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Hydrodechlorination of Carbon Tetrachloride

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The reaction of CCl_4 with H_2 over peripherally deposited Pt on η-Al_2O_3 catalyst proceeds as two parallel reactions, producing $CHCl_3$ and CH_4 at constant mole ratio, independent of process variables.

$$CCl_4 + H_2 \rightarrow CHCl_3 + HCl.$$

$$CCl_4 + 4H_2 \rightarrow CH_4 + 4HCl.$$

The intermediates CH_2Cl_2 and CH_3Cl were present only in trace quantities. Relative production rates were $CHCl_3 = 4.00$, $CH_2Cl_2 = 0.024$, $CH_3Cl = 0.0009$, $CH_4 = 1$. Separate experimentation showed that $CHCl_3$, CH_2Cl_2, and CH_3Cl were effectively unreactive, rather than being highly reactive intermediates.

The anomalous behavior was rationalized on the basis that formation of $CCl_3\cdot$ radical is the initiating step. Single step addition of hydrogen to $CCl_3\cdot$ accounts for $CHCl_3$. Concerted, rather than sequential, hydrogen addition to adsorbed $CCl_3\cdot$, with no important desorption of intermediates, accounts for CH_4. The study demonstrates that polysubstituted compounds may not react consecutively and that homologous series need not exhibit analogous behavior.

INTRODUCTION

In an earlier paper (*1*) on hydrodechlorination kinetics and reaction mechanisms, the reactions of the *cis*- and *trans*-dichloroethylenes and of vinyl chloride with hydrogen over platinum on alumina catalysts were reported. It was found that these olefinic chloride species were highly reactive at the carbon–chlorine bond. On the other hand, the aliphatic chlorides, ethyl chloride and dichloroethane, were effectively nonreactive. In the present work, the hydrodechlorination of chlorinated methanes is investigated.

The first hydrogenation of carbon tetrachloride reported in the literature was by Busch and Stove (*2*). Their interest in the reaction was as an analytical technique. Using palladium on calcium carbonate, they reacted carbon tetrachloride to completion in a liquid-phase reaction in potassium hydroxide solutions at room temperature and at atmospheric pressure.

Chadwell and Titani (*3*) studied the reaction with hydrogen atoms generated in a Wood's tube and found that methane and ethane were produced. A free radical mechanism involving replacement of a halide atom by a hydrogen atom was proposed:

$$CH_3X + H\cdot \rightarrow CH_3\cdot + HX, \qquad (1)$$

where X is a halogen atom.

Cremer, Curry, and Polanyi (*4*) and then Vance and Baumann (*5*) found that complete conversion of atomic hydrogen into HCl could be had by reaction with carbon tetrachloride.

Semeluk and Bernstein (*6,7*) studied the

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thermal decomposition of chloroform in a flow system in a temperature range of 450 to 525°C. Helium was used as a diluent. The principle products were hydrogen chloride and tetrachloroethylene. The following mechanism was proposed:

$$CCl_3H \rightarrow CCl_2H\cdot + Cl\cdot \qquad (2)$$

$$Cl\cdot + CCl_3H \rightarrow HCl + CCl_3\cdot \qquad (3)$$

$$CCl_2H\cdot + CCl_3H \rightarrow CCl_2H_2 + CCl_3\cdot \qquad (4)$$

The primary step was postulated to be the breakage of the C–Cl rather than a C–H bond. Studies made on chloroform and deuterium–chloroform indicated that the C–H bond was very stable in their temperature range.

Hickok (*8*) reacted methylene chloride and molecular hydrogen over palladium in a flow system in the temperature range 80 to 395°C. At low conversions corresponding to low temperatures (170°C), the hydrogenation products observed were methyl chloride and methane. Methyl chloride was present in larger quantities. At 287°C, methane appeared in larger quantities.

