Bromination of Fluoroalkanes

Part 4.—Kinetics of Thermal Bromination of Fluoroform and Pentafluoroethane

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The thermal brominations of CF_3H and C_2F_5H have been studied in the ranges 361-431° and 323-458°C respectively. The kinetics agree with the reactions

$$\mathrm{Br_2 \rightleftharpoons 2Br}$$

$$\left\{\begin{array}{l}\mathrm{Br+CF_3H \rightleftharpoons HBr+CF_3}(3,-3)\\ \mathrm{CF_3+Br_2 \rightarrow CF_3Br+Br}\ (9)\end{array}\right\} \text{ or } \left\{\begin{array}{l}\mathrm{Br+C_2F_5H \rightleftharpoons HBr+C_2F_5}\\ \mathrm{C_2F_5+Br_2 \rightarrow C_2F_5Br+Br.}\end{array}\right\} \qquad \begin{array}{r}(4,-4)\\ (15)\end{array}$$

From measurements of initial rates,

$$\log k_3(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}107 \pm 0{\cdot}035) - (22{,}320 \pm 110)/2{\cdot}303\ \boldsymbol{RT},$$
$$\log k_4(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}026 \pm 0{\cdot}020) - (19{,}305 \pm 61)/2{\cdot}303\ \boldsymbol{RT}.$$

The inhibition by added HBr was studied with both systems. For Br_2+CF_3H, the values of k_{-3}/k_9 obtained agree with previous independent data, the combined result being,

$$\log (k_{-3}/k_9) = (-0{\cdot}58 \pm 0{\cdot}04) - (2{,}130 \pm 90)/2{\cdot}303\ \boldsymbol{RT}.$$

For the system $Br_2+C_2F_5H$,

$$\log (k_{-4}/k_{15}) = (-0{\cdot}45 \pm 0{\cdot}06) - (2{,}750 \pm 250)/2{\cdot}303\ \boldsymbol{RT}.$$

The data for reactions (3) and (4) are combined with previous competitive results to give for the reference reactions,

$$\mathrm{Br+CH_4 \rightarrow HBr+CH_3,\quad Br+CH_3Br \rightarrow HBr+CH_2Br,}$$
$$\log k_{\text{CH}_4}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}991 \pm 0{\cdot}049) - (18{,}580 \pm 140)/2{\cdot}303\ \boldsymbol{RT},$$
$$\log k_{\text{CH}_3\text{Br}}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (14{\cdot}000 \pm 0{\cdot}058) - (16{,}310 \pm 170)/2{\cdot}303\ \boldsymbol{RT}.$$

Arrhenius parameters are tabulated for all bromination reactions studied to date.

From Arrhenius parameters for bromination reactions, the following bond dissociation energies are obtained: $D(CF_3—H) = 106{\cdot}7 \pm 0{\cdot}5$, $D(C_2F_5—H) = 102{\cdot}6 \pm 1{\cdot}2$ and $D(CH_3—H) = 104{\cdot}3 \pm 0{\cdot}7$, all in kcal mole^{-1} at 298°K. These figures are compared with results from other sources and recommended values of the three quantities are, $D(CF_3—H) = 106{\cdot}4 \pm 0{\cdot}5$, $D(C_2F_5—H) = 102{\cdot}9 \pm 1{\cdot}0$ and $D(CH_3—H) = 104{\cdot}2 \pm 0{\cdot}5$ kcal mole^{-1}.

Studies [1,2] of competitive bromination reactions of the type

$$\mathrm{Br}+\left\{\begin{array}{l}\mathrm{R_1H}\\ \\ \mathrm{R_2H}\end{array}\right. \rightarrow \mathrm{HBr}+\left\{\begin{array}{l}\mathrm{R_1}\\ \\ \mathrm{R_2}\end{array}\right. \qquad \begin{array}{r}(1)\\ \\ (2)\end{array}$$

have yielded ratios of A factors and differences in activation energies, i.e., A_1/A_2 and E_1-E_2 for many compounds. To assign absolute values of A and E to individual reactions, it is necessary to have absolute values of A and E for at least one particular reaction. These are best obtained by studying the thermal bromination of single compounds but such data are scanty for compounds which have also been studied

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competitively. Kistiakowsky and Van Artsdalen[3] measured rate constants for the reactions

$$Br+CH_4 \rightarrow HBr+CH_3$$
$$Br+CH_3Br \rightarrow HBr+CH_2Br$$

but at one temperature only and they combined the rate constants with activation energies obtained from the corresponding photobromination reactions to give absolute A factors. Only a few thermal runs were done and, in addition, their procedure is not entirely satisfactory since the photochemical determination of E involves the assumption that the reaction

$$Br+Br+M \rightarrow Br_2+M$$

has zero activation energy which is probably, but not certainly, true: this assumption is the main source of the error limits of $\sim \pm 1$ kcal mole^{-1} assigned to E.

The thermal bromination of CF_3H was studied by Corbett, Tarr and Whittle[4] and, although their results are consistent with later kinetic work,[5] there was a minor anomaly in the kinetics which prevented their results from being completely acceptable.

Thus, at present, the ratios A_1/A_2 and differences E_1-E_2 are accurately known for many compounds but individual A and E are much less accurately known. Further studies of thermal brominations of single compounds are desirable to remedy this. We have therefore repeated and extended the work of Corbett *et al.*[4] on the thermal bromination of CF_3H using improved methods and we have also studied the thermal bromination of C_2F_5H which has not previously been investigated. These compounds were selected because (i) the brominations of CF_3H and C_2F_5H yield only CF_3Br and C_2F_5Br respectively; in contrast to the alkanes, stepwise bromination to yield several products does not occur. (ii) the reactions

$$Br+CF_3H \rightarrow HBr+CF_3 \qquad (3)$$
$$Br+C_2F_5H \rightarrow HBr+C_2F_5 \qquad (4)$$
$$Br+CH_4 \rightarrow HBr+CH_3 \qquad (5)$$

were studied competitively by Coomber, Tarr and Whittle[6] who obtained accurate values of E_3-E_4, E_4-E_5, A_3/A_4 and A_4/A_5. Thus, if E and A are known for reaction (3) or (4), we can calculate A and E for the other two reactions. All these A and E are key reference data in competitive work.

EXPERIMENTAL

MATERIALS

These were as before[6] except that C_2F_5H was further purified by low-temperature fractional distillation. No impurities were detected in any material using i.-r. spectroscopy and gas-solid chromatography.

