

FUEL CELLS—II. PROPANE AND PROPYLENE ON ADAMS' PLATINUM CATALYST*

M. FUKUDA†, C. L. RULFS and P. J. ELVING
University of Michigan, Ann Arbor, Michigan, U.S.A.

Abstract—In order to control the quantity of previously adsorbed hydrogen in fuel electrodes to be used with hydrocarbons, the use of Adams' platinum catalyst was investigated. Preferred procedures for electrode preparation were developed. Adams' platinum oxide powder was intimately mixed with a silver powder and pressed to form a disk, which, fixed within a cell, was reduced with hydrogen in glacial HOAc and then treated with a water-proofing wax solution. Reduction could be stopped at a definite stage and the reduced electrode could be protected from air throughout all manipulative and measuring procedures. The potential behaviour of 15 electrodes reduced to differing degrees was studied in helium, propane, propylene and hydrogen at 80°C.

During flushing with propylene, the open-circuit potential increased quite rapidly after an induction period, which was related to the original degree of electrode reduction. The steady potential reached increased with the degree of reduction. The potential of an electrode initially saturated with hydrogen gradually decreased with propylene flushing, approaching a steady value.

The good discharge behaviour observed for propylene far exceeded that due to hydrogen adsorbed during electrode preparation. Propylene flushing for more than 20 h was necessary to reach a steady potential. On interruption of the discharges, the potential returned to almost the initial potential. The steady potential may represent an equilibrium potential between propylene, electrode and electrolyte, and may be called a "propylene potential".

Résumé—Etude du catalyseur platine d'Adams en vue du contrôle de l'hydrogène préalablement adsorbé sur une électrode de pile à combustible à hydrocarbures. Comparaisons de divers procédés de préparation de l'électrode. De l'oxyde de platine pulvérulent d'Adams est mêlé d'argent pulvérulent, pressé en disque, qui, fixé dans la cellule, est réduit par H₂ dans HCH₃CO₂ glacial. La réduction peut-être arrêtée à un stade défini et l'électrode protégée contre toute oxydation par l'air. On a ainsi étudié les comportements de 15 électrodes réduites à différents degrés, dans l'hélium, le propane, le propylène et l'hydrogène à 80°C. Dans le propylène, la tension croît rapidement après une période d'induction dépendant du degré initial de réduction et sa valeur stationnaire est d'autant plus grande que ce degré initial est élevé. Une électrode initialement saturée d'hydrogène a une tension qui décroît dans le propylène et tend aussi vers une valeur stationnaire. Il faut plus de 20 h pour atteindre la valeur stationnaire dans le propylène, les conditions de décharge de la pile étant alors bien meilleures que celles propres à l'hydrogène adsorbé au cours de la préparation de l'électrode. En interrompant la décharge, on revient à la tension initiale.

Zusammenfassung—Zum Zweck der Kontrolle des vorgängig adsorbierten Wasserstoffs in Brennstoff-Elektroden, welche für Kohlenwasserstoffe gebraucht werden sollen, wurde die Verwendung des Adams'schen Platin-Katalysators als Elektrodenmaterial untersucht. Es wurden speziell geeignete Methoden zur Herstellung der Elektroden entwickelt. Adams'sches Platinoxid-Pulver wurde mit Silberpulver innig vermischt und zu Scheiben gepresst, welche nach Fixierung in der Zelle mittels Wasserstoff in Eisessig reduziert und anschliessend durch eine Wachslösung hydrophobisiert wurden. Die Reduktion konnte an einem vorgewählten Punkt unterbrochen, und die Elektrode vor Luft während allen Manipulationen und Messoperationen geschützt werden. Das Potentialverhalten von 15 unterschiedlich reduzierten Elektroden wurde bei 80°C in Helium, Propan, Propylen und Wasserstoff verfolgt.

Während der Propylenbspülung steigt das stromlose Potential sehr rasch an nach einer mit dem Reduktionsgrad in Zusammenhang stehenden Induktionsperiode. Das erreichte stationäre Potential erhöhte sich mit zunehmendem Reduktionsrad der Elektrode. Das Potential einer mit Wasserstoff vorgängig gesättigten Elektrode ging beim Spülen mit Propylen-zurück auf einen stationären Wert.

Das gute Entladungsverhalten, welches bei Propylen beobachtet wurde, ging weit über dasjenige hinaus, welches dem während der Herstellung der Elektrode adsorbierten Wasserstoff entsprechen

* Manuscript received 20 March 1964.

† Present address: Central Research Laboratory, Matsushita Electric Industrial Company, Osaka, Japan.

würde. Eine Propylenbespülung von mehr als 20 Stunden war notwendig, um ein stationäres Potential zu erreichen. Bei Unterbruch der Entladung kehrte das Potential beinahe auf den ursprünglichen Wert zurück. Das stationäre Potential mag ein Gleichgewichtspotential zwischen Propylen, Elektrode und Elektrolyt darstellen und das 'Propylenpotential' genannt werden.

INTRODUCTION

PREVIOUS work¹ showed that the interpretation of fuel-cell experiments using a palladium catalyst reduced in hydrogen is complicated by the presence of hydrogen. This is obviously a basic problem in relation to the observed activity of catalysts and the observed potential on such catalysts of hydrocarbons less active than hydrogen. In order to isolate hydrocarbon phenomena from those due to the hydrogen-electrode reaction, it was decided to use an Adams' platinum catalyst² for the following reasons:

(a) Adams' catalyst powder can be prepared by a nearly stoichiometric reduction of $\text{PtO}_2 \cdot \text{H}_2\text{O}$ to Pt black by hydrogen. Hence, the quantity of adsorbed hydrogen is inferable from the experimentally determined total consumption of hydrogen.

(b) The activity of this catalyst is claimed to be due to the oxygen that still remains in the Pt black after reduction.

(c) Some preparations of Adams' catalysts are claimed to be the most active types of platinum catalysts.

In the present study, catalytic activities of electrodes based on Adams' catalysts are related to their method of preparation and an optimum procedure is described. The potential behaviour of propane and propylene on such catalysts is considered on the basis of distinguishing their electrode reactions from that of hydrogen adsorbed during preparation. The reduction of Adams' platinum oxide in the form of powder or contained in a pressed disk was investigated for different gaseous atmospheres, liquid media in which the oxide was soaked, shaking conditions *etc.* Electrodes prepared by the various procedures were subjected to potential measurements with propane and with hydrogen at 50°C. Electrode activities were evaluated on the basis of hydrogen potentials.