Besprozvannyi, Kononov, and Kharlamov (*9,10*) investigated carbon tetrachloride hydrogenation in n-heptene solvent in the pressure range of 4 to 20 atm and a temperature range of 80 to 110°C. The catalyst used was 0.04 wt % palladium on pumice. Mechanisms involving the formation of both hydrogen and chloroform radicals were proposed to account for the formation of both $CHCl_3$ and C_2Cl_6. The authors assumed molecular hydrogen dissociation on the catalyst surface. The mechanism they preferred accounted for the observed kinetics:

$$H_2 \overset{Pd}{\rightleftharpoons} 2H^*\cdot \qquad (5)$$

$$CCl_4 \overset{Pd}{\rightleftharpoons} CCl_4^* \qquad (6)$$

$$H^*\cdot + CCl_4^* \xrightarrow{k_1} HCl + CCl_3^*\cdot \qquad (7)$$

$$H^*\cdot + CCl_3^*\cdot \xrightarrow{k_2} CHCl_3 \qquad (8)$$

$$CCl_3^*\cdot + CCl_4 \xrightarrow{k_3} CCl_4^* + CCl_3\cdot \qquad (9)$$

$$2CCl_3\cdot \xrightarrow{k_4} C_2Cl_6 \qquad (10)$$

They postulated that the $CCl_3\cdot$ radicals are transferred from the catalyst surface to the surrounding liquid medium. Subsequent radical dimerization predominates, since more hexachloroethane than chloroform was formed. In the work of this article, which will be described now, no measurable amount of C_2Cl_6 was observed with Pt catalyst at atmospheric pressure.

EXPERIMENTAL

Materials

All gases used for this work were obtained from the Matheson Co. and had purities greater than 99.5%. Hydrogen was passed over palladium Deoxo catalyst and then over Houdry Process and Chemical Co. Type K nickel on alumina catalyst at 250°F to remove traces of oxygen. H_2O and CO_2 present in the gas streams were removed by passage over drierite and then ascarite. Except for the Deoxo catalyst, nitrogen and helium diluent gases received the same treatment as hydrogen.

Carbon tetrachloride, chloroform, and dichloromethane were obtained as the reagent and spectro grades from the Eastman Organic Chemicals Dept. of Distillation Products Industries. All liquids were greater than 99.9% purity.

The catalysts used for this study were 0.5% Pt on η-Al_2O_3. The η-Al_2O_3 pelleted support was supplied by Houdry Process and Chemical Co. It had a BET surface area of 213 m^2/g, a bulk density of 0.77 g/cm^3, and was in the form of extruded pellets $\frac{1}{16}$ inch in diameter and of variable lengths, nominally $\frac{1}{8}$ in.

Two separate identical preparations of catalysts, designated Catalyst I and Catalyst II, were made for this study. The catalyst was prepared by impregnating the dried η-Al_2O_3 support with aqueous chloro-platinic acid solution, the volume of solution being that just sufficient to wet the pellets. Using this procedure, the platinum was impregnated only on the outer periphery of the pellet. Prior to operation the catalyst was reduced for at least 1 day in flowing hydrogen at 270°C. Once reduced, the catalyst was maintained constantly under positive hydrogen pressure to avoid air leakage into the reactor.

The catalytic activity of Pt wire was also determined. A 70-in. length of 35 BWG wire was charged to the reactor and treated identically to the supported catalyst. The wire was loosely packed into a 1-in. length inside the reactor.

Equipment

Figure 1 is a flow diagram of the reaction system used for this study. Beginning with the point of chlorinated hydrocarbon addition only Pyrex and Teflon were used as materials of construction. Nitrogen was used as a diluent gas for Catalyst I, helium for Catalyst II. The adjustment of H_2 and diluent flow rates permitted study at various hydrogen partial pressures and residence times. Gas flow rates ranged from 8 to 260 cm^3/min and were measured by rotameters. The liquid chlorinated hydrocarbons were pumped by a Sage syringe pump equipped with either a 1 or a 5-cm^3 Hamilton Teflon plunger gas-tight syringe. Air dissolved in the chlorinated hydrocarbon was purged by backflushing hydrogen from the unit through the capillary line to the syringe and then through the liquid contained in the syringe.

The reactor was fabricated from 8-mm o.d. and 6-mm i.d. Pyrex tubing and was placed in a Sage Instrument Co. fluidized sand bath. Temperature uniformity in the bath was measured to be ±0.1°C at various locations. Gases entering the reactor were heated to reaction temperature in a 2-ft long coil of 2-mm i.d. Pyrex tubing. The liquid to gas ratio in all work was adjusted to maintain the vapor pressure of liquid below saturation at room temperature. Once liquid was vaporized in a simple nichrome wound tube, no condensation occurred anywhere in the remaining system.

A 3-mm Pyrex thermowell containing an iron constantan thermocouple was positioned immediately above the catalyst. The catalyst rested on Kimax beads which were supported on a fritted glass plate. The thermowell served the additional purpose of forming an annulus which effected rapid removal of the product stream from the high-temperature reaction zone. Temperature was both indicated and controlled with a precision of ±0.3°C by a Model 472P Barber-Colman controller.

