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Multiple Isotope Tracing of Methanation over Nickel Catalyst

II. Deuteromethanes Tracing

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The methanation of mixtures of carbon monoxide and hydrogen was studied by a novel isotope transient tracing technique using deuterium. Concentrations of $CH_{x\,\mathrm{ads}}$ intermediates on the surface of the working catalyst are estimated. The most abundant species are C_{ads} and CH_{ads} with $CH_{2\,\mathrm{ads}}$ and $CH_{3\,\mathrm{ads}}$ being present in smaller proportions. Evidence is presented that the mechanism involves sequential unidirectional hydrogenation of the intermediates by atomic adsorbed hydrogen.

INTRODUCTION

Elucidation of the mechanism of methanation of synthesis gas is an active field of study both because of its intrinsic interest and because of the close relationship of methanation to other syntheses based on carbon monoxide hydrogenation such as the Fischer–Tropsch synthesis of higher molecular weight hydrocarbons. Our earlier study (*1*) indicates that in the case of methanation carbon monoxide dissociates to form carbidic carbon atoms that subsequently react with hydrogen.

An area of current interest is the nature of the postulated CH_x intermediates produced by hydrogenation of the surface carbon species. Goodman *et al.* (*2*) suggested from preliminary X-ray photoelectron spectroscopy studies using nickel catalyst that a hydrogenated carbon rather than carbidic carbon may be present. Work by the Shell research group summarized by Biloen and Sachtler (*3*) indicates that methanation proceeds via rapid formation of a CH_x intermediate that is converted relatively slowly to methane as follows:

$$CO_{\mathrm{ads}} \xrightarrow[1]{\text{fast}} CH_x \xrightarrow[2]{\text{slow}} CH_4 \qquad (1)$$

These studies using ^{13}C tracing do not furnish information on the details of the CH_x species involved.

Galuszka *et al.* (*4*) carried out hydrogenations of predeposited carbon from dissociation of carbon monoxide. In these experiments the carbon was first partially hydrogenated by deuterium, followed by introduction of hydrogen into the system. Based on formation of CDH_3, it was concluded that CD groups were present on the surface suggesting that during methanation CH groups predominate.

Bonzel and Krebs (*5*) investigated several carbon deposits formed on iron after carbon monoxide hydrogenation using Auger and X-ray photoelectron spectroscopy. They concluded that the analytical power of XPS in the case of adsorbed hydrocarbons and their fragments is rather limited. However, their own studies and those of previous investigators in which C_2H_2 was decomposed on catalyst surfaces suggested that a major fraction of the CH_x peak consists of CH_{ads} species.

There still seem to be no data reported in which the intermediates were studied during methanation while the catalyst was in its working state. The transient tracer technique using deuterium presents an excellent opportunity to provide further useful information concerning this problem.

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METHODS

Apparatus and procedure. The apparatus is an improved version of that used in earlier studies (*1*). Figure 1 gives a schematic diagram of the present equipment which employs a gradientless recirculating reactor system often used in studies of this type to minimize external temperature and concentration gradients. Recent modifications include the incorporation of a diaphragm pump (Metal Bellows Corp. MB-41) in place of the all glass piston pump previously used. The recirculation rate was thereby increased from 3000 to 6000 ml/min. At the low temperature of the circulating stream which is heated and cooled before and after the reactor there is no problem with corrosion or catalytic activity introduced by the metal bellows. Two syringe pumps were installed in tandem on a movable stand so that it is possible with a single movement to simultaneously withdraw one feed stream containing a mixture of H_2 and CO and introduce the other (traced stream). This permits smooth and reliable step-up operation by a single operator.

Inlet and outlet gases were analyzed as previously using a Finnigan quadrupole mass spectrometer (Type 1015C). Data acquisition and manipulation have been improved by means of a data system (Finnigan 6000 Series). All raw data are recorded on a disk memory. In calculation of a sample composition from mass spectral data, information from the complete set of observable mass peaks is employed. This corresponds to a larger number of peaks than the components present and the computation procedure involves solving an overdetermined set of linear equations. A *prime* computer Model 350 was used for analysis of the experimental data.

The basic experimental procedure employed uses a so-called superposition technique. After steady state is reached with a given mixture of hydrogen, carbon monoxide, and helium, which may take several hours, the feed stream is rapidly switched to one containing D_2/CO in exactly the same proportion as that in the original H_2/CO feed while maintaining a constant forward flow of diluent helium. It was found by continuous monitoring of the effluent analysis that there was no kinetic isotope effect so that the rate of CO conversion remained the same except that a transient set of deuterated methanes was produced. Thus the data obtained correspond to the catalyst in its working state. A given set of data was modeled employing various assumed mechanisms.

A second technique, described as "wash-

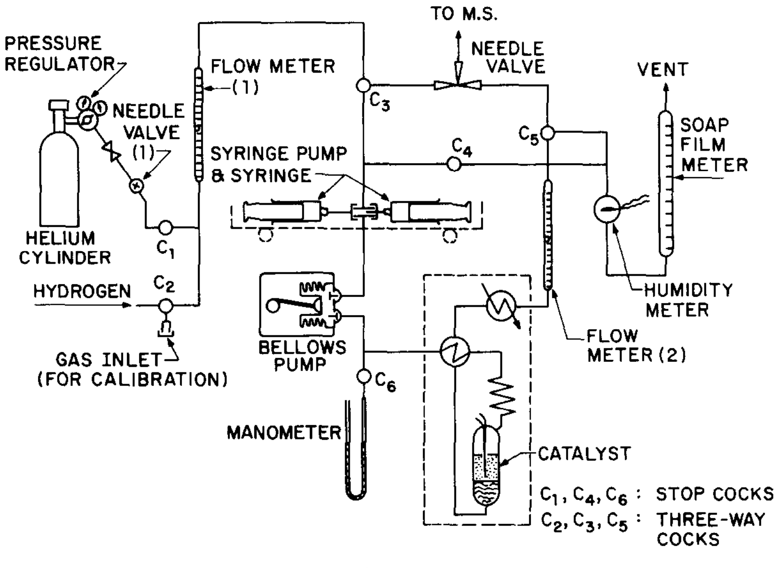

FIG. 1. Recirculating reactor system.