EXPERIMENTAL

The hydrogen furnace used to reduce metal oxide preparations, the air electrode, the flexible fuel-cell arrangement and instrumentation for potential measurement used have been described.¹

Attempts to use skeleton electrodes, *eg* porous carbon and porous sintered nickel disks, as supports for the platinum catalysts were unsuccessful since most of the products showed a tendency to powder. Consequently, pressed electrodes were used, the details of which are summarized in Tables 1 and 2.

Chemicals

Platinum oxide powder, $\text{PtO}_2 \cdot \text{H}_2\text{O}$, was prepared according to Adams². 3 g of chloroplatinic acid crystals (Mallinckrodt) was dissolved in 10 ml of distilled water in a casserole. After the addition of 25 g of NaNO_3 crystals and sufficient blending, the wetted crystals were dried in an oven. The casserole was heated to 550°C following Adams' temperature/time curve. After cooling, the sodium nitrate was dissolved in 50 ml of water, which resulted in the precipitation of platinum oxide as a brown powder. The oxide was washed by decantation and then on filter paper; a small amount of greenish colloidal powder was found in the filtrate (pH was *ca* 6). The powder was dried overnight in a desiccator containing Drierite and then stored over

fresh Drierite. Electrolytically prepared and precipitated silver powders (Mallinckrodt) were used as supporting agents in experiments 1–9 and 10–20, respectively, after being ground in an agate mortar. Reagent grade benzene or glacial acetic acid was used as liquid medium for reduction of the platinum oxide.

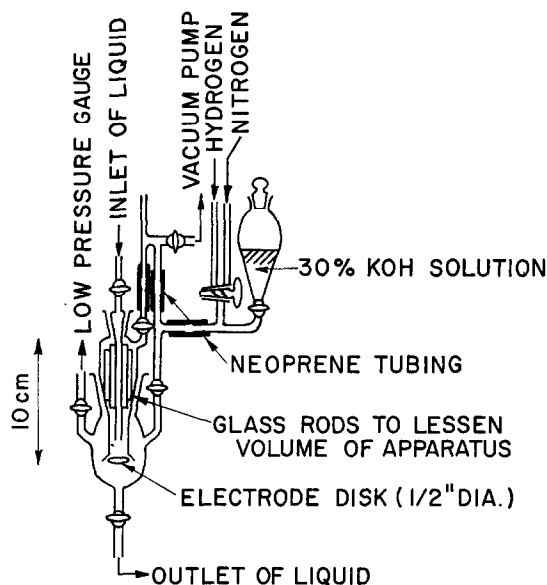


FIG. 1. Cell II for fuel electrode and apparatus for reduction and waterproofing treatment.

Apparatus

In experiments 1–9 a variety of glass apparatus, which could be evacuated, was used for reduction of the platinum oxide; the previously described¹ small glass cell (cell I) was used to test the products. Based on the results obtained, a glass reduction apparatus and accessories (Fig. 1) were constructed for experiments 10–20. This apparatus permitted the following operations to be performed without exposure to air: (a) evacuation, (b) introduction of N_2 and a measured quantity of H_2 from a gas burette, (c) introduction of a liquid medium, (d) separation of the reduction section from the pumping and gas-supply system for shaking, (e) introduction of a waterproofing wax solution, (f) solvent removal by drainage and evacuation, (g) introduction of 30% KOH solution in order to avoid direct exposure of reduced electrodes to air by covering the electrode surface with the solution. An inner part of the reduction apparatus (Cell II of Table 1), at the bottom of which an electrode was to be fixed, could be removed for potential measurements.

On the basis of experiments 1–20, a procedure was developed for the preparation of pressed electrodes (*cf* next sub-section), which were reduced and used in the apparatus shown schematically in Fig. 2. This apparatus consisted of the following units: (a) He and N_2 supply (purifying) trains, (b) propane and propylene supply (purifying) trains, (c) H_2 supply lines, including a gas burette, (d) gaseous pressure-controlling and oxygen-detecting train, (e) electrode reduction apparatus, including

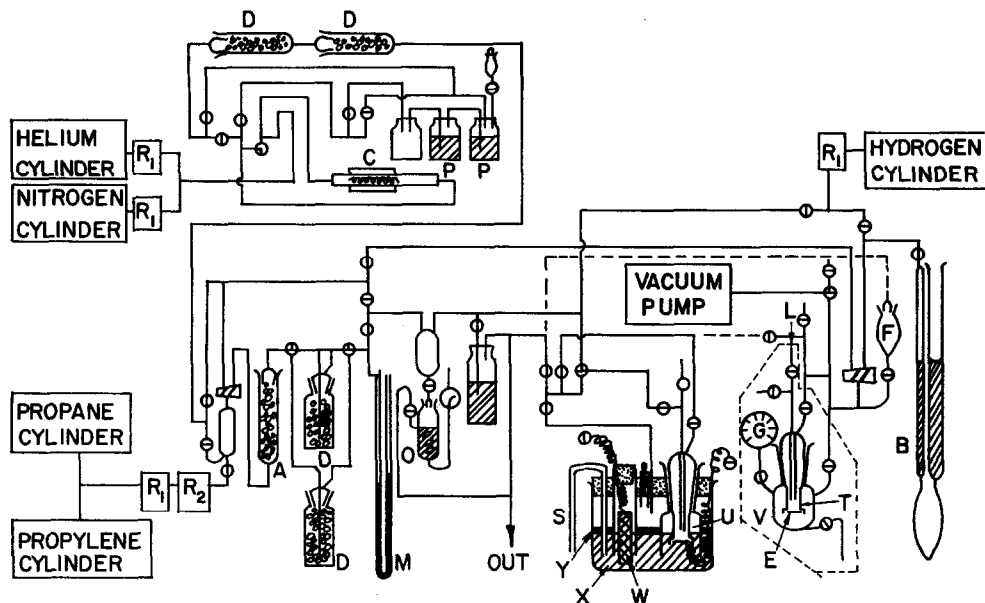


FIG. 2. Schematic diagram of experimental apparatus.

A: copper wire tube (to prevent explosion); B: gas-burette for supplying hydrogen; C: copper wire heated in furnace; D: Drierite; E: fuel electrode; F: reservoir for supplying hydrogen; G: low pressure gage; L: inlet for acetic acid; M: mercury manometer; O: oxygen detector; P: alkaline pyrogallol; R₁: high pressure gauge; R₂: low pressure gauge; S: salt bridge; T: fuel-electrode cell tube; U: outlet for gas bubbles; V: vessel for reduction and other treatment; W: air electrode; X: electrolyte solution; Y: mineral oil layer.

