this is observed for structurally similar pairs of iodine complexes such as diethyl ether–diethyl sulfide,[5] tetramethylurea–tetramethylthiourea,[15] and, from the present study, trioctylphosphine sulfide–diethylchlorophosphine sulfide.

Consequently, one would expect the charge-transfer band of the trichlorophosphine sulfide–iodine complex to be located at a somewhat shorter wavelength than that of the diethylchlorophosphine sulfide–iodine complex. Unfortunately, the charge-transfer band for the trichlorophosphine sulfide–iodine complex could not be located, probably because of overlapping iodine–solvent contact charge transfer and donor spectral absorption at wavelengths below about 235 nm. It will probably be very difficult to locate the charge-transfer band for most weak iodine complexes involving n donors (a weak iodine complex being defined as one having a K_c value less than 1.0) because the relatively large ionization potential of such an electron donor will most likely cause the charge-transfer band to be located in a spectral region where either, or both, iodine–solvent contact-charge-transfer absorption and donor absorption occurs.

For the two iodine complexes in the present study whose charge-transfer bands could be studied, the stronger complex has the more intense band, both in terms of the molar extinction coefficient at the absorption maximum and the integrated intensity parameters. This increase in intensity of the charge-transfer band with increasing strength of complex formation is predicted by theory.[18] It is experimentally also verified for iodine complexes with such pairs of structurally related n donors as tetramethylurea–tetramethylthiourea[15] and diethyl ether–diethyl sulfide.[5] Furthermore, for iodine complexes with n donors in general, the charge-transfer band intensity is greater for the relatively strong complexes ($K_c > 100$) than for the intermediate and weak complexes ($K_c < 100$).[5]

For the phosphine sulfide–iodine complexes the results of the present study show an increase in both the magnitude of the blue shift and the intensity of the shifted visible iodine band with increasing donor strength. These results for the shifted visible iodine band are in general agreement with the values reported for other iodine complexes with n donors.[5] An explanation for both the wavelength shift and the intensity change for this band has been proposed by Mulliken.[19]

Acknowledgments. This research was supported in part by the National Science Foundation under Grant No. GP-5470X. The author wishes to thank Mr. Michael Ribick and Mr. Michael Wavering for their assistance with the laboratory work.

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Chemistry of Transition Metals. I. Reactions of *n*-Alkyl Halides with Titanium[1a]

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Contribution from the Chemistry Department, McGill University, Montreal, Quebec, Canada. *Received November 20, 1970*

Abstract: The reactions of *n*-alkyl halides on clean titanium metal and on hydrohalided titanium surfaces have been studied. With the exception of alkyl fluorides, the *n*-alkyl halides react stoichiometrically with titanium at a conveniently measurable rate in the temperature range 150–250°, yielding olefin and a minor amount of paraffin in the gas phase, and a titanium hydride–halide phase at the surface. These latter reactions all followed a half-order rate law for disappearance of reactant. The reactivity of *n*-propyl fluoride was several orders of magnitude greater than that of the other *n*-propyl halides, and the reaction was first order in reactant. The activation energies for the reactions of *n*-propyl fluoride, chloride, bromide, and iodide were 20.5, 23.5, 27.5, and 29.5 kcal/mol, respectively. A mechanism is proposed to explain these experimental observations.

The point of departure for much organometallic chemistry is the reaction of an electropositive metal with an organic halide to yield a product containing a metal–carbon bond. As a general rule such reactions, in order to be useful, must yield a product which is either soluble or at least sufficiently easily detached from the surface of the metal to allow complete reaction. No transition metal has been so treated because of the intrinsic instability of organo(transition metal) halides in the absence of stabilizing ligands. However, the generally high reactivity of the surfaces of transition metals toward other molecules leads to the expectation that they should react readily with organic halides and that the transient organo species should have chemistry resembling, in many respects, that of unstable organo(transition metal) halides in solution.

The present study was originally undertaken to understand in part the mechanism of the reported polymerization of ethylene on metallic titanium subjected to ball milling.[2] A reasonable hypothesis as to the origin of such polymerization activity was that the ball milling

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(1) (a) This work was done in partial fulfillment of the requirements for a Ph.D. thesis (W. R. S.); (b) National Research Council of Canada Scholar, 1969–1970.

