

Reactions of Methyl Chloride and of Methylene Chloride at Metal Surfaces

II. Reactions over Evaporated Films of Titanium and Other Metals

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Received November 28, 1967

The reaction of methyl chloride and hydrogen, and of methylene chloride and hydrogen has been studied at the surface of a number of evaporated metal films in a static system. Adsorption of alkyl chloride resulted in rupture of all carbon-chlorine bonds before any carbon-hydrogen bonds were broken; thus in the reaction with deuterium, virtually no deuteroparent was formed. By the use of ^{13}C and ^{36}Cl it was shown that in the adsorption of methyl chloride on titanium, carbon-chlorine bond rupture was totally irreversible. Over nickel, tungsten, copper, platinum, cobalt, manganese, aluminum and silver, methane was the only hydrocarbon product. Over palladium and titanium higher hydrocarbons were formed. In the reaction of methylene chloride over titanium, polymer was also formed, and olefins were the main C_2 and C_3 products. The reaction of methyl chloride on titanium was shown to be first order in both methyl chloride and hydrogen pressures.

Adsorption measurements with the alkyl chlorides on the above metals gave surface hydrogen/carbon ratios which, in most cases, suggested the average surface hydrocarbon residue to be more extensively dehydrogenated than the group in the original alkyl chloride: the extent of dehydrogenation increased with increasing temperature. The exception to this was titanium where adsorption of methyl chloride and methylene chloride gave approximately CH_3 and CH_2 surfaces residues, respectively.

From the influence of hydrogen on the reaction product distribution, and from the results from reactions with deuterium it has been concluded that on palladium, chemisorbed hydrogen was directly involved in the process of product desorption, but on titanium this was not so, and inter-residue hydrogen transfer occurred in desorption.

Evidence has been adduced that carbon-carbon bond formation probably occurred by reaction of an alkyl chloride molecule with a surface CH_2 group.

Activation energies and frequency factors have been evaluated for the reactions of both alkyl chlorides on titanium.

INTRODUCTION

This paper reports work which was undertaken as part of a program for studying the behavior of hydrocarbon residues adsorbed at metal surfaces. In this work residues were generated by dissociative adsorption of

methyl or methylene chloride. This paper describes the products formed by desorption at low pressures from adsorbed residues of this sort, and also the reactions between these alkyl chlorides and hydrogen or deuterium occurring at higher pressures as catalytic processes.

EXPERIMENTAL

Experiments of two types were carried out. In the first type, reactions were studied with gas pressures in the range 1-30 mtorr

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at temperatures between 0° and 300°C. These experiments included measurements of products desorbed from a sorbed layer only, together with measurements of products formed in the presence of low pressures of reactant gases. In the second type, reactions were studied using gas mixtures in the torr pressure region between 200° and 300°C. In these reactions the standard reaction mixture in the reaction vessel at 0°C contained 60 torr of hydrogen or deuterium and 6.0 torr of alkyl chloride. The reaction volume (180 cc) was thus estimated to contain for a standard mixture (admitted at 0°C) 3.84×10^{20} molecules of H₂ or D₂ and 3.84×10^{19} molecules of alkyl chloride. In the low-pressure experiments, the apparatus and technique were similar to those used in Part I (1) of this series, while in the catalytic experiments at higher pressures the apparatus and technique were essentially the same as in other previous work (2, 3). Analyses were carried out by mass spectrometry and gas-phase chromatography (4).

Evaporated metal films were deposited by the techniques previously described (5, 6) with the reaction vessel at 0°C. Gas pressures during evaporation were in the region $2-5 \times 10^{-7}$ torr, so that the surfaces were probably subject to some degree of contamination. However, previous results (5) suggest that this should not have been too severe. In the low-pressure experiments, film areas were estimated at the end of an experiment using the BET method with xenon adsorption at 90°K, and assuming 20 Å² for the area per adsorbed xenon atom. The latter figure was adopted by assuming that the xenon monolayer was lattice-packed (5, 7), and that the low-order planes were approximately equally exposed. The assumption of lattice packing in xenon adsorption has recently been questioned by Delannois, Frennet, and Lienard (8), who also suggested (i) that the monolayer coverage should be measured at xenon relative pressures up to about 0.1, (ii) that the appropriate area per adsorbed xenon atom is 16.9 Å², based on close-packed xenon, (iii) that BET measurements with xenon relative pressures below 0.02 (as in

the present work), give monolayer values some 25% too low. We believe there to be strong evidence (5, 7) that the monolayer is in fact reached at a xenon relative pressure of about 0.02 and that the lattice packing model is correct. However, from an empirical standpoint, the two methods give very similar values for the film area, because the two factors (area per adatom and total uptake) differ in the two treatments by approximately equal amounts in opposite directions. Independent sintering experiments showed that under reaction conditions, film sintering proceeded to virtual completion. Where, in this paper, values are quoted for the number of surface sites for a film, these values have been set equal to the number of surface atoms, assuming that the low-order planes were equally exposed.

RESULTS

1. Low-pressure reactions with methyl chloride and with methylene chloride on titanium and palladium. With both of these metals, uptake of alkyl chloride proceeded to give a constant pressure over the film in 10-15 min at all temperatures in the range 0-300°C, and with alkyl chloride pressures over the film up to about 30 mtorr. When a constant pressure had been reached, the whole of the gas phase was removed for analysis. At this stage and at the same temperature, a dose of hydrogen was added. This dose was of about the same magnitude as the original alkyl chloride dose. After 10-15 min the gas phase was removed for analysis. The film temperature was established for about 10 min before the gas was admitted. Under these conditions, film sintering would be expected to be largely complete before gas was introduced.

In the following account, values are given for θ_c , which is intended to provide an *approximate* indication of the extent to which the surface was covered by hydrocarbon residues. Values of θ_c were computed using the measured film area to give the number of surface sites for the film. It was assumed that each carbon residue on the surface occupied one surface site. The hydrogen/carbon surface ratio was calculated from the mass balance.