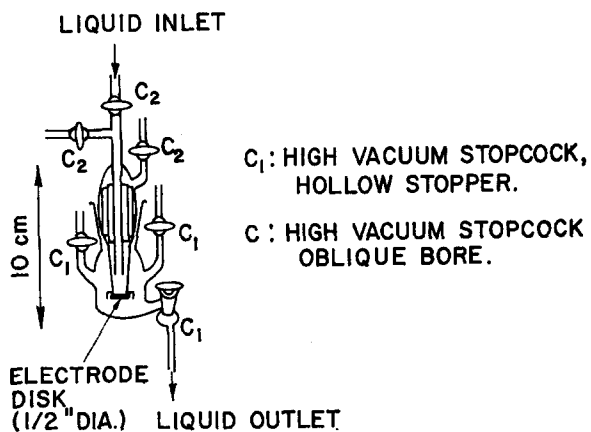


FIG. 3. Cell III for fuel electrode and reduction treatment.

an evacuating train and a 30% KOH solution supply train, and (f) cell for potential measurements.

During preliminary experiments, leakage sometimes occurred in Cell II in the case of overnight reduction at low pressure. This trouble was overcome in Cell III (Fig. 3), which used high vacuum stop-cocks; the tightness of the stop-cock used for the removal of HOAc and water-proofing solution from the apparatus is a critical feature.

A Carver laboratory press was used to prepare the pressed disks.

A shaker (3 strokes/s with a 45-mm excursion) was devised for shaking the reduction apparatus.

TABLE 1. PREPARATION PROCEDURES: ELECTRODES CONTAINING ADAMS' PLATINUM CATALYST

Expt.	Reduction apparatus and conditions	Type of sample	Constituents	
			PtO ₂ ·H ₂ O mg	Ag mg
<i>Reduction in presence of nitrogen</i>				
1	Cell I (not available for evacuation). Reduced in contact with KOH electrolyte.	Disk	42	1000
2	Glass vessel (100 ml) suitable for evacuation.	Piece	12	47
6	Cell I and glass vessel combined with Neoprene ring	Piece	42	170
<i>Reduction in presence of nitrogen and benzene</i>				
9	(Same as No. 6)	Disk	253	970
<i>Reduction in presence of hydrogen only</i>				
3	Abderhalden drying apparatus	Piece	6.3	24
4	Glass tube (5 ml)	Piece	7.1	26
5	Glass tube (5 ml)	Piece	52.4	214
12	Cell II, suitable for evacuation	Disk fixed at cell	87	348
14	(Same as No. 12)	Disk fixed at cell	153	615
<i>Reduction in presence of benzene</i>				
7	(Same as No. 2) Shaken	Piece	—	—
10	Cell II, shaken under connection with gas-supplying system.	Disk fixed at cell	246	978
<i>Reduction in presence of acetic acid</i>				
15	Cell II, shaken after separation from gas-supplying system.	Disk in a small beaker	143	—
16	(Same as No. 15)	Powder in a small beaker	149	—
17	(Same as No. 15)	(HOAc 0.25 ml) Powder in a small beaker	150	—
18	(Same as No. 15)	(HOAc 0.5 ml) Powder in a small beaker	150	—
20	Cell II, shaken after separation from gas-supplying system.	(HOAc 0.4 ml) Powder in a small beaker	150	—

TABLE 2. PREPARATION PROCEDURES AND OPEN-CIRCUIT POTENTIALS: ELECTRODES CONTAINING ADAMS' PLATINUM CATALYST

Expt.	Reduction with Hydrogen		Highest OCP vs HgO ^d	
	Ratio of introduced to stoichiometric ^a %	Ratio of consumed to stoichiometric ^b %	During propane flushing ^c V	During hydrogen flushing V
1	180 L	— (No colour change)	-0.05 (2 h)	—
2	2000 L	— (Slowly blackened above 0.1 atm)	—	—
6	500 L	— (Slowly blackened above 0.2 atm)	—	—
9	200 L	— (Very slow change)	-0.45 (3 h)	—
3	20000 L	— (Suddenly at 0.14 atm)	—	—
4	A (kept at 1 atm)	91 (Suddenly in 2 min)	—	—
5	A (kept at 1 atm)	103 (Suddenly in a few min)	—	—
12	120 L	— (Suddenly at 0.2 atm)	-0.61 (initially)	-0.90 (25 min)
14	83 A	— (Suddenly in a few s)	-0.26	-0.90 (65 min)
7	A (kept at 1 atm)	— (In a few min)	—	—
10	160 L	39 (67 min)	—	—
11	200 L (introduced through disk)	— (very slow)	-0.48 (10 min)	—
15	83 A (0.52 atm)	70 (46 h)	-0.35 (125 min)	-0.49 (85 min)
16	90 A (0.56 atm)	82 (100 min)	-0.70 (60 min)	-0.90 (50 min)
17	91 A (0.56 atm)	85 (97 min)	-0.10 (50 min)	-0.97 (3 h)
18	95 A (0.62 atm)	85 (58 min)	-0.33 (8 h)	-0.40 (3 h)
20	150 A (0.99 atm)	113 (100 min)	—	—

^a L indicates that the hydrogen was slowly introduced; A that the hydrogen was introduced all at once.

^b To determine the consumed hydrogen quantities, corrections were made for (1) variation of pressure with temperature, (2) solubility of hydrogen in glacial acetic acid, and (3) vapour pressure of glacial acetic acid which contains the small amount of water produced by the reduction.

^c Just after contact with electrolyte.

^d OCP = open-circuit potential; HgO = reference electrode of mercuric oxide in contact with 30% KOH solution.

Pressed fuel-electrode preparation

The pressed electrodes finally developed, which were used to study the potential behaviour of propane and propylene, were 12.7 mm in diameter and about 1.3 mm thick (including two 33-mesh silver screens), and contained 96–104 mg of platinum oxide. The following sequence illustrates a suitable electrode preparation procedure:

Weigh out $\text{PtO}_2 \cdot \text{H}_2\text{O}$ and fine Ag powders in the weight ratio of 1:2; mix intimately in agate mortar; press mixture (about 360 mg) to form a disk with two silver screens (33-mesh) and a silver wire lead (known wt) under a pressure of 60 lb/in² brush the disk surfaces; weigh to determine the weight of oxide (about 100 mg).

Fasten disk to bottom of the cell with silver wires; connect cell to the reduction apparatus; evacuate; introduce H_2 at 1 atm from a gas burette (measure by a low-pressure gauge); separate reduction apparatus from pumping and gas-supply system; shake reduction apparatus at room temperature; observe change of pressure during shaking by a low pressure gauge.

Reconnect reduction apparatus to pumping and gas-supply system; flush with He; introduce He; introduce through the stop-cock a water-proofing wax solution (flushed with He); evacuate for short time (dry); introduce He; introduce 30% KOH solution (flushed with He) through the side stop-cock to keep the electrode surface covered with solution.

