

## Electrocatalysis; Selective Electrogenenerative Reduction of Organic Halides

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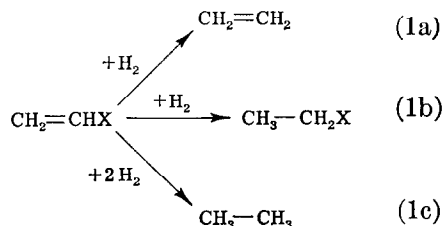
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Reduction of vinyl and ethyl fluorides and chlorides has been investigated under the operating conditions of the electrogenerative reactor. Reaction selectivity and rate were examined over palladium, platinum, ruthenium and silver black porous electrocatalysts operating at positive potentials with special attention given to vinyl fluoride reduction. Substrate partial pressure and flow rate as well as electrolyte concentration were considered as potential parameters for selectivity control. The effect of the position of the halide has also been studied. Results are compared and contrasted with conventional heterogeneous catalytic and electrochemical reduction. Palladium is the most selective electrocatalyst for double bond hydrogenation, while platinum catalyzes cleavage preferentially. Differences in selectivity are discussed in terms of an insertion-type mechanism and an electrochemical hydrodehalogenation step leading to cleavage.

The electrogenerative hydrogenation (1, 2) process involves the operation of an efficient hydrogen electrode in conjunction with an olefinic catalytic electrode so that favorable thermodynamic factors drive the cell to generate direct current. The two catalytic electrodes are separated by an electrolyte barrier phase and connected with a variable resistance external circuit. Substrate reduction by hydrogen ions with electrons takes place at the olefinic electrode or cathode where potential at a given current or rate is often dependent on the substrate and catalytic nature of the electrode. Use of electrocatalysts in electrogenerative processes offers the possibility of dual selectivity control through choice of catalyst and operating potential. The system differs further from conventional electrochemical hydrogenation in that reaction takes place at a positive potential relative to the hydrogen electrode, a region less explored in conventional electrochemistry.

In evaluating the electrogenerative reactor and comparing electrogenerative hydrogenation with conventional catalytic or electrochemical hydrogenation, the reduction of vinyl halides is of special interest because of the several paths by which reaction can proceed. Thus a simple vinyl halide,  $\text{CH}_2=\text{CHX}$ , may

1. Cleave to form the corresponding unsaturated hydrocarbon [Eq. (1a)], a process involving hydrodehalogenation (hydrogenolysis);
2. Add hydrogen to form a saturated haloalkane [Eq. (1b)]; or
3. Add hydrogen and cleave to give the corresponding saturated alkane [Eq. (1c)].



All paths are operable, dependent on conditions and catalyst. The products of partial cleavage of unsaturated halides are important for polymerization purposes while haloalkanes undergo reactions to yield coolants, hydraulic fluids, pharmaceuticals and other industrially important materials. Production of haloalkanes containing particular halides at specific positions may be difficult (3) while preparation of a corresponding alkene for further hydrogenation can sometimes be easier.

In this work we have studied reduction of several vinyl halides to investigate the role of electrocatalyst, potential, and other operating conditions on reaction selectivity control. In contrast to electrochemical reductions, where halide is dissolved in the electrolyte usually with the aid of organic solvents, low solubility of halocompounds in inorganic electrolytes is desired for the electrogenerative process, to avoid "chemical shorting" of the cell. Elimination of high resistivity organic solvents tends to decrease ohmic polarization and energy losses in the cell. In contrast to conventional heterogeneous catalysis, electrogenerative reduction often takes place without the presence of gaseous hydrogen and under relatively mild conditions.

Conventional electrochemical cleavage of organic halides was attempted by Kolbe as early as 1900 (4). However, Lingane *et al.* (5) demonstrated the possibility of selective electrolytic reduction of an aromatic ring without cleavage of iodine in the same compound, using a controlled potential mercury cathode. Fry and co-workers (6, 7) more recently used the same principle to reduce cyclic polyhalides and control the scission of the carbon-halogen bond. Von Stackelberg and Stracke (8) described a number of important factors which affected cleavage of the carbon-halogen bond at negative potentials and noncatalytic electrodes.

With the exception of some conventional investigations on copper, zinc or lead

cathodes (9-13), most work on halide reduction has been conducted on the mercury electrode (14, 15). The catalytically poisonous nature of mercury generally is ignored in favor of its advantages for electrochemical research. Possible catalytic action of a non-noble metal cathode was recognized by Plump and Hammett (9) in an early systematic investigation of carbon-halogen bond cleavage. Our interest in the problem was stimulated by an electrogenerative study of fluorobenzene electrocatalytic reduction which gave an equal mixture of benzene and cyclohexane (16). In comparison, aryl halide cleavage without aromatic ring hydrogenation was found by Wawzonek and Wagenknecht (17).

A brief examination of heterogeneous catalytic hydrogenation of halocompounds for comparison with the results from electrogenerative reduction shows that rhodium, palladium and nickel favor hydrogen addition to unsaturated halides with limited cleavage (18-20). Platinum favors replacement of the halogen by hydrogen and ruthenium is inactive (20). Vinyl fluoride and 1,1-difluoroethylene reduce quantitatively to the corresponding haloalkanes over Pd-on-carbon, while the chlorides do not hydrogenate before cleavage occurs (21). Haloethanes over the same catalyst give ethane.

## METHODS

*Cells.* Most of this study was conducted using a matrix cell (1, 2) with the electrolyte immobilized on a five-sheet filter paper matrix (Whatman No. 42). With alkaline electrolytes, however, a free electrolyte cell was used (22, 23). To avoid "chemical shorting" of the cells with electrolyte soluble substrates, or catalyst poisoning by cleaved chlorides (e.g., vinyl or ethyl chloride), a divided, flowing free electrolyte cell was designed, as shown in Fig. 1. The role of each cell component has been described previously (22-24). The

wettable polytetrafluoroethylene diaphragm was American Cyanamid Co., type TA-1 (25).