Catalyst I was charged to the reactor at two levels, 0.0893 and 0.3001 g. Catalyst II was charged at the larger figure. These amounts of catalyst corresponded to *L/D* (length to diameter ratio of the catalyst bed) of 0.684 and 2.30, respectively. Calculation of the degree of dispersion in the reactor (*11*) showed that for

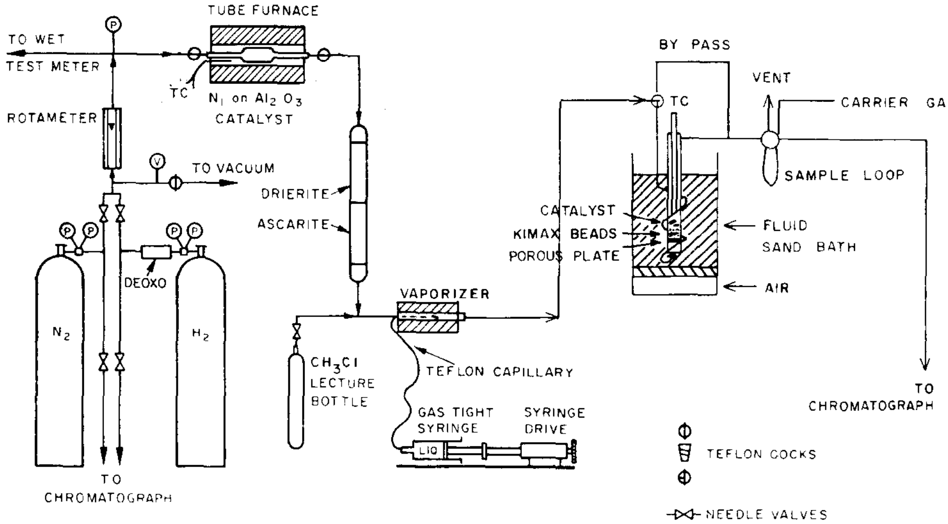


FIG. 1. Flow reaction system.

$L/D = 0.684$, the reactor was completely back mixed; and for L/D of 2.30, operation was intermediate between plug flow and back mixed. Catalyst activity did not change measurably over the period of use. This was established by testing the activity at a specified condition at regular intervals of time.

Operating conditions in the CCl_4 investigation ranged from 12 to 123°C, 0.0002 to 0.0181 min space time, 50 to 700 Torr H_2, and 8–90 Torr CCl_4.

The reactor effluent stream after the system had reached steady state (which usually required 1½ hr) or the charge stock (if the reactor were bypassed) then passed through a 10-cm^3 Teflon sample loop and then to a vent. The product or feed gas sample was trapped in the loop by a nylon sampling valve, and then passed into a chromatograph.

Analysis

A Perkin Elmer Model 880 Gas Chromatograph equipped with a dual flame ionization detector was used to analyze the products of the experiments using Catalyst I. Separation was effected by a 10-ft × ⅛-in. o.d. copper tubing column packed with 30% by wt squalane on Chromosorb W. Nitrogen was used as a carrier gas, and species were eluted in order of increasing boiling point. Methyl chloride and methane separated at 33°C, methylene chloride at 42°C following a program rate of 4°C/min. Chloroform and carbon tetrachloride separated at 90°C following a program rate of 48°C/min. Analyses for experiments on Catalyst II and for experiments on platinum wire were made using a Varian Aerograph Series 1200 flame ionization detector gas chromatograph. Helium was used as a carrier gas, and squalane on the support was reduced to 10%, which shortened the analysis time from 21 to 7 min.

RESULTS

CCl_4 Hydrodechlorination Rates

Experiments were made at constant feed conditions of 0.0084 min space time, 400 Torr hydrogen, and 6.9 Torr CCl_4 for the purpose of determining the activity of η-Al_2O_3 catalyst base, unreduced (H_2PtCl_6) impregnated base, and reduced Pt on η-Al_2O_3 catalyst. The fractional CCl_4 conversion at 35°C was 0.002, 0.002, and 0.182, respectively. This indicates that platinum metal is the active catalytic agent. At 118°C, which is near the upper temperature limits of this study, CCl_4 fractional conversion remained negligible at 0.004 over impregnated and 0.006 over unimpregnated base. The only product observed was CH_2Cl_2.