Separate cell from reduction apparatus; immerse the cell into 30% KOH electrolyte (flushed with He); measure potential.

DEVELOPMENT OF ELECTRODE PREPARATION PROCEDURE

Two systematic series of orientative experiments (Tables 1 and 2) were made to determine the relation between various parts of the electrode preparation procedure with each other and with the activities of the electrodes thus produced. These experiments are most conveniently classified on the basis of the environment in which the platinum oxide was reduced, *ie* of the atmosphere or solvent present in addition to the oxide and hydrogen.

Reduction in nitrogen

In experiments 1, 2, 6 and 9, the apparatus containing a disk or a piece of a disk was first filled with N_2 , into which H_2 was slowly introduced. In experiment 9, the disk was wetted with benzene by shaking the apparatus.

Almost no colour change occurred in the sample on the introduction of the stoichiometric quantity of H_2 when the H_2 pressure was below 0.2 atm. As the H_2 pressure increased, the sample very slowly blackened.

Reduction in an evacuated apparatus

In experiments 3–5, 12 and 14, the apparatus containing a disk or a piece of a disk was evacuated prior to introduction of H_2 . When H_2 at 1 atm was introduced all at once (experiments 4 and 5), reduction occurred in a few seconds or minutes, accompanied by the formation of water and a change in colour from brown to black, A nearly stoichiometric quantity of H_2 was consumed in the reaction and possible adsorption. When H_2 was slowly introduced (experiments 3 and 12), reduction began at a pressure of 0.2 atm.

When 83 per cent of the stoichiometric amount of H_2 was introduced all at once at 0.5 atm pressure (experiment 14), reduction, accompanied by a uniform change in

colour, occurred in a few seconds. The potential change of this electrode during propane flushing was from -0.11 to -0.21 V vs HgO; the highest potential obtained by hydrogen flushing was -0.90 V (Fig. 4).

When 120 per cent of the stoichiometric amount of H_2 was introduced in small amounts (experiment 12), reduction occurred at pressures exceeding 0.2 atm, leaving

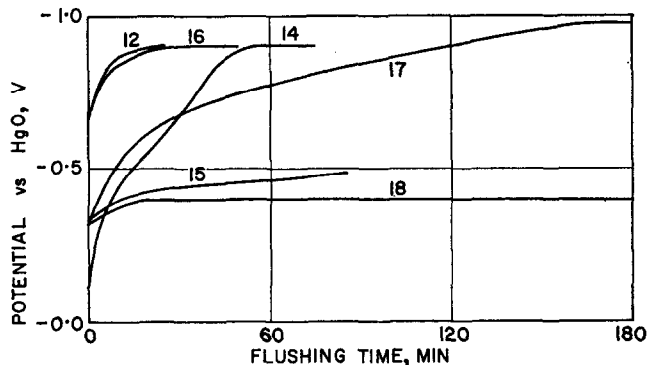


FIG. 4. Change of open-circuit potential during hydrogen flushing. (Experiment numbers on curves.)

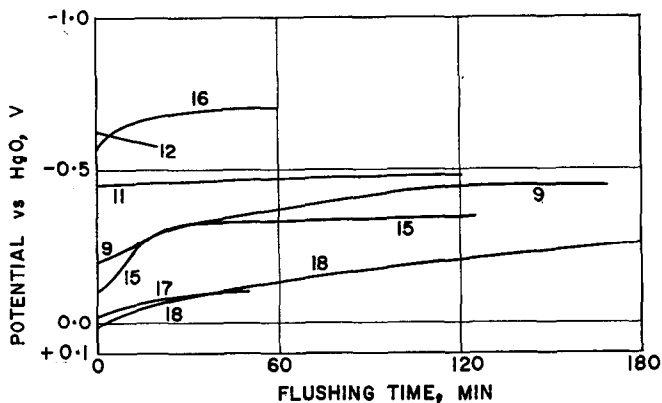


FIG. 5. Change of open-circuit potential during propane flushing after electrode/electrolyte contact is made. (Experiment numbers on curves.)

an area still brown. The potential change during propane flushing was from -0.61 to -0.57 V (Fig. 5); the highest potential on hydrogen flushing was -0.90 V (Fig. 4). Almost all of the reduced electrodes had a slight metallic lustre.

These results seemed to indicate that the potentials during propane flushing are affected by the hydrogen consumed during electrode preparation and that the activity of catalysts reduced in the absence of a liquid phase is low.

Reduction in presence of benzene

Experiment 7 showed that a disk soaked in benzene could be reduced by 1 atm H_2 pressure in a few minutes, when the apparatus was shaken. The H_2 consumption at 1 atm pressure was measured in experiment 10. After an hour, only 40 per cent of

the stoichiometric amount of H_2 was consumed; the inner layer of the disk was still brown. Reduction was even slow when the H_2 was introduced through the disk, which was wetted with benzene (Expt. 11). These results indicated the need of using as thin a disk as possible and of a thorough shaking of the apparatus.

Reduction in presence of acetic acid

Glacial acetic acid was investigated as a liquid medium, since it is claimed to be helpful in catalyst re-activation and in preparation of an active catalyst for some organic hydrogenations.

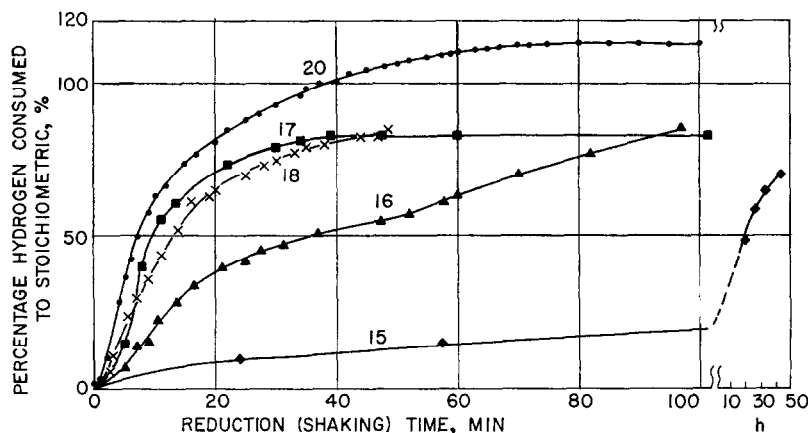


FIG. 6. Rate of reduction of Adams' platinum oxide with hydrogen in glacial acetic acid at room temperature. (Experiment numbers on curves.)

