The Pyrolysis of CCl₄ and C₂Cl₆ in the Gas Phase. Mechanistic Modeling by Thermodynamic and Kinetic Parameter Estimation

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ABSTRACT

A detailed radical reaction mechanism is proposed to describe the thermal reactions of CCl_4 and C_2Cl_6 in the gas phase quantitatively.

A consistent set of activation energies and preexponential factors for all elementary reactions, in combination with enthalpies of formation and entropies for all species involved, is computer optimized to fit experimental pressure-rise curves and concentration profiles.

For this purpose new experimental results on the pyrolysis of CCl_4 are used, together with published kinetic data on the pyrolysis of C_2Cl_6 (in the absence and in the presence of Cl_2).

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INTRODUCTION

Several kinetic studies have been reported on the thermal reactions of CCl_4 and C_2Cl_6 in the gas phase. However, most of them are incomplete and sometimes lead to conflicting mechanistic conclusions.

This article aims to propose one general radical mechanism, capable of describing the thermal reactions in the gas phase of both CCl_4 and C_2Cl_6 quantitatively. Most of the kinetic parameters for the elementary reactions of the model have already been measured, and thermochemical data for all species are available, too. So, constraints can be put on these parameters to ensure that, after modelling by computer simulations and optimizations, the physical meaning of the mechanism is maintained.

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Pyrolysis of C₂Cl₆

The most important kinetic results on the pyrolysis of C_2Cl_6 have already been described by Weissman and Benson [1].

Pyrolysis of CCl₄

Four kinetic studies have been reported for the pyrolysis of CCl_4 in flow systems [2-5].

Shilov and Sabirova [2] followed this reaction between 827 and 974 K in the absence and in the presence of toluene. The experiments were carried out in packed and unpacked quartz reactors at pressures below one atmosphere. The products were Cl_2 , C_2Cl_6 , and C_2Cl_4 . These authors concluded from their experimental results that CCl_4 was consumed in an essentially homogeneous, radical nonchain first-order process with an activation energy E of 55.1 kcal/mol and a preexponential factor A of 2.16 10^{12} s⁻¹. They proposed the following reaction mechanism

$$CCl_4 \longrightarrow CCl_3 + Cl$$

$$Cl + CCl_4 \longrightarrow CCl_3 + Cl_2$$

$$2CCl_3 \longrightarrow C_2Cl_6$$

$$C_2Cl_6 \longrightarrow C_2Cl_4 + Cl_2$$
(A)

As pointed out by Semenov [6], the value observed for E may not be assigned to the first reaction step because this leads to a value for the C--Cl bond energy in CCl₄ too low by about 15 kcal/mol.

Schiemann et al. [3] studied the pyrolysis of CCl₄ between 799 and 878 K with N₂ as carrier gas. The reactor was made of glass and the total pressure was about one atmosphere. The disappearance of CCl₄, calculated from the net reaction was first-order and its rate was not influenced by the amount of N₂. The Arrhenius parameters (E = 45.2 kcal/mol and $A = 4.5 \ 10^9 \ s^{-1}$) were much lower than those observed by Shilov and Sabirova [2].

Pyrolyses performed by Shinoda [4] between 893 and 1050 K suggest the occurrence of two parallel equilibrium reactions

$$2CCl_4 \Longrightarrow C_2Cl_6 + Cl_2 \tag{B}$$

$$2\text{CCl}_4 \rightleftharpoons \text{C}_2\text{Cl}_4 + 2\text{Cl}_2$$
 (C)

with still lower activation energies.

Antonov, Zalikin, and Rozhkov [5] carried out pyrolyses in a silica-glass tubular reactor at a pressure of one atmosphere between 673 and 853 K. These authors showed that the production of C_2Cl_4 and C_2Cl_6 at the beginning of the reaction can be explained at 833 K by a kinetic model consisting of the reactions given in eq. (B) and (C) and the reaction

$$C_2Cl_6 \rightleftharpoons C_2Cl_4 + Cl_2$$
 (D)

wherein the reversibility of the three processes is disregarded.