TABLE I
LOW-PRESSURE REACTION OF PALLADIUM WITH METHYL CHLORIDE AND METHYLENE CHLORIDE

Film weight (mg)	Temperature (°C)	Treatments	Final alkyl chloride pressure (mtorr)	Alkyl chloride reacted in each stage (10 ¹⁴ molec)	Number of carbon atoms in desorbed products in each stage (10 ¹⁴ molec)	Fraction of surface sites occupied by hydrocarbon residues after product desorption (θ_c)	Average H/C on surface	Composition of desorbed products (mole %)		
								CH ₄	C ₂ H ₄	C ₂ H ₆
21.1	0°	(i), CH ₃ Cl	14.2	88.0	54.4	0.09	1.40	98.5	0	1.5
		(ii), (i) + H ₂	—	—	2.4	0.06	—	10.5	0	89.5
9.8	0°	(i), CH ₂ Cl ₂	27.1	47.0	4.8	0.22	1.81	66.7	0	33.3
		(ii), (i) + H ₂	—	—	5.2	0.19	—	20.6	0	79.4
		(iii), (ii) + CH ₃ Cl	21.1	3.6	3.1	—	—	32.2	0	67.8
12.9	100°	(i), CH ₃ Cl	10.0	39.2	31.3	0.13	0	99.5	0	0.5
		(ii), (i) + H ₂	—	—	7.8	0	—	41.3	0	58.7
9.0	100°	(i), CH ₂ Cl ₂	35.9	24.7	4.2	0.35	1.70	86.4	0	13.6
		(ii), (i) + H ₂	—	—	10.2	0.18	—	87.7	0	12.3
		(iii), (ii) + CH ₃ Cl	13.8	4.2	3.0	—	—	32.4	0	67.6

^a Each film was dosed with the various gases in the order shown: for example, palladium, 21.1 mg at 0°C was dosed with methyl chloride to give $\theta_c = 0.09$ at a methyl chloride pressure of 14.2 mtorr and the gas phase was removed for analysis; hydrogen was then added, causing θ_c to fall to 0.06 and the desorbed gases were analyzed.

TABLE 2
 LOW-PRESSURE REACTION OF TITANIUM WITH METHYL CHLORIDE AND METHYLENE CHLORIDE

Film weight (mg)	Temperature (°C)	Treatments	Final alkyl chloride pressure (atorr)	Alkyl chloride reacted in each stage (10 ¹⁶ molec)	Number of carbon atoms in desorbed products in each stage (10 ¹⁶ molec)	Fraction of surface sites occupied by hydrocarbon residues after product desorption (%)	Average H/C on surface	Composition of desorbed products (mole %)		
								CH ₄	C ₂ H ₆	C ₂ H ₄
10.0	0°	(i), CH ₃ Cl	15.1	185	20.5	0.56	2.95	91.8	0	8.2
		(ii), (i) + H ₂	—	—	12.0	0.52	—	88.4	0	11.6
9.4	0°	(i), CH ₂ Cl ₂	12.2	118	3.6	0.35	1.87	62.8	28.0	9.2
		(ii), (i) + H ₂	—	—	4.2	0.34	—	60.4	31.1	8.5
		(iii), (ii) + CH ₃ Cl	14.3	1.8	1.2	—	—	57.2	21.4	21.4
10.0	200°	(i), CH ₃ Cl	6.9	105	12.0	0.78	2.95	79.4	18.1	2.5
		(ii), (i) + H ₂	—	—	6.0	0.73	—	72.4	20.8	6.8
8.6	200°	(i), CH ₂ Cl ₂	2.4	209	71.9	1.57	1.85	48.2	46.6	5.2
		(ii), (i) + H ₂	—	—	28.4	1.25	—	52.3	41.8	5.9
		(iii), (ii) + CH ₃ Cl	14.0	30.2	21.1	—	—	75.0	18.5	6.5
5.9	200°	(i), CH ₃ Cl	9.2	35.0	15.1	0.75	2.75	78.4	14.1	7.5
		(ii), (i) + CH ₂ Cl ₂	63.6	28.9	4.2	—	—	53.0	40.8	6.2
11.0	300°	(i), CH ₃ Cl	0	247	45.0	1.47	2.90	92.1	7.0	0.9
		(ii), (i) + H ₂	—	—	15.7	1.36	—	93.3	5.8	0.9
11.4	300°	(i), CH ₂ Cl ₂	0	256	21.0	3.43	1.68	72.3	26.2	1.5
		(ii), (i) + H ₂	—	—	11.3	3.20	—	76.7	22.8	0.5
		(iii), (ii) + CH ₃ Cl	0	58.6	28.4	—	—	91.5	7.1	1.4
9.5	300°	(i), H ₂ ^b	—	—	—	—	—	—	—	—
		(ii), (i) + CH ₂ Cl ₂	0	143	44.0	2.34	—	92.0	7.0	1.0
		(iii), (ii) + CH ₃ Cl	—	58.0	15.7	—	—	93.3	5.8	0.9

^a See Footnote a, Table 1.

^b Hydrogen adsorbed to give H/Ti = 2.54.

Over palladium at 0° and 100°C, the θ_c reached the quasi-limiting value of about 0.15 at a methyl chloride pressure of about 30 mtorr, while at 200°C θ_c did not exceed about 0.05. On the other hand, on titanium the corresponding values of θ_c were much higher; at 0° and 200°C θ_c reached values of about 0.5 and 0.75, respectively.

Analysis of the gas phase resulting from alkyl chloride adsorption indicated that no hydrogen or hydrogen chloride was desorbed. The desorbed products were totally accounted for by a mixture of hydrocarbons. Over titanium, the desorption products from both alkyl chlorides were methane, ethane, and ethylene: over palladium, the dominant desorption product was methane, accompanied by a small amount of ethane, but no ethylene. On titanium, the surface H/C ratio from adsorbed methyl chloride was in the range 2.7–3.0 at all temperatures and coverages, and from adsorbed methylene chloride this ratio was in the range 1.7–2.0. On palladium, the corresponding surface H/C ratios were lower, lying in the range 0–1.8 depending on conditions. Typically, the adsorption of methyl chloride at 0°C on palladium to $\theta_c \approx 0.05$ gave the surface H/C ratio equal to about 0.5, while at $\theta_c \approx 0.15$, the ratio was equal to about 1.8.

Typical results are given in Tables 1 and 2. The composition of the desorbed products depended, in reactions on palladium, on whether or not the products were formed by treatment of the adsorbed layer with hydrogen. In the absence of added hydrogen, the products from the reaction of methyl chloride on palladium contained a proportion of ethane that did not exceed about 1.5 mole % at 0°C, and this tended to decrease at higher temperatures. The reaction of methylene chloride with palladium gave comparable amounts of methane and ethane and again the proportion of ethane tended to decrease at higher temperatures. The products from the reaction of methyl chloride on titanium were in the molar ratios methane:ethylene:ethane as 1: 0.2: 0.2 at 0°C, and there was a general trend for the proportion of C₂ products to decrease at higher temperatures. From methylene chloride and titanium the corresponding molar ratios were 1: 0.6: 0.06, approximately independent of temperature.

