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# Reactions of Methyl Chloride and of Methylene Chloride at Metal Surfaces

## I. Reactions at a Sodium Surface

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Reactions of methyl chloride and of methylene chloride have been studied at the surface of clean evaporated films of sodium in the range −78° to 60°C. Reaction proceeded to give a surface tarnish layer into which was bound all of the chlorine and about half of the carbon from the reacted alkyl chloride, the balance of the carbon being returned to the gas phase as methane, ethane, and ethylene. Evidence is adduced that the surface product layer from methyl chloride and from methylene chloride can be considered as containing $CH_3^-$ and $CH_2^{2-}$, respectively.

The reaction of methyl chloride has been found to be strongly photoaccelerated by light of wavelength lying in the *F*-center absorption band of sodium chloride.

By the use of $^{13}C$- and $^{35}Cl$-labeled material, the reactions of methyl chloride (for instance) have been interpreted in terms of reactions at the surface (i) between two $CH_3^-$, (ii) between $CH_3^-$ and undissociated methyl chloride, the latter probably present as $CH_3Cl^-$, (iii) between two $CH_3Cl^-$. The effect of illumination is considered to be to facilitate reaction (iii) by a process analogous to M-center formation known for alkali halides. This M-center analogue forms a sterically favorable site for the required reaction.

### INTRODUCTION

One of the central problems in many areas of catalysis is the behavior of hydrocarbon residues of known structure on a metal surface. The present work was undertaken with this problem in mind and the experiments were designed to make use of the proposition that alkyl chloride adsorption would occur dissociatively to generate chemisorbed hydrocarbon residues. The present paper is devoted to reactions at a sodium surface, while Part II‡ will deal with reactions at transition metal surfaces. Sodium was chosen as a metal with respect to which the C–H bond is inert. (*1*).

We know of no previous work which has attempted to study the reactions of methyl chloride or methylene chloride with metals specifically as a surface process. The reaction of ethyl chloride with deuterium (*2*) has been studied previously over evaporated films of some transition metals, but under relatively high pressure conditions where the only detectable reaction was rupture of the C–Cl bond and the formation of DCl plus deuteroethanes. Of course, the reaction between alkyl halide and Group I metals has a long history as a synthetic method under the name of the Wurtz reaction. The synthetic reaction occurs in the liquid phase and it is likely (*3*, *4*) that with sodium and potassium the reaction proceeds via the formation of the corresponding alkylsodium or alkylpotassium molecule, while with lithium, free radicals can make some contribution to the reaction. The reactions of gaseous alkyl halides with lithium and magnesium have been reported previously, (*5*, *6*) but no mechanistic details were provided. The initial products were

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the corresponding organometallic compounds, together with hydrocarbon coupling products.

## EXPERIMENTAL

Sodium films were deposited onto the inside wall of a spherical reaction vessel using the technique and apparatus described previously (*7*). The reaction vessel was of about 250 ml volume and the geometric area of sodium film was about 190 $cm^2$. Films of 15-mg weight were used. A conventional high-vacuum system was employed. The reaction vessel was connected to the vacuum line via a U-trap. Prior to the preparation of a sodium film the reaction vessel was pumped and baked overnight at 450°C and the U-trap and connecting line were baked at 450°C for 3 hr; the trap was then cooled to —78°C and the reaction vessel cooled to room temperature. The pressure measured with an ion gauge was then about $10^{-7}$ torr.

Depending on the pressure of the experiment, gases were dosed into the reaction vessel either from a McLeod gauge or from a calibrated volume isolated between all-metal Hoke valves.

### *Gas Preparation*

**Hydrogen.** Cylinder hydrogen, purified by diffusion through a heated palladium thimble.

**Methyl chloride.** Refrigeration grade material, purified by fractional distillation.

**Methylene chloride.** BDH Analar grade sample, purified by fractional distillation.

**Hydrogen chloride.** Liberated using concentrated sulfuric acid, from thoroughly dried Analar grade potassium chloride which had been further purified by the method of Clusius and Dickel (*8*) to remove the last traces of bromide and iodide. The product was fractionally distilled before storage.

**Methane.** Philips Pure or Instrument Grade, further purified by fractionation on the line.

**Xenon.** Molecular-sieved material from Linde Air Products Co.

**Methyl chloride-$^{13}$C.** Prepared from methyl iodide-$^{13}$C (BioRad, 62.4 atom % $^{13}$C), by the reaction

$$CCl_4 + 4CH_3I \xrightarrow{AlCl_3} 4CH_3Cl + CI_4$$

Reaction according to the conditions recommended by Soroos and Hinkamp (*9*) gave a negligible yield of desired product, and the following method was adopted. Anhydrous aluminum chloride (Analar grade 0.3 g, 2.25 mmole), carbon tetrachloride (Analar grade, 1.0 ml, 1.59 g, 10 mmole), and methyl iodide-$^{13}$C (0.3 ml, 0.7 g, 5 mmole) were placed in a heavy-walled glass tube which had been necked down and flushed with dry oxygen-free nitrogen. After freezing the contents, the tube was sealed off and reaction was effected at 40°C for about 20 hr. The product was recovered in 50% yield by fractional distillation and was pure to both gas-chromatographic and mass-spectrometric analysis.

**Hydrogen chloride-$^{35}$Cl.** This was separated from a sample of normal pure hydrogen chloride by gaseous thermal diffusion using a 20-ft column and conditions similar to those described by Clusius and Dickel (*8*). A steady state at the top of the column was reached in about 24 days and the maximum enrichment in the material drawn off was 87.0 atom % $^{35}$Cl. The product was converted to potassium chloride for use in the preparation of methyl chloride-$^{35}$Cl.

**Methyl chloride-$^{35}$Cl.** This was prepared from enriched potassium chloride by treatment with dimethyl sulfate. Enriched potassium chloride (0.45 *g*, 6 mmole) in 1.5 ml of water was placed in a 100-ml flask, and dimethyl sulfate (0.7 ml, 7.5 mmole) with sulfuric acid (0.1 ml, 10 mmole) were held in a sidearm of the flask. The flask was connected to a tower containing potassium hydroxide and thence to cold traps successively at —78°C, and —195°C. After flushing with dry nitrogen, the reactants were mixed and heated to about 80°C. The product was evolved rapidly and condensed in the trap at —195°C whence it was purified by fractional distillation. The yield was 95% and isotopic composition of the final material was 85.8% $^{35}$Cl.

### *Analytical Methods*

In most experiments, the gas-phase composition was measured by gas-phase chromatography.