The experimental results on CCl_4 are somewhat contradictory and are too scarce to permit a quantitative analysis in terms of available thermochemical and kinetic data on elementary steps. It seemed therefore interesting to us to reinvestigate the reaction at lower temperatures (667 to 718 K) in a static system. Moreover, the proposed reaction model will be tested with experimental results of different laboratories using varying initial conditions of pressure, reaction temperature, and product composition.

EXPERIMENTAL

The experimental data chosen to test the model complement each other. They were obtained by several experimental techniques and are summarized in Table I.

For the pyrolysis of CCl₄, new concentration profiles of C_2Cl_4 and C_2Cl_6 were measured. CCl₄ (Aldrich, spectrophotometric grade, gold label) more than 99.9% pure, was used without further purification. The conventional static system, the reaction cell, and the technique were the same as in [9]. Preliminary experiments showed that the amount of C_2Cl_6 produced at the beginning of the reaction decreased with the number of experiments. The reaction cell was therefore aged by pyrolyzing samples of CCl₄ for several days at 697 K until reproducible results were obtained. The concentration profiles were determined from gas chromatographic analyses of the whole reaction mixtures of experiments carried out at the same

Table 1 Set of Experimental Results for Testing the Reaction Model. Initial Pressures are Given in torr and Reaction Temperatures T in K. GC stands for Gas Chromatography and Δ_p for Pressure Variation Measured with a Bourdon Manometer

	Experimental Conditions					
Starting Material (Pressure)	T	Reactor Type	Analytical Technique	Ref.		
CCl ₄ (83-162)	667718	STATIC (Quartz)	C_2Cl_4, C_2Cl_6 (GC)	this work		
C ₂ Cl ₆ (87.5)	671	STATIC (Pyrex)	Δp (Bourdon)	[7]		
$C_2Cl_6 + Cl_2$ (1096) (230)	651	STATIC (Pyrex)	CCl₄ (GC)	[8]		

temperature and initial pressure but with different reaction times. The analyses were performed on a 2-m column of 30% w/w Silicone OV-101 on 60-80 mesh Chromosorb PAW with a helium flow rate of 3.6 L/h between 70 and 200°C. In some experiments, the pressure of Cl₂ was also determined by measuring in the reaction cell the total pressure of the fraction of the products noncondensable at -84°C (more than 98% of Cl₂). As shown by the analyses the pyrolysis of CCl₄ yields Cl₂, C₂Cl₆, C_2Cl_4 , and a product that probably can be identified as $CCl \equiv CCl^1$. The amount of this product is less than 3% of the sum of the other products and will be neglected hereafter. Higher molecular weight-species $(C_3 \text{ or higher})$ are negligible. The mass balances have been checked.

A pressure-rise curve of Dainton and Ivin [7] was taken for the pyrolysis of C_2Cl_6 , together with

a CCl₄ concentration profile of White and Kuntz [8] for the pyrolysis of C_2Cl_6 in the presence of Cl_2 .

RESULTS AND DISCUSSION

The kinetic model used to describe the pyrolyses of CCl_4 and C_2Cl_6 is given in Table II. It involves 9 couples of elementary reactions and their back reactions, and 7 components, namely the 4 molecular species CCl_4 , Cl_2 , C_2Cl_4 , and C_2Cl_6 and the 3 radical species, Cl_1 , CCl_3 , and C_2Cl_5 . The reactions are numbered in a logical sequence for the pyrolysis of CCl_4 . They are couples of dissociation-recombination reactions, such as 1, 3, 6, and 8, the transfer reactions 5, and the disproportionation reaction 9. Table II also gives the known or estimated initial values of the Arrhenius parameters E and A before optimization, for one reaction of each couple. Also shown are the

Table II Kinetic Model for the Pyrolyses of CCl₄ and C₂Cl₆. The Activation Energies E are Expressed in kcal/mol and the Preexponential Factors A in L, mol, and s-units. Initial and Optim are Values before and after Optimization, Respectively. Correction corr = optim - initial. Cumulative Corrections Involving Thermodynamic Corrections from Table III are Not Mentioned

