

Detoxification of organic waste liquids by catalytic hydrogenation

Francesco Gioia

Dipartimento di ingegneria chimica, Università degli studi di Napoli Federico II, Piazzale Tecchio, 80125 Naples (Italy)

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Abstract

Catalytic hydrogenation is proposed here as a possible alternative to thermal incineration for the disposal of hazardous organic waste liquids. The validity of this proposal depends on the fact that the toxicity of organic liquid wastes is caused mainly by compounds containing heteroatoms in their chemical structure. Hydroprocessing, while converting these heteroatoms into easily removable inorganics, also produces non-toxic recyclable organic chemicals. The paper analyzes in detail, on the basis of the available results reported in the literature, both the chemistry and the chemical kinetics of hydrotreating of the most representative heteroatom-containing compounds. It thus provides the basic tools for the design of future detoxification plants based on hydroprocessing. Both the kinetic analysis reported here and, what is more important, the concrete realization of the proposed detoxification method are made possible by the fact that hydroprocessing is a well known technology in the petroleum and petrochemical industries.

Introduction

Millions of tons per year of hazardous waste liquids are produced throughout the world. Their safe disposal is one of the primary concerns of an environment-conscious society. The most widespread disposal method for these wastes is high-temperature incineration; in many cases, however, this method demonstrates an inefficient use of resources as these liquids may have an intrinsic value.

If the liquid waste largely comprises organic chemicals which have a high heat content, it can be used as a fuel for the production of energy. Its combustion, however, may be risky if inappropriate technologies are used because combustion by-products even more toxic than the waste being burnt may be produced. It is known, for instance, that the combustion of relatively harmless chlorinated compounds can give rise to PCDF and PCDD – polychlorinated dibenzofurans/dibenzodioxins [1,2] – which are highly toxic. Even the use of waste fuel in cement kilns is not without hazard, as shown by Mix and Murphy [3].

An extensive technical overview of the technology required for the safe disposal of hazardous wastes in boilers and furnaces is reported by Castaldini et al. [4]. To assure the continuous and complete destruction (99.99%) of a hazardous chemical under the safest conditions, conservative design of the combustion process is necessary. This unfortunately results in complex and oversized combustion units. Furthermore, close (and therefore complex and costly) monitoring of the whole combustion facility may be required to continuously assure complete destruction. Any transient deviation from the optimal combustion conditions called for when conventional fuels are used may have dramatic consequences on the environment if a hazardous waste is being burnt.

An alternative method for disposal of hazardous waste is to detoxify it (and hopefully to transform it into recyclable products) by chemical processing. Processes which have for long been used for production in the petroleum and petrochemical industries could equally well be applied to the detoxification of wastes formed primarily from organic liquids. Furthermore, the existing knowledge of these processes would permit the rapid design and development of detoxifying plants.

The toxic nature of most organic hazardous wastes arises primarily from the presence of chemical compounds containing heteroatoms (chiefly Cl, N, O and S), in their chemical structure. Catalytic hydroprocessing would therefore be an appropriate method for detoxifying these wastes because the heteroatoms are eliminated by hydrogenolysis as HCl, NH₃, H₂O and H₂S respectively (which are easily controlled inorganic species), leaving the host compound non-toxic and frequently in a recyclable form.

Catalytic hydroprocessing, which has long been used in industry for hydro-refining petroleum, has reached a stage of great reliability and is continuously advancing due to the intensive research being carried out all over the world. Elimination processes, by hydrogenolysis, of N, O and S are better known as HDN (hydrodenitrogenation), HDO (hydrodeoxygenation) and HDS (hydrodesulfurization). By analogy, HDC represents the process of hydrodechlorination.

Kalnes and James [5] have successfully hydroprocessed some hazardous liquid organic wastes in a pilot plant, and have demonstrated the economic and environmental advantages of hydrotreatment compared with thermal incineration. However, they do not report information on the kinetics of the process and on the catalyst used. It is therefore not possible on the basis of their results to estimate reaction times and to attempt the design of the reactors.

Fortunately, much well established research on the chemistry and kinetics of hydroprocessing of a variety of chemical compounds is available in the literature, and could serve as a valuable guide to developing hydrotreatment of hazardous organic wastes. However, a unified kinetic analysis of the numerous kinetic results reported on hydrotreatment, which is essential for comparing the detoxification rates of the chemicals containing heteroatoms, is lacking.

The aim of this paper is to gather consistent data from the literature on hydroprocessing the most representative compounds containing heteroatoms, and to make an attempt to analyze them unitarily so as to obtain a better understanding of the kinetics of hydroprocessing of this class of compounds. The analysis, through the calculation of reaction times, will lead to a quantitative evaluation of the influence that the kind of heteroatom present in the host molecule has on the detoxification rates of most representative toxic heterocycles. The hydrogen consumption for their complete detoxification will also be calculated.

