

Catalytic hydrodechlorination of 1,2,3-trichlorobenzene

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Abstract

Detoxification by catalytic hydrotreatment can be a valid alternative to thermal incineration for the disposal of hazardous organic waste liquids. With this aim, the hydrodechlorination of 1,2,3-trichlorobenzene on a Ni-Mo/ γ -Al₂O₃ catalyst has been investigated experimentally and theoretically. The behaviour of this chemical in hydrotreatment is hopefully representative of that of many toxic chlorinated compounds. The experimental reaction runs were conducted in a stirred batch reactor in the presence of hydrogen, at constant pressure ($p_{\text{H}_2} = 100$ bar), and using hexadecane as a reaction medium. The temperature, kept constant during each run, was varied in the range $200^\circ\text{C} \leq T \leq 350^\circ\text{C}$. The experimental results consisting of concentrations of reactant, reaction products and intermediates vs. time, permit the identification of the reaction network and its modification with temperature. The kinetic constants (and their temperature dependence) of the reactions which form the network are also determined.

1. Introduction

The threat posed to the environment by hazardous wastes, means there is an increasing need for research to be carried out on safe methods for their disposal. The present paper focuses on hazardous waste liquids formed mostly by organic chemicals. As discussed by Gioia [1], catalytic hydrogenation could be a possible alternative method for the disposal of such hazardous liquids. In fact, the toxic nature of most organic waste liquids is due primarily to the presence of chemical compounds containing heteroatoms (primarily 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 or H₂S (which are easily controlled inorganics), leaving the host compound non-toxic and frequently in a recyclable form.

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A great deal of research has been devoted to hydroprocessing. However, the most comprehensive results have been produced keeping in mind the upgrading of petroleum fractions and coal-derived liquids. Therefore, attention has been focused mostly on catalytic hydrotreatment of N-, O- and S-containing heterocycles (very refractory compounds). Naturally, the results of these investigations can also be used to design processes aimed at the detoxification of hazardous organic waste liquids containing such heteroatoms [1]. Unfortunately, however, catalytic hydrodehalogenation has not received comparable attention because the presence of chlorine-containing (or, in general, halogen-containing) chemical compounds in petroleum and in coal-derived liquids is a minor problem. Yet the presence of these compounds plays a fundamental role in the toxicity of organic waste liquids.

The problem of hydrodehalogenation has been dealt with in the literature with reference to both thermal and catalytic processes, even though to a limited extent. Louw et al. [2–4] have investigated the thermal hydrodechlorination of a variety of chlorinated compounds, both aliphatic and aromatic. These investigations provide the attainable conversion of chlorinated compounds for a given residence time and a number of temperature values. The experiments, all run in the gas-phase, show that dechlorination takes place to an appreciable extent in the temperature range 700–1000 °C. On the basis of the kinetic results, the authors speculate on the mechanism of elimination of chlorine from the host molecule.

Catalytic hydrodehalogenation, which could be more attractive due to the lower operating temperatures required, has also received some attention in the literature. Hagenmaier et al. [5] have studied the catalytic effect of copper on the decomposition (in the absence of H₂ gas) of some polychlorinated aromatics (octachlorodibenzo-*p*-dioxin (octaCDD), octachlorodibenzofuran (octaCDF), hexachlorobenzene, decachlorobiphenyl) and of some aromatics containing bromine (octabromodibenzo-*p*-dioxin, octabromodibenzofuran)). For many of these compounds the results are qualitative. Some quantitative results, though limited, are provided by Hagenmaier et al. [5] on the dechlorination of octaCDD and octaCDF. However, no information is provided on the reaction network.

Hiroaka et al. [6] have investigated the destruction of polychlorinated dibenzo-*p*-dioxins (PCDDs) in the gas phase. They provide results on the destruction (%) vs. temperature either with or without catalyst (Pt-supported). The temperatures to obtain appreciable destructions range between 700 and 900 °C without a catalyst and between 200 and 400 °C with a catalyst. No information is provided on the reaction network.

Mâthé et al. [7] describe the catalytic hydrodehalogenation of a few chlorobenzenes using a Pd-supported catalyst. The reaction intermediates are identified. However, the results must be considered as qualitative inasmuch as the kinetics of the process were not analyzed. On the other hand, the results of Mâthé et al. [7] cannot be used to evaluate the kinetic constants of the dechlorination reactions, inasmuch as some of the necessary operating conditions are not provided (e.g. the weight of catalyst).

