

Gas-phase Hydrogenolysis of Chloroethene: Rates, Products, and Computer Modelling†

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Hydrogenolysis of chloroethene (vinyl chloride, VC) has been investigated in a tubular-flow reactor at atmospheric pressure between 872–1 085 K. Ethene, ethyne, and HCl are major initial products of reaction. Hydrogen-atom addition to the substituted end of VC yields C_2H_4 after loss of a chlorine atom from the radical intermediate; addition to the unsubstituted end gives the 1-chloroethyl radical (1) and is reversible, but (1) may also be hydrogenated to chloroethane, which rapidly loses HCl. HCl elimination from VC to give C_2H_2 mainly occurs *via* a molecular reaction for which the parameters $\log k/s^{-1} = 14.0 - 290 \text{ kJ mol}^{-1}/\theta$, $\theta = 2.3 RT$ have been determined. Both C_2H_2 and C_2H_4 are hydrogenated and lead to C_2H_6 and, through splitting of the C–C bond in this product, to methane. Addition of HCl had only a small rate-enhancing effect on VC conversion, with increased production of ethene. A reaction model which accounts well for VC conversion rates and product, distributions has been developed. Features of VC hydrogenolysis have been compared with its pyrolysis.

Although the thermal conversions of chloroalkanes have been extensively studied, relatively little is known about the analogous behaviour of chloroalkenes. Chloroethene or vinyl chloride (VC) is the simplest compound with a chlorine bound to an sp^2 -hybridized carbon, and, as such, its behaviour should provide insight into the basic reactions of this class of compounds. Recently we have described the pyrolysis of VC in an inert atmosphere.¹ At 953 K, $\tau = 3$ s, about 35% decomposition took place, major products being HCl, ethyne (acetylene), 2-chlorobutadiene, and but-1-en-3-yne (vinyl-acetylene). Soot and tar were also produced and their proportions increased with temperature.

In hydrogen, the chemistry of chloroalkenes may be quite different. In a preliminary report² it was shown that, at 1 025 K, $\tau \sim 6$ s, (*E*)-1,2-dichloroethene gives a high degree of dechlorination, with HCl, C_2H_4 , and C_2H_6 as major products and little or no sooting, demonstrating that thermal hydrogenolysis is a promising method for conversion of chlorinated organic waste.

To the best of our knowledge, thermal hydrogenolysis of VC *per se* has never been directly studied, although there do exist some reports on the reactions of hydrogen atoms with VC. In 1968, Rennert and Wijnen photolysed HI at 298 K in the presence of VC and concluded that H atoms react with VC *via* addition and abstraction of chlorine and hydrogen; they suggested that the relative rates of these processes are 1:1.5:2.2, respectively.³ In 1971, Tanner and Jamieson used an electric discharge system to react hydrogen atoms with VC between 305–767 K.⁴ They reported the products HCl, C_2H_4 , C_2H_6 , and CH_4 and concluded that, at higher temperatures, a chain mechanism was involved. Finally, Ahmed and Jones recently reported the absolute rate constants for addition of hydrogen atoms to a series of halogenoethenes at 300 K; they found that the rate of addition followed the order $1,1-C_2H_2Cl_2 > C_2H_3Cl > C_2HCl_3$, with relative rates of 5.7:2.6:1.⁵

We have studied the thermal gas-phase hydrogenolysis of VC at atmospheric pressure between 872–1 085 K and report here on the rates, products, and mechanism of its reaction;

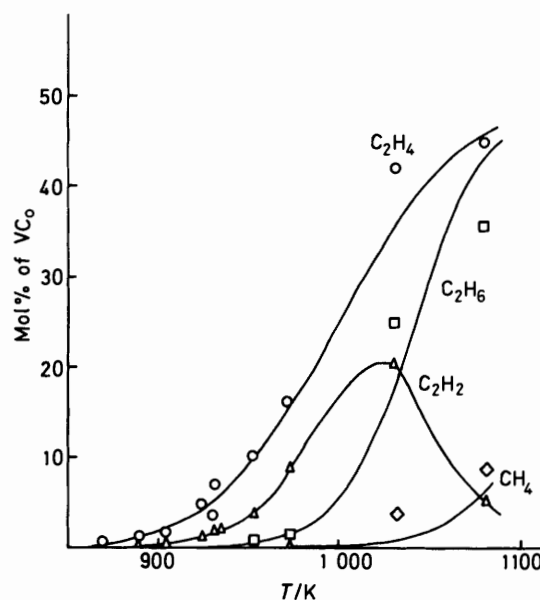


Figure 1. C_1 and C_2 products expressed as mol% of VC in; experiments without added HCl; C_2H_2 (Δ); C_2H_4 (\circ); C_2H_6 (\square); CH_4 (\diamond); smooth curves are values predicted on the basis of data in Table 2

further, we have developed a computer model that accounts well for the experimental data.

Results

Experiments were carried out at atmospheric pressure in a 13–15 fold excess of hydrogen. Residence times of *ca.* 3 s were obtained in a spirialized quartz tubular flow reactor of volume 29 ml (dimensions 0.4×232 cm). VC conversions ranged from 2.5% at 876 K to $\geq 99.8\%$ at 1 085 K. As we earlier found¹ that HCl, a major product, influences VC thermolysis in nitrogen, the effect of added HCl (equimolar with VC) was also studied. Data on representative runs are detailed in Table 1 and shown in Figures 1 and 2.

† This paper is Part 5 of the series 'Studies in Gas Phase Hydrogenolysis.' For Part 4 see ref. 28.

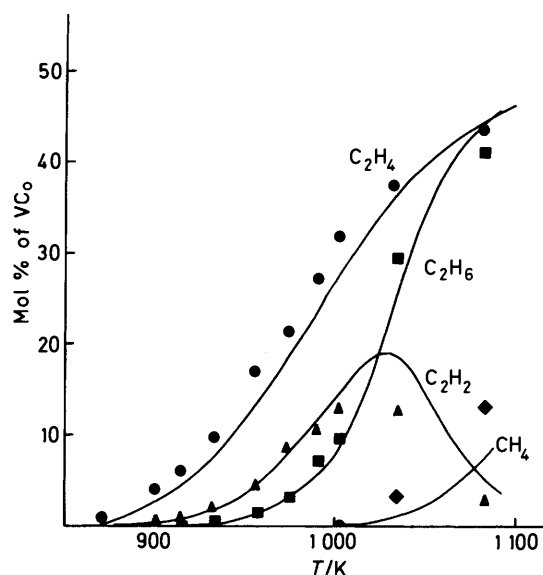


Figure 2. C₁ and C₂ products expressed as mol% of VC in; experiments with added HCl; C₂H₂ (▲); C₂H₄ (●); C₂H₆ (■); CH₄ (◆); smooth curves are values predicted on the basis of data in Table 2

The initial products of reaction are HCl, ethyne, ethene, buta-1,3-diene, butenes,* and chloroethane. On the g.c. column used, chloroethane was not separated from butene; both were shown to be present by mass spectrometry with C₄H₈ becoming increasingly important at higher temperatures. When HCl was added, we did not determine this compound in the effluent stream. Ethane and methane, barely visible at low conversions, become increasingly important products at higher temperatures; Figures 1 and 2 indicate that these are secondary products and stem from further conversions of C₂H₂ and C₂H₄. Small amounts of propene and traces of chloromethane, propane, and benzene were also observed.