On titanium there was no major alteration in the product hydrocarbons from either alkyl chloride by the addition of hydrogen after (or before) the adsorption of alkyl chloride. On palladium however, this treatment resulted at low temperatures in a large increase in the proportion of ethane, but

TABLE 3
ADSORPTION OF METHYL CHLORIDE ON VARIOUS METALS

Metal	Temperature (°C)	Number of surface sites $\times 10^{-16}$ or film weight	CH ₃ Cl uptake at 10 mtorr (molec. $\times 10^{-16}$)	Desorption products (molec. $\times 10^{-16}$)		Carbon retained on surface (atoms $\times 10^{-16}$)	Surface H/C ratio
				H ₂	CH ₄		
Nickel	0°	276	60.0	21.3	3.6	56.4	2.18
	100°	154	19.0	12.9	0.8	18.2	2.17
Tungsten	0°	430	158.2	11.5	21.8	136.4	2.67
	130°	430	95.7	46.0	48.9	46.8	0
Copper	0°	(14.2 mg)	49.3	43.0	0.7	48.6	1.22
	200°		49.3	61.0	4.7	44.6	0.16
Platinum	0°	145	38.4	12.1	16.3	22.1	1.16
	250°	—	86.5	35.4	34.7	51.8	0.97
Cobalt	0°	(20.2 mg)	34.0	3.2	9.4	24.6	2.36
Manganese	0°	(6.5 mg)	31.9	26.5	3.8	27.6	0.94
Aluminum	0° & 100°	(3.8 mg)	0	0	0	0	0
	200°	—	81.0	25.6	22.2	58.8	1.76
Silver	0° & 100°	(6.7 mg)	0	0	0	0	—
	230°	—	10.5	0	5.7	4.8	1.81

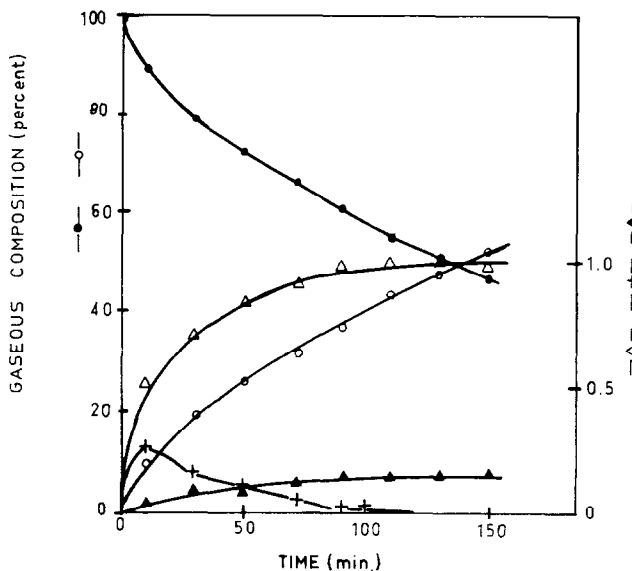


Fig. 1. Variation of gaseous composition with time from reaction of standard methyl chloride mixture on 4.9 mg of titanium at 275°C: \bullet , CH_3Cl ; \circ , CH_4 ; $+$, C_2H_4 ; Δ , C_2H_6 ; \blacktriangle , C_3H_8 .

at high temperatures there was no effect.

2. Low-pressure reactions with methyl chloride on various metals. The adsorption of methyl chloride was studied over a range of metals listed in Table 3, but in no case was any desorption product other than

methane and hydrogen detected. The data are recorded in Table 3.

3. Reaction between methyl chloride and hydrogen at higher pressures over titanium. This reaction was studied in the range 150–300°C. In all cases, C_2 and C_3 hydro-

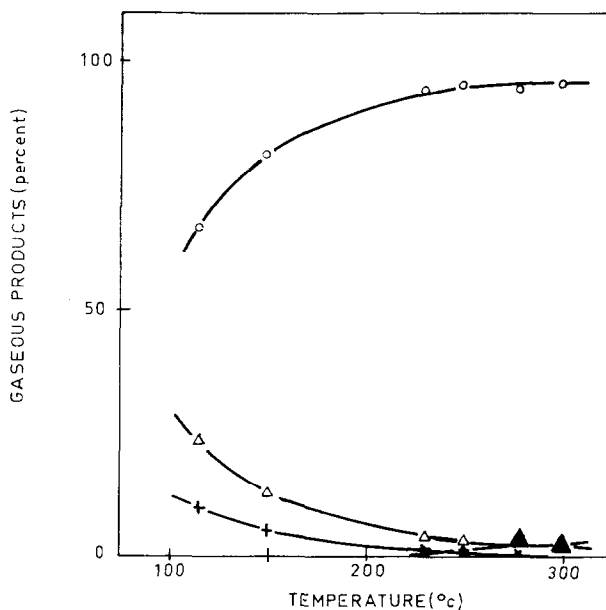


Fig. 2. Dependence of initial product distribution on reaction temperature for reaction of standard methyl chloride mixture on titanium; symbols as in Fig. 1.

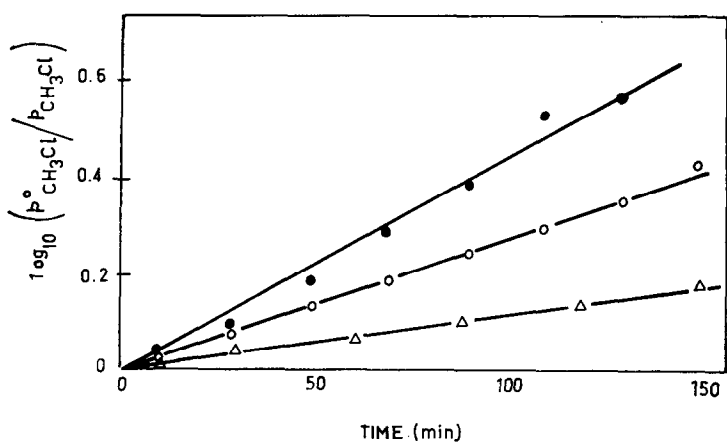


FIG. 3. First order kinetic plots for reaction of standard methyl chloride mixtures on titanium: ●, 300°C; ○, 275°C; Δ, 250°C; p° is the pressure at zero time.

