Rate Constants for the Recombination of CCl_3 Radicals and for their Reactions with Cl, Cl_2 and HCl in the Gas Phase

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The gas-phase photochlorination of $CHCl_3$ has been investigated between 303·2 and 425·5°K. The reaction was followed both by a conventional and a mass spectrometric technique. Rate measurements in steady light lead to

$$\log_{10}(k_3/k_8^{\frac{1}{2}}) = -5{,}000/4{\cdot}576\,T+3{\cdot}91, \tag{i}$$

and

$$\log_{10}(k_3k_2/k_7)^{\frac{1}{2}} = -3{,}700/4{\cdot}576T+3{\cdot}60, \tag{ii}$$

where k_2, k_3, k_7 and k_8 refer to

$$Cl+CHCl_3 \rightarrow CCl_3+HCl \tag{2}$$
$$CCl_3+Cl_2 \rightarrow Cl+CCl_4 \tag{3}$$
$$Cl+CCl_3 \rightarrow CCl_4 \tag{7}$$
$$2CCl_3 \rightarrow C_2Cl_6. \tag{8}$$

Rate measurements in intermittent light give

$$\log_{10}k_3 = -5{,}000/4{\cdot}576T+8{\cdot}74, \tag{iii}$$

which combined with eqn. (i) and (ii) and the known value of k_2 yields $\log_{10}k_7 = 10{\cdot}8$ and $\log_{10}k_8 = 9{\cdot}6_6$, independent of temperature. Using the values of k_2 and k_3 and thermodynamic data, one calculates $\log_{10}k_4 = -11{,}300/4{\cdot}576T+8{\cdot}65$ and $\log_{10}k_5 = -20{,}000/4{\cdot}576T+10{\cdot}93$, for the reverse of reactions (2) and (3) respectively. All rate constants are given in mole^{-1} l. sec^{-1}.

The rate constant for the gas-phase recombination of trichloromethyl radicals has been measured by Tedder and Walton [1] who found $\log_{10}k_8$ * = 10·9 between 350 and 446°K. This value is in line with those observed for methyl and trifluoromethyl radicals [2, 3] but is higher than would be expected from a comparison of the values observed for C_2Cl_5(8·6),[4] C_2HCl_4(9·3) [5] and C_2H_5(10·5) [2] radicals. It is also higher than a proposed value for CCl_3 radicals in the gas-phase (8·8) [6, 7] and observed values in the liquid phase (7·7→8·1).[8] It therefore seemed important to measure k_8 in a chemical system different from that used by Tedder and Walton (C_2H_4+CCl_3Br+$h\nu$). The gas-phase photochlorination of chloroform was chosen for this purpose.

This reaction has been investigated using steady illumination by Chiltz, Mahieu and Martens.[9] Between 360 and 430°K, the initial rate of chlorination is given by

$$v_s = -d[Cl_2]/dt = I_a^{\frac{1}{2}}k_3[Cl_2]/(k_8+k_7k_3[Cl_2]/k_2[CHCl_3])^{\frac{1}{2}} \tag{i}$$

* All rate constants are given in mole^{-1} l. sec^{-1}.

corresponding to the reaction mechanism

$$
\begin{array}{lll}
Cl_2 \xrightarrow{h\nu} 2Cl & I_a & \\
Cl + CHCl_3 \xrightarrow{(2)} CCl_3 + HCl & k_2 & \\
CCl_3 + Cl_2 \xrightarrow{(3)} CCl_4 + Cl & k_3 & \text{(ii)} \\
CCl_3 + Cl \xrightarrow{(7)} CCl_4 & k_7 & \\
CCl_3 + CCl_3 \xrightarrow{(8)} C_2Cl_6 & k_8 &
\end{array}
$$

