

tions. We estimate $\Delta S^\circ \approx -30$ eu.⁶ When the experimentally observed rate constant is equated to $K_{\text{eq}}k_u$ one obtains

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

so that

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

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 magnitude 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 $C \rightarrow$ products, the Arrhenius activation energy is related to the enthalpy

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

of activation by $E_a = \Delta H^\ddagger + RT$. Since $E_a = -(0.3 + \Delta H^\circ)$ kcal mol⁻¹, then $\Delta H^\ddagger = -\Delta H^\circ - (0.3 + RT)$ kcal mol⁻¹. Thus the difference between $-\Delta H^\circ$ and ΔH^\ddagger is 0.9 kcal mol⁻¹.

An apparent negative activation energy has been observed⁷ 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 vessels, 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).

(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 ($\text{HCl} + \text{CH}_2\text{N}_2 \rightarrow \text{CH}_3\text{Cl}^* + \text{N}_2$, $\Delta H^\circ \approx -68$ 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 ($\text{DCl} + \text{CH}_2\text{N}_2 \rightleftharpoons \text{CHDN}_2 + \text{HCl}$) 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, $\text{CH}_{3-n}\text{D}_n\text{Cl}$ ($n = 0-3$). It is necessary to introduce an exchange step ($\text{DCl} + \text{CH}_2\text{DCl}^* \rightleftharpoons \text{CHD}_2\text{Cl}^* + \text{HCl}$) between hot methyl chloride and DCl. Evidence for a similar reaction between hot methyl chloride and D_2O was also uncovered ($\text{D}_2\text{O} + \text{CH}_2\text{DCl}^* \rightleftharpoons \text{CHD}_2\text{Cl}^* + \text{HDO}$). 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 Setser² found that the reaction with hydrogen iodide produces methyl iodide energized above

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

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 estimated² to be 54 and 52 kcal mol⁻¹, respectively.

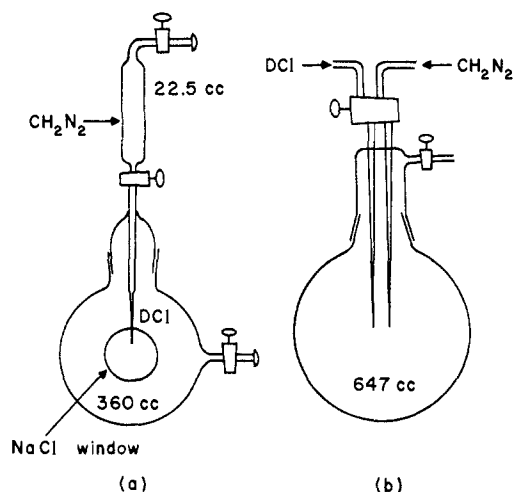


Figure 1. Reaction vessels used for the exchange studies: (a) single injection, with ir-transmitting windows; (b) double injection. Both reactants flow into the large bulb, which was either evacuated or (in most cases) filled with a third gas, such as Ar, D_2O , or D_2S . The injection time for this vessel was of the order of 2 min.

Until recently it has been generally assumed that the activation energy for a bimolecular reaction may be derived from all molecular energy sinks with essentially equal probability, or even that it may be all provided by the relative kinetic energy of the colliding pair. The fact that in a chemical reaction bonds are stretched and broken indicates that the available energy must eventually flow into the vibrational energy sink. Although the degree of adiabaticity which is associated with specific collisions is a current topic of theoretical analysis,³ a quantitative model for the flow of energy from translation, rotation, and vibration to the "critical" bonds has yet to be proposed. Vibrational relaxation data show that for the lowest states of excitation, in small molecules, the probability for transferring translational energy to vibration is relatively low,⁴ particularly for multiquantum vibrational excitation.⁵ The anharmonicity of vibrations and the higher density of states for energized molecules might be expected to smudge differences between various molecular energy sinks. However, this seems not to be the case, as recent trajectory calculations⁶ have indicated that in a chemical reaction the conversion of one form of energy to another is highly dependent on the shape of the potential function near the saddle point.