The design allowed continuous displacement of either or both anolyte and catholyte from a common electrolyte reservoir under gravity flow. The flow rate through each compartment (1–2 ml/min) could be controlled with Teflon needle valves at the chamber exits. A silver nitrate test verified chloride ion formation. The cell design was modified to remove anolyte chlorides by combining a catholyte supported on a filter paper matrix and a TA-1 Teflon diaphragm, with a flowing anolyte half cell. This eliminated gas bubble formation on the cathode at low potentials, which occurred with the design of Fig. 1. Reactant gas flow rates at each electrode were high enough to have no effect on cell polarization.

**Electrodes.** Commercial type polytetrafluoroethylene-bonded, partially wettable porous electrodes, supported on a tantalum screen were obtained from American Cy-

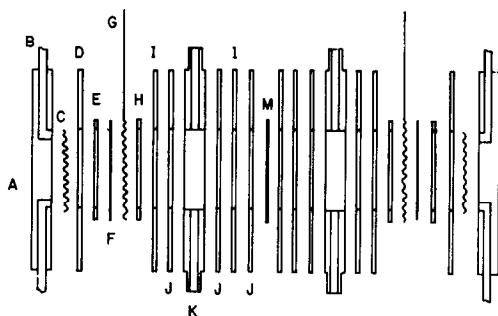


FIG. 1. Exploded view of divided free electrolyte cell: (A) Lucite face plate 2.5 in.<sup>2</sup>, 0.25 in. thickness; (B) stainless steel tubing,  $\frac{1}{8}$  in. diameter; (C) polypropylene screen spacer, 1 in. diameter; (D, I) Viton-A gaskets,  $\frac{1}{16}$  in. thickness; (E) polytetrafluoroethylene gasket, 1.25  $\times$  1 in. diameter,  $\frac{1}{16}$  in. thickness; (F) electrode, Cyanamid type LAA-2, 1.25 in. diameter; (G) Current collector, platinum screen 45  $\times$  45 mesh, 1.25 in. diameter; (H) Viton-A ring gasket, 1.25  $\times$  1 in. diameter,  $\frac{1}{16}$  in. thickness; (J) polytetrafluoroethylene film gasket, 0.002 in. thickness; (K) electrolyte chamber, KEL-F, 0.25 in. thickness; (M) separating diaphragm, 1.25 in. diameter.

TABLE 1  
Polytetrafluoroethylene-Bonded Catalytic  
Electrodes Used in This Work

Type <sup>a</sup>	Backing	Catalyst	Load (mg/cm <sup>2</sup> )	Cell design
AA-2	—	Pt-black	9	Matrix
AA-2	—	Pd-black	9	Matrix
AA-2	—	Ru-black	9	Matrix
2	Carbon	Ag-black	9–10	Matrix
AB-6 <sup>b</sup>	—	Pt-black	9	Matrix
LAA-2	Teflon-film	Pt-black	9	Free electrolyte
LSE <sup>c</sup>	Teflon-film	C	—	Free electrolyte

<sup>a</sup> Commercial designation of American Cyanamid Co.

<sup>b</sup> Supported on a golded-nickel screen, for use in alkaline electrolytes.

<sup>c</sup> Used in combination with a type AA-2 palladium electrode.

anamid (26–28) (see Table 1). Type L electrodes have a polytetrafluoroethylene film backing making them gas permeable and electrolyte impermeable, for use with a free electrolyte. To use Pd (AA-2) in a free electrolyte cell a type LSE carbon electrode was used as backing. Platinum black was used for all hydrogen anodes. All electrodes had 5.07 cm<sup>2</sup> of exposed geometric area.

**Materials.** Nitrogen and hydrogen were of prepurified grade. Other gases were >98% pure, and gas chromatography indicated negligible traces of impurities. Vinyl fluoride, 1,1-difluoroethylene and 1-chloro-2-fluoroethylene (*cis-trans* mixture) were supplied by P.C.R., Inc. Vinyl chloride was obtained from the Matheson Co. (CP grade), 1,1-Difluoroethane from K and K Laboratories, Inc. and 1-chloro-2-fluoroethane from Fairfield Chemical Co. Other materials have been described (22).

**Flow system.** The all-glass-and-Teflon gas system similar to an earlier one, allowed gas purging of anode and cathode without electrocatalyst exposure to air (22). Gas samples, obtained with a 250  $\mu$ l gastight syringe (Precision Sampling Corp.) at the cell exist, were analyzed immediately. Excess cathode reactant gas was passed through aqueous sodium carbonate solution to remove any HF.

**Product analysis.** A variety of gas chromatographic columns were used to separate

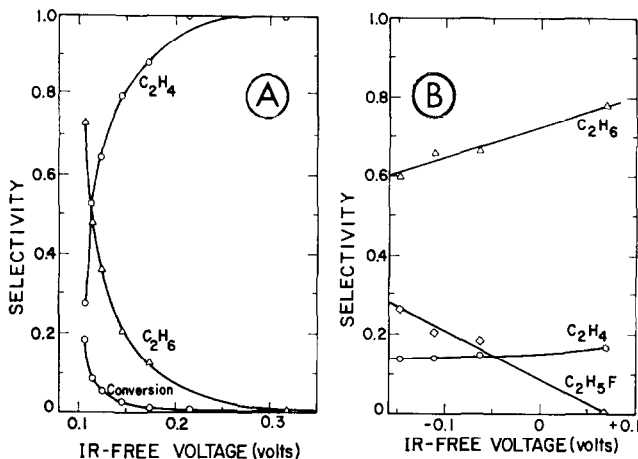


FIG. 2. Selectivity dependence on potential for electrogenerative reduction of vinyl fluoride on Pt (A) and Ru (B) in a matrix cell. Electrolyte, 2 *N* HClO<sub>4</sub>. Temp, 24°C.

and analyze the products of each reaction. Olefins were analyzed with a 6 ft long,  $\frac{1}{8}$  in. diameter Porapak QS column (73°C) or a similar alumina +5% KOH column. A Carle 8500 valve-fitted Basic gas chromatograph with a Durapak OPN-on-Porasil and a Porapak QS column in series, each 6 ft  $\times$   $\frac{1}{8}$  in. (75°C) was used for separation of the high boiling point compounds. By bypassing the Porapak QS column, efficient analysis of the less volatile halides was achieved on the Durapak OPN column except for 1-chloro-2-fluoroethane. The thermistor detectors were calibrated with 1–5% gas mixtures in air, using the absolute method. For quantitative analysis, a minimum of 0.5% total conversion of reactant was required, corresponding to about  $2.5 \times 10^{-7}$  mole/ml total concentration of products.

