selectivity is determined solely by the latter difference.

It has been suggested[1a] that the reactivity difference between the two diastereomeric adducts has its origin in the stability difference of the products of the oxidative addition of H_2 (i.e., $[RhH_2(dipamp)(mac)]^+]$), the order of stabilities of these diastereomeric products being opposite to that of the parent catalyst–substrate adducts. The reaction profiles depicting this behavior, which is characterized by crossing of the two profiles, are depicted in Figure 9. In the sense of the "Hammond postulate" this corresponds to the reaction being under "product control."[17]

Since the behavior depicted in Figure 9 appears to be quite general for this class of asymmetric hydrogenation reactions (i.e., involving ligands and substrates),[5,16] its origin must reflect some systematic feature of the reactions. A plausible suggestion is that the reason for the inverted order of stabilities of the initial catalyst–substrate adducts and the dihydrides derived from them is the trans disposition of the substrate and diphosphine chelate rings in the former case and the cis disposition in the latter (Figure 9). Unfortunately, all attempts to intercept and examine the dihydride intermediates in these reactions, and thus to probe this theme directly, have thus far been unsuccessful. This failure is consistent with the endothermicity of the H_2 oxidative addition step that is a feature of the behavior depicted in Figure 9.

Acknowledgment. Support of this research through a grant from the National Science Foundation (CHE 82-17950) and a generous loan of rhodium from Johnson-Matthey Co. are gratefully acknowledged. The NMR facilities used in this research were supported in part through The University of Chicago Cancer Center Grant No. NIH-CA-14599.

Registry No. 1, 75397-16-9; $\mathbf{2}^{maj}$, 75109-58-9; $\mathbf{2}^{min}$, 75109-57-8; $[Rh(DIPAMP)]^+BF_4^-$, 106502-35-6; methyl (*Z*)-α-acetamidocinnamate, 60676-51-9; toluene, 108-88-3; silane, 7803-62-5.

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Concerning the Mechanism of Formation of Oxygen Difluoride[1]

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Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received August 27, 1986*

Abstract: Passage of F_2 over ice at temperatures around −50 °C produces a mixture of O_2, HOF, and OF_2, along with small amounts of H_2O_2. The involvement of HOF in the formation of OF_2 has been demonstrated through the use of HOF labeled both with ^{18}O and with radioactive ^{18}F. The reaction that produces the OF_2 has been shown to be

$$F_2 + HOF \rightarrow OF_2 + HF$$

The OF_2 contains one fluorine atom from the F_2 and one from the HOF.

Oxygen difluoride was first synthesized by Lebeau and Damiens in 1927.[3] Although their initial method of preparation was electrochemical, they also observed that the compound was formed when fluorine was passed through aqueous alkali.[4] Cady, in his classic study of the reaction of fluorine with aqueous solutions, systematized our knowledge of the formation of OF_2.[5] He observed that it was formed to a negligible extent in water or acidic media and that its yield rose to a maximum of about 60% in 0.5–1 M alkali. Oxygen difluoride was subsequently observed to be formed when fluorine was passed through 60% $HClO_4$ in a graphite apparatus[6] or when it reacted with H_5IO_6.[7] A relatively recent study has shown that OF_2 can also be made in good yield by the reaction of fluorine with hydrated alkali fluorides.[8]

Despite this body of literature, there has been virtually no attempt made to elucidate the mechanism by which OF_2 is produced. If we think of the compound as the acid anhydride of HOF, its formation in dilute aqueous solutions seems particularly puzzling. In our previous study of the reaction of fluorine with aqueous media, we proposed a mechanism that accounted for the production of HF, HOF, H_2O_2, and O_2 but explicitly left open the question of OF_2 formation.[9] However, in the course of our studies of the production and utilization of hypofluorous acid, our attention was continually drawn to the fact that substantial amounts of OF_2 were always formed as a byproduct in the synthesis of HOF. We drew the tentative conclusion that HOF was probably involved in the production of OF_2, and we even suggested the thermodynamically plausible reaction[9]

$$F_2 + HOF \rightarrow OF_2 + HF \qquad (1)$$

In the present paper, we have undertaken to verify the involvement of HOF in the production of OF_2 and to attempt to shed some light on the overall mechanism of the reaction.

Experimental Section

Reagents. Fluorine was a standard industrial product (Matheson Co, minimum purity 98%). When necessary, it was freed of HF by passage through traps cooled with liquid nitrogen or liquid oxygen. Nitrogen used to transfer HOF was Airco "prepurified" grade. Water enriched in oxygen-18 (nominal 99 atom %) was obtained from Norsk Hydro, Oslo. Other chemicals were commercial products of analytical reagent grade.