A column was required that would resolve the hydrocarbon components up to $C_4$, yet have a reasonably short retention time for the alkyl chlorides. A low background was also necessary for using the flame-ionization detector at high sensitivity. For this purpose a 10 ft × ¼-inch ID column of tetraisobutylene 20 w/w% supported on 60/80 BSS Chromosorb P was used, the final 4 inches of which were packed with liquid paraffin on Celite to remove tetraisobutylene from the effluent stream. The tetraisobutylene was an Eastman Kodak sample, and the Chromosorb P was obtained from Johns Manville. The column was run at 0°C with a flame-ionization detector. Analysis was effected by expanding gas from the reaction vessel into the reservoir of a Toepler pump by which it was compressed into a modified Springham greaseless valve for introduction onto the column. The details of this injection system are described elsewhere (*10*). The sample-handling system was such that the background could be reduced below the limit of detection using the flame-ionization detector on maximum sensitivity: under these circumstances $10^{13}$ molecules would have been detectable. Using these techniques, accurate analytical data could be obtained for all components except methylene chloride, the peak from which was too broad for anything better than a semi-quantitative estimate.

Analysis for $^{13}C$ and $^{35}Cl$ was done using an AEI MSIO mass spectrometer. Samples for analysis were expanded from the reaction vessel into small demountable sample tubes for presentation to the introduction system of the MSIO.

Photoreactions were studied by illuminating the gas/ solid surface through a "window" in the sodium film. This window was of area about 20 cm² and was formed in the sodium layer at the side of the reaction vessel by local heating of the glass during sodium deposition. Intensity measurements were made with a calibrated thermopile, the mercury line at 3660 Å was isolated with a Wood's filter, mercury lines at 4358 and 5460 Å with sodium nitrite and cuprammine solutions, and a sodium lamp with a heat filter gave the sodium doublet at 5890 Å. Illumination experiments were initiated in the expectation that the reaction would be accelerated by light of wavelength lying within the absorption band of *F* centers in sodium chloride. The wavelengths listed above are shown in Fig. 1 in relation to the *F* center absorption band.

## RESULTS

### *Desorption from the Surface Product Layer*

Doses of alkyl chloride were added to the sodium film from the McLeod gauge in

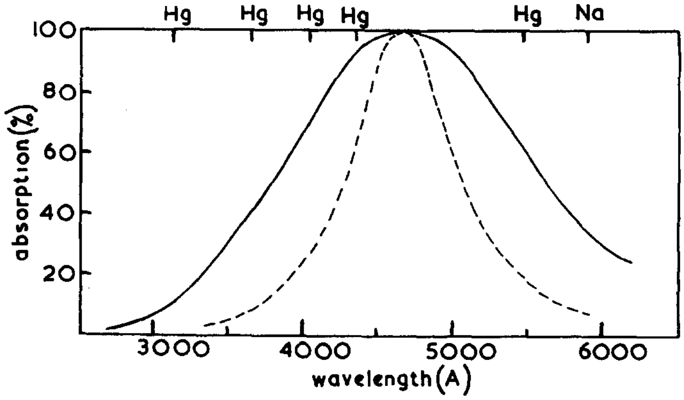

FIG. 1. The absorption spectra of F centers in sodium chloride: ——, 20°C; - - - -, −195°C [Mollow, E., *Z. Physik.* **85**, 56 (1933)]. The curves have been normalized to a relative absorption scale. The figure also shows the main exciting lines used for illumination in the present work.

the range $10^{15}$–$10^{17}$ molecules, and were added at temperatures in the range −78° to 20°C. Doses were taken up rapidly ($<1$ min) and completely, to a product layer thickness of several atomic layers. Maintaining the product layer at a constant temperature then resulted in hydrocarbon desorption; this was allowed to proceed until the product pressure had built up to a value in the range 1 to 10 mtorr, when the gas phase was transferred to the sample injector for gas-chromatographic analysis. We shall refer to this type of experiment as a *decomposition reaction.*

The course of a typical decomposition reaction at −23°C is given in Fig. 2, showing desorption with time for successive doses of methyl chloride. In the tabulated data contained in Fig. 2 is given the layer thickness ($L$), expressing the depth of product layer in terms of the equivalent number of sodium chloride unit cell dimensions. The latter is intended as an approximate index of layer thickness. It was calculated from the measured gas uptake assuming that the product layer consisted of sodium chloride with its normal lattice constant, but with some $Cl^-$ replaced by $CH_3^-$. For this purpose it was assumed that sodium chloride crystals with ⟨100⟩, ⟨111⟩, and ⟨110⟩ axes at right angles to the sodium surface were equally likely, so that an average unit layer of sodium chloride growing on 190 cm² of sodium would contain $1.1 \times 10^{17}$ $Cl^-$ and $Na^+$ ions. The original sodium film was assumed to expose geometric surface area. The composition of the surface layer in terms of the $Cl^-/CH_3^-$ ratio is included in Fig. 2. The justification for considering the existence of $CH_3^-$ ion is given later.

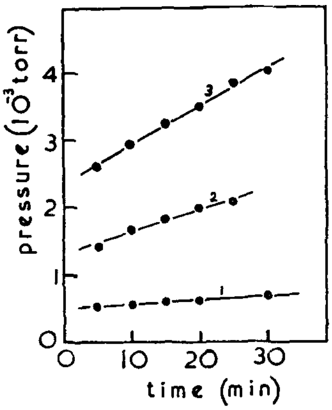

FIG. 2. Desorption of hydrocarbons from methyl chloride adsorbed on sodium; successive methyl chloride doses, −23°C. Composition of desorbed hydrocarbon given in table. $L$ is surface layer thickness in units defined in the text.

| Dose No. | Hydrocarbon (%) | | | $L$ | Ratio of chloride to $C_1$ in surface layer |
|---|---|---|---|---|---|
| | $CH_4$ | $C_2H_4$ | $C_2H_6$ | | |
| 1 | 100 | 0 | 0 | 4.2 | 1.1 |
| 2 | 82 | 11 | 7 | 11.6 | 1.3 |
| 3 | 69 | 3 | 28 | 22.4 | 1.8 |

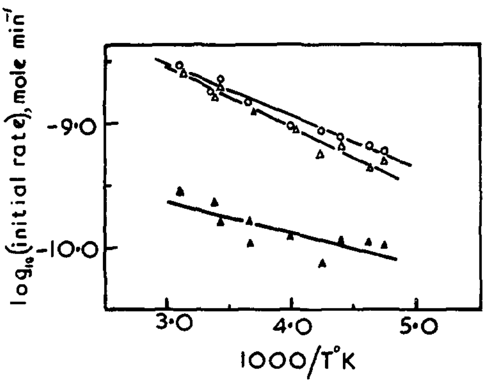

FIG. 3. Arrhenius plots for initial rates of hydrocarbon production from adsorbed methyl chloride: ○, $CH_4$; △, $C_2H_6$. ▲, $C_2H_4$.