Hydrogenatability of compounds with heteroatoms

The degree of difficulty of removing heteroatoms by hydrogenolysis depends on both the heteroatom and the chemical structure of the host compound, and reflects the strength of the chemical bond C-X (X = Cl, N, O, or S) that keeps the atom in the host molecule. A general picture of the difficulty of eliminating heteroatoms from classes of organic compounds can be obtained by inspecting the value of the C-X bond strength. Tables of these values are reported in the handbook by Weast [6].

Aliphatic compounds

The value of the strength of C-X bonds for some representative aliphatic compounds are (in parentheses, in kcal mol⁻¹): CH₃SCH₃ (77.2); CH₃-Cl (85); CH₃-NH₂ (85); and CH₃-OH (92). Values not too different are reported for higher molecular weight aliphatics. For aliphatic compounds, the strength of the bond increases in the order: C-S < C-Cl ≈ C-N < C-O. This suggests that the difficulty of removing the heteroatoms by hydrogenolysis should increase in the same order.

Other less stable compounds (ketones, aldehydes, amides etc.) would be rapidly converted at the operating conditions of hydrotreating which are necessary for the removal of heteroatoms from more refractory compounds.

Substituted aromatic compounds

When the heteroatom is bound to an aromatic carbon atom, the strength of the C-X bonds are larger than those reported above. According to the data reported by Weast [6] for some substances representative of this class of compounds, the bond strength (in parentheses, in kcal mol⁻¹) is: C₆H₅-SH (86.5); C₆H₅-Cl (96); C₆H₅-NH₂ (102), C₆H₅-OH (111). The reported values indicate that the difficulty of removing the heteroatom is larger than for aliphatic compounds, and in this case also increases in the order: S < Cl < N < O.

Aromatic heterocycles

When the heteroatoms O, N and S (Cl is not considered here; the detoxification of halogenated aromatic compounds will be dealt with in a specific section) are included in an aromatic ring (five-membered or six-membered depending on the heteroatom) the strength of the chemical bond C–X is noticeably larger than those previously reported. The high stability of this class of compounds is, in fact, well known. It is not easy to find the value of the bond strength which keeps the heteroatom in the aromatic ring structure. The lower limit of this strength can be estimated with the following simple (even though approximate) reasoning. It is known that the high stability of the aromatic structure is due to the π electrons which by resonance enhance the strength of the C=X double bond. It may therefore be safely assumed that the strength of the aromatic C=X bond is larger than the strength of the C=X double bond in an aliphatic structure. On the basis of the values of the bond dissociation energy of aliphatic C=X double bonds reported by Roberts et al. [7], the lower limit of the aromatic C=X bond strength is (in parentheses in kcal mol⁻¹): C=S (128); C=N (147); C=O (192). Even in this case the likelihood is that the difficulty of removing heteroatoms (which necessarily requires ring opening) increases in the order: S < N < O.

The previous discussion allows us to conclude that heterocycles are the most refractory chemicals to be detoxified by hydrogenation. Therefore our kinetic analysis will focus on the HDS, HDN and HDO of heterocycles. Naturally, a reactor designed to get rid of this class of hazardous chemicals would easily eliminate heteroatoms from more unstable compounds.

Kinetics of hydrogenation of aromatic heterocycles

The removal of the heteroatom from a heterocycle is indirect because it requires the opening of the aromatic ring. Irrespective of the specific heteroatom, there are a few common reaction steps which depend primarily on the structure of the host compound.

Five-membered aromatic heterocycles

The number of reaction steps for the removal of the heteroatom increases with the complexity of the heterocycle. Detailed information on catalytic hydrogenation of these heterocycles is available in the literature. The following are particularly important (when necessary, for clarity, the heteroatom X is indicated):

- (1) Single pentatomic ring: thiophene (X=S; Nag et al. [8]); pyrrole (X=N; Stern, [9]); furan (X=O; Furimsky [10]).
- (2) Pentatomic ring coupled with a benzene ring: benzothiophene [8]; indole [9]; benzofuran [10].
- (3) Pentatomic ring between two benzene rings: dibenzothiophene (Houalla

et al. [11]); carbazole (Sowiak [12]; Sarbak [13]); dibenzofuran (Krishnamurthy et al. [14]).

Inspection of the above papers shows that the highest complexity of the reaction network (in respect of the removal of the heteroatom) seems to be reached for compounds having the pentatomic ring between two benzene rings. Thus, for any choice of heteroatom, the reaction behavior of this structure is considered to be representative of that of any other five-membered ring heterocycle with the same X. To describe the reaction network for the catalytic hydrogenation of five-membered aromatic heterocycles, we will refer to the compound of Fig. 1 (carbazole if X=N; dibenzothiophene if X=S; dibenzofuran if X=O. Correspondingly, XH_n represents NH_3 , H_2S or H_2O).

The reaction network of Fig. 1 represents the hydrogenation of the model heterocycle **1** in the most general case. The principal intermediates which may form during the hydroprocessing of **1** are indicated in the same figure. To describe the kinetics of the overall reaction process, a few of these intermediates can be grouped in the boxed categories. All reactions, as determined experimentally, can be considered to be first order (see the results discussed below).