Reaction of Fluorine with Ice. The apparatus used to carry out reactions of fluorine with cold ice is shown in Figure 1. Of the plastic U-tube traps, trap B was the reaction vessel, trap A served to collect OF_2, traps C and D removed water and much of the HF, trap E collected HOF, and trap F protected trap E from impurities that might be evolved by the circulating pump G. The metal vacuum line served both to complete the circulation loop and as a reservoir for fluorine. By varying the number of segments of this line that were included in the loop, the

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[1] Work supported by the U.S. Department of Energy, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

[2] Present address, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

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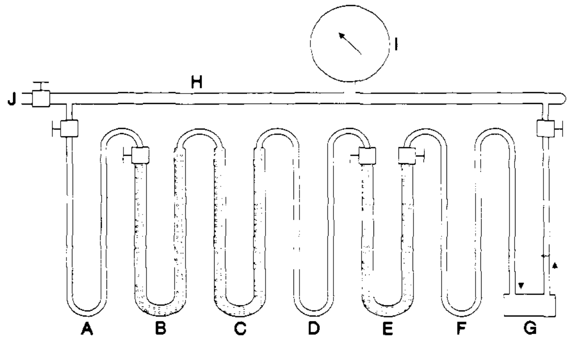

Figure 1. Apparatus for carrying out the reaction of fluorine with cold ice. U-tubes A–F are made of Kel-F or Teflon PFA plastic. Tubes B, C, and D are 1/2 in. o.d. × 3/8 in. i.d. and are packed with Teflon Raschig rings (cut from Teflon spaghetti tubing); the other U-tubes and connecting tubes are 1/4 in. o.d. × 3/16 in. i.d. Valves between A and F are also made of Kel-F or Teflon. Circulating pump G has Viton diaphragm and valves and a free-air flow of 15 L/min (Charles Austen Pumps, Ltd., Byfleet, Surrey, U.K.). Monel vacuum line H is equipped with Monel bellows valves and a Monel Bourdon pressure gauge (I). High vacuum pumps and fluorine cylinder are located to the left of inlet J.

total loop volume could be varied. This, in turn, permitted the production of varying quantities of product for the same initial fluorine pressure, up to a maximum of about 3 mmol each of O_2, OF_2, and HOF. In a typical experiment, the Teflon Raschig rings in reaction vessel B were wetted with 1–2 cc of water, which was frozen with dry ice. The apparatus was assembled and evacuated; trap A was cooled with liquid N_2, trap C with ethanol at −50 °C, trap D with dry ice, and traps E and F with liquid O_2. Then the reaction vessel was warmed to the desired operating temperature, and the system was charged with 200–300 torr of F_2, which was circulated for a period of several hours, until the fluorine was entirely consumed, as indicated by the fact that the pressure ceased to decrease.

The oxygen that was produced was removed and measured by successively filling a standardized volume of the metal vacuum line and measuring the pressure at each filling. Correction was made for the small partial pressure of OF_2 over liquid nitrogen, which was determined in separate experiments to be about 0.7–1 torr. After complete removal of the oxygen, the OF_2 collected in trap A was transferred from an ethanol bath at −105 °C and purified by redistillation from a vessel cooled in liquid O_2 to one cooled in liquid N_2. Its purity was verified by mass spectrometry, and its amount determined by gas volumetry. Correction was made for the small amount pumped away with the oxygen. The HOF collected in trap E was swept in a nitrogen stream into cold aqueous 1 M KI while the trap was allowed to warm slowly to room temperature. The solution was acidified, and the I_3^- was titrated with standardized sodium thiosulfate solution. Traps B, C, and D were washed with water into an acidified KI solution, ammonium molybdate was added, and the I_3^- formed was similarly titrated with thiosulfate to give the yield of H_2O_2.

If it was desired to mix HOF with the fluorine during the reaction, the U-tube that had been trap E in a previous reaction in which ca. 3 mmol of HOF were produced was inserted between traps A and B for the new reaction. This HOF-containing trap was warmed to dry ice temperature, so that a low concentration of HOF (probably less than 1 torr) was picked up in the F_2 stream during the circulation.

