The Kinetics of Radiation-Induced Hydrogen Abstraction by CCl_3 and CCl_3O_2 Radicals from Cyclohexane in the Liquid Phase

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The kinetics of the photolysis-induced free-radical reaction in carbon tetrachloride solution of cyclohexane in the absence and in the presence of oxygen were studied in the temperature range of 100–200 °C. It was found that the influence of the oxygen on the chloroform formation is significant, and a new mechanism which explains the results was suggested. The rate constants for the reactions $\cdot CCl_3 + O_2 \rightarrow \cdot CCl_3O_2$ (k_6), $\cdot CCl_3O_2 \rightarrow COCl_2 + ClO$ (k_7), and $\cdot CCl_3O_2 + C_6H_{12} \rightarrow CHCl_3 + \cdot C_6H_{11} + O_2$ (k_8) were found as log $(k_6/(M^{-1}\ s^{-1})) = 5.05 \pm 0.07$ and log $[(k_8/k_7)/(M^{-1}\ s^{-1})] = (3.0808 \pm 0.0973) - (3.7080 \pm 0.1857)/\theta$, where $\theta = 2.303RT$ kcal/mol.

Introduction

Previously, it was assumed that carbon tetrachloride toxicity is caused by the reduction of CCl_4 by the hemoprotein cytochrome P 450 which leads to lipid peroxidation and various biological damages, initiated by abstraction of hydrogen atoms from lipid molecules in a chain-reaction mechanism involving the CCl_3 radical. A new concept argues that the main radical involved in these chain reactions is the CCl_3O_2 radical.[1] This is one of the reasons why studies involving the CCl_3O_2 radical are so important.

Another system in which the CCl_3O_2 radical may play a role is stratospheric ozone destruction. According to Molina and Rowland[2] and other investigators,[3–5] the destruction of the ozone occurs in a chain-reaction mechanism, as follows:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

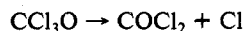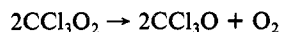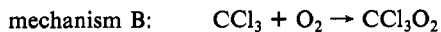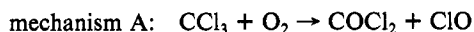net $\qquad\qquad O_3 + O \rightarrow O_2 + O_2$
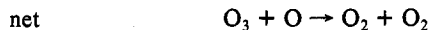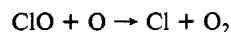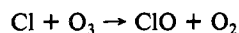
The source of chlorine radicals is usually attributed to chlorofluoromethanes such as CF_2Cl_2 and $CFCl_3$ which release chlorine atoms by photolytic dissociation.[2] However, Lovelock et al.,[6] who measured the concentration of halogenated hydrocarbons in and over the Atlantic, found that the CCl_4 concentration is higher than the $CFCl_3$ concentration and much higher than the CH_3I concentration.

Data on the presence of CCl_4 in the stratosphere and the upper troposphere were also reported. Thus, it is reasonable to assume that the chlorine radical should be attributed also to CCl_4.

So far, only a few studies have been performed on the kinetics of systems involving the CCl_3 radical and oxygen, and only one fact is clearly known, this being that phosgene is formed when oxygen is present with CCl_3 radicals.

There are two approaches to describe the reaction mechanism of the phosgene formation. The two possibilities are attributed to Heicklen and his co-workers.

mechanism A: $CCl_3 + O_2 \rightarrow COCl_2 + ClO$

mechanism B: $CCl_3 + O_2 \rightarrow CCl_3O_2$

$$2CCl_3O_2 \rightarrow 2CCl_3O + O_2$$

$$CCl_3O \rightarrow COCl_2 + Cl$$

While Heicklen previously favored mechanism A,[7] recently

Heicklen and co-workers preferred mechanism B.[8] Gillespie et al.[9] observed ClO formation following the flash photolysis of $CFCl_3$ and CCl_3Br in the presence of O_2. However, they attributed the ClO formation to byproduct reaction. Further studies have been made by Simonaitis and Heicklen[10] and also by Ohta and Mizoguchi.[11]
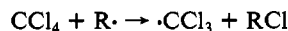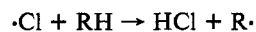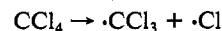
The radiolysis method (as well as the photolysis method) for measuring the rate constants and the Arrhenius parameters for the abstraction of hydrogen atoms by CCl_3 radicals from hydrogen-containing substrates had been used by several investigators[12,13] and proved to be a reliable method. This method involved the radiolyzing (or photolyzing) of liquid mixtures consisting of CCl_4 and an attackable hydrogen-containing substrate and is based on the competition between the abstraction of an H atom by a CCl_3 radical to form chloroform and the combination of two CCl_3 radicals to form C_2Cl_6. We use a similar method to measure the rate constants and the Arrhenius parameters for the abstraction of hydrogen atoms from hydrogen-containing substrates by the CCl_3O_2 radical.

