Vibrationally Excited Methyl Chloride. I. The Rate of Production of CH_3Cl^*

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Abstract: The overall rate of the gas-phase reaction between diazomethane and hydrogen chloride has been measured spectrophotometrically, and the bimolecular rate constant was found to be 7×10^5 cm^3 mol^{-1} sec^{-1} at room temperature. The heterogeneous contribution to the overall reaction has been evaluated based on a proposed mechanism for it, and the bimolecular rate constant has been obtained by an appropriate correction. The observation of a slight *negative* activation energy of 0.3 kcal mol^{-1} led to the conclusion that the reaction proceeds through the formation of an intermediate complex in equilibrium with the reactants.

The gas-phase reaction of diazomethane with hydrogen halides to produce methyl halides and nitrogen

$$HX + CH_2N_2 \longrightarrow CH_3X + N_2 \qquad (1)$$

was first reported by Hassler and Setser.[2] It appears that the methyl iodide produced through reaction 1 has sufficient internal energy above its critical limit to dissociate. During the course of their investigation of this unimolecular process, they found that the overall reactions between diazomethane and the hydrogen halides were very fast, even at room temperature. By making competitive studies using several combinations of acid pairs, relative rates for the reaction of the three hydrogen halides were obtained. However, these measurements did not achieve a high level of self-consistency, as reflected by the large scatter in the data, so that the derived quantities are only approximate.

Preliminary to the detailed study of the reactivity of vibrationally excited methyl chloride[3] produced by reaction 1, we measured the absolute rate of the reaction as controlled by the concentrations of reactants, the effect of added inert gas, and the temperature.

In the initial explorations, we attempted to follow the rate thermometrically, intending to utilize the large exothermicity of the reaction ($\Delta H_{300}{}^\circ \approx -68$ kcal mol^{-1}). Thermocouples were placed in a spherical reaction vessel at various radial distances from the tip of a fine injection tube located at the center. Tests were also made in a similarly instrumented flow tube. However, in both cases the superposition of thermal diffusion in a turbulent gas and the unknown rate of heat released by the reaction made the temperature history an extremely complicated one. This approach was abandoned in favor of a spectrophotometric method of analysis.

Experimental Section

Materials. Hydrogen chloride, hydrogen bromide, methyl chloride, and methyl bromide were obtained from the Matheson Co. Diazold (N-methyl-N-nitroso-*p*-toluenesulfonamide) was used as the precursor of CH_2N_2, which was generated by the technique of Dessaux and Durand.[4] It was dried by passing the gas through a column of potassium hydroxide pellets and stored as a solution in di-*n*-butyl phthalate[5] at −78°.

Determination of Concentrations. Concentrations were determined *in situ* after completion of the reaction, from the intensity of infrared absorption measured with a Perkin-Elmer Model 521 spectrometer. Four rotational lines in the fundamental band (P4–P7) were selected for determining the hydrogen chloride pressure. For methyl chloride, the C–Cl stretch at 732 cm^{-1} was scanned to determine its concentration. In this manner, pressures as low as 0.2 Torr could be measured for these gases. The initial concentration of diazomethane was assumed to be the same as the final methyl chloride concentration. As established by numerous blank runs, the presence of less than 2% side product, mostly C_2 hydrocarbons, justified this assumption. For these measurements, the cell was filled with argon to a total pressure of 600 Torr to develop reproducible pressure broadening of the lines.

Spectrometer. The rate of reaction 1 was measured by monitoring the decrease in the diazomethane absorption band, centered at 2100 cm^{-1}. The spectrometer slits were set at 150 μ, which gave 20-cm^{-1} resolution, more than sufficient to isolate this band. An early vintage Perkin-Elmer Infracord was modified to provide a moderately fast response instrument. The 11-Hz mirror–chopper was replaced by a four-spoked, silvered brass mirror, and a faster driving motor was inserted so that a 132-Hz chopping frequency was attained. The thermocouple detector was replaced by a liquid-nitrogen-cooled gold-doped germanium detector. A lock-in amplifier, tuned to the chopping frequency, led to an oscilloscope, and the traces were photographed with a Polaroid camera.

