If the propyl radicals undergo addition and disproportionation (in addition to (5) and (6))

$$2C_3H_7 = C_6H_{14} \tag{7}$$
$$= C_3H_6 + C_3H_8 \tag{8}$$

one obtains the following material balance equations

$$R_{H_2} - 3R_{N_2} = R_{C_3H_7NH_2} + R_{C_6H_{14}} + R_{C_2H_6} \tag{9}$$
$$-R_{C_3H_8} = R_{C_3H_7NH_2} + 2R_{C_6H_{14}} + R_{C_3H_6} \tag{10}$$

These equations are found not to be obeyed. Mass spectrographic analyses[8] showed 2,3,3,4-tetramethylpentane and an octene to be the principal products volatile above −80°. Reactions leading to such products may be postulated, usually by the addition of propyl radicals to propylene, but further speculation on this point is not warranted.

The existence of side reactions makes difficult the use of competitive rates to obtain ratios of rate constants. The ratio $k_8/k_7$ has values from 0.08 to 0.17 (Table I) which are lower than the 0.5 obtained at room temperature.[9] This can be explained by side reactions which use up propylene.

When oxygen is added to ammonia, hydrogen formation is suppressed but nitrogen formation is not. The reactions

$$NH_2 + O_2 = NO + H_2O \tag{11}$$
$$NH_2 + NO = N_2 + H_2O \tag{12}$$

have been suggested.[10] Reaction (12) must be rapid compared to (11) if nitrogen formation is to be explained in this way.

The values of $-R_{O_2}/R_{N_2}$ agree with those obtained by Bacon and Duncan[10b] 2.7 to 3.

The system ammonia–oxygen–propane is undoubtedly complex. Acetone is one of the products and undoubtedly results from the isopropyl radical–oxygen reaction, but there is no evidence for or against the formation of an intermediate hydroperoxide. Acetone is also one of the main products in the hydrogen bromide–catalyzed oxidation of propane.[11]

Acetone has strong absorption bands near the mercury lines at 1942 and 1995 Å.[12] Thus acetone will reduce absorption by the ammonia and photochemically give carbon monoxide, methane and ethane. This fact prevented a determination of the competitition between oxygen and propane for hydrogen atoms. Small amounts of acetone markedly decreased the rate of hydrogen formation from ammonia, due undoubtedly to radiation being absorbed by the acetone.

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ROCHESTER, N. Y.

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[8] The author wishes to express his appreciation to Mr. R. C. Wilkerson and his group at the Celanese Corporation of America, Clarkwood, Texas, for performing the mass spectrographic analyses.

[9] (a) R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953); (b) F. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 661 (1951).

[10] (a) C. H. Bamford, *Trans. Faraday Soc.*, **35**, 568 (1939); (b) H. E. Bacon and A. B. F. Duncan, THIS JOURNAL, **56**, 336 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER]

# The Study of Chlorine Atom Reactions in the Gas Phase

BY H. O. PRITCHARD, J. B. PYKE[1a] AND A. F. TROTMAN-DICKENSON[1b]

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The rates of chlorine atom attack on the following compounds: methane, ethane, propane, 2-methylpropane, 2,2-dimethylpropane, cyclopentane, methyl chloride and ethyl chloride, have been related to the rate of the reaction $Cl + H_2 \rightarrow HCl + H$. The rate factors listed in Table II were deduced from measurements made in the temperature range from 0 to 300°. The activation energies are lowest for those compounds which contain the weakest C–H bonds, but the activation energies and bond strengths are not linearly related. The most reactive compounds react with activation energies less than 1 kcal. No evidence is found for *A* (pre-exponential) factors greater than the collision rates.

The reactions of chlorine atoms with hydrogen-containing compounds are chain reactions, and as such their over-all rates are very sensitive to the presence of small traces of impurity, to the condition of the surface of the reaction vessel and, in photochemical systems, to the intensity of the absorbed light. Consequently the many attempts which have been made to determine rate constants for the elementary reactions of chlorine atoms have met with disproportionately little success. However, Tamura[2] was able to set an upper limit of 6 kcal. for the activation energy of reaction 1a.

$$Cl + CH_4 \longrightarrow HCl + CH_3 \tag{1a}$$

Schumacher and Wolff[3] obtained $E < 4.3$ kcal. for the similar reaction with chloroform.

