JOURNAL OF CATALYSIS 6, 167-185 (1966)

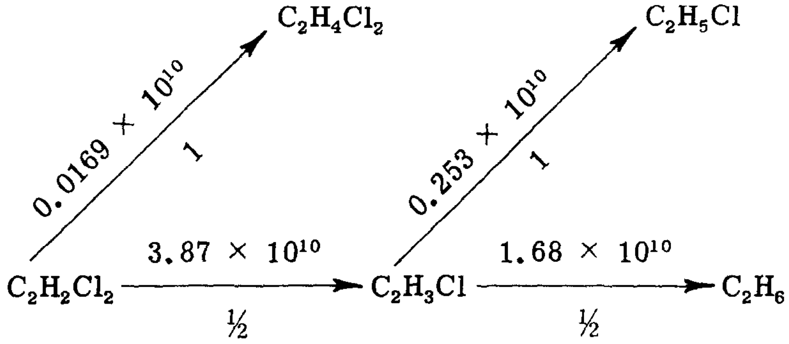
Hydrodechlorination Kinetics and Reaction Mechanisms

A. H. WEISS* AND K. A. KRIEGER

From the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania

Received June 22, 1965; revised February 3, 1966

The reactions of *cis*- and *trans*-dichloroethylenes with H_2 over platinum-on-alumina catalysts have been characterized. Both *cis*- and *trans*-dichloroethylenes react at identical rates, zero order in olefinic chlorides, according to the following scheme:



The reactions were fitted to an activation energy of 27 500 cal/mole. Frequency factors (gm mole/cc sec) at 1 atm H_2, and reaction order in H_2 are noted on each arrow for the zero order reactions. Above 1% conversion, the reactions commence a shift to first order pore-diffusion-controlled kinetics; and the fraction of vinyl chloride produced per mole of reactant converted falls from 50% to zero at complete conversion.

To explain the reactions, a mechanism has been proposed in which it is assumed that olefinic chlorides are adsorbed on the catalyst as stabilized tautomers, best represented as structures containing either —C═C— or $-\overset{-}{C}=\overset{+}{Cl}$ bonds. Hydrogenation proceeds by molecular hydrogen addition to the carbon–carbon double bond of the one tautomeric form; hydrodechlorination by proton addition to the carbon–chlorine double bond of the other form. The catalyst is regarded as a device which stabilizes the charge distribution of a resonating molecule into its possible canonical forms.

INTRODUCTION

Nonreactivity of Olefinic Chlorides

In reactions such as hydrolysis or the Grignard reaction, which involve carbon-chlorine single bonds, reactivity varies from C_{sp^2}–Cl to C_{sp^3}–Cl bond type. Fieser and Fieser (*1*) make the empirical generalization that a halogen atom is invariably deactivated by being joined to an ethylenic double bond. As an example, ethyl chloride undergoes substitution reactions readily, while vinyl chloride does not.

The difference in reactivity is not ascribable to bond energies calculated from heat of formation data. Cox (*2*) has shown that $E(C_{sp^3}\text{–Cl}) = 82.5$ kcal and $E(C_{sp^2}\text{–Cl}) \approx 83$ kcal. Both Pauling (*3*) and Fieser and Fieser attributed the diminished chemical reactivity of the vinyl chloride halogen atom

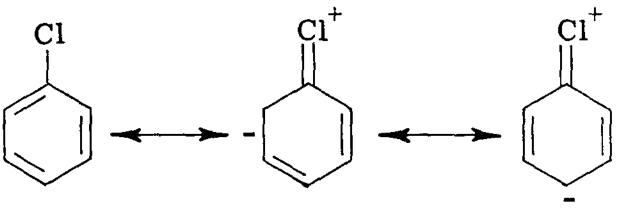
---

* Present Address: Department of Chemical Engineering and Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

to a resonance effect, resulting in the formation of a carbon–chlorine double bond

$$\mathrm{CH_2{=}CH{-}Cl} \longleftrightarrow \mathrm{\overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}} \qquad (1)$$

The comparably inert halogen of chlorobenzene [for which $E(\mathrm{C_{bz}{-}Cl}) = 85.7$ kcal) has also been explained by resonance



(2)

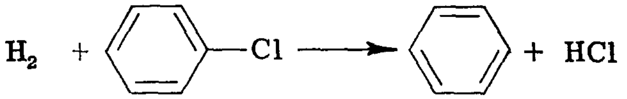
Coulson (*4*) suggests that the reactivity is better explained by hyperconjugation, involving π-electron delocalization. The C–Cl bond acquires a distinct double-bond character and, as a necessary corollary, the Cl atom loses π electrons.

The concept of the carbon–chlorine double bond requires that the carbon–chlorine bond distance of aliphatic chlorides be longer than that of olefinic chlorides. Pauling notes that aliphatic chlorides have a C–Cl bond distance of 1.76 Å, while the C–Cl distance in ethylene substituted by one or two chlorine atoms is 1.69 Å. Double-bond character in the latter compounds was calculated by Pauling from the bond shortening as 18%. Goldstein and Bragg (*5*) calculated the value from nuclear quadrupole interactions as 4%. Subsequently, Pitzer and Hollenberg (*6*) calculated by quantum mechanical valence theory a value of 9%, which is well within the 4%–18% range of the earlier authors. The calculation was based on the observed energy differences between *cis*- and *trans*-dichloroethylenes determined from infrared spectra.

The important point is that the concept of the carbon–chlorine double bond is well established and even the fraction of double-bond character has been measured by independent techniques. The carbon–chlorine double bond affects not only reactivity, but also physical properties, and causes anomalies such as the lower energy and the resulting greater stability of *cis*- than of *trans*-dichloroethylene. This particular phenomenon has been the subject of considerable recent interest (*7–10*).

Enhanced Reactivity of Olefinic Chlorides

The existence of the double-bonded nature of the carbon–chlorine bond in olefinic chlorides has been generally accepted as the reason for their decreased reactivity in reactions involving a C–Cl single bond. On the other hand, should one anticipate enhanced reactivity of olefinic chlorides for reactions peculiar to a double bond? Consider hydrogenation: Should one expect, because of its double-bonded nature, that the C–Cl bond of vinyl chloride will react much more readily than that of ethyl chloride; the C–Cl bonds of dichloroethylenes would be much more reactive than those of dichloroethane, etc.? Precisely these observations, which are the opposite of the usual rule in organic chemistry, were made by Kammerer *et al.* (*11*) and by Horner *et al.* (*12*), who studied, respectively, the hydrogenative dehalogenation of aromatic and aliphatic halogen compounds in the



(3)

$$2\,\mathrm{H_2} + \mathrm{CH_2{=}CHCl} \longrightarrow \mathrm{CH_3CH_3} + \mathrm{HCl} \qquad (4)$$

$$3\,\mathrm{H_2} + \mathrm{ClCH{=}CHCl} \longrightarrow \mathrm{CH_3CH_3} + 2\,\mathrm{HCl} \qquad (5)$$

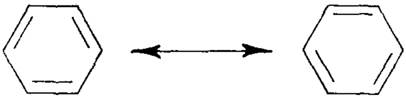
presence of Raney nickel and alkali. They found that the primary and secondary monochloroalkanes did not react under their experimental conditions, vicinal saturated dichloro compounds reacted slowly, and compounds with chlorine atoms adjacent to a double or triple bond reacted readily. The products of the reactions were the corresponding hydrocarbons and HCl. Examples are given in Eqs. (3)–(5).

These hydrodechlorination reactions should be distinguished from dehydrochlorination reactions, in which HCl is merely abstracted (by pyrolysis, e.g.) from the parent compound to produce a compound with a greater degree of unsaturation. A typical dehydrochlorination reaction is

$$ClCH{=}CHCl \xrightarrow{\Delta} ClC{\equiv}CH + HCl \tag{6}$$

Reaction with Tautomeric Forms

Pauling (*3*) has been scrupulous in pointing out the distinction between resonance and tautomerism in Section 57 of his text. When resonance determines the structure of a molecule, the nuclear configuration is not that for any canonical structure that can be drawn for a resonating molecule. On the other hand, if resonance can somehow be reduced so that it is insignificant relative to nuclear vibration frequency, a mixture of tautomers will result whose chemical properties are correctly described by the canonical structures. In the case of benzene resonance


(7)

if such a reduction of resonance were possible, there would result a pair of isomers, i.e., tautomers, corresponding to each Kekule structure.*

One may then note that factors such as thermal excitation or the formation of reaction intermediates may cause a molecule to assume an energy state that results in a shift from a resonating molecule to a tautomeric mixture. The results of the present study suggest that a shift from a resonance structure to tautomeric forms may very well be effected by a heterogeneous catalyst. Certainly a molecule chemisorbed on a catalyst surface is in a different energy state than a gaseous molecule. It is suggested that a nonuniform catalyst surface can be regarded as an array of charge centers, i.e., active sites, on which an adsorbed resonating species behaves like a mixture of tautomeric forms. As an example, vinyl chloride might be thought of as forms corresponding to $CH_2{=}CHCl$ at sites of one type, as $\overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}$ at sites of another type, and as the resonating molecule at other sites. The relative quantities of the tautomeric forms might be altered by varying the method of catalyst preparation.

