A Deuterium Isotope Study of Electrogenerative Hydrogenation. Mechanism of Hydrogenation of Ethylene at Positive Potentials[1]

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Abstract: The electrogenerative hydrogenation of ethylene has been studied in a flow system using deuterium in the anode compartment with $DClO_4$–D_2O electrolyte. Upon initiation of reaction by allowing the system to generate a variable controlled current, deuterium scrambling took place in the product stream in both ethylene and product ethane. The nature and extent varied with the current and potential of the system. Results were analyzed in terms of a Kemball model using statistical and computer techniques. Facile exchange and reversible reaction are indicated between ethylene and its half-hydrogenated state; the rate-determining step is the addition of a second hydrogen atom. Mechanistic implications are discussed. The characteristic open-circuit potential at the ethylene electrode is probably associated with the formation of a half-hydrogenated state. Electrogenerative systems are shown to be useful for carrying out controlled isotope studies at electrodes under steady-state conditions.

Some time ago we described the electrogenerative hydrogenation process[2a,b] by which hydrogen and an olefin react with the aid of a barrier electrolyte phase and electrodes to produce a saturated hydrocarbon product and external electrical current coulometrically equivalent to the reduction taking place. Reaction rate and generated current produced are very much dependent on the catalytic properties of both electrodes. For ethylene in the cell, the overall reaction may be represented by

anode
$$H_2 \rightarrow 2H^+ + 2e \text{ (external circuit)} \quad (1)$$

$$H^+_{(anode)} \rightarrow H^+_{(cathode)} \quad (2)$$

cathode
$$2H^+ + C_2H_4 + 2e \text{ (from external circuit)} \rightarrow C_2H_6 \quad (3)$$

A positive potential relative to the hydrogen electrode is produced at the cathode at open circuit and over the current range studied here.

In a preliminary investigation we found that: (a) no significant amount of hydrogen gas appeared in the cathode compartment during steady-state cell operation and (b) in a flow system with an operating cell at open circuit, no detectable deuterium exchange took place between a moving ethylene stream in the cathode compartment and ethylene adsorbed on the platinum-black electrode surface with an acidic deuterated electrolyte. The electrogenerative system is unusual in that it permits a controlled steady-state study at an operating electrode with an essentially invariant electrolyte and a hydrogenation study without the presence of free hydrogen or deuterium gas which complicates many catalytic investigations. Because of these factors and our general interest in catalysts and electrochemical processes, we undertook the present investigation of electrogenerative hydrogenation using deuterium gas and unlabeled ethylene with a deuterium oxide acidic electrolyte and platinum-black electrodes. The main objective was to ascertain the amount and nature of deuterium distribution in the electrochemical product and reactant, where possible, in order to characterize the electrode process and compare it with similar and related catalytic investigations. We chose perchloric acid as the electrolyte acid because it is one of the common, strongly ionized, unreactive, relatively nonadsorbing acids in which ethylene is not very soluble, so that the hydrogenation cell is operative.[2]

With the identification of "deuterium scrambling" in our reaction products, our study was influenced by previous work on conventional heterogeneous catalytic hydrogenation,[3,4] and was very strongly influenced by the views and approaches of Burwell,[5] Bond,[6] and Kemball[7] and their collaborators. Much of the previous related work on electrochemical hydrogenation has been noted earlier.[2]

Experimental Section

Cell Design. The hydrogenation matrix-type cells were similar to others which were previously used.[2] Cell components and construction are shown schematically in Figure 1. The assembly was held together by stainless steel screws through four $^3/_{16}$-in. diameter holes drilled on a 1.75-in. diameter circle through Lucite face plates and gaskets which held the stainless steel spacers, platinum current collectors, electrodes, and matrix in place. Gaskets allowed a 5.07-cm^2 working area. The cell was fed with excess gas well above the rate at which gas flow affected polarization. Reactant gases entered the inlet tubing and reached the reaction zone by flow through the spacers and current collectors and interdiffusion through the porous electrodes; with product, they were removed through the face-plate vents opposite the inlet. Electrolyte was held immobilized in the filter-paper matrix (Whatman 42, five sheets). The assembly was such that no stainless steel came in contact with electrolyte since only a moderate amount of electrolyte is used on the filter paper. On occasion, platinum or polypropylene spacers were also used with no effect on cell performance.

Materials. Rubber gaskets were made from silicone rubber No. 67 (Raybestos-Manhattan, Inc.). Gas lines generally were constructed of Teflon and glass tubing. The electrocatalyst was a platinum black–Teflon suspension supported on 50-mesh tantalum screen (American Cyanamid AA-1) containing 9 mg of platinum/

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[1] (a) We thank the National Science Foundation for support on this work; (b) taken in part from a Ph.D. thesis presented by I. Feiz in 1968.

[2] (a) S. H. Langer and H. P. Landi, *J. Amer. Chem. Soc.*, **85**, 3043 (1963); (b) *ibid.*, **86**, 4694 (1964).

[3] Earlier work reviewed in G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962.

[4] An excellent, concise, more recent review is found in A. S. Hussey, G. W. Keulkes, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968).

[5] R. L. Burwell, Jr., *Chem. Eng. News*, **44**, 56 (Aug 22, 1966).

[6] G. C. Bond, J. J. Phillipson, P. B. Wells, and J. M. Winterbottom, *Trans. Faraday Soc.*, 60, 1847 (1964).

[7] C. Kemball, *J. Chem. Soc.*, 735 (1956).

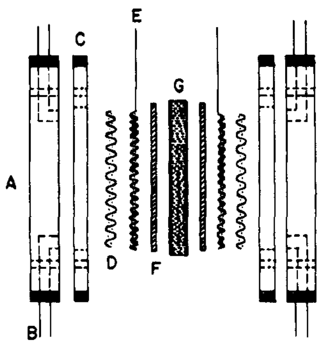

Figure 1. Cell components schematically represented relative to each other: (A) face plates, 2.5-in. diameter, 0.25-in. thickness; (B) stainless steel tubing, $^{1}/_{8}$-in. o.d., 4 in. long; (C) gaskets, $^{1}/_{16}$-in. thickness; (D) spacers, 1-in. diameter, 20 × 20 mesh; (E) current collectors, 1-in. diameter, 45 × 45 mesh, with cell terminals 0.003 in. thick, 2 in. in length; (F) Type AA-1 electrodes, 1$^{1}/_{8}$-in. diameter; (G) matrix containing electrolyte, 1.25-in. diameter.

cm^2 of electrode area.[8] All gases were CP grade; hydrogen and nitrogen were prepurified. The hydrocarbon gases contained no impurities detectable by our gas-chromatographic techniques.