Therefore a series of experiments in which the $[Cl_2]/[CHCl_3]$ ratio is varied yields the complex rate constants $k_3/k_8^{\frac{1}{2}}$ and k_3k_2/k_7. The life-time of the chains is given by

$$\tau = (1+\alpha)/\{2I_a^{\frac{1}{2}}(k_8+k_7k_3[Cl_2]/k_2[CHCl_3])^{\frac{1}{2}}\} \qquad \text{(iii)}$$

where

$$\alpha = k_3[Cl_2]/k_2[CHCl_3] = [Cl]/[CCl_3]. \qquad \text{(iv)}$$

τ can be determined by the rotating sector technique [10, 11] from a plot of $y = (v_i/v_s)(r+1)^{\frac{1}{2}}$ against $\log_{10}t$, where v_i and v_s are the rates of chlorination in intermittent and steady illumination respectively, r is the ratio of dark-to-light periods and t is the duration of the light flash. τ depends on several parameters and it is convenient to introduce a reduced time parameter [7]

$$t' = 2tI_a[Cl_2]/v_s. \qquad \text{(v)}$$

Then, if $\alpha \ll 1$, superimposing the theoretical curve [10] of y against $\log_{10} m = \log_{10}(t/\tau)$ on the experimental plot of y against $\log_{10}t' = \log_{10}(m/k_3)$ yields at $\log_{10}m = 0$ the value of $\log_{10}(1/k_3)$ (e.g., see fig. 3). This value combined with those of k_2 [12] and of $k_3/k_8^{\frac{1}{2}}$ and k_3k_2/k_7 leads to k_8 and k_7.

EXPERIMENTAL

Commercial tank chlorine (Solvay), chloroform (Merck, *pro analysi*) and trichloroethylene (Th. Schuchardt, *reinst*) were purified as described earlier (Cl_2,[13] $CHCl_3$,[9] C_2HCl_3 [5]). Gas chromatographic analyses of the $CHCl_3$ and the C_2HCl_3 showed less than 0·06 and 0·03 % impurity, respectively. The purities of hexachloroethane and carbon tetrachloride used for calibrating the gas chromatograph and the mass spectrometer were always better than 99 %.

The conventional kinetic apparatus and procedure have been described.[4] The rotating sector was a Perspex disc, three-quarters of which was painted black and one quarter left transparent, driven by a synchronous motor and a gear box. The nominal rotation speeds were accurate to better than 1 %. The light periods ranged from 5 to 640 msec. The ratio of the width of the sector opening to that of the image of the lamp focused in the plane of the sector was 40; therefore penumbra corrections [14] were neglected. Corrections for dark reactions,[15] non-uniform light absorption [14] and monomolecular chain breaking [16, 17] were also negligible. The values of y corresponding to the shortest light periods were $1{\cdot}00 \pm 0{\cdot}02$, therefore the dependence of the reaction rate on the light intensity is $0{\cdot}500 \pm 0{\cdot}015$.

Pressures were measured by a mercury manometer, a Bourdon gauge serving as a null instrument. Chlorine concentrations were determined continuously by measuring the absorption of a weak auxiliary light beam at about 3,600 Å by means of a logarithmic photometer [18] which was calibrated at each temperature: the smallest rate of chlorine consumption which could be detected was 0·02 torr in 1 min. The reaction rates were obtained by drawing tangents to the photometer curve. The concentrations of the reagents and the products during the course of the reactions were calculated using the stoichiometric equation

$$CHCl_3+Cl_2 \rightarrow CCl_4+HCl \tag{vi}$$

The absorbed light intensity (λ = 4,358 Å) was determined to within ±1 % using the reaction $Cl_2+C_2HCl_3$ as an actinometer and taking multiple reflections of the light into account.[19] The temperature T_0 of the reaction cell was measured by means of a calibrated chromel-alumel thermocouple. Due to the Draper-effect,[20] the effective temperature at which reaction occurred was $T = T_0+\Delta T$ with $\Delta T = v_T \Delta H r_0^2/8\kappa$, where v_T is the observed reaction rate (mole cm^{-3} sec^{-1}), ΔH the heat of reaction (cal $mole^{-1}$), r_0 = 1·85 cm the radius of the 11·9 cm long cylindrical cell and κ the thermal conductivity of the reacting mixture (cal cm^{-1} sec^{-1} $deg.^{-1}$). ΔH was calculated using the heat of formation of $CHCl_3$, CCl_4 and HCl from ref. (21). κ was obtained from the thermal conductivities of the components of the reacting mixture by means of the methods recommended by Reid and Sherwood.[22] ΔT depends on the reaction rate and the thermal conductivity of the reacting mixture. It therefore varies from one experiment to another and also in a reaction: the range of variation was 0·05-1·8°. All reaction rates in steady and intermittent illumination were normalized to the mean temperature of each set of n experiments,

$$\overline{T} = \sum_{i=1}^{i=n}(T_{0i}+\Delta T_i)/n,$$

using

$$v_{\overline{T}} = \frac{v_T(k_8/k_3^2+(k_7/k_3k_2)[Cl_2]/[CHCl_3])^{\frac{1}{2}}_{\overline{T}}}{(k_8/k_3^2+(k_7/k_2k_3)[Cl_2]/[CHCl_3])^{\frac{1}{2}}_{T}} = v_T C. \tag{vii}$$

Values of C ranging from 0·98 to 1·02 were obtained using values of $k_3/k_8^{\frac{1}{2}}$ and k_3k_2/k_7 calculated from uncorrected rates of reaction.