		E			$\log_{10}A$	
Reaction Steps	initial	optim.	corr.	initial	optim.	corr.
	69.6ª	67.8		16.63ª	16.74	-
$CCl_4 \rightleftharpoons CCl_3. + Cl$	0.0 ^b	0.0	_	10.80 ^b	10.86	0.06
	17.1ª	15.5		10.65ª	10.76	
$Cl + CCl_4 \rightleftharpoons CCl_3 + Cl_2$	5.0 ^b	5.1	0.1	8.74 ^b	8.70	-0.04
3 0 01	0.0 ^b	0.0		9.66 ^b	9.67	0.01
$2CCl_3 \rightleftharpoons C_2Cl_6$	68.7ª	66.8		17.17ª	17.29	
	17.54 ^a	17.3		11.15 ^a	11.12	
$Cl + C_2 Cl_6 \rightleftharpoons C_2 Cl_5 + Cl_2$	5.43°	5.4	-0.03	8.31°	8.26	-0.05
5 0 0 + 0	14.8ª	14.9		12.94ª	13.05	
$C_2Cl_5 \rightleftharpoons C_2Cl_4 + Cl_{-5}$	0.0 ^d	0.0		10.10 ^d	10.10	0.00
	0.0 ^e	0.0	—	10.40 ^e	10.39	-0.01
$C_1 + C_2 C_{15} \rightleftharpoons C_2 C_{16}$	69.6ª	69.5		17.13ª	17.09	
	14.3 ^f	14.1	-0.2	8.90 ^f	8.91	0.01
$CCl_3 + C_2Cl_6 \rightleftharpoons CCl_4 + C_2Cl_5.$	14.3ª	12.5		7.96ª	8.10	
	55.9ª	55.9		12.93ª	12.93	
$Cl_2 + M \rightleftharpoons 2Cl + M$	-1.63^{g}	-1.63	-	9.10 ^g	9.11	0.01
	0.0 ^h	0.0	—	10.40 ^h	10.39	-0.01
$C_1 + C_2 C_{15} = C_2 C_{14} + C_{12}$	42.7ª	42.6		11.38ª	11.26	

^aCalculated in the computer program from the thermodynamic data given in Table III and the rate constant of the back reaction. ^bFrom [11].

^cMean of two available values [1,14].

^fEstimated [1].

^gFrom [15].

^hArrhenius parameter of disproportionation reaction assumed to be equal to that of the corresponding recombination reaction (6).

¹The formation of this product has already been observed in the pyrolysis of mixtures of CCl₄ and C₂Cl₄ [10].

^cFrom [12].

^dFrom [13].

values of these parameters for each corresponding back reaction. These values were obtained according to the "principle of detailed balancing" from the equilibrium constants calculated at the reaction temperature using the thermochemical data given in Table III. Notice that this kinetic model contains only a few estimated values and that simulations have shown that: (i) the recombination reactions of C_2Cl_5 radicals with C₂Cl₅- and CCl₃-radicals missing in Table II are totally negligible for rate constants of 5 10⁸ [21] and 2 10⁹ L/mol.s (estimation), respectively; (ii) decreasing the rate constants of steps 5 and -5 has no consequences up to a factor of 10^3 so that "fall-off" effects are most probably excluded; and (iii) surface removal of Cl-atoms should have an efficiency of more than 3 10^{-5} to play a role. This suggests that the experimental data of Table I were obtained in well conditioned reactors (see [22]).

For modeling the mechanism 22 parameters were used, 3 activation energies, 9 A-factors, 5 enthalpies of formation, and 5 entropies. Only the zero-activation energies, and the thermodynamics of Cl_2 and Cl were fixed at initial conditions. The optimization procedure involves the "principle of detailed balancing" and is the same as in [23]. OPTKIN, a user friendly PC program for mechanistic modeling of reactions by kinetic and thermodynamic parameter optimization [24], has also been used.