The differences among the actual reaction networks of specific heterocycles (compound **1** with X=S, N, or O) will be due to different relative values of the kinetic constants k_{xij} . These will make some of the branches of the network of Fig. 1 more or less relevant for an individual heterocycle. Quantitative information on the hydrogenation of the specific heterocycles can be found in papers by Houalla et al. [11], for dibenzothiophene (X=S), Sowiak [12] for car-

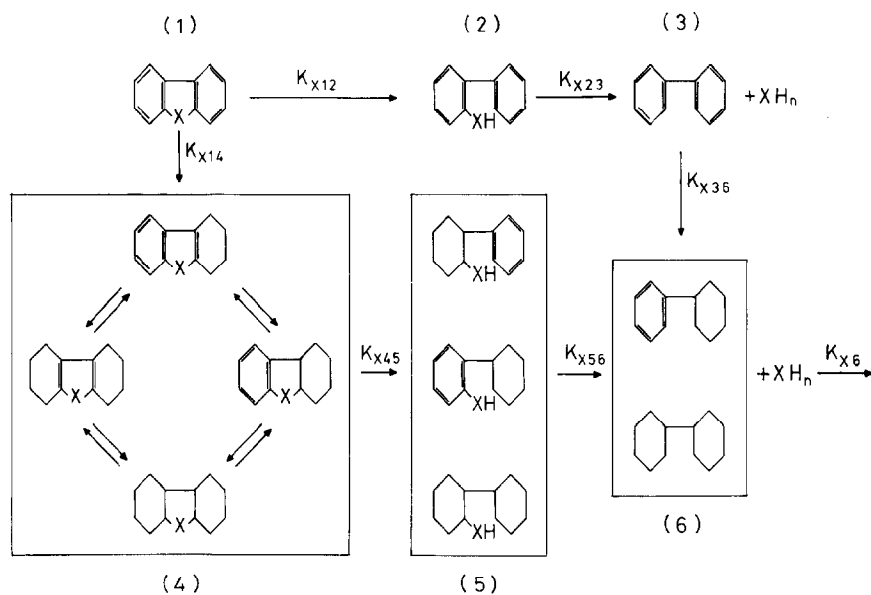


Fig. 1. Reaction network of the hydroprocessing of heterocycle **1** (general case)

bazole (X=N) and Krishnamurthy et al. [14] for dibenzofuran (X=O). The discussion of these authors in the light of the unified network of Fig. 1 will be based on the definitions reported in the Appendix.

To make the results uniform, the values of the kinetic constants k_{xij} have all been expressed (if differently reported) in the units: (g of solution)/(g of catalyst-min). Moreover, results based on runs carried out at the most nearly similar operating conditions are considered (particularly the temperature as it is the parameter with the strongest influence of the kinetic constant). Unfortunately, for dibenzofuran and carbazole, only in the work of Krishnamurthy et al. [14] and Sowiak [12] were runs carried out at almost the same temperature ($T=365^{\circ}\text{C}$ and 367°C). For dibenzothiophene, due to its greater reactivity, only data obtained at 300°C are available in the paper by Houalla et al. [11]. When necessary, the Arrhenius law will be used for reducing kinetic constants to a common temperature.

Dibenzothiophene (X=S)

Conditions used by Houalla et al. [11] were: catalyst: Co-MoO₃/γ-Al₂O₃; temperature: 300°C ; H₂ pressure: 103 bar.

Under these experimental conditions the following intermediates are not detected at all: *o*-phenylthiophenol (compound **2** of Fig. 1), 2-phenylcyclohexane-1-thiol, *o*-cyclohexylthiophenol and 2-cyclohexylcyclohexane-1-thiol (compounds grouped in box **5**). Furthermore, of the compounds grouped in box **4** only 1,2,3,4,-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene are detected (in trace amounts).

The absence of the cited intermediates implies the following relative values of the kinetic constants:

$$k_{S23} \gg k_{S12}; k_{S56} \gg k_{S45} \quad (1)$$

Inequalities (1) imply that the reaction network of Fig. 1 can be reduced to the three reactions: **1** → **3**, **3** → **6** and **1** → **6** (via compounds **4**).

Furthermore [11] at $T=300^{\circ}\text{C}$ and $p_{\text{H}_2} = 103$ bars (values in g of solution/g of catalyst-min):

$$k_{S13} = 1.34 \quad (2a)$$

$$k_{S14} = 2.1 \times 10^{-3} \quad (2b)$$

$$k_{S36} = 0.23 \quad (2c)$$

$$k_{S46} = 5.28 \quad (2d)$$

that is:

$$k_{S13} > k_{S36}; k_{S13} \gg k_{S14} \quad (3)$$

Inequalities (3) suggest that the reaction network for HDS of dibenzothiophene can be further simplified to the single reaction **1** → **3**.