It may be seen from Fig. 2 that the rate of product desorption increased as the layer thickness increased. However, it was found that at any given temperature the methyl chloride uptake reached a limiting value, so that the rate of product desorption reached a corresponding limit. Gas analyses at varying times during the desorption process showed that the hydrocarbon components were formed in relative proportions that were independent of time. In all cases, the desorption rates were independent of time (i.e., an apparent zero order process).

Table 1 shows for reactions at various temperatures the limiting methyl chloride uptake, the surface product composition, the rate of desorption and the distribution

TABLE 1

DATA FOR DECOMPOSITION REACTION OF ADSORBED ALKYL CHLORIDE

| | Temperature (°C) | Solid product layer | | % desorb.[a] ($C_1$ units) | Total decomposition rate ($10^{-9}$ mole $\text{min}^{-1}$) | Product distribution (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | $L$ | %Cl | | | $CH_4$ | $C_2H_4$ | $C_2H_6$ |
| $CH_3Cl$ | −78 | 8.6 | 68 | 52 | 0.65 | 79 | 10 | 11 |
| | −63 | 13.6 | 70 | 57 | 1.19 | 50 | 9 | 41 |
| | −55 | 19.7 | 75 | 66 | 1.22 | 55 | 9 | 36 |
| | −46 | 24.6 | 66 | 48 | 1.52 | 52 | 8 | 40 |
| | −36 | 14.0 | 72 | 60 | 1.53 | 57 | 5 | 38 |
| | −23 | 24 | 67 | 50 | 2.27 | 57 | 5 | 38 |
| | 0 | 70.5 | 57 | 25 | 3.06 | 48 | 4 | 48 |
| | 20 | 70 | 63 | 41 | 4.90 | 47 | 4 | 49 |
| | 50 | — | — | — | 6.29 | 48 | 5 | 47 |
| $CH_2Cl_2$ | −23 | 21 | 72 | 21 | 0.36 | 37 | 57 | 6 |
| | −15 | 28 | 72 | 19 | 0.47 | 53 | 43 | 4 |
| | 0 | 26 | 69 | 11 | 0.37 | 60 | 35 | 5 |
| | 11 | 45 | 69 | 11 | 0.40 | 52 | 43 | 5 |
| | 20 | 76 | 69 | 9 | 0.54 | 56 | 40 | 4 |

[a] % of adsorbed carbon that had desorbed in 1½–2 hr: a reasonably good approximation to infinite time, since the desorption rate was then very slow.

of desorbed products, for reactions with methyl chloride and methylene chloride. The overall C/H ratio in the surface product layer may be obtained from a mass balance, and for all experiments with methyl chloride the composition lay in the range $CH_{2.7}$ to $CH_{2.9}$, and for methylene chloride it was always close to $CH_{1.9}$.

From the variation in rate of formation of individual desorption products with temperature (Fig. 3), activation energies and frequency factors were obtained and the values are recorded in Table 2 for reaction from methyl chloride. With methylene chloride the data were not sufficiently extensive for activation energies and frequency factors to be evaluated with any accuracy. However, the available data showed that these parameters were of the same order of magnitude as from methyl chloride.

TABLE 2

KINETIC PARAMETERS FOR DECOMPOSITION REACTION OF METHYL CHLORIDE

| Product | $E$ (kcal $\text{mole}^{-1}$) | $\log_{10} A$ (molec $\text{sec}^{-1}$ $\text{cm}^{-2}$) |
|---|---|---|
| $CH_4$ | 1.9 ± 0.6 | 12.4 ± 0.2 |
| $C_2H_4$ | 1.2 ± 0.9 | 10.9 ± 0.4 |
| $C_2H_6$ | 2.4 ± 0.6 | 12.7 ± 0.2 |

Hydrogen chloride was rapidly and irreversibly adsorbed on a virgin sodium surface, but the presence of this adsorbed hydrogen chloride up to a thickness of $L \simeq 9$ was without effect on the subsequent behavior of a dose of methyl chloride. Similarly, hydrogen gas when activated by a hot wire is rapidly taken up by a virgin sodium film, (*11*) but this preadsorbed hydrogen had no effect on the rate or product distribution from the decomposition reaction of layers subsequently formed from methyl chloride or methylene chloride. On the other hand, the addition of a dose of hydrogen chloride, typically of about $3 \times 10^{17}$ molecules HCl, to a methyl chloride product layer of limiting thickness, resulted in the rapid desorption of methane and the rapid uptake of hydrogen chloride. After hydrogen chloride uptake had ceased, the decomposition reaction continued at approximately the same rate as prior to the admission of the hydrogen chloride dose.

### *Reactions in the Presence of Gaseous Alkyl Chloride*

At temperatures between 20° and 60°C and at pressures between 0.3 and 1.2 torr extensive reaction of gaseous methyl chloride was observed at the surface of a sodium film. Ethane was the dominant reaction product, together with a small amount of methane, the latter being typically 10% of the former. A mass balance showed that of the reacted methyl chloride, all of the chlorine, and about half of the carbon were incorporated into the film. The course of a typical reaction is shown in Fig. 4. The increasing ethane pressure and decreasing methyl chloride pressure were linearly related, as shown in Fig. 5 for a number of temperatures. The temperature dependences of the initial rates of methyl chloride reaction are shown in Fig. 6 and the corresponding Arrhenius parameters are recorded in Table 3. It was found that the initial rate of disappearance of methyl chloride and the initial rate of formation of ethane increased with increasing methyl chloride pressure, but the data were not sufficiently accurate at short reaction times for pressure dependence exponents to be obtained.

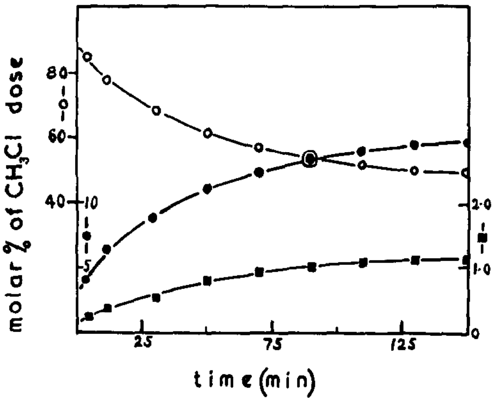

FIG. 4. Reaction in the presence of gas-phase methyl chloride on sodium at 40°C. Initial methyl chloride pressure 0.65 torr: ○, $CH_3Cl$; ●, $C_2H_6$; □, $CH_4$. The balance of the reacted methyl chloride formed the surface product layer.