The hydrodechlorination reaction is extremely exothermic; and, to avoid temperature gradients in either the reactor or catalyst pellets, experiments in which absolute rates were measured were confined to runs at conversions in the range 0.0007 to 0.08. Conversion of hydrogen was also differential.

Figure 2 shows log log plots of carbon tetrachloride conversion rate vs carbon tetrachloride partial pressure at parameters of temperatures and hydrogen partial pressures. At 32°C the lines drawn correspond to a slope of 0.11. For all practical purposes the reaction is zero order in CCl_4.

Figure 3 shows log log plots of CCl_4 conversion rate vs hydrogen partial pressure at constant temperature and CCl_4 partial pressure. The lines drawn on Fig. 3 correspond to an order of 0.12 in hydrogen

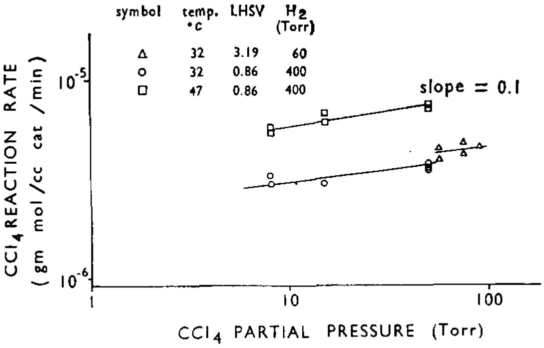


FIG. 2. The practically zero-order dependence of CCl_4 hydrodechlorination reaction rate on CCl_4 partial pressure. Catalyst I, $L/D = 0.68$, conversion = 0.007–0.05.

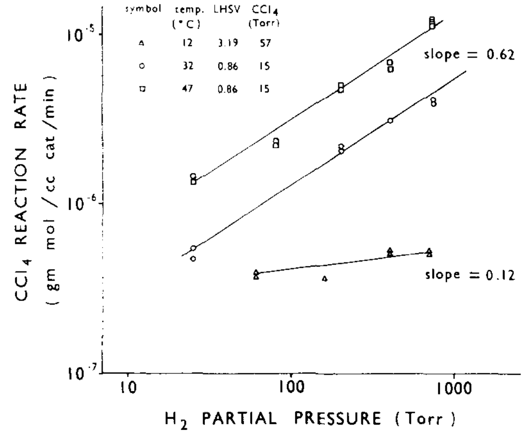


FIG. 3. CCl_4 hydrodechlorination reaction rate dependence approximates half order in hydrogen. Catalyst I, $L/D = 0.68$, conversion = 0.0007–0.08.

at 12°C and an order of 0.62 at 33 and 47°C. The transition to higher order as temperature increases is characteristic of Langmuir–Hinshelwood kinetics, which undoubtedly apply not only to hydrogen but also to CCl_4. The higher temperature value of 0.62 suggests 0.5 as the closest half-integral order; and this implies that dissociated hydrogen, rather than molecular hydrogen is the reacting species for hydrodechlorination. This is in accordance with the earlier observations on hydrodechlorination of olefinic chlorides.

Figure 4 is an Arrhenius plot of CCl_4 conversion rate vs reciprocal temperatures in the range 12 to 63°C and at constant CCl_4 and H_2 partial pressures of 57 and 60 Torr, respectively. The nonlinearity of the Arrhenius plot suggests that diffusional effects play a role in these fast reactions. The slope of the straight line portion corresponds to an activation energy of 19.25 kcal/mole.

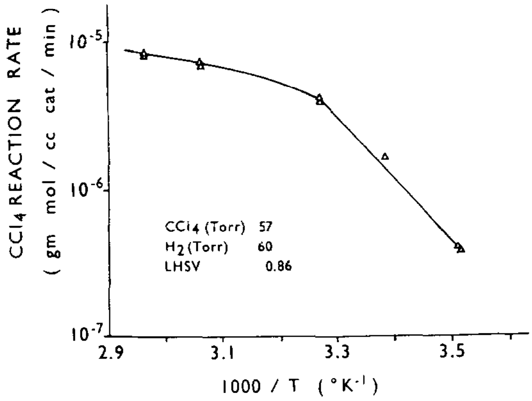


FIG. 4. The temperature dependence of CCl_4 hydrodechlorination suggests transport effects of significance. Catalyst I, $L/D = 0.68$, conversion = 0.0007–0.015.