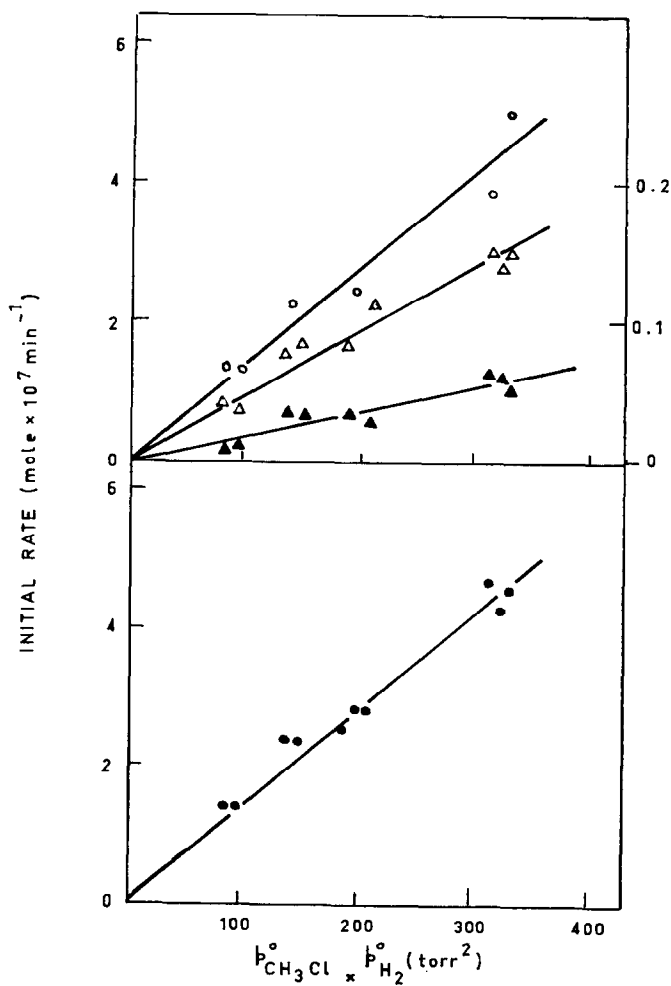


FIG. 4. Dependence on initial reactant pressure of initial rates of reaction from methyl chloride mixtures on titanium at 275°C; symbols as in Fig. 1; p° is the pressure at zero time. Top R.H. scale for Δ, ▲.

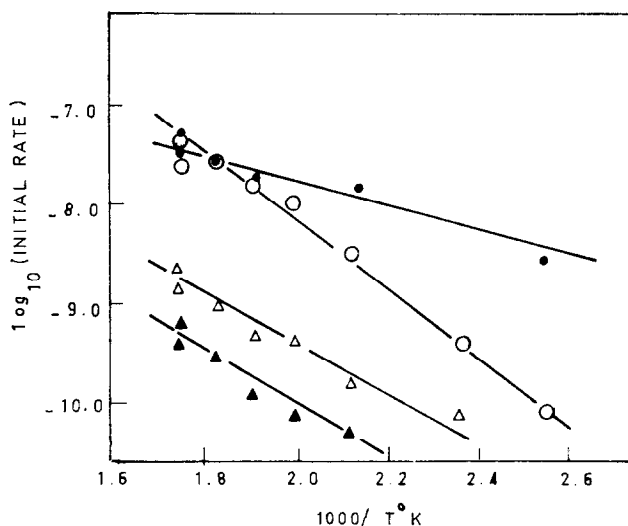


Fig. 5. Variation of reaction rate with temperature for standard methyl chloride reaction mixtures on titanium; symbols as in Fig. 1. Initial rates in mole $\times 10^7$ min $^{-1}$, and refer to films of estimated areas 500 cm 2 .

carbons were formed, and there was a significant loss of carbon by association with the catalyst. The course of a typical experiment is shown in Fig. 1. Figure 2 shows the dependence of initial product distribution on reaction temperature.

The disappearance of methyl chloride obeyed a first order rate plot, as shown in Fig. 3 for standard reaction mixtures at several temperatures. Since in these mixtures hydrogen was present in large excess, these results show that the rate of the overall reaction was proportional to the first power of methyl chloride pressure. A number of experiments were conducted at varying initial pressures of methyl chloride and hydrogen. Methyl chloride pressures were in the range 2 to 8 torr, and hydrogen in the range 20 to 80 torr. In these experiments, the initial reactant pressures were randomly related. The initial rates of methyl chloride reaction for various initial reactant pressures are contained in Fig. 4, which shows that the rate of this reaction is proportional to $p_{\text{CH}_2\text{Cl}} \times p_{\text{H}_2}$. In the same manner, the rates of formation of the individual saturated hydrocarbon products methane, ethane, and propane, are each proportional to $p_{\text{CH}_2\text{Cl}} \times p_{\text{H}_2}$; the data are included in Fig. 4. However, it will be seen from Fig. 1

that ethylene was produced rapidly in the early stages of the reaction, but the ethylene pressure quickly passed through a maximum. Because of this behavior, initial rates of ethylene formation could not be obtained with sufficient accuracy for the pressure dependences of the initial rate to be determined. An experiment in which 4 torr of HCl was initially added to a standard reaction mixture showed that at 275°C the rate was uninhibited by HCl.

TABLE 4
ACTIVATION ENERGIES AND FREQUENCY FACTORS
FOR THE REACTION OF METHYL CHLORIDE
ON TITANIUM

Process	Activation energy (kcal mole $^{-1}$)	log $_{10}$ (frequency factor) (frequency factor in molec. cm $^{-2}$ sec $^{-1}$)
Disappearance of CH $_2$ Cl	5.4 \pm 1	6.8 \pm 1
Formation of CH $_4$	16.1 \pm 2	11.0 \pm 1
Formation of C $_2$ H $_6$	12.5 \pm 2	8.3 \pm 2
Formation of C $_3$ H $_8$	12.4 \pm 2	7.7 \pm 2

4. Reaction between methylene chloride and hydrogen at higher pressures over titanium. The gas-phase chromatographic technique was of diminished accuracy for methylene chloride because of its very long