Electrolyte Preparation. Deuterioperchloric acid electrolyte was prepared by repeated electrolysis of a perchloric acid solution in deuterium oxide using bright platinum electrodes (3-cm separation) spotwelded to a platinum wire sealed in a glass tube. The U-shaped cell, of 12-mm glass tubing, contained 15 cm^3 of the electrolyte solution. Side-arm gas outlets were connected to the atmosphere through drying tubes. Initially, 60% CP perchloric acid was diluted with heavy water (Matheson Coleman and Bell, 99.5 mol % minimum purity) to give a 2 N solution. When solution volume was reduced to one-half by electrolysis, the solution was diluted to original volume with D_2O and mixed. The constant current electrolysis cycle was repeated five times after which the H/(H + D) content of the solution was judged to be less than 0.25%. No visible gas evolution occurred on introducing platinum-black powder to the solution, indicating little or no peroxide present in the final solution. No hydrogen was detected in the solution when subjected to nmr analysis (Varian A-60) using known weights of tetramethylsilane and $(CH_3)_3COD$ as internal standards.

Electrical System. Cell current was controlled with a load box containing decade resistors and monitored with an accurate ammeter (Sensitive Research Instrument Corp. Polyranger S). Potentials were measured with a 2730 Honeywell potentiometer or a digital voltmeter (United Systems Corp. Digitec 201). The internal resistance of the cell was measured before each run, with hydrogen flowing through both sides of the cell, with a 503 Keithly Instrument milliohmmeter.

Flow System. A schematic diagram of the flow system is shown in Figure 2. Both sides of the cell could be purged with hydrogen or nitrogen, and unsaturated gas introduced at the cathode without baring the system to the atmosphere. The inlet gases were passed through packed beds (D) of silica gel and Drierite before scrubbing and saturating with D_2O (S). Flow rates were adjusted with fine-control needle valves (F) and measured with bubble-type flowmeters (M) after the cell exits. Vents allowed purging of the lines. The heavy-water saturators, designed to minimize D_2O volume, were maintained at the cell temperature (laboratory at 25°). The gas sampling technique was similar to that of Cairns and Bartosik.[9] Gas streams from the cell exits could be diverted to 2-8-cm^3 sample bulbs (B) previously evacuated and filled with nitrogen using Teflon and glass three-way valves. The sample bulbs were fitted with two Kel-F grease-lubricated high-vacuum stopcocks and a 12/30 male standard glass joint for direct connection to the mass spectrometer inlet. A side arm sealed with a silicone rubber septum was provided when gc analysis or separation was required. Flow rates could be measured before or after the sample bulbs with the valves (T). Exit streams from the cell worked against a slight water pressure to prevent back-diffusion from the atmosphere and to regulate cell gas pressure.

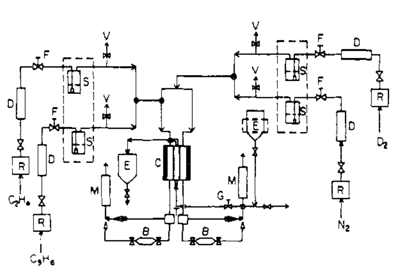

Figure 2. Flow diagram of electrogenerative hydrogenation system: R, regulator; D, drier and adsorbent; F, fine control valve; S, saturator (D_2O); V, vent; C, cell; M, flow meter; B, sample bulb.

Polarization Runs. In the electrogenerative hydrogenation system, oxygen should be completely eliminated from the electrode surface for satisfactory operation.[2] Presence of oxygen may be indicated by high values of the cell open-circuit potential. A systematic procedure was developed to obtain reproducible data. After purging the system with nitrogen, hydrogen was introduced on both sides of the shorted cell for 15 min to burn off catalyst surface oxide layers. The cathode compartment was then carefully purged with nitrogen before introducing olefin. Flow rates were about 5 cm^3/min. Preliminary polarization runs at higher potentials removed remaining traces of oxygen. With a conditioned cell, open-circuit voltage should not change more than 1 mV/5 min. Our data represent steady-state values after several minutes at a specific current and at least one earlier polarization run. Gas samples were obtained at conversions (controlled by current) corresponding to potentials of interest. The cathode exit gas mixture was passed through the sample bulb for 10 min before sealing to allow complete purging. Mass spectral and gas chromatographic analysis showed no ethylene leakage across the cell into the anode (deuterium) compartment.

Product Analysis. To avoid mass spectra overlap from deuterioethylenes and deuterioethanes, product ethylene and ethane fractions were separated by gas chromatography (Barber Colman Model 5122 thermal conductivity cell). The appropriate effluent stream from the detector was diverted to a Hamilton 870 fraction collector in a liquid nitrogen trap. The receivers contained inert 20–40-mesh ultrapure silica sand as the heat-transfer medium. For the separation of deuterioethylenes, a 6-ft 0.25 in. o.d.) column of 50–60 mesh Porapak Q (Waters Associates), was employed at about 50°. Water was retained strongly relative to the hydrocarbons, permitting complete removal prior to mass spectral analysis. Ethylene (4 min) is eluted before ethane (6.2 min). Passage of a deuterated hydrocarbon mixture through the thermal conductivity detector resulted in no appreciable effect on its mass spectrum. Collected samples were rechromatographed to verify that they were not contaminated or changed on collection. Good agreement was observed between the degree of conversion calculated from current and flow rate data of the electrogenerative cell and that indicated by the separation chromatograms. Sample receivers were filled with helium at 3 psi while immersed in liquid nitrogen to prevent air leakage during sample injection. After sample collection, the vials were reevacuated to about 1 mm while still in liquid nitrogen before warming to room temperature

Mass Spectral Analysis. The separated samples of deuterated ethylenes and ethanes were analyzed with a Consolidated Electrodynamics 21-103C mass spectrometer. The selected 12-eV ionization potential gave high parent peak sensitivity for accurate measurement and negligible ion currents for fragments formed by loss of more than two hydrogen or deuterium atoms from any hydrocarbon. The deuterioethylenes gave negligible fragmentation and good sensitivity. Because relative intensities were used instead of apparent intensities, distortion due to discrimination effects should be small.[10] A Hamilton 880 admission probe was used to introduce trapped samples from the chromatograph. Connecting lines to the receiver were evacuated by sealing the probe needle in the rubber section of the serum cap. Sample was injected by piercing at the appropriate time. Sample spectra are shown in Figure 3.