TABLE 3

KINETIC PARAMETERS FOR REACTIONS WITH GAS-PHASE METHYL CHLORIDE

| | $E$ (kcal mole$^{-1}$) | $\log_{10} A$ (molec sec$^{-1}$ cm$^{-2}$) |
|---|---|---|
| $CH_3Cl$ | 4.8 ± 2 | 15.1 ± 3 |
| $CH_4$ | 3.0 ± 2 | 13.2 ± 4 |
| $C_2H_6$ | 4.9 ± 2 | 15.4 ± 4 |

Reactions with methylene chloride were carried out at temperatures between 40° and 60°C and at a pressure of about 1 torr. Initial rates of formation of the reaction

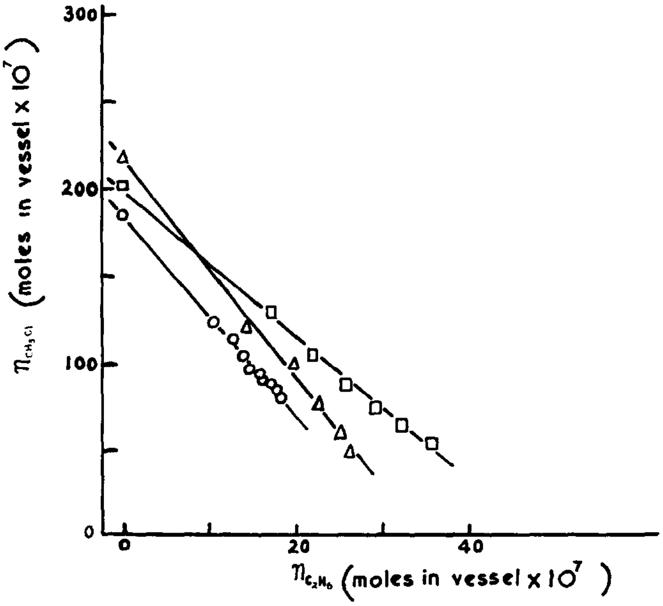

FIG. 5. Dependence of ethane concentration on methyl chloride concentration during course of the reaction: ○, 28°C; □, 50°C; △, 60°C.

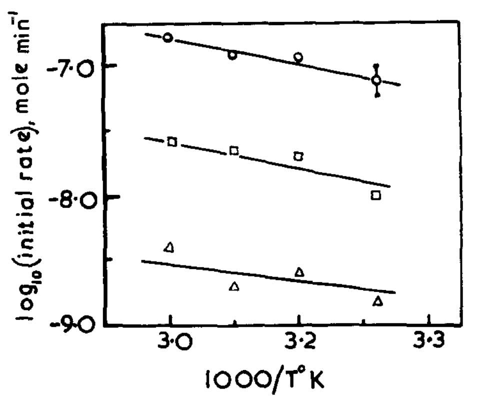

FIG. 6. Arrhenius plots for initial rates of reaction in the presence of gas-phase methyl chloride: ○, $CH_3Cl$; □ $C_2H_6$; △, $CH_4$.

products are contained in Table 4. The main reaction products were methane and ethylene together with a trace of ethane. Because of the relative inaccuracy in analysis for methylene chloride in the reaction mixtures, accurate rate data were not obtained; however, the data were sufficient to indicate that the activation energies and frequency factors were of the same order of magnitude as with methyl chloride.

TABLE 4
INITIAL RATES OF PRODUCT FORMATION FROM REACTION WITH GAS-PHASE METHYLENE CHLORIDE

| Temperature (°C) | Initial rate of formation ($10^{-9}$ mole min$^{-1}$) | |
|---|---|---|
| | $CH_4$ | $C_2H_4$ |
| 40 | 5.5 | 5.2 |
| 50 | 6.8 | 6.6 |
| 60 | 6.9 | 6.8 |

Reaction of gas-phase methyl chloride over a surface layer preformed from methylene chloride gave a product distribution generally similar to that arising from methyl chloride alone.

### *Isotopic Reactions*

The reaction was studied at 28° and 60°C between normal gas-phase methyl chloride at 0.6 torr, and a surface product layer previously formed from methyl chloride-$^{13}C$. After varying reaction times the gas phase was analyzed for the $^{13}C$ content of the ethane and of the methyl chloride. Under no circumstances was any of the surface $^{13}C$ returned into the gas-phase methyl chloride. The ethane reaction product contained ethane-1-$^{13}C$, and at 60°C the proportion ranged from 30% after 5 min reaction to 20% after 130 min; at 28°C the proportion ranged from 23% after 20 min reaction to 14% after 70 min. In no case was any ethane-1,2 $^{13}C$ detected above the amount expected from normal isotopic abundances.

The possibility of exchange between unfragmented methyl chloride molecules was checked by carrying out a reaction with a gas-phase mixture containing both methyl chloride-$^{13}C$ and methyl chloride-$^{35}Cl$. Reaction was carried out at 50°C with a gas pressure of 0.7 torr. No doubly labeled methyl chloride was detected in the gas phase for reaction periods up to 90 min.

### *Photoreactions*

The effects of light intensity and wavelength on the reaction were studied at temperatures of 28° and 40°C and with a methyl chloride pressure of 1.2 torr. The results from a typical experiment are shown in Fig. 7, where the reaction surface was illuminated with mercury radiation at 4358 and 5460 Å. It is seen that this illumination caused a marked increase in the rate of ethane production. Figure 8 shows the dependence of the rate of photoformation of ethane on the relative quantum intensity ($Q$), for light of varying frequencies. Figure 8 also shows that the effect was limited to wavelengths within the $F$-center absorption band of sodium chloride. Here, the rate of the photoreaction has been taken as the increase in the reaction rate due to illumination, over the corresponding prevailing dark rate. The relative intensity ($Q$) at a frequency is defined to be proportional to the rate of arrival of light quanta of that frequency which are incident upon the window of the reaction vessel. Values of $Q$ were obtained on a relative scale from the output of the thermopile. The rate of photoformation of ethane is best represented as a linear function of $Q^2$ although the precision of the data is not high. The photo-