A description of the mass spectrometric technique has been presented.[23] Mass spectra of the gas leaving the Pyrex reaction vessel through a 5 micron diam. sampling leak were taken at 5 sec intervals from m/e 70 to 121 and from m/e 130 to 220. The disappearance of chlorine and chloroform were obtained from the Cl_2^+ and CCl_2H^+ ions, the appearance of carbon tetrachloride from the CCl_3^+ ion and that of hexachloroethane from the $C_2Cl_4^+$ and $C_2Cl_5^+$ ions. The formation of C_2Cl_6 was also confirmed by gas chromatography. Known initial pressures of chlorine and chloroform provided an internal calibration for these substances. Sensitivity to carbon tetrachloride was calculated taking into account that at least 99 % of the chloroform was converted to tetrachloride. The relative sensitivity of C_2Cl_6 to CCl_4 was determined by introducing known pressures of the pure substances directly into the ionization chamber. The mass spectrometric experiment was performed with the unfiltered light from a medium pressure mercury vapour lamp (Philora HP 125). The experimental conditions were such that the quantum yields were always greater than 100.

RESULTS AND DISCUSSION

The photochlorination of chloroform in the gas-phase has been studied in steady and intermittent illumination at 303·2, 344·7,* 371·0 and 425·5°K in the conventional kinetic apparatus.

Eqn. (i) may be best represented graphically in the form

$$Y = I_a[Cl_2]^2/v_s^2 = k_8/k_3^2+(k_7/k_3k_2)[Cl_2]/[CHCl_3]. \tag{viii}$$

A plot of Y against $[Cl_2]/[CHCl_3]$ for the series of experiments at 371·0°K and a plot of Y against the % reaction for an experiment where $[Cl_2] = [CHCl_3]$ are given in fig. 1 and 2 respectively. It is apparent from these figures that eqn. (viii) describes not only the initial conditions, as has already been observed,[9] but also describes the

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* The results at this temperature have been published previously.[24]

reactions up to at least 70 % transformation: experiments at the other temperatures lead to the same conclusions. Thus the rate of the photochlorination is not influenced by the presence of the reaction products and reaction scheme (ii) and hence eqn. (iii) are valid up to at least 70 % transformation. This permits a considerable simplification of the rotating sector procedure which usually requires three experiments, one in intermittent illumination performed between two in steady illumination, to obtain

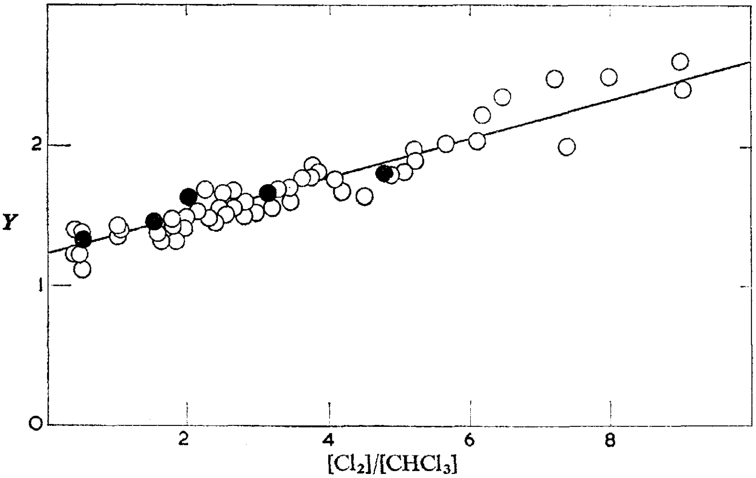

FIG. 1.—$Y = 10^2 I_a[Cl_2]^2/v_s^2$ against $[Cl_2]/[CHCl_3]$ (see eqn. (viii)) at 371·0°K. Y in einstein $l.^{-1}$ sec; initial conditions (●); 1-70 % transformation (○); the points at $[Cl_2]/[CHCl_3] = 1$ are mean values of Y during the course of a reaction (e.g., see fig. 2); straight line obtained by least squares; $p(CHCl_3)$ and $p(Cl_2)$ ranged from 13 to 100 torr and from 25 to 130 torr respectively.