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[8] S. H. Langer and H. P. Landi, U. S. Patent 3,248,267 (April 26, 1966); R. G. Haldeman, W. P. Colman, S. H. Langer, and W. A. Barber, *Advan. Chem. Ser.*, No. 47, 106 (1965).

[9] E. J. Cairns and D. C. Bartosik, *J. Electrochem. Soc.*, 111, 1205 (1964).

[10] D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, 19, 11 (1951).

Table I. Predicted Spectra of Deuterated Ethanes Based on Ethane-d_0[a]

m/e	d_0	d_1	d_2	d_3	d_4	d_5	d_6
28	177.1	88.55	31.99	0	0	0	0
29	11.72	59.26	88.55	31.99	0	0	0
30	*100*	5.86	59.26	88.55	31.99	0	0
31	0	*100*	5.86	59.26	88.55	31.99	0
32	0	0	*100*	5.86	59.26	88.55	31.99
33	0	0	0	*100*	5.86	4.98	0
34	0	0	0	0	*100*	5.86	4.98
35	0	0	0	0	0	*100*	0
36	0	0	0	0	0	0	*100*

[a] Ionization potential, 12 eV; gain, 10; pressure, 47 μ; current, 35 μA.

Table II. Total Product Distribution. Electrogenerative Hydrogenation of Ethylene with Deuterium[a]

		A	B	C	D	E	F
E_{obsd}, V	0.514	0.219	0.143	0.100	0.070	0.044	0.031
I, mA	Open circuit	5.3	46	118	180	265	330
% conversion	0	1.04	9.2	23.8	34.3	49.4	54.9
			Ethanes				
d_0	0	23.1	15.9	23.4	26.7	29.0	27.2
d_1	0	20.5	27.2	29.5	29.4	29.5	29.6
d_2	0	18.2	24.4	17.6	16.5	16.3	17.3
d_3	0	15.2	14.9	10.5	10.3	11.2	11.1
d_4	0	10.8	10.2	9.9	9.2	8.5	8.8
d_5	0	8.2	5.1	6.9	6.1	4.4	4.6
d_6	0	4.1	2.2	2.2	1.9	1.1	1.3
			Ethylenes				
d_0	100	98.5	93.8	91.0	90.1	87.1	93.2
d_1	0	0.8	3.4	4.9	5.6	7.2	3.3
d_2	0	0.3	1.4	2.1	2.3	3.3	1.9
d_3	0	0.2	0.9	1.3	1.4	1.8	1.1
d_4	0	0.2	0.5	0.7	0.6	0.7	0.5

[a] Run D54, temperature = 24°, pressure = 746 mm, R_{int} = 0.25 ohm, gas flow = 4–5 ml/min.

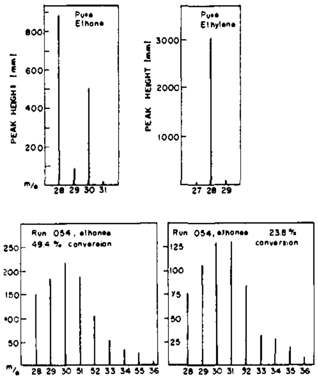

Figure 3. Sample spectra: ionization potential, 12 eV; gain, 10; current, 35 μA; pressure, 47 μ.

Spectra were corrected for the presence of naturally occurring isotopes by the statistical procedure of Beynon and Williams.[11] Saturated-hydrocarbon spectra were corrected for fragmentation by subtracting pure-component spectra from the mixture spectrum until "residuals" were zero or negligible. Because cracking patterns of all isotopic species were not available, the abundance of various ions was calculated on a statistical basis from the cracking pattern of ethane-d_0. By assigning two "isotope parameters" (P_H = 1.0, P_D = 0.85) to the probability of the loss of a deuterium or hydrogen atom, respectively, from a deuterated ethane species, the relative intensity of each ion was calculated by previously described methods.[10-12] Before each analysis, calibration runs were made with ethane-d_0. The matrix for the cracking pattern of ethanes is given in Table I. The partial pressures of unicomponent peaks were determined by dividing the observed relative intensity by the corresponding one in the pure-component spectrum. A computer program was used to process the raw data from the recorder charts, correct for natural isotopes, normalize the peaks, correct for fragmentation, and finally print partial pressure and mole fraction of the components in the unknown mixture.[1b] Two minutes of computer time (CDC 1604) was used to process six mixtures. It is difficult to assign possible limits of error involved in these calculations. However, satisfactory mass balances on the H/C ratio were obtained (less than 1% deviation) when the product gas composition was compared with the ethylene feed. Results and analyses for seven gas mixtures obtained at the indicated potentials and conditions are presented in Table II.