In the past few years an increasing body of evidence⁷⁻¹¹ has developed which points to the importance

(3) R. A. Marcus, *J. Chem. Phys.*, **45**, 4493, 4500 (1966); **49**, 2610, 2617 (1968).

(4) (a) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961, p 158; (b) B. Stevens, "Collisional Activation in Gases," Pergamon Press, Elmsford, N. Y., 1967, p 38.

(5) B. P. Curry, *J. Chem. Phys.*, **51**, 4951 (1969).

(6) (a) J. C. Polanyi and W. H. Wong, *ibid.*, **51**, 1439 (1969); (b) M. H. Mok and J. C. Polanyi, *ibid.*, **51**, 1451 (1969).

(7) (a) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Amer. Chem. Soc.*, **87**, 143 (1965); (b) W. Watt, P. Borrell, D. Lewis, and S. H. Bauer, *J. Chem. Phys.*, **45**, 444 (1965).

(8) (a) S. H. Bauer and E. Ossa, *ibid.*, **45**, 434 (1966); (b) A. Burcat and A. Lifshitz, *ibid.*, **47**, 3079 (1967); (c) D. Lewis and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 5890 (1968).

(9) A. Burcat, A. Lifshitz, D. Lewis, and S. H. Bauer, *J. Chem. Phys.*, **49**, 1449 (1968).

(10) A. Bar-Nun and A. Lifshitz, *ibid.*, **47**, 2878 (1967).

(11) A. Bar-Nun and A. Lifshitz, *ibid.*, **51**, 1826 (1969).

of the role of vibrational excitation in four-center exchange reactions. These data were obtained from shock tube experiments at temperatures between 1000 and 2000°K, where the molecules were vibrationally as well as translationally hot. Since the translational temperature rises within a few molecular collisions, while vibrational relaxation for the molecules studied (*e.g.*, H_2 , D_2 , H_2S , and N_2) requires many, there is coupling between vibrational excitation and the exchange reaction. The net rate appears to be limited by the rate of excitation to a critical vibrational level. This leads to an empirical rate law which includes a dependence on the ambient gas (generally argon) to an order between 0.5 and 1.0. Furthermore, the relative translational energy appears not to contribute significantly to the reaction probability.

In view of the fact that a large fraction of the energy released by the reaction of diazomethane with hydrogen halides resides initially (in the product methyl halide) as vibrational energy, there is the possibility that the nascent methyl halide may participate in an exchange reaction at room temperature, and this provides a test of one of the predictions of the "vibrational excitation" theory. Unfortunately, few homogeneous reactions involving methyl chloride are known; probably the major reason is that wall reactions both in static and flow systems tend to dominate the kinetics. Nevertheless, in this study two reactions were discovered which appear to take place as a direct result of the vibrational excitation of methyl chloride. Furthermore, quantitative estimates can be made concerning collisional deactivation probabilities for methyl chloride at intermediate energies of excitation.

Experimental Section

Materials. The preparation of diazomethane was described previously.¹² DCl, DBr, and CD_3Br were obtained from Merck Sharp and Dohme. DCl and DBr require special handling since they readily undergo D-H exchange on unseasoned glass walls. One section of the vacuum line was used exclusively for the deuterated acids to ensure purity levels of about 95%, as measured by infrared absorption. It was found that the absorption coefficient at the fundamental is three times as high for HCl as for DCl.

Argon, helium, and dimethyl ether were obtained from Matheson. The ether was distilled from a -156° trap into liquid nitrogen to remove butane impurities which interfered with the mass spectral analysis of the methyl chlorides. The liquid D_2O used had an isotopic purity of 99.7%. D_2S was prepared¹³ by adding D_2O to aluminum sulfide.