If reaction occurs by addition to the double bonds of stabilized tautomers, a tool is at hand that will predict and explain the products of complex reaction systems. The canonical resonance forms of a molecule will describe the reacting tautomers and provide an indication of the products that will result. In the present study, the reactions of dichloroethylenes with H_2 over platinum or alumina catalyst have been quantitatively characterized and used to provide a demonstration of the reactions of tautomerlike species.

EXPERIMENTAL

Equipment

Figure 1 is a flow diagram of the reaction equipment used in this study. Commencing

---

* To quote Pauling:

"When the magnitudes of the electronic resonance integral (or integrals) and of the other factors determining the electronic energy function of a molecule are such that there are two or more well-defined stable nuclear equilibrium configurations, we refer to the molecule as capable of existing in tautomeric forms; when there is only one well-defined stable nuclear equilibrium configuration, and the electronic state is not satisfactorily represented by a single valence-bond structure, we refer to the molecule as a resonating molecule."

with the points of chlorinated hydrocarbon addition, only Pyrex and Teflon were used as materials of construction (except for the chromatograph column). Bourdon gauges were used; and pressure drop across the unit was invariably less than 1 torr.

H_2 and N_2 flow rates ranged from 20 to 200 standard cc per minute (SCCM). Liquids, i.e., dichloroethylenes and dichloroethane, were pumped from a Hamilton Teflon-plunger gas-tight syringe at a rate equivalent to 1.9 SCCM.

The reactor was fabricated from standard 10-mm OD–8-mm ID Pyrex tubing positioned in a 38-mm ID by 30.5 cm long tube furnace. Radiant heating was utilized; and the ends of the furnace were plugged to prevent vertical convection. Gases were heated to reaction temperature while passing vertically upward through the empty tube and a 4.5 cm section of 3-mm Kimax Beads supported on a coarse porous glass plate. A 7-mm OD Pyrex thermowell containing an iron-constantan thermocouple was positioned immediately above the catalyst bed. Reaction temperature was measured at this point; and, in addition, the thermowell produced an annulus to effect rapid removal of the product stream from the high-temperature zone. Temperature was both indicated and controlled with a precision of ±0.1°C.

The product stream or, if the reactor were bypassed, the charge stream, then flowed through a 1-cc sample volume to a vent. When desired, the gas sample was trapped by the system of Teflon cocks indicated in Fig. 1 and was picked up by nitrogen carrier gas for analysis. Vented material could also be collected in bulbs for mass spectrometer analysis.

Materials

Hydrogen. Hydrogen was purchased in cylinders as the purified grade from the Liquid Carbonic Division of General Dynamics, Inc. Prior to use, the hydrogen was passed over Deoxo palladium catalyst and then over Houdry Process and Chemical Company Type K Nickel on Alumina catalyst to remove possible trace oxygen (Fig. 1). Any H_2O and CO_2 present were

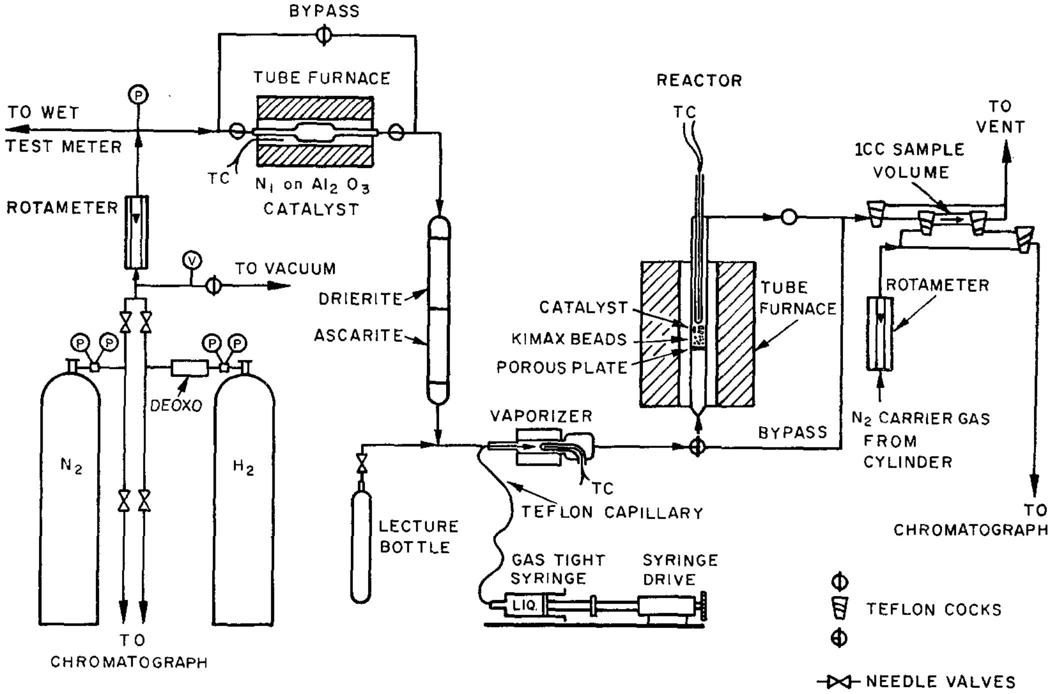


FIG. 1. Hydrodechlorination unit.

then removed by passage over Drierite and Ascarite, consecutively.

Nitrogen. Purified nitrogen was purchased in cylinders from the Air Reduction Company. Except for the Deoxo catalyst, nitrogen received the same purification as hydrogen.

Vinyl chloride. This material was purchased in lecture bottles as the pure gas from the Matheson Company, Inc. It was metered by a needle valve into the unit. Analysis, >99.9%.

Ethyl chloride. Same as vinyl chloride.

Dichloroethylenes. Both *cis*- and *trans*-dichloroethylenes were purchased as the practical grades from Eastman Organic Chemicals Department of Distillation Products Industries. Prior to use, *cis*- and *trans*-dichloroethylene were separately fractionated at 50:1 reflux ratio in a 100 theoretical plate column. P_2O_5 was added to the still pot and dry N_2 was bubbled at a low rate into the still pot. Middle fractions were collected in the dark at the appropriate boiling points and stored in the dark at −12°C until used. The analyses of these fractions, designated "Cis" and "Trans" for their major components, were as follows:

	"Cis"	*"Trans"*
Mole fraction *cis*-$C_2H_2Cl_2$	0.988	0.0271
Mole fraction *trans*-$C_2H_2Cl_2$	0.0121	0.973

Dichloroethane. Dichloroethane was purchased as the "spectro" grade from Eastman. Analysis >99.98% 1,2-$C_2H_4Cl_2$.

Catalyst. The catalyst used was Houdry Process and Chemical Company 3H Reforming Catalyst. This catalyst is 0.5 wt % Pt on eta-Al_2O_3, with a surface area of 250 m^2/g. The catalyst is in the form of extruded pellets 1/16-inch in diameter and of variable length, nominally 1/8 inch. Bulk density was measured to be 0.77 g/cc; and a single sample consisting of 0.335 cc of catalyst was used for all of the runs. The resulting bed, approximately 0.5 cm deep, was supported by the Kimax beads and positioned at the center of the furnace. Calculation of the degree of dispersion (*13*) in the reactor showed that it was completely back-mixed.

Prior to operation, the catalyst was reduced for at least 1 day in flowing hydrogen at 190°C. Once reduced, the catalyst was maintained constantly under positive H_2 pressure to avoid air leakage into the reactor.

The runs of the present study cover a H_2 partial pressure range of 39 to 760 torr. Dichloroethylene partial pressure ranged from 1 to 10 torr; and useful rate data were obtained within a residence time range of 0.08 to 0.16 sec and a temperature range of 26° to 120°C.

Analysis

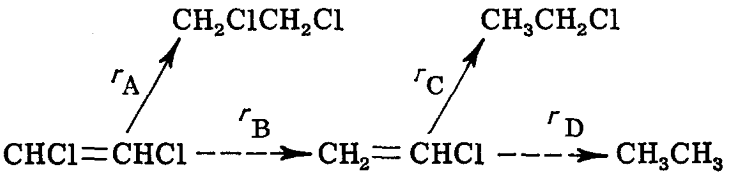
A Wilkens Instrument and Research, Inc., Aerograph Model 600-C gas chromatograph equipped with a flame ionization detector was used for all analyses. The lower limit of detection of the hydrocarbon components of interest in the gas stream corresponded to a partial pressure of 0.0005 torr for the lowest boiling component—ethane—and increased to 0.005 torr for the highest boiling component—dichloroethane. Analytical accuracy is estimated to be ±2% of the partial pressure measured, except for partial pressures approaching within a factor of 10 of the limit of detection. Repeatability is a function of the stability of gas and liquid flows; it was approximately ±10%.