Double-Labeling Experiment. Gaseous F_2, contained in a Monel pressure vessel, was labeled with ^{18}F by irradiation with fast neutrons produced in the Argonne 60″ cyclotron by bombardment of a beryllium target with 21 Mev deuterons. To avoid complications due to hot-atom reactions, we found it useful to include with the F_2 a small amount of OF_2 as a hold-back carrier. By cooling the fluorine-containing vessel with liquid nitrogen before extracting the irradiated F_2, significant contamination of the F_2 with the added OF_2 was avoided. As a further precaution, however, the added OF_2 was prepared in advance to have about the same ^{18}O enrichment as the subsequently prepared HOF.

The labeled F_2 was circulated over water that had been enriched in oxygen-18 in order to prepare HOF labeled both with ^{18}O and ^{18}F. The concomitantly formed OF_2 was reserved for use as a reference material in the subsequent oxygen isotope analysis. The doubly labeled HOF was then mixed into a stream of unlabeled F_2 and passed over unlabeled ice in a subsequent reaction, as described in the preceding section. Reaction was terminated after about 30 min, which we had established to be long enough to transfer all of the HOF through the reaction zone. The OF_2 produced in this reaction was isolated and purified as described previously, and its ^{18}O enrichment and ^{18}F activity were determined.

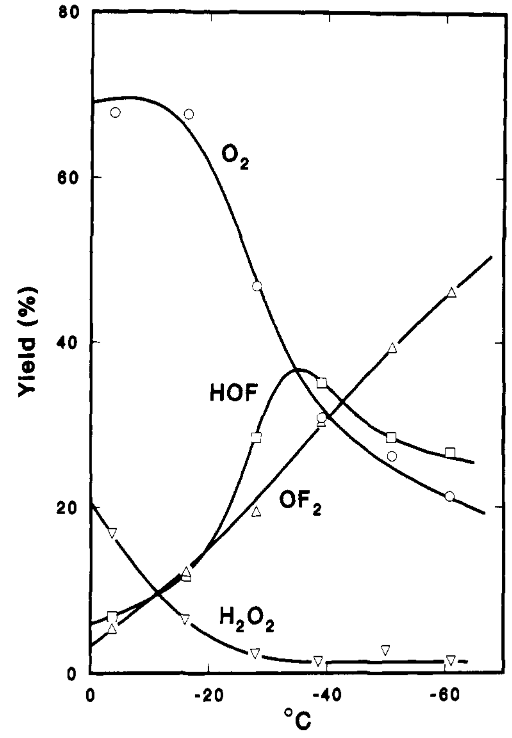

Figure 2. Effect of reaction temperature on yields of various products from the reaction of F_2 with ice (see also Table I).

The ^{18}O enrichment was determined mass spectrometrically with reference to the OF_2 that had been formed along with the labeled HOF. The ^{18}F activity was determined with reference to a sample of the labeled F_2. Samples for ^{18}F assay were placed in Kel-F vessels, and the 0.51 Mev annihilation radiation of ^{18}F was measured in a coincidence counter that made use of two thallium-activated sodium iodide scintillation detectors connected to single-channel pulse height analyzers.

Spectroscopic Measurements. Infrared and ultraviolet spectroscopic measurements of HOF were carried out in a Kel-F cell of 10-cm optical path length. Barium fluoride windows were used for infrared measurements, which were made with a Beckman IR 7 spectrophotometer; sapphire windows were used for measurements in the ultraviolet, which involved monitoring the HOF adsorption at 200–220 nm[10] with a Cary 14 spectrophotometer.

General Procedures. Pressures were measured with a Monel Bourdon gauge with 800 torr absolute full-scale range, ca. 1 torr resolution, and 0.25% of full scale relative accuracy. Mass spectrometry was carried out with a Finnigan Model 400 quadrupole mass spectrometer fitted with a Kel-F gas inlet. Isotope ratio measurements appeared to be accurate to about ±3%.

Results

Qualitative Observations. When HOF vapor is allowed to decompose in a Kel-F vessel, infrared and mass spectra of the decomposition products show no indication of OF_2. When HOF is carried in a stream of nitrogen through water or aqueous alkali and the effluent gas is passed into aqueous KI that is subsequently acidified, no significant amount of iodine is formed, again indicating the absence of OF_2. Passage of HOF in a nitrogen stream over ice or $KF{\cdot}2H_2O$ at −50 °C and examination of the product by mass spectrometry also failed to give any indication of OF_2 formation.

