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Heterogeneous Hydrogenolysis of Some Fluorocarbons

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The catalytic C—F hydrogenolysis of six fluorocarbons including $CH_2{=}CHF$, CH_3CH_2F, $CHF{=}CHF$, $CH_2{=}CF_2$, CH_3CHF_2, and CH_3CF_3 has been studied. C—F hydrogenolysis took place more readily for compounds with no more than one F atom attached to each carbon and much less readily for compounds with two or more F atoms attached to the same carbon. The apparent activation energy values range from 12 kcal mol^{-1} for CH_3CH_2F to 26 kcal mol^{-1} for CH_3CHF_2 and CH_3CF_3. Possible mechanisms for the C—F hydrogenolysis were also discussed.

INTRODUCTION

The processes of heterogeneous catalytic hydrogenolysis of organic species containing the C–C, C–N, and C–O bonds are all well established (*1–3*). There are also some studies on the hydrogenolysis of carbon–halogen bonds (*1*). In the case of chlorides and bromides, the reactions have been shown to follow reaction (1), where X represents Cl or Br (*4–6*).

$$RX + H_2 \rightarrow RH + HX. \qquad (1)$$

There is little published work referring to results of the heterogeneous hydrogenolysis of fluorocarbons (*5, 7*). A study of such systems may be useful in gaining information of mechanistic pathways and controlling parameters for catalytic hydrogenolysis. The introduction of an extremely electronegative, yet simple and nonbulky atom furnishes some useful means to obtain insights for such heterogeneous interactions.

Lacher and co-workers (*5*) studied the hydrogenation and hydrogenolysis of various C_1—C_3 fluorocarbons on palladium-on-carbon catalyst. The major findings are: (i) The lower members of a homologous series are more difficult to hydrogenate than the members of higher molecular weight. (ii) The hydrogenolysis of the C—Cl bonds occurs more readily than the hydrogenation of the C=C bonds, which in turn is more easily accomplished than the hydrogenolysis of the C—F bonds. (iii) The relative inertness of the C—F bonds persists in fluoroolefins as well as in fluorochloroolefins.

In the present work the C–F hydrogenolysis in six fluorocarbons on active carbon-supported palladium surfaces was studied at various temperatures. C–F hydrogenolysis took place more readily for compounds with no more than one F atom attached to each carbon and much less readily for compounds with two or more F atoms attached to the same carbon. From the data of the temperature variation studies, the activation energies and *A* factors of the complete C–F hydrogenolysis in the six fluorocarbons have been evaluated.

METHODS

Cell for catalytic hydrogenolysis. The hydrogenolysis of fluorocarbons was carried out in a flow-type catalytic cell with H_2 as the carrier gas. Active carbon-supported Pd (approximately 0.5 or 1.0 g) was mixed with glass beads (6 ml, 50/60 mesh) and packed into a U-shaped reaction cell equipped with a bypass for the carrier gas. The cell temperature was maintained at ±2°C of the temperature under study. The carrier gas flow rate through the cell was

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kept at 27 ± 3 ml/min. Prior to use the cell was activated under vacuum at 340–400°C for 12 h or longer. It was then reduced with H_2 before use.

General procedure. Fluorocarbons were introduced into an injection loop of known volume by the usual high-vacuum techniques. The pressure was accurately measured with a Validyne pressure transducer. The sample in the injection loop was then inserted into the carrier gas stream of the catalytic system. The eluted products were traced by a thermal conductivity detector with associated recorder and were immediately condensed into a trap. (It was observed when the catalyst cell temperature was 150°C or less, the products were sometimes eluted in more than one distinct peak.) The actual G.C. spectra of the trapped products were then quantitatively analyzed by another gas chromatographic device.

After each experiment the catalyst was put under vacuum at the reaction temperature for a minimum of ½ h followed by H_2 flow for at least 20 min.

Product analysis. Three gas chromatographic columns were employed for the analysis of the products: (i) a 4.6-m dimethyl sulfolene (DMS) column operated at 25°C, (ii) a 14.6-m DMS column operated at 25°C, and (iii) a 15.2-m propylene carbonate-coated-on-Alumina column operated at 0°C. Columns were chosen so that clean separation of the fluorocarbon products for each system was effected. The detected mass peaks were converted into the corresponding PV of the products in Torr-milliliter by employing calibrated thermal conductivity responses.