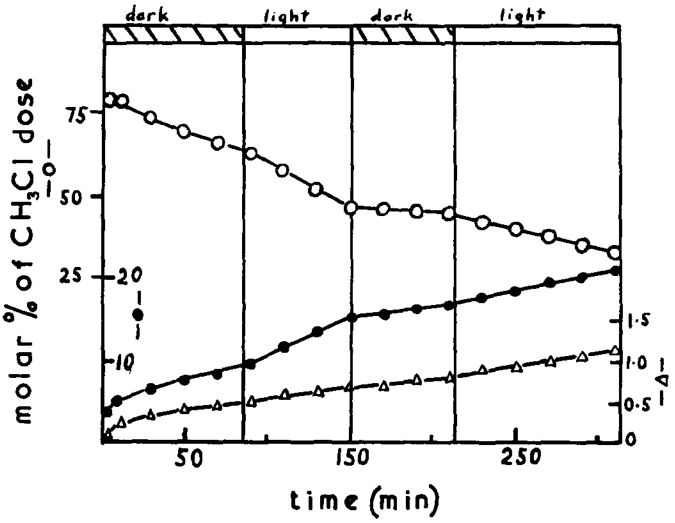

FIG. 7. Photoreaction of methyl chloride on sodium at 40°C. Initial methyl chloride pressure 0.8 torr. Illumination in the sodium chloride *F* band. ○, $CH_3Cl$; ●, $C_2H_6$; △, $CH_4$. The balance of the reacted methyl chloride formed the surface product layer.

rates did not depend significantly on temperature in the range 28° to 40°C.

During the photoreaction, the rate of carbon incorporated into the surface product layer remained the same as in the dark reaction.

The effect of illumination on the rate of decomposition of a surface product layer was determined (i.e., in the absence of gas-phase methyl chloride). Within experimental error, illumination was without effect.

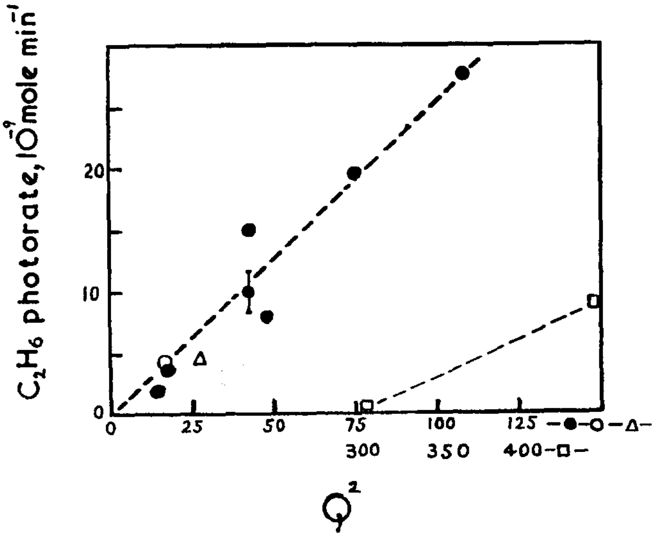

FIG. 8. Dependence on $Q^2$ of rate of photoformation of ethane from methyl chloride reaction with sodium: (a) ●, mercury light filtered in the *F* band of sodium chloride, 40°C reaction temperature; (b) ○ same as (a), but at 28°C; (c) △, mercury light filtered to yield only the 3660-Å line, 40°C; (d) □, light from sodium vapor lamp, 40°C. In all cases, the values for the quantum intensities *Q* are expressed on a relative scale.

### *Photoreactions with Isotopic Labeling*

The effect of illumination was studied on the reaction between normal gas-phase methyl chloride and a surface product layer previously formed from methyl chloride-$^{13}C$. The reaction was carried out at 40°C with a methyl chloride pressure of 0.6 torr, and with illumination using mercury lines at 4358 and 5460 Å. The results are given in Table 5 for the proportion of ethane-1-$^{13}C$ appearing in the ethane reaction product: for comparison, Table 5 also includes corresponding data for the simultaneous dark reaction. It is seen that the proportion of ethane-1-$^{13}C$ in the ethane product was substantially reduced in the photoreaction and in fact was equivalent to the ethane-1-$^{13}C$ arising from the dark reaction only.

## DISCUSSION

### *Dark Reactions*

We may assess the nature of the species by which carbon is incorporated into the surface product layer by referring to the properties of the alkali-metal alkyls. This problem has been reviewed by Morton (*3*) and by Coates (*12*), who concluded from an examination of physical and electrical properties that in lithium alkyls the Li–C bond is essentially covalent, but in sodium and potassium alkyls, the bond has a high degree of ionic character so that the organic group in them can be considered as a carbanion. This difference is probably due to the high polarizing power of the small lithium ion. In view of this, we propose to proceed on the assumption that all of the carbon that is incorporated into the surface product layer from methyl chloride is present as $CH_3^-$, while that from methylene chloride is $CH_2^{2-}$. These postulates are in approximate agreement with the observed carbon/hydrogen stoichiometry of the incorporated material. The likelihood of $CH_3^-$ in a product layer may also be judged in relation to the following $\Delta H$ values:

$$CH_3Cl(g) + e \rightarrow CH_3\cdot(g) + Cl^-(g) \qquad \Delta H_{298} = -5\text{kcal} \qquad (1)$$

$$CH_3Cl(g) + 2e \rightarrow CH^-(g) + Cl^-(g) \qquad \Delta H_{298} = -32\text{kcal} \qquad (2)$$

where the data have been taken from ref. (*13*), and in each case the free electron is assumed to be at zero kinetic energy and at zero electrostatic potential. In an ionic solid the formation of $CH_3^-$ would be energetically still more favorable relative to $CH_3\cdot$.

We thus propose that the overall processes by which the surface product layers are formed may be represented by

$$2Na + CH_3Cl \rightarrow (2Na^+ + Cl^- + CH_3^-) \text{ surface layer} \qquad (3)$$

$$4Na + CH_2Cl_2 \rightarrow (4Na^+ + 2Cl^- + CH_2^{2-}) \text{ surface layer} \qquad (4)$$

However, it must be recognized that these processes occur, in fact, as tarnishing reactions so that diffusion through the surface layer must occur for the reaction to be propagated. In the decomposition reactions the hydrocarbon products are then formed by further reaction from $CH_3^-$ and from $CH_2^{2-}$.

