox give a value of approximately 2 for this ratio, but fluorination gives a value of approximately unity, although this value is not very definite. For hydrogen abstraction by CD_3 radicals McNesby and Gordon get a value of exactly unity. The only apparent difference in the ΔS^\ddagger term would be due to a difference in symmetry factors. Approximate calculations indicate that the ratio should be greater than unity, as we have found for chlorination, but clearly further work is required.

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DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SHEFFIELD.

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¹⁶ McNesby and Gordon, *J. Amer. Chem. Soc.*, 1956, **78**, 3570.

¹⁷ Rice and Vanderslice, *J. Amer. Chem. Soc.*, 1958, **80**, 292.