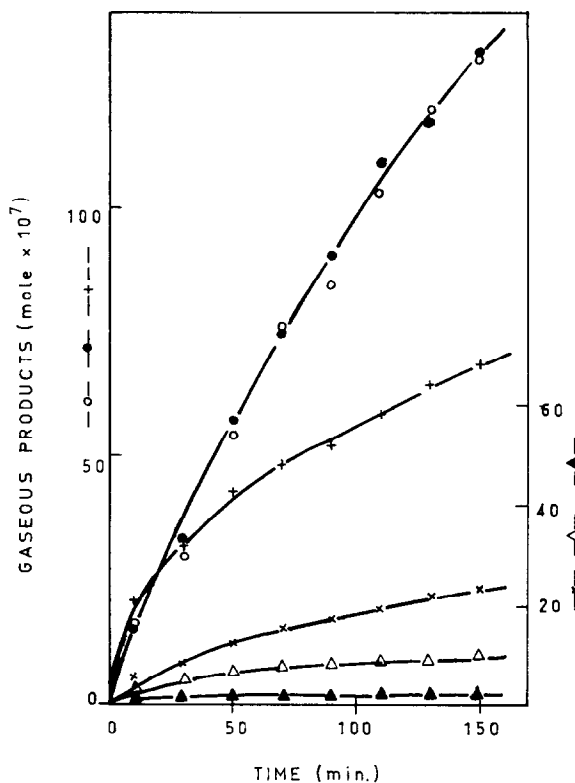


FIG. 6. Formation of gaseous reaction products with time from reaction of methylene chloride and hydrogen on 6.2 mg titanium at 275°C. Initial hydrogen pressure 82 torr, initial methylene chloride pressure 25 torr (both measured at 0°C) X, C₂H₆; other symbols as in Fig. 1.

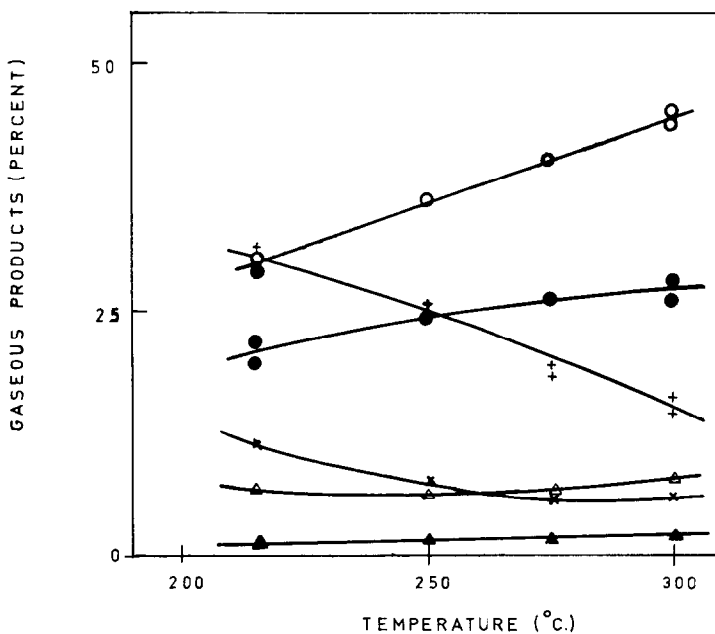


FIG. 7. Dependence of initial product distribution on reaction temperature for reaction of standard methylene chloride mixture on titanium; X, C₂H₆; other symbols as in Fig. 1.

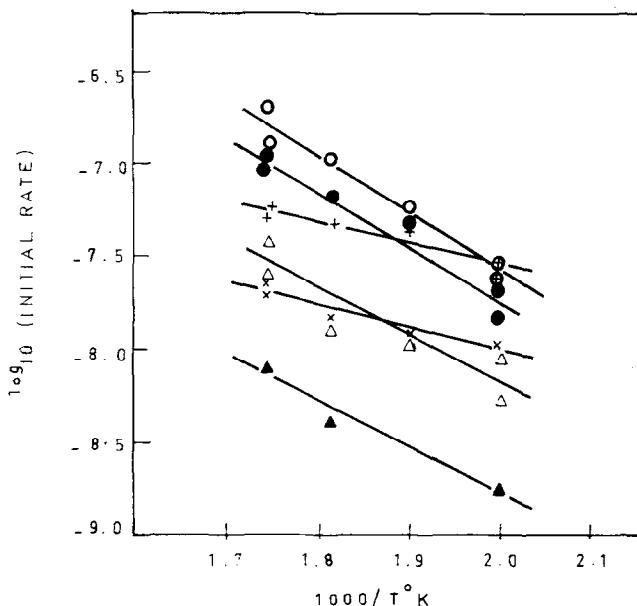


Fig. 8. Variation of reaction rate with temperature for standard methylene chloride reaction mixtures on titanium; X, C_2H_6 ; other symbols as in Fig. 1. Initial rates in mole $\times 10^7$ min, and refer to films of estimated areas 500 cm^2 .

retention time with consequent peak broadening. Hence, rate data for this component could only be obtained with reduced accuracy. Figure 6 shows the course of a typical reaction. Figure 7 gives the distribution of initial (gas-phase) reaction products formed in the range $215\text{--}300^\circ\text{C}$ for standard reaction mixtures. The temperature dependence of the initial rate of formation of the various reaction products is shown in Fig. 8, and the corresponding activation energies and frequency factors are recorded in Table 5.

In addition to the reaction products given in Fig. 7, a number of other gaseous prod-

ucts was observed, but in quantities insufficient for accurate analysis. These were identified as *n*-butane, *n*-butene, *n*-pentane, and probably chloroethane and chloroethylene. These extra products were estimated to total not more than 3 mole % of the gaseous product.

The surface of titanium films reacted with methyl or methylene chloride appeared visibly tarnished on inspection at the end of an experiment. However, reaction with methylene chloride produced an extremely thick surface layer which could be floated off the metal surface by immersion of the specimen in dilute hydrofluoric acid. An electron diffraction examination of this solid showed it to be amorphous which, taken with its insolubility in aqueous media, shows that it is probably a hydrocarbon polymer. Insufficient material was collected for further characterization.

5. Reactions of alkyl chlorides with deuterium over titanium. Reactions of methyl chloride and of methylene chloride with deuterium over titanium films were studied at 275°C using reaction mixtures of standard composition. The data indicating the course of the reaction are given in Table 6; the maximum extent of reaction was about 25%.