Although butadiene formation is substantial at moderate degrees of conversion, accounting for example, for 23% of the reacted VC at 902 K (Table 1, exp. 12), by 1 004 K (exp. 18) it accounts for less than 1%. Either its relative rate of formation decreases with increasing temperature, or it rapidly undergoes further conversion; as will be discussed, we believe that both explanations play a part.

The carbon mass balance was good, generally $\geq 95\%$ at lower temperatures with a gradual drop to about 90% at the highest. Material unaccounted for was probably present in the form of condensation products. Tar and soot formation, prominently featured in VC pyrolysis,¹ were of minor importance.

Addition of HCl increased the VC conversion at low temperatures by about a factor of two. Logically, at higher temperatures the effect becomes less noticeable due to increasing *in situ* generation of HCl. The catalytic properties of HCl were realized only through the C₂H₄ production pathway; the formation rate of C₂H₂ was unaffected.

Discussion

Thermally generated hydrogen atoms are prominently featured in the chemistry of hydrogenolysis and their concentration is

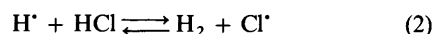
* G.C.—mass spectral analysis, utilizing a capillary column, showed three C₄H₈ species, but-1-ene and *cis*- and *trans*-but-2-ene. Butene formation will not be discussed in detail; butadiene hydrogenation in a manner analogous with that of C₂H₂ and C₂H₄ (*vide infra*) led to comparable results.

of critical importance. In a reactor similar to ours, Cao and Back⁶ have recently presented evidence that dissociation of H₂ [reaction (1)] is at equilibrium under their conditions (50—125



Torr, 876—1 016 K). This has also been indicated by our own study of phenol hydrogenolysis.⁷ We have assumed that this equilibrium is maintained during reaction with VC, an assumption which seems warranted at reasonably low VC concentrations. The hydrogen-atom concentration may thus be calculated from the well known thermodynamics of reaction (1).

In the presence of HCl, the metathesis reaction (2) is rapid⁸ and also assumed to be at equilibrium.



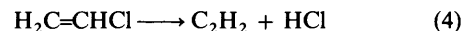
In this case, the ratio of chlorine to hydrogen atoms is given by equation (3):

$$[\text{Cl}^{\cdot}]/[\text{H}^{\cdot}] = K_2[\text{HCl}]/[\text{H}_2] \quad (3)$$

From the thermodynamic data,⁹ $\log K_2 = -0.16 + 2.7 \text{ kJ mol}^{-1}/\theta$, where $\theta = 2.3 RT$, between 900—1 100 K. As $K_2 \approx 1$, the ratio of these atomic species is very close to the ratio of HCl and H₂.

Although VC hydrogenolysis leads to a relatively small number of products, the chemistry may involve molecular reactions and the operation of a number of radical species: H atoms, Cl atoms, and various (chloro) alkyl and alkenyl radicals. Further, such species may react in different ways, *e.g.* H atoms may add to a double bond, combine with other radicals, or abstract either a hydrogen or chlorine atom from another molecule. Despite this, a judicious mix of thermokinetic analysis and reaction modelling allows an overall picture to be constructed. In the following analysis, the formation of each product or group of products is discussed; thereafter the results of the model are presented.

Ethyne.—Gas-phase molecular elimination of HCl from VC [reaction (4)] has been reported. Cadman and Engelbrecht¹⁰



published a brief communication in 1970 and gave the parameters $\log k_4/s^{-1} = 13.83 - 301 \text{ kJ mol}^{-1}/\theta$ over the temperature range 1 520—2 000 (°C or K, unstated in that publication). In a more thorough shock-wave study in 1977, Zabel¹¹ arrived at $\log k_{4,\infty}/s^{-1} = 14.0 - 290 \text{ kJ mol}^{-1}/\theta$ between 1 400—1 800 K.

If VC decomposition is assumed to be first- or pseudo-first-order, rate constants for C₂H₂ formation may be readily calculated from our data. An Arrhenius plot for lower temperature data is shown in Figure 3; owing to hydrogenation of C₂H₂ at increased temperatures, it is not possible to examine the entire range. At temperatures ≤ 980 K, the computer model indicates that further conversion of C₂H₂ is minimal, but a direct experimental check is not possible as C₂H₄, the initial hydrogenation product of C₂H₂, is also formed directly from VC (*vide infra*). What can be monitored is the hydrogenation of C₂H₄ to C₂H₆, which a separate study in this laboratory¹² has shown to be *ca.* twice as fast as that of C₂H₂ under these conditions. At 973 K (*cf.* Table 1, exp. 8) the C₂H₄/C₂H₆ ratio is still 11.2, which implies that C₂H₂ conversion is only about 4.5%. Making this minimal correction, and considering the data at lower temperatures only, leads to the parameters $\log k_{\text{C}_2\text{H}_2}/s^{-1} = 14.0 - 290 \text{ kJ mol}^{-1}/\theta$.