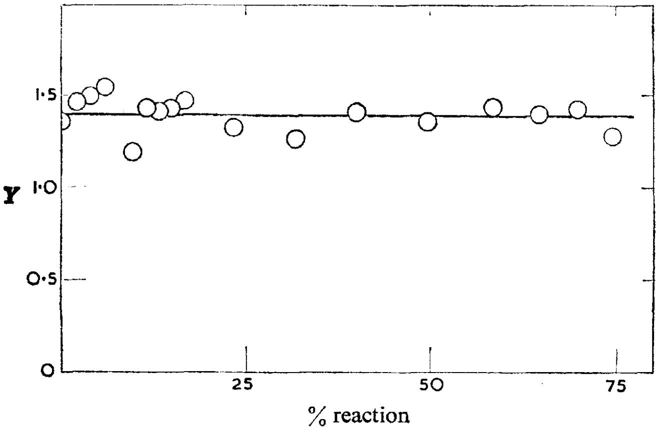

FIG. 2.—$Y = 10^2 I_a[Cl_2]^2/v_s^2$ against the % reaction with $[Cl_2] = [CHCl_3] = 100$ torr at 371·0°K.

only one point on the plot of y against log t'. Several such points can now be obtained from one experiment by illuminating the reaction mixture alternately with steady and intermittent light for times corresponding to about 5 % of reaction and using different flashing times t. Another advantage of this latter procedure is that the variation of the light intensity and the temperature is negligible during an experiment. Fig. 3 shows a plot of y against $\log_{10} t'$ for the series of experiments at 371·0°K. The results do not depend on the $[Cl_2]/[CHCl_3]$ ratio which was varied between 0·4 and 4·5 : this means that α is negligible in eqn. (iii). At 425·5°K experiments in intermittent illumination were performed with $[Cl_2]/[CHCl_3] \leqslant 1$ so that α was unimportant.

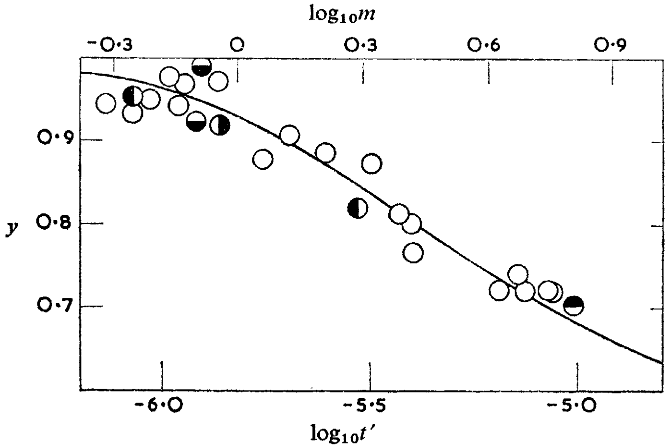

FIG. 3.—Photochlorination of chloroform in intermittent light at 371·0°K with sector $r = 3$. Theoretical sector curve superimposed on the experimental plot of y against $\log_{10}t'$; the definitions of t' (mole $l.^{-1}$ sec), Y and m are given in the introduction; at $\log_{10}m = 0$, $-\log_{10}t' = \log_{10}k_3 = 5·82$; $[Cl_2]/[CHCl_3]$ equals 0·4 (◐), 1·0(○), 1·7 (◒), 2·3 (◓) and 4·5 (◑); $p(Cl_2)$ ranged from 28 to 96 torr; incident light intensity $I_0 = 2·16 \times 10^{-10}$ einstein cm^{-2} sec^{-1}.

