

OF₂ FORMATION BY ELECTROLYSIS OF WET HF*

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INTRODUCTION

The best oxidizers for hydrocarbon fuels are: 1) a mixture of O₂ and F₂ (Flox), and 2) oxygen difluoride (OF₂) (1). Although F₂ is difficult to handle, much effort is being devoted to obtaining the benefits of Flox. On the other hand, OF₂ represents the optimum O/F ratio for hydrocarbon oxidation, and its use would reduce handling problems and lead to better performance because of higher density. However, because OF₂ is expensive and has a high flame temperature, interest in it has been limited.

The generally cited method for the preparation of OF₂ from F₂ and base (2) utilizes F₂ inefficiently. Although the presence of OF₂ in the electrolysis of HF has been known since 1927 (3), this process was not suggested as the preferred method for OF₂ production until 1955 (4). Yields of 60% OF₂ have been claimed for electrolysis of HF containing 1-20% water (5), but our results are quite different.

Our work to determine the mechanism of OF bond formation has provided data that not only are useful in evaluating the electrolytic process, but also establish operating conditions that ensure consistent yields of OF₂. In studying how the electrolysis variables affect the product distribution, we found that the concentration of H₂O in the HF is a significant variable, and that periodic interruption of the electrolysis will stabilize the otherwise erratic production of OF₂.

EXPERIMENTAL

Our initial experiments involved a basic procedure in which the electrolyte was 250 ml of HF containing about 1 mole % KF, and electrolysis was carried out with nickel anodes at 7.0-7.6 volts and 0-3°C in a static system. Our main purpose was to determine how the H₂O concentration in the electrolyte affected the product distribution. Thus, we added a known amount of water to the electrolyte, allowed the electrolysis to proceed through an induction period, and then collected and analyzed the gaseous products--H₂ at the cathode, and OF₂, F₂, O₂, and O₃ at the anode.

As our work progressed, we developed other electrolysis cells, a convenient method for monitoring and maintaining the H₂O concentration in the HF, and accurate methods for analyzing most of the products. Consequently our later experiments were more closely controlled.

Electrolysis Apparatus

Development of the electrolysis cell involved several designs. Generally, smaller anodes were used as the analyses were improved (presently 10 cm²), but the electrolyte volume was held constant at 250 ml to simplify monitoring of the H₂O concentration.

The present design is shown in Figure 1. The cell itself is a 300-ml Kel-F cup equipped with a stainless steel cap and a Teflon gasket. (The liquid level can be observed through the translucent Kel-F.) The cap includes a thermocouple well and electrode leads; separate ports for introducing electrolyte, adding H₂O, replacing anode, and flushing with helium; and separate lines for circulating the electrolyte to an infrared cell and for passing the gaseous products through a

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dry ice (-78°C) condenser. A NaF scrubber is located after the condenser to remove the last traces of HF from the gases. During the electrolysis, the cell is immersed in an ice bath. However, circulation through the infrared cell and electrolysis cause the electrolyte to stay at 12-15°C.

The power supply is an Electro Products Model D-612T. For automatic interrupted operation, it is connected to the electrolysis cell through a mercury relay that is operated by a flexopulse timer (Eagle Signal Corp.).

For study of surface deposits and weight changes, the anode is removed and rinsed with HF to remove KF. The HF is removed at reduced pressure.

Gas Analysis

In our early experiments, the gaseous products were allowed to react with KI solutions, which were then analyzed for I₂ and fluoride ion. In a later improvement, O₃ was trapped out on silica gel (6) and analyzed separately. Then, a dual-column gas chromatograph, one column to remove O₃ followed by one to separate other components, was added to increase the speed of analysis and include H₂ and O₂.

Further improvements in speed and sensitivity were obtained with the temperature-programmed, single-column setup shown in Figure 2. Because the products are oxidizers, the materials of construction are limited to dry and degreased metals and fluorocarbon plastics. Passivation with OF₂ and O₃ is also necessary. The 6-in. columns of silica gel used in the setup are a compromise in length--to minimize O₃ decomposition and still permit separation of H₂ and O₂ at a readily obtainable temperature.

