Hydrogenolysis of organochlorinated pollutants: Kinetics and thermodynamics

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Abstract

Hydrogenolysis is one of the most promising innovating technologies because it allows the toxic organic chlorides to change quickly into their corresponding hydrocarbons, under moderate conditions. The new contribution of this paper lies in that it offers a comprehensive view of the hydrogenolysis kinetics by collecting the Arrhenius equations of the main hydrodechlorination reactions based on the data available in the literature. Although the standard procedure used for the calculation of activation entropy cannot yield more but rough hints on the reaction mechanisms, it points out the possible simultaneous occurrence of two different reaction mechanisms for chloroderivatives of methane and enables to identify the causes of the prevalence of one mechanism over the other as well as the transition area where this change gradually takes place.

Introduction

The toxic wastes coming from the production and the use of organic chlorides may cause serious environmental problems, such as the contamination of groundwaters and air pollution.

Their incineration in a technically and environmentally acceptable way is a difficult task in fact, due to their high thermal stability, the complete incineration occurs at such high temperatures ($T > 1400°C$) as to be economically prohibitive [1]. On the other hand, incomplete combustion would be equally unacceptable for the possible environmental problems that can arise as a result of the formation of hazardous by-products [2]. Alternative incineration solutions, such as in rotary cement kilns, in specially designed plants for chemical wastes with HCl recovery, or in stirred-bed reactors [3] seem to improve the situation only slightly, whereas incineration at sea exposes the coastal environment to the risks of hazardous waste spills [4].

Among the non-thermal technologies, neither the direct adsorption of the pollutants on activated carbon [5,6], followed by stripping and air purification

[6], nor the solvent extraction processes [7], nor the use of ionizing radiations [8,9] constitute exhaustive solutions.

Lastly, as regards the biotechnological (or microbiological) degradations, several problems of culture stability are evident in the aerobic biofiltration [10-12], but better prospects of success seem possible in the use of anaerobic bacteria [13].

Hydrogenolysis is one of the most promising innovating technologies because it allows the toxic organic chlorides to change quickly (hydrodehalogenation) into their corresponding hydrocarbons, under moderate conditions. Furthermore, since the degradation of chlorinated hydrocarbons takes place in a closed system, no relevant emission is released, which represents an excellent advantage from an environmental point of view in comparison with incineration. Unfortunately, however, its mechanism of reaction is not yet fully understood.

The new contribution of this paper lies in that it offers a comprehensive view of the hydrogenolysis kinetics by collecting the Arrhenius equations of the main hydrodechlorination reactions based on the data currently available in the literature. Although the standard procedure used for the calculation of activation entropy cannot yield more but rough hints on the reaction mechanisms, it points out the possible simultaneous occurrence of two different reaction mechanisms for chloroderivatives of methane and enables to identify the causes of the prevalence of one mechanism over the other as well as the transition area where this change gradually takes place.

Theory of hydrogenolysis

Hydrogenolysis is an exoergic hydrodechlorination [14] which leads to the synthesis of hydrocarbons:

$$R-Cl+H_2 \longrightarrow R-H+H-Cl \qquad (1)$$

and generates, depending on the chloride structure, from 10 up to 25 kcal/mol (40-100 kJ/mol $R-Cl$).

Only a few seconds contact time at a temperature ranging from 700 to 1,000°C is enough to assure the complete hydrodechlorination of many organic chlorides (alkanes, alkenes or arenes, such as PCBs).

The donor of hydrogen atoms may consist not only in the expensive molecular hydrogen but also in alternative chemicals, such as butanol or methanol, which may be added separately or are produced *in situ*.

Because of the low specificity of the radical reactions and the concurrent occurrence of a cascade of secondary reactions [15-17], hydrodechlorination should be utilized not so much for synthetic purposes as for detoxifying chlorinated pollutants.

A study of the thermodynamic quantities referred to the reactants and the

products is not meaningfully exploitable for the following reasons. Since hydrogenolysis brings about simple bond transpositions from the reactants to the products, the entropy variations are presumably very little or, at least, nearly the same, and the enthalpy can (even though T is high) then be utilized, instead of the free energy of the reaction, ΔG_r, to evaluate the hydrodechlorination thermodynamics. Unfortunately, however, as the values of Table 1 show, the energy differences are not so relevant as to justify possible opposite thermodynamic trends of different categories of organic chlorides.