*Procedure.* The electrical equipment and the procedure for obtaining reproducible results have been reported (2, 22). The procedure incorporates techniques for surface oxide reduction of and elimination of oxygen and impurities from the system.

Although steady state cell operation was normally achieved after about 3 min at a specified current, samples were taken after 10 min. Correction for the hydrogen anode polarization is not significant [less

than 8 mV/decade (23)] and has been ignored here. The measured cell voltage should be corrected for electrolyte ohmic loss at the operating current (*I*). Such IR-free cell voltages are reported with reference to the dynamic hydrogen electrode (DHE) in the same electrolyte, unless otherwise noted. All current densities are based on apparent exposed electrode area.

## RESULTS AND DISCUSSION

### *Effect of Experimental Variables on Product Selectivity*

A useful criterion for comparing conditions favoring particular reaction paths is the *selectivity*,  $\phi_J$ , for product formation.

$$\phi_J = C_J / \sum_{J=1}^n C_J = C_J / (C_{R,0} - C_{R,F}) \quad (2)$$

where  $C_J$  is the concentration of product *J* in the cell effluent stream and  $C_{R,0}$  and  $C_{R,F}$  represent initial and final reactant concentrations.

Selectivity was calculated by accounting for all significant reaction products during steady state operation. Reactant conversions calculated from gas chromatographic analyses generally agreed within 5% with conversions calculated from Faraday's law. With silver electrodes for vinyl fluoride

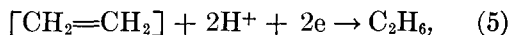
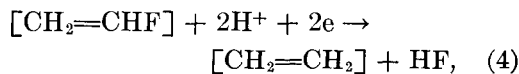
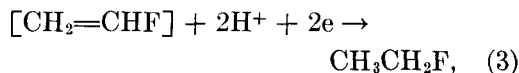
and with carbon-palladium cathodes for vinyl chloride, hydrogen evolution due to concentration cell processes (1) probably accounts for observed discrepancies between experimental and estimated conversions. Some alcohol formation or electrochemical oxidation of silver also may have occurred with these systems. The electrolyte was not tested for such reactions.

*Electrocatalyst.* The profound effect of metal catalyst in determining reaction path is illustrated in Figs. 2 and 3 for vinyl fluoride reduction. Platinum selectively cleaves the carbon-fluorine bond while failing to hydrogenate the double bond of vinyl fluoride. This, however, occurs readily on palladium, where selective addition of hydrogen is favored over cleavage even at +0.22 V. Above this voltage no products were observed, probably due to low conversion. Silver and ruthenium operate between the two extremes. Hydrogenation of vinyl fluoride over ruthenium at positive potentials yields ethane as the main product more nearly resembling platinum. Driving the ruthenium electrode to negative potentials with a constant current supply, increases ethyl fluoride formation, Fig. 2B. Then, operation

is no longer electrogenerative but energy requirements are lower than with conventional electrolysis.

Silver is more selective than ruthenium for hydrogen addition with no detectable ethylene in the product stream. Since ethylene and hydrogen do not adsorb on silver (29) the observed ethane might result from hydrogenolysis of ethyl fluoride. If vinyl fluoride is cleaved before hydrogen addition, hydrogenation is rapid in excess hydrogen. The unusual behavior and properties of silver compared to the other electrocatalysts and its low current efficiency suggests possible direct reduction without surface intermediates. Further investigation would be of interest, since silver catalytic properties for reductions are largely unexplored.

Potential electrochemical reactions on palladium, platinum and ruthenium may be represented by



where brackets designate adsorbed species.

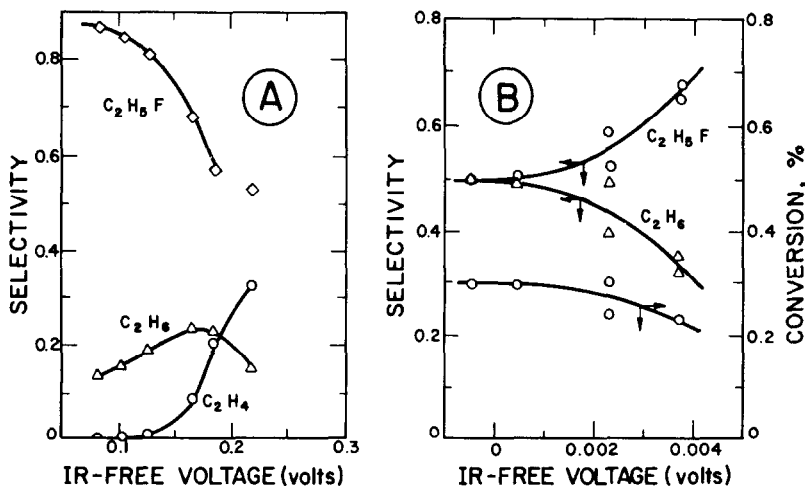


Fig. 3. Selectivity dependence on potential for electrogenerative reduction of vinyl fluoride on Pd (A) and Ag (B) in a matrix cell. Electrolyte, 2 *N* HClO<sub>4</sub>. Temp, 22°C.

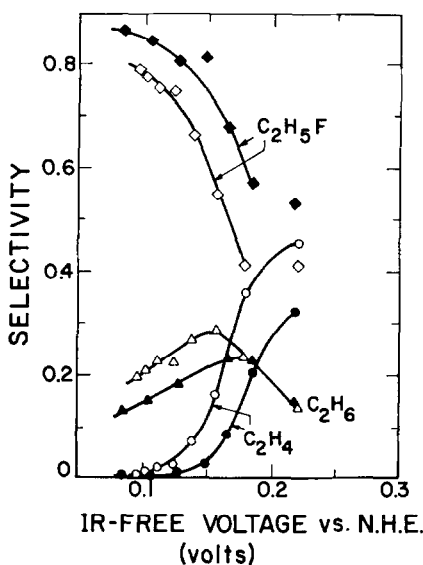


FIG. 4. Selectivity dependence on acid concentration for electrogenerative hydrogenation of vinyl fluoride on Pd. Electrolyte,  $\text{HClO}_4\text{-LiClO}_4$ . Temp,  $22^\circ\text{C}$ . Full symbols:  $2\text{ N HClO}_4$ . Open symbols:  $0.5\text{ N HClO}_4$ .