The principal product of the process (apart from H_2S) is biphenyl. Only at longer reaction times are cyclohexylbenzene and bicyclohexyl produced, and yields are low.

The hydrogen consumption is 2 mol of H_2 per mol of dibenzothiophene desulfurized.

Information of the HDS of sulfur heterocycles with a more complex structure (benzo[*b*]naphtho[2,3-*d*]thiophene and 7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene) is reported by Nag et al. [8] for a Ni-Mo/ γ - Al_2O_3 catalyst and at $T=300^\circ\text{C}$ and $p_{\text{H}_2}=71$ atm.

Dibenzofuran (X=O)

Krishnamurthy et al. [14] used the conditions: catalyst: Ni-Mo/ γ - Al_2O_3 ; temperature: 343, 365, and 376°C ; H_2 pressure: 103 bar.

The intermediate *o*-phenylphenol (compound **2**) and those grouped in box **5** (2-phenylcyclohexan-1-ol, *o*-cyclohexylphenol and 2-cyclohexylcyclohexan-1-ol) are not detected. Also, among the compounds of box **4**, only 1,2,3,4-tetrahydrodibenzofuran is detected (in trace quantities), thus implying:

$$k_{\text{O}56} \gg k_{\text{O}45} \gg k_{\text{O}14} \quad (4)$$

Therefore, the reaction network can be simplified to the three parallel reactions $1 \rightarrow 3$, $3 \rightarrow 6$ and $1 \rightarrow 6$ (via compounds **4**). Furthermore, since:

$$k_{\text{O}16} > k_{\text{O}13}; k_{\text{O}36} > k_{\text{O}13} \quad (5)$$

it follows that the principal deoxygenated organic products of the HDO of dibenzofuran are the compounds of box **6** (as opposed to the HDS of dibenzothiophene). The process takes place prevalently through the reaction $1 \rightarrow 6$.

In particular, at $T=365^\circ\text{C}$ and $p_{\text{H}_2}=103$ bar, Krishnamurthy et al. [14] report:

$$k_{\text{O}13} = 0.028 \quad (6a)$$

$$k_{\text{O}16} = 0.077 \quad (6b)$$

$$k_{\text{O}36} = 1.633 \quad (6c)$$

The hydrogen consumption, based on the reported deoxygenated product distribution (about 50% of bicyclohexyl and 50% of cyclohexylbenzene, besides the H_2O), is about 5.5 mol of H_2 per mol of dibenzofuran converted.

Carbazole (X=N)

Conditions used by Sowiak [12] were: catalyst: Ni-Mo/ γ - Al_2O_3 ; temperature: 367°C ; H_2 pressure: 34, 69 and 138 bar.

The intermediate **2** (*o*-phenylaniline) and those grouped in box **5** (2-phenylcyclohexylamine, *o*-cyclohexylaniline and 2-cyclohexylcyclohexylamine) are not detected; biphenyl is observed in trace amounts. Among the intermediates

of box 4, mainly 1,2,3,4-tetrahydrocarbazole is detected. This compound rapidly achieves equilibrium with carbazole. The equilibrium, at the operating conditions explored, is well shifted toward the hydrogenated form. The compounds of box 6 together with some lighter hydrocarbons (LH) are reported to be the principal denitrogenated products.

It may be assumed, therefore, that the HDN of carbazole is well represented by the consecutive reactions $1 \rightarrow 4$ and $4 \rightarrow 6$. The reaction $6 \rightarrow \text{LH}$, (LH is mainly cyclohexane) also takes place to some extent. The presence of these lighter compounds is not relevant in the HDS and HDO processes previously described.

In particular, at the operating conditions $T = 367^\circ\text{C}$ and $p = 69$ bar, Sowiak [12] reports:

$$k_{N13} = 0.12 \quad (7a)$$

$$k_{N14} = 6.06 \quad (7b)$$

$$k_{N46} = 4.12 \quad (7c)$$

Hydrogen consumption ranges between 7.5 and 9.5 mol of H_2 per mol of carbazole converted, the denitrogenated products being essentially (other than NH_3) bicyclohexyl and cyclohexane (arising from cracking of bicyclohexyl and cyclohexylbenzene).

Qualitatively similar results are reported by Sarbak [13]; it is not possible, however, to obtain quantitative kinetic information from this work as the k' kinetic constants are reported but the operating ratio W_c/W_L is not given.

In concluding this section, it is worth pointing out that the hydrogen consumption for the removal of the heteroatom increases in the direction $\text{S} \rightarrow \text{O} \rightarrow \text{N}$.

Comparison of rates of removal of heteroatoms in HDS, HDO and HDN of five-membered aromatic heterocycles

As shown in Fig. 1, the main reaction steps of the catalytic hydrogenation which lead to the removal of the heteroatom may be grouped into three categories: the first (branch $1 \rightarrow 3$ of Fig. 1) includes the reactions resulting in the direct extrusion of the heteroatom; the second comprises a few parallel reactions (having overall kinetic constant k_{X14}), which are representative of the saturation of aromatic rings; the third includes the reactions (with overall kinetic constant k_{X46}) which lead to the removal of the heteroatom from saturated (or partially saturated) aromatic rings.