The rate constant of reaction 1b is known accurately over the temperature range 273 to 1050°K.

$$Cl + H_2 \longrightarrow HCl + H \tag{1b}$$

from the work of Ashmore and Chanmugam,[4a] Steiner and Rideal[4b] and Rodebush and Klingel-

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[1] (a) College of Forestry, N. Y. State University, Syracuse 10, N. Y.; (b) Chemistry Department, The University, West Mains Road, Edinburgh 9.

[2] M. Tamura, *Rev. Phys. Chem. Japan*, **15**, 86 (1941).

[3] H. J. Schumacher and K. Wolff, *Z. physik. Chem.*, **B25**, 161 (1934).

[4] (a) P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953); (b) H. Steiner and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A173**, 503 (1939).

hoeffer.[5] When methane reacts with chlorine in the presence of hydrogen, it is possible to determine accurately the rate of the reaction 1a without any direct knowledge of the chlorine atom concentration, solely by measurement of the relative proportions of hydrogen and methane used up. Similarly the rate of reaction of methane can be compared with that of another hydrocarbon RH. Thus a whole series of reaction rates, based on the assumed value for the rate constant of reaction 1b, may be established.

When a mixture of two hydrocarbons and chlorine is illuminated, the following reactions are possible

$$
\begin{array}{rcll}
\mathrm{Cl_2} + h\nu & \longrightarrow & \mathrm{Cl} + \mathrm{Cl} & \\
\mathrm{Cl} + \mathrm{RH} & \longrightarrow & \mathrm{HCl} + \mathrm{R} & (1) \\
\mathrm{Cl} + \mathrm{R'H} & \longrightarrow & \mathrm{HCl} + \mathrm{R'} & (1') \\
\mathrm{R} + \mathrm{Cl_2} & \longrightarrow & \mathrm{RCl} + \mathrm{Cl} & (2) \\
\mathrm{R'} + \mathrm{Cl_2} & \longrightarrow & \mathrm{R'Cl} + \mathrm{Cl} & (2') \\
\mathrm{Cl} + \mathrm{Cl} + \mathrm{M} & \longrightarrow & \mathrm{Cl_2} + \mathrm{M} & (3) \\
\mathrm{R} + \mathrm{R} + \mathrm{M} & \longrightarrow & \mathrm{R_2} + \mathrm{M} & (4, 4', 4'') \\
\mathrm{R} + \mathrm{Cl} + \mathrm{M} & \longrightarrow & \mathrm{RCl} + \mathrm{M} & (5, 5') \\
\mathrm{RCl\ etc.} + \mathrm{Cl} & \longrightarrow & \mathrm{HCl} + \mathrm{etc.} & (6, 6')
\end{array}
$$

RH and R'H are only removed by reactions 1 and 1'. Now it can be readily shown[6] that if

$$-\frac{d[\mathrm{RH}]}{dt} = k_1[\mathrm{RH}][\mathrm{Cl}] \text{ and } -\frac{d[\mathrm{R'H}]}{dt} = k_1'[\mathrm{R'H}][\mathrm{Cl}]$$

then

$$\frac{k_1}{k_1'} = \log \frac{[\mathrm{RH}]_i}{[\mathrm{RH}]_f} \Big/ \log \frac{[\mathrm{R'H}]_i}{[\mathrm{R'H}]_f} \qquad \text{(I)}$$

where the subscripts i and f refer to the initial and final concentrations of the reactants. Equation I will only break down if there is a significant back reaction −1 or −1'; evidence on this point will be presented later.

We originally hoped to establish a complete series of reactivities starting from hydrogen and working upwards, but there was a large difference in the reactivities of methane and ethane. A number of likely substances were tried which we thought might be of intermediate reactivity, but it was found impossible to bridge the gap indirectly. We were forced to compete methane and ethane directly; this comparison is therefore rather less accurate than the others.