TABLE 5
ACTIVATION ENERGIES AND FREQUENCY FACTORS
FOR THE REACTION OF METHYLENE CHLORIDE
ON TITANIUM

Process	Activation energy (kcal mole ⁻¹)	log ₁₀ (frequency factor) (molec. cm ⁻² sec ⁻¹)
Formation of CH_3Cl	13.4 ± 2	10.4 ± 1
Formation of CH_4	13.3 ± 2	10.3 ± 1
Formation of C_2H_6	11.3 ± 2	9.5 ± 1
Formation of C_2H_8	10.9 ± 2	8.3 ± 1
Formation of C_2H_4	5.7 ± 1	7.1 ± 1
Formation of C_2H_2	6.7 ± 2	7.1 ± 1

TABLE 6
 PRODUCTS FROM THE REACTION OF METHYL CHLORIDE AND METHYLENE CHLORIDE WITH DEUTERIUM ON TITANIUM

Reactant	Reaction time (min)	Amount of parent reacted (mole X 10 ⁷)	Methylene chloride				Methyl chloride				C ₂ products*				Methane								
			D ₀ (%)	D ₁ (%)	D ₂ (%)	Amount formed (mole X 10 ⁷)	D ₀ (%)	D ₁ (%)	D ₂ (%)	Amount formed (mole X 10 ⁷)	D ₀ (%)	D ₁ (%)	D ₂ (%)	Amount formed (mole X 10 ⁷)	D ₀ (%)	D ₁ (%)	D ₂ (%)	D ₃ (%)	D ₄ (%)				
CH ₃ Cl	10	25	—	—	—	—	100	0	0	0	0	0	4.5	100	0	0	0	21	0	98.1	0	1.9	0
	30	65	—	—	—	—	99	0.9	0.1	0	0	0	6.5	50	50	0	0	50	0	94	2.3	3.7	0
	60	110	—	—	—	—	99	0.9	0.1	0	0	0	8.2	57	43	0	0	80	18.7	75	3.6	2.7	0
	120	170	—	—	—	—	99	1.0	0	0	0	0	11.4	57	43	0	0	116	22.2	69.5	5.6	2.7	0
CH ₂ Cl ₂	10	—	100	0	0	10	100	0	0	0	0	0	19	85	7.5	7.5	0	21	0	100	0	0	0
	35	—	100	0	0	22	98.5	0	1.5	0	0	0	27	77	12	11	0	38	31.5	68.5	0	0	0
	70	—	100	0	0	32	98	0	2.0	0	0	0	33	78	11	11	0	54	43.5	56.5	0	0	0
	120	—	100	0	0	48	98	0	2.0	0	0	0	39	78	13	9	0	69	51.7	48.3	0	0	0

* The C₂ product was mainly "ethane" from methyl chloride and "ethylene" from methylene chloride.

From methyl chloride monodeuteromethane (methane- d_1) was the primary C_1 product, and this underwent subsequent exchange to give higher deuteromethanes later in the reaction. Ethane- d_0 was the dominant initial C_2 product, and this subsequently underwent a single-step exchange to give ethane- d_1 . There was also a small amount of ethylene produced initially, but this was reacted away relatively quickly as the reaction proceeded (see Fig. 1). There was very little tendency for the production of deuteromethyl chloride: the amount of methyl chloride- d_1 reached about 1% of the methyl chloride- d_0 , and a very small amount of methyl chloride- d_2 was also formed.

The main primary products from ethylene chloride were methyl chloride- d_0 , methane- d_1 , and ethylene- d_0 . In the later stages of the reaction methane- d_0 was formed at the expense of methane- d_1 , but there were no deuteromethanes higher than methane- d_1 . At the same time there appeared somewhat increased amounts of ethylene- d_1 and ethylene- d_2 . Little or no significant further exchange of the methyl chloride- d_0 occurred. The deuterium content of the other minor reaction products was not determined.

6. Reaction of a mixture containing methyl chloride- ^{13}C , methyl chloride- ^{35}Cl , and hydrogen over titanium. This reaction was examined in order to test for possible reversibility in carbon-chlorine bond rupture. The methyl chloride- ^{13}C was 62.4 mole % $^{13}CH_3Cl$, and the methyl chloride- ^{35}Cl was 85.8 mole % $CH_3^{35}Cl$. Reaction was at 300°C using a mixture of standard composition and containing 32.6 mole % of the methyl chloride- ^{13}C and 67.4 mole % of the methyl chloride- ^{35}C (with, in each case, the isotopic purity given above). Reversibility in carbon-chlorine bond rupture would, provided there was sufficient mobility of the surface residues, result in a scrambling of the carbon and chlorine isotopes. At the temperature of the experiment, surface mobility would be expected. The results were obtained in terms of the measured relative peak heights in the mass range 50 to 53: the parent peak from $^{12}CH_3^{35}Cl$ lies at mass 50, the parent

from $^{13}CH_3^{37}Cl$ at mass 53. Over a reaction period of 100 min no significant change was detected in the relative peak heights in the range 50 to 53, and were different to a statistically scrambled distribution. It is concluded that no isotopic scrambling occurred and hence bond rupture was not reversible.

7. Structure of titanium catalysts. Transmission electron diffraction results taken on titanium films after reaction with alkyl chloride plus hydrogen mixtures, indexed with high accuracy as $TiH_{1.0}$ using evaporated gold as a calibrating standard.

8. Reaction between methyl chloride and hydrogen at higher pressures over palladium. This reaction was studied at 200° and 275°C. Reaction occurred mainly to give methane and hydrogen chloride. However, a small amount of ethane was also produced initially, but this subsequently decreased and disappeared presumably to methane. A mass balance

TABLE 7
REACTIONS OF METHYL CHLORIDE AND
HYDROGEN ON PALLADIUM

Temperature (°C)	Initial reaction rate (mole min ⁻¹ × 10 ⁷)		
	CH ₃ Cl reaction	CH ₄ formation	C ₂ H ₆ formation
200	3.0	2.8	0.07
275	12.4	11.2	0.48

showed no detectable carbon incorporation into the catalyst. Under reaction conditions, the stability of the palladium films was poor, and for this reason the collection of extensive data was not attempted. The available data are collected into Table 7 for reactions with standard mixtures. Film weights were about 10 mg in each case.

DISCUSSION

It is obvious from the range of products formed over titanium and palladium that these reactions are of considerable complexity. The most outstanding feature is the substantial tendency to carbon-carbon bond formation, particularly over titanium. Because of these complexities, we are only able to formulate an outline of the possible reaction paths.

Low-Pressure Reactions

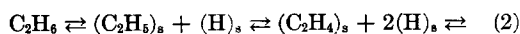
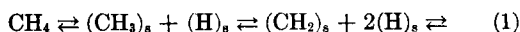
On all metals carbon-chlorine bond rupture occurred and virtually none of the chlorine was returned to the gas phase. Adsorption by rupture of a C-Cl rather than a C-H bond is likely in view of the bond energies, 76 kcal mole⁻¹ for C-Cl and 98 kcal mole⁻¹ for C-H (6). We shall thus proceed on the basis that in the adsorption process all of the C-Cl bonds in a molecule were ruptured before any C-H bond. This assumption is in agreement with deuterium exchange evidence discussed later.