APPARATUS AND PROCEDURE

Reactions occurred in a cylindrical quartz reaction vessel R.V. of length 10 cm, diam. 5 cm which was inside an oven similar to that used by Coomber and Whittle.[7] The oven was controlled by means of a Sirect regulator (C.N.S. Instruments) and the temperature was constant to better than ±0·2°C. The gradient along the R.V. was <0·2°C. Temperatures were measured with a chromel/alumel thermocouple calibrated as in ref. (7) so that temperatures quoted should be accurate to ±1°C and temperature differences to ±0·5°C.

Reaction rates were determined from the rate of disappearance of Br_2 measured photometrically. Along the axis of the R.V. passed a parallel beam of light, diam. 1 cm, from a 12V 24W car bulb run at 6V from a stabilized power pack. The beam passed through a cobalt-glass filter (λ_{max} = 4000 Å) so that light entering the R.V. roughly matched the λ_{max}= 4150 Å of Br_2. The transmitted light intensity was measured by means of an R.C.A. 931A photomultiplier connected to a logarithmic photometer of the type described by Ashmore *et al.*[8] This unit measures optical density so the output, when fed to a pen recorder, gives in effect a plot of bromine concentration against time. The photometer was calibrated with known pressures of Br_2 measured at the run temperature using a glass spiral gauge. A plot of pen-recorder deflection against bromine pressure was linear up to 60 mm at 320°C and became curved at higher pressures. When such pressures were used in kinetic runs, the measured recorder trace was corrected accordingly.

Materials were stored in a conventional high-vacuum system and were de-gassed before use. Pressures were measured with a glass spiral gauge and in this section of the apparatus, including the R.V., only Springham greaseless taps were used. In a run, Br_2 was admitted to the R.V. at a known pressure and CF_3H or C_2F_5H was then admitted at a pressure obtained from the total pressure and the Br_2 pressure (the latter was corrected for the small amount in the sidearm which was forced into the R.V. by the CF_3H or C_2F_5H). Reaction began at once and the curve of Br_2 concentration against time was smooth even at the start of the reaction which suggests that mixing was virtually instantaneous (in most runs, $[RH] \gg [Br_2]$). After each run, the R.V. was evacuated and the recorder pen always returned to zero (i.e., 100 % transmission).

RESULTS

The overall reactions are

$$Br_2 + CF_3H \rightleftharpoons HBr + CF_3Br \qquad (6)$$

$$Br_2 + C_2F_5H \rightleftharpoons HBr + C_2F_5Br. \qquad (7)$$

At the temperatures used in this work, the equilibria lie to the right-hand side since $K_6 \sim 14$ and $K_7 \sim 30$ at 700°K.[7] However, to avoid any back reaction, all results are based on measurements of initial rates. Preliminary experiments showed that the light beam of the photometer was too weak to initiate reactions (6) or (7) photochemically.

THERMAL BROMINATION OF CF_3H

The expected reactions are

$$Br_2 \rightleftharpoons 2Br \qquad (8, -8)$$

$$Br + CF_3H \rightleftharpoons HBr + CF_3 \qquad (3, -3)$$

$$CF_3 + Br_2 \rightarrow CF_3Br + Br. \qquad (9)$$

A steady-state treatment gives

$$-\frac{d[Br_2]}{dt} = \frac{k_3 K_8^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}[CF_3H]}{1 + k_{-3}[HBr]/k_9[Br_2]}, \qquad (10)$$

where $K_8 = K_c = k_8/k_{-8}$. If no HBr is initially present then, at zero time, eqn. (10) reduces to

$$-d[Br_2]/dt = k_3 K_8^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}[CF_3H], \qquad (11)$$

Before applying eqn. (11) to reaction (6), we summarize the work of Corbett, Tarr and Whittle,[4] CTW, who previously investigated the thermal bromination of CF_3H. They used an excess of CF_3H over Br_2 together with small conversions of Br_2 so that the following integrated form of eqn. (11) could be used,

$$k_3 K_8^{\frac{1}{2}} = (2/t)\{[Br_2]_0^{\frac{1}{2}} - [Br_2]_t^{\frac{1}{2}}\}/[CF_3H]_{ave}^{n}, \qquad (12)$$

where $[Br_2]_0$ and $[Br_2]_t$ are initial and final concentrations respectively and n is the order in CF_3H. Thus rate constants were obtained from analyses of reaction products rather than initial rates. The function ($\frac{1}{2}\log RT+\log k_3K_8^{\frac{1}{2}}$) was plotted against $1/T$ and the slope gave $E_3+\frac{1}{2}\Delta E_8 = 45{\cdot}58\pm0{\cdot}71$ kcal mole^{-1} from which $E_3 = 23{\cdot}0\pm0{\cdot}7$ kcal mole^{-1}, using a value of ΔE_8 calculated from thermodynamic data at the mean temperature of 670°K. From the intercept of the graph, they obtained $A_3 = 2{\cdot}9\times10^{13}$ cm^3 mole^{-1} sec^{-1}.*

CTW found an order in [Br_2] of 0·5, as expected from eqn. (11), (12) but the order in CF_3H was $0{\cdot}78\pm0{\cdot}03$ when the CF_3H pressure was varied in the range 29-370 mm; the expected order is 1·0. CTW could not explain this so their values of A_3 and E_3, while plausible, must be treated with reserve.

Our present study involves two improvements over that of CTW; (i) the differential eqn. (11) involving initial rates was used in preference to the integrated eqn. (12), (ii) Any given run leads to a value of $k_3K_8^{\frac{1}{2}}$ from which k_3 was calculated using thermodynamic data [9] on K_8. The quantities A_3 and E_3 were then obtained from an Arrhenius plot of k_3. This is more accurate than the procedure of CTW.