For a typical analysis, the columns are cooled to about -75°C by dry air which has been passed through a coil in liquid N₂. Then the gases to be analyzed are injected into one column by a Perkin-Elmer sampling valve, and the reference carrier gas is treated in the same way on the second column. After sampling is complete, the liquid N₂ is removed and the air flow is continued for about 5 minutes, or long enough to warm the columns to about -10°C and remove the O₃. Yields, as percent of current, are calculated from the gas chromatographic data and amperage, sample volume, and total gas flow measurements.

This analysis still has limitations with respect to H₂, F₂, and O₃. The thermal conductivity detector has a low sensitivity for H₂, and high concentrations cannot be allowed because response is not linear. Consequently, the flow of helium through the electrolysis cell must be adjusted to keep the H₂ concentration in the sensitive range. Also, even after prolonged passivation, the components of the system still react with F₂, so that only qualitative trace peaks are obtained for F₂. Because O₃ decomposes readily and is difficult to detect and determine reliably (7), the true O₃ yields may be higher than reported; O₂ yields would be correspondingly lower.

Analysis and Control of H₂O Concentration in Electrolyte

Because HF has a marked affinity for water, we could not analyze by ordinary Karl Fisher (8) or infrared (9) techniques. The difficulties were resolved by the closed system for continuous analysis shown in Figure 3. A diaphragm pump (with all parts that contact the electrolyte made of Teflon, except the Hasteloy C balls in the check valves) circulates the electrolyte to an Infracord through FEP or Kel-F tubing. The cells, shown in Figure 4, are made of tubing compressed to a thickness of about 2 mm between CaF₂ plates. The H₂O absorption is measured at 1.95μ, and to increase the sensitivity, a metal screen is placed at the widest aperture of the reference beam to balance the instrument to near full-scale reading when the cell containing the dry electrolyte is in the sample beam. However, because a gradual fogging of the tubing and the CaF₂ plates causes all cells to show a slow shift in base line, the usual absorbance vs. concentration calibration cannot be used. Instead, a "compensated" transmittance (T_c) vs. concentration was calculated from the absorption at 1.12μ, where H₂O does not absorb:

$$T_c = \frac{\%T_{1.95\mu \text{ of electrolyte vs. screen}}}{\%T_{1.12\mu \text{ of electrolyte vs. air}}}$$

The motor-driven syringe (Figure 3) is used to add H₂O to the electrolyte and thus to maintain a constant H₂O concentration during electrolysis.

Hydrogen peroxide is a possible component of the electrolyte, but, if present, its maximum concentration did not exceed 0.005 mole %. Our tests showed that added concentrations of 0.05 mole % had a negligible effect on the 1.95 μ absorption.

Although KF does absorb at 1.95 μ , its concentration was held constant and therefore was not a problem.

RESULTS

One of our early experiments to determine the effect of H₂O concentration on the product distribution is shown in Figure 5. Here, electrolysis was continuous and H₂O was added incrementally. The OF₂ yield dropped very rapidly as H₂O increased beyond about 0.5% and then leveled out at 7-10% OF₂. Ozone increased as OF₂ decreased and appeared to pass through a broad maximum. Oxygen apparently is largely independent of the other products, since it remained constant at 45-50%. Current efficiency for H₂ and total anode gas decreased as H₂O increased, possibly because the cathode was depolarized by dissolved anode products.

Figure 6 shows three sets of data for OF₂ yields. Curve A is the same run shown in Figure 5. Curve B is also a continuous run, except that the H₂O concentration of the electrolyte was high initially and then decreased as H₂O was consumed. Curve C is a run in which electrolysis was stopped after each sample had been taken for gas analysis, and H₂O was added before electrolysis was continued. Among these runs the yield of OF₂ was not the same at a given H₂O concentration and appeared to depend on the manner of operation. All three curves show maximum OF₂ yields over a narrow range of H₂O concentration centering below 1.0%. At higher H₂O levels, the interrupted electrolysis gave better OF₂ yields than the continuous. Continuous electrolysis at high H₂O concentration does not permanently affect the anode, because high OF₂ yields were restored as the electrolyte dried (Curve B).

