818. *The Reactions of Bromine Atoms with Alkanes and Methyl Halides.*

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The reactions of bromine atoms with alkanes and with methyl halides have been studied by competitive bromination in the gas phase and analysis of the products by gas chromatography. Absolute rate constants and Arrhenius parameters are given, based on those previously found for attack on methyl bromide. The activation energies for hydrogen abstraction are probably closely related to the strengths of the C–H bonds broken. The *A* factors predicted by transition-state theory agree well with those found. The deviations are similar to those obtained for chlorine- and fluorine-atom reactions.

Investigators have studied the hydrogen-abstraction reactions of bromine atoms both because of the intrinsic interest of the rate constants and the reaction systems and because measurement of the activation energies of the reactions could lead to more accurate values for bond-dissociation energies. The first rate constant of a reaction of an atom or radical with a molecule to be accurately measured was that of the bromine atom with hydrogen. Bodenstein and Lind [1] obtained expressions for the rate of disappearance of bromine from mixtures with hydrogen by thermal processes. The value of the rate constant for reaction (1) derived from their work is shown in Table 1. Their values of the activation

$$Br + H_2 = HBr + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

energy and *A* factor have been amply confirmed. Kistiakowsky and Van Artsdalen [2] showed that the gas-phase bromination of methane proceeded by the same mechanism as the reaction with hydrogen. The currently accepted value for $D(CH_3–H)$, the strength of the C–H bond in methane, is largely based on their activation energy for the attack

$$Br + RH = HBr + R \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

on methane (2). The heat of reaction (2) is related to the activation energies of the forward (E_2) and the reverse (E_{-2}) reaction by the equation:

$$\Delta H_2 = E_2 - E_{-2}$$

Since the heats of formation of H, Br, and HBr are accurately known, the value of $D(CH_3–H)$ can be derived from the equation

$$D(CH_3–H) = (E_2 - E_{-2}) + D(H–Br)$$

The principal uncertainty is in the value of E_{-2}. Andersen and Van Artsdalen [3] also deduced $D(C_2H_5–H)$ from less detailed studies and measured the activation energy for attack of bromine on methyl bromide.[2] Van Artsdalen and his collaborators later studied the reactions of bromine with neopentane,[4] isobutane,[5] and toluene.[6] Although the work was careful and yielded acceptable values for the bond strengths, the results have been suspected because the *A* factors of the abstraction reactions were very high. Benson and Buss [7] explained the discrepancies on the grounds that assumptions made in interpreting the results were invalid for the more reactive compounds. These necessary assumptions

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[1] Bodenstein and Lind, *Z. phys. Chem.*, 1907, **57**, 168.

[2] Kistiakowski and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469.

[3] Andersen and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 479.

[4] Schweitzer and Van Artsdalen, *J. Chem. Phys.*, 1951, **19**, 1028; Hormats and Van Artsdalen, *ibid.*, p. 778.

[5] Eckstein, Scheraga, and Van Artsdalen, *J. Chem. Phys.*, 1954, **22**, 28.

[6] Swegler, Scheraga, and Van Artsdalen, *J. Chem. Phys.*, 1951, **19**, 135; Andersen, Scheraga, and Van Artsdalen, *ibid.*, 1953, **21**, 1258.

[7] Benson and Buss, *J. Chem. Phys.*, 1958, **28**, 301.

were that steady-state concentrations of bromine atoms were reached in times short compared with the lengths of the runs. They calculated that a steady state was only attained for hydrocarbons less reactive than ethane. They also postulated that the reactions were partially heterogeneous, but there is no direct evidence for this.