Much more interesting is, on the other hand, the analysis of the thermodynamic quantities referring to the reaction intermediates, indeed more similar to the transition state rather than the reactants.

As regards the reaction mechanism proposed till now for hydrodechlorinations, alkyl monochlorides seem to be transformed into the respective hydrocarbons via concerted β-elimination with internal elimination of HCl (Fig. 1a), whereas polychlorinated compounds would preferentially follow radical substitutions. Two different radical mechanisms have been suggested by Louw et al. for polychlorides [18]: one supposes the reaction between hydrogen atoms and the chlorinated carbon of organic chlorides with the direct formation of hydrocarbons (Fig. 1b), the other one postulates, on the other hand, the direct attack of H· against the reactant, with the formation of free radical intermediates (Fig. 1c). Unfortunately, however, it is not clear, at present, what mechanism actually occurs or which predominates case by case, which constitute the aims of this study.

A radical addition/elimination has been proposed for chloroarenes [15,18] (Fig. 1d), for which the following kinetic equation has been proved:

$$-dc/dt = k_0 c [H_2]^{1/2} \tag{2}$$

where c is the organic chloride concentration. If H_2 is present in excess and its

TABLE 1

Enthalpy of formation values, ΔH_f (kcal/mol), of the C–Cl bonds involved in the hydrodechlorination reactions

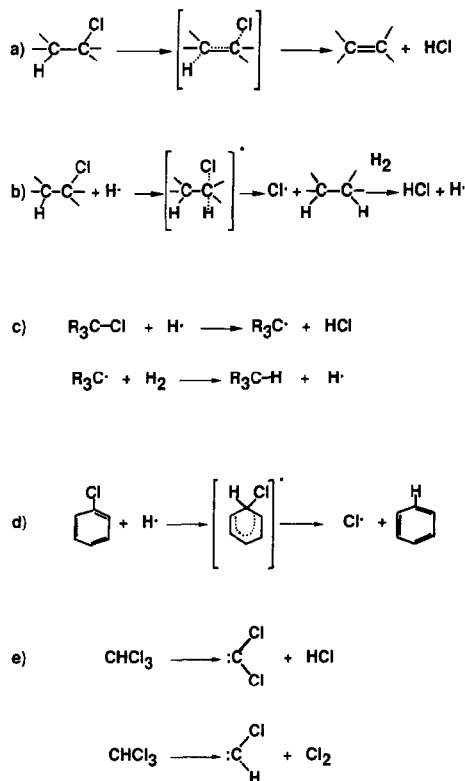| Compound	ΔH_f	Compound	ΔH_f
$CH_3–Cl$	85	$CH_2=CH–Cl$	84
$CH_3CH_2–Cl$	80	$CH_2=CH–CH_2–Cl$	60
$CH_3CH_2CH_2–Cl$	82	$C_6H_5–Cl$	96
$(CH_3)_2CH–Cl$	81	$C_6H_5CH_2–Cl$	72
$(CH_3)_3C–Cl$	82	$H–Cl$	103
$ClCH_2–Cl$	82	$H–H$	104
$Cl_2CH–Cl$	81	$Cl–Cl$	58
$Cl_3C–Cl$	73		

Fig. 1. Main reaction mechanisms proposed for hydrogenolysis of organo-chlorinated compounds. (a) β-elimination, (b) concerted radical substitution, (c) straightforward chain reaction with formation of free radicals, (d) radical addition/elimination, and (e) α-elimination with carbene formation.

concentration may assumed about constant eq. (2) becomes a pseudo-first order equation, one can write:

$$\log c/c_0 = -k_0 t [H_2]^{1/2}/2.303 \tag{3}$$

(where log is $\ln/2.303$) from which the specific rate constant k_0 can be easily calculated if sufficient data are available at different reaction times.

Independently of the type of mechanism actually involved, it is reasonable to assume, also for the other organic chlorides, that the reactant is actively present in the transition state; therefore, kinetics similar to the ones proposed for chloroarenes can be supposed.