ing," was employed in conjunction with the basic superposition technique to provide corroboration of the assumptions used in modeling and to provide a value for C*l*, the carbidic carbon deposit. In a typical experiment using this "washing" technique a mixture of hydrogen, carbon monoxide, and helium is fed to the reaction system until steady-state methane formation is attained. Then unreacted species are desorbed by purging for about 30 min with helium, leaving only chemisorbed intermediates that would require reaction with hydrogen to render them removable. These intermediates are then "titrated" by switching to a feed stream consisting of deuterium alone at the same rate as the original hydrogen feed and analyzing for deuterated methanes recovered in the effluent. Thus the total CD_4 content of the effluent stream would correspond to adsorbed carbidic carbon C*l* present on the catalyst; CHD_3 would correspond to CH*l* adsorbed; CH_2D_2 would correspond to CH_2l; CH_3D would correspond to CH_3l. This assumes that no reactions occur during this operation other than deuteration of adsorbed hydrocarbon species. Those apparent intermediates can be roughly compared with those predicted by modeling the superposition data assuming various mechanisms. The results of washing are, of course, not influenced by possible kinetic isotope effects. Washing provides an estimate for the C*l* species concentration which cannot be determined by deuterium tracing alone.

Method of correlation. As in previous studies in which ^{13}C and ^{18}O were used, the system is assumed to consist of a number of cells or compartments each containing one of the intermediates or terminal species. Reactants in one compartment are assumed to be equally accessible to those from another with which they interact. In earlier studies (*1*, *6*), the dependent variables for modeling were taken as fractional markings of tracer. In those cases the redistribution of tracer could be expressed in terms of systems of linear differential equations with constant coefficients.

With deuterium tracing such a simplification would result in the loss of information conveyed by the distribution of deuterium among species containing more than a single deuterium atom. Therefore the basic material balances were expressed in terms of the concentrations of deuterated species involved. It was possible to still retain a system of linear equations by expressing the fraction of hydrogen in the compartment involving chemisorbed hydrogen–deuterium as an observed known function of time.

Since in our experiments the hydrogen or deuterium taking place in the methanation reaction is adsorbed on the nickel component of the catalyst, it was assumed that the fraction of deuterium participating in reaction is the same as that observed in the gas phase. This assumption of equilibrium is supported by studies cited by Ozaki (*7*) in which it is indicated that adsorption of hydrogen on nickel is rapid and reversible. This assumption in addition to providing the desired relationship for modeling of the hydrogenation of carbonaceous species simplifies the modeling procedure by allowing reaction steps involving formation of deuteromethanes to be considered separately from intermediates containing oxygen.

It was found that the fractional concentration of hydrogen on the catalyst surface or in the gas phase could be accurately fitted by an exponential curve of the following form:

$$f = \frac{C^{Hl}}{C^0} = \exp(-kt) \tag{2}$$

where f = fraction of C^{Hl} on the surface of the total H*l* and D*l* species

C^{Hl} = concentration of H*l* on the catalyst surface, ml/g catalyst NTP

C^0 = concentration of H*l* + D*l* on the catalyst surface. It is assumed $C^0 = C^{Hl} + C^{Dl}$

k = a constant

t = time (min) ($t = 0$ when D_2 is introduced)

In our previous study (*1*) it was thought that an isotopic kinetic effect might be responsible for the observed deuterium distribution which was not random, but this did not prove to be the case. It was observed that the delays in marking of deuterated species and their maximum concentrations occurred sequentially. Therefore it was decided to attempt modeling on the basis of the assumption that hydrogenation occurred sequentially and unidirectionally. This resulted in good agreement with the data and is the model employed in the present study.

The model used was reported by us previously (*6*) and assumes the following mechanistic steps for methane production:

$$
\begin{aligned}
&H_2 + 2l \rightleftharpoons 2Hl\\
&CO + l \rightleftharpoons COl\\
&COl + l \rightarrow Cl + Ol\\
&Cl + Hl \rightarrow CHl + l\\
&CHl + Hl \rightarrow CH_2l + l\\
&CH_2l + Hl \rightarrow CH_3l + l\\
&CH_3l + Hl \rightarrow CH_4 + 2l
\end{aligned}
\tag{3}
$$

where l represents active surface sites. The first two steps are assumed to be rapid, and at equilibrium. The third step is taken as unidirectional because the low concentration of surface oxygen Ol would prevent the reverse reaction occurring to any great extent even if its rate constant were high, as indicated by studies of Biloen and Sachtler (*3*). Preliminary modeling calculations indicated that the concentration of adsorbed methane CH_4l was very small so it is not included in the mechanistic sequence.

The following 14 material balance equations can then be written corresponding to the 5 terminal species CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 and the 9 partially hydrogenated intermediate adsorbed species.

$$
\left.
\begin{aligned}
\frac{dC^{CDl}}{dt} &= V\left(1 - f - \frac{C^{CDl}}{C_2}\right)\\
\frac{dC^{CHl}}{dt} &= V\left(f - \frac{C^{CHl}}{C_2}\right)\\
\frac{dC^{CD_2l}}{dt} &= V\left(\frac{C^{CDl}}{C_2}(1 - f) - \frac{C^{CD_2l}}{C_3}\right)\\
\frac{dC^{CHDl}}{dt} &= V\left(\frac{C^{CHl}}{C_2}(1 - f) + \frac{C^{CDl}}{C_2}f - \frac{C^{CHDl}}{C_3}\right)\\
\frac{dC^{CH_2l}}{dt} &= V\left(\frac{C^{CHl}}{C_2}f - \frac{C^{CH_2l}}{C_3}\right)\\
\frac{dC^{CD_3l}}{dt} &= V\left(\frac{C^{CD_2l}}{C_3}(1 - f) - \frac{C^{CD_3l}}{C_4}\right)\\
\frac{dC^{CHD_2l}}{dt} &= V\left(\frac{C^{CHDl}}{C_3}(1 - f) + \frac{C^{CD_2l}}{C_3}f - \frac{C^{CHD_2l}}{C_4}\right)\\
\frac{dC^{CH_2Dl}}{dt} &= V\left(\frac{C^{CH_2l}}{C_3}(1 - f) + \frac{C^{CHDl}}{C_3}f - \frac{C^{CH_2Dl}}{C_4}\right)\\
\frac{dC^{CH_3l}}{dt} &= V\left(\frac{C^{CH_2l}}{C_3}f - \frac{C^{CH_3l}}{C_4}\right)\\
\frac{dC^{CD_4}}{dt} &= \frac{VW}{\beta}\left(\frac{C^{CD_3l}}{C_4}(1 - f) - \frac{C^{CD_4}}{C_5}\right).
\end{aligned}
\right\}
\tag{4a}
$$