When fluorine is added to HOF vapor, rapid decomposition of the HOF takes place. Thus when 50 torr of F_2 were added to a partially decomposed HOF sample at ca. 6 torr partial pressure in a Kel-F spectroscopic cell with sapphire windows, the remaining HOF decayed with a ca. 2-min half time, as monitored by the ultraviolet absorption spectrum.[10] In the absence of fluorine, a similar sample decayed with a half time of about 30 min. The infrared and mass spectra of the products of the decay of such a mixture of F_2 and HOF showed no evidence of OF_2.

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Table I. Products Formed from Circulation of F_2 over Ice[a]

temp,[b] °C	yield,[c] % OF_2	HOF	O_2	H_2O_2
−3	5	7	68	17
−16	12	12	68	7
−28	20	29	47	2
−39	30	35	31	2
−51	40	28	26	3
−61	46	27	22	2
−50[d]	52	f	f	f
−50[e]	80	2	f	f

[a] From reaction of 5.4 mmol F_2 at an initial pressure of ca. 200 torr. [b] Temperature of bath in which reaction vessel was immersed. Actual reaction temperature may be considerably different. [c] On the basis of initial F_2, assuming that 1 mol of F_2 can produce as much as 1 mol of HOF or H_2O_2 but only $^1/_2$ mol of O_2 or OF_2. [d] HOF added to F_2 stream. [e] $KF{\cdot}2H_2O$ used in place of ice. [f] Not measured.

Table II. Production of OF_2 from Reaction of Double-Labeled HOF with Unlabeled F_2 over Unlabeled Ice at −50 °C

	expt 1	expt 2
^{18}O enrichment (atom %)		
of labeled HOF (E_1)[a]	32.4	31.2
of OF_2 product (E_2)	23.6	19.6
$E_2/E_1 = R_O$	0.728	0.628
^{18}F activity[b] (counts/s/mmol F)		
of labeled HOF (A_1)[c]	12.2	7.9
of OF_2 product (A_2)	4.32	2.43
$A_2/A_1 = R_F$	0.354	0.308
R_O/R_F	2.06	2.04

[a] Assumed to be the same as that of the OF_2 produced as a byproduct in the preparation of the labeled HOF. The nominal enrichment, based on the manufacturer's analysis of the water used in the preparation, would be 33.0 atom % ^{18}O. [b] At a fixed, but arbitrarily chosen time. [c] Assumed to be the same as that of the F_2 from which the labeled HOF was made.

Addition of F_2 to liquid HOF at about 0 °C usually causes an explosion!

Production of OF_2 from the Circulation of Fluorine over Ice. Table I and Figure 2 give the yields of various oxidizing species that are formed when fluorine is circulated over ice at various temperatures. As the reactor temperature is lowered, yields of hydrogen peroxide and molecular oxygen decrease, while those of OF_2 and HOF increase, the last reaching a shallow maximum around −40 °C. The one experiment in the table in which HOF is mixed with fluorine before passage over the ice shows a modest but significant increase in yield of OF_2. The yield of OF_2 is also enhanced markedly in the one experiment in which $KF{\cdot}2H_2O$ is substituted for ice.

To determine the possible involvement of fluoride ion in the formation of OF_2, fluorine labeled with radioactive ^{18}F was passed over $KF{\cdot}2H_2O$ at −50 °C. The OF_2 product was found to have the same specific activity as the fluorine from which it was produced, indicating no significant incorporation of fluorine atoms from the unlabeled fluoride.

Experiments with Double-Labeled HOF. Table II shows the results of experiments in which HOF that has been labeled with both oxygen-18 and radioactive fluorine-18 is mixed with unlabeled F_2 and passed over unlabeled ice at about −50 °C. The ^{18}O analysis of the OF_2 product indicates that about $^2/_3$ of it derives from the labeled HOF, the balance necessarily deriving from the unlabeled ice, presumably through the intermediate production of unlabeled HOF. The ^{18}F analysis shows that about $^1/_3$ of the fluorine in the OF_2 derives from the labeled HOF. From the ratio of these two fractions, we are able to deduce the source of the fluorine atoms in those OF_2 molecules that have derived their oxygen from the labeled HOF. We see from Table II that this ratio is, within experimental uncertainty, equal to 2, which indicates that each of these OF_2 molecules contains one F atom from the labeled HOF and one from the unlabeled F_2. This, in turn, implies the reaction

$$F_2 + HOF^* \rightarrow FOF^* + HF \qquad (2)$$

where the asterisks indicate the labeled fluorine atoms.