The optimized pressure and concentration profiles are given in Figures 1-4. Therein, the time axes are always in s, the profiles are expressed as normalized variations relative to initial values, and the dashed and full curves represent the computer simulations before and after optimization, respectively². It should be pointed out here that the experimental points of Figure 1 belong to the same experiment whereas those of the other Figures are from different experiments. Further, the fittings shown were performed using simultaneously the experimental points from this work and the literature given in Figures 1-4 and not only those of the figure concerned. The quality of the fittings³ will be discussed later.

Figure 1 shows the results for the pyrolysis of C₂Cl₆ from Dainton and Ivin [7]. The pressure rise curve has a marked S-shape. After the induction period the rate of pressure variation increases to a maximum value and then decreases. Simulations and sensitivity analyses [25] show that the acceleration results mainly from reaction -2: this reaction converts CCl₃-radicals into Cl chain carriers due to the Cl₂ produced in reaction 4 (see Table II). It should be noted that before optimization the S-shape of the pressure rise curve is totally absent. The relative CCl₄ production is plotted in Figure 2 for the pyrolysis of C_2Cl_6 in the presence of Cl_2 [8]. As can be seen the rate of production is nearly constant but the initial and optimized parameter sets lead to values of it differing by more than a factor of 5. The profiles for C_2Cl_4 and C₂Cl₆ measured at 668 and 718 K in this work

Table III Heats of Formation ΔH_f° (kcal mol⁻¹), Heat Capacities C_p° , and Entropies S° (Gibbs mol⁻¹) Based on a 1-atm Standard State. Initial and Optim are Values before and after Optimization, Respectively, Correction corr = optim - initial

Compound	$\Delta H_{f.298}^{\circ}$		S ^o ₂₉₈			$C_{p,T}^{\circ}$					
	initial	optim.	corr.	initial	optim.	corr.	300 K	400 K	500 K	600 K	800 K
CCl ₄	-22.9ª	-22.2	0.7	74.1ª	73.8	-0.3	20.0ª	21.9ª	23.1ª	23.8ª	24.6 ^a
Cl ₂	0.0ª	0.0	-	53.3ª	53.3	-	8.1ª	8.4ª	8.6ª	8 .7ª	8.9ª
C_2Cl_6	-33.2 ^b	-33.2	0.0	95.3 ^b	95.2	-0.1	32.8 ^b	36.2 ^b	38.4 ^b	39.8 ^b	41.5 ^b
C_2Cl_4	-3.4°	-3.5	-0.1	81.5°	81.8	0.3	22.7°	25.1°	26.7°	27.9°	29.3°
Cl	29.0ª	29.0	_	39.5 ^a	39.5	~	5.2*	5.4ª	5.4ª	5.4ª	5.4ª
CCl ₃ .	19.0ª	18.0	-1.0 ^d	71.0ª	71.2	0.2	15.3ª	16.6ª	17.6ª	18.2ª	18.8ª
C_2Cl_5	8.7°	8.6	-0.1	96.5°	96.3	-0.2	27.6 ^f	30.6 ^f	33.0 ^f	34.8 ^f	37.2 ^f

^aFrom [16].

^bFrom [17].

^eRecalculated from data given in [13].

^fEstimated by group additivity methods developed in [20].

 $^{^{2}}$ This also holds for other figures of this work where a third root scale of the time is sometimes used to describe reactions from the beginning to a state close to the equilibrium.

³These "best" fittings were obtained by adjusting simultaneously the parameters shown in Tables II and III in order to minimize the sum of squares of the differences between experimental and calculated points.

^cFrom [18].

^dThis correction reduces to -0.1 ± 1.0 kcal/mol when a value of 18.1 ± 1 kcal/mol [19], recalculated from [16], is used for $\Delta H_{f,298}^{0}$ (CCl_{3.}) and becomes $\pm 1.0 \pm 0.6$ kcal/mol when $\Delta H_{f,298}^{0}$ (CCl_{3.}) = 17.0 ± 0.6 kcal/mol [19].