Separation was effected in order of increasing boiling point by a 10-ft by 1/8-inch OD copper tubing column packed with dinonyl phthalate on Chromosorb P and operated at 69°–71°C. The column was not capable of resolving ethylene and ethane; but mass spectrometer analysis of reaction products established that ethane, rather than ethylene, was produced.

RESULTS

It was found (*14*) that vinyl chloride and *cis*- and *trans*-dichloroethylenes reacted readily with H_2 in the presence of Pt on Al_2O_3 reforming catalyst according to the scheme of Eq. (8) (next page).

In the temperature range studied ethane, ethyl chloride, and 1,2-dichloroethane were shown by separate experiments to be effectively unreactive terminal products over the Houdry 3H Catalyst. No measurable isomerization of dichloroethylenes was detected in any of the studies made.



$$\begin{tikzcd} & \mathrm{CH_2ClCH_2Cl} & & \mathrm{CH_3CH_2Cl} & \\ \mathrm{CHCl{=}CHCl} \arrow[ur, "r_A"] \arrow[rr, dashed, "r_B"] & & \mathrm{CH_2{=}CHCl} \arrow[ur, "r_C"] \arrow[rr, dashed, "r_D"] & & \mathrm{CH_3CH_3} \end{tikzcd} \qquad (8)$$

Equivalence of Cis- and Trans-Dichloroethylenes

Figure 2 is a plot of *trans*- vs. *cis*-dichloroethylene conversion for runs made using a blend of 53.2 mole % *cis*- and 46.8 mole % *trans*-dichloroethylene. Figure 2 shows that these species are converted at identical rates in this reaction system. If they were converted at significantly different rates, the data would not fit the 45° line drawn on Fig. 2. In a kinetic analysis of the results of this study, *cis*- and *trans*-dichloroethylenes can be treated as one species. One may also infer that the rates of the reactions which occur in this system have no relationship to the *cis* and *trans* spatial configurations of the reactants, even though the adsorbed forms of the *cis* and *trans* species on the catalyst must differ, since no isomerization was observed. Free radical mechanisms,

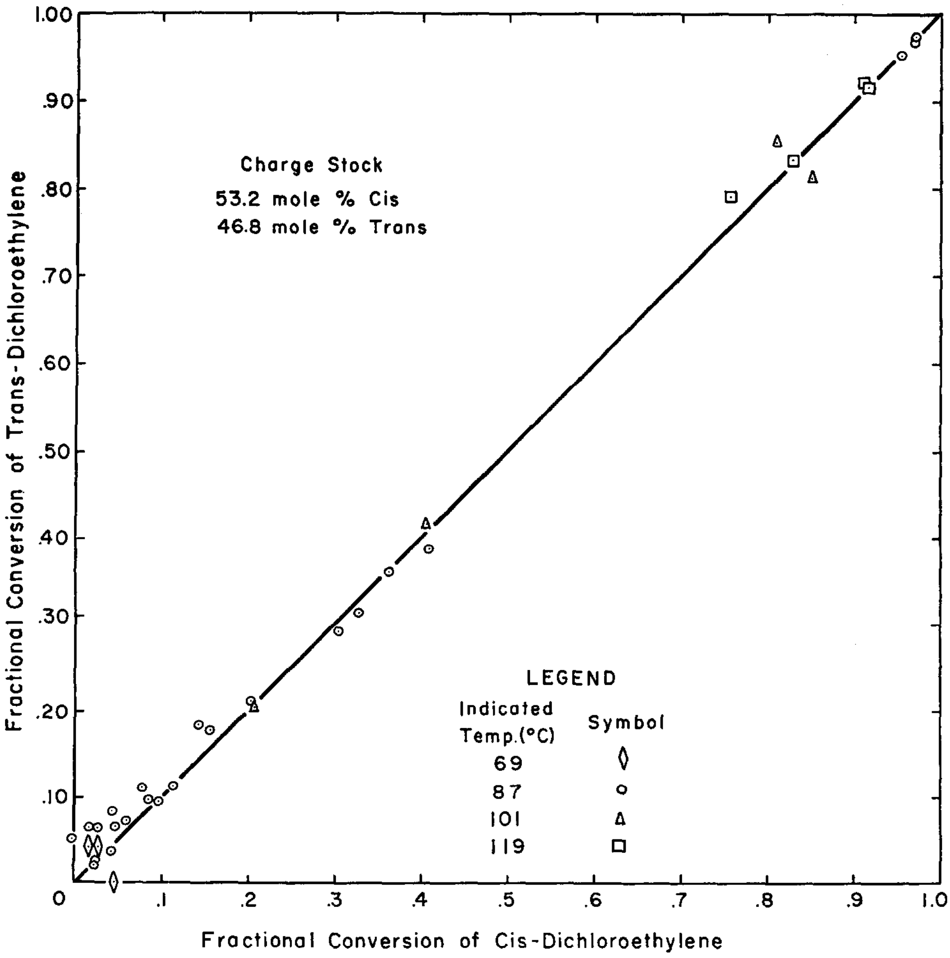


FIG. 2. *Cis*- and *trans*-dichloroethylenes react at identical rates; charge stock 53.2% *cis*-, 46.8% *trans*-dichloroethylenes.

involving formation of ClCH=CH· radicals, which would not necessarily return to a preferred *cis* or *trans* structure, are thus ruled out for this system.

Reaction Kinetics

Figure 3 shows the effect of varying dichloroethylene partial pressure when hydrogen partial pressure and temperature are maintained fixed at 760 torr and 86–87°C, respectively. Dichloroethylene conversion rate is zero order with respect to dichloroethylene partial pressure; and so are ethane, ethyl chloride, and dichloroethane production rates.

Figure 4 shows the effect of varying hydrogen partial pressure at 86–87°C. Dichloroethylene conversion (to ethane + vinyl chloride + ethyl chloride) and ethane production data are those that correspond to half-order hydrogen dependence. Least-squares analyses of the data used for Fig. 4

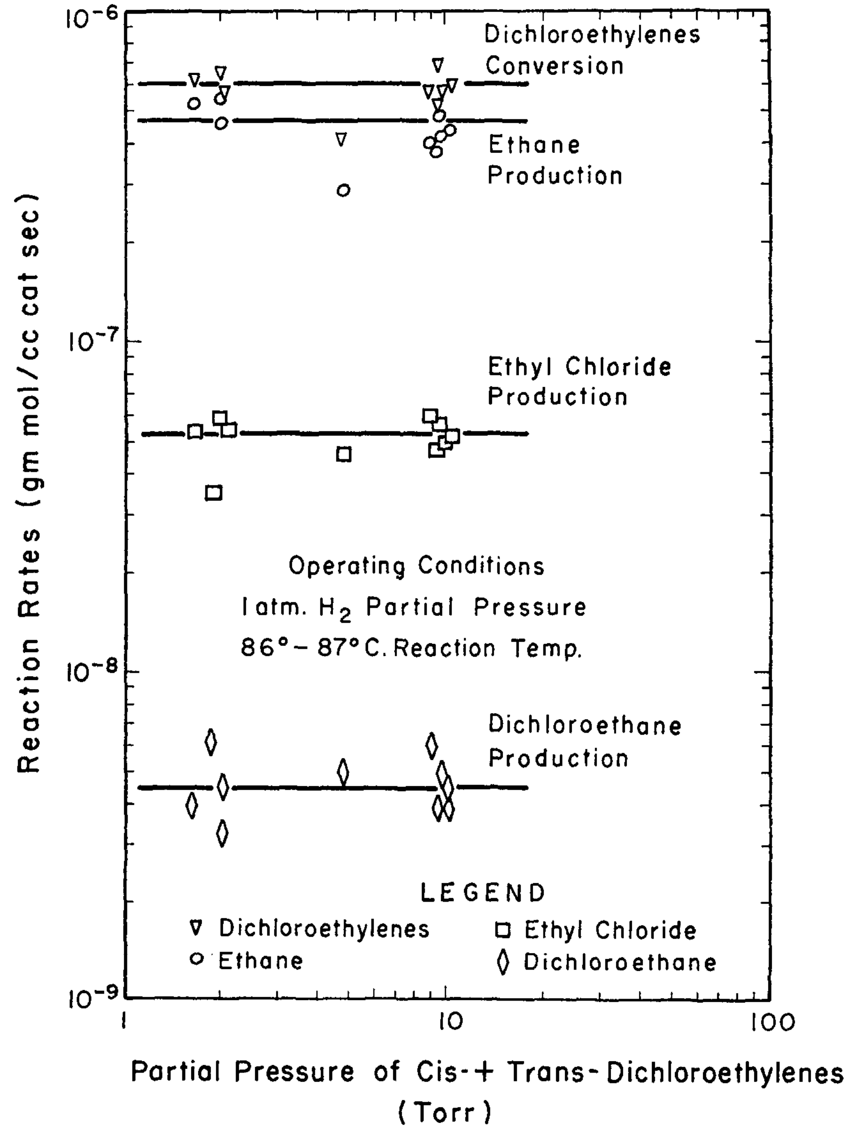


FIG. 3. The zero order dependence of reaction rates on dichloroethylene partial pressure; charge stock 53.2% *cis*-, 46.8% *trans*-dichloroethylenes.