In the decomposition reaction from a methyl chloride surface product layer, it was found that preadsorbed hydrogen was without effect on the product distribution, and in particular there was no increase in the proportion of methane. It thus appears that methane is not produced by reaction between methyl and hydride ions, but rather by a hydrogen absorption reaction between two methyl ions

TABLE 5

RESULTS FROM REACTION AT 40°C OF $CH_3Cl$ WITH SURFACE LAYER FORMED FROM $^{13}CH_3Cl$

| | Dark reaction | | Photoreaction | |
|---|---|---|---|---|
| Reaction time (min) | Total "ethane" formed ($10^{-7}$ mole) | % Ethane-1-$^{13}C$ in product | Total "ethane" formed ($10^{-7}$ mole) | % Ethane-1-$^{13}C$ |
| 14 | 0.52 | 27.0 | 3.2 | 4.1 |
| 37 | 0.84 | 24.8 | 3.4 | 3.4 |

$$2CH_{3(s)}^{-} \rightarrow CH_4 + CH_{2(s)}^{2-} \qquad (5)$$

Ethane was a major product from the decomposition of a methyl chloride layer, while ethylene was a major product from a methylene chloride layer. We formulate these reactions as

$$2CH_{3(s)}^{-} \rightarrow C_2H_6 + 2e_{trap(s)} \qquad (6)$$

$$2CH_{2(s)}^{2-} \rightarrow C_2H_4 + 4e_{trap(s)} \qquad (7)$$

where the electrons are trapped in the product layer, probably in the vacancies created by the reaction; in reactions (5)–(7) the subscripts (s) indicate that the reactions most probably occur at the surface. In the approximation of formulating the surface layer as having a sodium chloride lattice, we should formulate $CH_{3(s)}^{-}$ as existing in a surface anion site, that is as $CH_3^-|\square_{(s)}^-$. The ion such as $CH_{2(s)}^{2-}$ could be similarly sited, although being doubly charged it would be sited to energetic advantage with a di-vacancy, that is as $CH_2^{2-}|(\square_{(s)}^-)_2$.

It was found that addition of hydrogen chloride to a methyl chloride surface product layer resulted in rapid desorption of methane only during the process by which hydrogen chloride was being taken up. Inasmuch as surface hydride is inert, we propose that this methane desorption occurs by

$$HCl + CH_{3(s)}^{-} \rightarrow CH_4 + Cl_{(s)}^{-} \qquad (8)$$

and the occurrence of this reaction is in line with the reactions observed when gas-phase methyl chloride was present (see below).

It is instructive to compare from Table 6 the rates at which the various hydrocarbon products were formed in the decomposition reaction and in the reaction with gas-phase methyl chloride. In Table 6, initial rates are given for the comparison to be made. It will be seen that methane and ethylene were formed at comparable rates in both types of reaction and from this we conclude that, irrespective of the presence of gas-phase methyl chloride, methane and ethylene were formed by a decomposition reaction. Furthermore, the data in Table 1 show that at 20°C ethylene was formed in a decomposition reaction from a methylene chloride layer at about $0.2 \times 10^{-9}$ mole min$^{-1}$ and this is again close to the rate of formation from the decomposition reaction of a methyl chloride layer, in agreement with the suggestion that reaction (7) is responsible in both cases. On the other hand, Table 6 shows that in the presence of gaseous methyl chloride, ethane was formed at a very much faster rate than from the decomposition reaction. From this we conclude that in the presence of gaseous methyl chloride almost all the ethane is formed by a reaction directly involving methyl chloride molecules from the gas phase. On this basis, the formation of ethane-1-$^{13}C$ in the reaction between methyl chloride and a surface layer formed from methyl chloride-$^{13}C$ occurs via

TABLE 6

COMPARISON OF INITIAL RATES OF FORMATION OF VARIOUS PRODUCTS FROM DECOMPOSITION REACTION AND FROM REACTION IN THE PRESENCE OF GASEOUS METHYL CHLORIDE

| Product | Initial rate at 50°C ($10^{-9}$ mole min$^{-1}$) | | |
|---|---|---|---|
| | Decomposition reaction (A) | Reaction with gas-phase $CH_3Cl$ (B) | Ratio (B/A) |
| $CH_4$ | 2.6 | 2.0 | 0.8 |
| $C_2H_4$ | 0.2 | 0.2 | 1.0 |
| $C_2H_6$ | 2.9 | 23.7 | 8.2 |

$$^{13}CH_{3(s)}^{-} + CH_3Cl \rightarrow {}^{13}CH_3{-}CH_3 + Cl_{(s)}^{-} \qquad (9)$$

Reactions (8) and (9) are clearly analogous. However, the proportion of $^{13}CH_3$–$CH_3$ in the ethane was such that reaction (9) only accounted for up to 30% of the desorbed ethane; the only avenue for the formation of the balance of the ethane is from a reaction between a pair of adsorbed undissociated molecules. The fact that a significant amount of ethane-1,2-$^{13}C$ was not formed means that in the presence of gaseous methyl chloride, reaction (5) was of little relative importance, in agreement with the conclusion drawn previously from a comparison of rate data.

We now need to discuss in greater detail the precursors that lead to incorporation and to the required reaction between undissociated methyl chloride molecules. For the sake of simplicity the rest of the discussion will be formulated in terms of reactions with methyl chloride, and the electronic properties of the surface product layer will be discussed by reference to the known behavior of the alkali halides. In the reaction between a pair of undissociated methyl chloride molecules, it is most unlikely that the molecules should be merely physically adsorbed; adsorption involving substantial charge transfer would certainly be required to effect a sufficient modification in reactivity. The ionization potential of $CH_3Cl$, that is the energy required to form $CH_3Cl^+$, is certainly in excess of 200 kcal mole$^{-1}$ [cf. Field and Franklin (*14*)]. Since one could only expect to recoup a small fraction of this energy by Coulombic interaction with the surface, adsorption as $CH_3Cl^+$ is very unlikely. On the other hand, Harcourt (*15*) has calculated a favorable electron affinity for methyl chloride of about 2 eV, the electron entering the lowest unoccupied antibonding orbital, to give $CH_3Cl^-$. The effect of this would be expected to weaken the C–Cl bond and so enhance the reactivity. Since adsorption as $CH_3Cl^-$ must be at a crystallographically sensible site on the surface, we suggest that this ion occupies a surface anion vacancy. Since in the dark an alkali halide crystal is not an electronic conductor (*16*) there are no *free* electrons available. Therefore, we suggest that adsorption of methyl chloride occurs at a surface *F* center, so that we formulate adsorption as

$$CH_3Cl + \mathrm{e}|\square_{(s)}^- \rightarrow CH_3Cl^-|\square_{(s)}^- \qquad (10)$$