(2) A. S. Matlack and D. S. Breslow, *J. Polym. Sci., Part A*, 3, 2583 (1965).

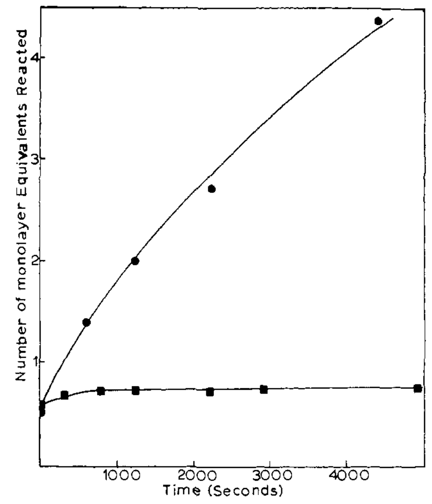

Figure 1. Reactions of *n*-propyl fluoride (●) and *n*-propyl chloride (■) at low temperature on a clean film.

served to generate an atomically clean metal surface which, either directly or after reaction with solvent, was the active species. A further interesting feature of this and similar systems is the considerable enhancement of polymerization activity in the presence of added alkyl halides.[2] If such enhancement of activity were due to oxidation of the clean metal to a polymerization-active alkyltitanium halide, this chemistry would obviously provide a novel approach to Ziegler-type catalysts. The latter are more conventionally produced by treating a transition metal compound in a high oxidation state with a reducing, alkylating agent.[3]

It became clear as our studies progressed that the reactions of halocarbons with transition metals were a fascinating study in their own right with both academic and practical implications far wider than the Ziegler chemistry which had initiated our interest. Using standard ultrahigh-vacuum techniques,[4] we have studied the reactions of many different types of alkyl halides with evaporated metal films and several classes of reactions have emerged. The present paper describes the noncatalytic reactions of *n*-propyl and ethyl halides with titanium films.

The hydrogenolysis of methyl chloride on metallic titanium has been previously reported.[5] The reaction of methyl chloride is more complex than the reactions of higher homologs, involving the removal of more than one hydrogen atom from some of the methyl radicals. Hydrogenolysis of alkyl halides on other metals has been quite extensively studied.[6] The only report of a study of direct reaction between an alkyl halide and a transition metal was due to Coeckelbergs, Frennet, and Gosselain[7] who detected methane production in a reaction of methyl chloride with tungsten surfaces, a reaction which we have observed on titanium surfaces.

Experimental Section

All reactions were performed in a standard ultrahigh-vacuum system capable of routinely achieving pressures of 10^{-9} Torr.[8] The reaction vessel consisted of a 300 ml Pyrex bulb equipped with tungsten feedthroughs. Film deposition occurred uniformly on the walls of the spherical bulb except at the neck ($\sim$10 cm^2). Contrary to indications in the literature,[9] no difficulty was experienced in evaporating pure titanium filaments by resistive heating. During evaporation the pressure in the system remained below 10^{-9} Torr. All experiments were performed on unsintered films deposited at room temperature with a thickness of about 10^{-5} cm. Sintering of films at the highest working temperatures (*ca.* 250°) prior to admission of reactant gas led to substantial loss of activity in initial low-temperature (0°) adsorption studies and erratic kinetic behavior in subsequent high-temperature reactions. The first reactant dose was normally admitted within a few minutes of the completion of film deposition.

Total pressure in the system was measured with a Granville-Phillips Model 03, Series 212 capacitance manometer. The composition of the gas phase was monitored by leakage into a C. E. C. Model 21-615 residual gas analyzer.

The temperature of the film was controlled to better than ±1° with a molten wax thermostated bath for temperatures >120° and an oil bath for lower temperatures.

All alkyl halides and hydrocarbons used for calibration or reaction were reagent grade materials, and liquids were distilled once before use. All reagents were tested for reaction in a blank system where all experimental steps except evaporation of a metal film were carried out. No reaction was detected up to 250° with any of the reactants investigated.