$$\left.\begin{aligned}
\frac{dC^{\mathrm{CHD_3}}}{dt} &= \frac{VW}{\beta}\left(\frac{C^{\mathrm{CHD_2}l}}{C_4}(1-f) + \frac{C^{\mathrm{CD_3}l}}{C_4}f - \frac{C^{\mathrm{CHD_3}}}{C_5}\right)\\
\frac{dC^{\mathrm{CH_2D_2}}}{dt} &= \frac{VW}{\beta}\left(\frac{C^{\mathrm{CH_2D}l}}{C_4}(1-f) + \frac{C^{\mathrm{CHD_2}l}}{C_4}f - \frac{C^{\mathrm{CH_2D_2}}}{C_5}\right)\\
\frac{dC^{\mathrm{CH_3D}}}{dt} &= \frac{VW}{\beta}\left(\frac{C^{\mathrm{CH_3}l}}{C_4}(1-f) + \frac{C^{\mathrm{CH_2D}l}}{C_4}f - \frac{C^{\mathrm{CH_3D}}}{C_5}\right)\\
\frac{dC^{\mathrm{CH_4}}}{dt} &= \frac{VW}{\beta}\left(\frac{C^{\mathrm{CH_3}l}}{C_4}f - \frac{C^{\mathrm{CH_4}}}{C_5}\right)
\end{aligned}\right\} \quad (4b)$$

where $C_2 = C^{\mathrm{CD}l} + C^{\mathrm{CH}l}$
$C_3 = C^{\mathrm{CD_2}l} + C^{\mathrm{CHD}l} + C^{\mathrm{CH_2}l}$
$C_4 = C^{\mathrm{CD_3}l} + C^{\mathrm{CD_2H}l} + C^{\mathrm{CDH_2}l} + C^{\mathrm{CH_3}l}$
$C_5 = C^{\mathrm{CD_4}} + C^{\mathrm{CHD_3}} + C^{\mathrm{CH_2D_2}} + C^{\mathrm{CH_3D}} + C^{\mathrm{CH_4}}$ this is an observed constant corresponding to the steady-state concentration in the product of $\mathrm{CH}_x\mathrm{D}_{4-x}$ ($x = 0$–4)
C^{il} = concentration of ith species on catalyst, ml/g (NTP) $i = \mathrm{CD, CH, CD_2, CHD, CH_2, CD_3, CHD_2, CH_2D, CH_3}$
C^i = concentration of ith species in vapor phase, vol fraction $i = \mathrm{CD_4, CHD_3, CH_2D_2, CH_3D, CH_4}$
$f = \dfrac{C^{\mathrm{H}l}}{C_0} = \exp(-kt)$
V = velocity of $\mathrm{CH}_x\mathrm{D}_{4-x}$ ($x = 0$ to 4) production, ml/min/g catalyst (NTP)
W = weight of catalyst, g
β = dead space, ml.

This set of differential equations describes the population distribution of all species, intermediates, and product components, according to the proposed mechanism. It can be expressed in matrix form as:

$$\frac{d\mathbf{x}}{dt} = \mathbf{A}\,\mathbf{x} + \mathbf{b} \quad (5)$$

where $\mathbf{x}$ = a vector of concentrations of all products and intermediates
$\mathbf{A}$ = a matrix containing all the constants and the time variant function f
$\mathbf{b}$ = a vector determined from the input of tracer in the feed that contains the time variant function f.

The 14 equations (4) are not all independent because the sum of the fractional concentrations for each of the compartmental components must equal unity. Thus for example,

$$\frac{C^{\mathrm{CH}l}}{C_2} + \frac{C^{\mathrm{CD}l}}{C_2} = 1. \quad (6)$$

There are four such relationships corresponding to the four parameters so that only 10 of the equations are independent.

In principle, a solution for one of the terminal species should provide sufficient information to determine C_2, C_3, and C_4. The parameter C_1 corresponding to Cl concentration cannot be determined by deuterium tracing. In practice the curves giving the $\mathrm{CH_4}$ and $\mathrm{CD_4}$ transients can be fitted to a high degree of accuracy by expressions involving only one or two exponentials so they do not furnish sufficiently accurate information for discrimination between the parameters. Therefore the intermediates that go through maxima in concentration are the most useful for providing information on values for assumed parameters which, of course, require expressions with several exponentials. Also all 10 of the independent differential equations are not required to fit the data for each separate observed deuteromethane. Thus, to fit the CH_2D_2 data requires eight equations, whereas the CH_3D or CD_3H concentration changes can be expressed by seven differential equations. In addition to requiring one additional equation for correlation, CH_2D_2 data showed the greatest scatter because of interference with other components. Therefore the basic modeling procedure was carried out with the data for CH_3D and CHD_3 transients taken together, which require eight equations. The surface concentrations thus obtained were used to plot values of the remaining species, $-CH_4$, CH_2D_2, and CD_4.

The method that we previously employed (*1*) could in principle be used to solve the sets of first-order linear equations with time-dependent coefficients but it proved difficult to obtain satisfactory convergence with the number of equations needed for deuterium tracing. We therefore took advantage of the fact that the reactions could be modeled as unidirectional by solving the equations analytically instead of using a computer routine to solve them numerically. Other features of the previously described method were retained including the statistical treatment that provides information on goodness of fit.

RESULTS

Adsorption Experiments

The same catalyst containing 60 wt% nickel on kieselguhr (supplied by Harshaw Chemical Co., Harshaw-104T) was used as in our previous studies. Because of the importance of chemisorption of species involved, additional data were obtained to supplement those previously reported. In conducting these experiments catalyst was initially reduced under a hydrogen flow at 480°C for 24 hr. Before each experiment, it was reduced again for 2 additional hr and degassed under less than 10^{-4} Torr for 1 hr at 227°C since adsorbed hydrogen is readily desorbed at this temperature (*8*). The surface area of this pretreated catalyst is 87 m^2/g.

Adsorption data were obtained using a method similar to that published by Vannice (*9*). In this method an isotherm is obtained between 50 and 200 Torr over a 15-min period; the apparatus is evacuated for 2 min to remove reversibly held gas, then a second isotherm is obtained in the same manner as the first. The difference between the two isotherms at 200 Torr is taken as the measure of chemisorption. For hydrogen this procedure yielded a value of 7.18 ml/g (STP) when adsorption was conducted at 27°C.