The adsorbed species $CH_3Cl^-|\square_{(s)}^-$ may then react to form ethane in two ways. A reformulation of reaction (9) is

$$CH_3Cl^-|\square_{(s)}^- + {}^{13}CH_3^-|\square_{(s)}^- \rightarrow {}^{13}CH_3\text{—}CH_3 + Cl^-|\square_{(s)}^- + \mathrm{e}|\square_{(s)}^- \qquad (11)$$

and the reaction between undissociated methyl chloride is now formulated as

$$2CH_3Cl^-|\square_{(s)}^- \rightarrow C_2H_6 + 2Cl^-|\square_{(s)}^- \qquad (12)$$

Of course, in the absence of $^{13}C$ surface layer, both reactions (11) and (12) occur simultaneously to give the same product, $C_2H_6$. The incorporation reaction also proceeds from $CH_3Cl^-|\square_{(s)}^-$ as a precursor, by reaction with another surface *F* center

$$CH_3Cl^-|\square_{(s)}^- + \mathrm{e}|\square_{(s)}^- \rightarrow CH_3^-|\square_{(s)}^- + Cl^-|\square_{(s)}^- \qquad (13)$$

It should be noted that all the species $\mathrm{e}|\square_{(s)}^-$, $CH_3^-|\square_{(s)}^-$, $CH_3Cl^-|\square_{(s)}^-$ carry approximately zero net charge with respect to the lattice, and thus there are no large Coulombic repulsions to be overcome as the reacting species in reactions (11)–(13) approach each other. *F* centers will be generated by solution of sodium into the product layer at the sodium/product layer interface, and in the absence of illumination, the number of these converted to a free anion vacancy and free electron will be vanishingly small. It may be noted that the surface product layer was always colored pink, and this color is similar to that of *F*-center-containing sodium chloride. Electron transfer adsorption of organic dyes at *F* centers has recently been observed by Rakityanskaya (*17*).

### *Reactions under Illumination*

The essentially important results from experiments under illumination are that neither the incorporation process via reactions (10) and (13), nor the mode of ethane formation that proceeds via reactions (10) and (11), are photoaccelerated; however, there does occur an ethane formation reaction which *is* photoaccelerated. In other words, the photoaccelerated ethane-producing reaction must involve reaction between adsorbed undissociated molecules. The immediate question is, What is the mechanism of this latter process? Sodium chloride *F*-band radiation (band center at 4650 Å) is a long way below the energy required electronically to excite a gas-phase methyl chloride molecule of which the long wavelength absorption edge is at about 1900 Å [Hertzberg and Scheibe (*18*)]. Furthermore, this difference is so great that it is inconceivable that mere physical adsorption could so modify the molecular energy levels that electronic excitation of a physically adsorbed molecule could result from *F*-band radiation.

Illumination of *F*-center-containing alkali halide with light in the *F* band has two consequences: (a) the creation of photoconductivity in the specimen by the ejection of electrons into the conduction band (*16*), and (b) the conversion of *F* centers in the crystal into aggregates (*19, 20*). The type of aggregate so formed depends on the conditions. Potassium chloride is the substance to have been most extensively studied, and using the results with this material by way of example (*19, 20*), we note that for illumination at about room temperature, the overwhelmingly dominant process is the formation of *M* centers, the latter being structurally specific dimers of *F* centers. We shall designate the surface *M* center as $(e|\square_{(s)}^-)_2$.

We consider that there is no reasonable mechanism for photoaccelerated ethane production which makes specific use of photogenerated electrons since (a) the presence of free electrons cannot accelerate ethane production via any of the reactions (10)–(13) and (b) the use of a free electron to produce $CH_3Cl^-$ adsorbed in some manner other than at a vacant anion site would result in an impossibly high Coulombic repulsion between the two adsorbed molecular ions which must react together to produce the ethane. We suggest that photoaccelerated ethane formation proceeds via methyl chloride adsorption at a surface *M* center

$$2e|\square_{(s)}^- \xrightarrow{h\nu} (e|\square_{(s)}^-)_2 \qquad (14)$$

$$(e|\square_{(s)}^-)_2 + 2CH_3Cl \rightarrow (CH_3Cl^-|\square_{(s)}^-)_2 \qquad (15)$$

followed by

$$(CH_3Cl^-|\square_{(s)}^-)_2 \rightarrow C_2H_6 + 2Cl^-|\square_{(s)}^- \qquad (16)$$

In suggesting reactions (14)–(16), we note that the possibility of illumination merely increasing the rate of reaction (12) by increasing the mobility on the surface of $CH_3Cl^-|\square_{(s)}^-$ must be rejected. If this were to occur, there is no apparent reason why reaction (11) should not be similarly photoaccelerated, yet this was not observed. The lack of photoacceleration with reaction (11) also argues against the possibility that illumination leads to enhanced reactivity of $CH_3Cl^-|\square_{(s)}^-$ by photoexcitation.

It is clear than on the postulated mechanism, the transition states for ethane production by reactions (12) and (16) must be virtually the same. The crux of the argument which distinguishes ethane formation by the photoreaction is that if free *F* centers are present, there exists a photomechanism by which a pair of *F* centers can be easily brought into adjacent proximity on the surface prior to methyl chloride adsorption. This model assumes that methyl chloride adsorption is relatively weak so that in the dark only a small fraction of all surface *F* centers are occupied by adsorbed methyl chloride, and those that are unoccupied are available for *M*-center formation upon illumination. This conclusion about the strength of methyl chloride adsorption is in agreement with kinetic model adopted in the next section. Alternatively, if *M*-center mobility is sufficient, they could be formed in the bulk and diffuse to the surface. Inasmuch as *F* centers are probably of higher mobility than *M* centers, the former is the more likely process.

It remains to comment upon the observed dependence of the rate of photoformation of ethane on light intensity, and its relation to the known dependence of the rate of *M*-center formation on light intensity. Both Bron and Norwick (*21*) and van Doorn (*22*) observed that the rate of *M*-center formation in potassium chloride was proportional to *F*-band light intensity to the first power, and at a sufficiently high intensity, it tended to become independent of intensity. Delbecq (*23*) found the rate of *M*-center formation proportional to about $(\text{intensity})^{0.3}$ suggesting he was limited to the intermediate intensity region. On the other hand, the present results show that the rate of photoformation of ethane is best represented by proportionality to $(\text{intensity})^2$, although the precision of the data is not high.