CCl_4 Hydrodechlorination Selectivity

The only two CCl_4 hydrodechlorination reaction products that were observed in studies ranging from 0.0007 to 0.08 CCl_4 conversion were methane and chloroform. The relative mole fraction of each of these are plotted vs CCl_4 fractional conversion on Fig. 5. The lines drawn on the log log plot correspond to a slope of unity, suggesting that at differential conversion levels the CCl_4 hydrodechlorination reaction behaves as if it were a set of parallel reactions,

$$CCl_4 + H_2 \rightarrow CHCl_3 + HCl, \tag{11}$$

$$CCl_4 + 4H_2 \rightarrow CH_4 + 4HCl. \tag{12}$$

The $CHCl_3/CH_4$ mole ratio is constant and equal to 4. The ratio is independent of process variables.

Catalyst loading was increased from $L/D = 0.684$ to $L/D = 2.30$ to effect more severe operation and to permit detection of trace products as well as CH_4 and $CHCl_3$. Figure 6 is a Cartesian plot of CH_4 and $CHCl_3$ relative mole fractions vs CCl_4 fractional conversion at integral rather than differential conversion levels. The linear relationship for each product is continued to approximately 70% conversion on Catalyst I and maintains the ratio of $CHCl_3/CH_4 = 4$. Linearity begins to disappear at higher CCl_4 conversion; 0.7 to 0.95. This is not surprising, particularly in view of the severe thermal gradients which must be inside the catalyst at these conversion levels.

The constancy of the molar ratio $CHCl_3/CH_4 = 4$ on Catalyst I over such a wide range of operating conditions suggests that the ratio is a function of the catalyst rather than the operating conditions. To illustrate this point, data for Catalyst II are also included on Fig. 6.

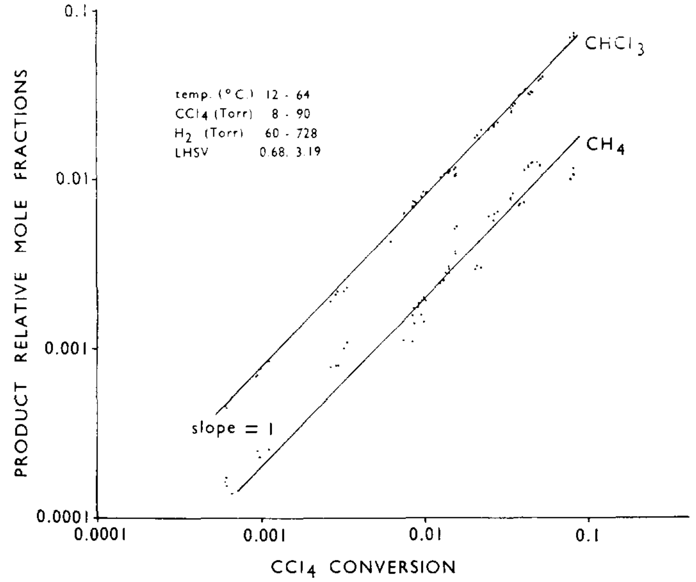


FIG. 5. CCl_4 hydrodechlorination at differential conversion levels behaves as a set of parallel reactions, producing $CHCl_3$ and CH_4 at a constant ratio of 4. Catalyst I, $L/D = 0.68$.

For this catalyst, the molar ratio is $CHCl_3/CH_4 = 3.3$. The fact that the molar ratio can be changed by changing catalyst suggests that a different site or process produces $CHCl_3$ than produces CH_4 in the range of process variables studied. The rate controlling step for the production of $CHCl_3$ is not the same mechanistically as that for CH_4.

Figure 7 is a log log plot of CCl_4 conversion vs all product mole fractions for Catalyst I at $L/D = 2.30$. Trace quantities of CH_3Cl and CH_2Cl_2 were detected by the chromatograph at these high conversion levels.

The production of $CHCl_3$ and CH_4 as

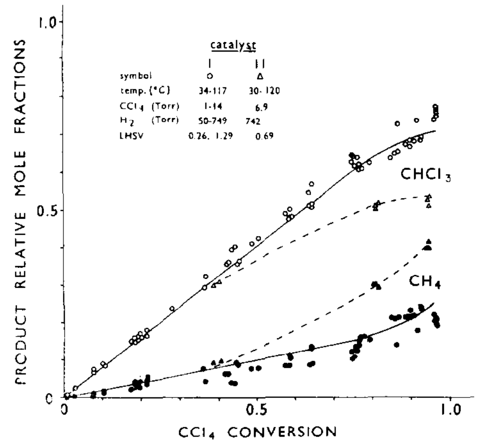


FIG. 6. The constancy of the $CHCl_3/CH_4$ mole ratio is lost at extreme integral CCl_4 conversion, where temperature effects may play a role, $L/D = 2.30$.