The overall response time of the system was limited by the chopper frequency and by the tuned amplifier to 0.08 sec. Since the reaction half-life was about 2 sec, the instrument response time was sufficiently short so that large corrections for finite response time were avoided.

Reaction Vessel. A portable glass reaction vessel with sodium chloride windows (Figure 1) was constructed to fit the Infracord sample space; it was easily attachable to the vacuum line. After the mixing chamber was thoroughly evacuated, CH_2N_2–Ar and HCl–Ar mixtures were expanded into their respective bulbs (volumes and pressures measured) and the cell was placed into the spectrometer sample space. A fast turn of the double stopcock allowed the gases to expand rapidly into the cylindrical mixing chamber. The injection time was measured by recording the diazomethane band while concurrently injecting argon rather than hydrogen chloride. Several trials indicated that the in-flow rate was exponential, with a characteristic time of about 0.1 sec. A typical absorption histogram is shown in Figure 2a. From such traces, the rate for the wall decomposition of diazomethane in a well-seasoned glass vessel was found to be about 10^{-3} sec^{-1}, which is at least two orders of magnitude less than the bimolecular reaction rate with hydrogen chloride.

Data Analysis. A typical trace obtained on mixing the two reagents is shown in Figure 2b. The experimentally measured quantity was the absorption intensity as a function of time. In-

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[2] J. C. Hassler and D. W. Setser, *J. Amer. Chem. Soc.*, **87**, 3793 (1965).

[3] Part II, T. Baer and S. H. Bauer, *ibid.*, **92**, 4773 (1970).

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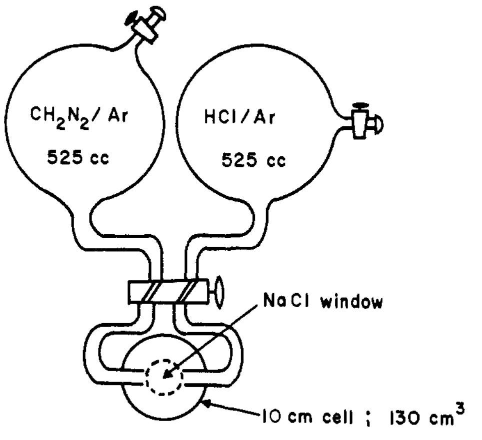

Figure 1. The reaction cell which was used for all the quantitative runs. The i.d. of the injection ports is 6 mm, giving a characteristic injection time of 0.1 sec.

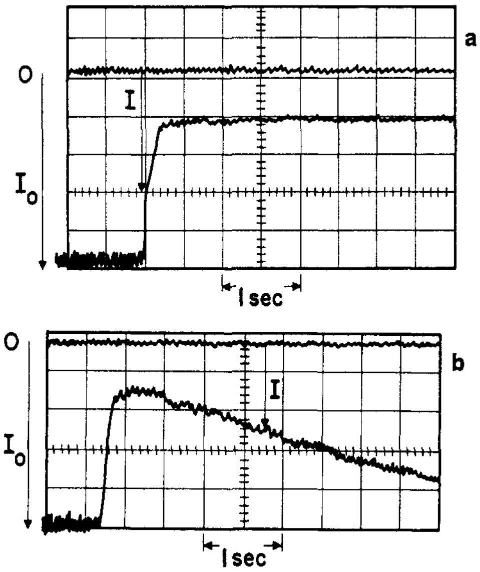

Figure 2. (a) The injection of diazomethane and argon into a well-seasoned mixing chamber. (b) A run showing the injection of diazomethane and its subsequent disappearance as a result of reaction with HCl. The peak of the curve is 1.35 Torr CH_2N_2.

tensity was converted to absorbance, and because the latter ranged from 0.0 to 0.20, it was assumed to be proportional to the concentration of diazomethane. The initial concentrations of this reagent were varied from 0.80 to 5.0 Torr. The result of such an analysis and the calculated variation of the bimolecular rate constant with time are illustrated in Figure 3. From this it is evident that a nonnegligible amount of diazomethane reacted during the injection period. In order to determine the diazomethane concentration at time t_0, the amount which reacted during the injection regime was estimated by assuming an exponential injection rate and a bimolecular reaction rate equal to that determined at t_0. The result of this calculation is shown as the dashed curve in Figure 3, for suitably selected magnitudes of the bimolecular rate constant and the characteristic injection time.