Figure 1 Pyrolysis of C_2Cl_6 at 671 K. Normalized variation of the total pressure p relative to the initial pressure p_0 of C_2Cl_6 vs. reaction time t in s. $p_0 = 87.5$ torr. The experimental points are from [7]. The dashed and full curves represent the computer simulations before and after optimization, respectively.

for the pyrolysis of CCl₄ are given in Figures 3 and 4, respectively. Here again a variation by more than a factor of 3 is noticed between simulation before and after optimization. The production rate of C_2Cl_4 increases with time and the curve is S-shaped. The production rate of C_2Cl_6 is maximum at the beginning. The profile goes through a maximum, followed by a less pronounced minimum. This minimum can be seen best from Figure 3 wherein after 5 10^4 s, the optimized concentration profile of C_2Cl_6 slowly increases again. This strange behavior of the C_2Cl_6 profile will be discussed in more detail later on in this work. It should be emphasized here again that all the experiments of Figure 1–4 were simulated using one



Figure 2 Pyrolysis of C_2Cl_6 in the presence of Cl_2 at 651 K. Normalized variation of the concentration C of CCl_4 relative to the initial concentration C_0 of C_2Cl_6 vs. reaction time t in s. The initial pressures of C_2Cl_6 and Cl_2 are 1096 and 230 torr, respectively. The experimental points are from [8]. The dashed and full curves represent the computer simulations before and after optimization, respectively.



Figure 3 Pyrolysis of CCl₄ at 667.6 K. Normalized variation of the concentration C of C₂Cl₄ and C₂Cl₆ relative to the initial concentration C₀ of CCl₄ vs. reaction time t in s. The initial pressure of CCl₄ is 161.6 torr. The experimental points for C₂Cl₄ (\bigcirc) and C₂Cl₆ (\triangle) are from this work. The dashed and full curves represent the computer simulations before and after optimization, respectively.

and the same optimized parameter set, so that the obtained result is quite convincing. The corrections which were applied to the initial values of the kinetic and thermodynamic parameters to arrive at this result are shown in Tables II and III, respectively. As can be seen, their maximum values are -0.2 kcal/mol for activation energies and 0.06 log units for A-factors. Corrections on the heats of formation and entropies do not exceed -1.0 kcal/mol and 0.3 cal/mol K, respectively. These small corrections are of the same magnitude as the experimental errors and prove that the optimized model is capable of describing all



Figure 4 Pyrolysis of CCl₄ at 718.4 K. Normalized variation of the concentration C of C₂Cl₄ and C₂Cl₆ relative to the initial concentration C₀ of CCl₄ vs. reaction time t in s. The initial pressure of CCl₄ in 83.3 torr. The experimental points for C₂Cl₄ (\bullet) and C₂Cl₆ (\blacktriangle) are from this work. The dashed and full curves represent the computer simulations before and after optimization, respectively.

the experimental results together without loss of its physical meaning. Notice that, as for the pyrolysis of 1,1,1-trichloroethane [23], the fitting of the model to the experimental data is rather insensitive to the choice of the initial values of the parameters. This results from the many degrees of freedom available for the optimization and prevents the choice between possible thermochemical and kinetic data.

A further proof of the reliability of the model is given by the simulation of the pyrolysis of CCl₄ in a vacuum flow system [2] at a temperature about 200°C higher than the highest temperature used for the optimization. The model predictions for the concentration-time profiles of Cl₂, C₂Cl₆, and C₂Cl₄ are shown in Figure 5 where the reaction time is less than 1 s. As can be seen the agreement with the experimental results is satisfactory for Cl₂ and C₂Cl₆ (the formation of C_2Cl_4 is mentioned in [2] but is not described quantitatively). It must be mentioned also that a simulation of the experiments of [5] yields for a residence time of 16 s at 833 K in a tubular reactor, 8.3 mass% C₂Cl₄ and 0.9 mass% C_2Cl_6 compared with the observed values 9-10 and 0.4 mass%, respectively.

The reaction model will now be used for short descriptions of some interesting mechanistic analysis of each experimental system.