Based on product formation, reduction of ethylene to ethane in the presence of vinyl fluoride apparently proceeds faster over palladium than over platinum, in agreement with results for pure ethylene (23). Since hydrodehalogenation of haloalkanes is slow on palladium, as shown below, hydrogen addition to double bonds on this catalyst must be competitive with the carbon-fluorine cleavage reaction.

Hydrogenolysis of the carbon-fluorine bond is especially noteworthy since this bond is stable under catalytic (30) or conventional electrochemical (14) conditions. Over palladium-on-charcoal catalysts, quantitative double bond reduction takes place (21). This behavior is approached on palladium with decreasing potential. However, the palladium electrogenerative potential can be controlled to give significant cleavage. Similarly, electrogenerative reduction and cleavage is possible over ruthenium which previously was found "inactive" for reduction of a chloride by heterogeneous catalysis (20).

Generally, at higher potentials with palladium, platinum and ruthenium, the reaction with hydrogen ions and electrons seems to facilitate the polar carbon-fluorine bond cleavage.

*Electrolyte.* Because of possible product variation, the palladium catalyst was chosen for further selectivity studies.

In studying the effect of acid concentration, potential effects across the diffuse layer were minimized by maintaining the ionic strength of the perchloric acid electrolyte constant, at that of a  $2\text{ N}$  solution, by addition of electrochemically unreactive ions such as lithium perchlorate (22, 23, 32). In the range of  $2$  to  $0.1\text{ N}$ , higher acid concentrations favor double bond reduction. Some trends are indicated in Fig. 4. Ethane selectivity on palladium shows a maximum with potential as a result of increasing selectivity for double bond saturation and decreasing halide cleavage at low cathode potentials. This combined with a counteracting decrease in hydrogenation selectivity at low acid concentrations causes a shift of the maximum to less positive potentials in such electrolytes.

Other tested electrolytes show behavior similar to perchloric acid. Tetrafluoroboric acid ( $2\text{ N}$ ), where some common ion effect might exist, has a small influence favoring ethyl fluoride formation relative to perchloric acid. An increase of about  $5\%$  in the selectivity for  $\text{C}=\text{C}$  bond reduction at high potentials diminishes as the cell voltage approaches zero. In neutral solutions ( $2\text{ N LiClO}_4$ ) over palladium, reduction of vinyl fluoride proceeds slower with product distribution of Fig. 4 shifted to less positive cathode potentials and ethylene the major product ( $\phi = 0.45$ ) at  $0.18\text{ V}$ . A single experiment with platinum in  $2\text{ N KOH}$  showed only carbon-halide cleavage with ethylene formation at higher potentials and slower reaction rates than with acid.

In conventional electrochemical hydro-

TABLE 2  
 Selectivity ( $\times 10^2$ ) Dependence on Partial Pressure; Vinyl Fluoride  
 Electrogenenerative Hydrogenation over Palladium Black

Cell IR-free voltage (V)	$P_{\text{C}_2\text{H}_2-\text{CHF}}$ (atm): 0.762			0.476			0.044		
	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{F}$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{F}$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{F}$
0.18	14	20	65	11	24	64	—	—	—
0.16	10	19	71	7	20	73	—	19	81
0.14	6	15	79	3	16	80	—	14	86
0.10	2	12	86	1	12	87	—	7	92
0.06	1	11	87	0.3	9	90	—	5	95

genation over mercury, fluoroalkene reduction also is dependent on hydrogen ion concentration but results only in halide cleavage (14).

*Partial pressure of substrate.* Variation of reactant partial pressures from 0.044 to 1 atm was achieved by dilution of the haloalkene in a nitrogen stream (22). Since pore diffusion may alter the intrinsic reaction kinetics (23, 31) selectivity for the hydrogenation or cleavage reaction paths will depend on the *apparent* reaction orders in haloalkene with lower orders favored by lower pressures (33).

The selectivity for hydrogen addition to vinyl fluoride increases by about 5% when haloalkene partial pressure is decreased by one order of magnitude, Table 2. The effect seems to be uniform throughout the potential region studied and, therefore, most important at high positive potentials, where haloalkane selectivities are low. No ethylene is detected below 0.1 atm of haloalkene despite ethane formation. This supports the view that ethylene product formation on palladium at 1 atm pressure is due to its surface displacement by vinyl fluoride before hydrogenation. Ethylene product also decreases with decreasing positive potential since the rate of reduction to ethane is increased at the catalyst surface (2, 22, 23).

*Flow rate.* Since the residence time of reactants and products can alter selectivity, flow rates generally were adjusted to give

maximum selectivity for ethyl fluoride formation as reported here. The optimum flow rate was 3.5 to 5 ml/min, regardless of electrode potential. Slower flow rates seem to result in mass transfer limitations and concentration polarization. The selectivity was less sensitive to faster flow rates but nevertheless decreased with flow rate.

*Halide.* With chloroalkenes, cleavage occurs more readily than with fluoroalkenes. The major products from electrogenerative reduction of vinyl chloride over platinum and palladium are ethylene and ethane, Fig. 5. However, to some extent palladium can selectively hydrogenate the double

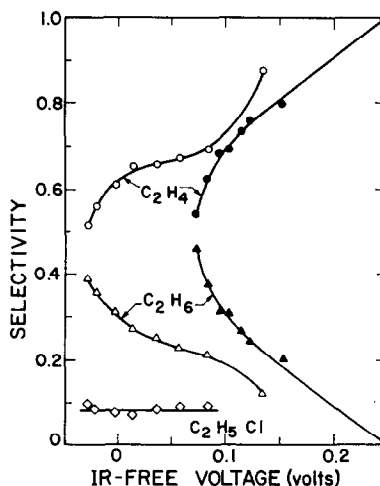


FIG. 5. Selectivity dependence on potential for electrogenerative reduction of vinyl chloride in 2 N HClO<sub>4</sub>. Open symbols: Pd-black, temp, 19°C. Full symbols: Pt-black, temp, 22°C.