Results

Low-Temperature Reactions. At 0° *n*-propyl and ethyl chloride, bromide, and iodide behaved similarly toward a clean, unsintered film of evaporated titanium. Rapid reaction occurred with retention of halide and some hydride at the surface and liberation of hydrocarbon to the gas phase. The hydrocarbon product consisted of an equimolar mixture of alkene and alkane. The reaction proceeded roughly to the extent of one monolayer equivalent and then stopped. Manometric analyses of runs with calibrated doses of reactant on clean films also indicated instantaneous adsorption of all alkyl halides to a level of about one monolayer equivalent.[10] The course of reactions of *n*-propyl chloride and *n*-propyl fluoride at 0° is illustrated in Figure 1. Similar data for bromide and iodide were virtually identical with those of the chloride.

The reactivity of *n*-propyl fluoride toward titanium was quite different from that of the other halides inasmuch as reaction proceeded beyond the level of a monolayer equivalent and yielded an 80:20 alkene: alkane product mixture. Indeed, the propyl fluoride reaction proceeded beyond the monolayer point even at 0°, a most surprising fact when compared to the high temperatures (*ca.* 200°) required to make the other halides react further. Adsorption and reaction of alkyl halides on clean films occurred too rapidly for meaningful kinetic measurements to be made.

High-Temperature Reactions. Once a clean titanium surface had been treated with *n*-alkyl chloride, bromide,

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[8] R. W. Roberts and L. E. St. Pierre, *Science*, 147, 1529 (1965).

[9] S. Dushman, "Scientific Foundations of Vacuum Technique," Wiley, New York, N. Y., 1962, p 709.

[10] Unsintered titanium films evaporated under conditions similar to those used in this work have a roughness factor of about 10. The value for a monolayer equivalent was obtained by dividing the geometrical area of the film × 10 by the area for the reactant obtained from published bond lengths and angles. The term "about one monolayer equivalent" indicates a number of molecules at least 50% of such a calculated number. Detailed B.E.T. surface area measurements were not made since we were not particularly interested in absolute rate constant determination.

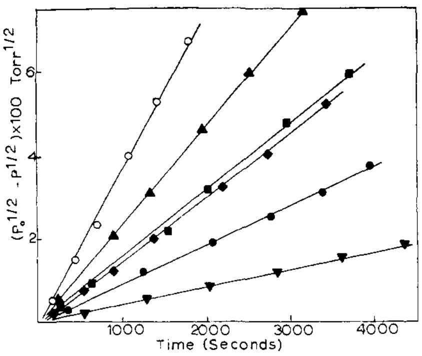

Figure 2. Disappearance of *n*-propyl chloride plotted as a half-order reaction at 220° (○), 210° (▲), 200° (◆, ■, duplicate runs), 190° (●), 180° (▼). $P_0 = 10^{-2}$ Torr.

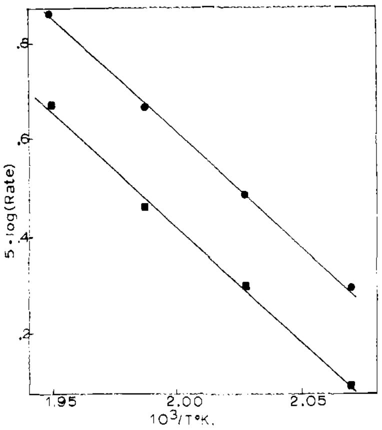

Figure 3. Arrhenius plots of rate data from half-order reactions of ethyl chloride for $P_0 = 2.5 \times 10^{-2}$ (●) and 5×10^{-2} Torr (■).