Figure 7 (Run 1) shows the effect of time on OF₂ yield during continuous electrolysis at 0.56 mole % H₂O. A fairly constant (35-36%) yield was obtained for about 3 hours, and then a sharp unexplained drop occurred. There was no break in the current density that might indicate an anode surface change. Even the 3-hour plateau was not reproducible, because the next run (Run 2) showed OF₂ yields that fell rapidly from the start. Nevertheless, the interrupted operation gave higher OF₂ yields, in that Run 2 started off at the same OF₂ yields as did Run 1. Thus the system showed no permanent effect from a run that lasted many hours and ended with a low OF₂ yield. The O₂ and O₃ showed slight increases with time, while H₂ was reasonably constant at 85-90% at this low water level. As anode total is less than H₂, some unidentified anode products are possible.

The consistent pattern in which off-on operation gives higher OF₂ yields suggested operating with planned interruption. The result was not only a higher OF₂ yield but a more constant yield with time (Figure 8). Moreover, only the OF₂ yields were higher; O₂, O₃, H₂, and current density were lower. The small effect of H₂O on OF₂ yields in this concentration range was consistent with the earlier results (Figure 5).

DISCUSSION

The high (45+%) OF₂ yields that we have observed for long periods (3-4 hours) show that we are approaching the consistent operation necessary for synthesis or detailed mechanism studies. Achieving maximum yields will require study of variables other than water.

In addition to yields, current density and anode life are also important in the evaluation of an electrochemical synthesis. Although the current density should depend on electrolyte concentration and should drop as water (a strong electrolyte in HF) is consumed in the electrolysis, it does not always. Instead for the first 15-30 minutes of electrolysis, whether or not water concentration is maintained, the current density increases in both continuous and interrupted electrolysis. This may be due to a breakdown in a resistive anode coating. Once

a maximum current is reached, the current density remains constant; however, it drops as the last few tenths percent water is consumed. Also, high water levels (> 3%) cause low current densities. The maximum current densities were noted at 0.5 to 1.0 mole % water.

We have observed that nickel anodes lose weight at low water concentration during continuous electrolysis:

Mole % H ₂ O	Volts	Faradays cm ²	OF ₂ Yield % of Current	Weight Loss % of Current
Mostly Continuous Operation				
0.2	5.0 - 8.2	.0132	6.0	5.0
0.2 - 0.5	7.6	.0324	20 - 47	1.0
0.5 - 1.5	7.6	.0670	25 - 10	.01
Automatic Interrupted Operation				
0.32	7.0	.0398	35 - 46	none
0.62	7.0	.1084	30 - 45	none

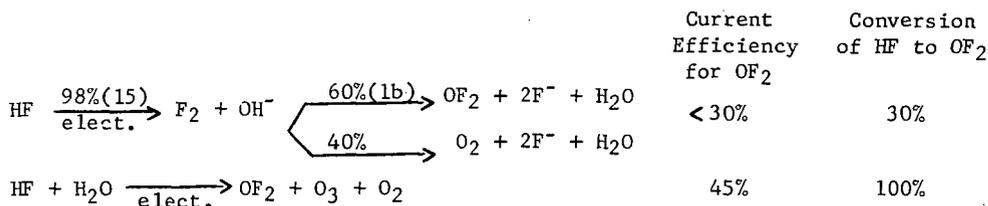
The surface of the nickel anode is quite different when electrolyzed at below 0.2% water, where F₂ is generated, and at higher water, where little or no F₂ is made. At low water a flaky deposit is formed, while at higher water a thin, uniform, adherent deposit is formed. At low water NiF₂ and KNiF₃ were detected by x-ray and electron diffraction, while only NiF₂ was found at higher water. Electron microscopy indicates a soft, porous, microcrystalline NiF₂ film when compared to that produced by action of F₂ on nickel at high temperature (10). With interrupted operation no weight losses were found at comparable water levels and faradays. However, the lower voltages and improved H₂O control may have also contributed to anode stability. While the times here (10-30 hours) are short, the data indicate that anode life should be long.