Values of $k_3/k_8^{\frac{1}{2}}$, $(k_3k_2/k_7)^{\frac{1}{2}}$ and k_3 were obtained from graphs such as fig. 1 and 3. The temperature dependences of these rate constants are shown in fig. 4 and are represented by

$$\log_{10}(k_3/k_8^{\frac{1}{2}}) = -5{,}000/4·576\,T + 3·91, \qquad \text{(ix)}$$

$$\log_{10}(k_3k_2/k_7)^{\frac{1}{2}} = -3{,}700/4·576\,T + 3·60, \qquad \text{(x)}$$

and

$$\log_{10}k_3 = -5{,}000/4·576\,T + 8·74. \qquad \text{(xi)}$$

These equations and the known value of k_2,[12]

$$\log_{10}k_2 = -3{,}350/4·576T + 9·84, \qquad \text{(xii)}$$

permits one to calculate

$$\log_{10}k_7 = -950/4·576\,T + 11·38 \qquad \text{(xiii)}$$

and

$$\log_{10}k_8 = 9·6_6. \qquad \text{(xiv)}$$

In eqn. (ix) to (xii), the standard errors on the activation energies and on the pre-exponential factors are 0·1 kcal $mole^{-1}$ and 0·06 logarithmic units respectively: they are twice as large in eqn. (xiv).

As eqn. (xiii) results from a combination of three experimental values (eqn. (x)-(xii)), it is not excluded that k_7 has no activation energy : we therefore propose

$$\log_{10}k_7 = 10·8. \qquad \text{(xv)}$$

The value of k_8 is about 7 times lower than that observed for CH_3 radicals. This agrees with the decrease of k_8 with increasing chlorine content of radicals observed for C_2H_5, C_2HCl_4 * and C_2Cl_5 radicals.

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* Applying the experimental technique described to the photochlorination of trichloroethylene, we obtained a value of $\log_{10}k_8 = 9·3$ at 371·0°K for the recombination of two C_2HCl_4 radicals in good agreement with the data of Dainton, Lomax and Weston (9·27).[5]

Fig. 5 shows the results of a mass spectrometric experiment performed with $p(CHCl_3) = p(Cl_2) = 82$ torr at 371·2°K. These results confirm the stoichiometric equation (vi) and the formation of C_2Cl_6 as a reaction product (see reaction scheme

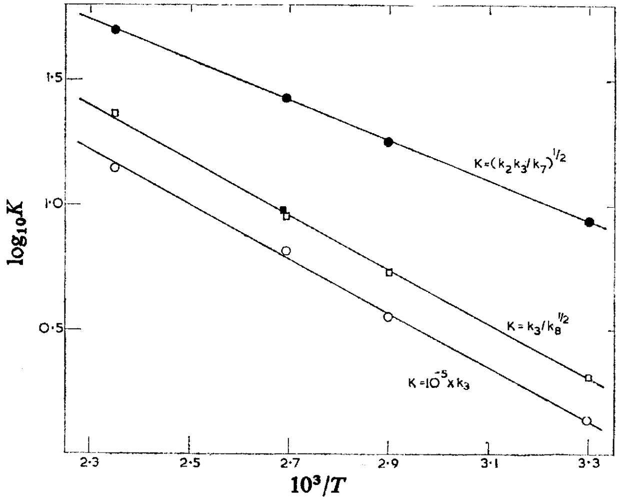

FIG. 4.—Arrhenius plots of rate constants k_3, $k_3/k_8^{\frac{1}{2}}$ and $(k_2k_3/k_7)^{\frac{1}{2}}$; mass spectrometric result for $k_3/k_8^{\frac{1}{2}}$ (■).

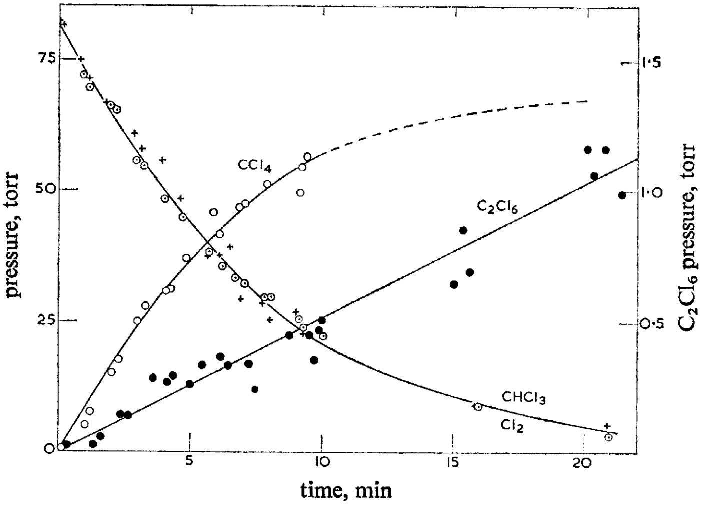

FIG. 5.—Photochlorination of chloroform at 371·2°K as followed by mass spectrometer.