Results

Initial Rates. At constant inert gas pressure, a general rate expression may be written in the form

$$\text{rate} = k[CH_2N_2]^{\alpha}[HCl]^{\beta} \qquad (2)$$

For a group of experiments in which the initial hydrogen chloride concentrations are nearly equal, β may be set equal to unity without biasing the results. On this basis nine runs were made over a range of diazomethane concentrations, but with similar hydrogen chloride and argon concentrations, to determine the order of the reaction with respect to diazomethane. The bimolecular rate constant was extrapolated to the time when about 95% of injection was completed. Figure 4 is a plot of log (rate/[HCl]) *vs.* log $[CH_2N_2]$. The resulting line with a least-squares slope of 0.97 ± 0.11 shows the reaction to be first order in diazomethane. A similar analysis of runs from which the order with respect to hydrogen chloride was determined is illustrated in Figure 5. Four runs with very low HCl pressure (1–2 Torr) were not included in Figure 5. As will be shown later, there is a significant surface component in this reaction, the net rate of which is controlled by diffusion. The low-pressure hydrogen chloride runs are particularly affected by this heterogeneity, which resulted in anomalously high initial rates for these four runs.

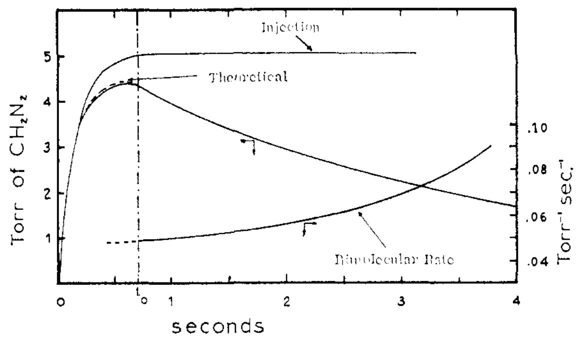

Figure 3. A complete analysis of a representative run, showing the calculated fit obtained in the injection region (dashed curve) as well as the variation of the bimolecular rate constant during the course of the reaction.

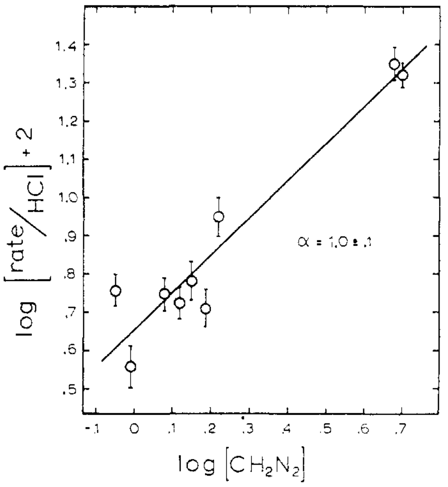

Figure 4. A plot of the initial rates for runs with constant HCl concentrations (6–7 Torr). The total argon pressure was 200 Torr. The calculated slope (least squares) represents the reaction order with respect to CH_2N_2.

The uncertainty in measuring the low diazomethane (methyl chloride) pressures is probably the major source of error. Although there is considerable scatter, the reaction as analyzed on the basis of initial slopes is clearly first order in diazomethane and first order in hydrogen chloride with an average rate constant of $(7.0 \pm 1.0) \times 10^5$ mol^{-1} cm^3 sec^{-1}. The correspond-

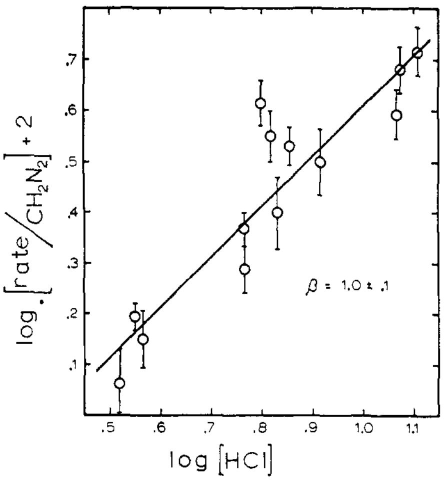

Figure 5. A plot of the initial rates for runs with constant CH_2N_2 concentrations (1–1.5 Torr). The total argon pressure was 200 Torr. The calculated (least squares) slope represents the reaction order with respect to HCl.