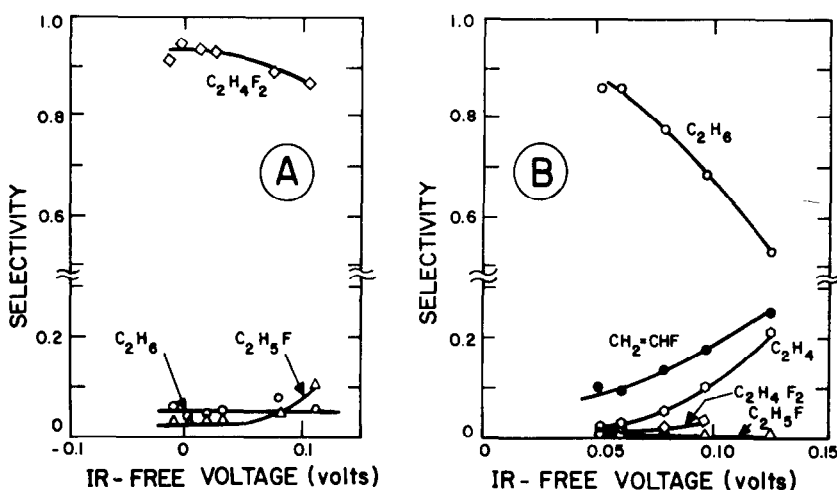


FIG. 6. Selective electrogenerative reduction of 1,1-difluoroethylene on Pd (A) and Pt (B) in 2 N HClO<sub>4</sub> in a matrix cell. Temp, 21°C.

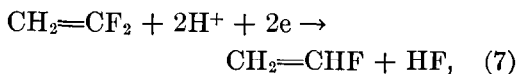
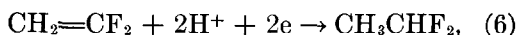
bond without hydrodehalogenation. This does not occur with catalytic hydrogenation (21) and electrolytic reduction over noncatalytic electrodes (14).

Here, and elsewhere (2, 22, 23) we have described several cell designs with electrolyte either supported on a matrix or "free," enclosed between liquid impermeable, gas permeable electrodes. All tested cell designs result in qualitatively similar selectivities for ethyl chloride for any given catalyst. The matrix cell yields up to 50% more ethylene, possibly due to chloride ion accumulation in the electrolyte which may inhibit the ethylene hydrogenation reaction.

Reduction of vinyl chloride proceeds through two parallel steps, as with vinyl fluoride [Eqs. (3)–(5)], but with cleavage on both platinum and palladium much faster than hydrogen addition. Dehydrohalogenation or halide cleavage of saturated halides can be ignored since ethyl chloride over palladium electrodes gives only traces of vinyl chloride and ethane, close to zero potential. Tests with 1,1-difluoroethane also resulted in small amounts of vinyl fluoride and ethane. Conversions are below 1% with hydrogen evolution at the cathode (1, 22, 34) explaining differences from yields expected

from Faraday's law (estimated conversion of ~10%).

With multihalide substitution on an olefinic carbon atom, cleavage takes place less readily on both palladium and platinum, Fig. 6. The absence of vinyl fluoride from the products of 1,1-difluoroethylene reduction over palladium indicates that hydrogen addition to adsorbed vinyl fluoride is faster than the cleavage of the difluoride. Reduction and stepwise cleavage of the *gem* dihalide apparently proceed in parallel on palladium and platinum,



with further vinyl fluoride reduction according to Eqs. (3)–(5). Hydrogenation of all products is strongly favored on palladium, while cleavage is still highly favored on platinum despite substantial subsequent olefinic hydrogenation.

The only *vicinal* dihaloalkene reduced electrogeneratively was 1-fluoro-2-chloroethylene on palladium. The primary product was vinyl fluoride accompanied by small amounts of ethyl fluoride, ethane and traces of ethylene. This is an indica-



TABLE 3  
Calculated and Observed Open Circuit Voltages for Electrogenative  
Reduction of Organic Halides

Main reaction	Catalyst	$E^{\circ}$ (V) <sup>a</sup>	OCV <sup>b</sup> (V)
$\text{CH}_2=\text{CHF} + 2\text{H}^+ + 2\text{e} \rightarrow \text{C}_2\text{H}_5\text{F}$	Pd	0.530	0.598-0.448
	Ru	0.530	0.600-0.400
	Ag	0.530	0.011-0.003
$\text{CH}_2=\text{CHF} + 2\text{H}^+ + 2\text{e} \rightarrow \text{C}_2\text{H}_4 + \text{HF}$	Pt	-0.044	0.466
$\text{CH}_2=\text{CF}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{CH}_3\text{CHF}_2$	Pd	0.613	0.676
$\text{CH}_2=\text{CF}_2 + 4\text{H}^+ + 4\text{e} \rightarrow \text{C}_2\text{H}_4 + 2\text{HF}$	Pt	0.253	0.585
$\text{CH}_3\text{CHF}_2 + 4\text{H}^+ + 4\text{e} \rightarrow \text{C}_2\text{H}_6 + 2\text{HF}$	Pd	0.208	0.077
$\text{CH}_2=\text{CHCl} + 2\text{H}^+ + 2\text{e} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$	Pd	0.124	0.445
	Pt	0.124	0.528
$\text{CH}_3\text{CH}_2\text{Cl} + 2\text{H}^+ + 2\text{e} \rightarrow \text{C}_2\text{H}_6 + \text{HCl}$	Pd	0.574	0.674
$\text{ClCH}=\text{CHF} + 2\text{H}^+ + 2\text{e} \rightarrow \text{CH}_2=\text{CHF} + \text{HCl}$	Pd	0.538	0.440

<sup>a</sup> Calculation based on free energy changes (35) except for vinyl chloride reduction (36).

<sup>b</sup> Observed open circuit voltage.

tion of strong adsorption of the original substrate and a tendency to cleave the carbon-chloride bond. No monochloride was observed. Irregularities in the chromatographic base line may have indicated slight polymerization.