Results

Polarization Data, Cell Operation. Polarization curves for the electrogenerative deuteration of ethylene on our platinum-black electrodes in 2 N $DClO_4$ at 25° are shown in Figure 4. As expected, the shapes of the curves are similar to those observed for hydrogen with perchloric acid electrolyte. The initial sharp drop of the potential and leveling of the ir-corrected curves are characteristic of the system. Variation between the cell performances for ethylene in the two runs shown in Figure 4 is due to differences in the internal resistances of the cells used; the curves become identical after ir

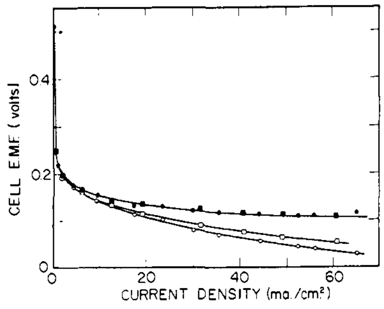

Figure 4. Electrogenerative hydrogenation: D_2–C_2H_4 with 2 N perchloric acid-d_1 in D_2O at 25°: ○, R_{int} = 0.25 ohm; □, R_{int} = 0.19 ohm. Solid symbols are ir corrected.

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(11) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier, Amsterdam, 1963.

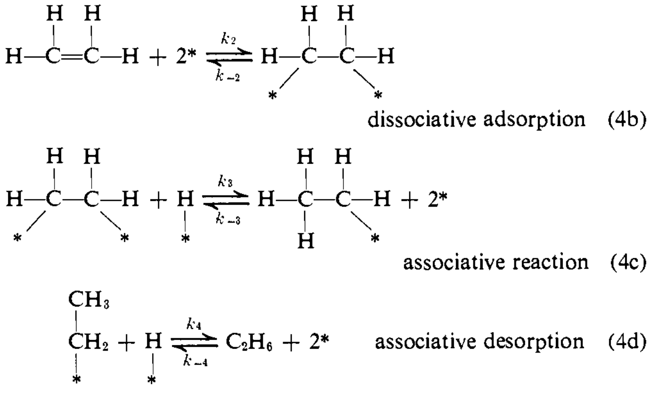
(12) J. Delfosse and J. A. Hipple, *Phys. Rev.*, **54**, 1060 (1938).

correction. They represent data obtained after two earlier polarization runs. Current density is reported in Figure 4 as compared to "total cell current" reported in our earlier work.[2] Techniques and conditions described here allow operation of the cell at a current density of about four times that first reported. For evaluation purposes, it should be noted that 1 mA of current is equivalent to about 5.17 × 10^{-9} mol/sec or about 1.27 × 10^{-4} cm^3 of hydrogen or ethylene/sec. Using as a basis the ethylene adsorption data of Niedrach,[13] a surface area of about 25 m^2/g of platinum black, and other assumptions,[14] a full surface coverage for the cell of about 0.15–0.25 cm^3 of ethylene is calculated for open circuit and higher cell operating potentials. The open-circuit voltage of 0.51 V observed here was close to that reported earlier.[2]

Treatment of Data. Analysis of the effluent ethylene stream at open circuit revealed no detectable amount of ethane. This would tend to rule against carbon–hydrogen dissociative adsorption[3,5,13] of ethylene on platinum under our conditions as a significant source of hydrogen in the electrogenerative hydrogenation process, especially at lower potentials.

When the electrogenerative reaction was allowed to proceed to even a slight extent (by adjustment to high resistance in the external circuit), all species of deuterated ethylenes and ethanes were detected in the effluent product stream (Table II). Such observations and related results are often a basis for hypothesizing a reaction scheme of the Horiuti–Polanyi type for the electrochemical hydrogenation of olefins such as ethylene. Beck and Gerischer[15] have reviewed and treated electrochemical hydrogenation from this viewpoint. Originally postulated for heterogeneous hydrogenation, this mechanism sequence involves initial dissociative surface adsorption of hydrogen followed by the reaction sequence depicted in eq 4 in the terminology of Burwell.[4,5] For an electrochemical reduction sequence, step 4a is usually replaced by an alternate discharge step involving formation of adsorbed hydrogen atoms[15] $H_{(a)}$ or H-*.

$$H_2 + 2^* \longrightarrow 2H^* \qquad (4a)$$



dissociative adsorption (4b)

associative reaction (4c)

associative desorption (4d)

While the Horiuti–Polanyi scheme is often applicable in catalytic situations and is convenient for introducing a number of catalytic intermediates and concepts for discussion, it considers a limited number of potential catalytic steps and is not always mathematically tractable. For our purposes, the general model of Kemball[7] would appear to be the most profitable initial approach for characterization of the steady-state reaction at the cathode. Without specifying a mechanism, the model assumes intermediate adsorbed species which react as shown in eq 5–7 (a indicates adsorbed species and g indicates gas phase), where p, q, r, and s are statistical parameters which refer to the ratio of the probabilities for the reactions indicated and X may be either a hydrogen or deuterium atom of unspecified origin. A theoretical distribution of deuterated species can be computed by assigning numerical values to the four parameters, p, q, r, and s, which have the following significance in terms of chemical processes

$$C_2X_4(g) \overset{1/(1+p)}{\rightleftharpoons} C_2X_4(a) \underset{r/(1+r)}{\overset{p/(1+p)}{\rightleftharpoons}} C_2X_5(a) \xrightarrow{1/(1+r)} C_2X_6(g) \qquad (5)$$

$$C_2X_4(a) + H \xrightarrow{1/(1+q)} C_2X_4H(a) \qquad (6a)$$

$$C_2X_4(a) + D \xrightarrow{q/(1+q)} C_2X_4D(a) \qquad (6b)$$

$$C_2X_5(a) + H \xrightarrow{1/(1+s)} C_2X_5H(g) \qquad (7a)$$

$$C_2X_5(a) + D \xrightarrow{s/(1+s)} C_2X_5D(g) \qquad (7b)$$

probability of adsorbed ethylene becoming ethyl = $p/(1 + p)$

probability of adsorbed ethylene desorbing = $1/(1 + p)$

probability of ethylene acquiring a D atom = $q/(1 + q)$

probability of ethylene acquiring an H atom = $1/(1 + q)$

probability of ethyl reverting to ethylene = $r/(1 + r)$

probability of ethyl becoming ethane = $1/(1 + r)$

probability of ethyl acquiring a D atom = $s/(1 + s)$

probability of ethyl acquiring an H atom = $1/(1 + s)$

By considering each of the possible adsorbed species and their probable fates, as defined above, it is possible, with the aid of appropriate mass balances,[1b,7] to generate 6 simultaneous equations for the adsorbed ethylenes and 12 for the adsorbed ethyl radicals. The coefficients of these equations are functions only of p, q, and r. Fractions of the products appearing as deuterioethanes are calculated using the fourth parameter s. Because positional deuterated isomers are not readily distinguishable, the number of predicted yields is reduced to 12.