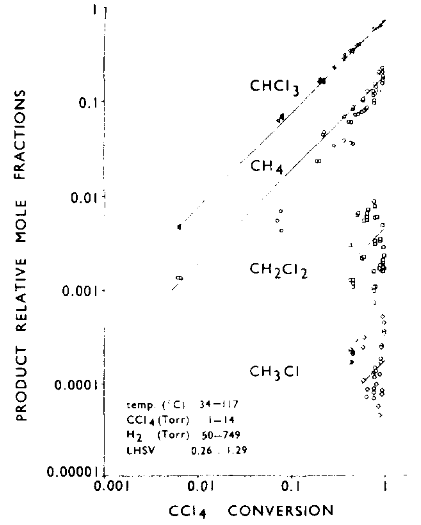


FIG. 7. CH_2Cl_2 and CH_3Cl can be detected as trace products of CCl_4 hydrodechlorination at high conversions. Catalyst I, $L/D = 2.30$. Relative production rates: $CHCl_3 = 4$, $CH_2Cl_2 = 0.024$, $CH_3Cl = 0.0009$, $CH_4 = 1.0$.

the major products and of CH_2Cl_2 and CH_3Cl as minor products of CCl_4 hydrodechlorination at first might be explained on the basis of the following set of consecutive reactions:

$$CCl_4 \xrightarrow{\text{Slow}} CHCl_3 \xrightarrow{\text{Fast}} CH_2Cl_2 \xrightarrow{\text{Very fast}} CH_3Cl \xrightarrow{\text{Very fast}} CH_4 \quad (13)$$

The addition of H_2 and production of HCl is implied, but, for simplicity, not shown in the above and subsequent equations of this paper.

Nonreactivity of Intermediates

Equation (13) suggests that CH_2Cl_2 and CH_3Cl are such highly reactive intermediates that they are converted the instant they are formed. Another possibility, in spite of the fact that the platinum was deposited on the outer periphery of the catalyst, is that this could be an example of pore diffusion controlling reaction where intermediates are reacted to extinction before they find their way out of a pore. (Type III selectivity defined by Wheeler (*12*)). However, studies in which $CHCl_3$, CH_2Cl_2, and CH_3Cl (rather than CCl_4) were charged to the reactor as feed showed that these species were effectively unreactive. *They are not highly reactive intermediates.* Table 1 shows such experimental data obtained for Catalyst I and II illustrating the surprising and unexpected nonreactivity of chloroform, methylene chloride, and methyl chloride, relative to carbon tetrachloride. Note that Table 1 lists sequential experiments in which carbon tetrachloride was charged to the system prior and subsequent to each test of the other reactant to ensure that the catalyst had not lost activity when charge stocks were changed during these tests.

To illustrate that this effect of intermediates nonreactivity was not peculiar to the supported catalyst, a further set of experiments was conducted using platinum

TABLE 1
Reactivities of Chlorinated Methanes

Charge stock	Temperature (°C)	Space time (min)	Relative mole fractions in product						Feed reaction rate × 10^6 (moles/cm^3 cat./min)
			CCl_4	$CHCl_3$	CH_2Cl_2	CH_3Cl	CH_4	C_2H_6	
			Catalyst I (683 Torr H_2, 56 Torr feed)						
CCl_4	↑	0.0129	0.296	0.569	0.0016	0	0.133	0	168.
$CHCl_3$	120	0.0107	—	0.9947	0.0028	0	0.0022	0	1.52
CCl_4	↓	0.0124	0.324	0.563	0.0025	0	0.110	0	161.
CH_2Cl_2	↑	0.0085	—	—	0.9967	0.0018	0.0015	0	1.19
CCl_4	96	0.0124	0.274	0.560	0	0.00012	0.167	0	173.
CH_3Cl	|	0.0034	—	—	—	0.999	0.001	0	0.90
CCl_4	↓	0.0124	0.218	0.635	0	0	0.146	0	187.
			Catalyst II (740 Torr H_2, 6.9 Torr feed)						
CCl_4	123	0.0031	0.052	0.533	0.018	0	0.396	0	113.
$CHCl_3$	↑	0.0026	—	0.9396	0.0262	0	0.0340	0	8.66
CCl_4	120	0.0031	0.097	0.581	0.008	0	0.313	0	108.
CH_2Cl_2	|	0.0020	—	—	0.992	0.00126	0.0067	0	1.44
CCl_4	↓	0.0031	0.088	0.572	0.025	0	0.314	0	109.
			Platinum wire (672 Torr H_2, 75 Torr feed)						
CCl_4	↑	0.081	0.9977	0.0015	0.000014	0.000038	0.00056	0.000048	0.115
$CHCl_3$	123	0.067	—	0.9998	0.000088	0	0.00011	0.000005	0.012
CH_2Cl_2	↓	0.054	—	—	0.99992	0.0000088	0.00003	0.000041	0.006