The disk (Expt. 15) or oxide powder (Expts. 16–18) was soaked in HOAc contained in a small beaker, which was placed in the main chamber of the reduction apparatus (Fig. 1). After evacuation and introduction of 83–95 per cent of the stoichiometric amount of H_2 , the apparatus was disconnected and shaken by hand. Reduction of the disk was very slow (45 h); that of the powder could be quite rapid (Fig. 6). The reduced powder was intimately mixed with fine silver powder and pressed to form a disk, which wetted with a waterproofing wax solution, was fixed at the bottom of the cell. Through all of these procedures, the reduced catalyst was carefully kept wetted with an organic solvent. The disk was dried by propane flushing (Expts. 15–17) or in an Abderhalden drying apparatus at 61.3°C (Expt. 18).

The potentials for propane (Fig. 5) are not reliable, probably because of the presence of a partially oxidized film at the catalyst surface, stressing the necessity of more completely protecting the reduced catalyst from exposure to air for accurate potential measurement of hydrocarbon electrodes. On the other hand, the highest potentials for hydrogen, -0.90 V (Expt. 16), -0.92 V (Expt. 17) and -0.40 V (Expt. 18 and Fig. 4), indicate that the use of glacial acetic acid can result in the preparation of a very active catalyst, but that the activity of the prepared catalyst decreases during the drying procedure used in experiment 18.

Electrode preparation procedure

On the basis of the results described, a procedure for electrode preparation was developed which included the following essential experimental conditions: (a)

Reduction of the platinum oxide after the disk has been fixed at the bottom of the cell, (b) use of glacial acetic acid as a liquid medium for reduction, (c) an initial H_2 pressure of about 1 atm in order for reduction to be as rapid as possible (the hydrogen consumption should be measured by a low pressure gauge), (d) use of oxygen-free helium as a flushing gas during both reduction and the subsequent potential experiments, (e) sufficient shaking of the reduction apparatus under definite, reproducible conditions, (f) drying, after waterproofing, as rapidly as possible at room temperature by evacuation and a brief flow of helium, (g) immediate covering of the reduced electrode with 30% KOH solution (flushed with helium and kept covered until commencement of electrode measurements).

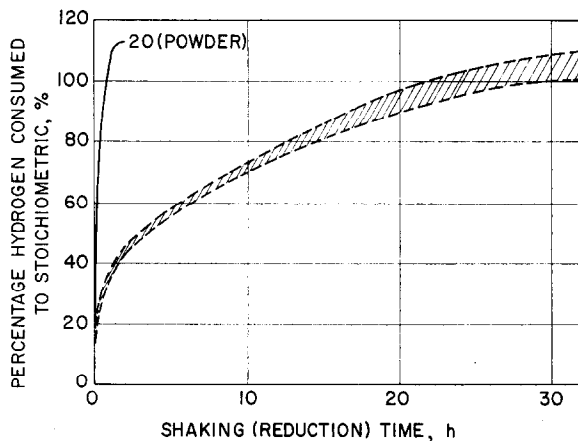


FIG. 7. Rate of reduction of Adams' platinum oxide contained in disk electrodes.

POTENTIAL MEASUREMENTS WITH PROPANE AND PROPYLENE

In these experiments, a pressed electrode containing Adams' platinum oxide was fixed at the bottom of cell III (Fig. 3). Reduction of the catalyst by shaking with HOAc in the presence of H_2 was stopped at a point where the percentage ratio of the amount of hydrogen consumed (due to reduction and/or adsorption) to the stoichiometric amount reached some definite value, *eg* 90 per cent (these percentages are corrected for the solubility of H_2 in HOAc at the temperature involved). As is evident from the relation between percentage H_2 consumed and shaking time (Expts. 20-41; Fig. 7), reduction of the powdered oxide proceeded quite rapidly, the hydrogen consumption approaching a steady value of about 113 per cent (the theoretical value for the formation of PtH is 125.2 per cent). Reduction of the oxide contained in a disk fixed in the cell, however, was very slow, a steady value of about 115 per cent being reached only after 47 h in experiments 22 and 23. In thirteen experiments (Expts. 25-41), the reduction was stopped at points in the range of 50-95 per cent.

The percentage "reduction" of the electrodes is indicated in Table 3. In the remainder of this paper, the percentage is conveniently referred to as "degree of electrode reduction".

After being treated with a waterproofing wax solution and covered with 30%

KOH solution, the reduced electrode was subjected to potential measurements under controlled atmospheres of helium, propane, propylene and hydrogen.

Open-circuit potentials

(a) *In helium, prior to use of other gases.* All electrodes were flushed with He for 20 min after contact between electrode and electrolyte was made, during which period their open circuit potentials were observed; these were in the range of -0.2 to -0.8 V

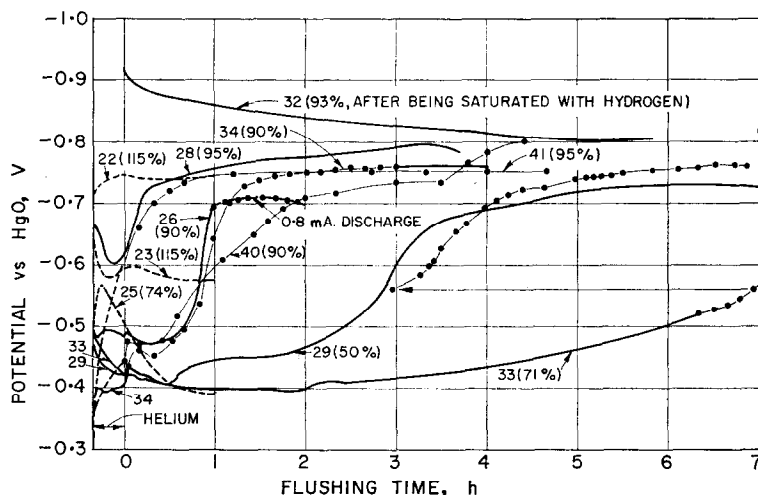


FIG. 8. Change of open-circuit potentials during flushing with helium, and propane or propylene.

Numbers not in parentheses refer to the experiment; numbers in parentheses to the percentage reduction of the electrode. Solid line: helium-propylene; dashed line: helium-propane. Dots: contact between electrode and electrolyte; dashes: no such contact.

(Table 3). No clear relationship was found between potential and degree of electrode reduction, although the surface protection from exposure to air was relatively effective compared to the preliminary electrode preparation experiments. For optimum control, a cell containing a reduced electrode should be inserted into the discharge cell in an oxygen-free helium atmosphere. In the present experiments, the time consumed in transfer from the reduction apparatus to the fuel cell location was less than 5 s; He was passed through the electrode during the transfer.

(b) *In propane and propylene.* After the 20-min helium flush, the electrodes were flushed with propane or propylene, while their open-circuit potentials were observed (Table 3 and Fig. 8).