Inert residence time. The inert residence time is defined as the time required for an inert, nonadsorptive compound to pass through the catalyst cell. This value was obtained from the difference in time required for helium to pass through the system with and without the cell. This time was found to be approximately ½ min at both 150 and 250°C.

Chemicals. The parent molecules $CH_2{=}CF_2$ (99.0%) and CH_3CHF_2 (98.0%) were obtained from Matheson Company. $CH_2{=}CHF$ (>97%), CH_3CH_2F (>97%), CH_3CF_3 (>97%), and a mixture of *trans*- and *cis*-$CHF{=}CHF$ (>97%) were obtained from PCR. All of these were used without further purification except several cycles of degassing. The catalyst, active carbon-supported Pd (10%), was obtained from Matheson, Coleman and Bell. Hydrogen (99.995%) was obtained from Airco.

RESULTS

Catalytic C–F Hydrogenolysis of Vinyl Fluoride and Ethyl Fluoride

A series of vinyl fluoride samples of various initial quantities was injected through the catalyst at 148 ± 2°C with H_2 as a carrier gas. The partial pressure of $CH_2{=}CHF$ ranged from 1 to 27 Torr (1 Torr = 123.3 N m^{-2}). Both the hydrogenation product CH_3CH_2F and the hydrogenolysis product C_2H_6 were observed, indicating the occurrence of the following reactions:

$$CH_2{=}CHF + H_2 \rightarrow CH_3CH_2F, \quad (2)$$

$$CH_2{=}CHF + 2H_2 \rightarrow CH_3CH_3 + HF. \quad (3)$$

The experimental results of this series of samples are shown in Fig. 1. The product yields are expressed as the percentage of the injected $CH_2{=}CHF$. As shown, when the sample size increased, the yield of the hydrogenation product increased while that of the hydrogenolysis product decreased.

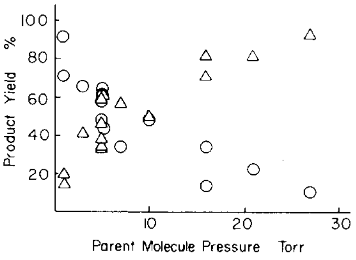


FIG. 1. Yield of hydrogenation and hydrogenolysis products from $CH_2{=}CHF$ as a function of the parent pressure. ○, C_2H_6; △, CH_3CH_2F.

For these samples the material balance for carbon atoms between the reactant and the products was always near 100%.

A corresponding series of experiments with CH_3CH_2F was performed. Similar decreasing trends of the hydrogenolysis product, C_2H_6, were also observed.

$$CH_3CH_2F + H_2 \rightarrow CH_3CH_3 + HF. \tag{4}$$

Catalytic C–F Hydrogenolysis of Other Fluorinated C_2 Hydrocarbons

The catalytic C—F hydrogenolysis of $CHF{=}CHF$, $CH_2{=}CF_2$, CH_3CHF_2, and CH_3CF_3 was carried out at 148 ± 2°C with sample pressure varying from 1 to 10 Torr. The $CHF{=}CHF$ used was a mixture of the *cis* and *trans* isomers in a 1 : 3 ratio. Preliminary results indicate these isomers undergo hydrogenation with similar efficiencies. The hydrogenation and C—F hydrogenolysis reactions of $CHF{=}CHF$ were all observed.

$$CHF{=}CHF + H_2 \rightarrow CH_2FCH_2F, \tag{5}$$

$$CHF{=}CHF + 2H_2 \rightarrow CH_3CH_2F + HF, \tag{6}$$

$$CHF{=}CHF + 3H_2 \rightarrow CH_3CH_3 + 2HF. \tag{7}$$

As the sample pressure increased the yield of the hydrogenation product, CH_2FCH_2F, increased, while that of the hydrogenolysis product, C_2H_6, decreased. The yield of the partial hydrogenolysis product, CH_3CH_2F, was always below 10%. The sum of the three products was near 100%.