TABLE 2
CARBON-CHLORINE BOND REACTIVITIES AND PROPERTIES

Compound	Relative reactivities		Force constant (*13*) × 10^{-5} (dyn/cm)	Bond length (*13*) (Å)	C-Cl Bond dissociation energy (*15*) (kcal)	Boiling point (*14*) (°C)
	Pt wire	Catalyst I				
CCl_4	1.0	1.0	2.00	1.755 ± 0.005	68.4	76.54
$CHCl_3$	0.104	0.009	2.47	1.77 ± 0.02	73.5	61.70
CH_2Cl_2	0.053	0.007	2.94	1.77 ± 0.02	78.5	40.0
CH_3Cl	—	0.005	3.12	1.77 ± 0.02	83.5	−24.2

wire rather than platinum on alumina catalyst. Because of the low surface area of the wire relative to the catalyst, carbon tetrachloride conversions at similar operating conditions are only on the order of 0.002 rather than 0.7. On the other hand, chloroform and methylene chloride conversions are only 0.0002 and 0.0001, respectively. A conclusion can be drawn that the alumina support neither affected the nature of the product nor the order of reactivity of CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl.

DISCUSSION OF RESULTS

Table 2 lists boiling points, force constants for bond stretching, and bond lengths for the chlorinated aliphatics and compares these to the relative reactivities observed over Catalyst I and over Pt wire. Table 2 also lists bond dissociation energies for removal of the first chlorine atom; and it is readily seen that reactivity order correlates with force constant and bond energy. However, chemical and physical considerations do not explain the parallel production of $CHCl_3$ and CH_4 from CCl_4. Apparently, two distinct processes occur; and we suggest a free radical mechanism proceeding in two manners.

As is well-known, adsorbed hydrogen dissociates readily to its atoms on platinum catalysts.

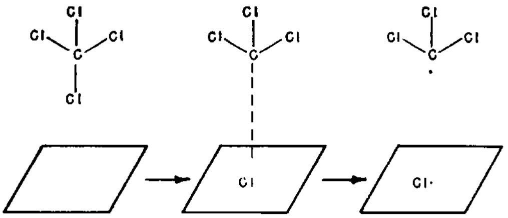
$$H_2^* \overset{Pt}{\rightleftarrows} H^*\cdot + H^*\cdot \qquad (14)$$

We believe that adsorbed carbon tetrachloride also dissociates on Pt catalyst.

$$CCl_4^* \overset{Pt}{\rightleftarrows} CCl_3\cdot(g) + Cl^*\cdot \qquad (15)$$

This reaction is probably the rate-controlling step, considering the constant ratio of $CHCl_3/CH_4$ and the observed zero order in CCl_4. Equation (15) suggests that $CCl_3\cdot$ is the reactive organic species of interest. The higher bond energies for removal of the first Cl from the other chlorinated methanes explains their nonreactivity. We rule out reaction of gaseous CCl_4 with adsorbed or gaseous hydrogen on the basis that, if such a reaction were preferred, $CHCl_3$, CH_2Cl_2, and CH_3Cl would also exhibit high reactivities, which they do not. The catalyst is needed to dissociate CCl_4 at the low temperatures of our study, where thermal reactions are negligible.