Adsorption of carbon monoxide was more complicated. Whereas in the case of hydrogen adsorption equilibrium at 27°C was attained in 30 min, in the case of carbon monoxide equilibrium was not reached even after 24 hr. Using the method of Vannice with 15 min adsorption time, we obtained a value of $V_m = 12.26$ ml/g (STP) at 27°C. This amounts to 1.71 times the amount of hydrogen adsorption at that temperature, in rough agreement with the ratio of 2.29 obtained by Vannice with a 5% Ni/Al_2O_3 catalyst. Apparently at room temperature carbon monoxide does not decompose upon adsorption because no carbon dioxide formation is detected. Whereas hydrogen is adsorbed dissociatively at both 27 and 227°C, carbon monoxide adsorption appears to involve single bonds. The amount of CO adsorbed at 27°C increases to more than four times that of hydrogen adsorption without reaching equilibrium, so that it is possible that more than one carbon atom is bound to a single surface nickel atom.

At higher temperatures decomposition of carbon monoxide occurs upon adsorption, evidently following the Boudouard reaction

$$2\,CO + l \rightleftharpoons CO_2 + Cl \qquad (7)$$

at 227°C this equilibrium is reached within 60 mins. Carbon deposition can be readily evaluated from the amount of CO_2 produced. Employment of a Langmuir plot gives $V_m = 17.26$ ml/g (STP) for carbon deposition, corresponding to slightly more than a monolayer based on hydrogen adsorption data.

Methane adsorption at 228°C was observed and equilibrium was attained within 45 mins. Employment of a Langmuir model for the adsorption gave V_m for methane of 0.75 ml/g (STP).

Deuterium Superposition and Washing

Four series of superposition and washing experiments are given in Tables 1 and 2. These runs were conducted under roughly parallel operating conditions for a range in temperature and concentration of reacting species. Values for outlet flow rates reported were obtained by utilizing C, H, and O material balances together with mass spectrometric analyses for hydrogen and CO_2.

It is difficult to exactly match deuterium superposition and washing runs taken at different times. Very slight changes in feed composition can result in large changes in steady-state composition of the recirculating stream. The steady state itself often requires several hours of operation to achieve. Therefore correspondence in these parallel runs is only approximate but still of sufficient accuracy to show that the two methods give essentially the same results as far as populations of surface species are concerned.

For the runs reported in Tables 1 and 2 for such parallel experiments, the concentrations of surface species reported were

TABLE 1

Deuterium Superposition and Washing—210°C[a]

	Series 1		Series 2	
	Run #021081	Run #020681	Run #021681	Run #021981
	Superposition (H during prereact. D during step-up)	Washing (H during prereact. only)	Superposition (H during prereact. D during step-up)	Washing (H during prereact. only)
Inlet flow rate, ml/min (NTP)				
H_2 or D_2	3.0	3.0	2.5	2.5
CO	1.0	1.0	1.0	1.0
He	84.15	83.56	79.9	79.9
Outlet flow rate, ml/min (NTP)				
$H_xD_{2-x}(x = 0-2)$	1.01	1.05	1.00	1.03
CO	0.24	0.29	0.43	0.41
CO_2	0.05	0.05	0.05	0.05
$H_xD_{2-x}O(x = 0-2)$	0.66	0.61	0.47	0.47
$CH_xD_{4-x}(x = 0-4)$	0.71	0.66	0.52	0.52
Calc. surf. conc., ml/g (NTP)[b]	Modeling	Wash. (integral of deut. wash. response)	Modeling	Wash. (integral of deut. wash. response)
Cl	Not modeled	2.41	Not modeled	1.97
CHl	4.41 ± 0.05	4.93	3.41 ± 0.06	4.09
CH_2l	0.66 ± 0.00	0.44	0.57 ± 0.00	1.59
CH_3l	0.75 ± 0.02	1.46	0.66 ± 0.02	1.32

[a] Weight of catalyst, 2.43 g; pressure, 1 atm; dead space, 118 ml.

[b] Derivatives for parameters are computed estimates of standard errors.

TABLE 2

Deuterium Superposition and Washing—230°C[a]

	Series 3		Series 4	
	Run #121980	Run #122280	Run #083181	Run #090981
	Superposition (H during prereact. D during step-up)	Washing (H during prereact. only)	Superposition (H during prereact. D during step-up)	Washing (H during prereact. only)
Inlet flow rate, ml/min (NTP)				
H_2 or D_2	2.5	2.5	1.0	1.0
CO	1.0	1.0	1.0	1.0
He	93.7	96.3	99.83	101.03
Outlet flow rate, ml/min (NTP)				
$H_xD_{2-x}(x = 0-2)$	0.36	0.40	0.35	0.52
CO	0.02	0.04	0.65	0.77
CO_2	0.20	0.20	0.10	0.08
$H_xD_{2-x}O(x = 0-2)$	0.58	0.56	0.15	0.17
$CH_xD_{4-x}(x = 0-4)$	0.78	0.76	0.25	0.15
Calc. surf. conc., ml/g (NTP)[b]				
	Modeling	Wash. (integral of deut. wash. response)	Modeling	Wash. (integral of deut. wash. response)
Cl	Not modeled	0.64	Not modeled	0.98
CHl	2.00	0.85	2.45 ± 0.40	1.59
CH_2l	0.44	0.50	0.51 ± 0.00	0.52
CH_3l	0.48	0.63	0.83 ± 0.04	0.39

[a] Weight of catalyst, 2.43 g; pressure, 1 atm; dead space, 118 ml.

[b] Derivatives for parameters are computed estimates of standard errors for Run #083181; an estimate was not possible for Run #121980.

obtained by quite different procedures. In the case of deuterium superposition they were computed according to the modeling procedure and reflect surface concentrations during steady-state methanation. Results obtained for deuterium washing were obtained by integrating the curves giving production of deuteromethanes during the washing period following methanation and purging.

It is seen that correspondence between superposition and washing is reasonable, providing confirmation of the basic assumptions used in deriving this information. In all cases the predominant surface intermediate is CHl with a smaller proportion of Cl. Measurable but considerably smaller proportions of CH_2l and CH_3l are present. At the higher temperature (230°C), a substantially increased production of CO_2 and reduced concentration of surface species was observed.