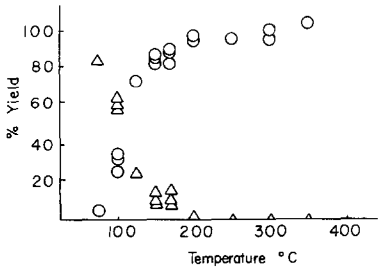


FIG. 2. Percentage yield of hydrogenation and hydrogenolysis products from $CH_2{=}CHF$ as a function of catalyst cell temperatures. ○, C_2H_6; △, CH_3CH_2F.

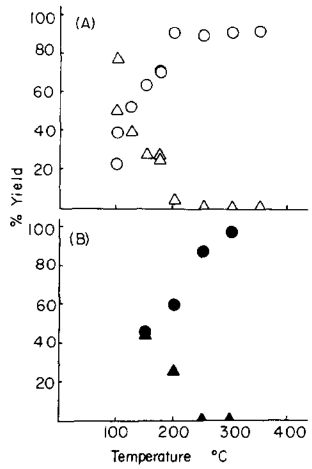


FIG. 3. (A) Percentage yield of hydrogenolysis product and remaining CH_3CH_2F as a function of catalyst cell temperature. ○, C_2H_6; △, CH_3CH_2F. (B) Percentage yield of hydrogenation and hydrogenolysis products from $CHF{=}CHF$ as a function of catalyst cell temperature. ●, C_2H_6; ▲, CH_2FCH_2F.

The hydrogenation of $CH_2{=}CF_2$ took place readily, giving essentially complete saturation. However, in contrast to the above results $CH_2{=}CF_2$, CH_3CHF_2, and CH_3CF_3 gave the hydrogenolysis products in only negligible amounts regardless of sample size.

Percentage Yields of C–F Hydrogenolysis Products as a Function of Temperature

The temperature effects on the catalytic C–F hydrogenolysis of the six fluorocarbons (partial pressure of 5 Torr) being used have been studied at 100, 150, 200, 250, 300, and 350°C. Selected studies were also made at 75, 125, 170, 375, and 400°C as needed. The observed yields of the hydrogenation product (or the remaining parent compound) and the hydrogenolysis product were plotted versus temperature in Figs. 2–5.

Three general patterns were observed for the complete hydrogenolysis product, C_2H_6. For molecules containing no more than one F atom on each carbon, $CH_2{=}CHF$, CH_3CH_2F, and $CHF{=}CHF$, the C_2H_6 yield rose very sharply in the 100 to 250°C range. For molecules containing

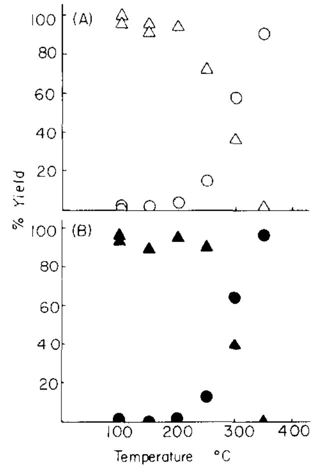


FIG. 4. (A) Percentage yield of hydrogenation and hydrogenolysis products from $CH_2{=}CF_2$ as a function of catalyst cell temperature. ○, C_2H_6; △, CH_3CHF_2. (B) Percentage yield of hydrogenolysis product and remaining CH_3CHF_2 as a function of catalyst cell temperature. ●, C_2H_6; ▲, CH_3CHF_2.

two F atoms on one of their carbons, $CH_2{=}CF_2$ and CH_3CHF_2, the C_2H_6 yield gradually rose to 100% in the 200 to 350°C range. For molecules with three F atoms on the same carbon, CH_3CF_3, C—F bond hydrogenolysis was insignificant at 300°C and rose sharply between 300 and 400°C. In each case the hydrogenation product or the remaining parent was observed to have a complementary decrease.