On the basis of the previous results it is possible to draw a few general conclusions on the chemistry and kinetics of HDS, HDO and HDN of five-membered aromatic heterocycles.

Firstly, it should be noted that the branch $1 \rightarrow 3$ is relevant, and indeed dominant, only for HDS. Due to the relatively low value of the $\text{C}=\text{S}$ bond energy, there are catalysts able to activate a primary extrusion of sulfur from the host compounds as a predominant reaction without requiring a preliminary satu-

ration of the aromatic structure. The rate of HDO, on the contrary, is determined primarily by route $1 \rightarrow 6$ because route $1 \rightarrow 3$ has slower kinetics.

The situation is completely reversed (in relation to sulfur) when nitrogen is considered. In fact, the reaction steps included in route $1 \rightarrow 3$ do not take place to any appreciable extent. The existing catalyst is not able to activate a primary extrusion of N from the heterocycle. The removal of this heteroatom (which takes place essentially through the pattern $1 \rightarrow 6$) requires as a prerequisite the hydrogenation (even though partial) of the aromatic rings so as to weaken the strength of the C=N bond, thus making its rupture possible.

It is of interest to make a quantitative comparison of the rates of the HDS, HDO and HDN processes. HDS reduces essentially to the first order reaction $1 \rightarrow 3$, HDO to the two first order parallel reactions $1 \rightarrow 3$ and $1 \rightarrow 6$ and HDN to the two consecutive reactions $1 \rightarrow 4$ and $4 \rightarrow 6$ having rate constants of similar magnitude.

The overall rates of the three reaction processes above can be compared by calculating the reaction times as defined in the Appendix.

To make the comparison consistent, k_{S13} [eqn. (2a)] must be reduced to 365°C by means of the Arrhenius equation. The activation energy may be assumed to be 30 kcal mol⁻¹ [15]. It follows that:

$$k_{S13} = 19.63 \text{ at } 365^\circ\text{C} \quad (8)$$

We will assume that inequalities (3) also hold true at 365°C, so that the HDS of dibenzothiophene is still represented by the single reaction $1 \rightarrow 3$.

Using eqns. (A.6) and (8) for the HDS of dibenzothiophene, eqn. (A.6) and the values of eqns. (6a) and (6b) for the HDO of dibenzofuran, and eqn. (A.10) and the values of eqns. (7b) and (7c) for the HDN of carbazole we calculate the reaction time values (in min):

$$t_{\text{HDS}} = 0.05 (W_L/W_C) \quad (9a)$$

$$t_{\text{HDO}} = 9.50 (W_L/W_C) \quad (9b)$$

$$t_{\text{HDN}} = 0.43 (W_L/W_C) \quad (9c)$$

Actually, the hydrogen pressure on which eqn. (9c) is based is about 30% smaller than for eqns. (9a) and (9b). This difference can, however, be ignored because the pressure does not have as strong an influence on rates as the temperature does.

Equations (9) show clearly that (at equal W_L/W_C ratios), for the case of pentatomic heterocycles, the HDO process is much slower than those of HDS and HDN.

HDN of six-membered aromatic heterocycles

The HDN of these compounds takes place through a large number of reaction steps and requires severe hydrotreating conditions. In short, to remove

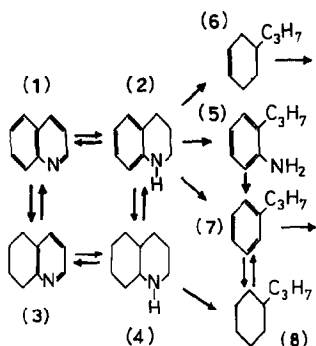


Fig. 2. Reaction network for the HDN of quinoline.

the nitrogen atom from the aromatic ring, a complete saturation of the ring is necessary to weaken the strength of the C=N bond.

As a good example, we will discuss in detail the HDN of quinoline. The reaction of this compound to hydrotreating is representative of the nitrogen six-membered aromatic heterocycles. We will refer to the results of Gioia and Lee [16]. The reaction network as identified by these authors is reported in Fig. 2.

Inspection of Fig. 2 shows that, before the nitrogen heteroatom is eliminated (as NH_3) from the host molecule, extensive hydrogenation at least of the benzenoid ring containing this atom must take place. The kinetics of the process can be described as follows.

Quinoline

Gioia and Lee [16] used the conditions: catalyst: Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$; temperature: 350°C; H_2 pressure: ten values ranging from 10.5–151.6 bar.

At the largest pressures ($p_{\text{H}_2} > 80$ bar, for example) the relative values of the kinetic constants are such that the kinetics of nitrogen removal are limited (with reference to Fig. 2) by the parallel reactions $2 \rightarrow 6$ and $2 \rightarrow 7$ and by the consecutive reactions $2 \rightarrow 4 \rightarrow 8$.