One reason for adopting a competitive method to study brominations in this investigation was that no assumption had to be made about the rate at which steady-state concentrations were attained. Two hydrocarbons, R^3H and R^4H, were mixed in known

$$Br_2 \longrightarrow 2Br$$

$$Br + R^3H \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R^3 + HBr \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$Br + R^4H \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R^4 + HBr \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$R^3 + Br_2 \longrightarrow R^3Br + Br \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$R^4 + Br_2 \longrightarrow R^4Br + Br \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

proportion and then admitted to a reaction vessel containing bromine. Alkyl bromides were formed by reactions (3), (4), (5), and (6). Reactions (5) and (6) are fast, so we can write, for low percentage consumption of the hydrocarbons:

$$k_3/k_4 = R^3Br[R^4H]/R^4Br[R^3H]$$

where R^3Br is the total amount of the bromide formed. The bromine-atom concentration does not appear in this expression; therefore steady-state conditions are unnecessary. The rate-constant ratio should also be independent of the molecular bromine and hydrocarbon concentrations in agreement with experiment. The back reactions (—3) and (—4) were found by previous workers to be sufficiently fast to influence the overall rate of bromination of several hydrocarbons. It would be expected that the back reactions should influence k_3/k_4 less than the overall rate because the effect on the formation of R^3Br and R^4Br would tend to cancel out. Experiment showed that k_3/k_4 could be only slightly altered by the addition of far greater quantities of hydrogen bromide than were normally formed in the reactions.

The competitive method yields only relative values of the Arrhenius parameters A_3/A_4 and $E_3 - E_4$ when the reactions are investigated over a range of temperature. Consequently, all values of A_2 and E_2 depend upon an absolute determination. All the results obtained in this work are related to the rate constants for the bromination of methyl bromide. It would have been more satisfactory if the bromination of methane could have been used as the standard but the present results with methane were not sufficiently reliable to justify this choice. For many purposes it is the relative rates of reaction of members of series of compounds that are of greatest interest. The competitive method is ideal for such determinations.

Table 1 lists the Arrhenius parameters and rate constants that have been found. The values obtained in this work are for reaction with the indicated hydrogen atoms; as they are much the most reactive atoms, the overall rates are very little different. Those values that are considered incorrect are placed in parentheses. The errors quoted are the 50% probable errors derived by the method of least squares.

Two comparisons can be made with results obtained by Anson, Fredricks, and Tedder.[8] They found that k^s(n-butane)/k^p(n-butane) = 82 and k^t(isobutane)/k^p(n-butane) = 1640 at 146°.* Our results give k^s(n-butane)/k(ethane) = 143 and k^t(isobutane)/k(ethane) = 1820 at 146°. The discrepancy between k^s/k^p is outside experimental error and it is surprising that the values of k^t/k^p which were found from $(k^t/k^s) \,.\, (k^s/k^p)$ agree so well.

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* k^p, k^s, k^t relate to reaction at a primary, secondary, or tertiary carbon atom, respectively. Where all the carbon atoms of a molecule are identical this suffix is omitted.

[8] Anson, Fredricks, and Tedder, *J.*, 1959, 918.

No explanation can be advanced for these observations. It may be noted that k^s(propane)/k(ethane) = 83 at 146°. Fredricks and Tedder [9] also found that attack on a hydrogen atom in the 1-position in n-butyl chloride occurred 34 times as fast as attack on a primary hydrogen in n-butane at 146°. The agreement with our value of k(methyl chloride)/k(methane) = 50 for each hydrogen atom is as close as could be expected.

TABLE 1. *Rate constauts,* A *factors, and activation energies for reactions of type* (2).

RH	log k_2 (100°) (mole^{-1} cm.^{3} sec.$^{-1}$)	log A_2	E_2 (kcal. mole^{-1})	Ref.
H_2	3·36	14·2	18·5	1, *a*
	3·43	13·8	17·7	*b*
	3·48	13·8	17·6	*c*
	3·28	13·7	17·5	2
	3·27	13·7	17·8	*d*
	3·32	14·0	18·3	
D_2	2·23	13·9	19·9	
CH_4	3·07	13·8	18·3	2
	3·3	14·0	18·3	This work †
C_2H_6	—	—	13·9	3
	6·05	13·895 ± 0·035	13·396 ± 0·088	This work
$C_3H_8{}^s$	7·76	13·712 ± 0·069	10·149 ± 0·139	This work
$C_4H_{10}{}^n$	7·23	13·221 ± 0·137	10·225 ± 0·234	This work
$C_4H_{10}{}^i$	(10·7)	(17·6)	(11·7)	5
	8·90	13·303 ± 0·112	7·509 ± 0·204	This work
Neo-C_5H_{12}	(6·3)	(17·0)	(18·2)	4
	5·87	14·244 ± 0·061	14·289 ± 0·132	This work
$C_6H_5{\cdot}CH_3$	(9·1)	(13·5)	(7·6)	6
CH_3Br *	4·33 *	13·730 *	16·050 *	2
CH_3Cl	5·15	13·616 ± 0·057	14·451 ± 0·156	This work
$CHCl_3$	6·8	12·3	9·3	*e*

* Taken as standard. † These values are less reliable than those given for other compounds.