Several additional observations during washing are pertinent since this technique represents a simple method of obtaining data once its validity has been established via the superposition technique. During washing experiments very little methane was recovered in the effluent, indicating that the high relative concentration of deuterium during washing tended to reduce hydrogenation of chemisorbed species. The fact that CHl produced during washing was no higher than that during superposition indicates that decomposition of carbonaceous intermediates did not occur during washing to produce less reactive *Cl* deposits as was probably the case in (1) when a long purging period was used.

After the washing experiment Run No. 090981 in Table 2, the temperature was raised to 300°C and deuterium flow was continued. There was no further evolution of CD_4, indicating that no very unreactive carbon remained on the catalyst. Though washing gives the total amount of surface carbon deposited on the catalyst, it does not distinguish between the reactivity of surface carbon species that are present under conditions of steady state methanation. According to studies by McCarty and Wise (*10*) several species with different reactivities can be obtained by CO decomposition.

In order to illustrate the type of information obtained by superposition and washing, detailed results are given for Run No. 021081 reported in Table 1. Figures 2–6 show the development of transient rates after substitution of deuterium. In each figure the smooth curve obtained by computer simulation is plotted along with the broken curve representing observed data. As discussed previously, the data for CH_3D and CHD_3 were modeled together to obtain the desired surface concentration parameters. Since the solutions were obtained analytically, the curves shown in Figs. 3 and 5 can be represented in closed form as follows, after division by the total flow rate:

$$C^{CH_3D} = \sum_{i=1}^{i=9} C_i e^{-k_i t} \tag{8}$$

$$C^{CHD_3} = \sum_{i=1}^{i=14} C_i e^{-k_i t}. \tag{9}$$

Table 3 gives values for the constants corresponding to the curves plotted in Figs. 3 and 5, together with the function *f* which is

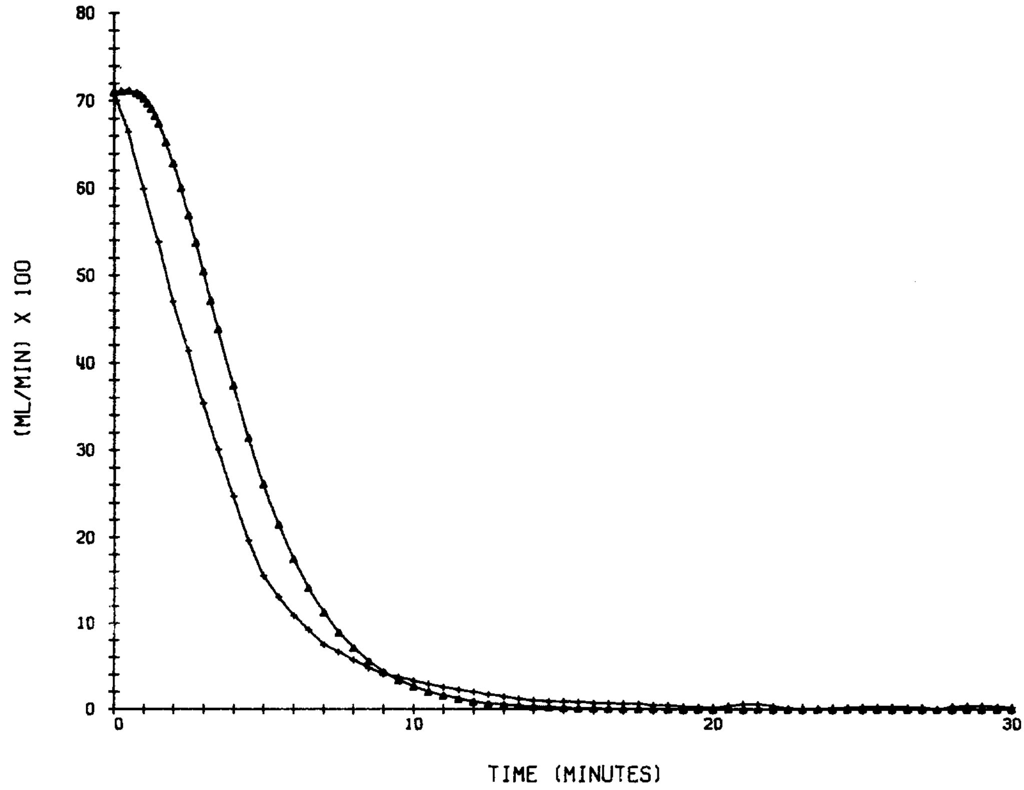

FIG. 2. Methane transient—Run #021081. Superposition: △, computed curve; ×, experimental data.