With the exception of titanium and palladium, all metals catalyzed the formation of methane as the only desorbed hydrocarbon product. The desorption of methane and the recorded H/C ratios for the surface make it clear that during adsorption there occurred partial dehydrogenation of surface carbon residues. Again, on all metals other than palladium and titanium some hydrogen was also returned to the gas phase from this dehydrogenation process, and there was thus no doubt some chemisorbed hydrogen present on the surface as well. In the case of titanium and palladium, although no gaseous hydrogen was produced, there was probably some hydrogen retained by the metal in solution and adsorbed on the surface. For these reasons, the recorded H/C ratios only give an upper bound to the average composition of the surface hydrocarbon residue. With this limitation in mind however, the data in Table 3 show that the degree of dehydrogenation increased with increasing temperature, and that if the average residue composition is written as CH_x, the upper limit to *x* seldom exceeded 2. The most consistent exception to this is titanium, where the upper limit to *x* from methyl chloride adsorption approached 3, and from methylene chloride adsorption, approached 2.

In contrast to the other metals, the desorption products from palladium, and particularly from titanium show that both C₁ and C₂ residues existed on the surface as the result of methyl chloride or methylene chloride adsorption.

On palladium the extent and distribution

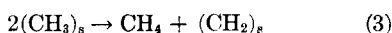
of desorption products depended strongly on treatment with hydrogen. It thus is likely that chemisorbed hydrogen was directly involved in the process of product desorption. Since C₁, and presumably C₂, species existed on the surface in varying stages of dehydrogenation, we may write the following relations between these surface residues and their corresponding desorption products:



where the notation (CH₃)_s, etc., represents a chemisorbed methyl group, without detailed specification of its mode of bonding to the surface. Reactions (1) and (2) are represented as reversible, but it is not necessarily implied that all are in established equilibrium: there is no satisfactory evidence about this latter point. However, in general one would expect the addition of surface hydrogen to shift both reactions (1) and (2) in the direction of hydrocarbon desorption. Furthermore, increased temperature should favor the formation of more highly dehydrogenated residues; there is some evidence for this in the measured surface H/C ratios from the low-pressure reactions, and there is also evidence from the temperature dependence of product distributions in the exchange between methane and deuterium over palladium (7). It has been observed from deuterium exchange data (8) that the activation energy for ethane adsorption/desorption is lower than for methane, and this may account for the increased proportion of ethane in the desorption product when this is induced by treatment with hydrogen.

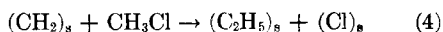
On titanium, the desorption product was insensitive to treatment with hydrogen; from this we conclude that surface hydrogen formed by adsorption of gas-phase hydrogen was not directly involved in hydrocarbon desorption, and that therefore this probably occurred by interresidue hydrogen transfer. There is no evidence to suggest whether interresidue hydrogen transfer occurred directly, or alternatively, if in the transfer process the hydrogen was for a short time

bonded to the surface. However, if the latter, it is clear that this "chemisorbed" hydrogen was not in equilibrium with the gas phase. The previous discussion concerning the surface H/C ratio on titanium suggests that adsorption of methyl chloride produced at least $(\text{CH}_3)_s$ and some $(\text{CH}_2)_s$ residues, while methylene chloride adsorption probably gave $(\text{CH}_2)_s$ together with more extensively dehydrogenated species. Thus, in the absence of gas-phase hydrogen we therefore formulate, for instance, the overall course of the primary methane-forming process in low-pressure reactions as

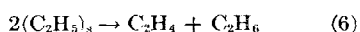


However, it should be noted (see next section) that in the reactions of methyl chloride on titanium at higher pressures, reaction (3) was certainly not the dominant methane-forming process [cf. reaction (8)].

On both titanium and palladium there was a tendency for preadsorption of methylene chloride to lead to an increase in the proportion of C_2 product from the reaction of methyl chloride. It is thus probable that surface C_2 residues were formed in the reaction of methyl chloride by



From $(\text{C}_2\text{H}_5)_s$, desorption of C_2 hydrocarbons may then proceed in two alternative ways



For reasons given previously in relation to the effect of added hydrogen, reaction (5) is probably dominant on palladium, in agreement with Stephen's (9) observations on the behavior of C_2 residues on that metal. On titanium, added hydrogen was found to be without effect on the product distribution and, moreover, ethylene was an important C_2 product. For these reasons, the interresidue hydrogen-transfer reaction (6) is probably favored on titanium. The $(\text{H})_s$ required in reaction (5) could be expected to be provided via dissociative adsorption of the parent. Evidence from reactions at higher pressures is considered in the next

section in support of reactions of the type of reaction (4).

The reaction of methylene chloride on titanium may be formulated in an analogous manner to reaction (4), and this system is discussed in greater detail in the next section.

The general trend towards a diminished C_2 yield at higher temperatures is ascribed to the general process



The state of hydrogenation of the surface residues involved in (7) is not known, although from previous related evidence (10, 11) it may well be low.

Reactions at Higher Pressures

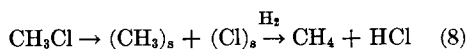
Unless otherwise specified, this discussion will refer to reactions over titanium. Under conditions in a higher pressure range, the extent of carbon-carbon bond formation was of enhanced importance, and there was produced material ranging from C_2 to polymeric. For instance, out of every 100 carbon atoms entering the reaction from methylene chloride, not less than 80 entered products of C_2 or higher. By comparison, the methyl chloride reaction was rather simpler in the sense that of every 100 carbon atoms entering the reaction about 85 went to form methane.

The lack of isotopic scrambling between ^{13}C - and ^{35}Cl -labeled methyl chloride on titanium clearly points to total irreversibility of carbon-chlorine bond rupture in the adsorption process, and also shows that scrambling by a direct bimolecular exchange between (say) adsorbed methyl chloride molecules is not possible. This behavior may be compared with the result of Cockerbergs *et al.* (12) who, using ^{36}Cl labeling, concluded that carbon-chlorine bond rupture was reversible in methyl chloride adsorption on chlorided surfaces of tungsten and molybdenum.

The observation that the reactions of deuterium with methyl or methylene chloride produced very little deuterio-parent, is in agreement with the behavior of ethyl chloride found for a number of metals by Campbell and Kemball (13), and of *n*- and

isopropyl chloride on palladium/pumice found by Addy and Bond (14), and supports the assumptions made in the previous section about the mode of adsorption. Under conditions of relatively high hydrogen or deuterium pressures one would expect the surface residues to be less extensively dehydrogenated than under low-pressure conditions; with this modification in mind we shall proceed with the same assumptions about the identity of the adsorbed residues as used in the previous section.