indicate that the exponents that best fit the data points are 0.64 for dichloroethylenes and 0.69 for ethane. With these exponents, rates are fitted with standard errors that are a factor of 1.18 and 1.13, respectively. Because of the complex nature of the reaction system, Langmuir-Hinshelwood effects are not considered in the data analysis. At low conversion levels, 0.5 is selected as the closest half-integral order that best represents the effect of hydrogen on dichloroethylene conversion and ethane production. As conversion increases, it was established that a shift from zero order reactions to first order pore-diffusion-controlled reactions occurs. The consequence is an apparent, but not true, increase in Fig. 4 of hydrogen order beyond the 0.5 level. This shift is also illustrated on Fig. 5, which shows that vinyl chloride yields at high conversion levels are best fitted by a first order pore-diffusion-controlling model. A significantly poorer fit of the data to the calculated lines on Fig. 5 resulted when the assumption was made that surface reaction, rather than pore diffusion, controlled at dichloroethylene conversions over 10%.

Figure 6 is a plot of ethane and vinyl chloride production versus reciprocal temperature for experiments at 732–762 torr H_2 partial pressure. Figure 7 is a similar plot showing ethyl chloride and dichloroethane production rates. Note that the total production rate of products—vinyl chloride, ethane, ethyl chloride, and dichloroethane—cannot exceed the charge rate of dichloroethylenes to the reactor.

At temperatures higher than those for the runs plotted on Figs. 6 and 7, production rates of terminal products—ethane, ethyl chloride, and dichloroethane—will level off to asymptotic values whose total approaches the charge rate. The production rate of vinyl chloride, the only reactive product, will ultimately fall towards zero to satisfy the material balance. The Arrhenius plots of

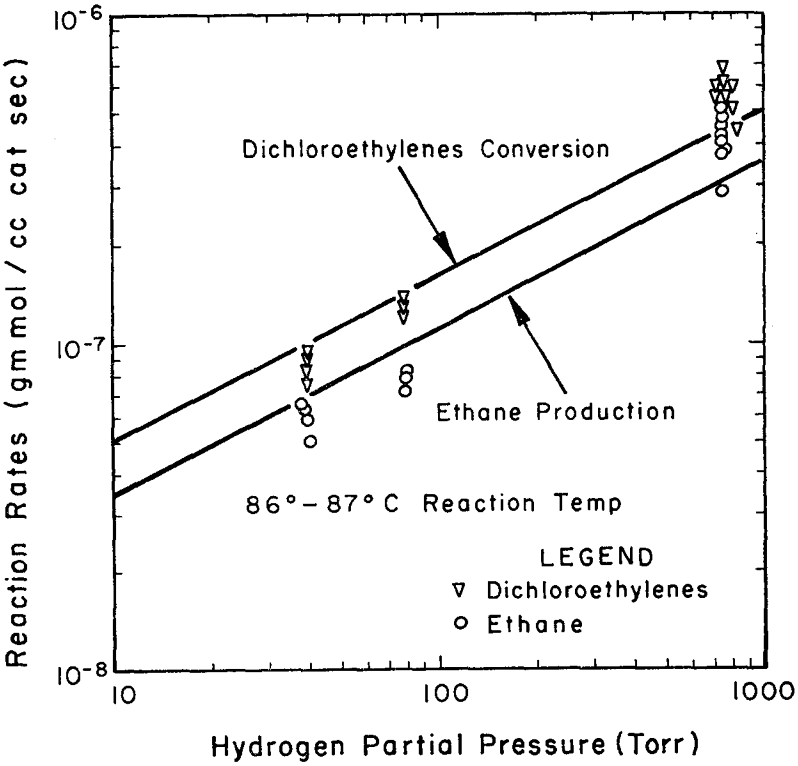


FIG. 4. The half-order dependence of dichloroethylene conversion rate and ethane production rate on hydrogen partial pressure; charge stock 53.2% *cis*-, 46.8% *trans*-dichloroethylenes.

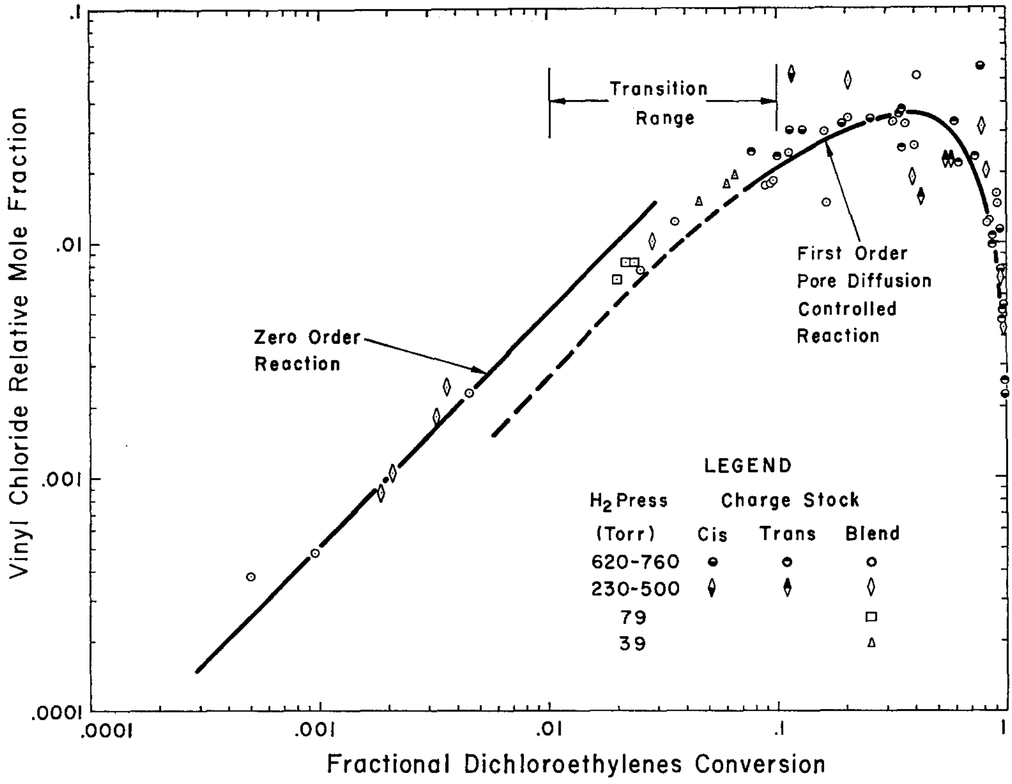


FIG. 5. Vinyl chloride Type III selectivity relationships; shift from zero order to first order reaction.

Figs. 6 and 7 are arbitrarily fitted with identical slopes, corresponding to an activation energy of 27 500 cal/mole.

For the purpose of both illustrating the hydrogen dependence of ethyl chloride and dichloroethane production and confirming the relative rates of ethane:ethyl chloride: dichloroethane shown on Figs. 6 and 7, for 732–762 torr H_2, plots have been made of ethyl chloride and dichloroethane production rates versus ethane production rates. The plots—Figs. 8 and 9—include the 760 torr H_2 data obtained using the blend of dichloroethylenes shown on Figs. 6 and 7 as well as data from lower hydrogen partial pressure runs and from runs on practically pure *cis*- and *trans*-dichloroethylenes. In both Figs. 8 and 9, partial pressures of each component in the effluent stream, rather than production rates, are plotted, since the ratios are equivalent in a back-mixed reactor.

Figure 8 shows the relationship between ethyl chloride and ethane. The lines drawn on the figure correspond to a first order dependence of ethyl chloride production on hydrogen partial pressure. Figure 9 shows the relationship between dichloroethane and ethane. Clear parameters for H_2 partial pressure can be drawn above 0.01 torr dichloroethane. Below this level, the yields of dichloroethane approach the limit of detectability of the chromatograph. Confidence limits are also noted on Fig. 9. Since dichloroethane production was only 1% of ethane production, the accuracy at low partial pressures is poor. It is concluded that dichloroethane and ethyl chloride show the same first order rate dependence on hydrogen partial pressure.