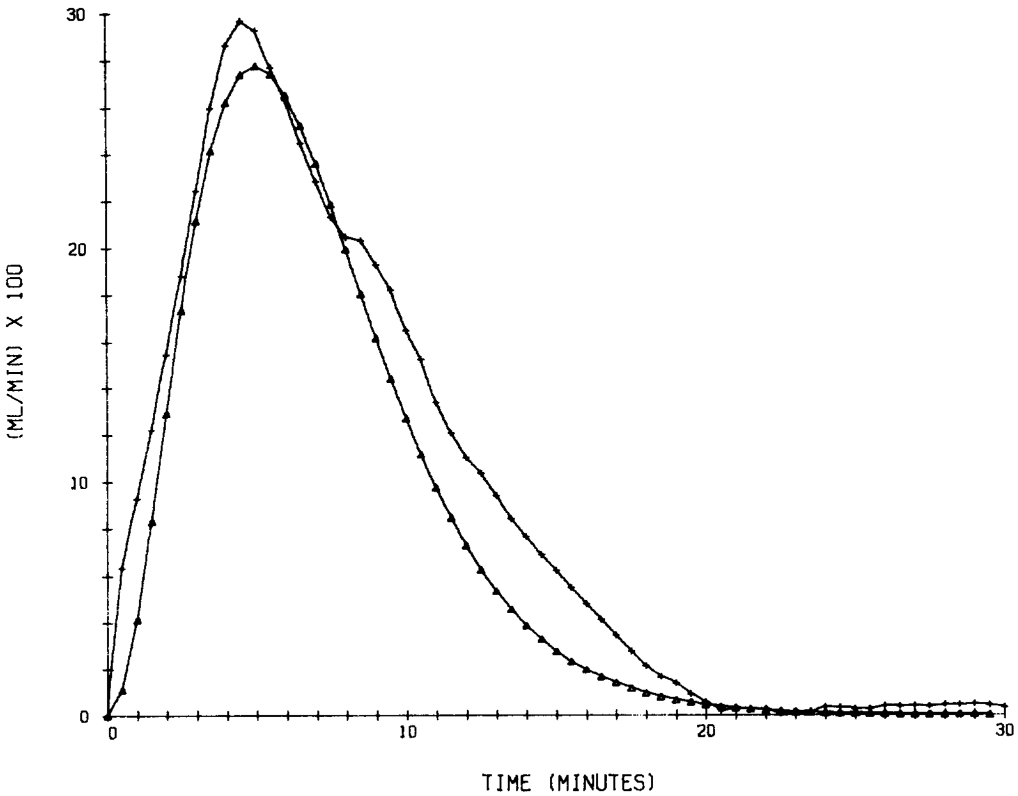

FIG. 3. Monodeuteromethane (CH_3D) transient—Run #021081. Superposition: △, computed curve; ×, experimental data.

obtained by modeling the deuterium–hydrogen variation with time. The curves for the other three components were also generated from analytical solutions corresponding to the same parameter values, Fig. 2 (CH_4), Fig. 4 (CH_2D_2), and Fig. 6 (CD_4). The calculated values are in good agreement with the independently obtained step-up data, although these data were not used to determine the parameters. It must be emphasized that the five computed velocity profiles are based on a model with only three free parameters and are not merely empirical data correlations.

Concentrations of methane shown in Fig. 2 include methane present in the dead space at the beginning of the step-up experiment. In modeling it was assumed that hydrogen in methane exchanges only to a negligible extent with deuterium as shown in our previous paper (*1*).

Experimental results for dideuteromethane in superposition experiments, such as plotted in Fig. 4, were obtained by difference from the overall material balance for methanes because of substantial scatter in the direct spectrometric determination due to interference of peaks from neighboring species. Such problems in CH_2D_2 determination account for the more irregular shape of experimental curves for this species.

Note the sequential delay in appearance of increasingly deuterated species and the corresponding appearance of maximum concentrations of these transitory intermediates. Calculations based on data shown in these figures and the value of *f* given in Table 3 show this effect more quantitatively. For example, at about 10 min after switching to D_2 the HD composition is about 80% D but the average D content of

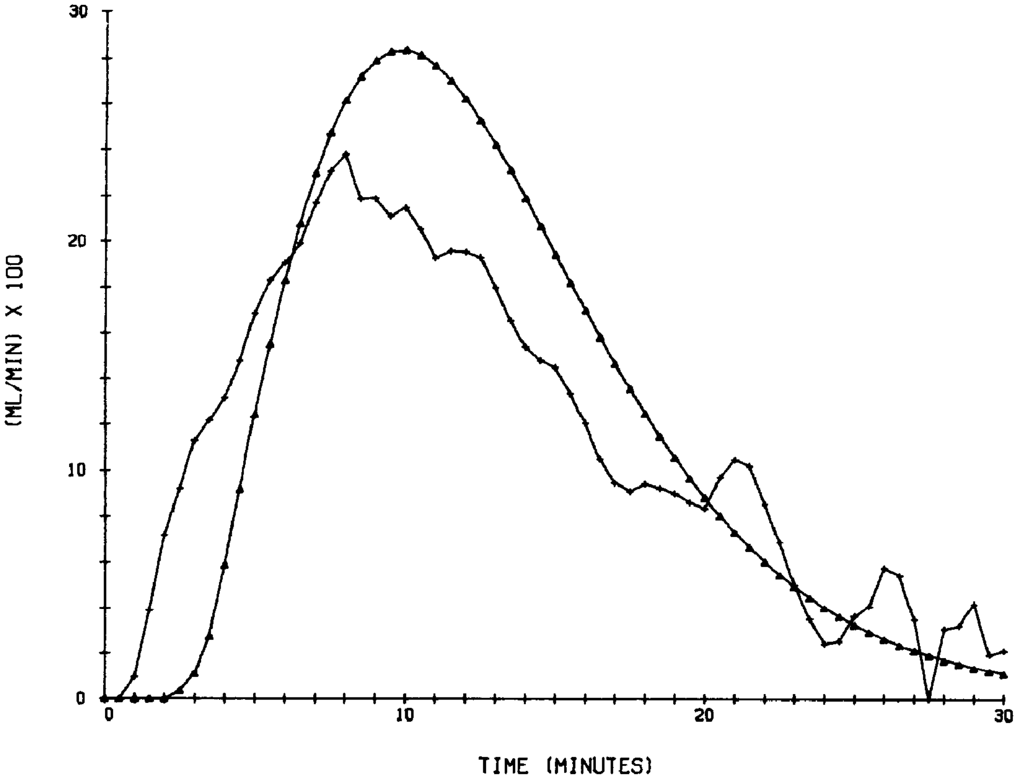

FIG. 4. Dideuteromethane (CH_2D_2) transient—Run #021081. Superposition: △, computed curve; ×, experimental data.