Initial rates of removal of Br_2 are difficult to measure accurately and we have therefore tried three methods of obtaining the slope at zero time of the experimental plots of Br_2 pressure against time; (i) the standard " mirror " method, (ii) the long face of a 90° prism is placed on the curve and the curve is viewed from vertically above the prism. A discontinuity in the curve is seen unless the side of the prism is parallel to a tangent at the point on the curve which is under the centre of the prism. Thus, the side of the prism gives the slope. This method cannot be used to measure slopes at or near to $t = 0$. Instead, slopes are measured at times t_1, t_2 etc. and a plot of log (slope) against t gives a curve which is readily extrapolated to $t = 0$, (iii) Lanczos [10] showed that, if values y_0, y_1, y_2 and y_3 of the quantity y are measured at equal intervals of time, each of h sec, then the slope of the curve at y_0 is given by

$$y_0' = (-21y_0+13y_1+17y_2-9y_3)/20h.$$

Lanczos recommends this 4-term eqn. where the slope of the curve is changing rapidly and in a complex way over a short-time interval. This is not so in our curves and we have therefore used the procedure of Lanczos to derive the following 6-term eqn.,

$$y_0' = (-165y_0+y_1+92y_2+108y_3+49y_4-85y_5)/280h.$$

This was used to calculate rates at $t = 0$ with y_0, y_1 etc. being Br_2 pressures read off from the experimental curve at equal intervals of time.

The three methods were compared for a number of curves. The results from methods (ii) and (iii) always agreed to within 1 % but they disagreed by up to 6 % with results obtained by method (i). This last method is highly subjective and results obtained by different workers using the same curve showed unacceptable scatter. Our kinetic results are based exclusively on method (iii) which is more convenient to use than method (ii).

KINETICS OF BROMINATION OF CF_3H

The order in CF_3H was first determined by using a constant pressure of 17 mm Br_2 at 426·1°C and varying the CF_3H pressure in the range 31-439 mm. A plot of log (initial rate of removal of Br_2) against log [CF_3H] is shown in fig. 1, curve B. When the CF_3H pressure was in the range 160-439 mm, the order in CF_3H was $0{\cdot}99\pm0{\cdot}01$ (by least squares) but, at lower pressures of CF_3H, the order became less than 1. Accordingly, the effect of varying the CF_3H pressure at other temperatures was investigated as follows: $T = 402{\cdot}8$°C, $Br_2 = 15{\cdot}6$ mm, $CF_3H = 106$-442 mm; $T = 447{\cdot}8$°C,

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* The left-hand side of eqn. (15) in ref. (4) should contain log k_2 instead of log k_9; this error is purely terminological and does not affect the results in ref. (4).

Br_2 = 16·5 mm, CF_3H = 52-137 mm. The results are given in fig. 1. As at 426·1°C, the order in CF_3H is unity provided that the CF_3H pressure exceeds $\sim$160 mm; below these pressures, the order becomes <1.

These observations are broadly in agreement with those of CTW but their data were not sufficiently precise to reveal the curvatures apparent in fig. 1 and they drew the best straight line through all the points and hence obtained an order in CF_3H of 0·78 rather than unity.

In view of the above effect, we determined the order in Br_2 at two different pressures of CF_3H, both at 426·1°C: the conditions were: (i) CF_3H, 37 mm; Br_2, 5·4-29·6 mm, (ii) CF_3H, 228·4 mm; Br_2, 5·4-40·1 mm. Both plots of log (initial rate) against log $[Br_2]$ were good straight lines with identical slopes of 0·51 ± 0·02, in excellent agreement with CTW.

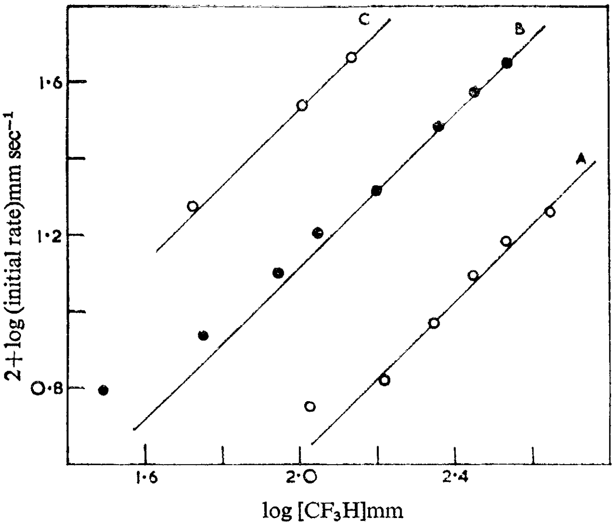


FIG. 1.—Variation with CF_3H pressure of initial rate of thermal bromination of CF_3H. Curve A, temp. = 402·8°C, Br_2 press. = 15·7 mm; curve B, 426·1°C, Br_2 press. = 17·0 mm; curve C, 447·8°C, Br_2 press. = 16·5 mm.

The observations of CTW are thus confirmed and extended but we now know that the rate law in eqn. (11) is accurately obeyed only if the CF_3H pressure is $> \sim 160$ mm. In consequence, we studied the variation of initial rate with temperature using CF_3H pressures in the range 160-440 mm so that rate constants can be calculated using eqn. (11). The Br_2 pressure was usually $\sim$16 mm. For each run, the use of eqn. (11) gave an experimental rate constant equal to $k_3K_8^{\frac{1}{2}}$: K_8 is known from standard data [9] so that k_3 could be calculated. The Arrhenius plot for 28 runs in the range 373-465°C was a good straight line leading to

$$\log k_3(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}107 \pm 0{\cdot}035) - (22{,}320 \pm 110)/2{\cdot}303\ RT. \qquad (13)$$

Error limits in this paper are $\pm\sigma$ unless otherwise stated.

CTW studied the reaction over the range 361-431°C using $\sim$11 mm Br_2 and $\sim$110 mm CF_3H and their result that

$$\log k_3 = (13{\cdot}46 \pm 0{\cdot}23) - (23{,}000 \pm 700)/2{\cdot}303\ RT \qquad (14)$$

is close to our present result in eqn. (13). However, the data in eqn. (13) are more reliable.

KINETICS OF BROMINATION OF C_2F_5H

The thermal bromination of C_2F_5H has not been previously studied. By analogy with the bromination of CF_3H, the expected reactions are (8, −8) and

$$Br+C_2F_5H \rightleftharpoons HBr+C_2F_5 \qquad (4,-4)$$
$$C_2F_5+Br_2 \rightarrow C_2F_5Br+Br. \qquad (15)$$

The procedure was similar to that for Br_2+CF_3H. The order in C_2F_5H was determined at 403·2°C using 17·4 mm Br_2 and varying the C_2F_5H pressure in the range 46-387 mm. A plot of log (initial rate) against log $[C_2F_5H]$ showed no curvature at low pressures, unlike the system Br_2+CF_3H, and the points all lay on a straight line of slope $0{\cdot}99 \pm 0{\cdot}01$. The order in Br_2 was determined at 403·2°C using 156·2 mm C_2F_5H and 5·8-84·5 mm Br_2. The order plot was a good straight line of slope $0{\cdot}51 \pm 0{\cdot}01$.