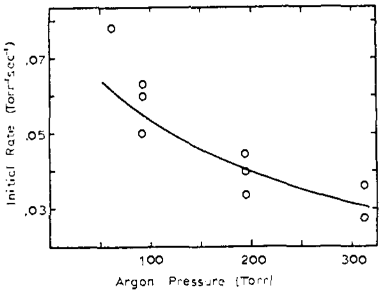

Figure 6. The effect of inert gas (argon) pressure on the *initial* rate of reaction.

ing reaction with HBr was found to be faster by a factor of 4, with a bimolecular rate constant of (3 ± 1) × 10^6 mol^{-1} cm^3 sec^{-1}. Hassler and Setser[2] collected data from which they estimated the rate for HBr relative to HCl to be 9 ± 2. However, their scatter was rather large; they cited values ranging from 1.8 to 22.4.

The Effect of Inert Gas. All of the above deductions are based on experiments made with a constant inert gas pressure of 200 Torr. Figure 6 shows that the rate does vary inversely with argon pressure. No mechanism based on complex formation, nor indeed any homogeneous mechanism that was tested, accounted for such a rate inhibition by argon. We concluded that part of the reaction takes place on the walls.

The increase in the bimolecular rate constant during the course of the reaction (Figure 3) also indicates that the reaction is not strictly bimolecular over the entire reaction period. But this does not contradict the conclusion based on consideration of *initial* rates, because the geometry of the reaction cell must be taken into account. The portion of gas which is monitored by the infrared beam is about 1 cm from the glass tube injection ports. It is plausible to assume that during the initial stage, the reaction, as sensed by the ir beam, is homogeneous, while the heterogeneous part of the reaction does not become significant until a steady state with respect to diffusion is established. This is supported by the following data.

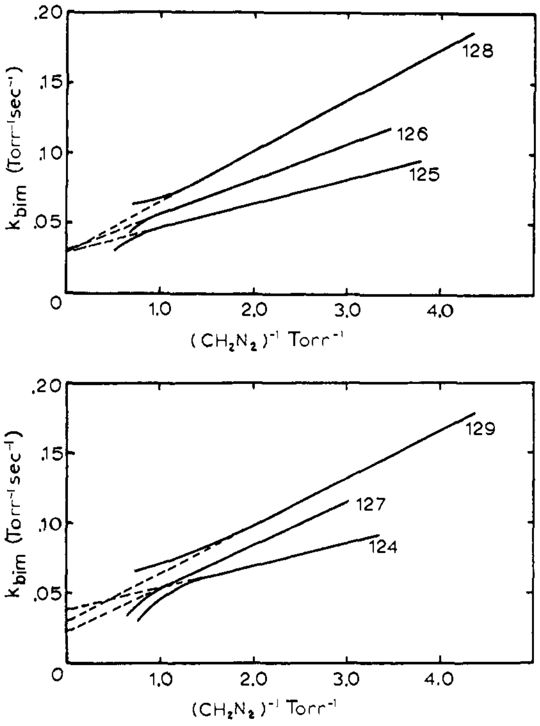

Figure 7. Runs 124–129 plotted according to eq 3. The slope is the heterogeneous rate constant which is first order in HCl, while the extrapolated intercept is the homogeneous bimolecular rate constant.