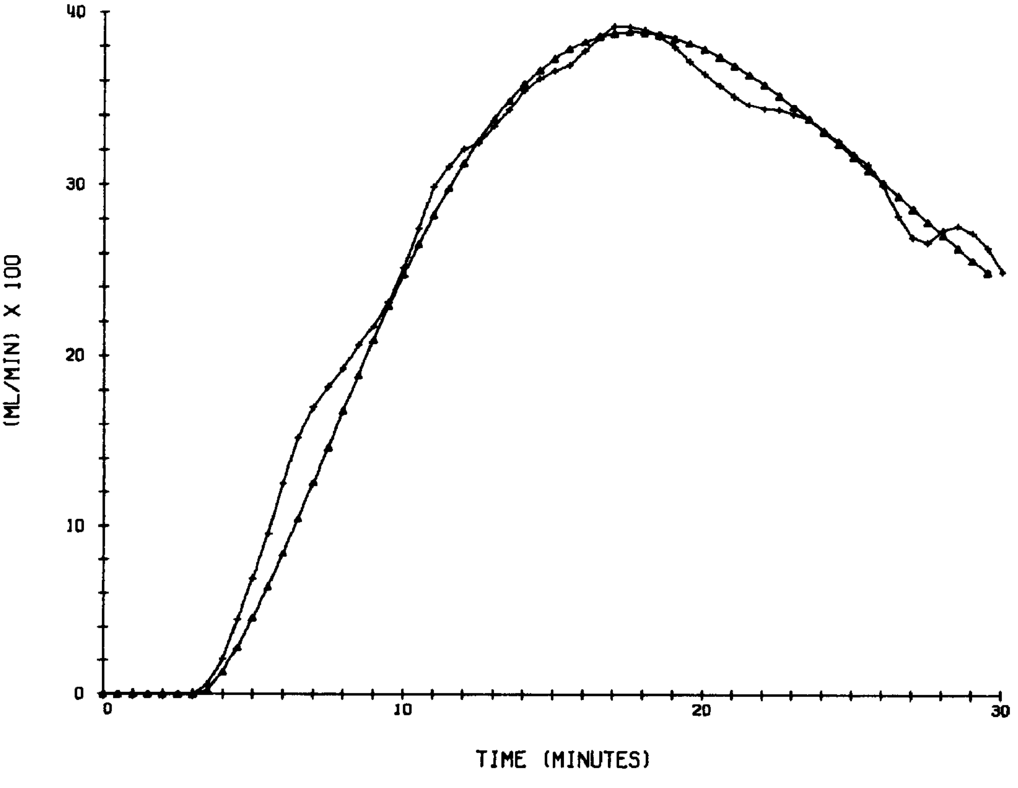

FIG. 5. Trideuteromethane (CHD_3) transient—Run #021081. Superposition: △, computed curve; ×, experimental data.

TABLE 3

Analytical Solutions for Surface Concentrations of CH_3D and CHD_3 during Superposition (Run #021081)

i	C_i	K_i
	$C^{CH_3D} = \sum_{i=1}^{9} C_i e^{-K_i t}$	
1	−20.41	0.49
2	−11.79	0.66
3	15.72	0.39
4	−1.97	0.58
5	2.18	0.75
6	75.74	0.56
7	−1.65	0.39
8	−57.80	0.52
9	0.001	118.17
	$C^{CHD_3} = \sum_{i=1}^{14} C_i e^{-K_i t}$	
1	2.70	0.16
2	29.71	0.33
3	−26.93	0.49
4	−28.97	0.66
5	1.48	0.06
6	−20.50	0.22
7	−86.76	0.39
8	142.80	0.55
9	−5.49	0.41
10	−11.79	0.58
11	3.36	0.75
12	70.04	0.36
13	−79.14	0.52
14	9.49	118.17

$f = e^{-0.165\,t}$

the deuteromethane mixture is only about 50% D. Also with unidirectional hydrogenation of Cl, it was not found possible to model the system by addition of H_2l instead of atomic Hl.

Statistical comparison (*11*) between our model and models with more than 10% backward velocity of a single step in Eq. (3) showed that the higher the ratio of N_{-}^{2}/V the poorer the latter models will be, indicating that little scrambling exists.

In the case of deuterium washing for the parallel experiment, Run No. 020681, Fig. 7 gives rates of evolution of the deuteromethanes. Quantitative interpretation of the kinetics is not possible in washing experiments because rates will change as individual species are removed from the catalyst. The results given in Tables 1 and 2 are obtained by integration of such curves to give the total amount of each species produced during the washing. The value of carbidic carbon corresponding to CD_4 production could not result from any process other than addition of deuterium to a carbon deposit, because "enolic" or partially hydrogenated CH_x species, if present, would contain hydrogen.

DISCUSSION

The present study was conducted well below temperatures at which formation of nonreactive graphitic carbon is reported to occur (370°C) in the comprehensive studies of Goodman *et al.* (*12*). Under our conditions (230°C), even the maximum carbon concentration deposited from carbon monoxide in the absence of hydrogen (approximately one monolayer) could be hydrogenated to methane. Therefore steady-state hydrogenation of CO could be conducted at all H_2/CO ratios with a range of surface coverages. However, the amount of carbonaceous deposit falls rapidly to a fraction of a monolayer as the H_2/CO ratio is increased and then remains relatively constant over a substantial range. Values for CH_xl are somewhat less at 230°C than at 210°C as reported in Tables 1 and 2. Data previously reported (*1*, *6*) using ^{13}CO tracing show similar effects of temperature. However, the CH_xl concentration obtained by ^{13}CO tracing agrees more closely with that measured in the present study by deuterium superposition rather than by inclusion of the additional Cl observed by washing. More study will be required to confirm this conclusion, which would indicate that the surface concentration of reactive carbon entering into the methanation mechanism is relatively small.

Coverages obtained by us are in approximate agreement with data obtained by Goodman *et al.* (*2*) under somewhat different conditions on a nickel (100) crystal surface. These authors did not report increased CH_xl deposition at lower temperatures but the time scale for their experiments (17 min) was somewhat shorter than we usually employed.

The low value of CHl reported for Run No. 122280 may be due to the low proportion of CO in the circulating gas stream which makes it difficult to attain steady-state conditions.

In the present studies with H_2/CO ratios in the circulating gas stream as low as 0.5/1 the concentration of Cl was always less than that of CHl. The high ratio of Cl to hydrogenated species reported in Table 6 of our first paper (*1*) is probably due to the extremely long time of 276 min of helium purging during which degradation of the adsorbed hydrocarbon intermediates could occur. In the present studies, we found that a much shorter period (about 30 min) sufficed to remove unreacted methane. In the earlier study we were especially interested in showing qualitatively the presence of hydrocarbon intermediates, since it had not then been possible to model the deuterium step-up data.

At higher temperatures and/or lower H_2/CO ratios than those employed in the present study it is, however, likely that the Cl concentrations would exceed that of CHl because under such conditions it is known that nickel catalysts are deactivated by graphitic carbon deposition. Study of the conditions under which this change occurs could be useful in optimizing catalyst operating conditions.