The influence of the presence of oxygen on hydrogen abstraction by the CCl_3 radical (or the CCl_3O_2 radical) has not been previously examined. We undertook this study in order to determine the Arrhenius parameters for the abstraction of the hydrogen atom from cyclohexane by the CCl_3–oxygen radical.
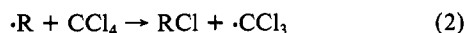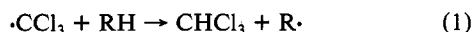
Method

The photolysis of CCl_4 in the presence of a hydrogen-containing substrate RH and in the absence of oxygen leads to chloroform and hexachloroethane formation through the following reaction mechanism:

initiation:

$$CCl_4 \rightarrow \cdot CCl_3 + \cdot Cl$$

$$\cdot Cl + RH \rightarrow HCl + R\cdot$$

$$CCl_4 + R\cdot \rightarrow \cdot CCl_3 + RCl$$

propagation:

$$\cdot CCl_3 + RH \rightarrow CHCl_3 + R\cdot \qquad (1)$$

$$\cdot R + CCl_4 \rightarrow RCl + \cdot CCl_3 \qquad (2)$$

(1) D. Brault and P. Neta, to be submitted for publication in *J. Phys. Chem.*
(2) M. J. Molina and F. S. Rowland, *Nature (London)*, **249**, 810 (1974).
(3) R. S. Stolarski and R. J. Cicerone, *Can. J. Chem.*, **52**, 1610 (1974).
(4) S. C. Wofsy and M. B. McElroy, *Can. J. Chem.*, **52**, 1588 (1974).
(5) P. Crutzen, *Can. J. Chem.*, **52**, 1569 (1974).
(6) J. E. Lovelock and R. J. Maggs, *Nature (London)*, **241**, 194 (1972).
(7) J. Heicklen, *Adv. Photochem.*, **7**, 57 (1970).

(8) R. K. M. Jayanty, R. Simontais, and J. Heicklen, *J. Photochem.*, **4**, 203 (1975).
(9) H. H. Gillespie, J. Garraway, and R. J. Donovan, *J. Photochem.*, **7**, 29 (1977).
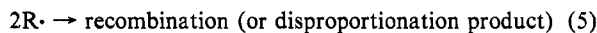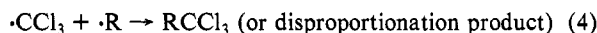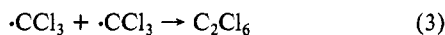(10) R. Simonaitis and J. Heicklen, *Chem. Phys. Lett.*, **62**, 473 (1979).
(11) T. Ohta and I. Mizoguchi, *Int. J. Chem. Kinet.*, **12**, 717 (1980).
(12) M. G. Katz, G. G. Baruch, and L. Rajbenbach, *Int. J. Chem. Kinet.*, **8**, 599 (1976).
(13) Z. B. Alfassi and L. Feldman, *Int. J. Chem. Kinet.*, **12**, 379 (1980).
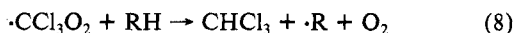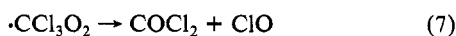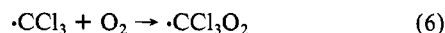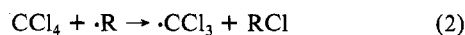
termination:

$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6 \tag{3}$$

$$\cdot CCl_3 + \cdot R \rightarrow RCCl_3 \text{ (or disproportionation product)} \tag{4}$$

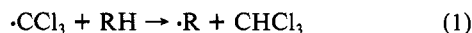$$2R\cdot \rightarrow \text{recombination (or disproportionation product)} \tag{5}$$

Alfassi and Feldman[14] showed that the two last termination reactions are important only if the abstraction reaction is very fast as in the case of allylic hydrogens or in a very high RH concentration case.

The above mechanism leads to the following correlation involving the yields of $CHCl_3$ and C_2Cl_6:
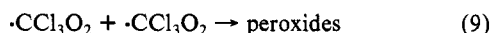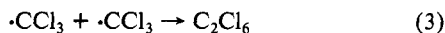
$$\frac{[CHCl_3]}{[C_2Cl_6]^{1/2}} = \frac{k_1}{k_3^{1/2}}[RH]t^{1/2} \tag{I}$$

where $[CHCl_3]$ and $[C_2Cl_6]$ are the concentrations of chloroform and hexachloroethane after time t of irradiation.