Table 1. Products in the thermal hydrogenolysis of VC^a

Exp.	T/K	Inflow/mmol h ⁻¹			τ/s^b	Products/mmol h ⁻¹								
		H ₂	VC	HCl		VC	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	EtCl/ C ₄ H ₈ ^c	C ₃ H ₆	C ₄ H ₆ ^d	HCl ^e
1	876	406	32.7	—	3.28	32.7	0.02	0.062	0.189	0.015	<i>f</i>	<i>f</i>	<i>f</i>	0.51
2	889	392	29.1	—	3.30	27.8	0.01	0.090	0.271	≤0.004	<i>f</i>	<i>f</i>	<i>f</i>	0.68
3	904	388	30.7	—	3.39	28.3	0.02	0.262	0.524	0.018	<i>f</i>	<i>f</i>	<i>f</i>	1.08
4	925	402	26.0	—	3.19	23.4	0.02	0.402	1.23	0.049	<i>f</i>	<i>f</i>	<i>f</i>	1.88
5	931	406	32.0	—	3.10	30.3	0.03	0.614	1.08	0.038	<i>f</i>	<i>f</i>	<i>f</i>	2.00
6	932	400	29.4	—	3.15	26.3	0.02	0.581	2.10	0.058	<i>f</i>	<i>f</i>	<i>f</i>	2.96
7	953	398	25.3	—	3.14	20.8	0.05	0.980	2.56	0.18	<i>f</i>	<i>f</i>	<i>f</i>	3.98
8	973	400	28.0	—	3.04	20.0	0.04	2.51	4.48	0.40	<i>f</i>	<i>f</i>	<i>f</i>	7.74
9	1 030	392	33.9	—	2.91	2.99	1.44	6.95	14.4	8.49	<i>f</i>	0.17	<i>f</i>	29.3
10	1 081	380	30.0	—	2.85	0.01	2.70	1.50	13.6	10.6	<i>f</i>	≤0.05	<i>f</i>	26.0
11	872	406	28.3	32	3.18	27.6	0.004	0.042	0.24	0.0040	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
12	902	390	22.6	23	3.26	19.7	0.002	0.122	0.72	0.0075	0.07	≤0.03	0.34	<i>f</i>
13	915	406	28.3	32	2.99	24.8	0.025	0.277	1.56	0.047	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
14	935	383	22.6	23	3.20	17.2	0.061	0.420	2.28	0.094	0.16	0.036	0.21	<i>f</i>
15	959	374	22.0	23	3.12	12.9	0.082	2.05	4.70	0.77	0.22	0.080	0.10	<i>f</i>
16	978	374	22.0	23	3.12	12.9	0.082	2.05	4.70	0.77	0.22	0.076	0.10	<i>f</i>
17	992	389	23.1	23	2.96	11.2	0.21	2.57	6.43	1.83	0.29	0.14	0.08	<i>f</i>
18	1 004	380	22.0	23	2.99	8.76	0.24	2.99	7.23	2.18	0.27	0.23	0.050	<i>f</i>
19	1 036	377	23.6	23	2.91	2.35	0.82	3.40	8.81	6.90	0.20	0.46	≤0.03	<i>f</i>
20	1 085	386	22.6	23	2.73	≤0.03	3.07	0.64	10.0	9.40	≤0.03	0.058	≤0.02	<i>f</i>

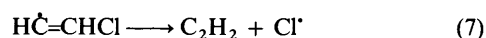
^a Tubular-flow reactor (0.4 × 232 cm); vol = 29.1 ml. ^b Determined from measured gas flow out. ^c Products not separated on g.c. column; molar response taken as that for EtCl (chloroethane). ^d Buta-1,3-diene. ^e Trapped in water and determined by titration. *f* Present but not quantitatively determined.

Table 2. Reactions used in the modelling of VC hydrogenolysis

Equation No.	Reaction	log <i>A</i> ^a	E ^a	Ref.
(4)	H ₂ C=CHCl → C ₂ H ₂ + HCl	14.0	290	<i>d</i>
(5)	Cl [•] + H ₂ C=CHCl → H \dot{C} =CHCl + HCl	10.7	29.3	13 ^b
(6)	H [•] + H ₂ C=CHCl → H \dot{C} =CHCl + H ₂	10.7	62.8	<i>b</i>
(8)	H [•] + H ₂ C=CHCl → C ₂ H ₃ [•] + HCl	10.6	38.9	15 ^b
(9)	C ₂ H ₃ [•] → C ₂ H ₂ + H [•]	13.0	172	<i>b</i>
-(9)	H [•] + C ₂ H ₂ → C ₂ H ₃ [•]	10.36	11.4	21
(10)	C ₂ H ₃ [•] + H ₂ → C ₂ H ₄ + H [•]	9.6	33.5	<i>c</i>
-(10)	H [•] + C ₂ H ₄ → C ₂ H ₃ [•] + H ₂	11.0	62.8	<i>b</i>
(11)	C ₂ H ₃ [•] + HCl → C ₂ H ₄ + Cl [•]	9.1	2.1	<i>c</i>
-(11)	Cl [•] + C ₂ H ₄ → C ₂ H ₃ [•] + HCl	11.0	29.3	13
(12)	H [•] + H ₂ C=CHCl → H ₂ C \dot{C} HCl	10.1	14.6	<i>b</i>
(14)	H [•] + H ₂ C=CHCl → H ₃ C \dot{C} HCl (1)	10.15	6.3	<i>b</i>
-(14)	(1) → H ₂ C=CHCl + H [•]	13.2	168	<i>c</i>
(15)	(1) + H ₂ → C ₂ H ₅ Cl + H [•]	9.1	67.8	<i>c</i>
-(15)	H [•] + C ₂ H ₅ Cl → (1) + H ₂	10.5	36.8	<i>b</i>
(16)	(1) + HCl → C ₂ H ₅ Cl + Cl [•]	8.5	33.5	<i>c</i>
-(16)	Cl [•] + C ₂ H ₅ Cl → (1) + HCl	10.15	3.5	22
(17)	C ₂ H ₅ Cl → C ₂ H ₄ + HCl	13.5	237	13
(18)	H [•] + C ₂ H ₄ → C ₂ H ₅ [•]	10.45	9.1	21
-(18)	C ₂ H ₅ [•] → C ₂ H ₄ + H [•]	12.95	159	23
(19)	C ₂ H ₅ [•] + H ₂ → C ₂ H ₆ + H [•]	9.15	54.8	<i>c</i>
-(19)	H [•] + C ₂ H ₆ → C ₂ H ₅ [•] + H ₂	11.0	40.2	24
(20)	C ₂ H ₅ [•] + HCl → C ₂ H ₆ + Cl [•]	8.7	10.7	<i>c</i>
-(20)	Cl [•] + C ₂ H ₆ → C ₂ H ₅ [•] + HCl	10.7	0.56	25
(21)	C ₂ H ₆ → 2CH ₃ [•]	16.75	372	13
(22)	[•] CH ₃ + H ₂ → CH ₄ + H [•]	9.4	43.5	14 ^c
(23)	[•] CH ₃ + HCl → CH ₄ + Cl [•]	8.5	3.9	26 ^c

^a Units: mol, kJ, dm³, K. ^b Estimated by analogy. ^c Calculated from reverse reaction. ^d This work.

Reaction (4) is not the only possible route to C₂H₂, however. Abstraction of a hydrogen from the unsubstituted end of VC by either Cl or H atoms [reactions (5) and (6)] leads to the 2-chlorovinyl radical, which rapidly loses Cl[•] [reaction (7)].