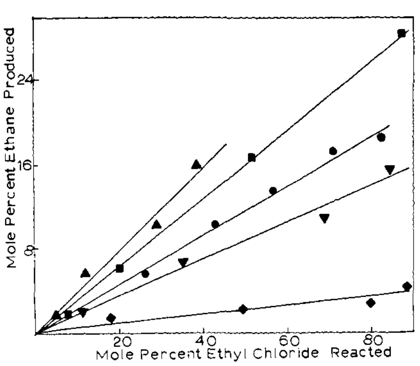

Figure 4. Dependence of mole per cent ethane produced on mole per cent ethyl chloride reacted at 240° on a slightly reacted film for $P_0 = 10^{-2}$ (◆), 2.5×10^{-2} (▼), 5.0×10^{-2} (■), and 10^{-1} Torr (▲); also for $P_0 = 10^{-2}$ Torr on the same film after extensive reaction (●).

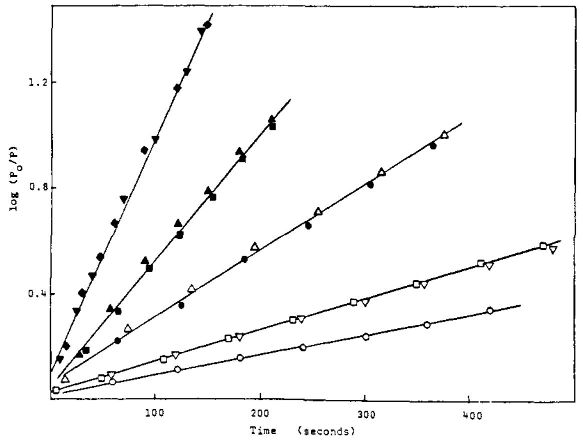

Figure 5. Reactions of *n*-propyl fluoride plotted as first-order reactions, $P_0 = 10^{-2}$ Torr: (○) 63°, (□) 70°, (△, ●) 78.5°, (▲, ■) 85°, (▼, ◆) 93°.

or iodide at room temperature, no further reaction could be detected at temperatures below *ca.* 150°. Above 175° all of these halides underwent smooth dehydrohalogenation, again with retention of hydrogen halide by the metal. This high-temperature dehydrohalogenation proved to be remarkable, both for its reproducibility and for the simplicity of the reaction kinetics. In all cases the rate of disappearance of alkyl halide was strictly half order in reactant over the range of temperatures and pressures which were studied. Linear plots such as those shown in Figure 2 for propyl chloride were obtained even after about 100 monolayer equivalents of reaction, and plots could be reproduced to within ±5% after cycling the temperature. Apparent activation energies were obtained from Arrhenius plots and were insensitive to pressure. Such plots for ethyl chloride at two different pressures are shown in Figure 3. The Arrhenius plots were obtained by doing runs at different temperatures on the same film, but activation energies thus obtained with several different films were constant to better than ±5%. The apparent activation energies for *n*-propyl chloride, bromide, and iodide were 23.0, 27.5, and 29.5 kcal. Within experimental error, the ethyl halides gave the same activation energies as the *n*-propyl analogs.

An interesting feature of the high-temperature dehydrohalogenation reaction was the increase in the amount of alkane in the product with increasing reactant pressure. It was also noted that the alkane:alkene ratio increased with the extent to which a film was allowed to react. A series of curves illustrating these variations for ethyl chloride are shown in Figure 4.

The reaction of 10^{-2} Torr of ethyl chloride was not affected in any way by addition of a 5×10^{-2} Torr dose of ethylene.

As in the case of its low-temperature reaction, *n*-propyl fluoride reacted at elevated temperatures in a markedly different manner from the other halides. Whereas significant reaction rates for the chloride, bromide, and iodide occurred only in excess of 175°, the reaction rates of the fluoride were so great that useful kinetic data could not be obtained at temperatures in excess of 110°. Kinetic data for this reactant were obtained within a temperature range of 60–100°. Furthermore, the disappearance of *n*-propyl fluoride obeyed a first-order rate law (see Figure 5).

The alkene:alkane ratio for *n*-propyl fluoride reactions was roughly the same (4:1) at higher temperatures on reacted films as it was on clean films at 0°. On the other hand, a considerable diminution in this ratio was observed for the other halides in the high-temperature reactions (*cf.* Tables I and II).