In general, the ease of cleavage of dissimilar halides in the same or similar molecules seems to follow the strength of the carbon-halogen bond, in agreement with conventional catalytic (30) and electrochemical (8, 14) reduction.

#### Electrochemical Behavior

*Open circuit voltage.* The open circuit voltage (OCV) of these cells are less well defined than those for simple alkenes (1, 2), declining somewhat in successive runs. No products were observed at OCV, in agreement with earlier work. Based on the major products observed on each electrocatalyst, thermodynamic rest potentials, referred to the normal hydrogen electrode,  $E^{\circ}$ , have been calculated from the standard free energy changes of the indicated reactions (298°K, 1 atm) as shown in Table 3 (35, 36). Calculated rest potentials for alternate observed reaction products are

shown in Table 4. With the exception of vinyl and ethyl chloride, the standard free energies of formation are not known precisely. Values reported in the literature sometimes differ from each other by an order of magnitude about equivalent to the difference between OCV and  $E^{\circ}$ . For some reaction products and reactants the standard free energy of formation was calculated from group contributions (36). Considering the fact that the reaction at the cathode is not thermodynamically reversible, the agreement between calculated and observed open circuit poten-

TABLE 4

Calculated Rest Potentials for Formation of Alternate Products from Electrogenative Reduction of vinyl Halides

Reaction	$E^{\circ}$ (V) <sup>a</sup>
$\text{CH}_2=\text{CHF} + 4\text{H}^+ + 4\text{e} \rightarrow \text{C}_2\text{H}_6 + \text{HF}$	0.382
$\text{CH}_2=\text{CF}_2 + 6\text{H}^+ + 6\text{e} \rightarrow \text{C}_2\text{H}_6 + 2\text{HF}$	0.343
$\text{CH}_2=\text{CF}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{CH}_2=\text{CHF} + \text{HF}$	0.646
$\text{CH}_2=\text{CHCl} + 4\text{H}^+ + 4\text{e} \rightarrow \text{C}_2\text{H}_6 + \text{HCl}$	0.323
$\text{CH}_2=\text{CHCl} + 2\text{H}^+ + 2\text{e} \rightarrow \text{C}_2\text{H}_5\text{Cl}$	0.733
$\text{ClCH}=\text{CHF} + 4\text{H}^+ + 4\text{e} \rightarrow \text{C}_2\text{H}_4 + \text{HF} + \text{HCl}$	0.247
$\text{ClCH}=\text{CHF} + 6\text{H}^+ + 6\text{e} \rightarrow \text{C}_2\text{H}_6 + \text{HF} + \text{HCl}$	0.339
$\text{ClCH}=\text{CHF} + 2\text{H}^+ + 2\text{e} \rightarrow \text{ClCH}_2-\text{CH}_2\text{F}$	0.613

<sup>a</sup> Calculation based on free energy changes; see footnote a on Table 3.

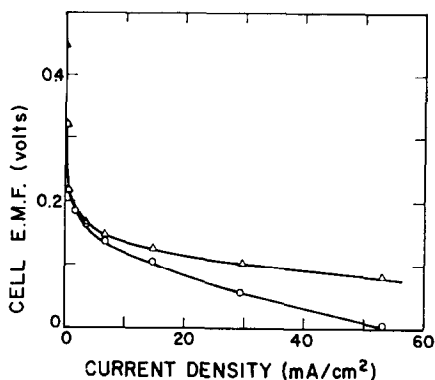
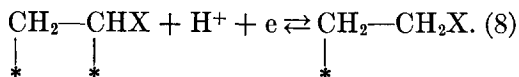


Fig. 7. Potential-current density curve for electrogenerative hydrogenation of vinyl fluoride on Pd in a matrix cell. Electrolyte 2 *N* HClO<sub>4</sub>. Cell internal resistance 0.284 ohm. Temp, 23.4°C. (○) Measured voltage; (Δ) IR-corrected voltage.

tials is fairly good, especially if one considers the reversible double bond reduction to the half hydrogenated state to be the potential determining reaction, exemplified by



Such a reaction does not require the formation of product (2). If reactions such as Eq. (8) do determine potential it does not follow that hydrogen addition is exclusively to the carbon atom attached to the halide atom.

It would appear from the OCV data on vinyl fluoride and the electrocatalysts examined that the potential determining reaction or adsorption on silver is quite different than with other catalysts. One difficulty with the calculated OCV presented here is that product distribution at or close to the open circuit potential is not known; it may be that a mixed rest potential calculation would be more appropriate for the system.

*Cell polarization.* A typical polarization curve for the reduction of vinyl fluoride on palladium is shown in Fig. 7. Similar curves are obtained with the other halides and electrocatalysts. In assessing these

curves, it should be noted that little polarization or voltage loss occurs at the hydrogen electrode (22, 26) so that almost all of the voltage loss is at the cathode. Though cell polarization is essentially independent of flow rate here, it increases with decreasing hydronium ion concentration and substrate partial pressure. The characteristic high initial voltage drop, at low current densities is indicative of activation polarization, a reflection of catalyst efficiency. From Fig. 7, it can be seen that reaction at the electrode can take place at a significant rate which can be controlled. Thus, our cell with its 5.07 cm<sup>2</sup> area of exposed electrodes produced currents as high as 0.35 A. Assuming a catalytic surface area of 20 m<sup>2</sup>/g (26) (1800 cm<sup>2</sup>/cm<sup>2</sup> electrode geometric area) and a current density of 50 mA/cm<sup>2</sup> geom., the rate of surface hydrogenation would be  $1.4 \times 10^{-10}$  mol/cm<sup>2</sup> sec. For an electrode of 5 cm<sup>2</sup> geometric area and a reactant flow rate of 5 ml/min (or  $3.7 \times 10^{-6}$  mol/sec), this rate corresponds to 35% reactant conversion.