Referring again to Fig. 6, note that at low temperatures the Arhennius line for vinyl chloride production rate approximates that for ethane, while at higher temperatures vinyl chloride production rate falls sharply below ethane production rate. This is a

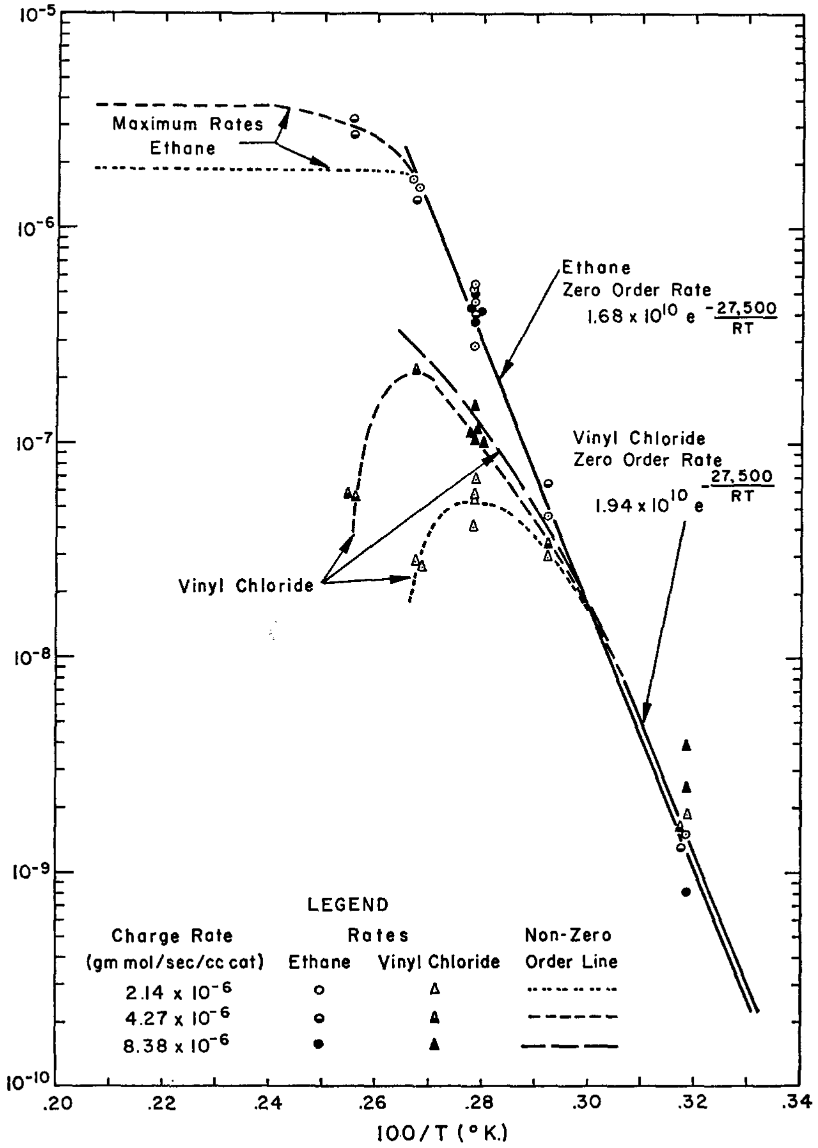


FIG. 6. Production rates of ethane and vinyl chloride at 1 atm H_2 partial pressure; parameters of 53.2% *cis*-, 46.8% *trans*-dichloroethylene blend charge rates.

reflection of the transition from zero order kinetics, where the catalyst has a plentiful supply of dichloroethylene, to the start of first order kinetics, where the catalyst is starved for dichloroethylenes.

At even more elevated temperatures, the dichloroethylene conversion rate must eventually equal the indicated charge rates.

Thus, Fig. 6 shows that the point at which vinyl chloride production rate begins to fall below its straight line Arrhenius plot is a function of the charge rate to the system, and hence, conversion. It is remarkable that even though dichloroethylenes are so strongly absorbed at these low temperatures, the transition from zero order kinetics commences at a very low conversion—less than 1%.

The reaction remains effectively zero order in vinyl chloride, which is evidenced by the

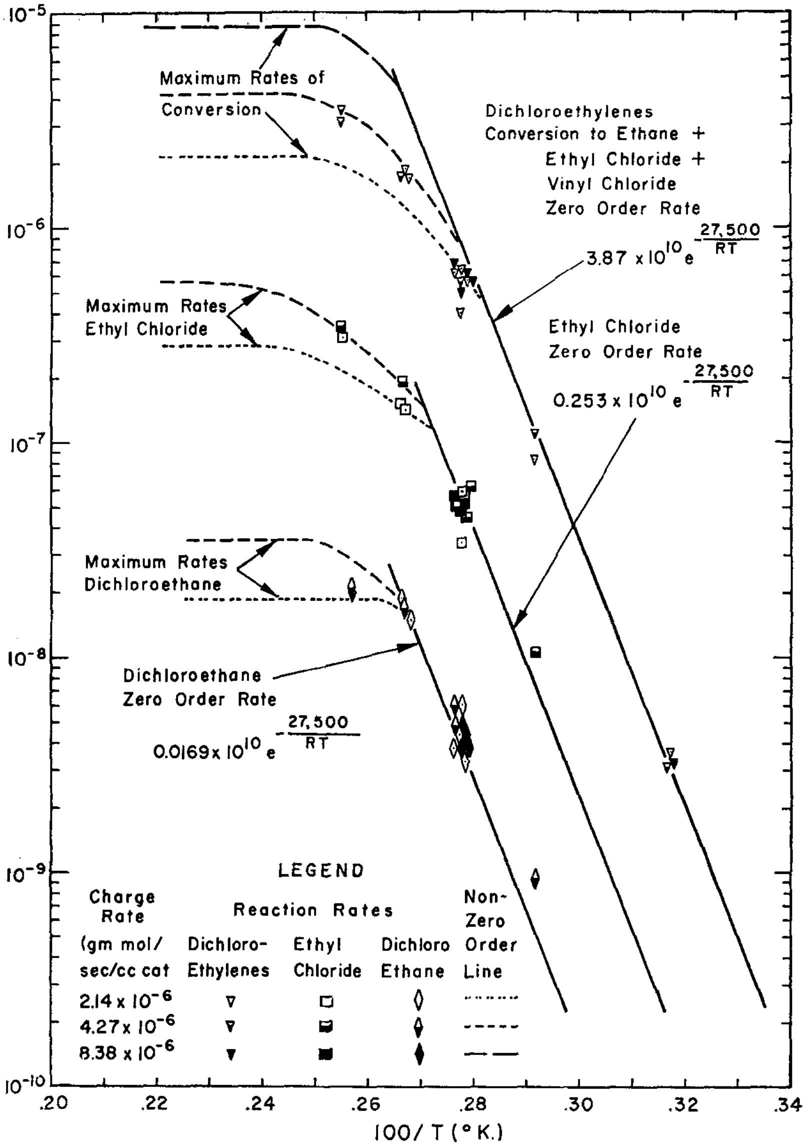


FIG. 7. Conversion rate of dichloroethylenes and production rates of ethyl chloride and dichloroethane at 1 atm H_2 partial pressure; parameters of 53.2% *cis*-, 46.8% *trans*-dichloroethylene blend charge rates.

zero order behavior of ethane production, to approximately 50% conversion (Fig. 6). The reason for such curious behavior, namely, a consecutive reaction remaining zero order in the intermediate step long after the shift to first order has begun in the first reaction step, is readily understandable, if vinyl chloride is *generated in excess at a site,* while dichloroethylenes must *diffuse* to the site. It will be shown subsequently that the mechanism proposed assumes just such a process.

At high conversion levels this system provides an example of pore-diffusion-controlled first order Type III Selectivity, described by Wheeler (*15*). The truly zero order Type III Selectivity (i.e., below 1% conversion) is independent of whether the system is surface-reaction-controlled or pore-diffusion-controlled. This can be shown