Because catalytic hydroprocessing of halogenated organics seems to be particularly suited for the destruction of such compounds, an increased effort in fundamental research on this topic would be valuable. The catalytic hydroprocessing of model chlorinated compounds (the most representative ones) should be investigated in detail.

The present paper follows this line of research. The catalytic hydrodechlorination of the model compound 1,2,3-trichlorobenzene has been investigated using a commercial Ni-Mo/ γ -Al₂O₃ catalyst. The study has been accomplished in the liquid phase because attention is focused on the detoxification of liquid organic wastes. The results of the present work provide an advancement over those of previous investigators inasmuch as for the first time all reaction products and intermediates have been identified and linked quantitatively in a complex network. Furthermore, the influence of temperature on the kinetic parameters of the reactions entering the network has been determined. The choice of 1,2,3-trichlorobenzene was made on the assumption that its behaviour in hydroprocessing can be considered to be representative of the upper bound of difficulty in hydrodechlorinating organic compounds. In fact, the C₆H₅-Cl bond is the strongest among the most usual organic chlorinated compounds [8].

2. Experimental procedure

The reaction was run in a batch reactor, a 300 ml autoclave with magnetic stirring (Autoclave Engineers), equipped with a sampling line of the liquid mixture and a catalyst loader (a small stainless steel cylindrical vessel) connected to the autoclave by a globe valve.

The main features of the apparatus and of the experimental procedure are as follows. A weighed amount (about 175 ml) of hexadecane (the reaction medium) is loaded into the autoclave and heating is started. At the end of the heating period, the catalyst is put into the loader together with the trichlorobenzene (the reactant) and another known amount of hexadecane (about 25 ml). Then the loader is assembled and connected to the autoclave. When the set temperature is reached the loader is pressurized, and the reactant and catalyst are injected into the autoclave by opening the globe valve. The set temperature of the heating period is about 10°C higher than the set temperature for the run, in order to take into account the temperature drop due to loading the cool reactant and catalyst. Immediately after injection, the pressure and temperature are precisely adjusted to the desired values. This is taken as the zero time of the reaction run. During the run both pressure and temperature are kept constant.

Liquid phase samples, averaging about 1.5 ml each, were then periodically collected, with the first sample taken just before the injection operation to check for the hexadecane decomposition products. The sampling line was flushed before each sampling (line volume < flush volume \approx 1.5 ml). A porous

seal at the opening of the sampling line inside the autoclave prevented loss of catalyst. Sampling frequency was adapted to the rate of trichlorobenzene disappearance. It decreased with time and increased with increasing temperature. Table 1 lists the materials used.

The samples were analyzed by GC-FID (Perkin Elmer 8500) equipped with a capillary column (crosslinked methyl silicone; 50 m long). The following chemical species were identified in the reaction samples; they are reported in order of increasing elution time: benzene (b; **5**); chlorobenzene (cb; **4**); 1,3-dichlorobenzene (1,3-dcb; **3**); 1,2-dichlorobenzene (1,2-dcb; **2**); 1,2,3-trichlorobenzene (tcb; **1**). Throughout the rest of the paper, compounds will be identified by means of either the short notation or bold face numbers, as reported in parentheses.

The experimental conditions of the reaction runs are reported in Table 2. Run 1, at 200 °C with catalyst, showed no appreciable reaction taking place, i.e. the conversion of tcb after 450 min was only 1.8%. The blank run 2 (without catalyst) at 350 °C was intended to check on the catalytic activity of the reactor walls. The results of this run showed that some reaction indeed took place, but

TABLE 1

Materials

Reaction medium	hexadecane (Aldrich Co.); vapour pressure at 350 °C \approx 3.24 bar
Reactants	1,2,3-trichlorobenzene, 98% (Aldrich Co.); the initial concentration ranged between 1.91 and 3.13 wt% Hydrogen GC grade, 99.999% (SIO ALPHAGAZ); the total pressure was the same for all runs and equalled 100 bar; the p_{H_2} was then dependent on the hexadecane vapour pressure at the temperature of the run; i.e. $96.76 \leq p_{H_2} \leq 99.9$. We will assume $p_{H_2} \approx 100$ bar
Catalyst	HDS-9A (American Cyanamid); ground and sieved 150-200 mesh. The slurry concentration in the reactor ranged between 0.5 and 0.63 wt%

TABLE 2

Experimental conditions for the runs ($p_{H_2} = 100$ bar)

Run no.	T (°C)	W_R (g)	W_C (g)	W_L (g)	Run time (min)
1	200	3.01	0.794	157.6	450
2	350	5.00	0	159.6	450
3	350	5.01	1.060	167.3	435
4	320	5.00	0.936	159.6	450
5	290	5.05	0.896	167.4	450

its extent could be neglected in the runs with catalyst. This point will be discussed further.