Theoretical distributions for the gas-phase hydrogenation of ethylene on alumina-supported platinum have been previously computed by initially intuitively assigning numerical values to the four parameters, considering experimental results, and systematically varying these parameters[6] in a manner similar to that used by Kemball.[7] This procedure is useful for examining the behavior of the distributions when varying parameter values, but is laborious.

The fraction of ethylene-d_0 produced in the reaction cannot be distinguished from that originally introduced to the system. In treating our data, therefore, it was omitted[6] so that 11 yields of deuterated species were calculated and renormalized. (Expressing the distributions in this manner exaggerates the magnitude and accuracy of ethylene exchange and introduces some

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(13) L. W. Niedrach, *J. Electrochem. Soc.*, 111, 1309 (1964).
(14) J. S. Mayell and S. H. Langer, *ibid.*, 111, 438 (1964).
(15) F. Beck and H. Gerischer, *Z. Electrochem.*, 65, 504 (1961).

Table III. Computed Statistical Parameters

Current, mA	p	q	r	s
5.3	46.9	0.47	84.5	0.55
46	18.1	0.58	15.8	0.39
118	31.8	0.57	15.4	0.27
180	27.4	0.58	10.4	0.20
265	34.7	0.53	10.1	0.17
330	57.0	0.56	9.1	0.20

Table IV. Comparison of Observed and Calculated Distribution of Deuterated Products from Ethylene and Deuterium in Electrogenerative Reaction with D_2O–2 *N* Perchloric Acid-d_1 Electrolyte

	A		B		C		D		E		F	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
						Ethylenes						
d_1	32.8	32.3	20.2	20.9	14.6	12.3	12.0	9.0	9.7	6.5	5.7	2.6
d_2	19.3	11.7	13.0	8.4	7.8	5.2	5.7	3.8	4.4	3.0	2.7	1.5
d_3	5.5	9.0	4.8	5.4	2.2	3.2	1.5	2.2	1.1	1.6	0.7	0.9
d_4	0.6	6.2	0.8	3.3	0.3	1.7	0.2	1.0	0.1	0.6	0.08	0.4
						Ethanes						
d_0	6.38	9.4	9.0	9.9	16.0	18.7	20.0	22.5	22.9	25.6	22.8	25.8
d_1	14.4	8.4	19.5	16.9	27.7	22.9	30.8	24.7	32.9	26.1	34.7	28.1
d_2	9.78	7.4	15.4	15.2	16.9	13.7	17.6	13.9	17.9	14.4	19.7	16.4
d_3	8.10	6.2	11.6	9.3	10.7	8.2	9.3	8.6	8.7	9.9	10.3	10.5
d_4	2.69	4.4	4.6	6.3	3.2	7.7	2.5	7.7	2.2	7.5	2.9	8.4
d_5	0.49	3.3	1.1	3.2	0.5	5.4	0.4	5.1	0.3	3.9	0.4	4.4
d_6	0.04	1.7	0.1	1.4	0.04	1.7	0.02	1.6	0.02	1.0	0.03	1.3

error, but no alternate procedure is available at this time.)

A computer program was designed to optimize the fitting of the parameters p, q, r, and s to the experimental data of Table II after an initial estimate of the parameters. The 18 mass-balance equations, obtained by considering the desorption or addition of each species, were solved by matrix inversion and the results reduced to the 11 values corresponding to the available experimental data. In the program,[1b] the resulting 11 calculated distributions and the experimental data were subjected to a regression analysis and search was made along a three-dimensional space for a better set of parameters. The estimates at each iteration were obtained by a method due to Marquardt[16] which combines the Gauss–Taylor series method and the method of steepest descent (subroutine GAUSHAUS) to search for another set of parameters. The final product distribution and the final parameters used in calculating the distribution were obtained at the iteration where the difference between the sum of the squares or the change in parameters was less than a prespecified value. Results obtained in this way are presented in Tables III and IV together with the experimental distributions expressed as a percentage of their sum for comparison. The olefin exchange is somewhat exaggerated as explained earlier, owing to the elimination of ethylene-d_0 from the calculations.

Evaluation of Data. It is difficult to assign limits of error to the steady-state product distributions reported in Table II in view of the numerous experimental variables governing their accuracy. However, the methods used seem to compare favorably with previous reports. Satisfactory carbon–hydrogen and isotopic mass balances usually obtained suggest that errors were not significant for interpretive purposes. Products containing more than two deuterium atoms per atom of hydrogen in the molecule are probably subject to larger errors, since their peak heights could not be measured with great accuracy. As we have indicated, the distributions represent the summation of all cis–trans and geometrical isomers, since these were not distinguishable in this investigation.

Deuterated ethylenes not being observed in the gas phase at open circuit suggests that olefin exchange and the exchange currents are small, or more probably desorption back to the gas phase is a slow step.[3,5,6,7] Since deuterated ethanes do not appear in the gas phase at open circuit, self-hydrogenation is not indicated. In contrast, the formation of ethane by self-hydrogenation is measurable[17] even at −78° for gas-phase hydrogenation of ethylene on nickel.

By assuming that hydrogenation was the only reaction and a 100% current efficiency,[2b] the degree of conversion, X, could be calculated from the current, i, by

$$X = i/nFr_j \tag{8}$$

where r_j is the molar flow rate of the entering species, ethylene, after correction for the presence of water vapor. Conversion was normally significantly below 0.6 in order to minimize concentration polarization.