Physically, reaction (15) may appear as follows:



(16)

Adsorbed chlorine can readily combine with adsorbed hydrogen (either molecular or radical) to form readily desorbed product HCl. The $CCl_3\cdot$ radical in the gas phase can either react with H_2 gas in propagation reaction

$$CCl_3\cdot(g) + H_2(g) \rightleftarrows CCl_3H(g) + H\cdot(g), \qquad (17)$$

or combine directly with adsorbed or gaseous $H\cdot$ radicals

$$CCl_3\cdot(g) + H\cdot(^* \text{ or } g) \rightleftharpoons CCl_3H(g). \qquad (18)$$

Since formation of $CCl_3\cdot$ from $HCCl_3$ is a far more difficult process than formation of $CCl_3\cdot$ from CCl_4, $CHCl_3$ will behave as a terminal product rather than as a reactive intermediate. Similar logic applies to abstraction of H· from CH_2Cl_2, CH_3Cl, and CH_4.

The formation of CH_4 can be explained on the basis that $CCl_3\cdot$ can readily readsorb on a Pt site and not desorb until it is converted to $CH_3\cdot$ by the H· atoms at the site.

This can be regarded as the following sequence of adsorbed organic radical reactions, bearing in mind that since hydrogen and its radicals are in equilibrium on the surface, we need not distinguish between them:

$$H_2^* + CCl_3^*\cdot \rightarrow HCCl_2^*\cdot + HCl(g), \qquad (19)$$

$$H_2^* + HCCl_2^*\cdot \rightarrow H_2CCl^*\cdot + HCl(g), \qquad (20)$$

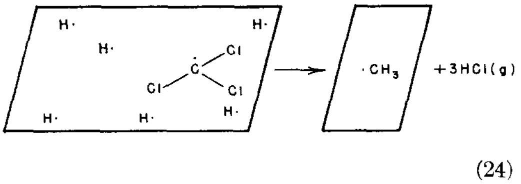
$$H_2^* + H_2CCl^*\cdot \rightarrow H_3C^*\cdot + HCl(g). \qquad (21)$$

No desorptions are involved, since we did not find significant amounts of intermediates that could readily form from gas-phase reactions with hydrogen

$$HCCl_2\cdot(g) + H_2 \rightarrow H_2CCl_2 + H\cdot \qquad (22)$$

$$H_2CCl\cdot(g) + H_2 \rightarrow H_3CCl + H\cdot \qquad (23)$$

Since desorption of intermediates and their subsequent readsorption does not occur, the reaction sequence of Eqs. (19–21), can also be regarded as a single concerted or multistep reaction:



(24)

Callahan, *et al.* (*16*), report this type of behavior in ammoxidation of propylene to acrylonitrile over bismuth molybdate catalyst. They demonstrated the mechanism does not involve acrolein as an isolatable vapor-phase intermediate.

Finally, methyl radicals can either react with hydrogen molecules or atoms to produce methane or even combine with themselves to account for the observed ethane at extreme conversions.

$$H_2 + CH_3\cdot \rightarrow CH_4 + H\cdot, \qquad (25)$$

$$H\cdot + CH_3\cdot \rightarrow CH_4, \qquad (26)$$

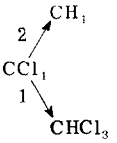
$$CH_3\cdot + CH_3\cdot \rightarrow CH_3CH_3 \qquad (27)$$

It should be noted that our lack of observation of C_2Cl_6 in measurable quantities does not preclude its formation, as reported by Besprozvannyi, *et al.* (*loc. cit.*) at higher pressures. Perhaps the low solubility of H_2 in their *n*-heptene solvent resulted in H_2 concentrations so low that recombination, rather than hydrogen addition, was favored in the solution.

$$2CCl_3\cdot \rightarrow C_2Cl_6 \qquad (28)$$

CONCLUSIONS

The hydrodechlorination of CCl_4 over Pt on alumina catalyst can be correctly written as a pair of parallel reactions



$$CCl_4 \xrightarrow{2} CH_4, \qquad CCl_4 \xrightarrow{1} CHCl_3 \qquad (29)$$

Reaction 1 involves a single step addition of hydrogen to a $CCl_3\cdot$ radical. Reaction 2 involves concerted addition of adsorbed hydrogen to adsorbed $CCl_3\cdot$ radical, with no need for desorption of intermediate species or for sequential addition of hydrogen. The peculiar parallel reaction behavior observed serves as a valid demonstration that adsorption–desorption of intermediates is not a rigid reaction requirement and that compounds in a homologous series may not necessarily exhibit analogous reaction behavior. Polysubstituted compounds may not react consecutively.

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