Figure 1 shows the concentrations of the single compounds vs. time for the runs at the highest (350 °C) and lowest (290 °C) temperatures. All other results, i.e. at 320 °C, the blank run at 350 °C and the run at 200 °C, are given in detail in a thesis [9]. The curves in Fig. 1 are model predictions to be discussed later.

3. Kinetic equations and reaction network

Since we are dealing with heterogeneous catalytic reactions, it is natural to assume for the hydrodechlorination reactions a Langmuir-Hinshelwood-type kinetic equation. In the assumption [10, 11] that there are two different types of active site: one for the organic species and the other one for the hydrogen; the rate r'_{ij} of the reaction leading from compound i to product j can be written as:

$$r'_{ij} = k'_{ij} f(p_{H_2}) c_i / (1 + \sum K_i c_i) \quad (1)$$

where the functional dependence on the hydrogen partial pressure is left undetermined. In fact, since all reaction runs were accomplished at constant p_{H_2} , the product $k'_{ij} f(p_{H_2})$ is constant during each run. Therefore, eq. (1) can be written as:

$$r'_{ij} = k_{ij} c_i / (1 + \sum K_i c_i) \quad (2)$$

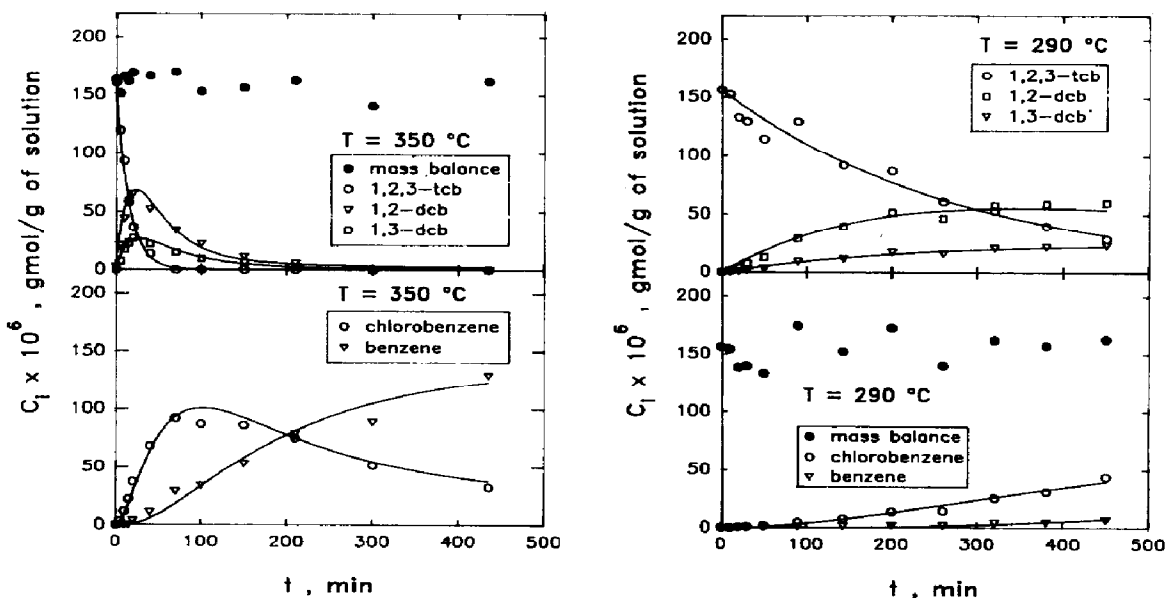


Fig. 1. Concentration of reactant, intermediates and product vs. time for two runs. Operating conditions: left panel $T = 350\text{ }^{\circ}\text{C}$, $p_{H_2} = 100\text{ bar}$; right panel $T = 290\text{ }^{\circ}\text{C}$, $p_{H_2} = 100\text{ bar}$. Filled symbols for checking material balance, they represent $\sum c_i (i = 1, 2, \dots, 5)$ vs. time.