DISCUSSION

Hydrogenation and C-F Hydrogenolysis of Fluorocarbons

The observed results from the unsaturated fluorocarbon systems indicate that C=C hydrogenation is probably much faster than C—F hydrogenolysis. The main support for this view is derived from the observation that at rather low temperatures the C=C hydrogenation is already quantitative while the C—F hydrogenolysis is still not observed.

An alternate way to interpret the results shown in Fig. 1 is to plot the actual yields of products instead of the percentage yields as a function of partial pressure of $CH_2{=}CHF$. In so doing it was detected that as the partial pressure of the parent increased the amount of observed product increased almost linearly up to a parent partial pressure of 10 Torr. Between 10 and 20 Torr a constant amount of the observed product was detected. This means that with a partial pressure of the parent compound less than 10 Torr, there is still an excessive amount of active sites on the catalyst surface for reaction. The reaction rate is thus dependent on the parent pressure. However, all available active sites are saturated if the partial pressure of the parent exceeds 10 Torr, and the reaction is converted into zero order.

Activation Energies for Complete C-F Hydrogenolysis

In this study H_2 was used as the carrier gas and was in large excess. Since the partial pressure of the sample employed for all the temperature studies was 5 Torr, where the product yield is definitely dependent on the fluorocarbon partial pressure, it is reasonable to assume that the C-F hydrogenolysis process would be pseudo first order. The fractional conversion, x, was normalized to account for the variation in the time the samples were within the catalyst cell. This normalization is necessary because the elution time for the products through the cell varies for different parent compounds and reaction temperatures. With these suppositions it is possible to

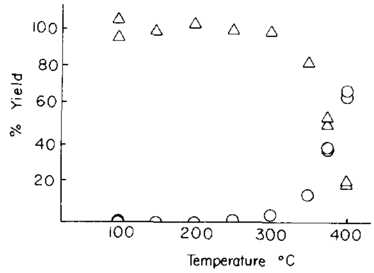


FIG. 5. Percentage yield of hydrogenolysis product and remaining CH_3CF_3 as a function of catalyst cell temperature. ○, C_2H_6; △, CH_3CF_3.

derive the following:

$$\ln \frac{1}{1-x} = Ate^{-E_a/RT},$$

where

$$x = \text{normalized fractional conversion} = \frac{\text{fractional conversion,}}{\tau_1/\tau_0}$$

τ_0 = inert residence time for He in catalyst cell in minutes,

τ_1 = adsorptive residence time for fluorocarbons in catalyst cell in minutes,

t = effective contact time,

E_a = apparent activation energy $= E_{\text{reaction}} - \Delta H_{\text{adsorption}}$.

Therefore,

$$\ln\left(\ln \frac{1}{1-x}\right) = -\frac{E_a}{RT} + \ln AT.$$

By plotting the left-hand side against $1/T$, the E_a value can be evaluated from the obtained slope. An example plot is given in Fig. 6 for the formation of the complete C—F hydrogenolysis product, C_2H_6, from $CH_2{=}CHF$.

The A factor can also be calculated from the intercept of the line by assuming the effective contact time, t, to be 0.2 sec. This time was estimated by considering the amount of catalyst, volume of the catalyst cell, and the rate of flow through the catalyst cell.

In Table 1, the evaluated apparent activation energies E_a and the A factor values for the complete C—F hydrogenolysis of the six fluorocarbons under study are listed. The slopes and intercepts from which these values were calculated are also included in Table 1. For fluorocarbons with a maximum of one F atom on each carbon, $CH_2{=}CHF$, CH_3CH_2F, and $CHF{=}CHF$, the E_a values are in the range of 12 to 17 kcal mol^{-1} (1 kcal mol^{-1} = 4.18 kJ mol^{-1}). The fluorocarbons with two or more F atoms on one of the carbon atoms, $CH_2{=}CF_2$, CH_3CHF_2, and CH_3CF_3, give E_a values in the range of 20 to 26 kcal mol^{-1}. The A factor values range from 5.8×10^5 to 2.4×10^{10} sec^{-1} with most of the values in the range 10^7 to 10^8 sec^{-1}.