In preliminary runs with vinyl halides, oscillations of current and voltage as high as  $\pm 10$  mV or  $\pm 0.5$  mA were observed with a frequency of  $\sim 10$  min<sup>-1</sup>. Their time dependence resembled the charge-discharge of a capacitor. Increased flow rate caused oscillations to diminish. In subsequent runs, few oscillations (less than 0.5 mV) occurred even at low flow rate. Oscillations have been reported for oxidation of alcohols and aldehydes over platinum (36) and have been attributed to formation and removal of oxide layers at the electrode surface. Here, oscillations seem to be related to conditioning of the catalytic surface with substrate and associated pore diffusion limitations possibly involving hydrogen from pretreatment.

This is supported by observed diminishing oscillations with flow rate increase.

Tafel plots, semilog plots of current versus potential, are frequently used in

electrochemical studies as indications of electrochemical mechanisms or representations of electrode activity. The position of Tafel plots on the potential scale and the slope of such plots can represent a measure of the difficulty with which a reaction proceeds over an electrocatalyst. Shift of Tafel lines to less positive potentials is indicative of more difficult reduction.

Tafel plots for vinyl chloride (Fig. 8) and vinyl fluoride (Fig. 9) indicate that these compounds are reduced over platinum at about the same rate as ethylene (22). Since ethylene is a major intermediate over platinum, its hydrogenation would seem to influence the polarization behavior of these reactants after the preferential cleavage reaction. This reasoning fails when applied to vinyl chloride on palladium. Although ethylene and ethane are the main products, substrate reduction proceeds significantly slower than ethylene hydrogenation. Vinyl fluoride hydrogenates over palladium at about the same rate that it cleaves over platinum, Fig. 9, but much slower than ethylene (23). Reduction over silver and ruthenium is significantly slower than over palladium.

Electrogenative saturation of the

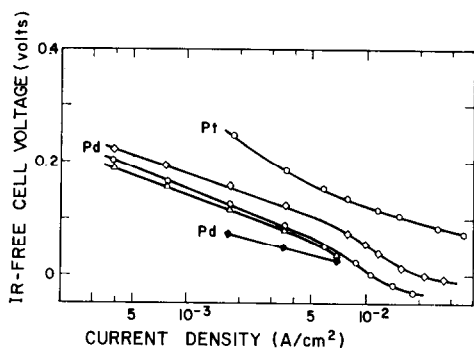


FIG. 8. Potential-current density plots for electrogenerative reduction of vinyl chloride ( $\circ$ ,  $\Delta$ ,  $\diamond$ ,  $\square$ ) and ethyl chloride ( $\blacklozenge$ ) on Pt and Pd in 2 N HClO<sub>4</sub>, at room temperature. ( $\circ$ ) Matrix cell; ( $\Delta$ ) half matrix cell (alkene cathode) and half static free electrolyte cell (H<sub>2</sub> anode), separated by a TA-1 membrane; ( $\diamond$ ) flowing anolyte and catholyte with a TA-1 separating diaphragm.

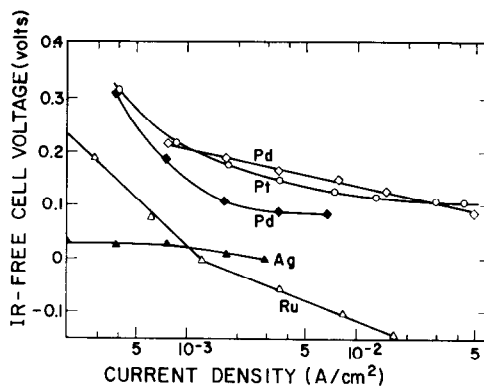


FIG. 9. Potential-current density plots for electrogenerative reduction of vinyl fluoride on Pd, Pt, Ru and Ag in 2 N HClO<sub>4</sub> [ $\blacklozenge$  2 N LiClO<sub>4</sub>], at room temperature.

double bond is easier with mono- than with polyhalides, occurring at more positive potentials. The rate of vinyl fluoride reduction over palladium (Fig. 9) is about an order of magnitude faster than the rate of 1,1-difluoroethylene reduction (Fig. 10). The rate of halide cleavage from the latter is also slow.

Reduction of dissimilar *vicinal* halides is slightly faster than of *gem* dihalides (Fig. 10), but saturation of the double bond is *not possible* without carbon-chloride cleavage. No free hydrogen has been found in the hydrogenation of 1,1-difluoroethylene and 1-chloro-2-fluoroethylene over palladium. However, the Tafel curves are similar to those found for the H<sub>2</sub>-N<sub>2</sub> cell (1, 22, 34) suggesting initial discharge to hydrogen atoms which react to give product [cf. hydrogen evolution reaction at positive potentials (22, 34)]. The electrogenerative mode is in contrast with catalytic (19) and electrochemical reduction at negative potentials (8), since these both proceed faster with polyhalides than with monohalides.

The very low conversions of saturated halides for current generated, and the similarity of Tafel plots, Figs. 8 and 10, to that for a H<sub>2</sub>-N<sub>2</sub> concentration cell indicate that hydrogen is transferred across

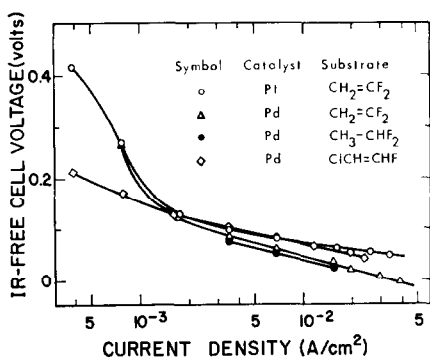


Fig. 10. Potential-current density plots for electrogenerative reduction of dihaloalkenes and a haloalkane in matrix cells with 2 *N* HClO<sub>4</sub> electrolyte. Temp, 21–22°C.

the cell and evolves on the cathode. Cleavage of saturated halides thus is less favored electrogeneratively and catalytically (19) than by conventional electrochemical reduction over noncatalytic cathodes and negative potentials (8).

Aside from indications of hydrogen discharge, Tafel slopes vary between 50 and 120 mV. The complexity and variety of electrode reactions in this survey study do not encourage further interpretation for the present.

Steric hindrance and surface utilization might explain the slower reduction of vinyl chloride on palladium compared with vinyl fluoride but not other results. Adsorption of halide ions, resulting from cleavage, with possible catalyst poisoning can affect reaction rate and cell polarization. Chloride ions are known to adsorb on platinum and retard hydrogenation in solution (38). Palladium also may be sensitive.