After a few attempts it became apparent that the adsorption of organic compounds was not relevant (i.e. $\Sigma K_i c_i \ll 1$). Thus eq. (2) reduces to:

$$r'_{ij} = k'_{ij} c_i \quad (3)$$

where $k'_{ij} = k'_{ij} f(p_{H_2})$ plays the role of a pseudo-first order kinetic constant.

The experimental data and the chemical structure of the compounds involved give clear indications on the direct reactions path. However, they are not sufficient to precisely identify the reaction network. In fact some alternatives remain.

By making use of the regression technique (HJB) proposed by Himmelblau et al. [12], which is a well-known powerful method [13] for analysing kinetic data, it was possible, by a trial and error procedure, to define the global network shown in Fig. 2 and to evaluate the kinetic constants k'_{ij} for all runs.

The procedure is as follows. A plausible network is assumed and the kinetic constants k'_{ij} of eq. (3) are evaluated by the HJB method. Then the set of differential equations describing the network is integrated by using the estimated k'_{ij} , and the resulting theoretical c_i vs. t curves are compared with the experimental c_i vs. t data. The procedure is repeated for other possible networks until that which best fits the data is identified.

The curves shown in Fig. 1 are computer-simulated based on the network of Fig. 2 and on the corresponding kinetic constants k'_{ij} as evaluated by the HJB method.

Inverse reactions have been considered in the statistical analysis of data. However, only the inclusion of the inverse reactions $5 \rightarrow 4$, $4 \rightarrow 3$ and $4 \rightarrow 2$ gave consistent results and improved the fit, but not at all temperatures. This inclusion has a theoretical support. In fact, chlorination reactions are reversible. The relative values of the equilibrium constants calculated on the basis of the data available in the literature [14] are reported in Fig. 3. It must be noted

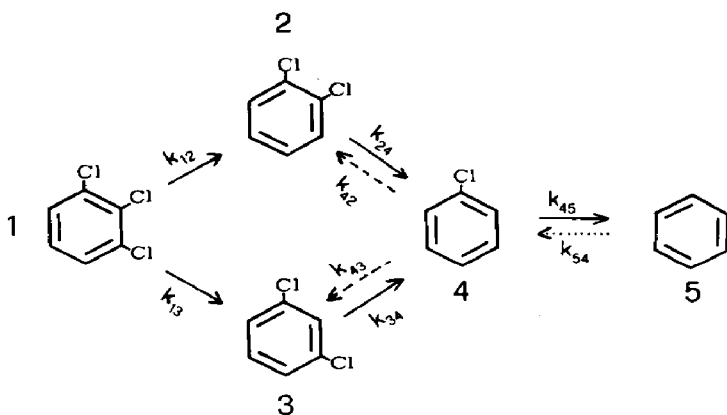


Fig. 2. Reaction network for 1,2,3-trichlorobenzene. Arrows: solid = at all temperatures; dotted = significant at 320 and 350 °C; dashed = significant at 350 °C.

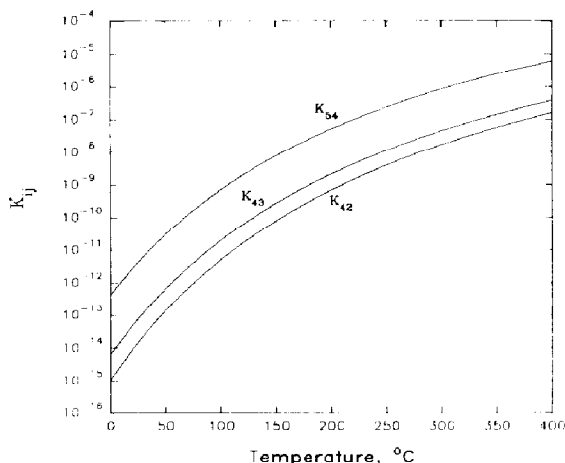


Fig. 3. Equilibrium constant K_{ij} (i and j as in Fig. 2) based on activities. Standard state: ideal gas state.

that inverse reactions, when compared to the direct ones, are favoured at higher temperatures for isothermic reactions. Reaction 5→4 which has a larger equilibrium constant is present at both $T=320$ and $T=350$ °C while reactions 4→2 and 4→3 are present only at $T=350$ °C.