The hydrogenolysis of methyl chloride was first order in both methyl chloride and hydrogen. The reaction is unlikely therefore to proceed by a path in which the reactants compete for the same surface sites. Hydrogenolysis leading to methane and hydrogen chloride (as occurs on both palladium and titanium) may thus be written



where it is assumed that reaction involves gas-phase or physically adsorbed hydrogen. Provided the surface coverage by $(\text{CH}_3)_s$ is not too high, this reaction accounts for the observed kinetics. Furthermore, the formation of CH_3D in the corresponding reaction with deuterium is also in agreement with reaction (8). At temperatures below 300°C the activation energy for methane formation was greater than for methyl chloride loss. This is probably due to the inclusion of a contribution from the changing steady state coverage of $(\text{CH}_3)_s$, since C_2 and C_3 products were of increased importance at lower temperatures. Moreover, the activation energy for methane formation was different from those for ethane and propane, which were similar. This suggests that methane was formed by a different mechanism to ethane and propane.

Although the residue $(\text{CH}_2)_s$ was probably formed from methylene chloride adsorption, no CH_2D_2 was returned to the gas phase during the reaction with deuterium, despite the ready formation of CH_3D from $(\text{CH}_3)_s$. There are two possible reasons for this. First, it may be a real reflection of the relative intrinsic reactivities of these residues toward deuterium; second, it is likely that methylene

chloride adsorption would give a higher surface coverage than methyl chloride, so that the chance of finding a vacant site adjacent to $(\text{CH}_2)_s$ would be low, and this would remove an avenue by which deuterium may attack the metal-carbon bond. Both effects probably contribute.

Deuterolysis of methylene chloride yields methyl chloride containing initially no deuterium, and up to 25% reaction the amount of deuteromethyl chloride was very small. It is difficult to see how this methyl chloride could be formed other than via $(\text{CH}_2\text{Cl})_s$, but the result with deuterium shows this residue certainly does not react with gas-phase deuterium, so that the reaction analogous to reaction (8) does not occur. The reason for this may again be due to the inaccessibility of the metal-carbon bond at high coverage, and this would be augmented by the steric shielding due to the large chlorine atom attached to the residue. It is possible that the hydrogen that enters to form the methyl chloride comes from a surface pool of chemisorbed hydrogen which was not in exchange equilibrium with the gas-phase deuterium, the pool having been formed by dissociative adsorption of the reactant. Such a "light" hydrogen pool can operate in the early stages of the reaction, but it is unlikely that it could continue to function at high conversions, since, with a large excess of gaseous deuterium, its deuterium content should slowly rise. The data in Table 6 are limited to the relatively early stages of the reaction (<25% conversion). However, it is also possible that CH_3Cl was formed from methylene chloride by an intermolecular hydrogen transfer between initial adsorption residues, this being facilitated by the high coverage, for instance

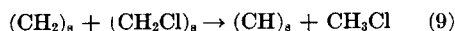
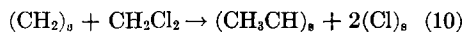


Figure 6 shows that methane is formed in the methylene chloride reaction on titanium as a primary product; thus the CH_3D formed in the presence of deuterium cannot arise as a secondary product from the readsorption of CH_3Cl . We suggest that the fact that this reaction with deuterium leads to CH_3D but, on the other hand, to CH_3Cl (i.e., the latter product undeuter-

ated) is due to steric hindrance in the vicinity of $(\text{CH}_2\text{Cl})_s$ on a surface already heavily covered with adsorbed methylene chloride.

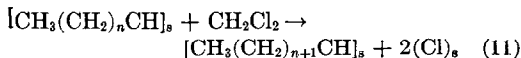
The reaction of methyl chloride and deuterium over titanium gave C_2H_6 (i.e., undeuterated as the main initial C_2 product). The discussion from the previous section suggests that this is formed via reactions (4) and (6), with the proportion of ethylene somewhat diminished from that expected from reaction (6) by hydrogenation. If the surface concentration of $(\text{CH}_2)_s$ is approximately independent of methyl chloride pressure, the rate of reaction (4) would be proportional to the first power of methyl chloride pressure, and this is in agreement with the observed pressure dependence of the rate of ethane formation. It should be noted that the observed dependence of the rate of ethane formation on the first power of methyl chloride pressure excludes the possibility of ethane formation by the recombination of two $(\text{CH}_3)_s$ groups. If an increasing hydrogen pressure favored the existence of $(\text{CH}_2)_s$ residues at the expense of more extensively dehydrogenated ones, this would explain the increasing rate of ethane formation with increasing hydrogen pressure (approximately a first order dependence), however, the complexity of the reaction is too great for this to be other than a tentative suggestion. The formation of deuterioethanes after the initial stages of the reaction was presumably due to an increasing proportion of deuterium in the surface hydrogen.

The reaction of methylene chloride on titanium may be formulated in an analogous manner to reaction (4). However in the high-pressure reactions with this system an extensive amount of surface polymer was formed, in addition to hydrocarbons in the range C_1 – C_5 . Thus, it is clear that the mechanism must allow for ready chain propagation. We thus formulate the reaction to give a C_2 surface residue as



Desorption of $(\text{CH}_3\text{CH})_s$ may give ethylene directly, and indeed ethylene was a major

product in this system. The general propagation step analogous to reaction (10) is



and HCl is formed by reaction of hydrogen with $(\text{Cl})_s$. We suggest that the relative facility for carbon-carbon bond formation from $(\text{CH}_2)_s$ is due to the formation of a quasi-free radical, $\cdot\text{CH}_2$ -surface. This is not dissimilar to the intermediate suggested by Nasini *et al.* (18) in the polymerization of diazomethane at metal surfaces. Such a free radical at a metal surface (where electrons would be expected to be freely available) may possibly only be formed as the transition state is approached.

The suggested mechanism for the formation of higher products from the reaction of methylene chloride over titanium agrees with the observation that C_2H_4 and C_3H_6 were formed with approximately the same activation energies, that the ethylene was produced mainly in the undeuterated form (the deuterium content of higher hydrocarbons was not measured), that the products are mainly olefinic, and that the reaction propagated readily to apparently higher polymerized species. If, as suggested previously, the accompanying saturates were formed by interresidue hydrogen transfer, this also accounts for the observation that, in the presence of deuterium, the saturates (e.g., ethane) were produced mainly in an undeuterated form.

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