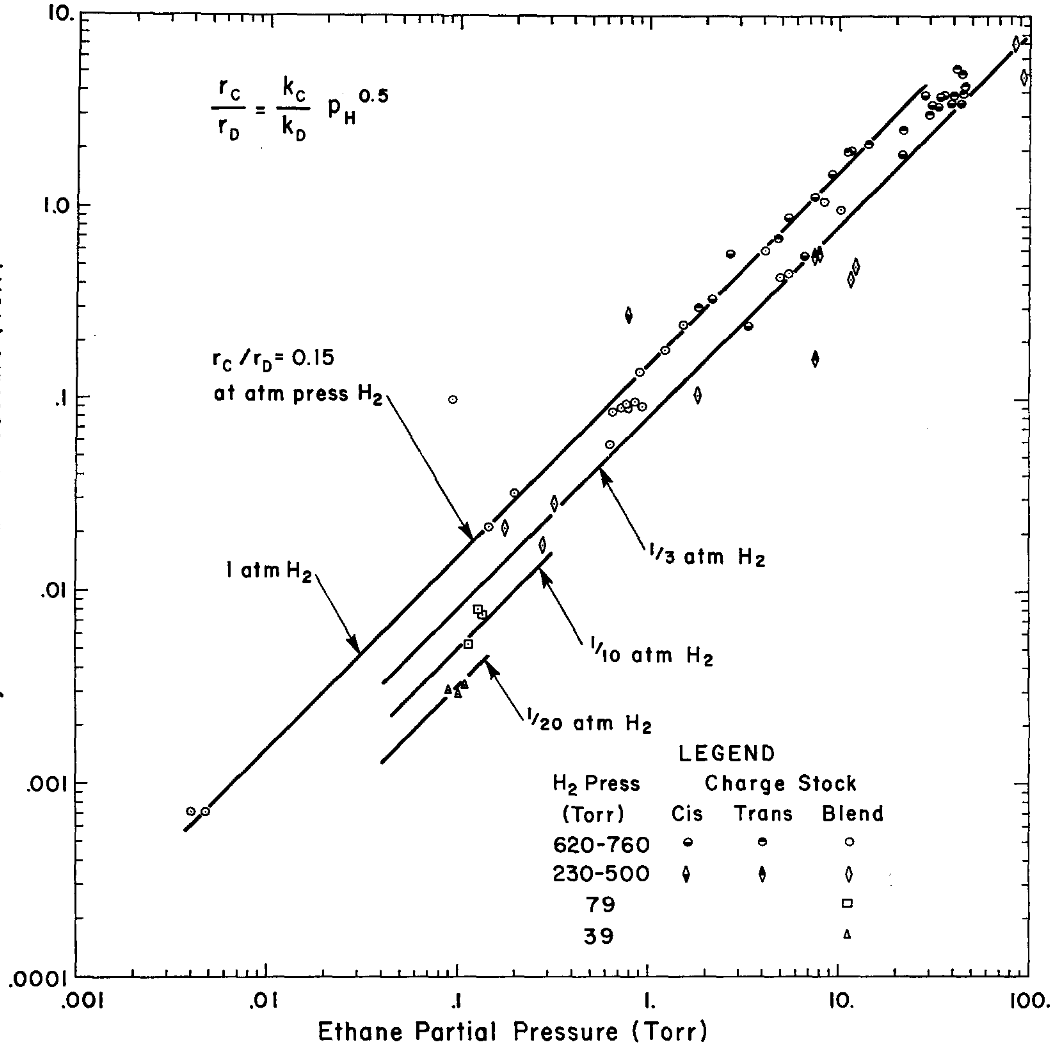


FIG. 8. Relative rates ethyl chloride to ethane production; parameters of hydrogen partial pressure noted.

readily using the method of Wheeler (for zero order, rather than first order reactions).

The zero order rate expressions and values of the rate constants (in g mole/cc cat sec) are obtained from Figs. 6 to 9 for the conversion range below 1%. H_2 partial pressure is expressed as atmospheres.

$$r_A = 0.0169 \times 10^{10} \exp(-27\,500/RT)p_H \quad (9)$$

$$r_B = 3.87 \times 10^{10} \exp(-27\,500/RT)p_H^{0.5} \quad (10)$$

$$r_C = 0.253 \times 10^{10} \exp(-27\,500/RT)p_H \quad (11)$$

$$r_D = 1.68 \times 10^{10} \exp(-27\,500/RT)p_H^{0.5} \quad (12)$$

Note that $r_B/r_D \cong 2$. This is a mathematical statement that the zero order rate of reaction of adsorbed dichloroethylenes is twice that for adsorbed vinyl chloride.

Effect of Catalyst Preparation

The Houdry Process and Chemical Company generously provided the 0.5% platinum on alumina 3H reforming catalyst for this study, and the unimpregnated eta-alumina pellets from which the catalyst was produced. Experimental catalysts were prepared con-

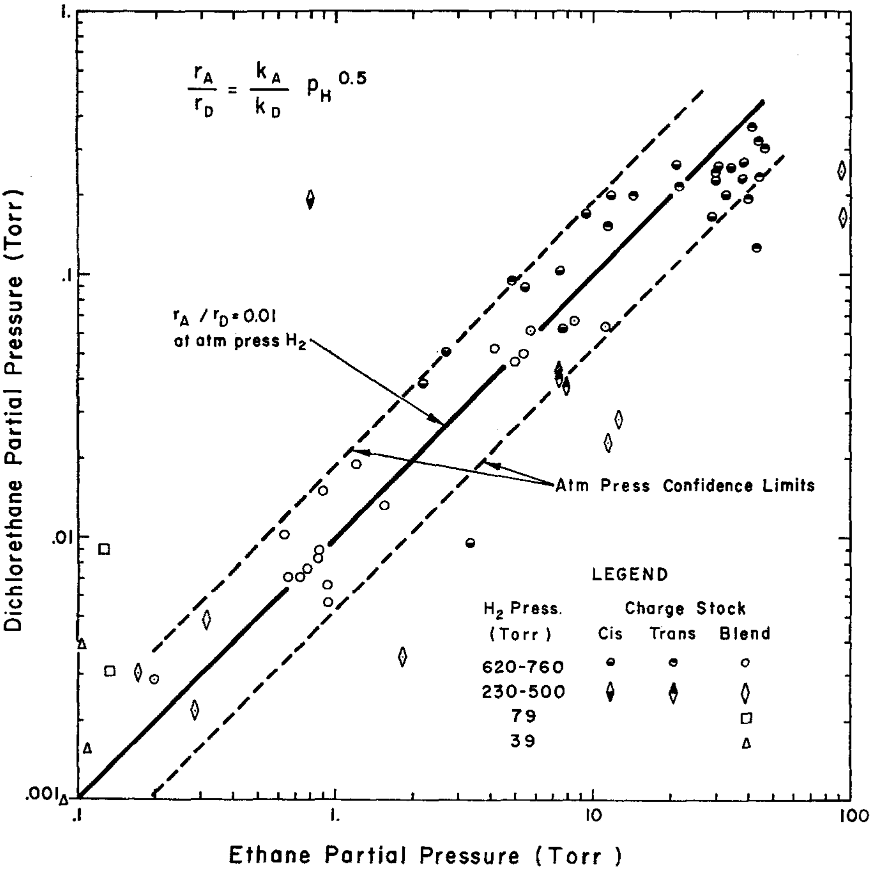


FIG. 9. Relative rates, dichloroethane to ethane production; confidence limits of data obtained at 1 atm hydrogen are a factor of 1.9; $\log r_A/r_D = -2 + 1/2 \log p_H \pm \log 1.9$.

taining 0.5% Pt on the same eta-alumina base; and Table 1 lists the catalysts studied and their preparation method in order of decreasing activity (as measured by ethane production rate from a blend of 46.4% *trans*–53.6% *cis*-dichloroethylenes).

Table 1 also lists the relative rates of dichloroethane to ethane and of ethyl chloride to ethane production, r_A/r_D and r_C/r_D. These values can be regarded as a measure of the relative amounts of the quasitautomeric reaction species that are on the catalyst and react to produce their respective hydrogenation and hydrodechlorination products. The fact that these values vary is an indication that the ratio of species is not an equilibrium distribution characteristic of the reactant alone. An external factor—the catalyst—is involved. Note that the relative rates of hydrogenation to hydrodechlorination do not vary consistently with catalyst activity.

DISCUSSION OF RESULTS

Hydrodechlorination Reaction Mechanism

It is possible to develop a catalytic hydrodechlorination mechanism on the basis of tautomerism and in accordance with the results of the present study that explains both aliphatic chloride and ethane production from olefinic chlorides. Since carbon–chlorine bond energies of aliphatic and olefinic chlorides are almost identical, they do not offer a satisfactory approach to the explanation of the great reactivity difference between the two species.