## Experimental

Approximately $2.5 \times 10^{-4}$ mole of chlorine was measured out and distilled into a 160-ml. Pyrex reaction vessel cooled in liquid nitrogen. Known quantities of the two competing gases were then admitted and the vessel was sealed off from the vacuum system. The reaction vessel was placed in one of a number of constant temperature baths and allowed to warm up to bath temperature in complete darkness. It was then strongly illuminated for about an hour with light from a tungsten filament lamp to ensure complete reaction of the chlorine. Finally the reaction vessel was reattached to the vacuum system, the seal broken and the contents analyzed by fractional distillation as follows (the optimum conditions being determined by trial on known mixtures).

**Methane-Hydrogen Mixtures.**—The contents of the vessel were hydrogen chloride, methyl chloride (and some polychlorinated methanes) together with the residual methane and hydrogen. The further chlorination of the methyl chloride does not invalidate equation 1, but means that the amounts of HCl and $\mathrm{CH_3Cl}$ produced cannot be used as a check on the results. The methane and hydrogen were separated easily from the other compounds because they are volatile at the boiling point of liquid nitrogen. They were pumped through a trap containing silica gel[7] at −193°; this removed the methane quantitatively, and upon warming up to room temperature released it completely. The volumes of residual hydrogen and methane were then measured separately. Runs were carried out at 20, 60, 100, 135, 146, 168, 211°; for range of concentrations used, see Table I.

TABLE I

Methane + hydrogen at 100°; amount of $\mathrm{Cl_2}$ added = 15.5 (±1.0) × $10^{-7}$ mole/cc.

| Initial concn., moles/cc. $10^7[\mathrm{H_2}]$ | $10^7[\mathrm{CH_4}]$ | Amount reacted, moles/cc. $10^7\Delta[\mathrm{H_2}]$ | $10^7\Delta[\mathrm{CH_4}]$ | $k_1/k_1'$ |
|---|---|---|---|---|
| 28.34 | 27.96 | 2.22 | 6.96 | 2.76 |
| 35.98 | 44.81 | 2.75 | 8.98 | 2.81 |
| 58.15 | 52.19 | 4.72 | 7.54 | 3.01 |
| 66.57 | 33.80 | 5.27 | 6.46 | 2.57 |
| 76.77 | 33.27 | 5.24 | 7.72 | 2.88 |
| 81.34 | 51.16 | 4.09 | 8.62 | 2.79 |

**Methane-Methyl Chloride Mixtures.**—The residual methane was removed by pumping at liquid nitrogen temperature. The rest of the contents were then distilled on to solid KOH to remove the HCl leaving methyl chloride and substituted methyl chlorides, the former being collected by controlled distillation at −125°. Runs were carried out at 25, 76, 100, 146, 211°; range of concentrations used; $[\mathrm{CH_4}] = 30\text{–}90 \times 10^{-7}$, $[\mathrm{CH_3Cl}] = 25\text{–}72 \times 10^{-7}$ mole/cc.

**Methane-Ethane Mixtures.**—The procedure was as for methane-methyl chloride mixtures except that ethane for analysis was pumped off at −165°. Runs were carried out at 76, 100, 146, 211, 290°; range of concentrations used: $[\mathrm{CH_4}] = 65\text{–}81 \times 10^{-7}$, $[\mathrm{C_2H_6}] = 14\text{–}20 \times 10^{-7}$ mole/cc.

**Ethane-Ethyl Chloride Mixtures.**—After the HCl had been removed the ethane was pumped off at −165° and the ethyl chloride at −102°. Runs were carried out at 25, 100 146, 211°; range of concentrations used: $[\mathrm{C_2H_6}] = 34\text{–}64 \times 10^{-7}$, $[\mathrm{C_2H_5Cl}] = 43\text{–}95 \times 10^{-7}$ mole/cc.

**Ethane-Propane Mixtures.**—The propane was removed at −133°. Runs were carried out at 25, 100, 146, 211°; range of concentrations used: $[\mathrm{C_2H_6}] = 18\text{–}36 \times 10^{-7}$, $[\mathrm{C_3H_8}] = 19\text{–}66 \times 10^{-7}$ mole/cc.