In particular, at $P_{\text{H}_2} = 100$ bar and $T = 350^\circ\text{C}$, Gioia and Lee report:

$$k_{26} = 1.35 \quad (10a)$$

$$k_{27} = 0.57 \quad (10b)$$

$$k_{24} = 4.0 \quad (10c)$$

$$k_{48} = 12.0 \quad (10d)$$

A further approximation is possible. The relative values of rate constants k_{24} and k_{48} are such that reaction $2 \rightarrow 4$ may be considered limiting with respect

to **4**→**8**. In fact, the ratio between the reaction time obtained by applying eqn. (A.10) to the reactions **2**→**4**→**8** and that obtained by applying eqn. (A.6) to the single reaction **2**→**4** (considered limiting) is 1.4.

Therefore, on the hypothesis that the reactions **2**→**4**→**8** can be approximated to the single reaction **2**→**8**, having the rate constant $k_{28}=k_{24}$ the reaction time of the HDN of quinoline can be calculated from eqn. (A.6) and is (in min):

$$t_{\text{HDN}} = [1/(1.35 + 0.57 + 4.0)] (W_L/W_C) = 0.17 (W_L/W_C) \quad (11)$$

According to the results of Gioia and Lee [16] at the largest hydrogen pressures, the hydrogen consumption, for complete denitrogenation, is about 8 mol of H₂ per mol of quinoline.

Studies on the HDN of other specific six-membered heterocycles are available in the literature. In particular, the HDN of pyridine (one six-membered ring) has been studied by McIlvried [17] and by Sarbak [18]. The HDN of heterocycles more complex than quinoline has been studied by Bhide et al. [19], who report on acridine, and by Shabtai et al. [20], who report on the HDN of 5,6-benzoquinoline.

For all these other compounds, however, the principal reaction steps during HDN are essentially analogous to those for quinoline.

Hydrogenation of halogenated aromatic compounds

Unlike the HDS, HDO and HDN processes, the catalytic HDH (hydrodehalogenation) of aromatic compounds has not been extensively studied. In fact, detailed information on the kinetics of HDH is not available in the literature. In particular, neither the reaction networks nor the rate constants of the overall HDH process for any aromatic halogenated compounds are known.

The feasibility of catalytic hydrogenation for the detoxification of these compounds, some of which are particularly toxic, can be evaluated on the basis of the results of Hagenmaier et al. [21]. These authors have studied the catalytic effect of copper on the decomposition of some polychlorinated aromatics: octachlorodibenzo-*p*-dioxin (octaCDD), octachlorodibenzofuran (octaCDF), hexachlorobenzene and decachlorobiphenyl, and of some aromatics containing bromine: octabromodibenzodioxin and octabromodibenzofuran.

The compounds whose dechlorination Hagenmaier et al. consider in most detail are octaCDD and octaCDF. The dechlorination experiments were carried out in test tubes at different temperatures (in the range 150–300°C) and for different reaction times (1, 5 and 30 min) in the absence of hydrogen. The authors assume that the hydrogen necessary for the reaction is supplied by the water in the air present in the reaction vessel.

Relevant information reported in Ref. [21] is that the removal of chlorine atoms from PCDD and PCDF takes place gradually: thus, at intermediate re-

action times, the presence of lower chlorinated PCDD and PCDF is detected. By reaction of either octaCDD or octaCDF, the lower chlorinated compounds present at intermediate times are tetra- to octaCDD or tetra- to octaCDF.

The results of Hagenmaier et al. [21] concerning the kinetics of decomposition are largely qualitative. A few quantitative results are, however, reported which make it possible to obtain an estimate of the kinetic parameters of dechlorination of octaCDD and octaCDF so that the rates of the dechlorination process and the rates of the HDS, HDO and HDN of heterocycles may be compared.

Octachlorodibenzodioxin and octachlorodibenzofuran

Hagenmaier et al. [21] used as catalyst copper metal, and their W_L/W_C ratio was 1.6 (g/g). They report the following reaction times at $T=285^\circ\text{C}$.

- Reactant octaCDD: after 1 min, less than 1% of the octaCDD remains as tetra- to octaCDD.
- Reactant octaCDF: after 1 min, about 6% of the octaCDF remains as tetra- to octaCDF.

These figures, assuming that the overall dechlorination process is first order, permit the calculation of the kinetic constant k' (min^{-1}) by means of eqn. (A.4) and then the kinetic constant k (g solution/g catalyst-min) by eqn. (A.5) ($W_L/W_C=1.6$) for the dechlorination of the compounds under consideration.