In Fig. 8, the Tafel plots for vinyl chloride reduction over palladium are shown for three cell designs. When the free electrolyte catholyte was continuously replaced, ethylene hydrogenation was fastest and polarization smallest. With immobilized catholyte, either in a matrix or half-matrix cell, incorporation of a diaphragm had little effect. With the moving free electrolyte, selectivity for ethylene was low ( $\sim 0.30$ ) and ethane

high; for immobilized electrolyte, ethylene was favored ( $\phi \simeq 0.70$ ) indicative of some chloride poisoning for double bond hydrogenation. Fluoride ions probably do not adsorb on platinum (39), while possible adsorption on palladium, ruthenium and silver cannot account for all of the experimental results.

It is difficult to find an overall correlation into which to fit the metals and substrates studied here. However, examination of metal catalyst sublimation heats and rates of reactions on these metals suggests a possible "volcano" relationship. Heats of sublimation are sometimes assumed to be related to adsorption strength for hydrogen or possibly substrate. For reaction, adsorption strength is often believed to have an optimum value (40). Some indication of a "volcano" correlation is found in the tabulated values of cathode potential at particular current levels and heats of sublimation of Table 5. Platinum and palladium give a relatively high potential while silver and ruthenium give lower potentials. With such a relationship, vinyl fluoride would adsorb weakly on silver and strongly on ruthenium relative to some optimum adsorption level.

*Catalyst specificity.* Among the most notable differences between palladium and platinum in this study has been in the tendency for hydrogenation relative to cleavage of vinyl fluoride as illustrated by Eqs. (1a) and (1b). A possible explanation

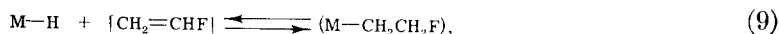
TABLE 5

Voltage Variation with Heat of Sublimation of Electrocatalyst for Electrogenerative Reduction of Vinyl Fluoride

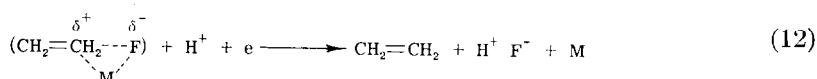
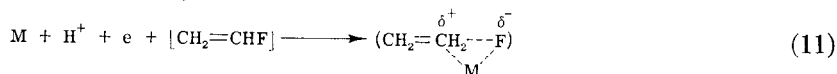
Electro-catalyst	Heat of sublimation (kcal/g-atom)	Cell IR-free voltage (V)	
		0.8 mA/cm <sup>2</sup>	2.0 mA/cm <sup>2</sup>
Ag	68	0.02	0.002
Pd	91	0.21	0.18
Pt	135	0.23	0.17
Ru	160	0.05	-0.03

is available from the examples of homogeneous catalysis and from a realization that hydrogen addition can take place either through addition of a hydrogen

atom or by addition of a proton and an electron (2, 22) as well as by other mechanisms. Thus reaction can take place as follows



or possibly



where brackets indicate adsorbed species and parentheses intermediates. M would represent a metallic catalyst site.

The reaction sequence illustrated by Eqs. (11) and (12) can take place either on platinum or palladium and might occur to varying degrees on both at higher potentials. However, in homogeneous catalysis palladium is known to participate much more readily in "insertion reactions" as compared to platinum (41, 42); hence, its use in the Wacker process. Reactions (9) and (10) can be considered to be analogous with adsorption of interacting species on different catalyst sites. The capacity of palladized electrodes for hydrogen atom storage in the lattice may similarly relate to their catalytic promotion of Reactions (9) and (10) (43).

With decreasing potential, the number of hydrogen atoms on the palladium electrocatalyst increase with a corresponding increase in selectivity for hydrogenation as seen in Fig. 3. While significant hydrogen surface coverage might occur on platinum, ethylene insertion Eq. (9) takes place with considerably less facility especially with fluorine substituted in this alkene. While presently we have no clear analysis of the kinetics of the cleavage reaction, it does seem to be first order in hydrogen ion which would be consistent

with Eqs. (11) and (12) with the first step being rate limiting and the postulated intermediate short lived if it exists discretely at all. The capacity for a possible insertion mechanism may also account for the capacity for partial hydrogenation to give fluoroalkane with silver and ruthenium.

The heterogeneous catalytic cleavage of the carbon-chlorine bond in vinyl halides with nickel has been explained in terms of adsorption of a hyperconjugated form of these compounds,  $\overset{\delta^-}{\text{C}}-\overset{\delta^-}{\text{C}}=\overset{\delta^+}{\text{Cl}}$ . This adsorbed form is then postulated to hydrodechlorinate in a manner similar to hydrogenation of a double bond (44). Even if this explanation is accepted, an analogous form for vinyl fluorides is unlikely in view of the special properties of fluorine and its electronegativity.

## CONCLUSIONS

Electrogenerative reduction of vinyl halides does not operate either purely catalytically or purely electrochemically, but it incorporates features of each mode of operation. Electrocatalyst, cathode potential, nature of halide and electrolyte are important parameters that determine the selectivity for either hydrogen addition or hydrodehalogenation.

In general, vinyl halides reduce more readily than haloalkanes, with cleavage favored by high positive potentials, high substrate partial pressures and alkaline electrolytes. Monohalides reduce easier than *vicinal* dihalides which in turn reduce easier than *gem* dihalides. Cleavage of polyhalides proceeds stepwise following the strength of the carbon-halogen bond ( $F \gg Cl$ ).

The reaction rate for vinyl halide reduction regardless of selectivity, follows the order  $Pd \sim Pt \gg Ag \sim Ru$ . However, the selectivity of the electrocatalysts for reducing the carbon-carbon double bond decreases in the order  $Pd \gg Ag > Ru > Pt$ .

The action of palladium for catalyzing the hydrogenation of the double bond of vinyl fluoride preferentially over cleavage of the carbon-fluorine bond may be a result of hydrogen atom adsorption followed by an insertion reaction. Platinum apparently catalyzes an electrochemical reaction between substrate and protons to cause halide hydrodehalogenation.

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