At moderate conversions when HCl was added, the concentration of Cl[•] was at least five-fold higher than in the H₂-only experiments, yet the rate constant for C₂H₂ formation

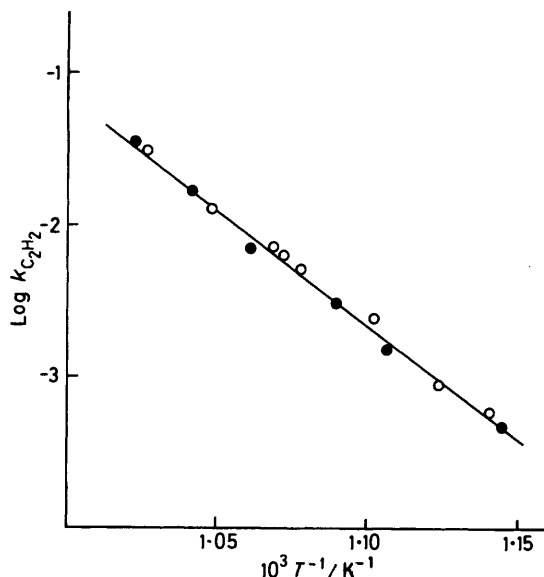
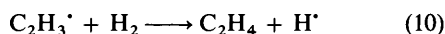
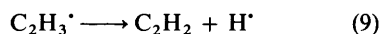
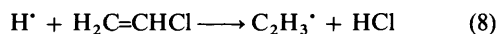


Figure 3. Arrhenius plot for C_2H_2 formation between 872–978 K; filled symbols \bullet added HCl; unfilled \circ , no added HCl. Least-squares analysis: $\log k/s^{-1} = 14.0 - 290 \text{ kJ mol}^{-1}/2.3 RT$.

was unaffected (see Figure 3). Apparently reaction (5) is unimportant. This conclusion may be checked by using the rate parameters estimated by Weismann and Benson¹³ for abstraction of an ethenic hydrogen by $Cl\cdot$, $\log k$ (per H)/ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10.4 - 29 \text{ kJ mol}^{-1}/\theta$. The contribution to ethyne production by reaction (5) is given by $R_5 = k_5 [Cl\cdot][VC]$. For exp. 12, Table 1, and using equation (3) and an equilibrium value of $10^{-11.84} \text{ mol dm}^{-3}$ for $[H\cdot]$, we find $[Cl\cdot] = 10^{-13.1} \text{ mol dm}^{-3}$. With $[VC] \approx 10^{-3.2} \text{ mol dm}^{-3}$ and $k_5 \approx 10^{9.0}$, we find $R_5 = 10^{-7.3} \text{ mol dm}^{-3} \text{ s}^{-1}$, which is only about 4% of the observed value of $10^{-5.9} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Reaction (6) is more problematic as the equilibrium concentration of $H\cdot$ is almost unaffected by HCl, and abstraction rates of sp^2 C–H bonds by $H\cdot$ are unknown. However, the rate of reaction (6) should be lower than that for abstraction of the more weakly bound hydrogen of CH_4 . This reaction has been well studied and, after a review of the literature, Sephrad, Marshall, and Purnell¹⁴ suggest $\log k$ (per H)/ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10.28 - 49.9 \text{ kJ mol}^{-1}/\theta$. If k_6 were equally large reaction (6) would account for *ca.* 5% of the acetylene at 875 K and *ca.* 3% at 975 K. Bond strength considerations suggest that these are maximum values, with the actual contribution being lower.

As a final alternative, chlorine abstraction from VC by $H\cdot$ [reaction (8)] leads to the vinyl radical, which may lose $H\cdot$ to give C_2H_2 or abstract H from either H_2 or HCl [reactions (10) and (11)] leading to C_2H_4 .

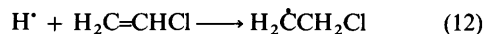


If we take k_8 as that reported for abstraction of the more weakly bound Cl of CH_3Cl ,¹⁵ $\log k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10.6 - 39 \text{ kJ mol}^{-1}/\theta$, we calculate that reaction (8) could account for up to 15% of the total C_2H_2 at 902 K (*cf.* Table 1, exp. 12). This is, however, a maximum value and further, the relative rates of

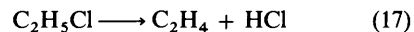
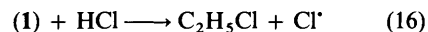
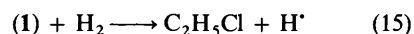
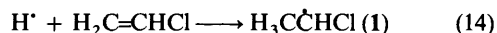
reactions (9)–(11) (see Table 2) indicate that, at temperatures $\leq 975 \text{ K}$, more than 90% of the vinyl radicals will ultimately give C_2H_4 and not C_2H_2 . We also note that, if reaction (8) were an important route to C_2H_2 , the addition of HCl would be expected to have an effect as it functions as an important H-transfer agent *via* reaction (11). Hence, it should affect the decomposition–hydrogenation ratio for $C_2H_3\cdot$ and, thereby, the total C_2H_2 formed. Again, this is contrary to the experimental result.

We therefore conclude that molecular elimination of HCl from VC accounts for $\geq 90\%$ of the C_2H_2 formed and the measured Arrhenius parameters may be ascribed to this reaction. The perfect agreement between our results and $k_{4\infty}$ reported by Zabel¹¹ may not be as good as it appears, as he also reports a strong pressure dependence, up to about 10 atm at 1 600 K. Such pressure dependence will, however, decrease with temperature; given the differences in the type of study, the difference of more than 600 K in average temperature, and the short temperature range covered here, the two sets of results are in satisfactory agreement.

Formation of C_2H_4 .—There are several possible routes leading to C_2H_4 . The reaction sequence (8) followed by (10) or (11) has been previously discussed. However, taking k_8 as before, this could account for only about 2% of the observed C_2H_4 at *e.g.* 902 K (Table 1, exp. 12). Hydrogen-atom addition to VC is the most reasonable alternative. Such reaction at the substituted end of VC results in the 2-chloroethyl radical which readily loses $Cl\cdot$ [reactions (12) and (13)].



It is well known, however, that radicals prefer to add to the unsubstituted end of alkenes.^{16,17} This addition [reaction (14)] creates a ‘sterile’ 1-chloroethyl radical (1) which is unable to lose $Cl\cdot$. This reaction is reversible, but (1) may also abstract hydrogen from H_2 or HCl [reactions (15) and (16)]. The resulting chloroethane rapidly loses HCl to give C_2H_4 [reaction (17*)]. It is clear from the small amounts of C_2H_5Cl observed that reactions (14)–(16) do indeed take place. The presence of



C_2H_6 , inarguably the hydrogenation product of C_2H_4 (*vide infra*), serves, by analogy, as independent evidence for the importance of this pathway. Chloroethane never becomes a major end product simply because its further conversion is rapid; the reported rate parameters (see Table 2) entail $t_{1/2} \approx 0.05 \text{ s}$ for reaction (17) at 1 000 K.