Discussion

The variation of deuterated ethylenes with conversion is represented in Figure 5. At conversions above 0 and below 20%, the total observed labeled ethylenes approximately equal the total observed labeled ethanes. Above 20% conversion, the ratio is about 1:2 or 1:3, indicating that the major portion of adsorbed ethylene is converted to ethane at lower potentials and higher currents. However, significant ethylene exchange takes place in contrast to open-circuit observations. The concentration of unlabeled ethylene in the total ethylene stream generally decreases with higher conversion, while total labeled ethylenes increase. Labeled d_2 and d_3 are the source of increase while d_4-labeled ethylene is more or less constant outside of the low-conversion region. This tends to rule against any significant carbonium mechanism involved in the

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(16) D. L. Marquardt, *J. Soc. Ind. Appl. Math.*, **2**, 431 (1963).

(17) D. W. McKee, *J. Amer. Chem. Soc.*, **84**, 1109 (1962).

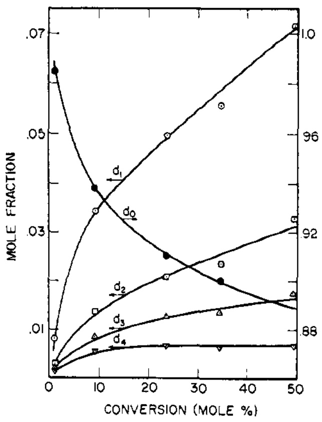


Figure 5. Product distribution of deuterioethylenes as a function of conversion at 25°.

exchange reaction. Gaseous isotope exchange seems to increase with current, and exchange and hydrogenation must be associated with a mechanism wherein electron transfer takes place before or during the exchange reaction.

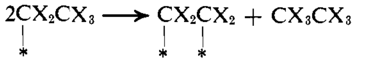
The fact that ethylene exchange is associated with surface reaction and moderate current densities rather than open-circuit or low-current conditions would suggest that some ethylene is desorbed in the course of reacting surface, dynamic reorganization involving surface species of all types. The data presented earlier would indicate an average turnover rate of the order of six to ten adsorbed volumes per minute per unit area of catalyst at 50% conversion. Labeled ethylene then would be of the order of 10% of ethane produced.

Our experimental procedure and the reproducible open-circuit potential of 0.51 V would be evidence against the presence of surface oxides.[14]

Figure 6 presents a semilogarithmic plot of yield of deuterated ethanes *vs.* the number of deuterium atoms in these ethanes as higher conversions. The plot is approximately linear in the d_1–d_3 range and somewhat less so at higher deuterated substitution. No such linearity is apparent at higher potentials and conversions lower than 23%. The linear logarithmic decrease of deuterated paraffins with deuterium content has been noted frequently[3,18] and has been expressed in terms of

$$\frac{\text{yield of } C_nH_{2n+2-x}D_x}{\text{yield of } C_nH_{2n+3-x}D_x} = \sigma$$

If a significant final step in hydrogenation is a reaction such as



$$2\underset{\vert \atop *}{\mathrm{C}}\mathrm{X_2CX_3} \longrightarrow \underset{\vert \atop *}{\mathrm{C}}\mathrm{X_2}\underset{\vert \atop *}{\mathrm{C}}\mathrm{X_2} + \mathrm{CX_3CX_3} \qquad (9)$$

then additional labeling reactions such as (4c) can occur with the diadsorbed olefin of reaction 9 to give a more highly deuterated product. With this mechanism operative, σ might be expected to have a value of 0.5. In Figure 6 the solid line is drawn for a σ value of 0.63. The fact that plots are not linear above d_4 and the occurrence of highly deuterated species can be attributed to the existence of other addition mechanisms.[3] However, the presence of labeled species constantly exceeding predicted occurrence (Table IV) can be explained by the porous nature of the electrode, especially at the electrode–matrix interface. Ethylene molecules trapped at the most inaccessible regions of the interface would be most likely to readsorb and exchange further and finally react to form alkanes in a region where the flux of discharging deuterium atoms from the matrix might be greatest. The Kemball model assumes that neither olefins nor paraffins readsorb. For the major portion of our flow system, this assumption is probably more true than for static systems used elsewhere. The entering olefin stream in this system constantly displaces and sweeps out reacted paraffin and exchanged ethylene in the more accessible reaction zones provided by a rather highly porous, loose, thin-electrode structure.

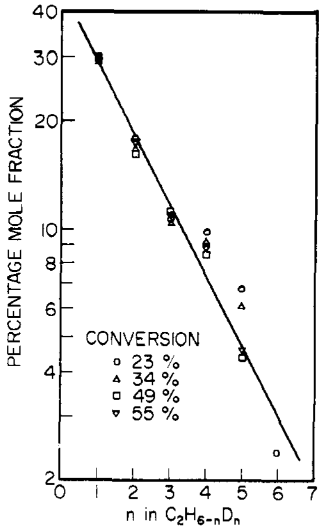


Figure 6. Distribution of deuterated ethanes plotted semilogarithmically.

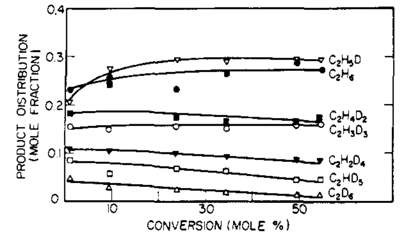
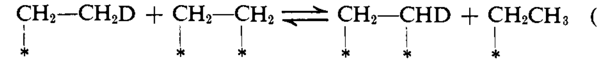


Figure 7. Product distribution of deuterioethanes as a function of conversion at 25°.

Figure 7 illustrates the overall distribution of labeled ethanes which do not vary greatly over conversions of more than 10%. In the ethane distributions, ethane-d_0 and ethane-d_1 are produced to a large extent, as is the case in other studies of platinum-catalyzed hydrogenations.[6] Rapid deuterium exchange such as this is often taken as evidence for[3,19] reaction such as



$$\underset{\vert \atop *}{\mathrm{CH_2}}\text{—}\mathrm{CH_2D} + \underset{\vert \atop *}{\mathrm{CH_2}}\text{—}\underset{\vert \atop *}{\mathrm{CH_2}} \rightleftharpoons \underset{\vert \atop *}{\mathrm{CH_2}}\text{—}\underset{\vert \atop *}{\mathrm{CHD}} + \underset{\vert \atop *}{\mathrm{CH_2}}\mathrm{CH_3} \qquad (10)$$

Subsequently, a rapid surface reversible reaction such as (4c) could result in the scavenging of deuterium from the surface and replacement of adsorbed surface deuterium atoms by hydrogen which has its origin in

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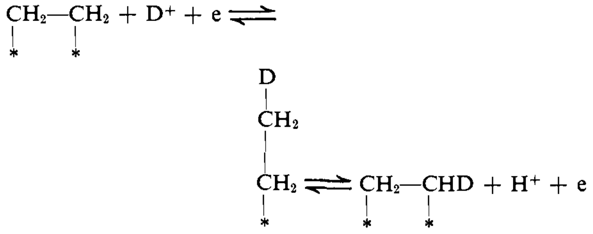
(18) G. C. Bond, *Trans. Faraday Soc.*, 52, 1235 (1956).