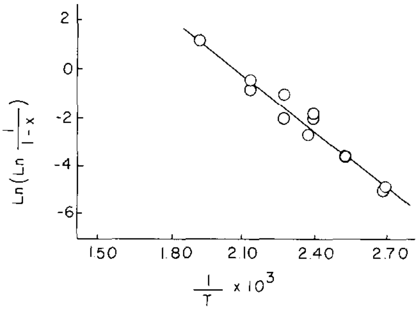


FIG. 6. Arrhenius plot for the evaluation of kinetic parameters for the catalytic C—F hydrogenolysis in $CH_2{=}CHF$ to give C_2H_6 as final product.

Possible Mechanism of C–F Hydrogenolysis

In the study of C–Cl hydrogenolysis on evaporated Pd films, Campbell and Kemball have proposed two possible mecha-

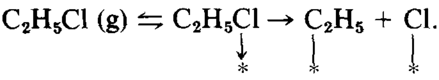
TABLE 1

Apparent E_a and A Factor Values for the Complete C–F Hydrogenolysis of Fluorocarbons

Compound	Slope	Apparent E_a (kcal mol^{-1})	Intercept	A factor (sec^{-1})
$CH_2{=}CHF$	−7685	15	15.825	3.7×10^7
CH_3CH_2F	−6154	12	11.670	5.8×10^5
$CHF{=}CHF$	−8774	17	16.503	7.3×10^7
$CH_2{=}CF_2$	−10176	20	17.272	1.6×10^8
CH_3CHF_2	−12964	26	22.309	2.4×10^{10}
CH_3CF_3	−12854	26	19.073	9.6×10^8

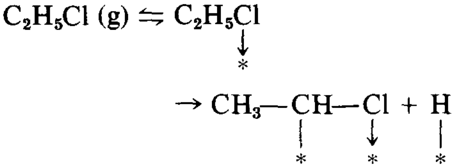
nisms which are illustrated below with C_2H_5Cl (*6*):

Mechanism 1



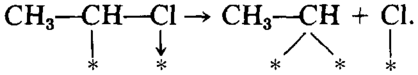
$$C_2H_5Cl\,(g) \rightleftharpoons \underset{\underset{*}{\downarrow}}{C_2H_5Cl} \rightarrow \underset{\underset{*}{|}}{C_2H_5} + \underset{\underset{*}{|}}{Cl}. \quad (8)$$

Mechanism 2



$$C_2H_5Cl\,(g) \rightleftharpoons \underset{\underset{*}{\downarrow}}{C_2H_5Cl}$$

$$\rightarrow \underset{\underset{*}{|}}{CH_3}—\underset{\underset{*}{\downarrow}}{CH}—\underset{\underset{*}{|}}{Cl} + \underset{\underset{*}{|}}{H}, \quad (9)$$

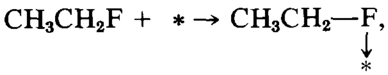


$$\underset{\underset{*}{|}}{CH_3}—\underset{\underset{*}{\downarrow}}{CH}—Cl \rightarrow CH_3—\underset{*\diagup\diagdown *}{CH} + \underset{\underset{*}{|}}{Cl}. \quad (10)$$

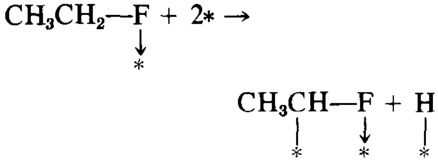
A reliable way to distinguish between these two mechanisms would be the addition of D_2 to the hydrogenolysis system. If Mechanism 1 predominates, C_2H_5D would be formed from the adsorbed C_2H_5 radicals. On the other hand, the adsorbed CH_3CH radicals produced in Mechanism 2 would give rise to CH_3CHD_2. The fact that large amounts of CH_3CHD_2 were indeed detected means that Mechanism 2 is likely to be the predominant one (*6*).

It is highly possible that C-F hydrogenolysis proceeds in a similar fashion to the C-Cl hydrogenolysis. This means that Mechanism 2 may also predominate in the hydrogenolysis of fluorocarbons; however, certain refinements could be introduced to slightly modify the mechanism.