References: *a*, Bodenstein and Jung, *Z. phys. Chem.*, 1926, **121**, 127. *b*, Bach, Bonhoeffer, and Moelwyn-Hughes, *Z. phys. Chem.*, 1934, *B*, **27**, 71. *c*, Bodenstein and Lütkemeyer, *Z. phys. Chem.*, 1924, **114**, 208. *d*, Campbell and Fristrom, *Chem. Rev.*, 1958, **58**, 173. *e*, Sullivan and Davidson, *J. Chem. Phys.*, 1949, **17**, 176.

A Factors of Bromine-atom Reactions.—According to transition-state theory the *A* factor for a bimolecular reaction is given by

$$A = e^2(\boldsymbol{k}T/\boldsymbol{h}) \exp [(\Delta S^{\ddagger}_{tr} + \Delta S^{\ddagger}_{rot} + \Delta S^{\ddagger}_{vib})/\boldsymbol{R}]$$

The translational entropy of activation for reaction

$$RH + Br \rightleftharpoons RHBr \longrightarrow R + HBr$$

is given exactly by

$$\Delta S^{\ddagger}_{tr} = 1{\cdot}5\boldsymbol{R} \ln (M^{\ddagger}/M) - 19{\cdot}02 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

where $M^{\ddagger}$ and M are the molecular weights of RHBr and RH respectively and the standard state is 1 mole cm.$^{-3}$.

The rotational entropy of activation can be obtained from

$$\Delta S^{\ddagger}_{rot} = 0{\cdot}5\boldsymbol{R} \ln (A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHBr and RH. This value is for reaction at a single hydrogen atom of any type; inclusion of the symmetry numbers in the expression would yield $\Delta S^{\ddagger}_{rot}$ appropriate to all the hydrogen atoms of a given type in the molecule. The ABC values can be evaluated graphically with sufficient accuracy by assuming suitable configurations and bond lengths in RH and RHBr. C–H and C–C distances have been taken as 1·10 and 1·54 Å except for the half-order bonds in the complexes, *i.e.*, the bonds $>$C–H–Br. Following Pauling, we have

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[9] Fredricks and Tedder, *J.*, 1960, 144.

assumed that they are 0·18 Å longer than the corresponding single bonds, *i.e.*, C–H = 1·28 Å, H–Br = 1·59 Å. All bond angles have been taken as tetrahedral with the exception of ∠CHBr which has been taken as 180°. It was found that the results of similar calculations for the reactions of chlorine and fluorine atoms depended little on the precise dimensions assumed for the complex. The products of the moments of inertia are therefore unlikely to be in error by more than a few units %.

The calculation of the vibrational entropies of activation is much less certain. The procedure followed is that adopted for the chlorine [10] and fluorine atoms.[11] Briefly, it was assumed that most of the molecular motions of the complex would be the same as those of the reactant. Hence they could be disregarded in calculating the change of vibrational entropy. Only those vibrations most intimately associated with the site of the reaction should be greatly altered. The alteration will be similar for the members of a series such as the paraffins. It has been assumed that the only new vibrations that have to be considered are the symmetrical stretching and double degenerate bending of the R–H–Br bond. The stretching of the C–H bond that becomes the reaction co-ordinate makes a negligible contribution to the initial vibrational entropy. This simplification might introduce an error into the absolute values calculated for the A factors but should have little effect on the accuracy of the relative A factors calculated for different members of a series. The frequencies of the bending motion of the R–H–Br bonds were calculated in the same way as those for fluorine atoms, the same force constant being assumed. This is a straightforward application of classical mechanics; the frequency is simply a function of the masses of R, H, and Br and the internuclear distances. The force constants selected were those derived by Pitzer [12] to equate the calculated and experimental A factors for the reaction $Cl + H_2 = HCl + H$. The calculations are summarized in Table 2, and the results for log $(A_{exp.}/A_{calc.})$ for bromine atoms are compared with the equivalent quantities for chlorine and fluorine atom reactions.