Addition of HCl increases C_2H_4 production by about a factor of two at low conversions. This is explainable by the increased operation of reaction (16), further supporting that steps (14)–(17) are significant. The model predicts (*vide infra*, Figure 6) that $H\cdot$ additions to both the substituted and unsubstituted ends of VC contribute to C_2H_4 formation, but that

* Chloroethane may also be converted into C_2H_4 *via* $Cl\cdot$ ($H\cdot + C_2H_5Cl \longrightarrow HCl + \cdot CH_2CH_2Cl \longrightarrow C_2H_4 + Cl\cdot$). However, relative rate analysis indicates that this path will account for $< 1\%$ of reaction under our conditions.

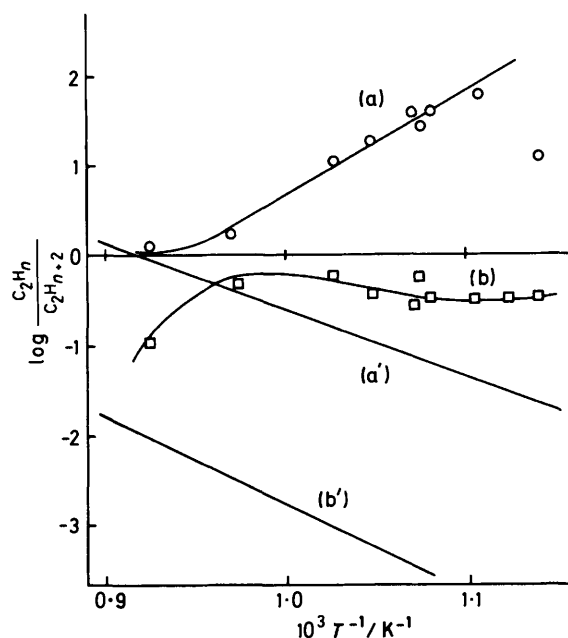


Figure 4. Formation of C_2 hydrocarbons vs. temperature. Experiments without added HCl: (a) $\log C_2H_4/C_2H_6$ (○); (b) $\log C_2H_2/C_2H_4$ (□); straight lines show equilibrium composition for $H_2 = 0.85$ atm, smooth curves are model results

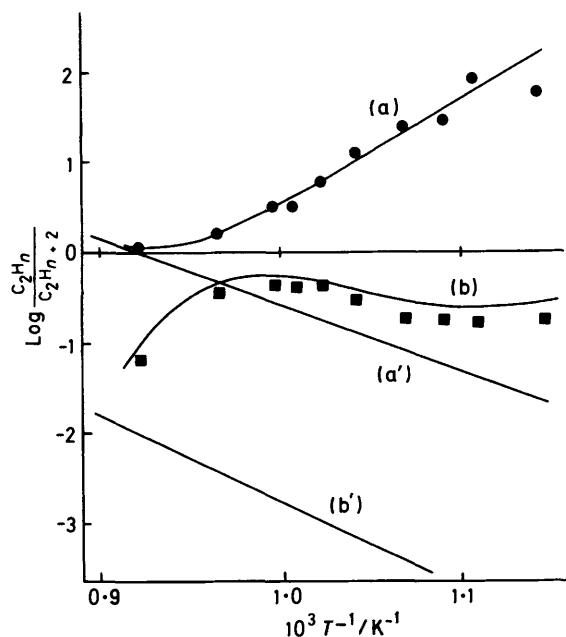
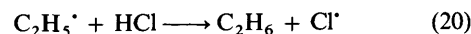
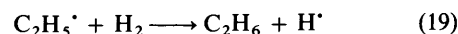
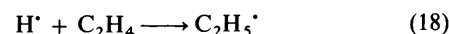
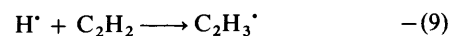


Figure 5. Formation of C_2 hydrocarbons vs. temperature. Experiments with added HCl: (a) $\log C_2H_4/C_2H_6$ (●); (b) $\log C_2H_2/C_2H_4$ (■); straight lines show equilibrium composition for $H_2 = 0.85$ atm, smooth curves are model results.

the latter pathway is somewhat dominant, especially at lower temperatures.

Further Product Conversions.—Both C_2H_2 and C_2H_4 are subject to further reaction. Addition of H^\cdot to C_2H_2 [reaction (9)] leads to vinyl radical. As previously discussed, this species may be converted into C_2H_4 through reactions (10) and

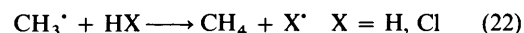
(11). Similarly, C_2H_4 may be hydrogenated to C_2H_6 through reactions (18)–(20).



Reactions (19) and (20) both appear to be important in the final hydrogenation step. HCl is the better hydrogen-transfer agent; from the data in Table 2, $k_{21}/k_{20} \approx 70$ at 1 000 K. However, the H_2/HCl ratio is large (≥ 10), which means that both reactions play a role.

In Figures 4 and 5 $\log(C_2H_4/C_2H_6)$ and $\log(C_2H_2/C_2H_4)$ are plotted vs. reciprocal temperature. The straight lines show the thermodynamic equilibrium values calculated for an 85% H_2 environment, while the curved lines represent the values predicted by the reaction model. It is apparent that the C_2 distribution is kinetically controlled over most of the temperature range, although equilibrium is being approached at the highest temperatures studied.

Methane, a trace product at low temperatures, does not become important except at high temperatures. More significant, its build-up closely follows that of C_2H_6 (Figures 1 and 2). Thus, it would seem to stem at least partly from C–C bond fission in this molecule [reaction (21)] followed by H abstraction from H_2 or HCl [reaction (22)]. Experimental

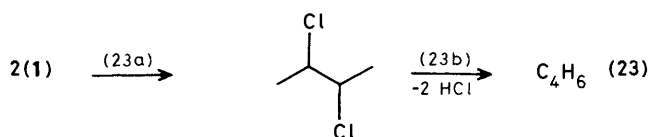


methane values at higher temperatures are, however, close to a factor two higher than those reproduced by inclusion of this scheme in the model. Reaction (21) has been studied several times,¹⁸ and the rate parameters are in good agreement, which suggests that additional pathways to CH_4 exist. This is confirmed by small amounts of methane found in the early stages of reaction, where (21) is unimportant.