The $Br_2+C_2F_5H$ system is therefore simpler than Br_2+CF_3H since the theoretical rate law in eqn. (11) is obeyed at all pressures of C_2F_5H used. The effect of temperature on the rate was investigated using ~15 mm Br_2 and 26·5-410 mm C_2F_5H. The C_2F_5H pressure was varied because, in order to cover the maximum temperature range, we used high pressures of C_2F_5H at low temperatures to obtain measurable reaction rates and, for the same reason, low pressures of C_2F_5H were used at high temperatures. The rate constant k_4 was calculated using the analogue of eqn. (11) and an Arrhenius plot was a good straight line. From 43 runs in the range 323-458°C,

$$\log k_4(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}026 \pm 0{\cdot}020)-(19{,}305 \pm 61)/2{\cdot}303\ RT. \qquad (16)$$

INHIBITION EXPERIMENTS

Br_2+CF_3H

Bromination reactions are inhibited by HBr because of competition between reactions such as (−3) and (9); this gives rise to the second term in the denominator of eqn. (10). No HBr is present at zero time hence our results based on initial rates are unaffected by the inhibition. To obtain information about the inhibition reactions (−3) and (−4), it is therefore necessary to add HBr to the initial mixture of reactants.

For Br_2+CF_3H, runs were done using 17 ± 1 mm Br_2, 133-323 mm CF_3H and 197-333 mm HBr so that the ratio $[HBr]/[Br_2]$ was ~15-20. The ratio $k_{-3}/k_9 \sim 1/20$ so the second term in the denominator of eqn. (10) was ~1 and the inhibited rates were approximately half the uninhibited rates. From 9 runs in the range 392-482°C, we obtain the Arrhenius plot in fig. 2 (dashed line) from which

$$\log (k_{-3}/k_9) = (-0{\cdot}33 \pm 0{\cdot}08)-(3{,}000 \pm 260)/2{\cdot}303\ RT. \qquad (17)$$

These data supersede those obtained by CTW using the inhibition method although the results of the two studies agree within experimental error.

The ratio k_{-3}/k_9 was measured by Tucker and Whittle [11] using an independent method in which hexafluoroacetone was photolyzed with a mixture of Br_2+HBr in the range 55-334°C. They obtained

$$\log (k_{-3}/k_9) = (-0{\cdot}58 \pm 0{\cdot}08)-(2{,}170 \pm 160)/2{\cdot}303\ RT \qquad (18)$$

in fairly good agreement with our results in eqn. (17). Ratios such as k_{-3}/k_9 obtained by inhibition experiments and the use of eqn. (10) are sensitive to errors in measuring initial rates hence the results in eqn. (18) are more reliable than those in eqn. (17). However in fig. 2, we give values of k_{-3}/k_9, both from the present work and from

Tucker and Whittle, and it is clear that for $10^3/T \sim 1{\cdot}55$, which is the point at which the temperature ranges of the two studies meet, the respective values of k_{-3}/k_9 are in excellent agreement. In view of this, we have *combined* the two sets of results into a single Arrhenius plot which is the solid line in fig. 2. From the combined data,

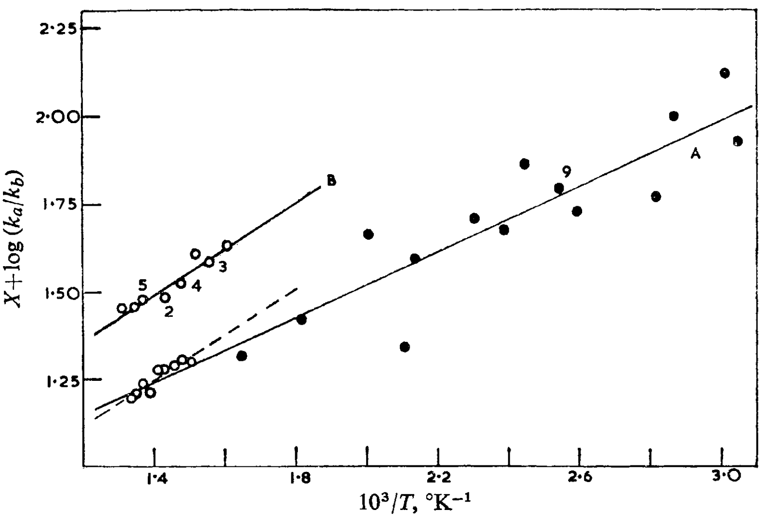


FIG. 2.—Arrhenius plots for inhibited reactions. Curve A, $X = 0$, $k_a/k_b = k_{-3}/k_9$; ●, results of Tucker and Whittle;[11] ○, present work. Solid line is best line through *all* points. Dashed line fits results of present work. Curve B, $X = 0{\cdot}2$, $k_a/k_b = k_{-4}/k_{15}$. A number by a given point indicates the number of runs done at that temperature (see fig. 3).

$$\log(k_{-3}/k_9) = (-0{\cdot}58 \pm 0{\cdot}04) - (2{,}130 \pm 90)/2{\cdot}303\,RT. \tag{19}$$

This result involves the large temperature range of 55-482°C and is the best available data on k_{-3}/k_9.

INHIBITION OF THE REACTION BETWEEN Br_2 AND C_2F_5H

There are no previous data on the ratio k_{-4}/k_{15} so we have studied this inhibition in some detail. If an experiment is done with HBr added to the initial mixture of $Br_2 + C_2F_5H$, then the inhibited initial rate R_{in} is given by eqn. (10). If the HBr were absent, then the uninhibited rate R_{un} is given by eqn. (11). If two experiments are done with the same pressures of Br_2 and C_2F_5H and at the same temperature so that k_4 and K_8 are the same for both, we may then combine eqn. (10) and (11) to give

$$[(R_{un}/R_{in}) - 1] = (k_{-4}/k_{15})[\mathrm{HBr}]/[\mathrm{Br_2}]. \tag{20}$$