The results of the analysis for the blank run (at 350 °C without catalyst) showed that the k'_{ij} s ranged between 3 and 10% of the corresponding k'_{ij} of the run at 350 °C with catalyst. The only exception was for reaction 4→5 whose constant k'_{45} without catalyst was about 40% of that with catalyst. However, at lower temperatures, due to the presumably lower activation energy of the non-catalyzed reactions, their influence will be even lower. Therefore, we will neglect the influence of the non-catalyzed reactions. Naturally less confidence will be attributed to the values of k'_{45} .

The kinetic constants k'_{ij} were reduced to the weight of catalyst by the relationship:

$$k_{ij} = (W_L/W_C)k'_{ij} \quad [\text{g of solution/g of catalyst} \cdot \text{min}] \quad (4)$$

The k_{ij} values are reported in Table 3. Not too much confidence can be given to k_{54} , which is about one order of magnitude lower than the other constants. The constants of Table 3 have been regressed according to the Arrhenius law. The calculated Arrhenius parameters are included in the last two columns of the table. For an overall picture of the behaviour of the reaction process with temperature, the Arrhenius equations for all constants are reported in Fig. 4. For further details on the kinetic analysis of data see Famiglietti [9].

Inspections of Table 3 and/or Fig. 4 indicate the following trends:

- (1) For all temperatures in the investigated range, the dechlorination of chlorobenzene is the slowest step.

TABLE 3

Kinetic constants and Arrhenius parameters

k_{ij}	350 (°C)	320 (°C)	290 (°C)	k_{ij}^0 (gsol/gcat · min)	ΔE_{ij} (kJ/mol)
k_{12}	7.53	1.99	0.50	8.24×10^{11}	131
k_{13}	2.70	0.59	0.14	3.54×10^{12}	145
k_{24}	3.92	1.28	0.41	6.01×10^9	110
k_{34}	2.77	1.11	0.11	7.39×10^{13}	159
k_{45}	0.85	0.55	0.19	1.38×10^6	74
k_{42}	0.15	—	—	—	—
k_{43}	0.18	—	—	—	—
k_{54}	0.03	0.17	—	—	—
k_0	1.15	0.75	0.20	2.02×10^7	86

k_0 is the kinetic constant of the overall reaction (5) for $n = 1$.

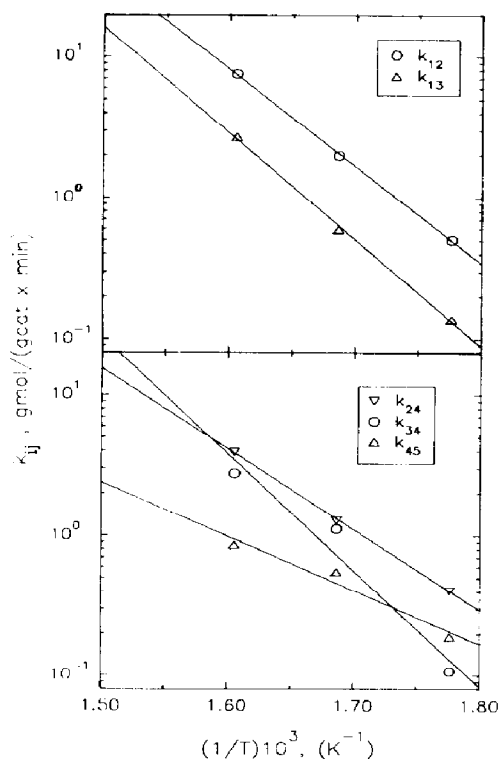


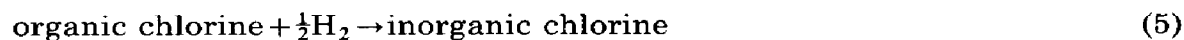
Fig. 4. Arrhenius plots for the k_{ij} s.

- (2) The dechlorination path 1→2, 2→4 is preferred with respect to path 1→3, 3→4. However, the gap between the rates of the two paths tends to become smaller at higher temperatures.

These considerations allow us to draw the main conclusion that the more chlorine atoms bonded to the benzenic ring the larger is the rate of removal of a chlorine atom. Whether the chlorine atom to be removed is in the ortho or meta position plays but a minor role on the reaction rate, particularly at higher temperatures.

4. Overall dechlorination reaction

From a practical point of view it may be of interest to synthesize the dechlorination process, represented in detail by the network of Fig. 2, as:



where for "organic chlorine" we mean the chlorine atom bonded to the benzenic ring, and for inorganic chlorine we mean HCl.