The absolute rate constant for the reaction of chlorine atoms with hydrogen was determined between 25° and 700°. Pitzer's calculations refer to the mid-temperature of this range. The discrepancy in Table 2 between the calculated and experimental values for the reaction arises because the calculated value here was for 25°. No rate constant of a fluorine-atom reaction has been measured absolutely. The values in Table 2 are based on the assumption that the calculated and experimental A factors for ethane are equal.

TABLE 2. A *Factors for bromine-, chlorine-, and fluorine-atom reactions.*

Bond type RH	Br						Cl	F
	$\Delta S^{\ddagger}_{tr}$ + 19·02	$\Delta S^{\ddagger}_{rot}$	$\Delta S^{\ddagger}_{vib}$	log A (calc.)	log A (exp.)	$\log \frac{A_{exp.}}{A_{calc.}}$	$\log \frac{A_{exp.}}{A_{calc.}}$	$\log \frac{A_{exp.}}{A_{calc.}}$
H_2	11·05	6·85	1·1	13·66	13·90	+0·24	+0·23	+0·54 *
CH_4	5·34	7·06	7·2	13·78	13·42	−0·36	−0·68	+0·29 *
Primary C–H bonds								
C_2H_6	3·86	5·50	9·0	13·53	13·12	−0·41	−0·10	0·00 †
neo-C_5H_{12} ...	2·22	3·34	11·3	13·20	13·17	+0·03	+0·31	+0·06
Secondary C–H bonds								
C_3H_8	3·08	4·90	9·0	13·23	13·41	+0·18	+0·52	−0·03
n-C_4H_{10}	2·58	4·05	10·5	13·26	13·62	+0·36	+0·50	+0·08
Tertiary C–H bonds								
iso-C_4H_{10}	2·58	3·66	10·5	13·18	13·30	+0·12	+0·41	+0·15
Halides								
CH_3Cl	2·83	6·61	10·3	13·82	13·14	−0·68	−0·29	—
CH_3Br	1·83	6·90	11·6	13·95	13·25	−0·70	—	—

S in cal. mole^{-1} deg.$^{-1}$; A in mole^{-1} cm.^{3} sec.$^{-1}$.

* The figure in ref. 11 is incorrect. † Assumed, see ref. 11.

No adjustable parameters were involved in the calculations of the A factors for the

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[10] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

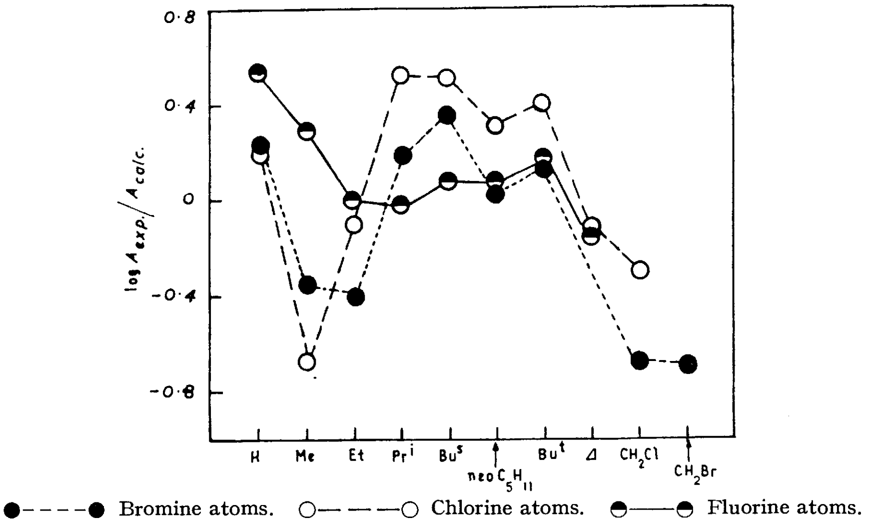
[11] Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 1064.