Reaction in the Presence of Oxygen. The photolysis of CCl_4 in the presence of oxygen and hydrogen-containing substrates RH leads to $CHCl_3$, C_2Cl_6, ClO, and phosgene formation. As usual, the reaction mechanism can be described by three steps. The initiation step is assumed to be the same as described previously for the reaction in the absence of oxygen. We may describe the propagation step by the following scheme, assuming mechanism A for the phosgene formation:

$$\cdot CCl_3 + RH \rightarrow \cdot R + CHCl_3 \tag{1}$$

$$CCl_4 + \cdot R \rightarrow \cdot CCl_3 + RCl \tag{2}$$

$$\cdot CCl_3 + O_2 \rightarrow \cdot CCl_3O_2 \tag{6}$$

$$\cdot CCl_3O_2 \rightarrow COCl_2 + ClO \tag{7}$$

$$\cdot CCl_3O_2 + RH \rightarrow CHCl_3 + \cdot R + O_2 \tag{8}$$

The termination step will be as without oxygen.

$$\cdot CCl_3 + \cdot CCl_3 \rightarrow C_2Cl_6 \tag{3}$$

$$\cdot CCl_3O_2 + \cdot CCl_3O_2 \rightarrow \text{peroxides} \tag{9}$$

We used steady-state kinetic analysis for both radicals CCl_3 and CCl_3O_2 which leads to the following expressions: from reactions 1 and 8

$$[CHCl_3] = k_1[CCl_3]_{ss}[RH]t + k_8[CCl_3O_2]_{ss}[RH]t$$

from reactions 6, 7, and 8 and assuming $k_9[CCl_3O_2] << k_7 + k_8[RH]$

$$[CCl_3O_2]_{ss} = \frac{k_6[CCl_3]_{ss}[O_2]}{k_7 + k_8[RH]}$$

and from reaction 3

$$[C_2Cl_6] = k_3[CCl_3]_{ss}^2 t$$

Thus, the concentration ratio $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ is given by

$$\frac{[CHCl_3]}{[C_2H_6]^{1/2}t^{1/2}} = \frac{k_1}{k_3^{1/2}}[RH] + \frac{k_8k_6}{k_3^{1/2}}\frac{[O_2][RH]}{k_7 + k_8[RH]} \tag{II}$$

The determination of the various rate constants appearing in eq II can be done by two methods:

1. Approximation Method. For a high concentration of RH which fulfills the requirement $k_8[RH] >> k_7$, eq II can be approximated by the expression

$$\frac{[CHCl_3]}{[C_2Cl_6]^{1/2}t^{1/2}} = \frac{k_1}{k_3^{1/2}}[RH] + \frac{k_6}{k_3^{1/2}}[O_2] \tag{III}$$

The above expression predicts that the plot of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ vs. [RH] should yield a straight line with a slope

of $k_1/k_3^{1/2}$ (which is equal to the slope in the absence of oxygen) and a positive intercept of $k_6[O_2]/k_3^{1/2}$. A plot of $\ln (k_6/k_3^{1/2})$ vs. T should yield a straight line with a slope of $-(E_6 - E_3/2)/R$ and an intercept of $\ln (A_6/A_3^{1/2})$.

For a low concentration of RH which fulfills the requirement $k_8[RH] << k_7$, eq III can be approximated by

$$\frac{[CHCl_3]}{[C_2Cl_6]^{1/2}t^{1/2}} = \left(\frac{k_1}{k_3^{1/2}} + \frac{k_8k_6}{k_3^{1/2}k_7}[O_2]\right)[RH] \tag{IV}$$

The last expression predicts that a plot of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ vs. [RH] should yield a straight line with a slope of $k_1/k_3^{1/2} + k_8k_6[O_2]/(k_3^{1/2}k_7)$ which passes through the origin. By using the calculated values of $k_1/k_3^{1/2}$ and $k_6/k_3^{1/2}$ (from eq III) for various temperatures together with the obtained slopes from eq IV, we can easily obtain the k_8/k_7 values for the various temperatures. A plot of k_8/k_7 vs. T should yield a straight line with a slope of $-(E_8 - E_7)/R$ and an intercept of $\ln (A_8/A_7)$.

2. Direct Method. The form of eq II can be changed to the following form

$$\frac{1}{\alpha} = \frac{k_3^{1/2}k_7}{k_8k_6[O_2]}\frac{1}{[RH]} + \frac{k_3^{1/2}}{k_6[O_2]} \tag{V}$$

where

$$\alpha = \frac{[CHCl_3]}{[C_2Cl_6]^{1/2}t^{1/2}} - \frac{k_1}{k_3^{1/2}}[RH] \tag{VI}$$

or in a different form

$$\alpha = \left(\frac{[CHCl_3]}{[C_2Cl_6]^{1/2}t^{1/2}}\right)_{O_2} - \left(\frac{[CHCl_3]}{[C_2Cl_6]^{1/2}t^{1/2}}\right)_{noO_2}$$

Equation V predicts that a plot of $1/\alpha$ vs. $1/[RH]$ should yield a straight line with a slope of $k_3^{1/2}k_7/(k_8k_6[O_2])$ and an intercept of $k_3^{1/2}/(k_6[O_2])$, and thus the ratio of rate constants k_7/k_8 can also be obtained. By analyzing those values for various temperatures, we will obtain the Arrhenius parameters.