Further conversion of buta-1,3-diene is most likely responsible. Butadiene hydrogenolysis appears to proceed through two pathways, one leading to two C_2 species and the other to C_3 and C_1 . In the same reactor used in the VC experiments, and similar conditions ($T = 913$ K, $[C_4H_6] = 0.25$ vol % in H_2 , $\tau = 3.2$ s) the hydrogenolysis of C_4H_6 proceeds for ca. 50% and leads to the following product ratios (mol/mol) $C_3:C_2:C_1 = 1:2.4:2.1$. The observation that the $C_3:C_1$ ratios in the VC experiments at low temperatures are similar, e.g. at 935 K (Table 1, exp. 14), $C_3:C_1 = 1:1.7$, lends strong support to the idea that these products stem from C_4H_6 .

Formation of Butadiene.—At moderate conversions of VC, C_4H_6 is a relatively important product, comprising 23% of the reacted VC at 902 K (Table 1, exp. 12). However, by 1 004 K (Table 1, exp. 18), it accounts for <1% of the converted VC. This must be due to its rapid conversion and/or a marked slowing in its relative rate of formation.

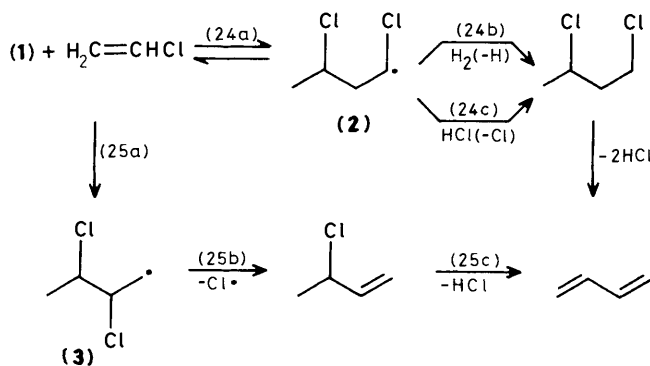
A priori there are two likely pathways leading to C_4H_6 . First, reaction (23), the combination of two 1-chloroethyl radicals followed by elimination of 2 moles of HCl, is a possibility, but it can be shown that this is of minor importance. If reaction (14) is approximately at equilibrium, the concentration of (1) is given by $[(1)] = K_{14} [H^\cdot][VC]$, which, using the parameters in Table 2, leads to $[(1)] \approx 10^{-8.6}$ mol dm^{-3} at 902 K. Taking k_{23a} as 10^{10} dm^3 mol^{-1} s^{-1} , the maximum rate of C_4H_6 formation



is $R(\text{C}_4\text{H}_6) = k_{23a} [(1)]^2 = 10^{-7.2} \text{ mol dm}^{-3} \text{ s}^{-1}$. The observed value at this temperature (Table 1, exp. 12) is $10^{-5.5} \text{ mol dm}^{-3} \text{ s}^{-1}$, some 50 times higher.

An alternative route, *via* addition of (1) to VC is put forth in the Scheme.

Addition to the substituted end of VC [reaction (25a)] is followed by loss of Cl[•] and HCl elimination [reaction (25b) and (25c)] to give C₄H₆. Polar and steric effects, however, favour attack at the unsubstituted carbon [reaction (24a)].¹⁶ This step is reversible, but the intermediate 1,3-dichlorobutyl radical (2)



Scheme.

can be hydrogenated and, after loss of two HCl molecules, lead to buta-1,3-diene.

The rate of formation of C₄H₆ from these reactions may be estimated as follows; because $k_{25b} \gg k_{-25a}$, and (3) will irreversibly lead to buta-1,3-diene, the rate for reaction (25) is given by $R_{25} = k_{25a} [(1)] [\text{VC}]$. At low VC conversions (*e.g.* 902 K, exp. 12), $[\text{VC}] \approx \text{constant} = 10^{-3.2} \text{ mol dm}^{-3}$ and, as before $[(1)] = 10^{-8.6} \text{ mol dm}^{-3}$; taking $k_{25a} = 7.9 - 29 \text{ kJ mol}^{-1}/\theta$, similar to the experimental values for isopropyl radical addition to various alkenes,¹⁹ leads to $R_{25} = 10^{6.2} \cdot 10^{-8.6} \cdot 10^{-3.2} = 10^{-5.6} \text{ mol dm}^{-3} \text{ s}^{-1}$. For the alternative route, $R_{24} = [(2)] (k_{24b} [\text{H}_2] + k_{24c} [\text{HCl}])$; (2) is essentially (1) with a β substituent and we take the rate parameters k_{24b} and k_{24c} as equal to those for (1) (*i.e.* k_{15} and k_{16} , see Table 2). Finally, estimating K_{24a} (902 K) = $10^{0.4}$ *via* thermochemical kinetics,²⁰ and filling in the appropriate concentrations as before, we obtain $R_{24} \approx 10^{-7.4} \text{ mol dm}^{-3} \text{ s}^{-1}$. It thus appears that addition to the substituted carbon [path (25)] is the only important mechanism and the calculated rate of $10^{-5.6} \text{ mol dm}^{-3} \text{ s}^{-1}$ is very close to that observed, $10^{-5.5} \text{ mol dm}^{-3} \text{ s}^{-1}$.

The relative importance of C₄H₆ formation depends on the concentrations of (1) and VC and, ultimately, therefore, on $[\text{H}^*]$, the value of K_{14} , and the square of $[\text{VC}]$. While $[\text{H}^*]$ increases with temperature, K_{14} decreases and, except at low conversions, $[\text{VC}]$ decreases rapidly throughout the reaction. The interplay of these factors is complex, but trial incorporations of reaction (25) into the model show that C₄H₆ formation is expected to go through a maximum at about 975 K, and may account for *ca.* 15% of the total VC at this point. This is not observed experimentally due to rapid conversion of C₄H₆. Buta-1,3-diene hydrogenolysis is complex and not well understood at this time. We therefore refrained from attempting to build this chemistry into the model, although we note here that it must be occurring and will be relatively more important at lower temperatures and high VC concentrations.