[12] Pitzer, *J. Amer. Chem. Soc.*, 1957, **79**, 1804.

bromine atoms. The good agreement with the experimental values is therefore most satisfactory. Wilson and Johnston [13] calculated a similar value for the reaction of hydrogen (log $A_{calc.} = 14{\cdot}1$) but a rather lower value for isobutane (12·4). The smallness of log ($A_{exp.}/A_{calc.}$) for the reactions is a strong argument that the experimental values obtained in this work are approximately correct and that those previously reported for the higher hydrocarbons are wrong.

The probable errors for the log $A_{exp.}$ derived by the method of least squares are lower than those usually found in kinetic studies. Nevertheless, little significance can be attached to the fourth significant figure, and there must frequently be an error in the third figure even if relative values only are considered. The parallelism, shown in the Figure, between the values of log ($A_{exp.}/A_{calc.}$) for the three series of halogen-atom reactions is more marked than could resonably have been expected. Two features that were noted for chlorine and fluorine are again found for bromine, *viz.*: (1) There is a fall in log ($A_{exp.}/A_{calc.}$) from hydrogen to ethane followed by a slight rise as the hydrocarbons become more complex.

log $A_{exp.}/A_{calc.}$ *for the reactions of bromine, chlorine, and fluorine atoms with hydrocarbons.*



(2) The values of log ($A_{exp.}/A_{calc.}$) are slightly higher for attack on a hydrogen atom attached to a secondary than to a primary carbon atom. It was suggested that these features could be attributed to the part played by alterations in the frequencies of the chain deformations that were ignored in the calculations. The bromine results support this conclusion. The fact that the bromine results resemble those for chlorine more closely than those for fluorine was also expected. It is therefore reasonable to suppose that a coherent theory could be developed that would reduce the size of log ($A_{exp.}/A_{calc.}$) and that their present sizes are not solely determined by experimental error.

Activation Energies of Bromine-atom Reactions.—The activation energies found for the attack of bromine atoms on the hydrocarbons are close to those that might have been expected, for the activation energies for the abstraction reactions of all the more selective radicals are in the order methyl > primary > secondary > tertiary.[14] The value of E_2 for neopentane is perhaps high but it lies within the limits of the experimental error of most work with other radicals. The strengths of the C–H bonds cannot be directly deduced until the activation energies of the back reactions, E_{-2}, have been measured. Some information can be derived if the Polanyi relation $E = \alpha\Delta H + c$, where c is a constant, is accepted.

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[13] Wilson and Johnston, *J. Amer. Chem. Soc.*, 1957, **79**, 29.

[14] Shaw and Trotman-Dickenson, unpublished work.

The difference in ΔH for the reactions of methyl and t-butyl is equal to $D(\text{Me–H}) - D(\text{Bu}^t\text{–H}) = 12{\cdot}5$ kcal. mole^{-1}.[21] This figure is derived from electron-impact measurements and may be in error by 2 or 3 kcal. mole^{-1}. Hence α lies between 0·72 and 1 (α cannot be greater than unity) with a most probable value of 0·86. This value has been used to obtain the intermediate values of D(R–H) shown in Table 3. The bond strengths are very reasonable and agree well with those obtained by electron impact. On the other hand, the Polanyi relation has not been clearly established for any series of reactions, largely because of the lack of an adequate knowledge of bond strengths. It would be expected that the relation would hold best when α is high, as in the present instance. At the moment the use of the relation should be regarded as no more than a plausible method of interpolation.

TABLE 3. D(R–H) *for alkanes and Arrhenius parameters for the reaction of alkyl radicals with hydrogen bromide.*

Alkyl	S	E_{-2}	$\log A_{-2}$	D(R–H)	Alkyl	S	E_{-2}	$\log A_{-2}$	D(R–H)
Methyl	47·2	1·8	12·2	102·5 *	Isopropyl ...	65·9	(3·1)	12·2	93·1
Ethyl	58·5	(2·5)	11·9	96·9	s-Butyl	76·8	(3·1)	12·4	93·2
Neopentyl ...	78·2	(2·4)	12·0	97·9	t-Butyl	70·4 †	(3·6)	12·1	90·0

S is in cal mole^{-1} deg.$^{-1}$, D and E in kcal. mole^{-1}, and A_{-2} in mole^{-1} cm.^{3} sec.$^{-1}$.