Experimental Section

Samples of 5 cm^3 of CCl_4 solution of cyclohexane at concentrations of 0.05–0.5 M were prepared in quartz ampules.

After degassing under liquid nitrogen (only in cases of reaction in the absence of oxygen) through three turns of thawing and freezing, the ampules were irradiated with ultraviolet rays (Oriel 350-W universal arc lamp power supply, Model 8500) from mercury lamp (HBO 850 W/2 Oriel 6283) at various temperatures (100–200 °C) in a tabular oven. The temperature during irradiation was kept by a chromel–constantan thermocouple within ±1 °C.

The $CHCl_3$, RCl (i.e. $C_6H_{11}Cl$), and C_2Cl_6 concentrations after irradiation were measured gas chromatographically with a flame-ionization detector by using columns of 15% carbowax on Chromosorb P and 15% DC-200 on Chromosorb P for the determination of $CHCl_3$ and RCl and for the determination of C_2Cl_6, respectively.

Basic Literature Data

The Solubility of Oxygen in CCl_4. Wilhelm and Battino[15] gave the solubility of gas in pure solvent as a function of temperature by using the expressions

$$\Delta \bar{G}° \simeq -RT \ln X_2(\text{sat}) \tag{VII}$$

$$\Delta \bar{G}° = \Delta \bar{H}° - T\Delta \bar{S}° \tag{VIII}$$

where $\Delta \bar{G}°$, $\Delta \bar{H}°$, and $\Delta \bar{S}°$ are the change in Gibbs energy, enthalpy, and entropy for isothermic solutilization process of 1 mol of pure gas in 1 atm and $X_2(\text{sat})$ is the saturated solubility of the gas in a pure solvent in mole fraction units (assuming ideal

(14) Z. B. Alfassi and L. Feldman, *Int. J. Chem. Kinet.*, **13**, 771 (1981).

(15) E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973).

TABLE I: The Arrhenius Parameters for the Hydrogen Abstraction from Cyclohexane by the CCl₃ Radical according to Several Studies

phase	E, kcal/mol	log $(A/$ $(M^{-1} s^{-1}))$	ref
gas	10.7	8.79	21
gas	10.0 ± 1.0	8.86 ± 0.13	22
liquid	11.1 ± 0.2	8.8 ± 0.2	23
liquid	10.85 ± 0.5	9.24 ± 0.34	18

behavior of the gas and validity of the laws for ideal dilute solutions).

The above expressions lead to the following expression:

$$-\ln X_2 = \frac{\Delta \bar{H}^{\circ}}{RT} - \frac{\Delta \bar{S}^{\circ}}{R} = \frac{1}{R}\left(\frac{\Delta \bar{H}^{\circ}}{T} - \Delta \bar{S}^{\circ}\right) \quad \text{(IX)}$$

The solubility X_2 for various gases and solvents can be calculated by using tabulated values of $\Delta \bar{H}^{\circ}$ and $\Delta \bar{S}^{\circ}$. The given values of $\Delta \bar{H}^{\circ}$ and $\Delta \bar{S}^{\circ}$ for the oxygen–CCl₄ system are 8 cal/mol and -13.34 cal/(mol K), respectively.[15] When those values are substituted in eq IX, it can be easily seen that above 298 K (or even for lower temperatures) the $\Delta \bar{H}^{\circ}/T$ is negligible relative to the term $\Delta \bar{S}^{\circ}$. Thus, above room temperature, eq IX can be approximated by

$$\ln X_2 \simeq \Delta \bar{S}^{\circ}/R \quad \text{(X)}$$

The last equation predicts that the solubility of oxygen in CCl₄ is almost independent of the temperature.

The molar concentration of oxygen can be calculated from the mole fraction X_2 of the dissolved gas by assuming ideal-gas behavior throughout the expression:[15]

$$X_2 = [RT/(Lp_2 v_i^{\circ}) + 1]^{-1} \quad \text{(XI)}$$

where L is the Oswald coefficient (defined by V_2/V_1, where V_2 is the volume of gas absorbed in volume V_1 of solvent), v_i° is the molar volume of the pure solvent, and p_2 is the partial gas pressure.