Reaction Vessel and Procedure. The primary concern in the design of the reaction vessel was the elimination of the surface component¹² to the overall reaction. The reaction flask was a 360-cc spherical Pyrex bulb connected to the vacuum line through a stopcock. A 22.5-cc sample bulb was connected to the flask *via* a stopcock and a finely drawn-out feed glass tube, which extended to the middle of the reaction bulb. For some runs, another spherical flask of similar size but equipped with NaCl windows was used, to allow for the *in situ* determination of the HCl and DCl concentrations (ir absorption) before and after reaction with diazomethane (Figure 1). All glass surfaces which came in contact with diazomethane were thoroughly seasoned by repeatedly subjecting them to aliquots of the diazomethane heated to about 100°.

The procedure was to expand a mixture of DCl and a diluent gas (Ar, D_2 , ether, etc.) into the 360-cc flask. A diluted mixture of diazomethane (usually with Ar) was then placed in the 22.5-cc vessel at several times the total pressure of the DCl and diluent present in the larger bulb. A turn of the stopcock connected the

(12) Part I, T. Baer and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 4769 (1970).

(13) C. R. Bailey, J. W. Thompson, and J. B. Hale, *J. Chem. Phys.*, **4**, 625 (1936).

Table I. Initial Concentrations (Torr) of Reactants for Runs 34–37

	Run 34	Run 35	Run 36	Run 37
HCl	0.95 ± 0.05	0.36 ± 0.05	0.61 ± 0.08	0.29 ± 0.03
DCl	24.8 ± 0.50	9.50 ± 0.30	19.1 ± 0.40	2.85 ± 0.20
CH ₂ N ₂	0.84 ± 0.06	0.99 ± 0.06	0.99 ± 0.06	0.99 ± 0.06
Ar	180.4	197.2	186.3	205.0
M (total)	207.0	208.0	207.0	209.0

two vessels, allowing the diazomethane to flow through the capillary tube into the acid. In such an experiment the average temperature rise in the region of highest reaction was measured to be less than 0.5°. Furthermore, the low injection rate (≈ 60 sec) and the considerable excess of acid essentially eliminated the heterogeneous reaction. The deuterium content of the final product was established by mass spectroscopy. The total yield of methyl halide was determined by vapor phase chromatography.

Mass Spectra. Analysis for the deuterated methyl halides was carried out with a Model 21-103 Consolidated Engineering Corp. mass spectrometer. The ionizing voltage was set at 70 eV. The cracking patterns of authentic samples of methyl chloride and methyl bromide and their fully deuterated analogs were determined, and from these the cracking pattern for CH₂DCl, CHD₂Cl, CH₃Cl, CH₂DBr, and CHD₂Br could be calculated. A number of studies^{14–19} have dealt with the effects of deuteration on the cracking patterns of deuterated analogs, and several trends have been discerned.

(a) Because the ionizing voltage is considerably higher than the ionization potential of the molecules, the small difference in the ionization potential of deuterated and nondeuterated molecules is negligible. Thus the total number of ions produced in the ionizing chamber per unit pressure is the same for both species.

(b) An isotope effect is observed in the breaking of a hydrogen *vs.* a deuterium bond. This is known as the π effect, and represents the ratio of the probability of breaking a Y–D bond in a deuterated molecule to that of a Y–H bond in a nondeuterated molecule. Reported^{14,15,17,18} values for π vary from 0.55 to 0.67.

(c) A smaller isotope effect is due to the tendency of partially deuterated molecules to break more easily at a Y–H bond than their nondeuterated analogs. This is designated as the γ effect, and has been reported for methane¹⁴ (1.10), acetylene¹⁵ (1.30), water¹⁷ (1.33), and hydrogen sulfide¹⁸ (1.27). The value for methane was obtained by studying CH₃D and CH₄. Meyerson¹⁹ found that as the deuterium content decreased the γ effect decreased as well. Hence the low value reported for methane may reflect this trend.