The anode is a key component in the electrolysis. The surface influences product formation and at the same time is influenced by electrolysis reactions. The restoration of high OF₂ yields as excess H₂O is electrolyzed away (Figure 6, Curve B) indicates that the surface is formed reversibly. The nickel-nickel fluoride anode is unique and essential to OF₂ formation. We have found other metals (Cu, Al) either passivate completely and require very high voltages, or disintegrate (Pt) rapidly (11). Only O₂, no O₃ or OF₂, was found with these metals. The nature of changes in the nickel-nickel fluoride anode surface, such as occur during start-up, is still uncertain. Several possibilities exist, i.e., mechanical break-up of the film, different forms of NiF₂ (α , β , γ) (12), or mixed oxide-fluoride films.

Speculation (13) on electrochemical fluorination considers free F₂ as a possible intermediate in product formation. Our data appear to eliminate this route for OF₂. In cases where F₂ is found in the products, adding H₂O does not increase OF₂ yields until the current is interrupted. Another route to OF₂ is fluorination of water by K₂NiF₆ or K₃NiF₆ in the film. However, this path is unlikely because K₂NiF₆ and K₃NiF₆ react with water to give only O₂ (14).

The formation of O₃ along with OF₂ and the absence of O₃ as well as OF₂ with anodes other than nickel suggest that the oxygen atom is a reaction intermediate. Increase in O₃ yield when OF₂ yield drops suggests that oxygen atoms are being diverted from OF₂ to O₃ formation. Further study may reveal the precise nature of the intermediate species.

The overall current yield of OF₂ and conversion of HF to OF₂ are higher with the one-step electrolysis than the two-step process of reacting F₂ with base:



Therefore in our opinion, much lower cost OF₂ would result from a development of this electrolysis. Our present study has provided the necessary analysis, control techniques, and yield data and has indicated areas for further possible improvements.

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FIGURE 1

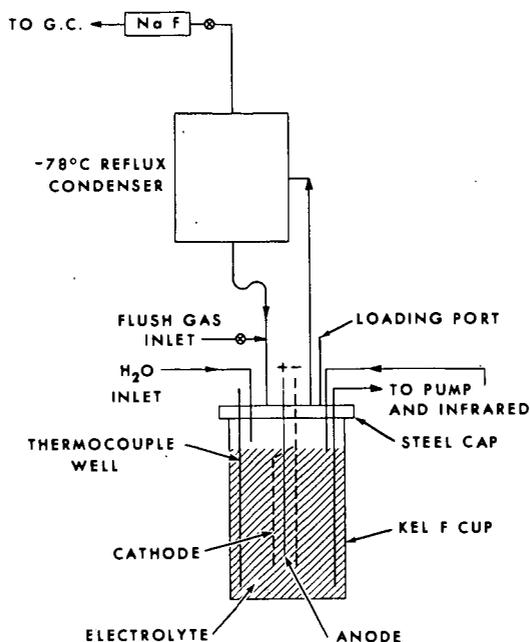
HF ELECTROLYSIS CELL

FIGURE 2

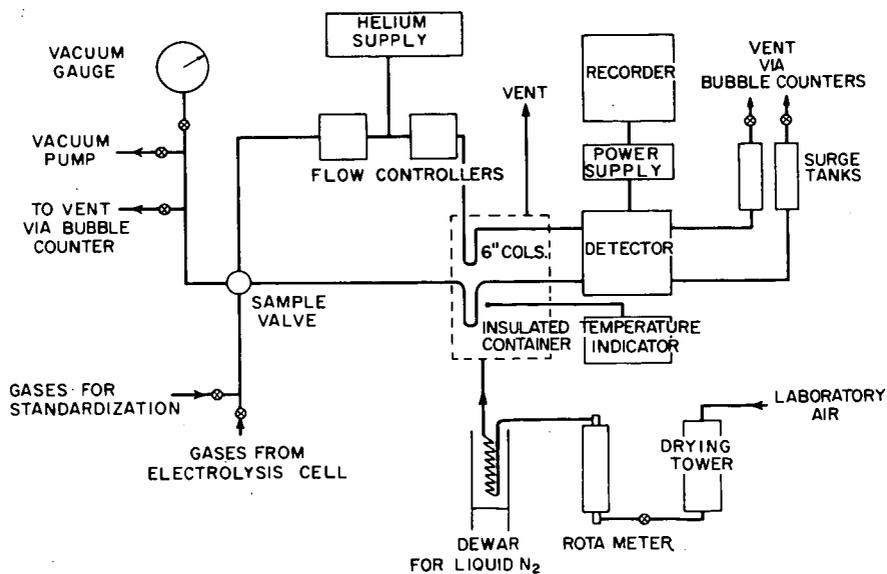
LOW TEMPERATURE PROGRAMED GAS CHROMATOGRAPH