**Ethane-Butane and Ethane-Pentane Mixtures.**—Because the heavier hydrocarbons and ethyl chloride have similar boiling points, they were collected together and measured. The amount of the heavier hydrocarbon was then found by subtraction of the amount of ethyl chloride present, which was calculable from the amount of ethane used up. Runs with these mixtures were carried out at 25, 76, 146, 211°; range of concentrations used: $[\mathrm{C_2H_6}] = 20\text{–}60 \times 10^{-7}$, $[\mathrm{C_4H_{10}}] = 20\text{–}28 \times 10^{-7}$, $[\mathrm{C_5H_{10}}] = 18\text{–}29 \times 10^{-7}$, $[\mathrm{C_5H_{12}}] = 33\text{–}65 \times 10^{-7}$ mole/cc.

Very considerable care was taken in all cases that the components of the reacting mixtures were of the highest possible purity.

## Results

The calculation of results according to equation I was quite straightforward except when methane-methyl chloride and ethane-ethyl chloride mixtures were being investigated. Then one of the products of chlorination was the other member of the mixture. Consequently equation I had to be modified. Some three to six runs were performed at each temperature. A specimen set of results for methane and hydrogen are given in Table I. The complete activation energy difference plot is shown in Fig. 1.

When R'H ≡ RCl a more complicated form of expression is needed, *viz.*

$$\frac{k_1}{k_1'} = \frac{\log (A_i/A_f)}{\log \dfrac{B_i - k_1A_i/(k_1' - k_1)}{B_f - k_1A_f/(k_1' - k_1)}} \qquad \text{(II)}$$

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[5] W. H. Rodebush and W. K. Klingelhoeffer, THIS JOURNAL, **55**, 130 (1933).

[6] W. M. Jones, *J. Chem. Phys.*, **19**, 78 (1951).

[7] R. Delaplace, *Compt. rend.*, **205**, 664 (1937).

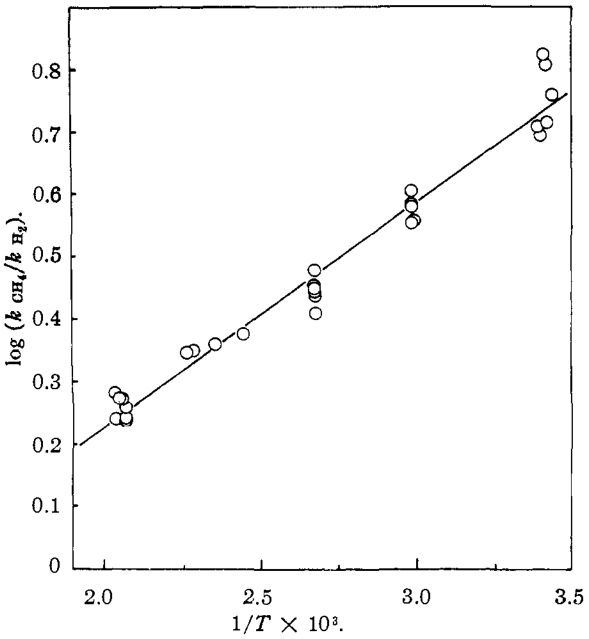

Fig. 1.—The relative rates of chlorination of hydrogen–methane mixtures.

where $A$ is [RH] and $B$ is [RCl]. The expression cannot be simplified to obtain $k_1/k_1'$ explicitly. Furthermore, in our experiments, it was found that the optimum experimental conditions for ease of analysis led to a situation where $A/B$ was of the same order of magnitude as $(k_1' - k_1)/k_1$, so that expression II became extremely sensitive to small experimental errors. This difficulty was overcome by considering the two limiting cases (a) that the RCl produced from RH does not react, and (b) that all the RCl produced from RH is available for reaction from the commencement of the run, leading to

$$\frac{k_1}{k_1'} = \frac{\log (A_i/A_f)}{\log \dfrac{B_i}{B_f - (A_i - A_f)}} \qquad \text{(IIa)}$$

and

$$\frac{k_1}{k_1'} = \frac{\log (A_i/A_f)}{\log \dfrac{B_i + (A_i - A_f)}{B_f}} \qquad \text{(IIb)}$$

In practice these two estimates of the rate ratios did not differ by more than 12% when R was $CH_3$ and they were often much closer than this. When R was $C_2H_5$, the differences were of the order of 10–20%. In each case, the average result from (IIa) and (IIb) was used to calculate activation energy differences.