* Long, *Proc. Roy. Soc.*, 1949, **198**, 62. † Benson and Buss [7] recommend 79·5 cal. mole^{-1} deg.$^{-1}$, which seems much too high.

E_{-2} for methyl radicals has been estimated kinetically on a rather dubious basis. E_{-2} for the other radicals has been deduced from E_2 and ΔH_2 and is given in parentheses in col. 3 of Table 3. Values of A_{-2} have also been calculated from A_2 and ΔS_2 on the assumption that the entropies of the radicals are as listed in col. 2. The entropies have been derived from those of the parent hydrocarbon; 1·4 cal. mole^{-1} deg.$^{-1}$ have been added to allow for the electron degeneracy, and the symmetry numbers have been calculated on the assumption that the bonds from the carbon atom carrying the free electron are coplanar. Free rotation may occur slightly more readily in some of the radicals than in the parent molecules, hence the entropies may be slightly underestimated. Direct experimental evidence on reaction (—2) is clearly needed.

EXPERIMENTAL

Apparatus.—The apparatus was of Pyrex glass. Stopcocks were lubricated with Silicone grease. The reaction vessel (92 c.c.) was contained in a vapour-jacket that could be kept at suitable temperatures by filling it with different liquids. The temperature was measured with a thermocouple that had been calibrated against standard thermometers, placed in a well down the centre of the reaction vessel. The reaction vessel was joined by capillary tubing to the rest of the apparatus through a three-way stopcock. The hydrocarbons were generally measured in quantities sufficient for a series of runs into a 500 c.c. spherical mixing vessel that had a cold finger to contain liquid oxygen let into it. Small quantities were mixed in a toroidal trap with a flame applied to one side to induce convection. This trap was also used for degassing and remixing the hydrocarbons before each run. The stopcock on the reaction vessel separated the hydrocarbon dosage and storage system, from the bromine storage and the analysis system. Pressures in the former were measured by a mercury manometer.

The detector for the chromatography system was a katharometer made from a brass block with coiled tungsten filaments. Hydrogen was the carrier gas.

Procedure.—Known amounts of hydrocarbons were mixed with the less reactive hydrocarbon in considerable excess. Bromine was admitted into the reaction vessel up to a pressure determined by the temperature of the storage vessel. The pressure was 4 cm. (0°) for most runs. The hydrocarbon mixture was then expanded into the reaction vessel. The vapour-bath was painted black except for a window fitted with a shutter. Slow reactions were accelerated by illumination with a 125 w mercury arc. At the end of the reaction, the products were frozen into the injection trap of the chromatography system. The products were then injected into the column through a short tube of 30% *NN*-dimethyl-*p*-toluidine on 52/72 mesh firebrick or a mixture of tetramethyldiaminodiphenylmethane with dinonyl phthalate on firebrick which absorbed the bromine.

Materials.—The rate-constant ratios were very sensitive to impurities in the bromine which was stored for several weeks over potassium bromide. Small samples were distilled from potassium bromide and phosphoric oxide with rejection of head and tail fractions. They were degassed many times by distillation under a high vacuum into traps cooled with liquid oxygen.

The methane generally contained some impurities which made it difficult to obtain reproducible results. B.O.G. methane passed over heated copper and subsequently degassed was unsatisfactory. Some satisfactory work was done with methane obtained from the National Chemical Laboratory, Teddington, but only a limited supply was available. Prebromination of the methane in the presence of ethane partially removed the impurity. Manganese dioxide that had been reduced by hydrogen at 300° was a more convenient and equally effective reagent for removing the impurity. The purifications were followed by several trap-to-trap distillations (−183° to −210°) under a high vacuum. The nature of the more successful methods of purification indicates that the impurity is probably oxygen and that it is very difficult to remove it completely. Ethylene was removed from B.O.G. ethane with an absorbent. Propane was an N.C.L. sample. n-Butane and isobutane were given by the British Petroleum Co.; the latter contained 0·3% of propane. The neopentane (Phillips Petroleum pure grade) contained 1% of isobutane that was removed by bromination of the mixture for 10 min. in diffused sunlight. The product was distilled from a trap at −80° through tubes of potassium hydroxide and Anhydrone. The residual bromine was removed by passage through a tube filled with *NN*-diethyl-*p*-toluidine supported on three times its weight of firebrick. The methyl chloride (B.O.G.) and methyl bromide (B.D.H.) were degassed. All gases were dried (P_2O_5).