Using $v_i^{\circ} = 97.09$ cm³/mol and $X_2 = 12.01 \times 10^{-4}$ for 1 atm of partial gas pressure,[15] we get $X_2 = 2.5244 \times 10^{-4}$ for 0.21 atm of partial oxygen pressure, which means $[O_2] = 2.601 \times 10^{-3}$ M.

The Arrhenius Parameters for the CCl₃ Radical Recombination. The activation energy for CCl₄ self-diffusion was measured by Watts et al.,[16] who found a value of 3.3 kcal/mol for that process.

According to Katz et al.,[12] the recombination of radicals in the liquid phase are diffusion controlled and the activation energy is assumed to be equal to that of the self-diffusion of the solvent. Thus, in our case $E_3 = 3.3$ kcal/mol, and adopting this idea, Katz et al. obtained log $A_3 = 11.40$.

Those Arrhenius parameter values are supported by Paul's result,[17] who measured A_3 in methanol using the electron spin resonance method and obtained log $A_3 = 11.42$.

Using these values, Alfassi and Feldman[13,18] showed a good agreement for the A factors and activation energies of hydrogen abstraction by a CCl₃ radical from several substrates, between the liquid and gas phase. That fact may be additional evidence for the diffusion-controlled rate of the CCl₃ recombination reaction in the liquid phase. Thus, the rate constant for recombination of CCl₃ yielding C₂Cl₆ can be expressed by the Arrhenius equation:

$$\log k_3 = 11.42 - 3.30/\theta$$

where $\theta = 2.303RT$ kcal/mol.

Results and Discussion

Reaction in the Absence of Oxygen. Several studies have been performed on the kinetics of γ-irradiation-induced free-radical reactions in mixtures of CCl₄ and cyclohexane. Most of these

(16) H. Watts, B. J. Adler, and J. H. Hildebrand, *J. Chem. Phys.*, **23**, 659 (1955).

(17) H. Paul, *Int. J. Chem. Kinet.*, **11**, 495 (1979).

(18) Z. B. Alfassi and L. Feldman, *Int. J. Chem. Kinet.*, **13**, 517 (1981).

TABLE II: The [CHCl₃]/[C₂Cl₆]¹ᐟ²ᵃ Values for Various Cyclohexane Concentrations in the Presence of Oxygen after 1-h Irradiation Time

[RH], M	temp, °C 100	125	150	175	200
0.05	0.2516	0.3032	0.3626	0.6021	0.7377
0.10	0.3821	0.5127	0.7008	1.0035	1.4139
0.15	0.5057	0.3880	0.8579	1.2246	1.9248
0.20	0.5530	0.6808	1.0966	1.5509	2.5744
0.30	0.6629	0.9276	1.4282	2.3622	3.4370
0.40	0.7122	1.0621	1.7335	2.9677	4.6499
0.50	0.8248	1.1875	2.1570	3.5660	5.8845

^{a} In M¹ᐟ².

TABLE III: The Various Rate Constant $(k)^a$ Ratios for Hydrogen Abstraction from Cyclohexane by the CCl₃ and CCl₃O₂ Radicals for Various Temperatures

	temp, °C 100	125	150	175	200
$k_1/k_3^{1/2}$	0.01288	0.02931	0.06149	0.11206	0.18766
$k_6/k_3^{1/2}$	2.6033	2.2146	1.9592	1.7942	1.4997
$k_8 k_6 [O_2]/(k_3^{1/2} k_7)$	0.05506	0.06312	0.06894	0.08621	0.09242
k_8/k_7	8.1321	10.9588	13.5296	18.4748	23.6949

^{a} In M⁻¹ s⁻¹.

TABLE IV: Ratio and Values of Arrhenius Parameters for Hydrogen Abstraction from Cyclohexane in the Presence of Oxygen^a

related prod	log $(A_1/A_3^{1/2})$	$\Delta E = E_1 - E_3/2$	log A_1	E_1
CHCl₃	3.6445 ± 0.311	9.3965 ± 0.1415	9.3545	11.046

^{a} E and A in kcal/mol and M⁻¹ s⁻¹, respectively.

studies showed a good agreement with regard to the values of the Arrhenius parameters for abstraction reaction 1. The obtained values in the liquid phase are very similar to those found for the gas phase, as shown in Table I. However, no work on the abstraction of hydrogen from cyclohexane using the CCl₃ radical was done by photolysis, which has the advantage over radiolysis because it eliminates the possibility of the formation of positive ions (which may lead to unfavorable reactions). This is due to the lower energy of the photons obtained in photolysis irradiation. Some of the ratios of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ and $[RCl]/([C_2Cl_6]^{1/2}t^{1/2})$ were plotted against the cyclohexane concentration in Figures 1 and 2. The linearity of the curves proves the adequacy of eq I, thus supporting the proposed mechanism.