The cracking patterns for the deuterated methyl halides were generated by making use of these empirical findings. The π effect was directly observed by comparing the cracking patterns of CH₃Br and CD₃Br. The average value found experimentally was $\pi = 0.65$, which agrees well with that reported for other molecules. γ could not be determined experimentally because we lacked authentic samples of the partially deuterated methyl halides. Thus a reasonable value of 1.3 was assumed. Use of these empirical findings made it possible to calculate mass spectra for all the deuterated methyl bromides and chlorides. Concentrations of the deuterated methyl halides calculated on the basis of these cracking patterns are subject to a standard error of about 0.5%.

Results

DCl Exchange. Exchange Reaction in Unseasoned Vessels. The first group of experiments was carried out in unseasoned vessels. HX (X = Cl, Br) was treated with diazomethane in the presence of D₂ and CD₄ by allowing diazomethane to flow into a mixture of HX and excess D₂(CD₄). Mass spectral analyses of the methyl halide thus generated indicated that a

(14) O. Schaeffer, "Mass Spectroscopy in Physics Research," National Bureau of Standards Circular 522, U. S. Government Printing Office, Washington, D. C., 1966, p 249.

(15) V. H. Dibeler and H. M. Rosenstock, *J. Chem. Phys.*, **39**, 1326 (1963).

(16) P. Natalis, *Bull. Soc. Chim. Belg.*, **73**, 389 (1964).

(17) F. Fiquet-Fayard and P. Guyon, *J. Chim. Phys.*, **60**, 1069 (1963).

(18) F. Fiquet-Fayard and P. Guyon, *Advan. Mass Spectrom.*, **3**, 489 (1966).

(19) S. Meyerson, *Advan. Mass Spectrosc.*, **2**, 313 (1962).

significant amount of deuterated methyl halides was formed. These data were reported as a preliminary communication by Bauer, Marshall, and Baer.²⁰ However, work done since then has shown that this deuteration occurred on the walls. A sequence of runs starting with an initially unseasoned vessel exhibited a decreasing amount of deuteration, demonstrating that as the walls were increasingly seasoned the extent of the wall reaction decreased. Once the vessel was seasoned with diazomethane, no significant amounts of exchange products were found when the diluent was D₂, CD₄, CD₃Br, or C₂D₄.

The nature of the wall reaction was not investigated and as yet is not well understood. It may be that the unseasoned glass wall catalyzed the production of CH₂ radicals which desorbed and reacted with D₂. The other possibility is that the entire exchange reaction occurred on the walls.

Reaction Products from DCl–CH₂N₂ Mixtures. Many experiments were carried out with mixtures of DCl and diazomethane. Mass spectrometric analyses of the products showed not only that these contained large amounts of *all* the deuterated species of methyl chloride, but also that these experiments were quantitatively reproducible. Because HCl and DCl exchange readily on the glass walls, the concentrations of these species were always in some doubt, although their total concentration was known. The use of NaCl windows in the reaction cell made it possible to determine the HCl and DCl concentrations before and after an experiment by their infrared absorption. The initial concentrations of all species for runs 34–37 are shown in Table I. Since the diazomethane was injected much more slowly (≈ 60 sec) than the rate of reaction, the "concentration" shown is a hypothetical one, calculated as though all the diazomethane were injected before any reaction took place. It is therefore equivalent to the final methyl chloride concentration.

Table II gives the resulting distributions of methyl chloride found in the products and the calculated distributions, assuming complete randomization of H–D for an equivalent deuterium content. The random distribution for a set of CH_{3–n}D_nCl ($n = 0–3$) with total hydrogen = h and total deuterium = d is given by the binomial coefficients h^3 , $3h^2d$, $3hd^2$, and d^3 . When these are normalized to 100% the "random distribution" is obtained.

Inert Gas Pressure Dependence. An attempt was made to determine the role of the inert gas on the product distribution in the deuterated methyl chlorides. The effect of increasing pressure was small but consistent. Two trends were observed: (1) the deuterium incorporated in the methyl chloride decreased slightly and (2) the distribution of deuterated methyl

(20) S. H. Bauer, D. Marshall, and T. Baer, *J. Amer. Chem. Soc.*, **87**, 5514 (1965).