FIGURE 3

ARRANGEMENT FOR CONTINUOUS WATER CONTROL
AND ANALYSIS BY INFRARED

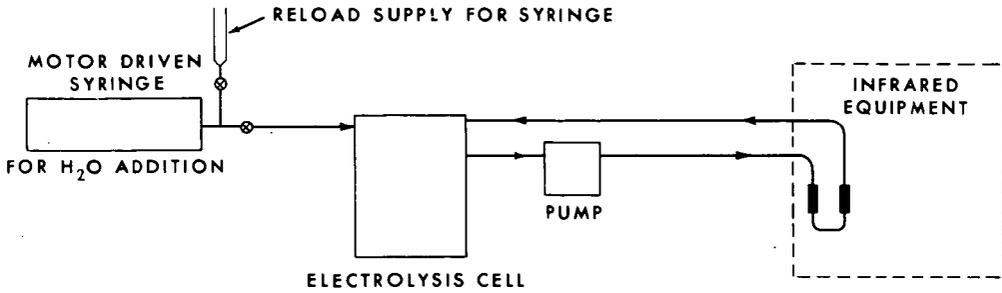


FIGURE 4

INFRARED CELL

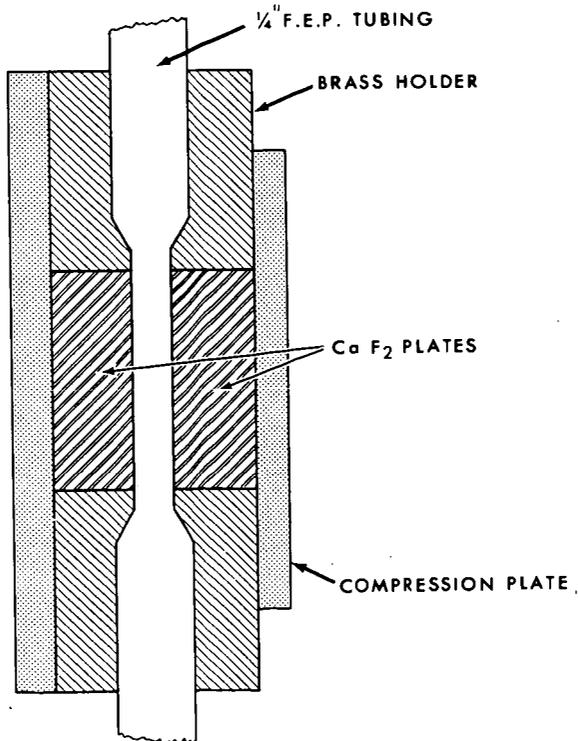


FIGURE 5
 YIELDS AT CHANGING WATER CONCENTRATION

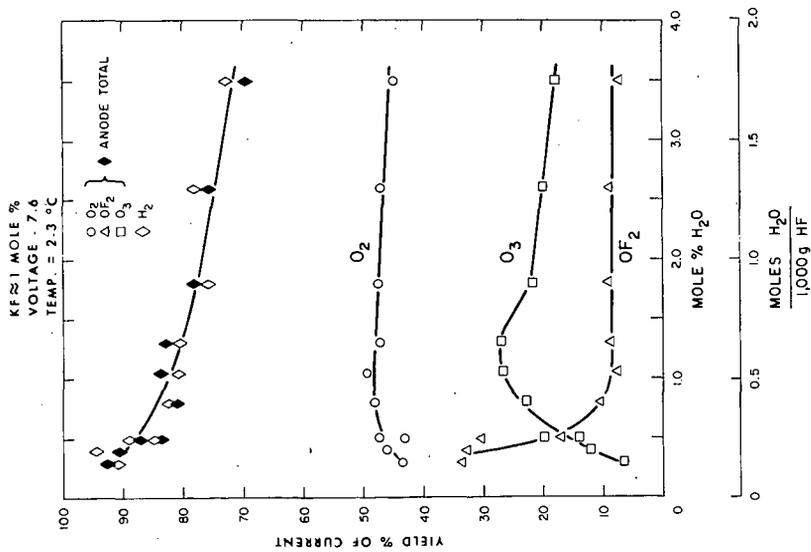


FIGURE 6