When $B_i = 0$, equation II becomes

$$B_f = \frac{k_1 A_f}{k_1' - k_1}\left\{1 - \left(\frac{A_i}{A_f}\right)^{(k_1 - k_1')/k_1}\right\} \qquad \text{(IIc)}$$

Sometimes the ethyl chloride produced was not separable from the residual gases, as when the ethane–pentane systems were studied. Then the amount of ethyl chloride was estimated from equation IIc, using the values of $k_1$ and $k_1'$ which had previously been determined.

The mixtures investigated and the experimental temperature coefficients are listed in Table II and the experimental points are plotted in Fig. 2. The experimental uncertainties are represented by an error quoted on the activation energy differences; these errors were estimated from the scatter of the Arrhenius plots. The values in the columns headed $A_1'$ and $E_1'$ are calculated from columns two and three of the table together with the rate expression for hydrogen itself, *viz.*, $k/_{1b} = 0.79 \times 10^{14}$ exp. $(-5500 \pm 200/RT)$ mole$^{-1}$ cc. sec.$^{-1}$.

TABLE II

| Mixture RH + R'H | $A_1'/A_1$ | $E_1 - E_1'$, cal./mole | $A_1'$ × $10^{-14}$, moles$^{-1}$ cc. sec.$^{-1}$ | $E_1'$, cal./mole |
|---|---|---|---|---|
| $H_2 + CH_4$ | 0.32 | 1650 ± 150 | 0.26 | 3850 |
| $CH_4 + CH_3Cl$ | 2.22 | 490 ± 150 | 0.57 | 3360 |
| $CH_4 + C_2H_6$ | 4.67 | 2850 ± 370 | 1.20 | 1000 |
| $C_2H_6 + C_2H_5Cl$ | 0.38 | −490 ± 90 | 0.46 | 1490 |
| $C_2H_6 + CH_2(CH_3)_2$ | 1.47 | 330 ± 200 | 1.76 | 670 |
| $C_2H_6 + CH(CH_3)_3$ | 1.64 | 140 ± 20 | 1.96 | 860 |
| $C_2H_6 + C(CH_3)_4$ | 1.03 | 300 ± 40 | 1.23 | 700 |
| $C_2H_6$ + cyclo-$C_5H_{10}$ | 2.45 | 420 ± 40 | 2.93 | 580 |