The manner in which the bimolecular rate increases, first slowly and then more rapidly as diazomethane is depleted, suggests that an empirical rate law of the form (3) represents the data. Hence, a plot of

$$\begin{aligned}\text{rate} &= k_1[CH_2N_2][HCl] + k_2[HCl] \\ &= \left[k_1 + \frac{k_2}{[CH_2N_2]}\right][CH_2N_2][HCl]\end{aligned} \tag{3}$$

k_{bim} against $[CH_2N_2]^{-1}$ should result in a straight line for which k_1 is the intercept and k_2 is the slope. Figure 7 shows that such an expression is obeyed, particularly toward the end of the reaction period. The initial portions do not fall on the line as a result of the failure to achieve steady state with respect to diffusion. Further evidence for this explanation is the observation that the initial deviation is more pronounced in the high-pressure runs than those at low pressures.

A mechanism in which a homogeneous bimolecular reaction is augmented with a heterogeneous reaction between gaseous CH_2N_2 and HCl adsorbed on the walls (eq 4) accounts for this behavior. If one assumes

$$CH_2N_2 + HCl \xrightarrow{k_h} CH_3Cl + N_2 \tag{4a}$$

$$HCl + \text{wall} \underset{k_{-w}}{\overset{k_w}{\rightleftharpoons}} HCl(\text{wall}) \tag{4b}$$

$$CH_2N_2(g) + HCl(\text{wall}) \xrightarrow{k_{4c}} CH_3Cl(g) + N_2 \tag{4c}$$

a steady-state concentration of HCl(wall) and that k_{-w} is much less than $k_{4c}[CH_2N_2]$, then eq 3 follows directly, wherein k_1 is identified with k_h and k_2 with k_w. If the maintenance of a steady-state concentration of adsorbed hydrogen chloride is diffusion controlled, k_w will be inversely proportional to the pressure, thus

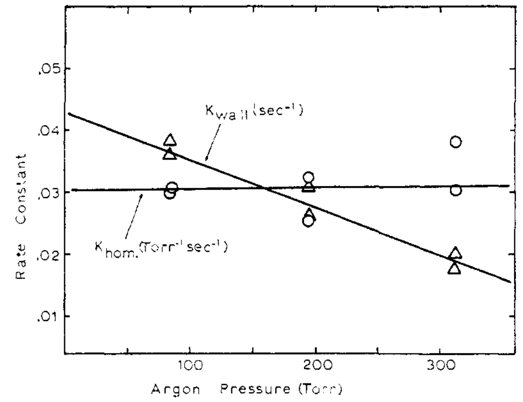

Figure 8. Dependence of the homogeneous (second-order) and the heterogeneous (first-order) rate constants on the inert gas pressure.

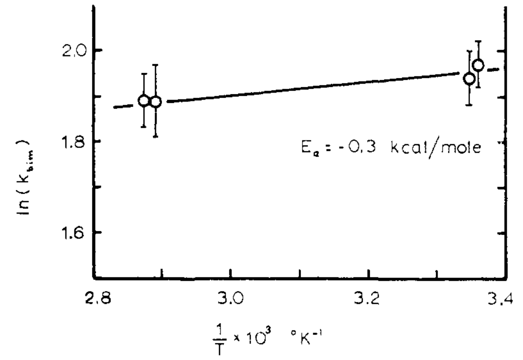

Figure 9. An Arrhenius plot of four runs at 24 and 75°. The HCl and CH_2N_2 pressures were 5.35 and 1.80 Torr, respectively, while the argon pressure was 200 Torr (room-temperature values).

giving rise to the observed pressure dependence of the overall rate.

An analysis of six runs in which only the argon pressure was varied gave the values for k_h and k_w shown in Table I. The two constants are plotted against the total pressure in Figure 8; k_h is independent of the pressure, while k_w varies inversely with the pressure.