In Fig. 5 the weight percentage of these two forms of chlorine are reported vs. time for the run at 350 °C. The overall reaction has been regressed by the kinetic equation

$$dc_{cl}/dt = -k'_0(c_{cl})^n \quad (6)$$

where c_{cl} is the molar concentration of organic chlorine and k'_0 is the kinetic constant of the overall reaction (5).

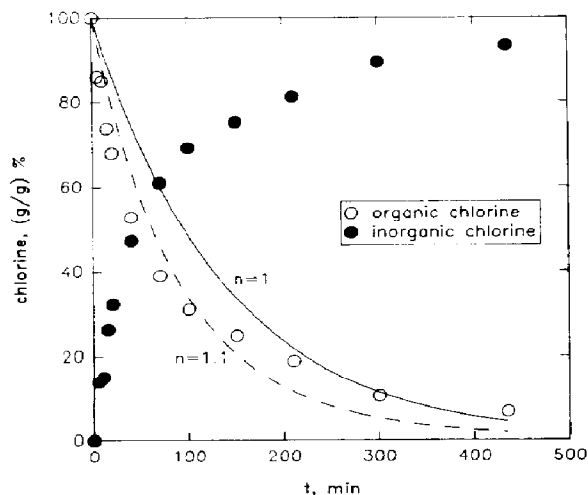


Fig. 5. Overall chlorine conversion. Operating conditions $T=350\text{ }^{\circ}\text{C}$, $p_{\text{H}_2}=100\text{ bar}$.

The regression of data indicate that $n=1$ is a good approximation for the overall dechlorination reaction at all temperatures investigated. The corresponding values of the overall kinetic constant k'_0 (for $n=1$) have been reduced to the weight of catalyst and reported in Table 3 as k_0 .

5. Conclusions

The investigation has shown that catalytic hydrogenation can be a suitable method for making waste trichlorobenzene inert, producing recyclable chemicals (i.e. benzene). At 350 °C, which is a reasonably low temperature, the conversion of the organic chlorine is more than 90% after 435 min, with only 0.63 wt% of a commercial hydrogenation catalyst.

It is worthwhile remarking that the 1,2,3-trichlorobenzene can be considered as a good model compound for predicting the kinetic behaviour of chlorinated organic compounds in general. The dechlorination rates evaluated for the trichlorobenzene can just as well be applied to other practical cases.

The overall kinetic constant k_0 could be directly and safely adopted for the design of the detoxification process of non-aromatic organic compounds containing chlorine. In fact, C_6H_5-Cl has the strongest C-Cl bond of the most usual chlorinated non-aromatic compounds [8].

For the design of the detoxification process for most toxic aromatic organic compounds with a chlorine bond to the benzene ring (e.g. PCDDs, PCDFs for which direct experimentation would be more difficult due to the high level of hazard connected with their handling), k_0 could still be adopted, but with a safety coefficient.

Notation

c_{cl}	concentration of organic chlorine (mol/g of solution)
c_i	molar concentration of compound i in liquid solution (key as in Fig. 2) (mol/g of solution)
ΔE_{ij}	activation energy of the reaction leading from organic compound i to product j in the reaction network of Fig. 2 (kJ/mol)
K_{ij}	equilibrium constant based on activities (i and j as above)
k'_{ij}	pseudo-first-order kinetic constant (i and j as above) (min^{-1})
k_{ij}	kinetic constant (i and j as above) (g of solution/(g of catalyst · min))
k_{ij}^0	pre-exponential factor (i and j as above) (g of solution/(g of catalyst · min))
k'_0	kinetic constant of the overall reaction (5) ($(\text{gsol/mol})^{n-1} \text{min}^{-1}$)
k_0	kinetic constant of the overall reaction (5), $k_0 = k'_0(W_L/W_C)$ ($\text{gsol}^n/(\text{mol}^{n-1} \cdot \text{gcat} \cdot \text{min})$)
n	order of overall reaction (5)
p_{H_2}	hydrogen partial pressure (bar)

R	gas law constant (8.314 J/mol · K)
r'_{ij}	rate of reaction (i and j as above) (mol/(g of solution · min))
T	temperature (K)
W_C	catalyst loaded in the reactor (g)
W_L	weight of liquid solution in the reactor (g)
W_R	weight of 1,2,3-tcb loaded in the reactor (g)

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