The transient superposition technique used in this study maintains a steady-state reaction throughout a set of observations as

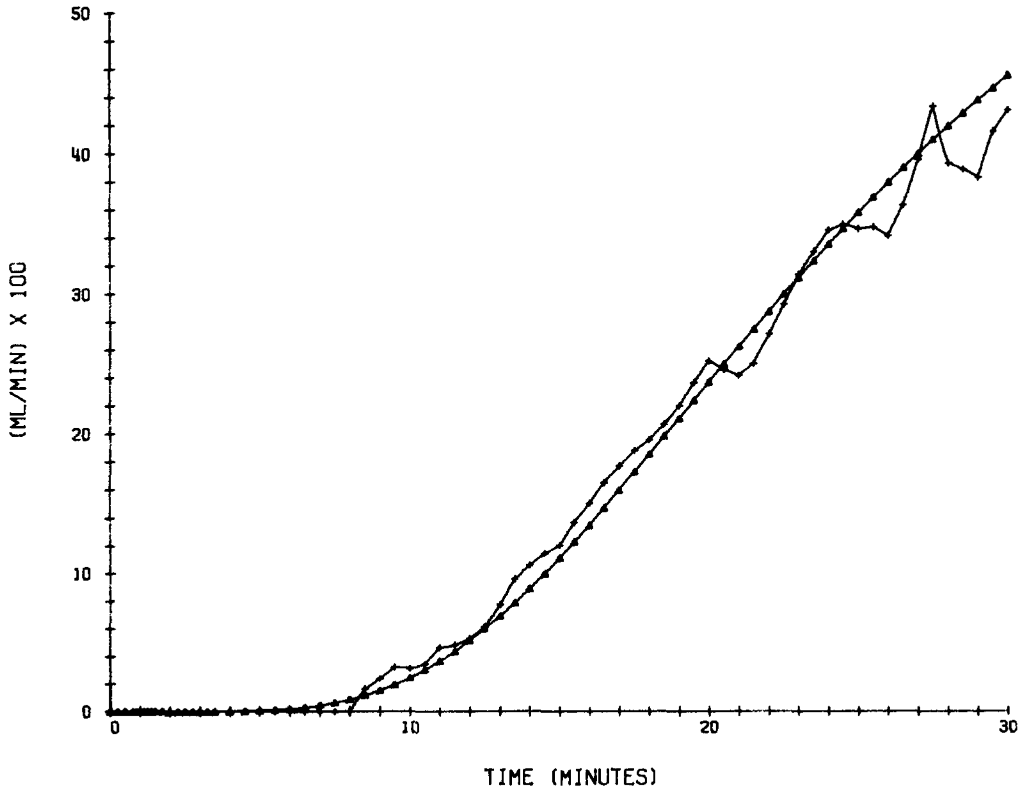

FIG. 6. Tetradeuteromethane (CD_4) transient—Run #021081. Superposition: △, computed curve; ×, experimental data.

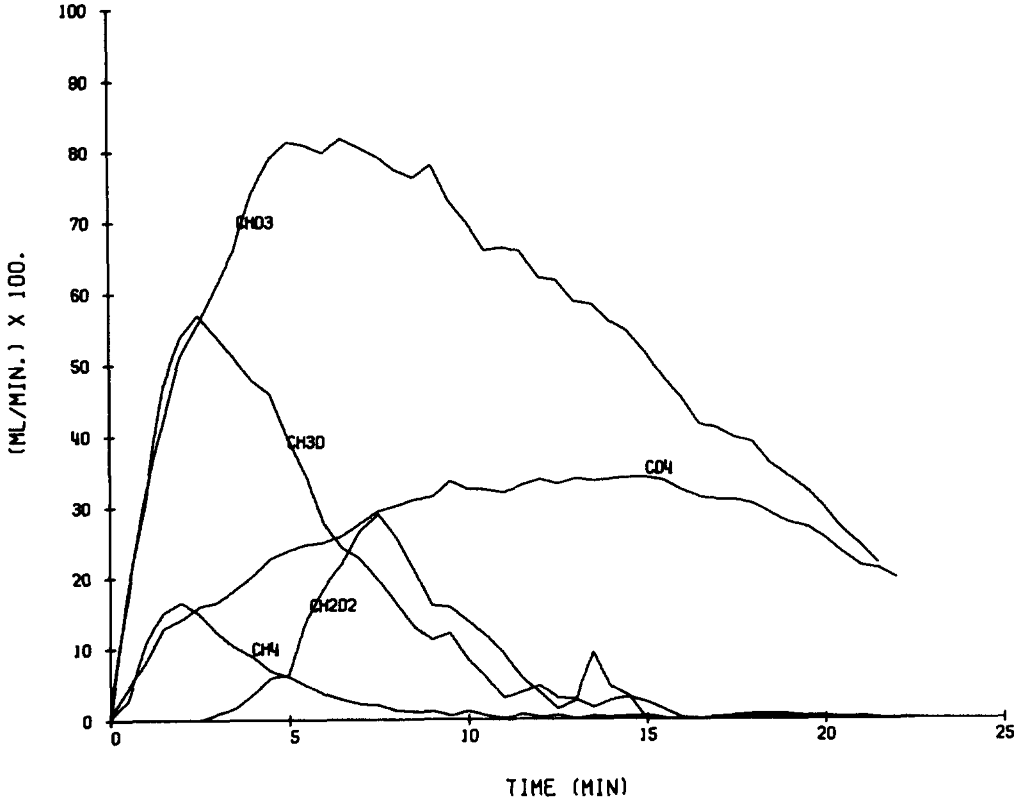

FIG. 7. Deuteromethanes produced during washing—Run #020681.

contrasted with pulse and XPS techniques. This has the advantage that intermediates will not change in concentration once the system has been brought to steady state. It is thus easier to model the data obtained.

Since a correspondence has been found in this case between superposition and washing, the latter technique could be employed to obtain data more rapidly with similar catalysts. If similar mechanisms apply with other catalysts, it might be possible to use this procedure as a screening technique. Postreaction analysis via the spectroscopy of choice might very well correlate with parallel superposition results.

Another profitable direction for application of these methods should be in the study of the Fischer–Tropsch reaction. It is thought (*3*) that CH_x intermediates similar to those generated in the formation of methane are precursors for the production of higher molecular weight hydrocarbons. Identification of the mechanisms involved in Fischer–Tropsch synthesis could be readily conducted by extension of the present methodology.

The results presented here do not depend on kinetic relationships for rates of methane production as a function of pressure, temperature, and concentrations of ambient species. Thus it is not necessary to employ the usual assumptions involved in Langmuir–Hinshelwood kinetics or to specify a rate-controlling step. From the results reported here it is clear that a number of intermediates can exist at appreciable concentrations. Evidently the rates of hydrogenation of Cl and CHl are important factors in the determination of reaction rate.

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