Table 3. Sensitivity coefficients ($10^3 S$) for major products of VC hydrogenolysis at 900 and 1 000 K^a

Rate constant (k_i)	900 K				1 000 K			
	H ₂ C=CHCl	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	H ₂ C=CHCl	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
(4)	-5	996	3	6	-269	840	-9	-5
(5)	0	52	-2	-3	-9	32	-1	-3
(6)	0	1	0	0	-3	9	0	0
(8)	0	0	54	64	-27	-11	36	43
(9)	0	0	-1	-2	0	3	-2	-5
-(9)	0	-11	2	0	0	-228	123	84
(10)	0	0	1	2	0	0	1	3
-(10)	0	0	-1	-2	0	1	-1	-3
(11)	0	0	1	2	0	-1	0	-2
-(11)	0	0	-1	-2	0	1	-1	-3
(12)	-8	-4	421	492	-166	-67	220	269
(14)	-20	-10	530	461	-179	-81	332	375
-(14)	5	3	-145	-125	114	53	-216	-249
(15)	0	0	18	14	-37	-18	69	81
-(15)	0	0	-1	-2	1	1	-1	-4
(16)	0	0	43	36	-78	-35	146	161
-(16)	0	0	-1	-2	1	1	-1	-4
(17)	0	0	309	314	0	0	6	20
(18)	0	0	-12	994	0	0	-260	827
-(18)	0	0	4	58	0	0	65	-222
(19)	0	0	-1	10	0	0	-20	54
-(19)	0	0	1	-2	0	0	0	-8
(20)	0	0	-2	4	0	0	-53	170
-(20)	0	0	1	-2	0	0	6	-27
(21)	0	0	-1	-2	0	0	-1	-5

^a $S = \delta \ln \psi_i / \delta \ln k_i$; $\psi_i = i^{\text{th}}$ product; $k_i = i^{\text{th}}$ rate constant; calculated for 5% increase in k_i at indicated temperature with following inflows (mmol h^{-1}): H₂ = 375, VC = HCl = 25, $\tau = 3 \text{ s}$. Results with no added HCl are similar.

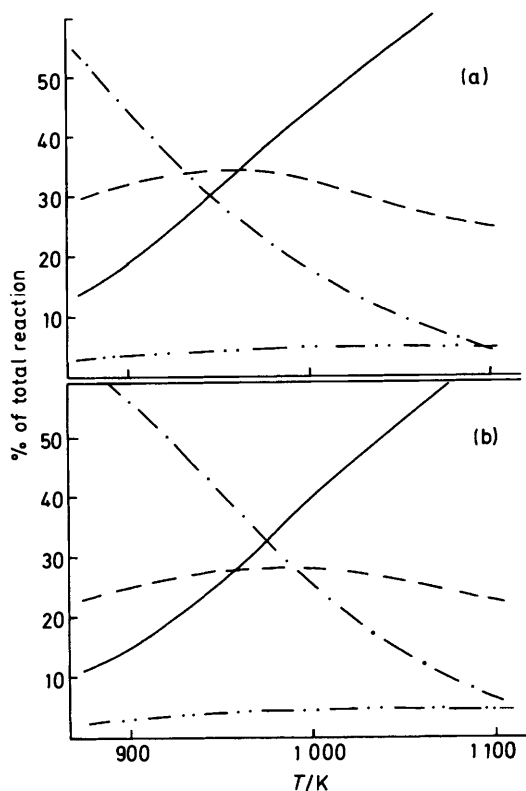


Figure 6. Relative importance of VC dechlorination pathways as predicted by model, expressed as a percentage of total reaction: (a) no added HCl; inflows (mmol h^{-1}): $\text{H}_2 = 375$, $\text{VC} = 25$, $\text{HCl} = 0$; (b) added HCl; inflows: $\text{H}_2 = 375$, $\text{VC} = \text{HCl} = 25$. Molecular loss of HCl —; hydrogenation to $\text{C}_2\text{H}_5\text{Cl}$ (followed by HCl loss) - - -; displacement of Cl^- via H atom addition to substituted end of VC — · —; abstraction of Cl^- by H atom · · ·

Reaction Modelling.—The reactions used in the computer modelling of VC hydrogenolysis are listed in Table 2 along with their rate parameters. If available, the Arrhenius values were taken directly from the literature, if not they were either estimated by analogy or from the reverse reaction and transition-state theory. Literature parameters were not altered in order to obtain a 'best fit'. As stated earlier, reaction (1) was taken to be at equilibrium throughout; the steady-state assumption was used for radical concentrations. No radical/radical reactions (e.g. $\text{R}^\cdot + \text{R}^\cdot \rightarrow \text{Products}$ or $\text{R}^\cdot + \text{H}^\cdot \rightarrow \text{Products}$) are presented in Table 2, as their inclusion in the model was found to have a negligible effect on the results.

The sensitivity coefficients for the major products are presented in Table 3. The indirect (brute-force) method was used for their calculation; that is, the input parameters were varied one by one, the equations re-solved, and the coefficients calculated by the finite difference approximation.

The most critical rate constants affecting the overall VC conversion and initial product distribution are k_4 , k_{12} , k_{14} , k_{-14} , k_{15} , and k_{16} . Of these, k_4 , determined in this work, agrees well with other studies and was assumed to be correct. The parameters for H^\cdot addition to VC, reactions (12) and (14), were estimated by analogy with those for C_2H_4 , which are well known. A theoretical study on the activation energies for these additions has also been carried out by Schlegel and Sosa;¹⁷ they propose $E_{14} = 4.2 \text{ kJ mol}^{-1}$ and $E_{12} = 17\text{--}25 \text{ kJ mol}^{-1}$.

Our values are similar, although we have chosen a slightly lower value of $E_{12} = 15 \text{ kJ mol}^{-1}$. This is not unreasonable as

it is well known that calculated barriers for H-atom addition are usually slightly overestimated; it is also in line with the 10–13 kJ mol^{-1} barrier for H addition to the substituted carbon of propene.¹⁹ Further, a comparison of the experimental data of references 5 and 27 show that at 298 K, $(k_{12} + k_{14})/k_{19} = 1.44$, similar to the value of 1.58 obtained by extrapolation of our values. The values also suggest that, at room temperature, H^\cdot adds mostly to the unsubstituted end of VC. With regard to k_{-14} , the chosen value is dependent on the thermodynamic properties of VC and (1), the uncertainties of which are discussed in the Appendix.

Rate constants for hydrogen abstraction by (1) from H_2 and HCl [reactions (15) and (16)] were, in the former case, estimated by analogy with those for $\text{C}_2\text{H}_5^\cdot$, for which both the forward and reverse reactions have been well studied and subject to a recent review.²⁴ The parameter set for $\text{C}_2\text{H}_5^\cdot$ appears to be sufficiently accurate, judging by the excellent fit between experimental and calculated values for the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratios (Figures 4 and 5), which is heavily dependent on these values. In the case of HCl, reaction (16) has been experimentally studied.²² In conjunction with the thermodynamic properties of (1) (Appendix), this allows a reasonably confident estimation of the forward reaction.

In general, the model slightly underestimates the conversion rate of VC. This may in part be due to uncertainties in the thermodynamic properties of VC, $\text{C}_2\text{H}_5\text{Cl}$, and (1) (Appendix), which lead to variations in the most important rate constants. We also note, however, that while the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio is well reproduced by the model for both systems, the predicted $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ ratio is approximately correct only in the absence of HCl. Variations in selected rate constants were found to improve the fit with either one of the two systems, but not both. Two possible explanations are that added HCl increases ethene formation [via reaction (16)] more than predicted by the model, or that the parameters affecting C_2H_2 hydrogenation are incorrect.