(19) T. B. Flanagan and B. S. Rabinovitch, *J. Phys. Chem.*, 61, 664 (1957).

the ethylene stream. Given the possible formation of hydrogenated radicals in a manner similar to eq 10, the formation of C_2H_6 could then be explained by eq 9.

Alternatively or additionally, the following type of reaction could be significant at the surface under reaction conditions and accomodated by the Kemball model.



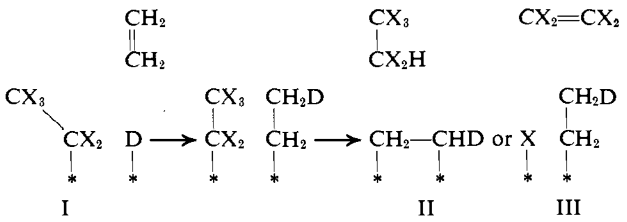
$$\underset{*}{\overset{}{CH_2}}\!-\!\underset{*}{CH_2} + D^+ + e \rightleftharpoons \underset{*}{\overset{\overset{D}{|}}{\overset{CH_2}{|}}}\!\!CH_2 \rightleftharpoons \underset{*}{CH_2}\!-\!\underset{*}{CHD} + H^+ + e \quad (11)$$

Such a reaction could change the composition of the hydrogen–deuterium pool at the surface of the electrodes to favor hydrogen statistically.

The mean deuterium number[3] of the ethane distributions lies between 1.6 and 1.7, which means that there are, on the average, fewer than two deuterium atoms in each molecule formed, the deficiency due to the net hydrogen exchange with the ethylene stream. The observed distributions were not in statistical equilibrium in contrast to the relatively unique observations of Wilson, *et al.*,[20] on nickel.

Values of *p*, *q*, *r*, and *s* tabulated in Table III are qualitatively similar to those reported for platinum-catalyzed deuteration of similar chemical systems. This is especially true for comparable conversions. Generally these values can be interpreted as indicating that (1) the probability of ethylene desorbing is small; (2) the probability of an ethylene molecule becoming an ethyl radical is high; (3) the conversion of an ethyl radical to gaseous ethane is difficult and not favored. Quantitatively, there are general trends, dependent on potential and current, which also may be associated with a change in dominant mechanism. Values of *p* and *q* at the higher potential of 0.22 V and lower current are consistent with fast initial formation of ethyl radicals and faster reversal; this would assist a "quasi-equilibrium" distribution of hydrogen and deuterium atoms, indicated by *r* and *s* values, originating from ethylene adsorption and deuterium discharge, respectively. Strong ethylene adsorption is also indicated from the high value of *p* and *r* at 0.22 V. At lower potentials and currents, the trend is toward higher ethyl production and concentration with relatively lower reversal reaction. The values of *q* would indicate an initial tendency to react with discharging deuterium atoms at the surface, but lower values of *s* would indicate relatively newly arrived ethylene molecules at the surface to be the source of the second hydrogen atom to give ethane.

It is attractive at lower potentials and higher currents to postulate conversion-type reactions involving surface reorganization with ethyl-type radicals and an impinging ethylene molecule. Such a process would explain high concentration of d_0-type species, the appearance by displacement of some labeled ethylene molecules in the gas phase, and the favoring of hydrogen on the second addition to form ethane. Intermediate sequences can be conjected, such as



$$\begin{array}{ccc} CH_2{=}CH_2 & CX_3{-}CX_2H & CX_2{=}CX_2 \end{array}$$

$$\underset{\text{I}}{\underset{*}{\overset{CX_3\diagdown}{CX_2}}\;\;\underset{*}{D}} \longrightarrow \underset{*}{\overset{\overset{CX_3}{|}}{CX_2}}\;\;\underset{*}{\overset{\overset{CH_2D}{|}}{CH_2}} \longrightarrow \underset{\text{II}}{\underset{*}{CH_2}\!-\!\underset{*}{CHD}} \text{ or } \underset{\text{III}}{\underset{*}{X}\;\;\underset{*}{\overset{\overset{CH_2D}{|}}{CH_2}}}$$

and similar types which might involve ethylene reacting with two ethyl groups attached to platinum. It should be remembered that reaction does take place in an environment in which total hydrogen and deuterium atoms are limited by acid ion discharge and that the sequences proposed are variants of Rideal–Eley-type mechanisms.[21]

Our results only help to characterize the mechanisms of hydrogenation at positive potentials. However, they also illustrate the strong potential that electrogenerative processes possess for the study of surface-catalyzed chemical and electrochemical systems at steady-state operating conditions. Additional results will assist interpretation considerably and we are continuing our investigations. An attractive feature of this and other electrogenerative systems is the simplicity of operation and the capacity for varying operation over a wide range of conditions to obtain chemical and electrochemical information simultaneously and at steady-state conditions. Despite the present sophisticated development of electrochemical approaches, information concerning attendant chemical processes in many studies is woefully lacking.