Figure 3 expresses log $(k_1/k_3^{1/2})$ vs. T for both CHCl₃ and RCl. Only a slight difference was found between the two straight lines, as was expected. Using the Arrhenius parameters of the termination reaction, i.e. $E_3 = 3.3$ kcal/mol and log $A_3 = 11.42$, we obtained the following rate expressions (log $(k_1/(M^{-1} s^-))$) for the related product of the abstraction reaction: CHCl, 9.3–11.0/θ; RCl, 10.2–12.6/θ.

It is clear that the Arrhenius parameters based on the formation of chloroform are more reliable than those based on the chlorocyclohexane concentration and are quite similar to those obtained in previous studies. This proves the reliability of the earlier results, since no dependence on the irradiation method was found.

Reaction in the Presence of Oxygen. A. The Arrhenius Parameters of Reaction 1. The values of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ for various cyclohexane concentrations at various temperatures are given in Table II. These values were measured for various light intensities and measurement times, changing the conversion by at least a factor of 3. The conversion of CCl₄ was always less than 2%. These values are higher than those obtained in the absence of oxygen. Some of these values were plotted against the cyclohexane concentration (Figure 4). It can be seen that, for high RH concentration (in which the requirement $k_8[RH] \gg k_7$ is probably fulfilled), a linear dependence between the RH concentration and $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ was found.

The slopes of these "high RH concentration" lines are given in Table III (as $k_1/k_3^{1/2}$ values) for various temperature and
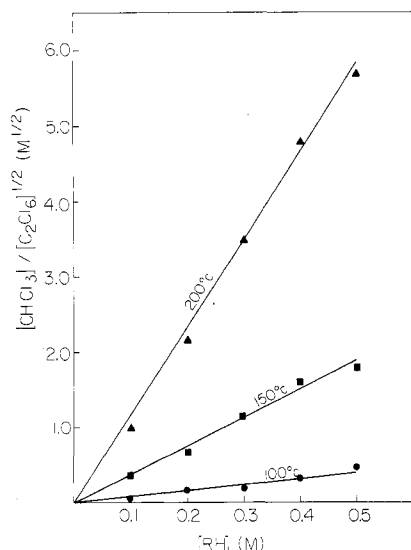
Figure 1. The dependence of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ on the concentration of cyclohexane at 100, 150, and 200 °C in the absence of oxygen.

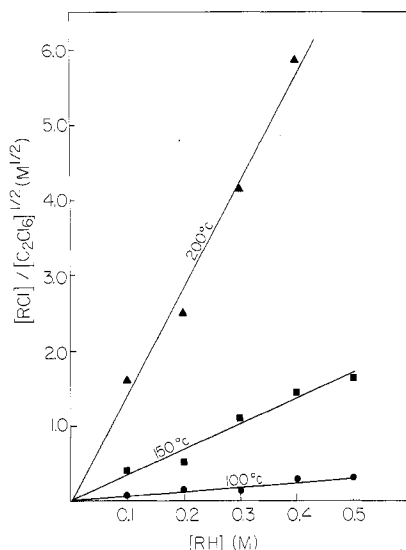**Figure 2.** The dependence of $[RCl]/([C_2Cl_6]^{1/2}t^{1/2})$ on the concentration of cyclohexane at 100, 150, and 200 °C in the absence of oxygen.

Figure 3. The Arrhenius plot of $k_1/k_3^{1/2}$ in the case of cyclohexane in the absence of oxygen for both products (CHCl₃ and chlorocyclohexane).

Figure 4. The dependence of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ on the concentration of cyclohexane at 100 and 150 °C in the presence of oxygen.

Figure 5. The Arrhenius plot for the various rate constant ratios for cyclohexane in the presence of oxygen.

appear in Figure 5 which expresses log log($k_1/k_3^{1/2}$) vs. T. The values of log ($A_1/A_3^{1/2}$) and $E_1 - E_3/2$ together with the respective values of log A_1 and E_1 based on least-squares analysis are given in Table IV.

It can be seen quite clearly that the $k_1/k_3^{1/2}$, E_1, and log A_1 values obtained in the presence of oxygen are quite similar to those obtained in the absence of oxygen, thus proving the adequacy of eq II.

It should be noted that while in the reaction in the absence of oxygen, the yield of chlorocyclohexane was almost the same as that of chloroform. It was found that in the presence of oxygen the yield of chlorocyclohexane was the same as that of chloroform only for reactions at low temperatures. At higher temperatures the deviation between the yields of the two products was significant, probably due to the formation of other products as RO₂ radicals which might also abstract hydrogen. Thus, only the yields of chloroform were used to determine the various rate constants.