The apparent activation energy (measured over the temperature range from 60 to 110°) for the *n*-propyl fluoride reaction was 20 ± 1.0 kcal/mol. Details of various reactions of *n*-alkyl halides on titanium at low and high temperatures are summarized in Tables I and II, respectively.

Table I. Alkyl Halide Interactions with Virgin Films

Reactant	No. of reactant molecules × 10^{17}	Pressure equiv, Torr, × 10^2	Film temp, °C	Reactant			Gaseous products and product ratios
				Mol % adsorbed	Mol % reacted	Mol % unaffected	
Ethyl chloride	3.7	1.0	20	32.5	18.5	49.0	Ethane:ethylene 20:80
n-Propyl fluoride	3.7	1.0	0	70.4	29.6	0.0	Propane:propylene 20:80
n-Propyl chloride	3.7	1.0	0	64.0	26.6	9.4	Propane:propylene 50:50
	3.7	1.0	20	17.5	15.3	67.2	Propane:propylene 50:50
n-Propyl bromide	3.7	1.0	0	41.0	18.5	40.5	Propane:propylene 50:50
n-Propyl iodide	3.7	1.0	0	61.0	15.0	24.0	Propane:propylene 50:50

Table II. Alkyl Halide Interactions with Previously Reacted Films

Reactant	Reaction order	Apparent $E_a \pm \sigma$	Gaseous products and product ratios	$P_0 \times 10^2$, Torr
Ethyl chloride	Half	23.5 ± 1.5	Ethylene:ethane 90:10	1.0
Ethyl chloride	Half	21.4 ± 0.4	Ethylene:ethane 80:20	2.5
Ethyl chloride	Half	21.9 ± 0.7	Ethylene:ethane 70:30	5.0
n-Propyl chloride	Half	23.4 ± 0.9	Propylene:propane 90:10	1.0
n-Propyl bromide	Half	27.3 ± 0.6	Propylene:propane 90:10	1.0
n-Propyl bromide	Half	27.9 ± 0.2	Propylene:propane 85:15	3.3
n-Propyl iodide	Half	28.9 ± 0.3	Propylene:propane 90:10	1.0
n-Propyl iodide	Half	29.8 ± 0.3	Propylene:propane 85:15	3.3
n-Propyl fluoride	First	20.4 ± 0.6	Propylene:propane 80:20	1.0
n-Propyl fluoride	First	20.8 ± 0.7	Propylene:propane 80:20	1.0

Reproducibility of Kinetic Measurements. The reactions described herein exhibited a quite exceptional reproducibility for heterogeneous reactions. For a given film many doses of reactant caused virtually no change in the reactivity of the film, even after wide variations in temperature and reactant pressure. The duplicate runs illustrated in Figure 5 were performed in a cycle of increasing temperature followed by decreasing temperature. Runs were frequently performed over a period of several days on the same film with little change in activity, suggesting that the product layer formed on the surface was extremely coherent and stable.

In addition to the constant and reproducible activity of a given film, reactions on different films laid down under more or less identical conditions showed little variation in activity. Also, we have never found activation energies measured at different times by different operators to differ by more than ±5%.

Discussion

The marked difference in reactivity between initial clean-film reactions at low temperature and subsequent high-temperature reactions suggests that the high-temperature reactions do not involve direct reaction with metallic titanium. More probably a titanium halide, or hydride–halide species, is involved. No loss of carbon from the reacting species to the surface was observed.

Half-Order Reactions. Although previous isotopic mixing experiments have indicated that the dissociative adsorption of methyl chloride on titanium is irreversible,[5] we have been unable to reconcile the half-order rate laws observed in our reactions with any mechanism involving an irreversible adsorption of alkyl halide.

The half-order noncatalytic reactions of alkyl halides with halided titanium films may be explained by the following reaction sequence.

A rapid dissociative adsorption–associative desorption equilibrium is postulated as the initial step.

$$\text{R-CH}_2\text{CH}_2\text{-X} + 2^* \overset{k_1}{\rightleftarrows} \text{R-CH}_2\text{CH}_2\text{-}^* + \text{X}^* \qquad (1)$$

In equation 1, the asterisk represents a nondesignated univalent surface site.