The specific rate constant is related to the thermodynamic temperature, T, by the Arrhenius equation:

$$k_0 = A \exp - (E_{act}/RT) \tag{4}$$

TABLE 2

Experimental data and main relative conditions found in literature for the hydrodechlorination of several chlorinated compounds

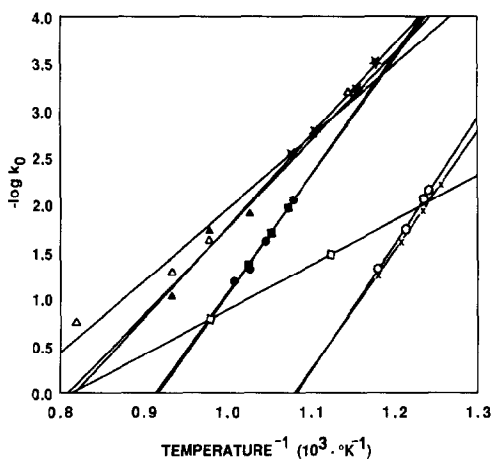| Compound	Temperature (°C)	Residence time (s)	Yield (%)	Reference
CH_3Cl	604–840	11	19.6–98.4	[19]
CH_2Cl_2	650–720	11	12.0–88.0	[19]
$CHCl_3$	526–550	11	44.5–78.5	[19]
CCl_4	532–573	11	16.4–74.7	[19]
$CH_2=CH-Cl$	660–800	11	43.2–80.0	[19]
$Cl-CH=CH-Cl$	610–750	6.2- 8.0	50.0–96.0	[15,18]
C_6H_5Cl	604–840	7.5-11.0	19.6–98.4	[15,18,19]
$C_6H_4Cl_2$	600–950	4.6- 8.8	0.7–93.0	[15,18]

Fig. 2. Dependence on temperature of the specific rate constant of thermal hydrogenolysis of different organo-chlorinated compounds. (△) Dichlorobenzene, (▲) chlorobenzene, (□) dichloroethylene, (■) vinyl chloride), (○) carbon tetrachloride, (×) chloroform, (●) dichloromethane, (★) chloromethane.

where

$$A = (kT/h) \exp (\Delta S_{act}/R) \tag{5}$$

is the Arrhenius pre-exponential factor, where k is Boltzmann's constant, h is Planck's constant, while ΔS_{act} and E_{act} are the activation entropy and enthalpy, respectively.

The values of $-\log k_0$, calculated for several pure chlorides at different temperatures from the literature data of Table 2, have been plotted in Fig. 2 versus $1/T$ according to eq. (4); from the resulting values of the pre-exponential fac-

tor the entropy of activation has been calculated through eq. (5). By inspection of the trend of this quantity with the chemical structure of the reactant, rough hints on the prevailing kinetic mechanism of the thermal hydrogenolysis of organic chlorine compounds are suggested case by case.

In order to achieve this, a reference temperature of 973.15 K (700°C) has been assumed in order to compare the thermodynamic quantities of reactants showing different reactivities at various temperature ranges.

Results and discussion

Table 2 summarizes the experimental data and the relative main experimental conditions found in literature for several pure chlorides [15,18,19]. Although these data have been often obtained under different conditions, some important generalizations can nevertheless be made. Runs were all performed at normal pressure in quartz flow-stirred tank pyrolysis reactors [15] through which the vapourized reactants were passed mixed with pure hydrogen as H donor. Depending on the different chlorocarbons, the residence time in the pyrolysis chamber varied from 5 to 11 s, the temperature from 873 to 1223 K (600 to 950°C) and the molar ratio of H_2 to substrate from 4 to 14. The reaction yield was continuously monitored by HCl recovery from the samples' exit gas, while organic products were detected by on-line gas-liquid chromatography.