Table II. Product Distributions (%) for the Reaction
 $\text{CH}_2\text{N}_2 + \text{DCI} \rightarrow \text{CH}_n\text{D}_{3-n}\text{Cl} + \text{N}_2$

	Experi- ment	Random distribu- tion	Experi- ment	Random distribu- tion
	—Run 34—		—Run 36—	
CH_3Cl	3.9	4.0	4.5	4.3
CH_2DCI	34.8	23.1	32.8	23.8
CHD_2Cl	22.6	44.4	25.2	44.4
CD_3Cl	38.6	28.4	37.4	27.5
D/H	1.89		1.87	
	—Run 35—		—Run 37—	
CH_3Cl	7.0	7.6	17.2	20.7
CH_2DCI	38.6	31.1	50.2	42.9
CHD_2Cl	28.7	42.2	24.7	29.6
CD_3Cl	25.6	19.1	7.8	6.8
D/H	1.36		0.70	

chlorides became more random. This applied both to argon and to dimethyl ether used as pressuring gases. The latter was chosen because the frequency of one of its vibrational modes (250 cm^{-1}) is close to one-third of the carbon-chlorine stretching frequency (732 cm^{-1}) in methyl chloride. Lambert²¹ found for methyl chloride that the collisional deactivation probability increased by a factor of 6 when the collider was methyl ether compared to methyl chloride. This increased efficiency was attributed to a resonant vibration-vibration (V-V) energy transfer. Even with such an efficient collider, the pressure dependence was small. The results for two representative runs are summarized in Table III.

Table III. Effect of Inert Gas Pressure on the Product Distribution

Reactants	High-pressure run, Torr		Low-pressure run, Torr	
HCl	0.12		0.085	
DCI	2.07		2.03	
CH_2N_2	0.49		0.52	
$(\text{Me})_2\text{O}$	587.0		33.0	
Ar	20.0		24.0	
Products	Experiment distribution, %	Random distribution, %	Experiment distribution, %	Random distribution, %
CH_3Cl	32.2%	33.0%	11.9%	19.0%
CH_2DCI	47.2	44.2	56.4	42.2
CHD_2Cl	18.3	19.4	24.0	31.2
CD_3Cl	2.4	2.9	7.0	7.7
D/H	0.45		0.74	

Deuteration of Diazomethane. A critical experiment which revealed part of the mechanism for the hydrogen-deuterium exchange led to the conclusion that diazomethane itself became deuterated during the course of the reaction. DCI was injected in excess diazomethane. After 5 min the remaining diazomethane was treated with excess HBr, which converted it to methyl bromide. This experiment was carried out a number of times in a variety of ways to ensure its reliability and reproducibility. Were deuteration confined to the nonreversible part of the reaction path which produces methyl chlo-

ride, only CH_3Br would have resulted. Mass spectrometric analysis showed that the product methyl bromide was about 20% deuterated, indicating that some diazomethane contained deuterium prior to reaction with the HBr.

Possibility of Surface or Free-Radical Reactions. Before presenting a homogeneous gas-phase mechanism for the production of all the deuterated methyl chloride species in well-seasoned vessels, the possibility of a surface reaction must be ruled out. It was indicated previously¹² that in the rapid mixing cell 30–40% of the reaction appeared to take place on the surface. In those experiments a large amount of the surface was made easily accessible to the reactants by the turbulence resulting from the sudden injection of the gases into an evacuated ir cell. The reaction vessels used in these exchange studies were designed to minimize these effects. The slow injection of diazomethane reduced turbulence to a minimum, and the large excess of DCI over diazomethane promoted reaction before the diazomethane diffused to the walls. Hassler² used a similar reaction vessel and found no evidence for a surface contribution. In fact, he ruled out such a reaction because the presence of hot methyl iodide ($\text{CH}_3\text{I}^* \rightarrow \text{CH}_3 + \text{I}$) clearly could not be reconciled with a wall reaction.