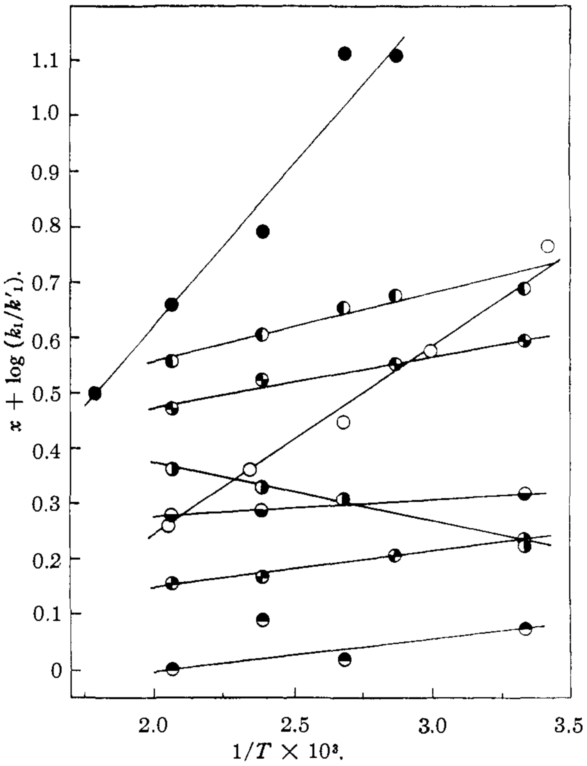

Fig. 2.—The relative rates of chlorination of mixtures: ○, hydrogen + methane ($x = 0$); ◐, methane + methyl chloride ($x = 0$); ●, methane + ethane ($x = -1.3$); ◑, ethane + ethyl chloride ($x = 1.0$); ◓, ethane + propane ($x = -0.3$); ◒, ethane + isobutane ($x = 0$); ◕, ethane + neopentane ($x = 0$); ◔, ethane + cyclopentane ($x = -0.1$). (Each point represents the mean of all experiments carried out at that temperature; the relative rate equations were calculated from the data for the individual experiments by the method of least squares.)

Returning to the problem of bridging the gap in reactivity between methane and ethane, it might be thought from the results in Table II that methyl chloride would provide the answer. But the values of $k_{MeCl}/k_{EtH}$ apparently showed a maximum at 100° and fell away at both higher and lower temperatures. Probably this strange result was obtained because it was impossible to separate ethyl chloride, methyl chloride and methylene dichloride by distillation, so that the extent of the reaction had to be estimated indirectly. Experiments were also carried out with ethane and chloroform, ethane and dimethyl ether and with ethane and benzene mixtures. Dimethyl ether chlorinates approximately twice as fast as ethane both at 25 and 146°; benzene and chloroform appeared to react at about the same rate as ethane, but more moles of ethane were used up than the number of moles of chlorine originally added. We have not sufficient analytical evidence to account satisfactorily for this.

The possibility that "hot" chlorine atoms may be involved was investigated by adding about 20 cm. of argon to some of the ethane–isobutane mixtures. No difference in rate ratios was observed. The addition of an inert gas to hydrogen–methane mixtures would have been a more rigorous test, but it is difficult to analyze hydrogen and methane in the presence of large quantities of argon.

## Discussion

The results listed in Table II exhibit several interesting features. The activation energies for attack of chlorine atoms on ethane and larger molecules are very small. The large drop in activation energy from hydrogen to methane to ethane followed by the near constancy for other hydrocarbons shows that there is no direct parallelism between activation energy and bond strength, whatever system of dissociation energies one uses. It is also satisfying to note that although the errors in determining the activation energy for higher hydrocarbons could accumulate to quite large totals, none of the activation energies calculated for these compounds is negative. Another point worthy of mention is the fact that the chlorination of methyl chloride is easier than the chlorination of methane, but ethyl chloride is more difficult to chlorinate than ethane.

From a knowledge of the heat of a reaction and its activation energy, the activation energy of the reverse reaction may be calculated. The only case meriting discussion at the present time is reaction 7a

$$\mathrm{Cl} + \mathrm{CH_4} \longrightarrow \mathrm{CH_3} + \mathrm{HCl} \qquad (7a)$$

which, if $D(\mathrm{CH_3{-}H})$ is 102.5 kcal./mole, is exothermic to the extent of about 650 cal./mole; we find that the activation energy of the reaction is 3850 cal./mole, so that the activation energy of reaction −7a

$$\mathrm{CH_3} + \mathrm{HCl} \longrightarrow \mathrm{Cl} + \mathrm{CH_4} \qquad (-7a)$$

must be 4.5 kcal. The reaction of methyl radicals with hydrogen chloride has been studied recently by Cvetanović and Steacie[8] who concluded that the activation energy was about 2.1 kcal./mole, but their results were not very reproducible. From their experiments at 28° they quote an upper limit of 5.1 kcal. which is consistent with our observations.[9]

Because of the closeness of the activation energies for forward and back reactions, it is possible that an equilibrium may be set up in the reaction with say RH. Consequently, the reaction with R'H will be favoured. This can only occur in the experiments with hydrogen and methane where the reactions are thermally neutral, perhaps with methyl chloride and possibly with neopentane where, by analogy with the primary bonds in *n*-butane, the C–H dissociation energy could be as high as 102 kcal./mole. However, we have found no experimental evidence that the back reactions are at all important; if one of the reactions were approaching equilibrium, variation of the ratios of RH and R'H would lead to a corresponding variation in the resulting $k_1/k_1'$ values. No such variation was observed in experiments with any of the molecules mentioned.