In one experiment a measurement was made of the specific activity of the fluorine that remained unreacted after reaction 2 was terminated. It was found to be less than 0.25% of the specific activity of the HOF (per F atom), indicating that the F_2 was not exchanging fluorine to any appreciable extent with either HOF or OF_2.

Discussion

It appears that HOF by itself does not decompose to OF_2 under any conditions that we have attempted. In this respect HOF differs from the other hypofluorites NO_3F ("fluorine nitrate") and SO_4F^- (the fluoroxysulfate ion), both of which have been reported to form OF_2 by reaction with alkali.[11-13] Nor does HOF behave like HOCl, which is in labile equilibrium with Cl_2O and water.

Gas-phase mixtures of HOF and F_2 do not interact to produce OF_2, i.e., reaction 1 does not proceed in the gas phase. However, the parallel production of HOF and OF_2 when fluorine is passed over cold ice suggests that HOF is in some way involved in the formation of OF_2, and this suggestion is confirmed by the enhancement of OF_2 yield when the fluorine is mixed with HOF before passage over the ice. Finally, our double-labeling experiments establish conclusively that reaction 1 is responsible for the production of OF_2 when fluorine is passed over ice.[14] It does not seem too great a leap of faith to generalize this conclusion and to add reaction 1 to the scheme for the overall interaction of F_2 with water that we proposed in our previous study.[9]

$$F_2 + H_2O \rightarrow HOF + HF \qquad (3)$$

$$HOF + H_2O \rightarrow H_2O_2 + HF \qquad (4)$$

$$F_2 + H_2O_2 \rightarrow O_2 + 2HF \qquad (5)$$

$$HOF + H_2O_2 \rightarrow O_2 + H_2O + HF \qquad (6)$$

$$F_2 + HOF \rightarrow OF_2 + HF \qquad (1)$$

A number of our observations, however, are not really explained by this scheme. Why, for example, should reaction 1 take place when fluorine is passed over ice but not occur in the gas phase? We have seen that in the gas phase fluorine catalyzes the decomposition of HOF, and we suggest the free-radical mechanism

$$F_2 + HOF \rightarrow F + OF + HF \qquad (7)$$

$$F + HOF \rightarrow OF + HF \qquad (8)$$

$$2OF \rightarrow O_2 + 2F \qquad (9)$$

Reaction 7 should be only slightly endoergic,[15-17] while reactions 8 and 9 are both exoergic and are known to proceed rapidly.[18,19] In this scheme, formation of OF_2 would require recombination of F and OF, which would be relatively improbable in the gas but

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which might proceed as a "cage" reaction on the surface of ice. Alternatively, reaction 1 may take place on the ice surface as a concerted, one-step process.

It is also remarkable that substantial quantities of OF_2 are produced when fluorine is passed over cold ice, but not when it is passed into liquid water.[5] We can only conjecture that on the surface of ice it may be possible for relatively large concentrations of F_2 and HOF to build up, allowing the two to interact before either can react with the solvent, whereas in liquid water the steady-state concentrations of F_2 and HOF are too low to permit reaction 1 to proceed to any appreciable extent. The formation of OF_2 from passage of fluorine over H_5IO_6 or hydrated alkali fluorides may have a similar explanation. It is interesting that $KF{\cdot}2H_2O$ is more effective than ice for producing OF_2.

It is well-known, of course, that fluorine does react with aqueous alkali to produce OF_2 in good yield.[5] This suggests possible involvement of the OF^- anion. We have not attempted to address this question in our present study, but we hope to take it up in a future investigation.

In conclusion, therefore, though we have succeeded in identifying the stoichiometric reaction that is responsible for the production of OF_2 from fluorine and water, a great deal of the "why" of this reaction remains shrouded in mystery.

Acknowledgment. We thank Professor Richard C. Thompson of the University of Missouri-Columbia and Professor Robert E. Connick of the University of California, Berkeley for their continuing interest and helpful discussions. We are particularly indebted to Professor Connick for the suggestion that an isotopic tracer experiment might identify the reaction that produces OF_2. We thank Milan Oselka for carrying out the cyclotron irradiations and James Frogge for effecting transport of the fluorine-18 samples. Dr. Irshad Ahmad provided considerable assistance and advice in the setting up of a coincidence counter for fluorine-18. A.W.J. acknowledges the support of a Faculty Research Leave Appointment at Argonne.

Registry No. F_2, 7782-41-4; H_2O, 7732-18-5; O_2, 7782-44-7; HOF, 14034-79-8; OF_2, 7783-41-7; H_2O_2, 7722-84-1.