B. The Arrhenius Parameters of Reaction 6 Yielding CCl₃O₂ Radicals. Some questions may be asked about the constancy of the oxygen concentration (in the solution) during irradiation (due to reaction 7 yielding phosgene and ClO). However, for various reasons, which we shall discuss later, we concluded that there is negligible variation of the oxygen concentration with time and no change of the oxygen concentration with temperature (as discussed previously).
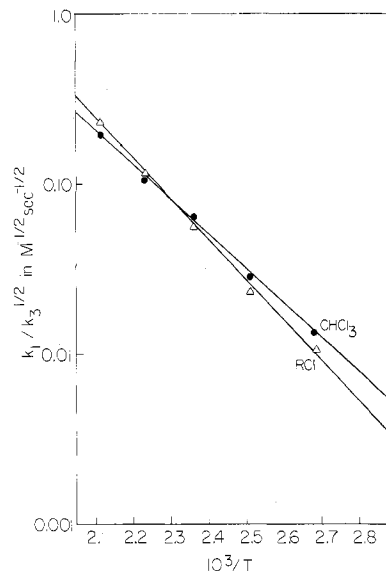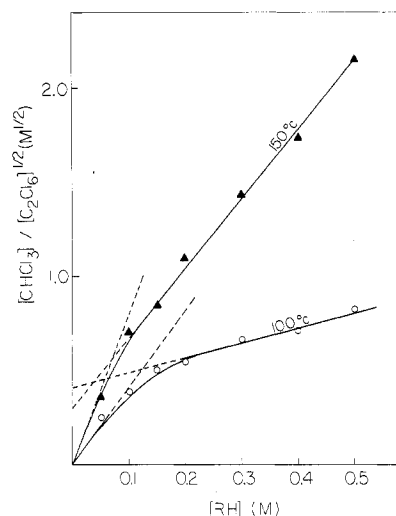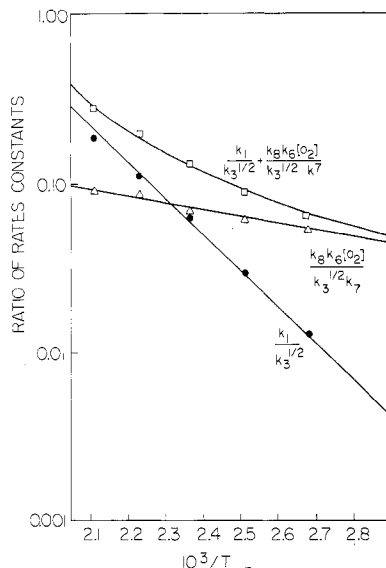
According to the proposed approximation method scheme, the $k_6/k_3^{1/2}$ value can be calculated from the intercept of the high

TABLE V: Ratio and Values of Arrhenius Parameters for the Addition Reaction Yielding $\cdot CCl_3O_2$ and the Competition between Phosgene Formation and Hydrogen Abstraction[a]

$\log (A_6/A_3^{1/2})$	$\Delta E = E_6 - E_3/2$	$\log A_6$	E_6	$\log (A_8/A_7)$	$\Delta E = E_8 - E_7$
-0.6595 ± 0.0685	-1.8309 ± 0.1307	5.0505 ± 0.0685	-0.1810 ± 0.1307	3.0808 ± 0.0973	3.7080 ± 0.1857

[a] E and A in kcal/mol and M^{-1} s^{-1}, respectively.
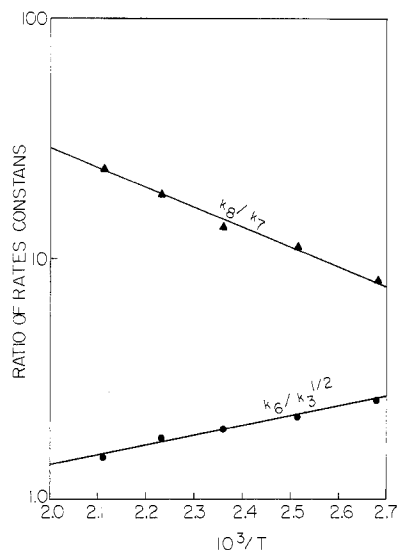
Figure 6. The Arrhenius plot for $k_6/k_3^{1/2}$ and k_8/k_7 in the case of cyclohexane.

RH concentration line which is equal to $k_6[O_2]/k_3^{1/2}$. The values of $k_6/k_3^{1/2}$ based on those intercepts and the concentration of O_2 in CCl_4 (equal to 2.601×10^{-3} M) are given in Table III and appear in Figure 6 which expresses $\log (k_6/k_3^{1/2})$ vs. T. The values of $\log A_6/A_3^{1/2}$ and $E_6 - E_3/2$, together with the respective $\log A_6$ and E_6 values, based on least-squares analysis are given in Table V.