The results obtained in this research throw some light on the problem of frequency factors in bimolecular reactions. In Table III we compare the observed frequency factors ($A$) with the collision frequencies ($Z$) of the reacting species. These collision numbers are for a temperature of 400°K. and are calculated on the basis of collision diameters taken from a recent paper by Rowlinson[11]; the collision diameter for chlorine has been taken to be the same as that for argon (3.42 Å.). In the final column of Table III, the quantities $A/Z$ are listed and we will loosely identify these ratios with the steric factors for the reactions; to attach any precise significance to the ratio $A/Z$ involves a knowledge of the number of square terms contributing to the reaction. The quantity $A/Z$ is never significantly greater than unity and we may therefore conclude that the chlorine atom reactions studied here do not have steric factors greater than unity. However, steric factors considerably greater than unity have been reported for the corresponding reactions of bromine atoms.[12] It is interesting that bromine should react with 2-methylpropane or 2,2-dimethylpropane with frequency factors of the order of $10^{17}$ mole$^{-1}$ cc. sec.$^{-1}$ whereas chlorine reacts with the same substances with "normal" frequency factors. This large difference cannot be

TABLE III

| Reactant | Collision diameter, Å. | $10^{-14}Z$, moles$^{-1}$ | $10^{-14}A$ cc. sec.$^{-1}$ | $A/Z$ |
|---|---|---|---|---|
| $H_2$ | 2.93 | 4.04 | 0.79 | 0.20 |
| $CH_4$ | 3.85 | 2.20 | .26 | .12 |
| $CH_3Cl$ | 4.1$^a$ | 1.69 | .57 | .3 |
| $C_2H_6$ | 4.30 | 2.04 | 1.20 | .6 |
| $C_2H_5Cl$ | 4.5$^a$ | 1.79 | 0.46 | .3 |
| $C_3H_8$ | 4.75 | 2.07 | 1.76 | .9 |
| Iso-$C_4H_{10}$ | 5.20 | 2.18 | 1.96 | .9 |
| Neo-$C_5H_{12}$ | 5.45 | 2.23 | 1.23 | .6 |
| Cyclo-$C_5H_{10}$ | 5.4$^a$ | 2.21 | 2.93 | 1.3 |

$^a$ Estimated.

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[8] R. J. Cvetanović and E. W. R. Steacie, *Can. J. Chem.*, **31**, 518 (1953).

[9] A preliminary note[10] on this topic contained some arithmetical errors. $k_{7a}$ was given as $10^{14.5}$ exp. $(-3800/RT)$ mole$^{-1}$ cc. sec.$^{-1}$, whereas $10^{13.4}$ exp $(-3850/RT)$ is correct. Consequently, $k_{-7a}$ should have been $10^{12.1}$ exp. $(-4510/RT)$ which is equal to $10^{9.8}$ at 150°. The agreement with the value of $10^{10.4}$ given by Cvetanović and Steacie is as good as was reported previously.

(10) H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, THIS JOURNAL, **76**, 1201 (1954).

(11) J. S. Rowlinson, *Quart. Rev.*, **8**, 168 (1954).

(12) B. H. Eckstein, H. A. Scheraga and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 29 (1954).

TABLE IV

$A$'s in mole$^{-1}$ cc. sec.$^{-1}$, $E$'s in kcal./mole.

| Reaction | log $A$ expt. | $E$ | Ref. | log $A$ calc. | Ref. |
|---|---|---|---|---|---|
| $Cl + CH_4 \rightarrow HCl + CH_3$ (7a) | 13.4 | 3.9 | This work | 13.0 | This work[a] |
| $H + CH_4 \rightarrow H_2 + CH_3$ (7b) | 12.5 | 9.0 | See discussion | 13.3 | 16 |
| $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ (7c) | 11.5 | 14.3 | 14 | 10.9 | 16 |
| $Br + CH_4 \rightarrow HBr + CH_3$ (7d) | 13.7 | 18.3 | 15 | 13.7 | 15 |

[a] The transition state calculation was made by standard methods.[16] The H–Cl distance was assumed to be 1.65 Å. and the C–H–Cl doubly degenerate bending frequency was taken as 500 cm.$^{-1}$.

accounted for by experimental errors, but the possibility still remains that there may be an error in the assumed reaction mechanisms (the bromination of neopentane experiments were criticised on these grounds by Benson and Graff[13] who suggested that the neopentyl radicals produced in the reaction might decompose to methyl radicals and isobutene; they showed that such an assumption would reduce the frequency factors to the same order of magnitude as the collision number).