The model makes a steady-state assumption for the concentration of (1). As a result, HCl reduces [(1)], with a concomitant, but relatively mild, increase in the rate of C_2H_4 formation. If equilibrium (14) were more quickly established (say via wall reactions with surface-absorbed H atoms), the effect of HCl would be larger and could lead to the observed curves. Given, however, that the same steady-state assumption was made for $\text{C}_2\text{H}_5^\cdot$, and the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio is well reproduced in both systems, we feel this is not likely. Regarding C_2H_2 hydrogenation, it is certainly possible that the actual parameters are somewhat different from those used here. Still, the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ ratio is also incorrect in the lower temperature region, where hydrogenation is minor.

Another explanation must exist. Our current impression is that the equilibrium assumption for $[\text{H}^\cdot]$, although approximately correct, may not hold at low temperatures where the equilibrium H-atom concentration is very small. In such cases, free-radical chains may be initiated, leading to a higher than equilibrium steady-state concentration of H^\cdot , and resulting in complications due to wall effects, impurities, etc. This is discussed in more detail in a separate article on chlorobenzene hydrogenolysis.²⁸ In the present instance, if the H-atom concentration is allowed to vary by 0.15 log units, the experimental data can be much better reproduced.

The variation in the relative importance of each reaction pathway with temperature is shown in Figure 6. While it must be emphasized that these results are based on the model, and may vary considerably under conditions where equilibrium (1) is not established, we think they present a reasonably accurate view of the reactions involved in VC conversion.

The other primary shortcoming of the present model stems from non-inclusion of condensation routes and the subsequent

reactions of the resulting products. This leads to a 10–15% overestimation of the total C₂ product at the highest temperatures (Figures 1 and 2). Before a more complete analysis is possible, however, further study of radical addition processes is required, particularly in the region of 1 000 K, and particularly involving unsaturated radicals such as C₂H₃[•], about which little is known.

Pyrolysis and Hydrogenolysis Compared.—VC behaviour in hydrogenolysis is quite different from that in pyrolysis. While the overall rates are similar, the product distributions are very different. This is so despite the major importance of reaction (4) in both systems.

As we have previously discussed,¹ pyrolysis leads to high concentrations of carbon-centred radicals, largely through the presence of highly reactive chlorine atoms. The carbon-centred radicals, in turn, add to other unsaturated centres, resulting in polymerization and tar. Some of the products, e.g. 2-chlorobuta-1,3-diene, are still chlorinated. Sooting is important in pyrolysis, possibly due to the presence of large quantities of ethyne, a known soot precursor.²⁹

In hydrogenolysis, by contrast, hydrogen serves as a source of hydrogen atoms, and also functions as a radical buffer. To a large extent, chlorine atoms and carbon-centred radicals are replaced by H atoms *via* metathesis reactions with H₂. Hydrogen atoms result in rapid dechlorination and the splitting and hydrogenation of unsaturated C–C bonds, thus preventing or slowing the build-up of polymeric material and soot.

Carried to an extreme, the end result of pyrolysis is some HCl and partially chlorinated tar and soot; extreme hydrogenolysis leads to HCl and to C₁ and C₂ hydrocarbons in equilibrium proportions.

Experimental

Experimental and analytical details were as previously described.¹

Acknowledgements

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Appendix

Thermodynamic Properties of Selected Species.—Thermodynamic properties for C₂H₅[•] were taken from (ΔH_f°) or calculated from (C_p° terms) the recent work of Brouard, Lightfoot, and Pilling.³⁰ These values differ considerably from older recommendations,²⁰ but lead to considerable improvement between calculated and experimental parameters for the forward and reverse rates for C₂H₄ + H[•] \rightleftharpoons C₂H₅[•] and H[•] + C₂H₆ \rightleftharpoons C₂H₅[•] + H₂. Cao and Back²⁴ have discussed in detail the latter reaction in this light. They retained, however, the C_p° values of ref. 22; the newer values given here lead to still further improvement.

The changes in S° and C_p° terms are as significant as the revised ΔH_f° when used for estimating rate constants from the reverse reaction. The revised S° and C_p° values stem primarily from measurements by Pacansky and Coufal,³¹ which indicate free rotation about the C–C bond in C₂H₅[•], in contrast to the old assumption of a *ca.* 8 kJ mol⁻¹ barrier.²⁰ At our temperatures, such changes lead, through the *A*-factor, to a factor of three reduction in the calculated rate constants for H abstraction by C₂H₅[•] from H₂ and HCl. In a broader sense, the above is illustrative of the uncertainties in reaction modelling

Table 4. Thermodynamic data^{a,b}

Species	$\Delta H_f^\circ(300)_g$	$S^\circ(300)$	C_p°			
			300	500	800	1 000
H ₂ C=CHCl	20.9	264.0	54.0	74.5	89.5	101.7
C ₂ H ₅ Cl	-111.7	276.6	63.2	90.8	114.6	131.8
C ₂ H ₅ [•]	118.7	248.1	51.6	72.8	96.4	108.1
H ₃ CCHCl	75.3	287.9	61.3	84.1	102.5	116.7

^a References as discussed in text. ^b ΔH_f° in kJ mol⁻¹; S° and C_p° in J mol⁻¹ K⁻¹.

and demonstrates the need for more precise measurements of the thermodynamic properties of radicals.

For (1), entropy and C_p° terms were estimated using the methods of Benson,²⁰ assuming a 0 barrier to C–C rotation and from the calculations of Schlegel and Sosa.¹⁷ The above values are interpolations between the two results. Schlegel and Sosa estimate $\Delta H_f^\circ(1) = 79.5$ kJ mol⁻¹,¹⁷ while, based on the activation energy for the α -photobromination of C₂H₅Cl, Tschuikow-Roux and Salomon³² report a value of 70.1 kJ mol⁻¹. In the latter study the authors were concerned that the measured *A*-factor seemed too low. If this were due to a measured activation energy which was also too low, $\Delta H_f^\circ(1)$ would be correspondingly increased; we have therefore chosen an intermediate value.

The thermodynamic properties of C₂H₅Cl and VC have also been included, as the values in commonly available sources^{20,33} are somewhat different, generally with regard to ΔH_f° s, but also, apparently due to typographical errors, in certain C_p° terms. After review, we feel the above parameters are the best currently available; preferred values for ΔH_f° (C₂H₅Cl)³⁴ and ΔH_f° (VC)^{1,17,34} have been previously discussed.

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