For saturated fluorocarbons such as CH_3CH_2F and CH_3CHF_2, the initial interaction between the gas-phase molecules and the catalytic surface is likely to be through the physical adsorption of the electronegative F atoms on the Pd surface. This is followed by the metalation of the C-H bonds involving the α carbon on which the F atom is attached.



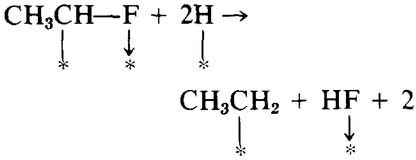
$$CH_3CH_2F + * \rightarrow CH_3CH_2—\underset{\underset{*}{\downarrow}}{F}, \quad (11)$$



$$CH_3CH_2—\underset{\underset{*}{\downarrow}}{F} + 2* \rightarrow$$

$$\underset{\underset{*}{|}}{CH_3CH}—\underset{\underset{*}{\downarrow}}{F} + \underset{\underset{*}{|}}{H}. \quad (12)$$

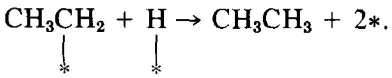
Some recent studies on the chemisorption of halogenated olefins on the Pt single-crystal surfaces indicate that the dehydrofluorination of the fluorocarbons is likely to be an intermolecular process (*8, 9*). Since H_2 was employed as a carrier gas in the present system, the Pd surface must be saturated with adsorbed H atoms for the intermolecular dehydrofluorination process. Because of this, the next step in the C-F hydrogenolysis mechanism is modified from an equivalent of Eq. (10) to



$$\underset{\underset{*}{|}}{CH_3CH}—\underset{\underset{*}{\downarrow}}{F} + \underset{\underset{*}{|}}{2H} \rightarrow$$

$$\underset{\underset{*}{|}}{CH_3CH_2} + \underset{\underset{*}{\downarrow}}{HF} + 2*. \quad (13)$$

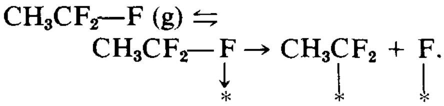
After the adsorbed CH_3CH_2 radicals combine with surface H atoms, the resultant C_2H_6 molecules may desorb from the surface.



$$\underset{\underset{*}{|}}{CH_3CH_2} + \underset{\underset{*}{|}}{H} \rightarrow CH_3CH_3 + 2*. \quad (14)$$

In the case of CH_3CHF_2, the two stages of C-F hydrogenolysis could be either simultaneous or stepwise, but both stages must be completed before desorption from the surface. This is the reason why the yield of CH_3CH_2F from CH_3CHF_2 is negligible.

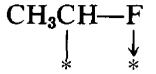
The mechanism for the C-F hydrogenolysis of the other four fluorocarbons differs from the above pair mainly in the initial adsorption stage. For CH_3CF_3, because of the lack of H atom on the α carbon, the initial step is likely to be the direct dissociation of a C-F bond similar to what has been shown in Mechanism 1 for C_2H_5Cl.



$$CH_3CF_2—F\,(g) \rightleftharpoons$$

$$CH_3CF_2—\underset{\underset{*}{\downarrow}}{F} \rightarrow \underset{\underset{*}{|}}{CH_3CF_2} + \underset{\underset{*}{|}}{F}. \quad (15)$$

In the case of the three unsaturated fluorocarbons, either the F atom or the C=C double bond could be physically adsorbed on the surface as the initial step. This will immediately lead to chemisorption. In fact, it has been established from the Pt single-crystal studies that CHF=CHF undergoes associative chemisorption while CH_2=CHF and $CH_2=CF_2$ undergo dissociative adsorption followed by elimination of F-containing species (*8, 9*). In the present experiments, the situation is quite different. Since the Pd surface is originally saturated with chemisorbed H atoms, such H atoms may add efficiently to the double bonds of the unsaturated fluorocarbons to enhance immediate saturation. As a result, compounds such as CH_2=CHF will be immediately converted to the adsorbed half-hydrogenated states such as



$$\underset{\substack{| \\ *}}{CH_3CH}\text{—}\underset{\substack{\downarrow \\ *}}{F}$$

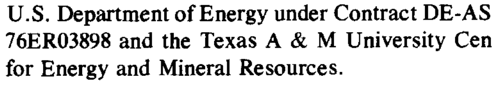
which is essentially identical to what has been derived from CH_3CH_2F as shown in Eq. (12).