Pyrolysis of C₂Cl₆

In this pyrolysis, it can easily be demonstrated that at any time the C_2Cl_4 profile equals the pressure rise and is also equal to the amount of $Cl_2 + 1/2$



Figure 5 Pyrolysis of CCl₄ at 891 K. Normalized variation of the concentration C of Cl₂, C₂Cl₆, and C₂Cl₄ relative to the initial concentration C₀ of CCl₄ vs. reaction time t in s. The initial pressure of CCl₄ is 20 torr. The experimental points for Cl₂ (O) and C₂Cl₆ (\blacktriangle) are from [2]. The curves represent computer simulations not only for these two products but also for C₂Cl₄ (lowest curve) for which no quantitative experimental data are available (see text).



Figure 6 Pyrolysis of C_2Cl_6 at 671 K. Computer simulation. Normalized variation of the concentration C of the products C_2Cl_4 , Cl_2 , and CCl_4 relative to the initial concentration C_0 of C_2Cl_6 vs. reaction time t in s. Initial pressure of $C_2Cl_6 = 87.5$ torr.

CCl₄ (CCl₄ is a minor product initially formed at constant rate). This is illustrated in Figure 6 (see also Fig. 1). Further it appears that the length of the induction period is very sensitive to pressure and temperature and decreases when pressure and temperature increase. The simulated pressure rise curves are shown in Figure 7 for 10, 30, and 100 torr of C_2Cl_6 at 671 and 691 K. All these predictions are confirmed experimentally in [25].

The pyrolysis of C_2Cl_6 is sometimes described in terms of two parallel equilibria [1]. The first equilibrium (see eq. (D)) is quickly attained, is quite reversible, and yields equal amounts of C_2Cl_4 and Cl_2 . It is then followed by a further reaction of Cl_2 , the reverse reaction given in Eq. (B), which slowly converts almost all the C_2Cl_6 into CCl_4 . This is supported by the results of a simulation at 703 K given in Figure 8. In the initial stage of the reaction



Figure 7 Pyrolysis of C₂Cl₆. Computer simulation. Normalized variation of the total pressure p relative to the initial pressure p_0 of C₂Cl₆ vs. reaction time t (in s) at 671 (full curve) and 691 K (dashed curve). $p_0 = 10$, 30, and 100 torr.



Figure 8 Pyrolysis of C_2Cl_6 at 703 K. Computer simulation. Normalized variation of the concentration C of CCl_4 , C_2Cl_4 , Cl_2 , and C_2Cl_6 relative to the initial concentration C_0 of C_2Cl_6 vs. reaction time *t* in s. Initial pressure of $C_2Cl_6 = 200$ torr.

equal amounts of Cl_2 and C_2Cl_4 are formed. Then the Cl_2 profile goes through a maximum and further tends to zero. At the same time the C_2Cl_6 is totally consumed. CCl_4 , which is a minor product at the beginning, gradually builds up and at the end reaches a level which is twice that of C_2Cl_4 according to the global equilibrium

$$2C_2Cl_6 \Longrightarrow 2CCl_4 + C_2Cl_4.$$
(E)

Figure 9 shows pressure rise curves calculated for different initial pressures at 703 K. As can be seen, these curves all tend to a relative pressure increase of 0.5 according to the global equilibrium, but when the pressure becomes low enough, from about 200 torr, they go through a maximum which lies about 50% higher than the final pressure rise. Below 50 torr, the pressure rise curve becomes totally different. Such phenomena have already been observed [25].



Figure 9 Pyrolysis of C_2Cl_6 at 703 K. Computer simulation. Normalized variation of the total pressure *p* relative to the initial pressure p_0 of C_2Cl_6 vs. reaction time *t* in s. $p_0 = 10$, 50, 100, 200, 400, and 800 torr.



Figure 10 Pyrolysis of CCl₄ at 696.6 K. Computer simulation. Normalized variation of the concentration C of CCl₄ relative to the initial concentration C_0 of CCl₄ vs. reaction time t in s. The initial pressures of CCl₄ are 40, 80, 160, and 320 torr.