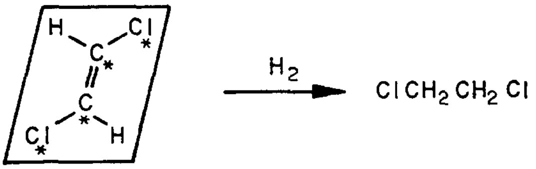
Suppose that a resonating olefinic chloride

TABLE 1
0.5% PT ON HOUDRY ETA ALUMINA BASE CATALYSTS

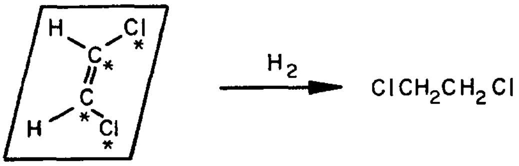
Catalyst designation	Preparation method	Activity	r_A/r_D	r_C/r_D
H_2PtCl_6	Impregnation from aqueous H_2PtCl_6 soln.; dried at 140°C, reduced 10 hr at 190°C in H_2	20	0.07	0.45
$PtBr_4$	Impregnation from alcoholic $PtBr_4$ soln; reduction occurred while drying at 140°C; reduced 23 hr at 190°C in H_2	3	0.0054	0.07
Houdry 3H	Commercially prepared, reduced 24 hr at 190°C in H_2	1	0.01	0.15
PtI_4	Reduced H_2PtCl_6 catalyst heated 16 hr at 250°C with I_2; PtI_4 reduced by heating 7 hr at 190°C in N_2; reduced 14 hr at 190°C in H_2	0.05	0.10	0.30
Fired H_2PtCl_6	Dried H_2PtCl_6 catalyst fired and reduced in air at 770°C for 2 hr, reduced 24 hr at 190°C in H_2	0.02	0.01	0.095

is stabilized as adsorbed tautomers on the catalyst surface, to account for production of both hydrogenation and hydrodechlorination products. In the case of *cis*- and *trans*-dichloroethylenes, the adsorbed species must differ in that no isomerization of desorbed products was observed. However, the reactive bonds of the adsorbed species must be identical, in that no differences in reaction rates between the two isomers were measured. The fact that dichloroethylenes hydrodechlorinate at twice the rate of vinyl chloride suggests that adsorption takes place at both chlorine atoms, rather than at a single atom.

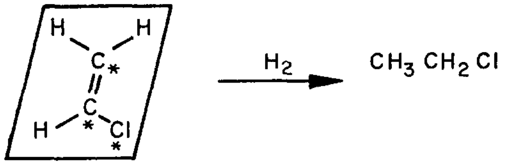
On the basis of these considerations, four-point adsorption of dichloroethylenes and three-point adsorption of vinyl chloride become the allowable forms of the adsorbed molecules. To explain hydrogenation, it is assumed that a certain percentage of the molecules are adsorbed on sites in such a manner that their charge distribution corresponds to the normally written canonical form of olefinic chlorides. Reaction products are readily desorbed.



(13)



(14)



(15)

The strongly polar nature of the reactants, and reaction temperatures not greatly different from their boiling points would account for the observed zero order rate dependence on dichloroethylene and vinyl chloride partial pressure. Addition of molecular hydrogen to the carbon–carbon double bond is in accord with the observed first order dependence of hydrogenation on hydrogen partial pressure.

Hydrodechlorination can be explained on the basis that adsorbed olefinic chlorides on sites other than those at which hydrogenation took place are in a form whose charge distribution corresponds to the quasitautomeric species containing carbon–chlorine double bonds. The hypothesis that certain sites are capable of effecting one charge distribution for an adsorbed species, others another, is supported by the observation that varying the method of catalyst preparation (independent of catalyst activity) varied the relative amounts of hydrogenation and hydrodechlorination products.

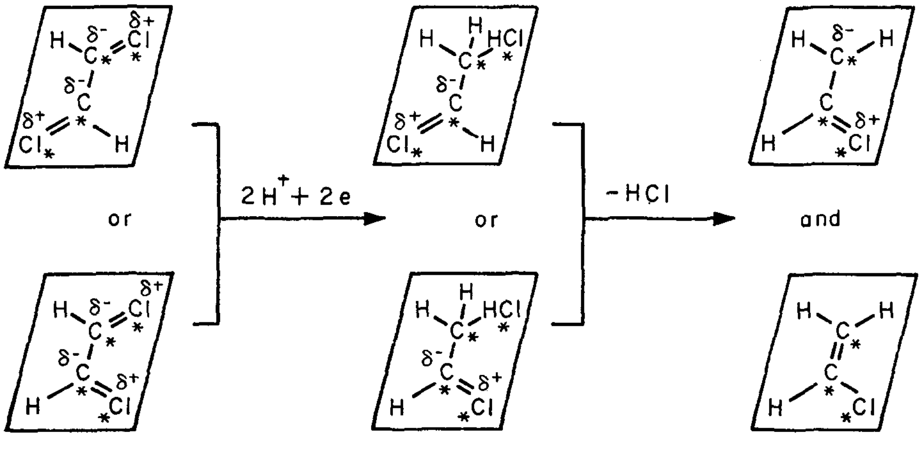
The observed half-order dependence of hydrodechlorination rate on hydrogen partial pressure suggests that addition of a dissociated form of H_2, rather than of molecular hydrogen, is the rate-controlling step for hydrodechlorination. Since the carbon–chlorine double bond is highly polar, we believe (but cannot prove in this intrinsically acid system) that the dissociated H_2 is adsorbed on the catalyst surface in the form of protons (rather than atoms).

Although the experimental evidence does not uniquely establish a hydrogen addition mechanism, it is suggested that the rate-controlling step in hydrodechlorination is the addition of the first proton to the carbon–chlorine double bond of the adsorbed olefinic chloride tautomer at the location where the electronic charge density is the greatest.

Nothing in this study provides a guide to subsequent steps. Possibly this "half-hydrogenated" cation dissociates with the adsorbed Cl^+ subsequently converted to an anion by the acquisition of electrons from the metal, followed by combination with a second proton to form HCl.

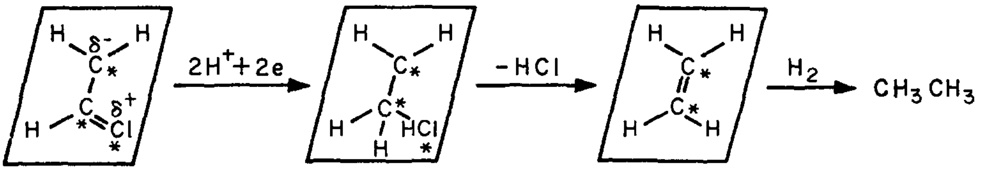
In any case, to account for the persistence of zero order kinetics in vinyl chloride long after dichloroethylene conversion has begun to shift to first order, it is necessary to assume that the hydrocarbon moiety which results is *adsorbed* vinyl chloride.

It is now possible to write an overall reaction scheme to explain the observed hydrodechlorination of *cis*- and *trans*-dichloroethylenes. The adsorbed molecules, in the form of quasitautomers having charge distributions most closely resembling molecules containing carbon–chlorine double bonds, react with protons in the sequence just described to form unstable HCl addition products which break down to produce adsorbed vinyl chloride in its two tautomeric forms:



(16)

The olefinic form of adsorbed vinyl chloride is hydrogenated to ethyl chloride, as mentioned previously. The form containing the carbon–chlorine double bond hydrodechlorinates through the same proton addition sequence as above to produce adsorbed ethylene, which is readily hydrogenated to the observed ethane.



(17)

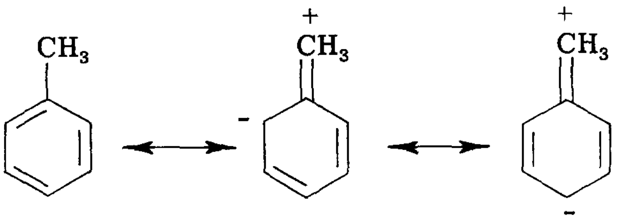
Hydrodealkylation

The logic that has been employed in this study can be utilized in what is, at first glance, an apparently unrelated process. Consider hydrodealkylation, which has become a major petrochemical process for the production of benzene and naphthalene from their alkyl homologs. The reactions, exemplified by that for toluene,

$$H_2 + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_4 \qquad (18)$$

occur both thermally and catalytically at elevated temperatures and pressures. The literature on hydrodealkylation is extensive; reviews are provided by Weiss (*16*) and by Asselin (*17*). Free radical chain mechanisms have been proposed by Silsby and Sawyer (*18*) and, more recently, by Amano *et al.* (*19*).

The present approach to the hydrodealkylation reaction considers hydrogen addition to double bonds that are written in the canonical structures for toluene. It presumes that toluene is stabilized as these forms as a result of thermal or catalytic excitation. Toluene hyperconjuation is well known and is discussed in depth by Coulson (*4*). Toluene hyperconjugation can be represented by two ionic structures



(19)

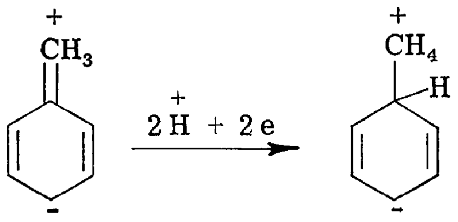
and a hydrodealkylation mechanism analogous to hydrodechlorination and proceeding via hydrogen addition to the double bond of a stabilized tautomer can be formulated. [Eqs. (20), (21)].

In support of such a mechanism, observed phenomena are readily described by addition to the stabilized tautomeric structures that are not explained by chain mechanisms. Consider the fact, shown by Szwarc (*20*), that the aliphatic C–C bond is the weakest bond in ethylbenzene, e.g., pyrolysis of ethylbenzene takes place by a unimolecular process in which the rate-determining step is Eq. (22).