New Mechanistic Probes of Hydride Abstraction from Rhenium–Alkyl Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ by $Ph_3C^+PF_6^-$; Evidence for Initial Electron Transfer

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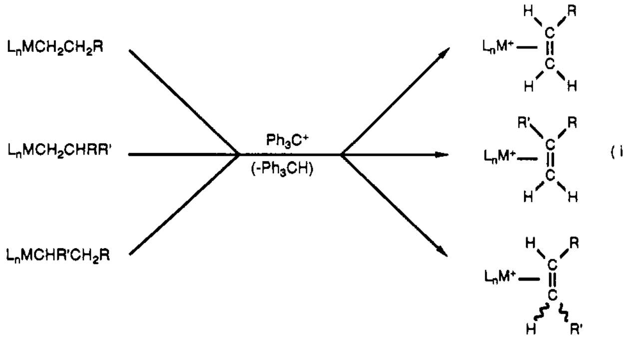
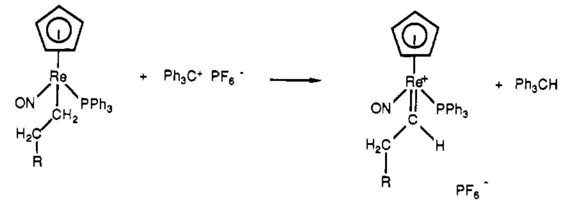
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and Institute for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, 7034 Trondheim-NTH, Norway. *Received August 1, 1986*

Abstract: The mechanism of hydride abstraction from rhenium–alkyl complexes R–(Re) ((Re) = $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$) by $Ph_3C^+PF_6^-$ is probed by study of the equilibrium $R\text{–}(Re) + Ph_3C^+ \rightleftarrows R\text{–}(Re)^{\bullet+} + Ph_3C^\bullet$ (eq v) and the effect of oxygen on the rate and deuterium kinetic isotope effect. Equilibrium constants K_5 are determined in CH_2Cl_2 at 208 K from reversible potential measurement for R = $PhCH_2$ (**1**, 2.5×10^{-5}), $(CH_3)_2CHCH_2$ (**2**, 7.9×10^{-3}), and $Ph(CH_3)CH$ (**3**, 5.0×10^{-2}). When generated electrochemically in separate experiments, $R\text{–}(Re)^{\bullet+}$ and $Ph_3C^\bullet$ are stable under the reaction conditions. Upon mixing CH_2Cl_2 solutions of the reactants in (v), rapid reactions ensue giving Ph_3CH and hydride abstraction products derived from R–(Re). Thus, if an electron transfer mechanism is operative, very rapid hydrogen atom exchange must take place between $R\text{–}(Re)^{\bullet+}$ and $Ph_3C^\bullet$ to displace the unfavorable equilibria (v) to the right. Nearly diffusion controlled rate constants are found for the reaction between $Ph_3C^\bullet$ and O_2, suggesting that $Ph_3C^\bullet$ formed in (v) could be trapped by O_2 and diverted from the pathway leading to Ph_3CH. Rate enhancements of ca. an order of magnitude are observed when reactions are carried out in the presence of oxygen, while the rhenium products are essentially unchanged. A deuterium kinetic isotope effect, $k_H/k_D = 5.4$, is found for reactions of $PhCH_2\text{–}(Re)$ and $PhCD_2\text{–}(Re)$ under nitrogen but not in the presence of oxygen. This indicates that in the presence of O_2 rate control switches from hydrogen atom transfer to electron transfer. In the presence of O_2, as much as 70% of the organic product is benzophenone, arising from decomposition of Ph_3COOH. It is concluded that hydride transfer from R–(Re) to $Ph_3C^+PF_6^-$ most likely takes place by an initial electron transfer followed by hydrogen atom transfer to either $Ph_3C^\bullet$ or $Ph_3COO^\bullet$, depending upon whether O_2 is present.

Transition-metal–alkene complexes are frequently prepared by β-hydride abstraction from alkyl complexes $L_nMCH_2CH_2R$, L_nMCH_2CHRR', or $L_nMCHR'CH_2R$ by the trityl cation (Ph_3C^+), as shown in eq i.[2] Surprisingly, when rhenium–alkyl complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2R)$ (R = H or alkyl) are treated with $Ph_3C^+PF_6^-$, α-hydride abstraction to give *alkylidene* complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH_2R)]^+PF_6^-$ rapidly occurs (eq ii).[3-6] However, with rhenium–alkyl complexes of the formulas



(i)



(ii)

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