Table I. Runs at Constant HCl and CH_2N_2 Pressures (Torr)

Run	HCl	CH_2N_2	Ar	k_h, Torr^{-1} sec^{-1}	k_w, sec^{-1}
124	5.74	1.24	85	0.0380	0.0200
125	5.87	1.48	85	0.0300	0.0170
126	5.82	1.32	196	0.0317	0.0258
127	5.83	1.53	196	0.0250	0.0308
128	5.54	1.35	314	0.0290	0.0375
129	5.93	1.38	314	0.0290	0.0350

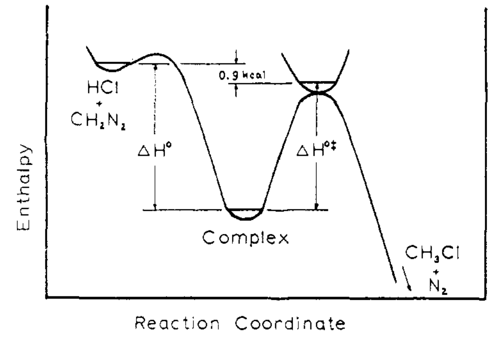

Figure 10. Schematic diagram of the enthalpy surface which accounts for the observed negative activation energy.

Activation Energy. Four runs were made at two different temperatures in order to obtain an estimate of the activation energy. The reaction vessels were wrapped with heating tape and uniform heating was obtained. The results shown in Figure 9 indicate a slight negative activation energy, which can be interpreted in two ways. A small apparent negative activation energy may be observed for a simple bimolecular reaction when $E_a = 0$, but there is an inverse temperature term in the preexponential coefficient. However, all such known cases involve fast reactions with rate constants near the collision frequency. The zero activation energy found for this much slower reaction cannot be explained in this manner. It is more plausible to assume the formation of an intermediate complex, in equilibrium with the reactants. Such a mechanism can be written in detail by postulating one transition state, C*, for the complex formation, an intermediate complex, C, and another transition state, C‡, for stable product formation (Figure 10).

$$\begin{gathered} A + B \underset{k_{-a'}}{\overset{k_{a'}}{\rightleftharpoons}} C^* \\ C^* + M \underset{k_{-a''}}{\overset{k_{a''}}{\rightleftharpoons}} C + M \end{gathered} \tag{5a}$$

$$C + M \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} C^{\ddagger} + M \tag{5b}$$

$$C^{\ddagger} \xrightarrow{k_c} \text{stable products} \tag{5c}$$

If a steady state is assumed for C*, C, and C‡, and it is assumed that $k_{-b}(M) > k_c$, it can be shown that

$$[C]_{ss} = \frac{k_{a'}k_{a''}}{k_{-a'}k_{-a''}}[A][B] = K_{eq}[A][B] \tag{6}$$

and

$$[C^{\ddagger}]_{ss} = \frac{k_b[C][M]}{k_{-b}[M] + k_c} \tag{7}$$

which reduces at high inert gas pressures to

$$[C^{\ddagger}]_{ss} = \frac{k_b}{k_{-b}}[C] \tag{8}$$

Therefore the overall rate is

$$\frac{d[P]}{dt} = \left(k_c\frac{k_b}{k_{-b}}\right)[C] = \left(k_c\frac{k_b}{k_{-b}}\right)K_{eq}[A][B] \tag{9}$$

The expression $(k_b/k_{-b})k_c$ corresponds to the high-pressure limit for the unimolecular rate constant (k_u) associated with steps 5b and 5c. The reasonableness of the proposed mechanism can be tested by estimating K_{eq} and thereby obtaining a value for k_u. The equilibrium constant for complex formation has the form $\exp(\Delta S°/R - \Delta H°/RT)$. The association reaction of the type proposed has a large negative entropy increment due to the loss of three translational and three rotational degrees of freedom and a gain of six vibrations. We estimate $\Delta S^\circ \approx -30$ eu.[6] When the experimentally observed rate constant is equated to $K_{eq}k_u$ one obtains

$$(e^{-30/R}e^{-\Delta H^\circ/RT})k_u = 10^{5.6}e^{+0.3/RT}$$

so that

$$k_u = 10^{12.2}\exp[(0.3 + \Delta H^\circ)/RT] \qquad (10)$$

This is an acceptable unimolecular rate constant, since ΔH° is certainly negative and of the order of 5–10 kcal mol^{-1}.