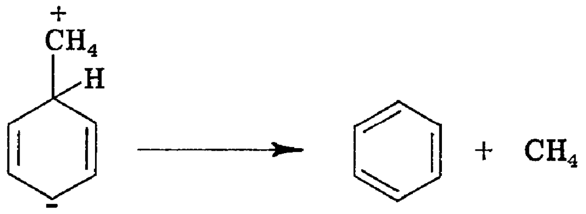
Hydrodealkylation free radical chain mechanisms infer, from such a consideration, that one could expect that toluene would be the major product to be produced by ethylbenzene hydrodealkylation. But this is not the case. Morii *et al.* (*21*) report that the quantity of toluene formed is only 10–20% of that of benzene. This is understandable from the viewpoint of Eqs. (23) and (24). Weiss and Doelp (*22*) have characterized catalytic ethylbenzene hydrodealkylation with the assumption that benzene is the sole product formed.

The utility of considering the canonical forms is that the double-bond locations show where hydrodealkylation will take place. In the case of cumene, the hyperconjugated structures and reaction products of Eq. (25) are possible.

According to Doelp (*23*), the indicated products are produced from hydrodealkylation of cumene. The important conclusion

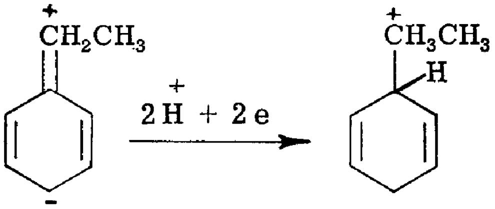


(20)

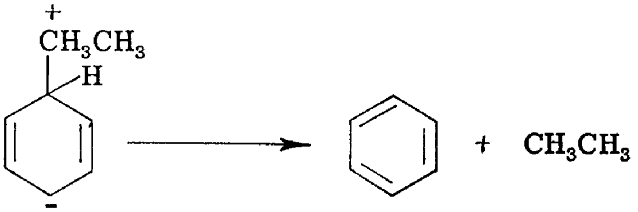


(21)

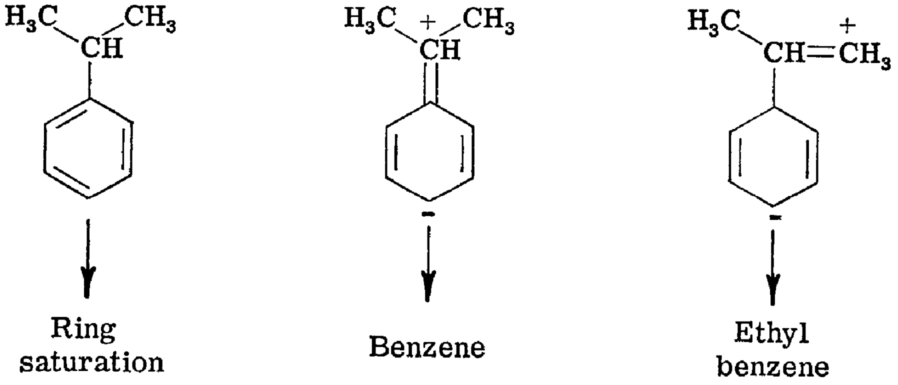
$$C_6H_5CH_2CH_3 \dashrightarrow C_6H_5CH_2\cdot \quad + \quad CH_3\cdot \tag{22}$$



(23)



(24)



(25)

that results is that charge distribution, rather than bond energies, has dictated the location of hydrogen addition and the resulting hydrodealkylation products.

CONCLUSIONS

It has been shown that *cis*- and *trans*-dichloroethylenes and vinyl chloride are simultaneously hydrogenated and hydrodechlorinated in the presence of platinum-on-alumina catalysts to produce dichloroethane, ethyl chloride, and ethane as terminal products. Dichloroethylene hydrodechlorination is a consecutive reaction in which vinyl chloride is produced as a reactive intermediate. No isomerization of *cis*- and *trans*-dichloroethylenes was detected. Hydrogenation reactions are first order and hydrodechlorination reactions are half-order with respect to hydrogen partial pressure; and, at conversion levels below 1%, all reactions are zero order with respect to hydrocarbon partial pressures. This reaction system may be of further interest as a model system for studying the transition range from zero order to first order pore-diffusion-controlled kinetics, in that the vinyl chloride rate provides a sensitive indication of the shift.

The products and rates of the observed reactions could not be explained using conventional bond energy or free radical mechanistic approaches. In line with the known fact that olefinic chlorides are hyperconjugated structures, a mechanism based on the premise that olefinic chlorides are adsorbed on the catalyst as stabilized tautomerlike structures has been proposed. Two species of adsorbed olefinic chlorides are envisioned. In one the molecular charge distribution (caused by a catalyst site in proximity to the adsorbed molecule) can best be represented as a structure containing carbon–chlorine double bonds. The other structure (occurring at a different site) corresponds to the normally written olefinic form containing a carbon–carbon double bond. The nature of the adsorbed species varies from site to site on the catalyst surface and the relative amounts of the two species are dependent on the catalyst structure, rather than activity. With these hypotheses, it has been possible to explain the phenomena observed in the present study and to predict products in hydrodealkylation thermal and catalytic systems.

This mechanistic approach, in which the canonical forms of an adsorbed resonating molecule are treated as the reacting species, can then be altered to provide a view of a catalyst's role in multiproduct addition reactions. The catalyst can be regarded as a device for stabilizing the charge distribution of a ground state resonance structure into stable species corresponding to the possible canonical tautomers.

ACKNOWLEDGMENTS

Financial support for the equipment and materials used in this study was provided by the Advanced Research Projects Agency of the Department of Defense Contract SD 69. The authors wish to gratefully acknowledge this support, which was administered by the Laboratory for Research on the Structure of Matter of the University of Pennsylvania. The research was also supported in part by the Institute for Cooperative Research of the University of Pennsylvania, which provided the necessary academic appointments, clerical services, and digital computer facilities.

REFERENCES

1. Fieser, L. F., and Fieser, M., "Organic Chemistry," 1st ed., pp. 154, 569. D. C. Heath and Co., Boston, Massachusetts, 1944.
2. Cox, J. D., *Tetrahedron* **18,** 1337–1350 (1962).
3. Pauling, L., "The Nature of the Chemical Bond," 2nd ed. Cornell Univ. Press, Ithaca, New York, 1945.
4. Coulson, C. A., "Valence," 2nd. ed., pp. 356–365. Oxford University Press, London, 1963.
5. Goldstein, J. H., and Bragg, J. K., *Phys. Rev.* **75,** 1453 (1949); **78,** 347 (1950).
6. Pitzer, K. S., and Hollenberg, J. L., *J. Am. Chem. Soc.* **76,** 1493–1496 (1954).
7. Morokuma, K., Fukui, K., Yonezawa, T., and Kato, H., *Bull. Chem. Soc. Japan* **36,** 47–53 (1963).
8. Saito, S., *Bull. Chem. Soc. Japan* **35,** 1483–1485 (1962).
9. "Cis Isomers can be More Stable Than Trans," *Chem. Eng. News,* pp. 38–39, October 7, 1963.

10. Burnelle, L., *Bull. Classe Sci., Acad. Roy. Belg.* **47**, 357-361 (1961).
11. Kammerer, H., Horner, L., and Beck, H., *Chem. Ber.* **91**, 1376-1379 (1958).
12. Horner, L., Schlafer, L., and Kammerer, H., *Chem. Ber.* **92**, 1700-1705 (1959).
13. Levenspiel, O., "Chemical Reaction Engineering," Chap. 9. Wiley, New York, 1964.
14. Weiss, A. H., "Structure Dependent Catalysis," Dissertation in Chemistry, Graduate School of Arts and Sciences, University of Pennsylvania, Philadelphia, Pa. (1965).
15. Wheeler, A., *Advan. Catalysis* **3**, 249-327 (1952).
16. Weiss, A. H., *Petrol. Refiner.* **41**, 185-188 (1962).
17. Asselin, G. F., *Advan. Petrol. Chem. Refining* **9**, 91-95 (1964).
18. Silsby, R. I., and Sawyer, E. W., *J. Appl. Chem. (London)* **6**, 347-356 (1956).
19. Amano, A., Tominaga, H., and Tokuhisa, H., "Mechanism of Thermal Hydrogenolysis of Toluene." To be published in *Bull. Petrol. Inst. (Japan)*.
20. Szwarc, M., *J. Chem. Phys.* **17**, 431-435 (1949).
21. Morii, H., Hashimoto, A., and Tominaga, H., "Hydrogenolytic Dealkylation of Alkylaromatics." Presented at the Sixth World Petroleum Congress, Frankfurt am Main, June 19, 1963.
22. Weiss, A. H., and Doelp, L. C., *Ind. Eng. Chem., Proc. Design Develop.* **3**, 73-78 (1964).
23. Doelp, L. C., Houdry Process and Chemical Co., Linwood, Pennsylvania, private communication.