The fact that CH_3CH_2F was actually observed as a product from the catalytic hydrogenation and hydrogenolysis of CHF=CHF but not from $CH_2=CF_2$ means that when the α carbon is chemisorbed on Pd surface it is compulsory for all the C—F bonds of this carbon to undergo hydrogenolysis. But, it is not necessary for the F atoms on the β carbon to be affected. Whenever the α carbon is chemisorbed on the Pd surface, the β carbon in some adsorbed molecules may be standing in a rather vertical position away from the Pd surface. If the β carbon does not interact with the surface through adsorption, the resulting partial hydrogenolysis product, such as CH_3CH_2F from CHF=CHF, would have a chance for desorption after reactions are completed on the α carbon.

The Observed Kinetic Parameters

The observed apparent activation energies for the complete hydrogenolysis of the six fluorocarbons as shown in Table 1 probably reflect the dissociation energies of the cleaved C–F bonds. This is because the likely rate-determining step in the reaction mechanism is the cleavage of the C–F bonds as shown in Eq. (13) (*6*). The actual values of the dissociation energies of the C–F bonds in the adsorbed fluororadicals are unknown. For the stable molecules, it has been determined that $D(CH_3CH_2\text{–}F) = 107.5$ (*10, 11*) and $D(CH_3CF_2\text{–}F) = 124.8$ kcal mol^{-1} (*12*). This implies that for a carbon atom with more F atoms attached, the C–F bond strength will be higher. This could explain the general trend observed in Table 1 for the apparent E_a values of the C–F hydrogenolysis processes.

The apparent E_a values for C–F hydrogenolysis are similar for CH_3CHF_2 and CH_3CF_3. This could be attributed to the supposition that both molecules will give rise to a similar adsorbed CH_3CF_2 radical [see Eqs. (15) and (16)] whose dehydrofluorination reaction might be rate determining.



$$CH_3CHF\text{—}F\ (g) \leftrightarrows CH_3CHF\text{—}\underset{\substack{\downarrow \\ *}}{F} \rightarrow CH_3\underset{\substack{| \\ *}}{C}F\text{—}\underset{\substack{\downarrow \\ *}}{F} + \underset{\substack{| \\ *}}{H}. \quad (16)$$

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REFERENCES

1. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
2. Bond, G. C., *in* "Heterogeneous Catalysis: Principles and Applications" (P. W. Atkins, J. S. E. Holker, and A. K. Holliday, Eds.). Oxford Univ. Press (Clarendon), London/New York, 1974.
3. Ozaki, A., "Isotope Studies of Heterogeneous Catalysis." Academic Press, New York/London, 1977.
4. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 377 (1957).

5. Lacher, J. R., Kianpour, A., Oetting, F., and Park, J. D., *Trans. Faraday Soc.* **52,** 1500 (1956).
6. Campbell, J. S., and Kemball, C., *Trans. Faraday Soc.* **57,** 809 (1961).
7. Lacher, J. R., Kiampour, A., and Park, J. C., *J. Phys. Chem.* **60,** 1454 (1956).
8. Mason, R., Textor, M., Iwasawa, Y., and Gay, I. D., *Proc. Roy. Soc. Ser. A* **354,** 171 (1977).
9. Clarke, T. A., Gay, I. D., and Mason, R., *Chem. Phys. Lett.* **27,** 562 (1974); *J. Chem. Soc. Chem. Commun.,* 331 (1974).
10. Golden, D. M., and Benson, S. W., *Chem. Rev.* **69,** 125 (1969).
11. Chen, S. S., Rodgers, A. S., Chao, J., Wilhoit, R. C., and Zwolinski, B. J., *J. Phys. Chem. Ref. Data* **4,** 441 (1975).
12. Pickard, J. M., and Rodgers, A. S., *J. Amer. Chem. Soc.* **99,** 691 (1977).