There is another argument against a wall reaction. It was found that mixtures of methyl chloride and DCI did not exchange in either a seasoned or unseasoned reaction vessel even after days of contact. Therefore, unless one accepts the proposition that wall exchange with diazomethane occurs prior to methyl chloride formation, he would have to argue that a complex sticks to the surface where it is repeatedly hit by DCI molecules and thus becomes successively deuterated. It is difficult to conceive of such an unstable complex existing long enough to undergo such an exchange sequence. It is in fact more likely that a wall reaction would lead to a single product, CH_2DCI . This was indeed the case when the reaction was carried out in the presence of about 20 Torr of D_2O (the equilibrium vapor pressure at room temperature). It is reasonable to suppose that the latter reaction took place on the walls, which under those conditions were covered with a layer of liquid water; further details are given below. For the present, we shall accept the implication that if a wall reaction in the presence of D_2O leads to a single deuterated product, then in the absence of D_2O that wall reaction could not produce the observed sequence of deuterated methyl chlorides.

Another explanation for the deuterated products is the possibility of free-radical reactions. If any free radicals were present in the reaction cell, then one would expect to find CH_2 , which is the primary gas-phase decomposition product of diazomethane. It is well documented²² that reactions between methylene (CH_2) and unsaturated hydrocarbons are very fast, on the order of collision frequencies. To test for the presence of methylene, the reaction between HCl and diazomethane was carried out in a tenfold excess of propylene. The limit of detectability (by vpc and mass spectrometry) of C_4 hydrocarbons in methyl chloride is about 0.1%. To that level of sensitivity, no C_4

(21) J. D. Lambert, D. G. Parks-Smith, and J. L. Stretton, *Proc. Roy. Soc., Ser. A*, **282**, 380 (1964).

(22) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 238 (1964).

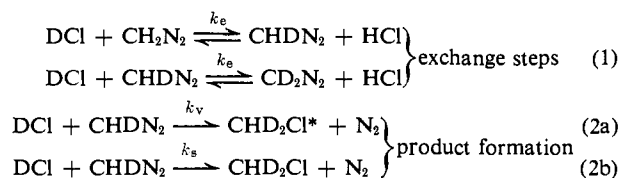
hydrocarbons were found in the reaction products. Since the reactions of methylene with HCl and propylene are not expected to differ by more than a factor of 10, the conclusion drawn is that no methylene is produced during the course of the reaction.

Hassler and Setser² tested for methyl radicals (CH_3) by introducing scavengers (O_2 and excess HX). Their results indicated that methyl radicals were produced during the reaction of diazomethane with HI, but as a consequence of the decomposition of energized CH_3I^* . However, no methyl radicals were detected when diazomethane was reacted with HBr and HCl. These findings were indirectly confirmed by the experiments described above.

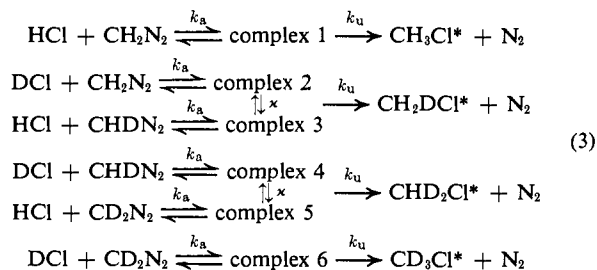
The Exchange Mechanism. DCI- CH_2N_2 Exchange Mechanism. A simple mechanism for the production of various deuterated methyl halides is to assume that DCI exchanges very rapidly with diazomethane, producing CHDN_2 and CD_2N_2 , and then more slowly to give methyl chloride. In this way all the deuterated diazomethane isomers could be generated first, subsequently producing all the deuterated isomers of methyl chloride. The plausibility of such an DCI- CH_2N_2 exchange rests on work reported by Pimentel,²³ who found that diazomethane could be deuterated by heavy water in the liquid phase (no rates were given) with only minor losses due to the formation of methane.