This eqn. was tested by performing several runs with various HBr and Br_2 pressures at each of the temperatures 370·0, 403·2, 426·6 and 457·6°C. The measured initial rate gave R_{in}, whereas R_{un} was calculated using the known Br_2 and C_2F_5H pressures together with K_8 and k_4 obtained as described above. Plots of $[(R_{un}/R_{in}) - 1]$ against $[\mathrm{HBr}]/[\mathrm{Br_2}]$ which are shown in fig. 3 verify eqn. (20) within experimental error. The ratio k_{-4}/k_{15} was therefore calculated for each experiment in fig. 3, using eqn. (20) and also for further experiments at temperatures other than those of fig. 3. An Arrhenius plot of k_{-4}/k_{15} is shown in fig. 2 and, from 18 runs in the range 349-471°C.

$$\log(k_{-4}/k_{15}) = (-0{\cdot}45 \pm 0{\cdot}06) - (2{,}750 \pm 250)/2{\cdot}303\,RT. \tag{21}$$

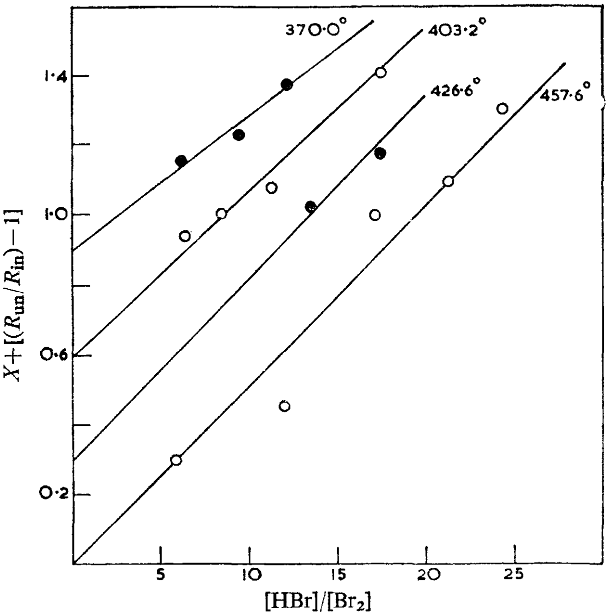


FIG. 3.—Tests of rate law in eqn. (20). $X = 0{\cdot}0$, 0·3, 0·6 and 0·9 at 457·6, 426·6, 403·2 and 370·0°C respectively.

DISCUSSION

We have attempted to measure accurate Arrhenius parameters for reactions (3) and (4) hence it is important to cross-check the results. Reactions (3), (4) and (5) and

$$Br + CF_3CF_2CF_2H \rightarrow HBr + CF_3CF_2CF_2 \qquad (22)$$

were studied by Whittle and co-workers [2,6] using competitive methods; their results were

$$\log (k_4/k_3) = \log (k_{C_2F_5H}/k_{CF_3H}) = (-0{\cdot}091 \pm 0{\cdot}022) + (3{,}040 \pm 60)/2{\cdot}303\,RT, \qquad (23)$$
$$\log (k_5/k_4) = \log (k_{CH_4}/k_{C_2F_5H}) = (0{\cdot}941 \pm 0{\cdot}042) + (720 \pm 90)/2{\cdot}303\,RT, \qquad (24)$$
$$\log (k_{22}/k_3) = \log (k_{C_3F_7H}/k_{CF_3H}) = (-0{\cdot}156 \pm 0{\cdot}031) + (3{,}240 \pm 80)/2{\cdot}303\,RT, \qquad (25)$$
$$\log (k_5/k_{22}) = \log (k_{CH_4}/k_{C_3F_7H}) = (1{\cdot}074 \pm 0{\cdot}035) + (470 \pm 80)/2{\cdot}303\,RT. \qquad (26)$$

Combination of eqn. (23) with (24) and (25) with (26) gives

$$\log (k_5/k_3) = \log (k_{CH_4}/k_{CF_3H}) = (0{\cdot}850 \pm 0{\cdot}050) + (3{,}760 \pm 110)/2{\cdot}303\,RT \text{ from (23) and (24),} \qquad (27)$$
$$= (0{\cdot}918 \pm 0{\cdot}047) + (3{,}710 \pm 110)/2{\cdot}303\,RT \text{ from (25) and (26).} \qquad (28)$$

Thus, the ratio k_{CH_4}/k_{CF_3H} has been measured by two independent methods using C_2F_5H and n-C_3F_7H respectively as " bridge " compounds. The results, given in eqn. (27), (28) agree well which suggests that *all* the data in eqn. (23) to (26) are reliable.

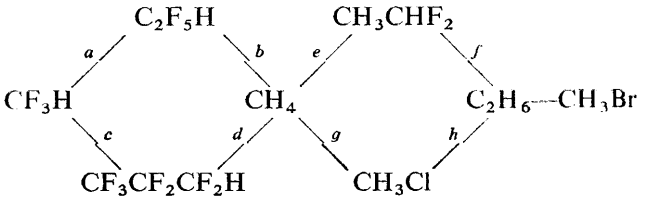
The data in eqn. (23) were obtained by brominating a mixture of $CF_3H + C_2F_5H$ and we compare the result with the corresponding ratio $k_{C_2F_5H}/k_{CF_3H}$ calculated from the results of the present work on the *separate* brominations of CF_3H and C_2F_5H. Combining data on k_{CF_3H} in eqn. (13) with that on $k_{C_2F_5H}$ in eqn. (16), we have

$$\log (k_{C_2F_5H}/k_{CF_3H}) = (-0{\cdot}081 \pm 0{\cdot}040) + (3{,}020 \pm 130)/2{\cdot}303\,RT. \qquad (29)$$

The agreement between this result and that of eqn. (23) is good since the absolute

Arrhenius parameters in eqn. (13) and (16) are much more susceptible to error than the competitive results in eqn. (23). Thus the reliability of the data in eqn. (13) and (16) is confirmed.