In experiments 22, 23 and 25, the open-circuit potential during a 60-min propane flush was either similar to the potential observed during the prior He flushing or gradually decreased; no marked increase was observed. The potential seems to be related to that observed during He flushing and seems to involve the hydrogen potential of the electrode.

In the case of propylene flushing, however, a significantly increasing potential was observed in experiments 26, 28, 29, 33, 34, 36, 40 and 41; the potential increased

TABLE 3. POTENTIAL BEHAVIOUR OF ELECTRODES CONTAINING ADAMS' PLATINUM CATALYST WHEN HELIUM, PROPANE, PROPYLENE AND HYDROGEN ARE PASSED OVER THEM

Degree of electrode reduction %	Expt.	Change of OCP during flushing		Potential change during discharge at 0.8 mA V	Highest OCP during H ₂ Flush V
		With He for 20 min ^a V	With C ₃ H ₈ or C ₃ H ₆ V		
			Order of gases: He-C ₃ H ₈ -H ₂		
115	22	-0.715	-0.745 (1 h)	-0.745 (20 s)	-0.927
		-0.747		-0.525 (1 h)	
115	23	-0.643	-0.578 (1 h)	-0.575 (20 s)	-0.928
		-0.594		-0.506 (1 h)	
74	25	-0.520	-0.386 (1 h)	-0.375 (20 s)	-0.928
		-0.569 ^b		-0.267 (1 h)	
		-0.503			
			Order of gases: He-C ₃ H ₆ -H ₂		
50	29	-0.478	-0.726 (6.9 h)	-0.712 (30 s)	-0.905
		-0.418	steady	-0.412 (1 h)	
71	33	-0.503	-0.762 (11 h)	-0.715 (1 min)	-0.892
		-0.423	-0.785 (6 h) ^c	-0.360 (1 h)	
			-0.730 (1 h) ^d		
			steady		
90	26	-0.487	-0.694 (1 h)	-0.699 (30 s)	-0.934
		-0.495		-0.710 (30 min)	
		-0.483		-0.700 (1 h)	
90	34	-0.374	-0.762 ^e (3 h)	-0.746 (30 s)	
		-0.401	-0.760 ^d (1 h)	-0.594 (1 h)	
			steady		
90	36	-0.655	-0.537 (20 min)	-0.527 (1 min)	
		-0.524	not yet steady	-0.611 (69 min, max)	
				-0.336 (4 h)	
				-0.309 (6.7 h)	
90	40	-0.351	-0.801 (4.5 h)	-0.789 (1 min)	
		-0.428	-0.796 (20 min)	-0.710 (1 h)	
			not yet steady	-0.500 (4 h)	
				-0.437 (6.7 h)	
95	28	-0.659	-0.795 (3.4 h)	-0.802 (10 s)	-0.928
		-0.602	steady	-0.545 (1 h)	-0.930
			-0.807		
95	41	-0.425	-0.753 (6.7 h)	-0.722 (2 min)	
		-0.602	-0.740	-0.717 (1 h)	
				-0.590 (16 h)	
93	32	-0.481	-0.920 (by H ₂)	-0.796 (30 s)	
		-0.450	-0.804 (5.4 h)	-0.680 (1 h)	
			steady		
			Order of gases: He		
90	35	-0.625		-0.570 (20 s)	
				-0.714 (40 min)	
				-0.512 (4 h)	
				-0.284 (5 h)	
92	39	-0.557		-0.310 (20 s)	
		-0.390		-0.010 (5 h)	
		-0.312 ^a			
95	37	-0.243		-0.336 (20 s)	
		-0.344		-0.190 (58 min)	

^a Values on the upper and lower lines indicate the initial and final potentials respectively.

^b This value indicates the maximum potential.

^c As shown in Fig. 8, flushing was carried on for 6.4 h during continuous contact between electrode and electrolyte, and then under intermittent contact between the two (contact made only at

either quite rapidly (95 per cent electrode) or after a certain period of time (90, 70 and 50 per cent electrodes). The following flushing method was helpful in controlling the gas-flushing effect. As used in experiment 34 (90 per cent reduced electrode), contact between electrode and electrolyte was made only at the times of potential measurement, *ie* approximately every 10 min (measurement was actually made within 5 sec after contact); after the potential reached a steady value, the electrode was flushed until the potential reached a new steady value under continuous contact. In experiment 33, for example, after reaching a steady potential of -0.79 V by flushing under intermittent contact, the potential decreased to -0.73 V when flushed with continuous contact for 1 h. This phenomenon was independent of the presence of the oxygen counter-electrode in the cell.

On the other hand, in experiment 32 using a 93 per cent reduced electrode, a test of the electrode pre-saturated with H_2 resulted in a slow potential decrease during propylene flushing, which approached a steady value of -0.80 V.

Summarizing, the initial increasing-potential phenomenon caused by propylene flushing seems to be related to the degree of reduction attained during electrode preparation; the greater the reduction, the higher the steady potential (-0.80 V for the 95 per cent electrode, -0.76 V for the 90 per cent, -0.73 V for the 50 per cent). The highest steady potential reached with propylene was approximately the same as that of the lowest potential when the hydrogen-saturated electrode was flushed with propylene.

(c) *In hydrogen.* In seven experiments (22, 23, 25, 26, 28, 29 and 33 of Table 3), after discharge tests in propane or propylene the electrodes were flushed with H_2 until their potential reached a limiting steady high value. Though these values are much affected by the electrode history, *eg* flushing time with propane or propylene, degree of discharge, wet condition *etc*, they are indicative of the activities of the electrodes at the end of the experiments. The 90 or 95 per cent reduced electrodes (-0.93 V for H_2) were more active than the 50 or 71 per cent (-0.90 V for H_2), comparable with the results described in the next section on the steady potentials for propylene.

Discharge characteristics in propylene. Electrodes were subjected to 0.8-mA discharges while under a propylene atmosphere at 80°C as follows, for 1 h for cases (a) to (c): (a) After 1 h propylene flushing for a 90 per cent reduced electrode (Expt. 26); (b) after several hours of propylene flushing, which resulted in steady potentials for 50 per cent (Expt. 29), 71 per cent (Expt. 33), 90 per cent (Expt. 34) and 95 per cent (Expt. 28) reduced electrodes; (c) after pre-saturation with hydrogen and sufficient propylene flushing (*ca* 4.8 h), which resulted in a steady potential for a 93 per cent reduced electrode (Expt. 32); (d) for 6.7 h after 20 min propylene flushing for a 90 per cent reduced electrode (Expt. 36); (e) for 6.7 h after about 5 h propylene flushing, which resulted in a potential increase for a 90 per cent reduced

times of potential measurement) for 4.6 h, when the potential reached a steady value of -0.762 V. On the next day, flushing was continued with intermittent contact for 6 h, when the potential reached a steady value of -0.785 V; flushing was then continued under continuous contact for 1 h, when the potential reached a new steady value of -0.731 V.