We may now consider the rate factors of the four reactions of methane listed in Table IV. All are taken directly from the sources except the rate factors of reaction 7b. We have estimated these as follows: The activation energy of reaction −7b is 10.0 kcal./mole,[17] and reaction 7b is approximately 1 kcal./mole exothermic. Therefore the activation energy of reaction 7b is 9 kcal./mole. The $A$ factor of reaction −7b is $10^{11.5}$ mole$^{-1}$ cc. sec.$^{-1}$. From considerations of the entropies of the substances involved in the reaction[18] we can show that $A_{7b}/A_{-7b} \approx 10$. Therefore $A_{7b}$ is $10^{12.5}$ mole$^{-1}$ cc. sec.$^{-1}$; if anything this value is likely to be a little high. These rate factors give $k_{7b} = 10^{7.7}$ mole$^{-1}$ cc. sec.$^{-1}$ at 140°, which value agrees far better than could be reasonably hoped with the value of $10^{7.6}$ mole$^{-1}$ cc. sec.$^{-1}$ measured by Berlie and LeRoy.[19] They found that $k_{7b} = 10^{10.0} \exp.(-4500/RT)$ mole$^{-1}$ cc. sec.$^{-1}$, but placed much more reliance on their measurement of the reaction rate than of its temperature dependence. Indeed, measurements of rates are generally much more reliable than measurements of temperature coefficients. It can be seen from the table that all of these $A$ factors are in reasonable agreement with the predictions of transition state theory listed in the fifth column.

It is often suggested, as a rough corollary of the supposed activation energy-dissociation energy relationship, that in a reaction of the type

$$X + RH \longrightarrow HX + R \qquad (7)$$

the stronger the HX bond, the lower the activation energy and it is instructive to examine this hypothesis in the light of data now available. Consider the activation energies of the three reactions 7a, 7b and 7c. The bonds formed in the three reactions have identical dissociation energies to within about ±1%; hence thermochemistry alone cannot account for the steady gradation in activation energy along the series 7a, 7b and 7c. It is interesting to speculate on the cause of the wide variation in activation energy for these reactions. Presumably it arises from differences in the repulsion energies upon close approach of the reacting particles, chlorine being the least repelled and methyl the most. If we are to retain the idea that the "transition state" in these reactions is a fairly localized affair and that the methane molecule does not fly apart when a chlorine atom passes nearby, we must accept that the chlorine atom can approach very close to the methane molecule without any marked repulsion. We imagine that this is only possible because the free electron on the chlorine atom has a significant attraction for the electrons in the methane molecule. Therefore, we should expect that the greater the electroaffinity of the singly occupied orbital, the easier the close approach of the two centers would be. If the methyl radical is flat, it should have an electroaffinity of about 6 e.v.[20]; the values for the hydrogen and chlorine atoms are 7.2 and 9.5 e.v., respectively.[21] Thus the relative values of the activation energies of reactions 7a, 7b and 7c can be understood in terms of the electroaffinities of the approaching particles. It seems that we can distinguish at least two factors which govern the activation energy of reaction 7 for a constant RH, these being the thermochemistry of the reaction and the electroaffinity of the abstracting particle.

In spite of the difficulties in analysis without resort to mass-spectrometric techniques, we feel that the numerical results presented here are essentially correct: the further exploitation of the competitive method using physicochemical methods of analysis is not feasible. But with a mass-spectrometer available, the range of substances investigated could be considerably extended, the accuracy improved, and interesting results on the relative rates of reactions 2 and 4 could be collected.

MANCHESTER, ENGLAND

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