Using the plot of Figure 4, it is possible to formally calculate a small exchange current of the order of 10^{-11} A/cm^2, correcting for roughness factors. However, the calculation of this current would be dependent on the overall two-electron reaction, including the second rate-determining hydrogen or deuterium addition of eq 4d or other operative processes which give ethane. From the data of Table III, at 0.22 V it is apparent that exchange and addition of the first hydrogen atom to ethylene is proceeding faster than the measured current by about a factor of 10^2. Given the trends of the table, and the ease of obtaining an approximate open-circuit rest potential, it seems reasonable to estimate the ethylene exchange current at open circuit to be a factor of 10^4 or more ($>10^{-7}$ A/cm^2) greater than the formally calculated exchange current. The ethylene electrode potential is probably poised by the surface reaction

$$CH_2{=}CH_2(a) + D^+ + e \rightleftharpoons {}^*C_2H_4D \qquad (12)$$

or with H*

$$CH_2{=}CH_2(a) + H^+ + e \rightleftharpoons {}^*C_2H_5$$

which is appreciable and relatively reversible. Evidence is strong that the ethylene or olefin electrode does have a characteristic open-circuit potential or potential range.[3,22,23]

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[20] J. N. Wilson, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953); *J. Chem. Phys.*, 20, 338 (1952).

[21] E. K. Rideal, *Proc. Cambridge Phil. Soc.*, **35**, 130 (1939); A. Couper and D. D. Eley, *Proc. Roy. Soc., Ser. A*, **211**, 536 (1952); G. I. Jenkins and E. K. Rideal, *J. Chem. Soc.*, 2490, 2496 (1955).

[22] M. Fukuda, C. L. Rulfs, and P. J. Elving, *Electrochim. Acta*, **9**, 1581 (1964).

[23] S. H. Langer and S. Yurchak, *J. Electrochem. Soc.*, **117**, 510 (1970).

At lower cell operating potentials, it seems to be reasonable to assume, with considerably diminished positive potentials at the ethylene electrode, that hydrogen or deuterium ions discharge to give atoms. The reaction system then more nearly resembles a conventional heterogeneous catalytic chemical system.[3,4]

It is difficult to compare the results of other workers in systems similar to ours. In one instance surface adsorption of ethylene was studied in an aqueous sulfuric acid solution[24] where sulfuric acid surface-catalyzed olefin addition reactions might take place and where olefin might exist in a semihydrogenated state at the electrode surface. We also do not find that acetylene and ethylene are equivalent in our cells, as has been observed at bright platinum electrodes at lower ethylene partial pressures[25] than those used here. Actually, acetylene either poisons or reduces electrode performance significantly under our experimental conditions.[1b]

(24) E. Gileadi, B. T. Rubin, and J. O'M. Bockris, *J. Phys. Chem.*, **69**, 3335 (1965).

(25) S. Gilman, *Trans. Faraday Soc.*, **62**, 461 (1966).

Electrostatic and Resonance-Energy Effects in Proton Ionization from Pyridinecarboxylic and Anilinesulfonic Acids

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Abstract: For proton-transfer reactions of the type $AH^+ + A\text{–}X^- \rightarrow A + {}^+HA\text{–}X^-$, where A is pyridine or aniline and X^- is carboxylate or sulfonate, respectively, the entropy change is found to result largely from electrostatic effects. The enthalpy change is a result of both electrostatic and resonance effects, and the magnitudes of these effects are calculated.

The pK, $\Delta H°$, and $\Delta S°$ values for proton ionization from the protonated nitrogen in anilinesulfonic and pyridinecarboxylic acids would be expected to differ from the corresponding values for proton ionization from aniline and pyridine, respectively, for three reasons: (a) the charge on the sulfonate or carboxylate group will exert an electrostatic-field effect on the ionizing proton, (b) the presence of a sulfonate or carboxylate group should increase the resonance stabilization of the anion over that of the zwitterion, and (c) the presence of the substituent will affect the specific hydration around the ionizing group. It is the purpose of this paper to evaluate the effects of each of these factors on the $\Delta H°$ and $\Delta S°$ values for proton ionization from the above acids.

The anilinesulfonic and pyridinecarboxylic acids were chosen as a model system for three reasons: (a) accurate pK, $\Delta H°$, and $\Delta S°$ values are available in the literature for the proton ionization reactions,[2–5] (b) the molecules are rigid and of known geometry, and (c) there are three isomers (*i.e.*, ortho, meta, and para) available in each case.

Data

The thermodynamic data used in this study for proton ionization from the 2-, 3-, and 4-pyridinecarboxylic acids, the 2-, 3-, and 4-anilinesulfonic acids, pyridine, and aniline were taken from ref 2a.

The data given in ref 2a for the pyridinecarboxylic acids must be corrected for the presence of microspecies in order to obtain the true values of the thermodynamic quantities for proton ionization from the protonated nitrogen.[6] The microconstants (k_n), microenthalpies (Δh_n), K_z, and the relationships among these quantities are shown in Figure 1. The K_z values used in the

Table I. Microconstant, Microenthalpy Change, and Microentropy Change Values for 2-, 3-, and 4-Pyridinecarboxylic Acids

Acid	K_z[a]	pk_3	Δh_3, kcal/mol	Δs_3, cal/(mol deg)
2-Pyridinecarboxylic acid	0.07	5.29	2.48	−15.9
3-Pyridinecarboxylic acid	0.16	4.75	3.08	−11.4
4-Pyridinecarboxylic acid	0.05	4.84	3.16	−11.5

[a] The K_z values given are the average of independently determined values given in P. O. Lumme, *Suom. Kemistilehti B*, **30**, 168 (1957), and R. W. Greenwood and K. H. Tong, *J. Amer. Chem. Soc.*, **78**, 4896 (1956).

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(1) (a) University of New Mexico; (b) Brigham Young University.

(2) (a) J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969); (b) F. J. Millero, J. C. Ahluwalia, and L. G. Hepler, *J. Phys. Chem.*, **68**, 3435 (1964).

(3) H. P. Hopkins, Jr., C.-H. Wu, and L. G. Hepler, *ibid.*, **69**, 2244 (1965).

(4) W. F. O'Hara, H. C. Ko, M. N. Ackerman, and L. G. Hepler, *ibid.*, **71**, 3107 (1967).

(5) P. J. Conn and D. F. Swinehart, *ibid.*, **69**, 2653 (1965).

(6) D. P. Wrathall, R. M. Izatt, and J. J. Christensen, *J. Amer. Chem. Soc.*, **86**, 4779 (1964).

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