In particular, for octaCDD, it follows that:

$$k_{\text{DCD}} = 7.4 \quad (12)$$

and for octaCDF

$$k_{\text{DCF}} = 4.5 \quad (13)$$

The reaction times (min) calculated by eqn. (A.6) are for octaCDD:

$$t_{\text{rDCD}} = 0.14(W_L/W_C) \quad (14a)$$

and for octaCDF:

$$t_{\text{rDCF}} = 0.22(W_L/W_C) \quad (14b)$$

Comparing eqns. (14) with eqns. (9) and (11) it appears that (with the operating conditions adopted by Hagenmaier et al.) the rate of HDC of polychlorinated dibenzodioxins and of polychlorinated dibenzofurans is of the same order of magnitude as the rates of HDS and HDN of heterocycles. In reality, the HDC rate will be larger because the results leading to eqns. (14) are based on runs at 285°C , lower than those on which eqns. (9) and (11) are based.

Other relevant information reported by Hagenmaier et al. [21] is that the final products of the dechlorination reaction are neither the dibenzo-*p*-dioxin nor the dibenzofuran to which the chlorine atoms were attached. Thus, attack of the host molecule takes place during the process.

It can be inferred that the reaction network of polychlorinated dibenzodioxins and polychlorinated dibenzofurans is particularly complex, inasmuch as the reaction steps for the removal of chlorine atoms are accompanied by attack on the dibenzodioxin or dibenzofuran molecule. Presumably this attack, as far as dibenzofuran is concerned, takes place according to the reaction network of Fig. 1. At any rate, the previous result seems to indicate that the limiting step for the *complete* detoxification of polychlorinated dibenzofurans (and, perhaps, of polychlorinated dibenzodioxins) is the destruction of the dibenzofuran molecule rather than the removal of chlorine. This is consistent with the fact that the strength of the C-Cl bond is less than that of the C=O bond in the aromatic ring. Presumably the hydrogen consumption (for PCDF) necessary for both dechlorination and deoxygenation must be larger than that for the HDO of dibenzofuran; i.e., if we call N_{Cl} the number of chlorine atoms in the molecule, the hydrogen consumption may be estimated as: $\approx (5.5 + N_{Cl}/2)$ mol H_2 per mol of PCDF dechlorinated and deoxygenated. For PCDD no estimate is possible, as to the best of our knowledge, the reaction network of the deoxygenation of dioxins is unknown.

To conclude this section it must be pointed out that all processes of heteroatom removal by hydrogenolysis have rates which increase with hydrogen pressure (see, e.g., Ref. [16] for HDN). It may be expected, therefore, that the reaction times of eqn. (14) (based on results of experiments in the absence of hydrogen gas) may decrease if the reaction process takes place in the presence of hydrogen. Better kinetic results could also be expected if more appropriate catalysts than the simple copper metal adopted by Hagenmaier et al. [21] were used.

Conclusions

The above analysis has shown that aromatic heterocycles are the most refractory chemicals to be detoxified. Both the difficulty in the removal of the heteroatom from these compounds and the hydrogen consumption depend on the kind of heteroatom and on the structure of the host compound.

A quantitative kinetic analysis based on reaction networks and rate constants, obtained from a careful search of the literature, has permitted a comparison of the rates of the HDC, HDN, HDO, and HDS for some model heterocycles whose reaction behavior can be assumed to be representative of the kinetics of hydrogenation. The model compounds have been chosen as those whose reaction network, with specific reference to the removal of the heteroatom, shows the greatest complexity. We conclude from the results of the analysis that the expected removal rates are in the order: $HDO \ll HCD \approx HDN < HDS$ (HDC refers only to the removal of Cl atoms; the destruction of the eventual furan or dioxin molecule on which these atoms are attached is a HDO case). Correspondingly, the hydrogen consumption in-

creases in the order: HDS → HDO → HDN; for HDC the consumption depends on the number of Cl atoms present on the host molecule and is in a molar ratio 1:1.

The above progression on the rates of detoxification of heterocycles has been primarily attributed to the different strengths of the bonds between the carbon atom and the heteroatom. For example, due to the comparatively low C=S bond strength, the available catalysts are able as a predominant reaction to activate a primary extrusion of sulfur from the host compounds. In contrast, the removal of different heteroatoms showing a larger value of bond energy requires a preliminary saturation of the aromatic structure, which promotes a weakening of the bond strength between the heteroatoms and the carbon and makes the bond rupture possible. Consequently, hydrodesulfurization requires the minimum quantity of hydrogen compared with that required for the hydroremoval of other heteroatoms from similar host compounds.

The results of the kinetic analysis of the detoxification of polychlorinated dioxins and furans are based on a few, fragmentary data. Although investigations on HDO, HDN, HDS processes are numerous and advanced, this is not true for hydrotreating of these compounds. As these compounds are known to be among the most toxic and difficult chemicals to dispose of, there is an increasing need for research to be carried out on their hydrodetoxification.

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Appendix

In experiments such as those discussed above, the reaction rate r_i is defined as moles of reactant i converted per unit mass of catalyst and per unit time; i.e.

$$r_i = (1/W_C) (dn_i/dt) \quad (\text{A.1})$$

where W_C is the mass of catalyst loaded into reactor.