RESULTS

Calibrations.—The relative sensitivity of the katharometer to the products was determined by measurements on known mixtures of selected pairs of bromides. The sensitivities found (relative to ethyl bromide) were as follows: EtBr, 1; CH_2ClBr, 0·98; MeBr, 1·08; CH_2Br_2, 1·11; Pr^iBr, 1·02; Bu^sBr, 1·02; Bu^tBr, 1·10. Neopentyl bromide was assumed to have the same sensitivity as Bu^tBr.

The reaction systems are described in the order in which they were studied.

n-Butane–Isobutane.—Between −6° and 98° the only measurable products were t- and s-butyl bromide. They were separated on a 50 cm. column of 25% dimethyl phthalate–Celite (80—100 mesh). Details of the conditions and results are given in Table 4, which shows that the relative rate constants are independent of the proportions of the reactants, their total pressure, the amount of bromine, and the presence of added hydrogen bromide. Tests showed that no bromination occurred in the chromatography system and that the products did not decompose. A least-squares treatment gave

$$k^t(\text{isobutane})/k^s(\text{n-butane}) = (0{\cdot}132 \pm 0{\cdot}009) \exp (2716 \pm 30/\boldsymbol{R}T)$$

Propane–Isobutane.—In 27 runs between 34° and 148°, the only measurable products were isopropyl and t-butyl bromide. They were separated on a 60 cm. column of 25% dimethyl phthalate–Celite. The total pressure of hydrocarbon was 6·6 cm. in most runs with propane/isobutane = 3·45. Variation of hydrocarbon pressure between 4 and 8 cm. and of the proportion between 2 and 4 did not affect the results; nor did the addition of hydrogen bromide.

$$k^t(\text{isobutane})/k^s(\text{propane}) = (0{\cdot}418 \pm 0{\cdot}04) \exp (2640 \pm 65/\boldsymbol{R}T)$$

Propane–Ethane.—In 32 runs between 12·5° and 145°, the only measurable products were isopropyl and ethyl bromide which were separated on the column used in the previous experiment. The total pressure of hydrocarbon was 7·6 cm. in most runs, with ethane/propane = 4·9. Variation of hydrocarbon pressure from 5 to 8·4 cm., of the proportion from 4·9 to 1·43, and of the bromine pressure from 3·4 to 15 cm. had no effect. As the proportion of propane was normally small, the extent of the reaction was kept low to restrict its relative depletion. The addition of 20 times the normal amount of hydrogen bromide formed had only a very small effect.

$$k^s(\text{propane})/k(\text{ethane}) = (0{\cdot}669 \pm 0{\cdot}053) \exp (3247 \pm 51/\boldsymbol{R}T)$$

Methyl Bromide–Ethane.—In 23 runs between 58·5° and 199°, the only measurable products were methylene dibromide and ethyl bromide. These were passed through 150 cm. of 25% dinonyl