(ii)). Further, it can be shown that the rates of formation of CCl_4 and of C_2Cl_6 * are represented respectively by

$$d[CCl_4]/dt = -d[Cl_2]/dt = -d[CHCl_3]/dt = 1·9 \times 10^{-3}[Cl_2] \text{ mole l.}^{-1} \text{ sec}^{-1}, \quad \text{(xvi)}$$

and

$$d[C_2Cl_6]/dt = 3·9 \times 10^{-8} \text{ mole l.}^{-1} \text{ sec}^{-1}, \quad \text{(xvii)}$$

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* These rates were determined from the curves of fig. 5 and corrected for the pressure drop in the reactor of 0·5 %/min, due to the sampling leak.

up to at least 30 % of reaction where I_a is practically constant. The experimental rate eqn. (xvi) and (xvii) are of the same form as those resulting from a steady-state treatment of reaction scheme (ii) assuming long chains from which

$$(\mathrm{d}[\mathrm{CCl_4}]/\mathrm{d}t)/(\mathrm{d}[\mathrm{C_2Cl_6}]/\mathrm{d}t)^{\frac{1}{2}} = k_3[\mathrm{Cl_2}]/k_8^{\frac{1}{2}}. \tag{xviii}$$

Combining eqn. (xvi) to (xviii) one obtains a value of $\log_{10}(k_3/k_8^{\frac{1}{2}}) = 0{\cdot}98$ at 371·2°K in good agreement with eqn. (ix) which yields 0·97 (see fig. 4). The fact that two completely different methods of determination of $k_3/k_8^{\frac{1}{2}}$, one requiring a measurement of I_a (see eqn. (i)) and the other not (see eqn. (xviii)), lead to the same result, indicates no error in the actinometry and hence no I_a error in the determinations of the rate constants k_3, k_7 and k_8.

From eqn. (xi) and (xii) and from the entropies and the heats of formation of Cl, $\mathrm{Cl_2}$, HCl, $\mathrm{CHCl_3}$ and $\mathrm{CCl_4}$ given in ref. (21) and those of $\mathrm{CCl_3}$,* one obtains for the reverse of reactions (2) and (3) of reaction scheme (ii)

$$\mathrm{CCl_3 + HCl \xrightarrow{(4)} Cl + CHCl_3} \qquad k_4 \tag{xix}$$

and

$$\mathrm{Cl + CCl_4 \xrightarrow{(5)} CCl_3 + Cl_2}, \qquad k_5 \tag{xx}$$

$$\log_{10}k_4 = -11{,}300/4{\cdot}576T + 8{\cdot}65, \tag{xxi}$$

and

$$\log_{10}k_5 = -20{,}000/4{\cdot}576T + 10{\cdot}93. \tag{xxii}$$

These rate constants are compatible with the fact that reactions (xix) and (xx) are not observed during the course of a reaction.

Using eqn. (iv), (xi), (xii) and (xiv) and the known value [28] of the rate constant for

$$\mathrm{Cl + Cl + M \xrightarrow{(6)} Cl_2 + M} \qquad k_6 \tag{xxiii}$$

one calculates that, under our experimental conditions, the rate of the three-body recombination of Cl atoms is at least 10^4 times lower than that of the recombination of $\mathrm{CCl_3}$ radicals.

An evaluation of rate constants by the transition state theory [29] gives

$$\log_{10}k_3 = -5{,}100/4{\cdot}576T + 9{\cdot}1, \tag{xxiv}$$

and

$$\log_{10}k_7 = 10{\cdot}7, \tag{xxv}$$

in satisfactory agreement with the experimental eqn. (xi) and (xv). For k_8, calculated values [29, 30] are much higher than the present experimental value: this has also been observed for $\mathrm{C_2HCl_4}$ and $\mathrm{C_2Cl_5}$ radicals.[29]

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* The values S°_{298} $(\mathrm{CCl_3}) = 70{\cdot}8$ cal/mole deg. and $\Delta H^{\circ}_{f,\,298}$ $(\mathrm{CCl_3}) = 18$ kcal/mole were chosen as mean values of existing data.[25-27]

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