^a As explained in footnote (c), a potential value indicates one observed under a continuous contact between electrode and electrolyte. The time described in parenthesis indicates the length of flushing time after an intermittent contact is replaced by continuous contact.

* An attempt was made to raise the potential by repetition of small discharges; it was unsuccessful.

electrode (Expt. 70); (f) for 35 h after about 7 h propylene flushing with a 95 per cent reduced electrode (experiment 41).

The discharge behaviour observed is summarized in Table 3 and Fig. 9. For the 1-h discharge, the potential was nearly constant at -0.7 V in the case of (a), gradually decreased in the case of (b), and, in the case of (c), seemed to hold at near -0.7 V after an initial rapid decrease from -0.8 V.

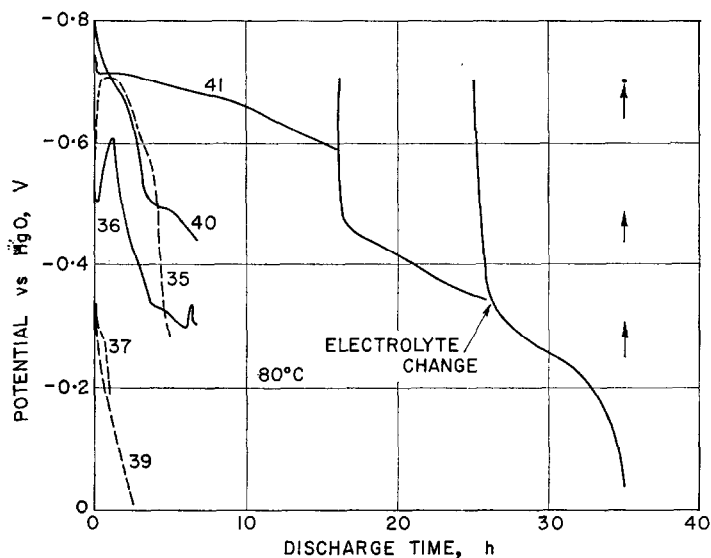


FIG. 9. Discharge behaviour at 0.8 mA in propylene and helium.

Solid line: propylene; short dashed line: helium; discontinuities show the open-circuit potential after interruption in helium. (Numbers refer to experiments.)

With the longer discharge times, the potential in the case of (d) decreased markedly after reaching a maximum (-0.61 V) and then held at near -0.3 V. In case (e), a sharp initial decrease (for about 4 h), and subsequent constancy (for about 3 h) as in the case of (d), were observed. However, in case (f) the potential held nearly constant (*ca* -0.7 V for 7 h), decreasing only very slowly and reaching -0.59 V after 16 h. After interruption of the discharge, which resulted in recovery of the open-circuit potential of about -0.7 V, the discharge was continued for a further 10 h to a total discharge time of 35 h, after which the open-circuit potential again returned to about -0.7 V, as described in the next section on temperature coefficients.

In other experiments, a steady 0.8-mA discharge was applied to three electrodes, which were flushed only with helium. In experiment 35, the potential increased quite rapidly at the beginning of the discharge from -0.47 to -0.71 V (1 h). This was not observed in experiments 37 and 39, where the discharge behaviours were very poor. After reaching maximum value, the potential decreased very rapidly for 3–4 h. The discharge capacities of these three electrodes may be ascribed to H_2 strongly adsorbed in the electrodes. These results might indicate that the maximum discharge capacity of the adsorbed hydrogen was near 4 mA h.

Temperature coefficient of propylene potential. The electrode used in experiment

41 exhibited excellent discharge behaviour; its capacity was far beyond that of the pre-adsorbed hydrogen, and the open-circuit potential on interruption of the discharges always returned to about -0.7 V. Consequently, this electrode was used for accurately measuring open-circuit potentials over the temperature range of 20 to 80°C (Figs. 10 to 12).

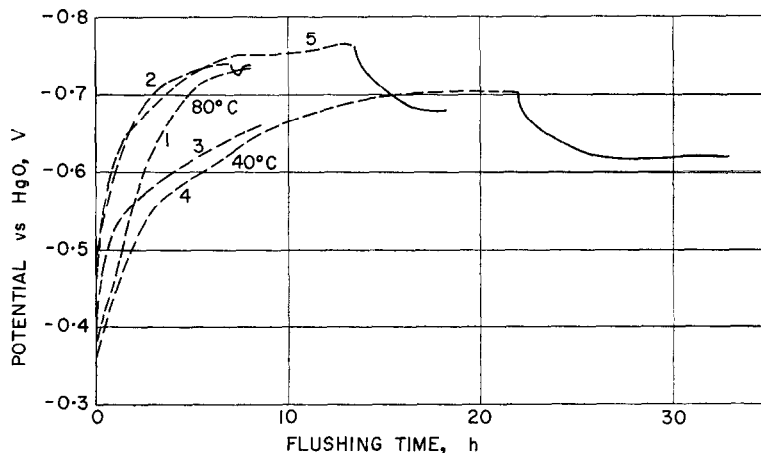


FIG. 10. Preliminary tests of variation of open circuit potentials during propylene flushing at 40 and 80°C .

The numbers indicate the experimental order. Solid line: continuous contact between electrode and electrolyte; dashed line: intermittent contact.

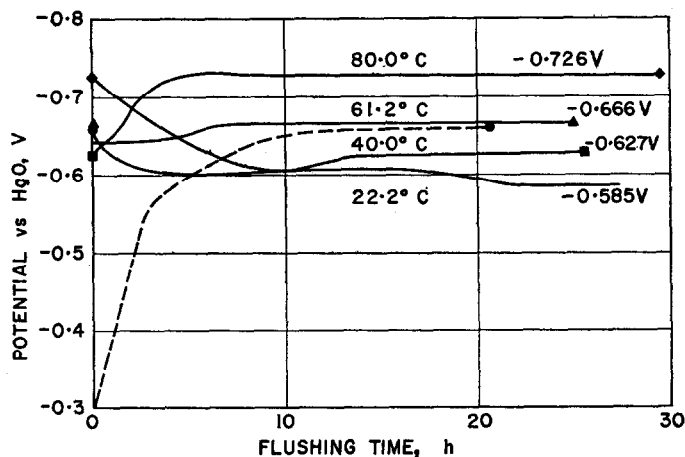


FIG. 11. Time needed to reach steady open circuit potential at various temperatures during propylene flushing.

Dashed line: intermittent contact between electrode and electrolyte. Sequence of experiments: 61.2, 40.0, 80.0, 22.2°C .