Olefin is produced by the reactive desorption of the surface alkyl by β-hydride elimination, as shown in eq 2.

$$\text{R—CH}_2\text{CH}_2\text{—}^* \xrightarrow{k_2} \text{R—CH=CH}_2 + \text{H}^* \qquad (2)$$

Excess surface halide is lost by formation of a bulk metal halide phase. Its disappearance is assumed to have a first-order dependence.

$$\text{X}^* \xrightarrow{k_3} {}^* + \text{X}_{\text{lattice}} \qquad (3)$$

Excess surface hydride also must be lost into the metal lattice, but discussion of how this may occur will be postponed to the latter part of this kinetic argument.

Several mechanisms must be considered for the formation of paraffin. These include: (a) reactive desorption of two adjacent surface alkyls (*i.e.*, disproportionation)

$$2\text{R—CH}_2\text{CH}_2\text{—}^* \xrightarrow{k_{4\text{a}}} \text{R—CH}_2\text{CH}_3 + \text{R—CH=CH}_2 + 2^* \qquad (4)$$

(b) quasisorbed reaction of olefin and two surface hydrides

$$\text{R—CH=CH}_2 + 2\text{H}^* \xrightarrow{k_{4\text{b}}} \text{R—CH}_2\text{CH}_3 + 2^* \qquad (5)$$

(c) quasisorbed reaction of alkyl halide and surface hydride

$$\text{R-CH}_2\text{CH}_2\text{-X} + \text{H}^* \xrightarrow{k_{4c}} \text{R-CH}_2\text{CH}_3 + \text{X}^* \qquad (6)$$

(d) associative desorption of surface hydride and surface alkyl

$$\text{R-CH}_2\text{CH}_2^* + \text{H}^* \xrightarrow{k_{4d}} \text{R-CH}_2\text{CH}_3 + 2^* \qquad (7)$$

Generation of paraffin by disproportionation of surface alkyls is most unlikely. This mechanism would require a substantial surface alkyl concentration, which is not indicated by experimental observations. It does not explain the experimentally observed increase in paraffin production as the extent of film reaction is increased and does not rationalize the invariant olefin : paraffin product ratio during the reaction of a particular dose of reactant.

The production of paraffin by the quasisorbed reaction of olefin with two surface hydrides can also be discounted. We have shown that the reaction of ethyl chloride in the presence of excess ethylene does not result in enhanced ethane production. In addition, if paraffin production were occurring by this mechanism, then a continuing reaction of olefin and surface hydride after complete consumption of alkyl halide should have been observed, but was not. Also, the probability of finding two adjacent surface hydride species in a hydrogen-deficient system should be low.

The quasisorbed reaction of alkyl halide and surface hydride can also be discounted, since it would require a first-order dependence of the rate of paraffin production on alkyl halide pressure. It has been demonstrated that both paraffin and olefin production occur with half-order kinetics.

The production of paraffin by the associative desorption of surface alkyl and surface hydride is the remaining possibility and will be shown to be a plausible alternative in the following elaboration of this kinetic scheme.

According to the mechanism outlined above and in agreement with experimental observation, the net rate of reaction of alkyl halide may be equated to the sum of the rates of formation of alkane and alkene, thus

$$\frac{-\text{d}[\text{RCH}_2\text{CH}_2\text{X}]}{\text{d}t} = \{k_2 + k_{4\text{d}}[\text{H}^*]\}[\text{RCH}_2\text{CH}_2^*] \qquad (8)$$

From (1) we obtained

$$[\text{X}^*] = \frac{k_1}{k_{-1}}\frac{[\text{RCH}_2\text{CH}_2\text{X}][^*]^2}{[\text{RCH}_2\text{CH}_2^*]} \qquad (9)$$

A further reasonable assumption is that the net rate of reaction may be equated to the net rate of loss of halide into the lattice. If it is assumed that the latter step is effectively irreversible, we may write

$$\{k_2 + k_{4\text{d}}[\text{H}^*]\}[\text{RCH}_2\text{CH}_2^*] = k_3[\text{X}^*] \qquad (10)$$