TABLE 4. *Results of isobutane–n-butane bromination.*

Temp.	Hydrocarbon press (cm.) n-Butane	Isobutane	Peak areas (units) Bu^tBr	Bu^sBr	$\frac{k^t \text{ (isobutane)}}{k^s \text{ (n-butane)}}$
−11·5°	4·73	1·88	9·48	1·00	23·93
,,	,,	,,	12·30	1·12	27·60
,,	,,	,,	8·36	0·82	25·84
,,	,,	,,	8·59	0·86	25·12
−6·0	,,	,,	11·73	1·29	22·89
,,	,,	,,	10·33	1·28	20·30
11·38	5·29	1·51	6·20	1·40	15·58
,,	4·10	2·72	10·30	0·95	16·35
,,	5·80	2·31	5·36	0·86	15·65
,,	3·00	1·20	5·34	0·77	16·94
,,	4·73	1·88	9·03	1·38	16·46
,,	,,	,,	5·57	0·88	15·92
,,	,,	,,	11·25	1·67	16·95
,,	,,	,,	6·04	0·96	15·83
35·0	5·19	2·07	7·68	1·81	10·63
,,	3·82	1·52	3·05	0·69	11·09
,, [a]	3·26	1·30	2·11	0·49	10·80
,, [b]	4·73	1·88	3·03	0·68	11·16
,, [c]	3·51	1·40	16·04	3·61	11·14
58·3	4·73	1·88	6·04	1·73	8·78
,,	,,	,,	3·14	0·98	7·96
,,	,,	,,	2·77	0·79	8·83
,,	,,	,,	5·21	1·65	7·94
,,	,,	,,	9·08	3·02	7·56
98·0	,,	,,	5·08	2·29	5·58
,,	,,	,,	1·86	0·93	5·03
,,	,,	,,	3·17	1·46	5·45
,,	,,	,,	1·60	0·77	5·23
,,	,,	,,	1·29	0·61	5·32
,,	,,	,,	2·52	1·13	5·61

[a] Bromine pressure = 15 cm. [b] Bromine pressure = 3·4 cm. Bromine pressure for all other runs = 6 cm. [c] 3 mm. HBr also present.

phthalate–Celite (70°) and on to 50 cm. of 25% dimethyl phthalate–Celite (25°). When the ethyl bromide was eluted the second column was by-passed, and the methylene bromide carried through a column of glass beads that maintained the flow of carrier gas constant. The pressure of reactants was between 6 and 9 cm., and the methyl bromide/ethane ratio between 2·1 and 4·3. Variation of the bromine pressure between 3·4 and 15 cm. had no effect. Previous work had shown that hydrogen bromide had no effect on these reactants separately.

$$k(\text{ethane})/k(\text{methyl bromide}) = (1{\cdot}364 \pm 0{\cdot}050) \exp (2654 \pm 88/\boldsymbol{R}T)$$

Neopentane–Ethane.—In 23 runs between 57° and 200°, the only products were ethyl bromide and a compound with an elution time appropriate to neopentyl bromide. They were separated on a 60 cm. column of 25% dimethyl phthalate–Celite (20°). Hydrocarbon pressures were between 4 and 8 cm., with ethane/neopentane between 1·5 and 0·67. The bromine pressure was between 3·4 and 15 cm.

$$k(\text{neopentane})k(\text{ethane}) = (2{\cdot}235 \pm 0{\cdot}117) \exp (-893 \pm 44/\boldsymbol{R}T)$$

Methyl Chloride–Ethane.—In 26 runs between 58·5° and 200° the only measurable products were ethyl bromide and bromochloromethane. The column was 60 cm. of 25% dimethyl phthalate–Celite (20°). Total reactant pressure was 4—8 cm., methyl chloride/ethane = 2·9—1, and bromine pressure 3·4—15 cm. Addition of more hydrogen bromide than was formed in a normal run did not affect the rate constants.

$$k(\text{ethane})/k(\text{methyl chloride}) = (1{\cdot}897 \pm 0{\cdot}109) \exp (1055 \pm 68/\boldsymbol{R}T)$$

Methane–Methyl Chloride.—23 Runs were carried out between 204° and 341°. The products were analysed on a 150 cm. column of 25% diethyl phthalate–Celite (37°). Most of the runs were done with a total reactant pressure of about 7·6 cm., made up in the proportions $MeCl : CH_4 : C_2H_6$ of 1·3 : 5 : 0·7. The addition of the ethane greatly improved the reproducibility and yield of the C_1 products, presumably because the ethyl radicals formed reacted with the impurities. Total pressure was varied between 5 and 10 cm., CH_3Cl/CH_4 between 2 and 5, and ethane between 0·3 and 2 cm. The bromine pressure was kept at about 10 cm. Many runs were wasted because the precautions taken to eliminate impurities were insufficient. The amounts of products found were then small, and the ratio of rate constants was low. The scatter of the points obtained when reasonable quantities of products were formed was not excessive. From the mean points at each temperature we found

$$k(\text{methyl chloride})/k(\text{methane}) = 0{\cdot}36 \exp (3800/\boldsymbol{R}T)$$

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