Pyrolysis of CCl₄

In contrast with the pyrolysis of C₂Cl₆ where the starting material is almost totally converted (see Fig. 8), only a small fraction of CCl₄ is consumed at equilibrium (see Fig. 10). The degree of conversion decreases when the initial pressure is raised. So it goes from 17% for 40 torr of CCl₄ to about 9.5% conversion for 320 torr of starting material (see Fig. 10). This is in agreement with the overall equilibrium given in eq. (C). It also appears from Fig. 10 that the profiles of CCl₄ fall together up to about 7% conversion, so that it can be concluded that the pyrolysis of CCl₄ is first-order at the beginning. At the start of the reaction equal amounts of Cl₂ and C₂Cl₆ are formed (see Fig. 11). The C₂Cl₆ is unstable and goes through a maximum and at the final equilibrium the amount of Cl_2 is nearly twice that of C_2Cl_4 . So the reaction is sometimes



Figure 11 Pyrolysis of CCl₄ at 696.6 K. Computer simulation. Normalized variation of the concentration C of Cl₂, C₂Cl₄, C₂Cl₆, and CCl₄ relative to the initial concentration C₀ of CCl₄ vs. reaction time t in s. Initial pressure of CCl₄ = 84.1 torr.

described in terms of the equilibrium reactions given in eqs. (B) and (C) [4]. However, as afore mentioned, the C_2Cl_6 profiles of the pyrolysis of CCl_4 shown in Figures 3 and 4 seem to exhibit a strange behavior. It was therefore decided to study this system with much care⁴ from the beginning until equilibrium was reached. All the experimental results for C₂Cl₆ and C_2Cl_4 , obtained from independent experiments with different reaction times, for an initial pressure of CCl_4 of 84.1 ± 2.3 torr at 696.6 ± 0.7 K are given in Figure 12. A third root scale is used for the reaction time since the ratio between the longest experiment of about 1 week and the shortest of 5 min is about 2000. So at the beginning, the shape of all profiles is distorted. The optimized profiles are shown as full curves together with the experimental data. As can be seen, the concentration of C_2Cl_6 goes indeed through a maximum, followed by a less pronounced minimum, to finally reach a constant value. A detailed analysis of the rates of the elementary reaction steps given in Table II shows that: (i) in the course of the reaction, the reaction couple 3/-3always produces C_2Cl_6 and the reaction couples 4/-4, 6/-6, and 7/-7 always consume C_2Cl_6 ; the observed C_2Cl_6 profile is therefore induced by differences between the rates of the couple 3/-3and the other couples and (ii) at the end of the profile all reaction steps have practically attained their equilibrium. The profile shows no oscillatory behavior. The parallel equilibrium reactions given in

⁴Both storage and analysis of the reaction mixtures were carried out in the complete darkness in order to avoid any photochlorination of C_2Cl_4 yielding C_2Cl_6 [26].



Figure 12 Pyrolysis of CCl₄ at 696.6 K. Normalized variation of the concentration of C_2Cl_4 and C_2Cl_6 relative to the initial concentration C_0 of CCl₄ vs. reaction time t in s. The initial pressure of CCl₄ is 84.1 torr. The experimental points are from this work. The full curves represent the computer simulations after optimization.

eqs. (B) and (C) cannot explain this C_2Cl_6 profile but well the consecutive reaction scheme

$$2CCl_4 \rightleftharpoons C_2Cl_6 + Cl_2$$

$$C_2Cl_6 \rightleftharpoons C_2Cl_4 + Cl_2$$
(F)