The only absolute Arrhenius parameters available before the present work were for the reactions of Br with CH_4 and CH_3Br (we do not include $Br+H_2$ or D_2 since these have not been linked competitively to other reactions). The Arrhenius parameters for $Br+CH_4$ and CH_3Br can be obtained independently from the present work using the sequences,



where each linked pair of compounds has been studied competitively. The pairs *ab* and *cd* give the results in eqn. (27) and (28) respectively, the mean being

$$\log (k_{CH_4}/k_{CF_3H}) = (0{\cdot}884\pm0{\cdot}034)+(3{,}740\pm80)/2{\cdot}303\ RT. \tag{30}$$

Using Arrhenius parameters for reaction (3) in eqn. (13), we have

$$\log k_5 = \log k_{CH_4}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}991\pm0{\cdot}049)-(18{,}580\pm140)/2{\cdot}303\ RT. \tag{31}$$

From the pairs *ef* (ref. (2)) and *gh* (ref. (13)), we obtain

$$\log (k_{C_2H_6}/k_{CH_4}) = (0{\cdot}144\pm0{\cdot}027)+(4{,}920\pm40)/2{\cdot}303\ RT \text{ from } ef, \tag{32}$$

$$= -0{\cdot}105+4{,}900/2{\cdot}303\ RT \text{ from } gh, \tag{33}$$

which agree well. However, Fettis *et al.*[13] point out that the result in eqn. (33) is less accurate than usual, probably because of impurities in the CH_4. Combining the data in eqn. (31) and (32) with data on $k_{C_2H_6}/k_{CH_3Br}$ (ref. (13)), we get

$$\log k_{CH_3Br}\ (\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (14{\cdot}000\pm0{\cdot}058)-(16{,}310\pm170)/2{\cdot}303\ RT. \tag{34}$$

Fettis and Knox [1] recommended *

$$\log k_{CH_4}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}78\pm0{\cdot}26)-(18{,}180\pm550)/2{\cdot}303\ RT, \tag{35}$$

$$\log k_{CH_3Br}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = (13{\cdot}70\pm0{\cdot}30)-(15{,}850\pm600)/2{\cdot}303\ RT. \tag{36}$$

These results are based on the work of Kistiakowsky and van Artsdalen [3] and they agree within experimental error with our new results in eqn. (31) and (34). However, we believe our results to be more accurate since they do not involve the combination of thermal and photobromination results which leads to larger error limits than ours.

One further check can be applied to our results in eqn. (31) and (34). Kistiakowsky and van Artsdalen [3] (KA) studied the thermal bromination of CH_4 and CH_3Br at 570°K and, using eqn. (10), they obtained $k_{exp} = k_{CH_4} K_8^{\frac{1}{2}} = 0{\cdot}0248$ from 6 runs with CH_4 and $k_{exp} = k_{CH_3Br} K_8^{\frac{1}{2}} = 0{\cdot}160\ \text{cm}^{\frac{3}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec}^{-1}$ from 3 runs with CH_3Br. They calculated K_8 from thermodynamic data of Gordon and Barnes [14] and hence obtained k_{CH_4} and k_{CH_3Br}, both at 570°K. KA do not give the actual values but instead use them to derive Arrhenius parameters. We repeated their calculation using data from ref. (14) and also using more accurate data [9] on equilibrium

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* Throughout this paper, we give experimental A factors whereas Fettis and Knox [1] generally give A factors per reacting H atom. Where we quote from Fettis and Knox's review, their A factors have been converted back to the experimental figures where appropriate.

TABLE 1.—RATE CONSTANTS AT 570°K FOR THE REACTIONS

$Br+CH_4 \rightarrow HBr+CH_3$ k_{CH_4}
$Br+CH_3Br \rightarrow HBr+CH_2Br$ k_{CH_3Br}

	KA(GB)	KA(J)	present work
$k_{CH_4} \times 10^{-6}$	5·96	6·53	7·45
$k_{CH_3Br} \times 10^{-7}$	3·84	4·21	5·39

Rate constants in cm^3 $mole^{-1}$ sec^{-1}. Figures under KA(GB) and KA(J) are from kinetic data of Kistiakowsky and van Artsdalen [3] re-calculated by us using thermodynamic data of Gordon and Barnes [14] and from the JANAF tables.[9]

TABLE 2.—ARRHENIUS PARAMETERS FOR THE REACTION

$Br+RH \rightarrow HBr+R$

RH	log A(cm^3 $mole^{-1}$ sec^{-1})	E(cal $mole^{-1}$)	ref.
CF_3H	13·107 ±0·035	22,320 ±110	this work
C_2F_5H	13·026 ±0·020	19,310 ±60	this work
$CF_3CF_2CF_2H$	12·951 ±0·047	19,080 ±140	2
CH_4	13·991 ±0·049	18,580 ±140	2,6
CH_3F	13·736 ±0·052	16,100 ±140	6
CH_2F_2	13·369 ±0·052	16,585 ±140	6
CH_3CH_3	14·135 ±0·056	13,660 ±140	2,6,13
$CH_3\overset{*}{C}H_2F$	13·121 ±0·079	11,590 ±170	2
$CH_3\overset{*}{C}HF_2$	13·361 ±0·052	14,550 ±140	2
CH_3CF_3	14·011 ±0·044	23,460 ±130	2
CF_3CH_2F	13·587 ±0·060	19,500 ±160	2
CF_2HCF_2H	13·601 ±0·063	19,350 ±160	2
$CH_3\overset{*}{C}H_2CH_3$	13·960 ±0·066	10,410 ±150	13
$CH_3\overset{*}{C}H_2\overset{*}{C}H_2CH_3$	14·460 ±0·084	10,490 ±170	13
$(CH_3)_3\overset{*}{C}H$	13·581 ±0·078	7,770 ±160	13
$(CH_3)_4C$	14·484 ±0·061	14,460 ±150	13
CH_3Cl	13·857 ±0·061	14,720 ±160	13
CH_3Br	14·000 ±0·058	16,310 ±170	13
H_2	14·43 ±0·14	19,700 ±400	1
D_2	14·29 ±0·14	21,400 ±400	1
$CHCl_3$	12·36 ±0·15	9,300 ±300	22
$\overset{*}{C}H_3OH$	12·5	7,500 ±1000	*a*
$CH_3\overset{*}{C}H_2OH$	—	3,600 ±2000	*b*
CF_3CHO	12.447 ±0·081	6,600 ±200	23
†CCl_3Br	13·91 ±0·15	10,200 ±300	22
†CF_3Br	13·8 ±0·5	24,300 ±2000	15

* Indicates H abstracted.

† for these two compounds, the reactions are $Br+CCl_3Br \rightarrow Br_2+CCl_3$ and $Br+CF_3Br \rightarrow Br_2+CF_3$: for the latter process, Arrhenius parameters are based on kinetic data on the reverse reaction combined with thermodynamic data.[15]

Results in the first part of the table are all from kinetic studies using the two reactions at the head of the table as standards. The references give the source of competitive results. In ref. (13), there are some inconsistencies between the absolute Arrhenius parameters and the competitive results hence we have used only the latter.