The present *F*-band light intensities are of the order $10^{14}$ to $10^{15}$ quanta $cm^{-2}$ $sec^{-1}$, and this lies in the range where, from the data of Bron and Norwick (*21*) and van

Dorn (*22*) a linear dependence of rate of *M*-center formation on intensity would be expected. If this is so, it is clear that if a steady state in the concentration of surface species $(e|\square_{(s)}^-)_2$ and $(CH_3Cl^-|\square_{(s)}^-)_2$ is established, the rate of ethane production would, from reactions (14)–(16), be proportional to the first power of light intensity. However, there is reason to believe that, with the time scale of the present photoexperiments up to 60 min or so, such a steady state was not reached. For instance, Delbecq (*23*) showed that with *F*-center concentrations in potassium chloride in the range $1.8 \times 10^{17}$ to $0.27 \times 10^{17}$ centers $cm^{-3}$ and at temperatures in the range 0–30°C, the time required for the *M*-center concentration to reach its maximum value was in the range 12-160 min, with lower *F*-center concentrations needing longer times. In potassium chloride, an *F*-center concentration of $10^{17}$ centers $cm^{-3}$ requires for its generation, for instance, a potassium pressure of about 0.5 torr at 440°C (*24*). From this rough comparison, we believe it is reasonable to expect the surface *M*-center concentration to be rising throughout the course of an experiment. The effect of this would be to raise the power of the apparent exponent of the intensity in its relation to the rate of ethane production: on this basis the observed value of about 2 is merely fortuitous.

### *General Comments*

It is the incorporation reaction that results in growth of the surface product layer thickness, and since the rate decreases as the thickness grows, the reaction behaves as a typical tarnishing reaction which is probably controlled by the rate of arrival of *F* centers at the gas/solid interface. We shall assume that the constant pressure growth law for the product layer is parabolic, i.e., $dX/dt = kX^{-1}$, where $X$ is the layer thickness, since this law corresponds to diffusion under a linear concentration gradient. Since the incorporation reaction (13) is reached via reaction (10), the rate of incorporation would be proportional to the first power of methyl chloride pressure, provided methyl chloride adsorption is not too strong. Thus, the rate of decrease of the amount of methyl chloride and done up in the reaction vessel due to the incorporation reaction is given by

$$-\frac{dn_m}{dt} = \frac{k_1 n_m}{n_m^0 - n_m - n_e} \qquad (17)$$

where $n_m$ and $n_e$ are the numbers of moles of carbon contained in methyl chloride and ethane, respectively, in the reaction vessel at time $t$, $n_m^0$ is the initial value of $n_m$, and $(n_m^0 - n_m - n_e)$ is proportional to $X$. It was found that $n_e$ and $n_m$ were linearly related during the course of an experiment as shown in Fig. 5. Moreover, this relation includes the point $n_m = n_m^0$ when $n_e = 0$. Thus, this relation may be expressed as

$$n_e = b(n_m^0 - n_m)$$

where $b$ is the slope of the plot of $n_e$ vs. $n_m$ from Fig. 5. Note that only a fraction of the reacted methyl chloride yielded methane and this is reflected in the value of $b$. Equation (17) thus becomes

$$-\frac{dn_m}{dt} = \frac{k_1 n_m}{(1 - b)(n_m^0 - n_m)} \qquad (18)$$

Integration of Eq. (18) with $n_m = n_m^0$ when $t = 0$, gives

$$\log_{10}(n_m^0/n_m) - (n_m^0 - n_m)/2.303 n_m^0 = k_1 t/2.303 n_m^0 (1 - b)$$

The general validity of the model adopted to represent the reaction is demonstrated by the ability of Eq. (19) adequately to represent the observed dependence of $n_m$ on time, as shown in Fig. 9. Values of $b$ were taken from the data in Fig. 5 and these values, together with the corresponding values of $n_m^0$ are given in the legend to Fig. 9. The values of $k_1$ evaluated from Fig. 9 lead to an activation energy of $6 \pm 2$ kcal $mole^{-1}$ which is, within the (large) limits of error, not significantly different from the value found from initial rates (Table 3).

Despite the apparent complexity of this

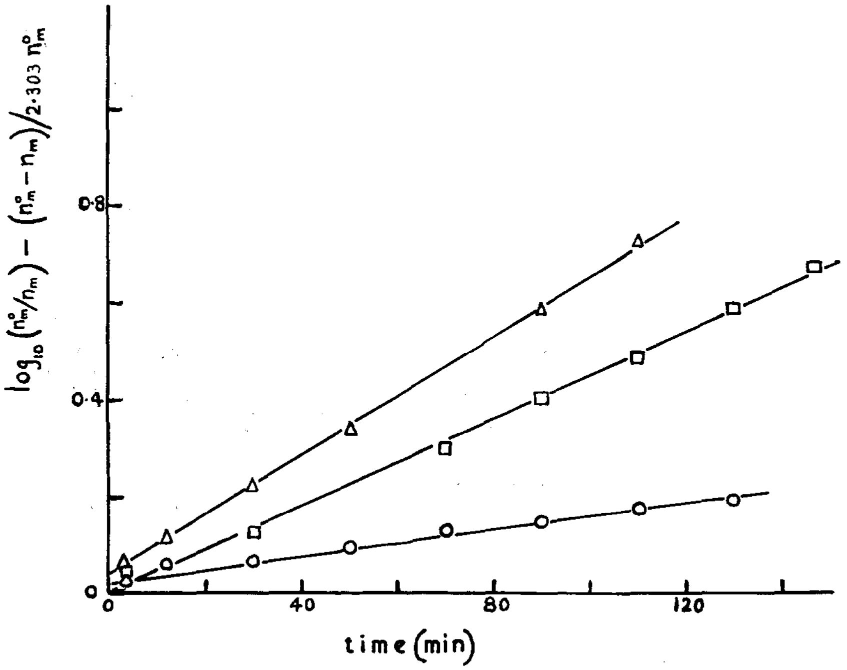

FIG. 9. Data plotted according to Eq. (19). The values for $b$ and $n_m^0$ were taken from data in Fig. 5: ○, 28°C, $b = 0.176$, $n_m^0 = 1.84 \times 10^{-5}$ mole; □, 50°C, $b = 0.233$, $n_m^0 = 2.03 \times 10^{-5}$; △, 60°C, $b = 0.158$, $n_m^0 = 2.17 \times 10^{-5}$.

reaction, we suggest that it is a reasonable model system to show how specific information available in great detail from studies in solid state physics can be of direct use for mechanistic interpretation.

The reaction between alkali-metal-doped alkai halide and methyl chloride may prove a system of great interest since, from the present results, one would expect to be able to incorporate $CH_3^-$ ions into the alkali halide matrix, and it should be possible to acquire these in sufficient concentration for them to be studied by optical and resonance spectroscopy.

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