Another possibility must be considered. If the entire reaction were heterogeneous, the total rate would be diffusion controlled. Although one should then anticipate a positive activation energy, its magntiude might be small enough to be within the experimental error of the data. However, comparison of the reaction with HBr and HCl shows that the former reagent is faster than the latter by a factor of 4. If diffusion were the controlling factor, the HBr rate would be slower by about a factor of 2, because of its higher molecular weight. Thus one is forced to the conclusion that the apparent activation energy for the homogeneous reaction is indeed close to zero. A schematic potential energy surface for this system is shown in Figure 10.

For the unimolecular reaction C → products, the Arrhenius activation energy is related to the enthalpy of activation by $E_a = \Delta H^{\ddagger\circ} + RT$. Since $E_a = -(0.3 + \Delta H^\circ)$ kcal mol^{-1}, then $\Delta H^{\ddagger\circ} = -\Delta H^\circ - (0.3 + RT)$ kcal mol^{-1}. Thus the difference between $-\Delta H^\circ$ and $\Delta H^{\ddagger\circ}$ is 0.9 kcal mol^{-1}.

An apparent negative activation energy has been observed[7] for a similar reaction between ketene and HCl. However, the extensive heterogeneous component for that reaction precluded quantitative measurements.

Conclusion

A kinetic analysis of the rates of reaction between diazomethane and hydrogen chloride mixtures shows that the reaction, even in well-seasoned vessles, is in part homogeneous and in part heterogeneous. The homogeneous portion is first order in each of the reactants and appears to have a small negative activation energy. This makes the diazomethane–hydrogen chloride reaction similar to that for ketene–hydrogen chloride studied by Setser, who also found evidence for a surface component to the overall rate. The negative activation energy is consistent with the proposed formation of a nearly equilibrated complex between hydrogen chloride and diazomethane. Additional support for the existence of such a complex is presented in part II.[3]

Acknowledgment. T. B. expresses his thanks to Proctor and Gamble for a Fellowship (1967–1968).

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[6] A. Shepp and S. H. Bauer, *J. Amer. Chem. Soc.*, **76**, 265 (1954).

[7] D. W. Setser, unpublished results, private communication.

Vibrationally Excited Methyl Chloride. II. Reactions of Vibrationally Hot but Translationally Cold Methyl Chloride

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Abstract: The highly exothermic gas-phase reaction a ($HCl + CH_2N_2 \rightarrow CH_3Cl^* + N_2$ ($\Delta H^\circ \approx -68$ kcal mol^{-1})) was used to produce vibrationally hot but translationally cold methyl chloride. Tracer studies with the deuterated acid showed that the rate of reaction b ($DCl + CH_2N_2 \rightleftarrows CHDN_2 + HCl$) was comparable to that of reaction a. However, analysis showed that reactions a and b by themselves cannot account for the distribution of D in the product methyl chloride, $CH_{3-n}D_nCl$ (n = 0–3). It is necessary to introduce an exchange step ($DCl + CH_2DCl^* \rightleftarrows CHD_2Cl^* + HCl$) between hot methyl chloride and DCl. Evidence for a similar reaction between hot methyl chloride and D_2O was also uncovered ($D_2O + CH_2DCl^* \rightleftarrows CHD_2Cl^* + HDO$). Along with these experimental results, a discussion of the significance of these observations with respect to the vibrational excitation mechanism for homogeneous atom switching is presented.

The gas-phase reaction of diazomethane with the halogen acids to yield methyl halides and nitrogen is highly exothermic. The enthalpy increment is about equal to the heat of formation of diazomethane. Hassler and Setser[2] found that the reaction with hydrogen iodide produces methyl iodide energized above its "critical energy" of 54 kcal mol^{-1}. From product distributions, obtained as a function of inert gas pressure, they estimated by means of the RRKM theory that the internal energy of the nascent methyl iodide is about 58 kcal mol^{-1}. The corresponding reactions with hydrogen bromide and chloride produced stable products. If the total energy released is assumed to distribute itself in these reactions as it does in the case of methyl iodide, the internal energies of the nascent methyl bromide and chloride may be estimated[2] to be 54 and 52 kcal mol^{-1}, respectively.

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