Results in the second part of the table are all from direct independent measurements. *a*, Buckley and Whittle [24] obtained for the reaction $Br+CH_3OH \rightarrow HBr+CH_2OH$, E = 7·5 kcal $mole^{-1}$ which they corrected to 6·2 kcal $mole^{-1}$; however, we now prefer the uncorrected figure. *b*, E obtained from $E(Br+CH_3OH)$ = 7·5 kcal $mole^{-1}$ together with $E(Br+CH_3OH)-E(Br+C_2H_5OH)$ = 3·9 kcal $mole^{-1}$, ref. (25).

(8) and we find values of k_{CH_4} and k_{CH_3Br} given in table 1. In the last column, we give k_{CH_4} and k_{CH_3Br} calculated from our data in eqn. (31) and (34). The agreement between the figures in the last two columns supports our data in eqn. (31) and (34).

If the figures in eqn. (31) and (34) are accepted, then previous data on Arrhenius parameters require correction. Fettis and Knox [1] give a table of A and E using data in eqn. (36) as standards; we have corrected these using our data in eqn. (34) as standards and the results are given in table 2 which also includes values of A and E for Br+ fluoroalkanes. These were given in ref. (2) using data in eqn. (35) as standards whereas the new results are based on eqn. (31). The first part of table 2 therefore includes corrected results, all of which are derived from competitive studies plus the absolute Arrhenius parameters given in eqn. (13) and (16) of this paper. It is difficult to estimate the absolute uncertainties in the various A and E but cross-checks have been applied in several cases [2,6] by competing pairs of reactants AB, BC and AC and the discrepancies were always of the same order as the statistical errors. Hence it seems likely that the absolute uncertainties are of the same order as the statistical errors. In the second part of the table are given other independent results with error limits estimated by the various authors. The whole table covers all bromination reactions which have been studied directly and also includes some indirect results in which Arrhenius parameters of the reaction of interest are calculated by combining experimental data on the *reverse* of the bromination reactions with thermodynamic data. This type of calculation utilizes entropies of free radicals and an improved entropy of the CF_3 radical was calculated by Amphlett and Whittle [15] using the new A factor for reaction (3) given in eqn. (13).

ARRHENIUS PARAMETERS FOR REACTIONS OF CF_3 AND C_2F_5 RADICALS WITH HBr AND Br_2

For CF_3+Br_2, Whittle and co-workers [11,16] obtained $\log k_9(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = 12{\cdot}36-700/2{\cdot}303\ RT$ and combination of this result with that of eqn. (19) gives for CF_3+HBr

$$\log k_{-3}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = 11{\cdot}94-(2{,}830\pm500)/2{\cdot}303\ RT. \qquad (37)$$

The value of A_{-3} in this eqn. supersedes $\log A_{-3}(\text{cm}^3\ \text{mole}^{-1}\ \text{sec}^{-1}) = 11{\cdot}78$ from ref. (16) owing to our use of the new result in eqn. (19); the corresponding change from $E_{-3} = 2{\cdot}9$ kcal mole^{-1} in ref. (16) is negligible.

The absolute Arrhenius parameters for the reactions of the C_2F_5 radical with HBr and Br_2 are unknown but from eqn. (21), $E_{-4}-E_{15} = 2{\cdot}94\pm0{\cdot}28$ kcal mole^{-1}. Now for the reaction between CF_3 and Br_2, $E_9 = 0{\cdot}7\pm0{\cdot}5$, consequently we estimate that for $C_2F_5+Br_2$, $E_{15} = 1{\cdot}0\pm1{\cdot}0$ kcal mole^{-1}, since both reactions are exothermic by $\sim$21 kcal mole^{-1}. Thus $E_{-4} = 2{\cdot}9+E_{15} = 3{\cdot}9\pm1{\cdot}2$ kcal mole^{-1}.

BOND DISSOCIATION ENERGIES

$D(CF_3—H)$

Previous studies by Whittle and co-workers lead to $D(CF_3—H) = 106{\cdot}4$ kcal mole^{-1} from chlorination reactions [5] and $D(CF_3—H) = 106{\cdot}2$ kcal mole^{-1} from bromination reactions [5] (unless otherwise stated, all dissociation energies are at 298°K): the bromination result must now be amended as follows.

The previous value $D(CF_3—H) = 106{\cdot}2$ kcal mole^{-1} was obtained from ΔH_3° using the activation energies $E_3 = 21{\cdot}9$ and $E_{-3} = 2{\cdot}9$ kcal mole^{-1}. The value of E_3 was based on a competitive determination of the difference $E_3—E_5$ together with $E_5 = 18{\cdot}2$ kcal mole^{-1} as suggested by Fettis and Knox.[1] However, we have now measured E_3 directly and with greater accuracy, the result from eqn. (13) being $22{\cdot}32 \pm 0{\cdot}11$ kcal mole^{-1}. On combining this with $E_{-3} = 2{\cdot}83 \pm 0{\cdot}5$ kcal mole^{-1} from eqn. (37), we get $\Delta H_3^\circ = 19{\cdot}5 \pm 0{\cdot}5$ kcal mole^{-1} at a mean temperature of 617°K whereas the previous result was $\Delta H_3^\circ = 19{\cdot}0$ kcal mole^{-1} at 520°K. Using standard thermodynamic data,[9] D(H—Br) = 88·4 kcal mole^{-1} hence $D(CF_3$—H) = 107·9 kcal mole^{-1}, both at 617°K, which becomes 106·7 kcal mole^{-1} at 298°K using heat capacities from ref. (9).

The current position with regard to $D(CF_3$—H) at 298°K is therefore as follows:

$D(CF_3$—H) = $106{\cdot}7 \pm 0{\cdot}7$ kcal mole^{-1}, from bromination work;
= $106{\cdot}4 \pm 0{\cdot}5$ kcal mole^{-1}, from chlorination work;[5]
= $105{\cdot}6 \pm 3{\cdot}0$ kcal mole^{-1}, from iodination work.[17]

We suggest as a weighted mean of these results, $D(CF_3$—H) = 106·4 kcal mole^{-1} with an uncertainty of about ±0·5 kcal mole^{-1}. Following Pritchard and co-workers,[17] we neglect other reactions from which $D(CF_3$—H) can be derived. However, Coomber and Whittle[5] used data on the reactions

$$CD_3 + CF_3H \rightleftharpoons CD_3H + CF_3$$

to obtain $D(CF_3$—H) = $D(CH_3$—H) + 0·4 kcal mole^{-1} so that, using $D(CH_3$—H) = 104·2 kcal mole^{-1} (see below), we have $D(CF_3$—H) = 104·6 kcal mole^{-1} with error limits of about ±1·5 kcal mole^{-1}. This result agrees within experimental error with that proposed above.