Substituting [X*] from (9) yields

$$[\text{RCH}_2\text{CH}_2^*] = \left\{\frac{k_3k_1[\text{RCH}_2\text{CH}_2\text{X}][^*]^2}{k_{-1}(k_2 + k_{4\text{d}}[\text{H}^*])}\right\}^{1/2} \qquad (11)$$

Substitution of (11) into (8) yields

$$\frac{-\text{d}[\text{RCH}_2\text{CH}_2\text{X}]}{\text{d}t} = \left\{\frac{k_1k_3(k_2 + k_{4\text{d}}[\text{H}^*])}{k_{-1}}\right\}^{1/2}[^*][\text{RCH}_2\text{CH}_2\text{X}]^{1/2} \qquad (12)$$

The experimental observations require that both [H*] and [*] remain effectively constant during reaction if the above treatment is valid. The constancy of [*] is readily rationalized by the assumption that $k_{-1} \gg k_1$, but the constancy of [H*] is more difficult to explain. It is well known that hydrogen reacts readily with clean, metallic titanium[11-13] and the reaction

$$\text{H}^* \xrightarrow{k_5} \text{H}_{\text{lattice}} + {}^* \qquad (13)$$

is expected to be fast under the conditions of our experiments. If reactions 13 and 7 are fast compared to reaction 2, but of comparable rate to each other, a steady-state condition will exist for [H*]. Although [H*] may remain effectively constant during reaction of a few doses at the pressures used in our experiments, reaction of large amounts of alkyl halide will eventually begin to saturate the solid phase with hydrogen and the surface concentration, [H*], may increase, giving rise to production of larger amounts of alkane (see Figure 4).

Little or no difference between *n*-propyl chloride and ethyl chloride rates and apparent activation energies would be expected on the basis of these rate equations and no significant differences were found experimentally. Lack of activation energy dependence on initial pressure, and therefore lack of dependence on the olefin : paraffin product ratio, suggests that temperature dependence of k_2 and $k_{4\text{d}}$ are similar.

Rate Control in Half-Order Reactions. The noncatalytic, half-order reactions of *n*-propyl chloride, bromide, and iodide and ethyl chloride all occurred with similar rates and in the same temperature region. This, coupled with the similar activation energies, suggests that the reactions are all occurring with the same general mechanism and have the same rate-controlling step. This is also supported by the much more rapid reaction of *n*-propyl fluoride. The extremely rapid *n*-propyl fluoride reaction makes it unlikely that reactive desorption of the *n*-propyl surface radical is the rate-controlling step of the half-order reactions. Further evidence against reactive desorption as the rate-controlling step is close similarity in rate between alkyl monochlorides and 1,2- or 1,3-dichloroalkanes. In these latter cases the reactive desorption involves β- or γ-chloride elimination.[14]

Since hydride diffusion into the surface phase must be occurring in the *n*-propyl fluoride reaction as in the other noncatalytic reactions of monohalo compounds, it must occur rapidly and therefore is unlikely to be the rate-controlling step.

Hauffe and Rahmel[15] have described conditions wherein the reaction of gaseous sulfur, S_2, with nickel proceeds with half-order dependence on sulfur pressure and linear dependence on the thickness of the nickel sulfide layer. The mechanism which they propose is similar to the mechanism proposed for the half-order reactions described in the present investigation. For this sulfidation reaction, rate control was ascribed to equilibrium dissociative chemisorption of the S_2 molecule. Hauffe and Rahmel noted that incorporation of an S

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(11) B. M. W. Trapnell, *Trans. Faraday Soc.*, **52**, 1618 (1956).

(12) R. W. Roberts, *Brit. J. Appl. Phys.*, **14**, 4851 (1963).

(13) S. Dushman, "Scientific Foundations of Vacuum Technique," Wiley, New York, N. Y., 1962, p 544.

(14) J. F. Harrod and W. R. Summers, unpublished results.

(15) K. Hauffe and A. Rahmel, *Z. Phys. Chem. (Leipzig)*, **199**, 152 (1952).

atom into the surface is a step which may be distinguished from chemisorption onto the surface. The incorporation step may also be distinguished from bulk diffusion which would occur after incorporation.