Indeed, both maximum and minimum on this profile can be simulated using appropriate rate constants for the overall reactions and the thermochemical data given in Table III. These rate constants are such that: (i) in the region of the maximum the main reactions are the forward reactions, (ii) in the region of the minimum the back reaction of the second reaction is no longer negligible, and (iii) after the minimum and until equilibrium is reached the first reaction couple produces more C₂Cl₆ than is consumed by the second reaction couple. Using Figure 12 and the reaction scheme F, the final (equilibrium) concentrations of CCl_4 and Cl_2 can be deduced from those of C_2Cl_4 and C₂Cl₆. Hence, equilibrium constants K at 696.6 K can be calculated from which, using the "third law method", enthalpies of reaction can be estimated. The results are given in Table IV together with other determinations. As can be seen the results for the reaction (D) of this work are supported by those of Puyo et al. [27,28]. These are different from those of Bushneva et al. [30] (see Table IV) but have been used by most evaluators to fix the relative heats of formation of C₂Cl₄ and C₂Cl₆. Owing to the determination of the enthalpy of reaction (B) (or reaction (C), which is a combination of reactions (B) and (D)) (see Table IV), absolute values can be obtained for these heats of formation from that of CCl₄. From an analysis of the results it appears that $\Delta H_{f,298}^{\circ}$ (C₂Cl₄) = -4.5, $\Delta H_{f,298}^{\circ}$ (C₂Cl₆) = -34.0, and $\Delta H_{f,298}^{o}$ (CCl₄) = -22.5 kcal/mol are compatible with the experimental results of this work and those of Puvo et al. [27,28] within ± 1 kcal mol⁻¹ (see Tables III and IV).

Figure 13 shows the profiles of C_2Cl_6 as a function of the initial pressure of CCl_4 at 696.6 K. As can be seen, the maximum in the curve is more pronounced at lower pressures, while the opposite is valid for the minimum in the curve. For 320 torr, e.g., the concentration level of the final equilibrium is nearly equal to the first maximum value. These profiles of C_2Cl_6 are believed to be worthy of further investigation. Note at least that their pressure dependence can be simulated quantitatively in equilibrium conditions using the simple reaction scheme given in eq. (F). However, when the reaction proceeds a more elaborated mechanistic model as given in Table II is needed.

In conclusion, this study has led to a thermochemically consistent optimized reaction mechanism

Table IV Equilibrium Constants $K_{696.6}$ at 696.6 K (atm-units) and Enthalpies of Reaction ΔH_{298} at 298 K (kcal mol⁻¹) for Gas-Phase Reactions

Reactions	K _{696.6}	ΔH_{298}						
$C_2Cl_6 = C_2Cl_4 + Cl_2$ (D)	0.28ª	28.8 ^b	29.7°	30.3 ^d	30.4°	33.4 ^f	29.5 ^g	
$2CCl_4 = C_2Cl_6 + Cl_2 (B)$	$6.2 \ 10^{-4a}$	10.7 ^b	11.2°		_	-	11.0 ^g	
$2CCl_4 = C_2Cl_4 + 2Cl_2 (C)$	1.74 10 ⁻⁴ ª	39.5 ^b	40.9°	-			40.5 ^g	

^aCalculated from the equilibrium pressures $p(C_2Cl_6) = 3.8 \ 10^{-4}$, $p(C_2Cl_4) = 7.22 \ 10^{-3}$, $p(Cl_2) = 1.48 \ 10^{-2}$, and $p(CCl_4) = 9.55 \ 10^{-2}$ atm (see text).

^bObtained from $K_{690.6}$ using the "third law method" and "initial" entropies and heat capacities from Table III. ^cCalculated from "Optimized" $\Delta H_{f,298}^{o}$ of Table III.

^dCalculated using the same procedure as in b (this work) from $K_{776} = 0.8$ measured by Puyo et al. [27,28].

^eCalculated by Kolesov and Papina [29] from $K_{776} = 0.8$ [27,28], using the "third law method."

^fCalculated by Kolesov and Papina [29] from values of K measured in the range 773-873 K by Bushneva et al. [30].

^gCalculated using $\Delta H_{f,298}^{o}(C_2Cl_6) = -34.0$, $\Delta H_{f,298}^{o}(C_2Cl_4) = -4.5$, and $\Delta H_{f,298}^{o}(CCl_4) = -22.5$ kcal mol⁻¹ (see text).



Figure 13 Pyrolysis of CCl₄ at 696.6 K. Computer simulation. Normalized variation of the concentration C of C_2Cl_6 relative to the initial concentration C_0 of CCl₄ vs. reaction time t in s. The initial pressures of CCl₄ are 40, 80, 160, and 320 torr.

which fits the pyrolyses of CCl_4 and C_2Cl_6 under rather extreme experimental conditions. Moreover the ability of computer aided design of new experiments which may further elucidate the mechanism has also been demonstrated.

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