The obtained E_6 values (-0.1810 ± 0.1307 kcal/mol) indicate a zero activation energy for the reaction yielding the CCl_3O_2 radical, thus leading to the rate expression

$$\log k_6 = \log A_6 = 5.05 \pm 0.06$$

C. The k_8/k_7 Ratio. The k_8/k_7 ratio, which is the measure of the competition between the abstraction of H atoms by the CCl_3O_2 radical and the decomposition of the CCl_3O_2 radical to form phosgene and ClO, is given in Table III for various temperatures.

The calculation for these values is based on eq VI which requires the fulfillment of the condition $k_8[RH] \ll k_7$.

The plot of $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ vs. [RH] for four RH concentrations yields straight lines with slopes of $k_1/k_3^{1/2} + k_8k_6[O_2]/(k_3^{1/2}k_7)$. From the calculated values of $k_1/k_3^{1/2}$ we calculated the $k_8k_6[O_2]/(k_3^{1/2}k_7)$ values which are given in Table III). By using the calculated values of $k_6/k_3^{1/2}$, we obtained the values of k_8/k_7.

The k_8/k_7 values prove that the hydrogen abstraction reaction by CCl_3O_2 is the preferred one and not the decomposition reaction of CCl_3O_2, which is almost negligible at high-temperature values.

Conclusions and Critical Notes

The Zero Activation Energy of the Addition Reaction Yielding $\cdot CCl_3O_2$. It is quite attractive to compare the kinetics of the reactions of CH_3 radicals and the CCl_3 radical. In such a comparison which was made in earlier studies,[19] it was found that the

(19) S. Mosseri and Z. B. Alfassi, to be submitted for publication.
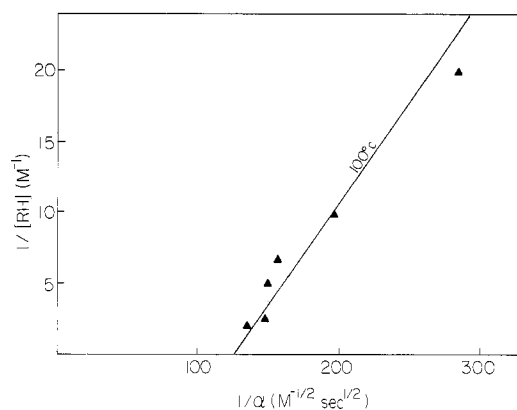
Figure 7. The $1/[RH]$ vs. $1/\alpha$ plot at 100 °C in the case of cyclohexane for reaction in the presence of oxygen.

activation energy of reactions involving the CH_3 radical is usually higher than that of similar reactions involving CCl_3 radicals. Marcotte and Noyes[20] found that the addition reaction of the methyl radical to an oxygen molecule yielding $\cdot CH_3O_2$ has a zero activation energy. Thus, our result for the CCl_3 radical also having a zero activation energy for the addition reaction of $\cdot CCl_3$ to the oxygen molecule yielding the CCl_3O_2 radical seems quite reasonable.

The Reliability of the k_8/k_7 Values. Testing the k_8/k_7 values with respect to eq III yields the conclusion that the obtained k_8/k_7 from the plotted lines by using the $[CHCl_3]/([C_2Cl_6]^{1/2}t^{1/2})$ values in low RH concentration do not fulfill the $k_8[RH] \ll k_7$ requirement.

For example, the k_8/k_7 values obtained at 100 °C (equal to 8.13) were based on a 0.05 and 0.10 M RH concentration. Thus, k_8/k_7 should be much lower than $1/[RH] = 10$ (since the requirement $k_8[RH] \ll k_7$ is similar to the requirement $k_8/k_7 \ll 1/[RH]$). However, 8.13 is not much lower in comparison to 10. Thus, the concentration at which the requirement $k_8[RH] \ll k_7$ may be fulfilled should be much lower. So, it can be expected that the k_8/k_7 ratio will be higher. However, the determination of these values is somewhat difficult due to the larger experimental error in detection of very low product concentrations. The direct method for the rate constants' determination was also proved to be an unsuitable method due to the large standard deviation in the calculated values of $1/\alpha$ (eq VII), as shown in Figure 7 (although the $k_6/k_3^{1/2}$ value was found similar to those found in the approximation method).

The "Constant Oxygen Concentration Assumption". Since $k_8 \gg k_7$ (as shown in Table 8 and as discussed in the previous section), it can be assumed that the yields of phosgene and ClO are very small, and thus the concentration of oxygen in CCl_4 is reduced very little, if at all. Thus, the above assumptions holds.

Registry No. CCl_3 radical, 3170-80-7; CCl_3O_2 radical, 69884-58-8; cyclohexane, 110-82-7; hydrogen, 1333-74-0.

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