 OF₂ YIELDS AT CHANGING WATER CONCENTRATION

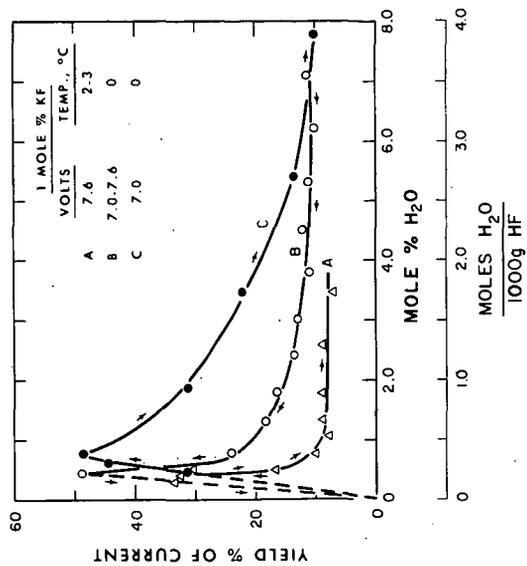


FIGURE 7

CONTINUOUS ELECTROLYSIS

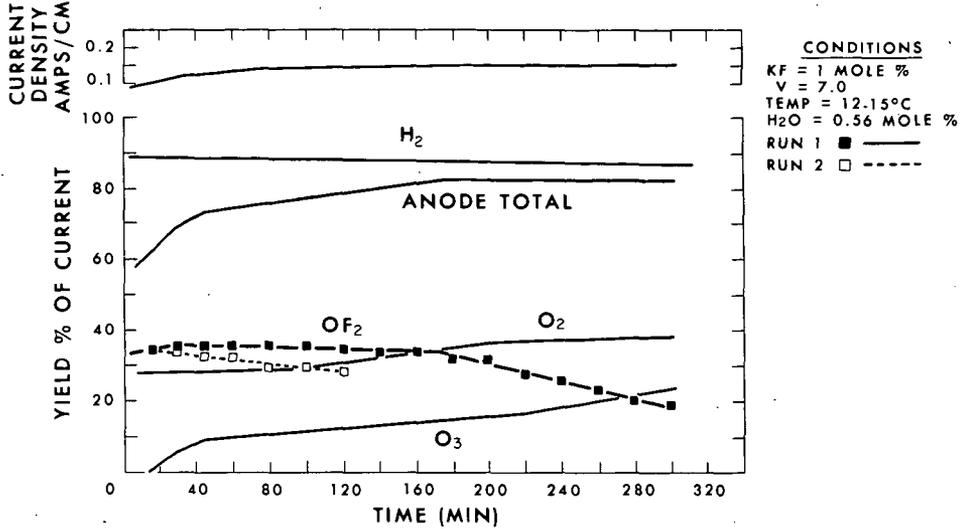


FIGURE 8

INTERRUPTED ELECTROLYSIS

RUN NO.	KEY	MOLE % H ₂ O	INTERRUPTION RATE
1	■ ———	0.62	1/60
2	— - - - -	0.56	NONE
3	□ - - - - -	0.31	1/60