The exchange could take place in two ways; by a single step bimolecular exchange reaction or through the formation of a short-lived complex between DCI and diazomethane. The complex would have to rearrange and decompose either to HCl and CHDN_2 , or to nitrogen and methyl chloride. The fact that the rate study¹² strongly favors the assumption of complex formation lends further support to this proposal. However, the two mechanisms differ only in the structure of the transition states and cannot be distinguished on the basis of their product distribution. The two mechanisms are explicitly stated below; the asterisk on the methyl chloride indicates vibrational excitation. The correspondence between symbols used here and in part I¹² is: $(k_v + k_s) = (k_a/k_{-a})(k_b/k_{-b})k_c = (k_a/k_{-a})k_u$ and $k_e = (k_a/k_{-a})\alpha$.

Mechanism I may be represented by



and further isotopic variations of product-forming reactions. Mechanism II follows.



(23) (a) T. D. Goldfarb and G. C. Pimentel, *J. Amer. Chem. Soc.*, **82**, 1865 (1960); (b) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **40**, 329 (1964).

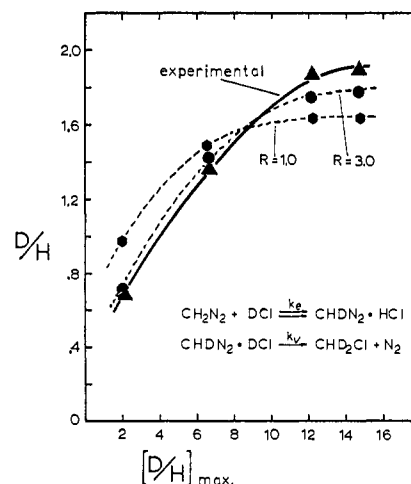


Figure 2. Comparison of the predicted (---) and experimental (—) ratios D/H for the DCI- CH_2N_2 exchange mechanism. R is the isotope effect on the product formation step.

Because the two mechanisms lead to identical distributions, the numerical analysis was made for the first one, which is simpler to formulate. The differential equations which describe this mechanism were solved by numerical integration on an IBM 360/65 computer. Nine rate equations were set up for the concentrations of HCl, DCI, $\text{CH}_n\text{D}_{2-n}\text{N}_2$ ($n = 0, 1, 2$), and $\text{CH}_n\text{D}_{3-n}\text{Cl}$ ($n = 0-3$). An approximation was introduced in that the solution was assumed to be in the form of a truncated Taylor expansion

$$y = y + \left(\frac{dy}{dt}\right)\Delta t$$

The time interval Δt was chosen so that the total integration required between 12,000 and 16,000 iterations. The size of the step was varied to test its effect on convergence. An interval of 5×10^{-4} sec was found to be sufficiently small to make the solutions accurate to about 0.5%.

A kinetic isotope factor (R), which measures the relative rate of product formation for the steps 2a and 2b, was included; R is defined as the ratio of the rate of the reaction with HCl to the rate with DCI. These are the only steps which are expected to exhibit an isotope effect. In the DCI- CH_2N_2 exchange mechanism, the steps 2a and 2b do not lead to different products, so that only the sum of their rates ($k_v + k_s$) is significant. Hence, the two independent parameters are the ratio $k_e/(k_v + k_s)$ and R , while the corresponding independent parameters in the complex mechanism are the ratio α/k_u and the isotope factor for the production of methyl chloride. In both cases, rate constants for the deactivation of $\text{CH}_n\text{D}_{3-n}\text{Cl}^*$ were assumed to be relatively large.

The two parameters, $k_e/(k_v + k_s)$ and R , were varied until a best fit was obtained between the theoretically predicted and the experimental product distributions. These were found to be $k_e/(k_v + k_s) = 4.0 \pm 0.2$ and $R = 3.0 \pm 0.4$. The corresponding distributions are shown in Table IV. A maximum D/H ratio can be calculated²⁴ by assuming that all the deuterium and hydrogen which are not in the stable product

(24) T. Baer, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1969.