$D(CH_3$—H)

This is obtained using E_5 and E_{-5}. The " old " value of E_5 = 18·2 kcal mole^{-1} (see eqn. (36)) leads to $D(CH_3$—H) = 103·8 kcal mole^{-1} (Kerr [18] uses E_5 = 18·3 to get $D(CH_3$—H) = 103·9 kcal mole^{-1}). The more accurate result $E_5 = 18{\cdot}58 \pm 0{\cdot}17$ kcal mole^{-1} from eqn. (31) together with $E_{-5} = 1{\cdot}37 \pm 0{\cdot}50$ kcal mole^{-1}, ref. (12), gives $D(CH_3$—H) = 105·5 kcal mole^{-1} at a mean temperature of 544°K which becomes $D(CH_3$—H) = 104·3 kcal mole^{-1} at 298°K, with an uncertainty of about 0·7 kcal mole^{-1}. The main source of error is the uncertainty of the assumption that $E(CH_3 + I_2) = 0$ which is used in deriving E_{-5}. The previous bromination result of $D(CH_3$—H) = 103·9 kcal mole^{-1} is superseded by the new result which is more accurate. The iodination work of Benson and co-workers and Pritchard and co-workers was reviewed by Kerr [18] who gives $D(CH_3$—H) = 104·1 (with an uncertainty of about ±0·5 kcal mole^{-1} being proposed in ref. (19)). The mean result from the bromination and iodination work is $D(CH_3$—H) = $104{\cdot}2 \pm 0{\cdot}5$ kcal mole^{-1}, compared to $D(CH_3$—H) = $104{\cdot}0 \pm 1{\cdot}0$ kcal mole^{-1} adopted by Kerr.[18] The most significant change is the reduction in error limits.

$D(C_2F_5$—H)

Taking $E_4 = 19{\cdot}31 \pm 0{\cdot}06$ kcal mole^{-1} from eqn. (16) and $E_{-4} = 3{\cdot}9 \pm 1{\cdot}2$ kcal mole^{-1} recommended above, we get $\Delta H_4^\circ = 15{\cdot}4 \pm 1{\cdot}2$ kcal mole^{-1} at a mean temperature of 673°K. Using D(H—Br) = 88·6 then $D(C_2F_5$—H) = $104{\cdot}0 \pm 1{\cdot}2$ kcal mole^{-1}, both at 673°K. Assuming that ΔC_p is the same for reactions (3) and (4), the corrected result at 298°K is $D(C_2F_5$—H) = $102{\cdot}6 \pm 1{\cdot}2$ kcal mole^{-1}.

Previous values are: Coomber and Whittle [7] obtained $D(C_2F_5$—H) = $103{\cdot}5 \pm 2{\cdot}0$ kcal mole^{-1} from bromination studies (not corrected to 298°K); this result is superseded by the one given above. Pritchard and Thommarson [20] obtained $D(C_2F_5$—H)—$D(CH_3$—H) = $-1{\cdot}1 \pm 1{\cdot}0$ kcal mole^{-1} and, taking $D(CH_3$—H) = $104{\cdot}2 \pm 0{\cdot}5$ kcal mole^{-1}, we have $D(C_2F_5$—H) = $103{\cdot}1 \pm 1{\cdot}1$ kcal mole^{-1}, in good agreement with the bromination result. The mean value $D(C_2F_5\text{—}H) = 102{\cdot}9$ is probably reliable to $\pm 1{\cdot}0$ kcal mole^{-1}.

RELATED BOND DISSOCIATION ENERGIES

Coomber and Whittle [21] give a table of bond dissociation energies, many of which are based on $D(CF_3\text{—}H) = 106{\cdot}3$ kcal mole^{-1} and $D(C_2F_5\text{—}H) = 103{\cdot}0$ kcal mole^{-1}. Using the amended values given above, the results in their table should be increased by 0·1 kcal mole^{-1} if based on $D(CF_3\text{—}H)$ and decreased by 0·1 kcal mole^{-1} if based on $D(C_2F_5\text{—}H)$.

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[1] G. C. Fettis and J. H. Knox, *Progr. in Reaction Kinetics*, 1964, **2,** 1.
[2] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1966, **62,** 1553.
[3] G. B. Kistiakowsky and E. R. van Artsdalen, *J. Chem. Physics*, 1944, **12,** 469.
[4] P. Corbett, A. M. Tarr and E. Whittle, *Trans. Faraday Soc.*, 1963, **59,** 1609.
[5] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1966, **62,** 2183.
[6] A. M. Tarr, J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1965, **61,** 1182.
[7] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1967, **63,** 608.
[8] P. G. Ashmore, B. P. Levitt and B. A. Thrush, *Trans. Faraday Soc.*, 1956, **52,** 830.
[9] *JANAF Interim Thermochemical Tables* (Dow Chemical Co., Midland, Michigan, 1965).
[10] C. Lanczos, *Applied Analysis*, (Pitman, London, 1957) p. 323.
[11] B. G. Tucker and E. Whittle, *Trans. Faraday Soc.*, 1965, **61,** 866.
[12] G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 3037.
[13] G. C. Fettis, J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4177.
[14] A. R. Gordon and C. Barnes, *J. Chem. Physics*, 1933, **1,** 692.
[15] J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1967, **63,** 2695.
[16] J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1966, **62,** 1662.
[17] C. A. Goy, A. Lord and H. O. Pritchard, *J. Physic. Chem.*, 1967, **71,** 1086.
[18] J. A. Kerr, *Chem. Rev.*, 1966, **66,** 465.
[19] D. M. Golden, R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87,** 4053.
[20] G. O. Pritchard and R. L. Thommarson, *J. Physic. Chem.*, 1964, **68,** 568.
[21] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1967, **63,** 2656.
[22] J. H. Sullivan and N. Davidson, *J. Chem. Physics*, 1951, **19,** 143.
[23] J. C. Amphlett and E. Whittle, unpublished work.
[24] E. Buckley and E. Whittle, *Trans. Faraday Soc.*, 1962, **58,** 536.
[25] A. M. Tarr and E. Whittle, *Trans. Faraday Soc.*, 1964, **60,** 2039.