From the values of the kinetic parameters listed in Table 3, one can observe that the activation enthalpy ranges from 35 to 61 kcal/mol, except for Cl-CH=CH-Cl, and that also the bond formation enthalpy values of C-Cl bonds, listed in Table 1, are not very different from one another, barring some cases not considered in this study. Furthermore, the activation enthalpy always ranges from one half to one third of the enthalpies of formation of the reactant bonds. For these reasons hydrodechlorination takes place very quickly,

TABLE 3

Thermodynamic properties calculated for the hydrodechlorination of different organic chlorides and scaled to 973.15 K

Compound	E_{act} (kcal/mol)	ΔS_{act} (cal/mol K)	ΔG_{act} (kcal/mol)	k_0 ($s^{-1} \cdot 10^3$)	$\log A$
CH_3Cl	44.1	−24.8	68.2	9	7.88
CH_2Cl_2	56.8	−9.0	65.5	40	11.35
$CHCl_3$	58.2	2.0	56.2	4790	13.74
CCl_4	61.3	5.5	56.0	5517	15.52
$CH_2=CH-Cl$	58.4	−7.3	65.4	41	11.72
$Cl-CH=CH-Cl$	21.7	−43.2	63.8	96	3.86
C_6H_5Cl	41.9	−27.0	68.2	10	7.40
$C_6H_4Cl_2$	35.0	−34.9	68.9	7	5.68

with low specificity, and shows similar reaction rates for different types of chlorocarbons; these characteristics belong to both homolytic and concerted exoergic reactions. Little variations in the reaction rate, which are imputable to the prevalence of one mechanism rather than the other, should then be highlighted by differences in the Arrhenius pre-exponential factor, i.e. in the activation entropy.

A more careful evaluation of the thermodynamic quantities at the transition state shows that for methane derivatives reaction rate increases with increasing number of chlorines, which is just opposite to what one would expect from the increase observed in activation enthalpy. This emphasizes the importance of the activation entropy in calculating the total activation free energy, which is the parameter to be considered in kinetic terms.

As the values of Table 3 show, the difference between the activation entropies of the activated complex and the reactant system increases with increasing number of chlorine atoms. This phenomenon is so important as to invert the Gibbs free energy trend in comparison with that of the activation enthalpy.

These results give useful information about the reaction mechanisms of thermal hydrogenolysis. The negative activation entropy variations, observed for both chloromethane and dichloromethane, suggest the formation of transition states having more rigid structures with respect to the reactants.

For the absence of β-hydrogens in chloroderivatives of methane, this behaviour cannot be explained with the β-elimination mechanism of Fig. 1a. For these compounds, a concerted mechanism with the formation of free radicals (Fig. 1c) or an α-elimination with the formation of carbenes like :CCl$_2$ or :CHCl followed by further rapid reactions of these intermediates with the other species present in the system (Fig. 1e) would both be consistent with the observed negative values of the activation entropy. The first mechanism, proposed by Louw et al. [20], should take place more likely if one also considers the increase of activation entropy with increasing number of chlorines in the reactants. In fact, the positive values of activation entropy of chloroform and carbon tetrachloride are consistent with homolytic scission of C-Cl bonds in the rate determining step, with the subsequent formation of free radicals as intermediates (Fig. 1c). This gradual change from concerted to homolytic reaction mechanism can be ascribed to overlap of the p-orbital on carbon with a vacant d-orbital on the chlorine atoms, which tends to stabilize more the radicals having the greater number of chlorines. This effect is probably so prominent in chloroform as to provoke C–Cl homolysis prior to attack by hydrogen.

A different trend is observed, on the other hand, for polychloroarenes: the reactants containing the highest number of chlorine atoms show by and large the same reactivity at 973.15 K as the partially hydrogenated products. This kinetic behaviour might be due to the temporary loss of aromaticity of the benzene ring during each radical addition/elimination step (Fig. 1d), that requires a relatively high free energy of activation.

As regards to chloroalkenes, a surprising feature is the very low E_{act} value for dichloroethylene, when compared with vinyl chloride. Vinyl chlorides are expected to be much less reactive to hydrogenolysis than alkylchlorides, as indeed observed in the case of $CH_2=CH-Cl$, but dichloroethylene behaves anomalously in this respect.

Conclusions

In conclusion, by inspection of the values of the activation free energy, all polychlorinated hydrocarbons undergo spontaneously successive dechlorination steps, which makes the whole reaction self-sustained; in fact, each substitution generates sufficient energy to get over barriers of all C-Cl bonds. This is also the reason for the observed low specificity of these reactions, the proportions between partially and completely dechlorinated products being dependent on the relative free energy barriers. This supposition is consistent with the incomplete hydrodechlorination observed at low temperatures [18] for either polychloroarenes or alkenes.

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