The potential recovery behaviour was examined at 80 and 40°C relative to the time necessary to reach a steady potential and other factors (Fig. 10). Potential observations were conducted in the sequence noted in the figure. Propylene was

flushed through the electrode, using both intermittent contact of electrode and electrolyte as previously described and continuous contact. The reproducibility of the data was quite good at both 80 and 40°C. After the electrode had been flushed for nearly 20 h, which was necessary to reach a steady potential (-0.77 V at 80°C; -0.70 V at 40°C), the potential decreased markedly on flushing under continuous contact

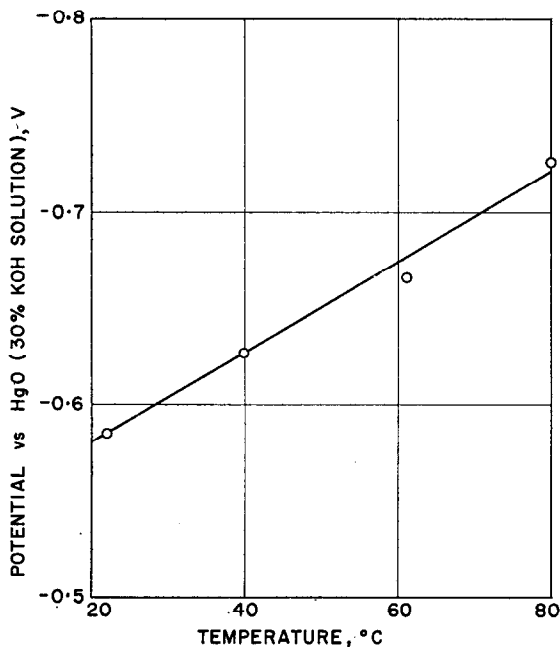


FIG. 12. Effect of temperature on open-circuit potential of propylene.

(-0.68 V at 80°C; -0.62 V at 40°C). Although this unusual decrease was not thoroughly examined, one probable cause is the contamination of the batch charge of KOH electrolyte with discharge products.

Consequently, the electrolyte was replaced at intervals. The electrolyte present in the cell-insertion tube of the discharge cell (U in Fig. 2) was lowered as much as possible by control of the propylene pressure, causing separation of electrolyte from electrode. Three-quarters of the electrolyte in the discharge cell could be removed *via* a pipette temporarily inserted under a protecting mineral oil layer; the same volume of fresh, pre-flushed electrolyte was introduced into the cell. This exchange procedure was repeated five times. The electrolyte in the cell was pre-saturated by bubbling propylene for 20 min without contact between electrode and electrolyte, and then for 10 min after making contact between the two, in order to remove old electrolyte contained in the electrode. The entire electrolyte exchange procedure was twice repeated.

A steady potential of -0.661 V at 60°C was obtained after flushing for about 20 h under intermittent contact (Fig. 11). On subsequent flushing for about 25 h under continuous contact, a steady potential of -0.661 V was observed at 61.2°C. The propylene flushing involved passing 4 bubbles/s through the electrode at a pressure

of 4 mm of dibutyl phthalate higher than 1 atm. Without interruption of the propylene flushing, the temperature was lowered to 40°C in 10 min; a steady potential of -0.627 V was reached after 25.5 h. Subsequent potential measurements at 80 and 20°C were made without interruption of the propylene flushing; steady potentials were observed of -0.726 V at 80.0°C (30.5 g) and -0.585 V at 22.2°C (25.5 h). These potentials are approximately linearly related to temperature, exhibiting a temperature coefficient of -2.33 mV/deg C (Fig. 12).

DISCUSSION

The present and preceding papers have been primarily concerned with an experimental investigation of the potential behaviour of gaseous propane and propylene in 30% KOH solution at temperatures below 80°C from the standpoint of distinguishing the electrode reaction of a hydrocarbon from that of previously adsorbed hydrogen.

If propylene can be cracked to produce hydrogen at the catalyst surface as predicted by the carbonium ion theory, the hydrogen will accumulate to a degree corresponding to an equilibrium and, at the same time, will reduce the oxygen which remains in the partially reduced platinum catalyst. Based on this assumption, the differences between the starting time and the time needed to reach the steady potential may be reasonably explained. The period of time necessary to reach equilibrium for the 50 per cent reduced electrode should be longer than that for the 90 per cent reduced electrode. In addition, the activity of the 50 per cent electrode, after reaching equilibrium should be lower than that of the 90 per cent one because a large amount of the oxygen contained in the Adams' oxide will be reduced in the KOH solution rather than during preparation in the acetic acid medium. From this point of view, the steady potential observed may be regarded as a potential characteristic of the equilibrium between propylene, intermediate products and the catalyst surface under propylene flushing.

However, as indicated by experiments on the discharge capacity due to adsorbed hydrogen, it is obvious that the prepared electrode contains some hydrogen even in the case of less than 100 per cent reduction. It is possible that a slightly oxidized surface film of catalyst is broken during propylene flushing, resulting in contact between electrolyte and newly exposed surface, which has an effectively higher hydrogen concentration. From this point of view, the steady potential may be considered to be due to hydrogen which is strongly bound to the platinum, though it is significant that propylene has such an "activating" property.

The discharge behaviour in propylene is particularly significant. In one case, the capacity of three consecutive discharges in propylene exceeded 28 mA h (35 h at 0.8 mA). This value corresponds to 71 per cent of the theoretical discharge capacity calculated from the quantity of hydrogen consumed in reduction of the platinum oxide. The maximum discharge capacity of hydrogen adsorbed on electrodes was considered to be near 5 mA h based upon the discharge behaviour in helium; therefore, the discharge capacity obtained in propylene is far beyond that due to the previously adsorbed hydrogen. Moreover, upon interruption of discharge, the open-circuit potential returns to the initial steady potential obtained prior to discharge. From these results, a steady potential obtained on propylene flushing can be interpreted as involving an equilibrium between propylene and intermediate products containing hydrogen at the electrode surface and electrolyte. This potential can be called a

“propylene potential”. The following points appear to be critical in identifying whether an observed potential is due to a hydrocarbon or not:

- (a) Confirmation of the electrical dischargeability of the hydrocarbon to be used.
- (b) Determination of the flushing time needed for reaching a steady value, eg at least 20 h for propylene.

On this basis, all the steady potentials observed on flushing 50, 70, 90 and 95 per cent reduced electrodes with propylene are propylene potentials, the differences being due to differences in the activity of the electrodes. The activity of the 95 per cent reduced electrode used for the determination of the temperature coefficient of the potential is rather low, because its initial steady potential was about 50 mV lower than that obtained in the case of other electrodes reduced to the same degree.

Acknowledgement—The authors thank Sinclair Research, Inc., which helped to support this work.

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