Because i is made to react diluted in a mass W_L of inert solvent, eqn. (A.1) (as usually $W_L/W_i \gg 1$) can be written as:

$$r_i = (W_L/W_C) (dC_i/dt) \quad (\text{A.2})$$

where C_i is the concentration of i as moles per unit mass of solvent (or, which is the same, of solution). Correspondingly, the first order kinetic equation is written as:

$$r_i = -k_i C_i \quad (\text{A.3})$$

where k_i is a kinetic constant with the dimensions (mass of solution)/(mass of catalyst-time). Combining eqns. (A.2) and (A.3) we obtain:

$$dC_i/dt = -k'_i C_i \quad (\text{A.4})$$

where

$$k'_i = (W_C/W_L) k_i \quad (\text{A.5})$$

k'_i has the units 1/time.

It must be noted that:

- (1) The constant k_i is strictly representative of the activity of the catalyst.
- (2) The constant k'_i , which also includes the ratio W_C/W_L , is representative of the rate of the reaction as taking place (for a given catalyst) at the operating value of W_C/W_L .

Comparisons of kinetic results from different experiments are consistent when based on k_i constants, which are independent of the operating ratio W_C/W_L .

Unfortunately, sometimes the constants k'_i are reported in the literature without specifying the ratio W_C/W_L thus rendering the investigation useless for reactor design purposes.

Reaction time

When, as in the present case, reaction processes are composed of many steps (parallel and/or consecutive reactions), a comparison of their overall rates may be consistently performed by resorting to the reaction time t_r , which is a measure of the time necessary for the reactions to accomplish an assigned chemical change. If ϕ is the destruction ratio (defined as the ratio between the moles of heterocycle converted to compounds free of heteroatom and the initial moles of heterocycle) at any time t , the reaction time may be defined as the time necessary for the reaction(s) to achieve the assigned change of concentration ϕ .

Reaction times can be easily calculated by integration of rate equations such as eqn. (A.4). Setting for convenience $\phi = 1 - e^{-1}$, the following equations are obtained for the cases of interest here.

Parallel reactions

The heterocycle is transformed into products free of heteroatoms through n parallel first order reactions with 1:1 stoichiometry. The reaction time t_r is then:

$$t_r = \left(\sum_{i=1}^n k'_i \right)^{-1} \quad (\text{A.6})$$

which, by using eqn. (A.5), can also be written as:

$$t_r = \left[(W_C/W_L) \sum_{i=1}^n k_i \right]^{-1} \quad (\text{A.7})$$

Consecutive reactions

The heterocycle is transformed to products free of heteroatom through two first order consecutive reactions having kinetic constants k'_1 and k'_2 (the in-

termediate, produced with 1:1 stoichiometry, is a compound still containing the heteroatom). Naturally, the most interesting situation exists when the reactions have comparable kinetic constants; otherwise the rate of the overall process is limited by the reaction having the smallest rate constant (the other reaction being considered at equilibrium). Then, writing

$$k_1 = k' \quad (\text{A.8})$$

$$k_2 = k'(1 + \delta) \quad (\text{A.9})$$

The reaction time t_r (for $\phi = 1 - e^{-1}$) is given by the implicit equation:

$$e^{-1} = [1 + \delta]/\delta \exp(-k't_r) - (1/\delta) \exp[-k'(1 + \delta)t_r] \quad (\text{A.10})$$

In the special case that the two reactions have equal rate constants

($\delta = 0$), eqn. (A.10) becomes:

$$e^{-1} = (1 + k't_r) \exp(-k't_r) \quad (\text{A.11})$$

which gives:

$$t_r = 2.14/k' \quad (\text{A.12})$$

Making use of eqn. (A.5), eqn. (A.12) becomes

$$t_r = 2.14 / [(W_C/W_L)k] \quad (\text{A.13})$$

Notation

C_i	concentration of compound i ; mol/g of solution
k	first order kinetic constant for a catalytic reaction, see eqn. (A.3); g of solution/(g of catalyst·min)
k'	true first order kinetic constant, see eqn. (A.5); min^{-1}
k_{ij}	kinetic constant of the reaction leading from organic compound i to product j in the reaction network of the HDN of quinoline; g of solution/(g of catalyst·min)
k_{Xi}	kinetic constant of the reaction leading from organic compound i to product j in the reaction network of the heterocycle containing the heteroatom X; g of solution/(g of catalyst·min)
PCDF	polychlorinated dibenzofurans
PCDD	polychlorinated dibenzo- <i>p</i> -dioxins
r_i	reaction rate; moles of reactant i converted per unit mass of catalyst and per unit time.
t_r	reaction time; min
W_C	mass of catalyst loaded in the reactor; g
W_L	mass of solution in the reactor; g

Greek symbols

ϕ	destruction ratio: ratio between the moles of heterocycle converted to compounds free of heteroatom and the initial moles of heterocycle, at any time t
δ	see eqn. (A.9)

Subscripts

DCD	dechlorination of dibenzodioxin
DCF	dechlorination of dibenzofuran
HDC	hydrodechlorination
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
i	compound i
X	heteroatom: X = O, S or N