Further work which suggests that incorporation of chemisorbed species into the gas–metal halide phase boundary may be the rate-controlling step has been reported by Stout and Gibbons.[16] These workers studied the sorption of oxygen, nitrogen, carbon dioxide, air, water vapor, hydrogen, and methane into titanium metal. They found that gas pressure above the metal decreased linearly with time during sorption of large concentrations of nitrogen and carbon dioxide and for small concentrations of oxygen. In order to account for the linear time–pressure relationship, they postulated a surface-barrier-limited sorption.

A second phase boundary exists at the metal–metal halide interface. If rate control were ascribed to abstraction of titanium atoms from the metal lattice with subsequent rapid diffusion through the metal halide layer, then similar rates would exist for the various halides and no diffusion control would be observed. In fact, of the first-row transition elements, titanium is the most likely metal to follow this reaction pattern. It has one of the highest metal lattice energies, which would make abstraction of atoms from the lattice difficult. It also has the lowest metal dihalide lattice energies, which might allow lattice disruptions, such as diffusion of titanium cations, to occur relatively easily. In order to maintain a first-order disappearance of surface halide, it would be necessary to postulate that the rate of titanium abstraction across this phase boundary must be proportional to the surface halide population. Precedent for a rate-controlling step of this type can be found in sulfidation reactions of silver and copper. Rickert and Wagner have shown that passage of silver cations across the silver–silver sulfide phase boundary was the rate-controlling step in the reaction of sulfur with silver surfaces. In this system, the silver sulfide layer therefore grew with linear time dependence.[17,18]

Ionic diffusion occurs more readily when there is a large number of lattice vacancies. The Ti^{2+} ions in a titanium dihalide crystal occupy half the available lattice sites and also have a considerably smaller ionic radius than the halide ions, which would facilitate their movement in the halide lattice.

In conclusion, it should be pointed out that the rates of dehydrochlorination of ethyl and propyl chlorides are substantially faster than the rate of reaction of HCl with hydrochlorided titanium. The latter reaction does not occur at a significant rate below 220°, and it follows first-order kinetics.[14] We believe this behavior is due to the larger bond energy of H–Cl, relative to C–Cl, and a slowing of the dissociative desorption step to the point where it becomes much slower than the solid-state transport processes which govern the rates of the alkyl halide reactions. A similar explanation may account for the anomalous behavior of *n*-propyl fluoride, where the dissociative adsorption step may become rate controlling as a result of unusually rapid solid-state transport steps (eq 3 and 13) and slow dissociative adsorption. There is no *a priori* reason for expecting a much higher rate of solid-state transport in the titanium hydrofluoride phase, and any attempt to explain this on the basis of presently available evidence would be purely speculative.

Conclusions

Although the details of the various steps remain obscure, we can suggest the following on the basis of analogy between the present reactions and others whose mechanisms are more completely understood.

(1) Alkyl halides undergo facile reaction with Ti(0) at low temperatures and with a titanium hydride–halide phase at high temperature in which the titanium is most probably in a low oxidation state. The initial step is probably scission of the carbon–halogen bond resulting from electron transfer from the metal. The electron transfer may be two one-electron transfers, by analogy with the Co(II)[19] and Cr(II)[20] reduction of alkyl halides, or a single two-electron transfer step analogous to the so called "oxidative addition" reaction.[21]

(2) The alkyltitanium species produced as a result of the initial electron-transfer step exhibits a mode of decomposition similar to that of known molecular alkyltitanium complexes. The β-hydride elimination resulting in olefin and surface hydride finds many analogs in alkyl(transition metal) chemistry,[22] as does the reaction of alkyl with hydride to produce alkane.[23]

(3) The transport of atoms, or ions, across the reacted surface layer does not present a serious barrier to reaction in the case of titanium. The known stability of titanium hydride phases and the high affinity of metallic titanium for hydride undoubtedly contribute to the unique reactivity of titanium reported in the present paper. Other transition metals behave quite differently, largely as a result of their inability to scavenge hydrogen.[24]

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