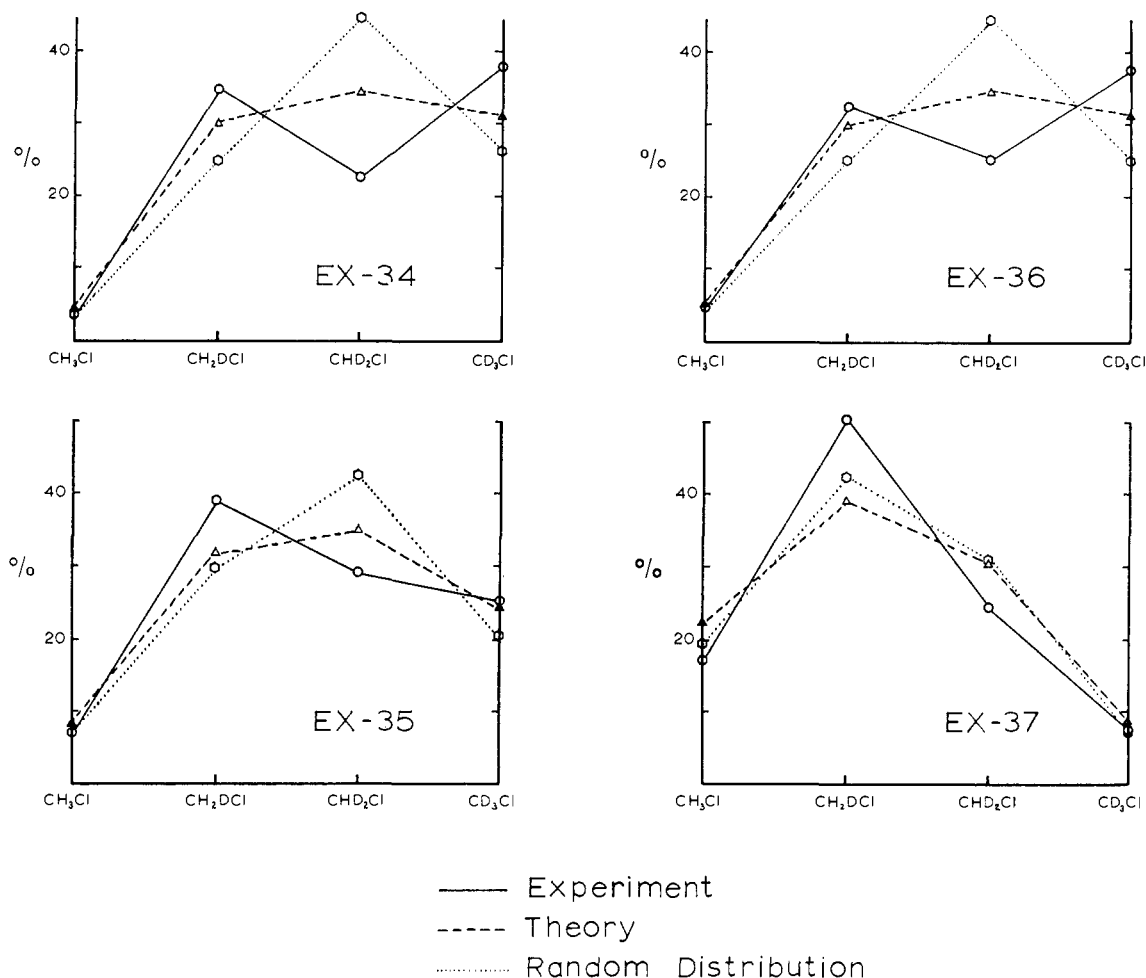


Figure 3. Comparison of the observed isotopic distributions in methyl chloride with those predicted by the $\text{DCI}-\text{CH}_2\text{N}_2$ exchange mechanism.

(methyl chloride) equilibrate during the course of the reaction. When the experimental D/H is plotted against this maximum D/H , the correspondence between theory and experiment is rather good. This is shown in Figure 2 for the optimized values of k_e ,

Table IV. Theoretical $\text{CH}_n\text{D}_{3-n}$ Cl Distributions for Runs 34-37

	Run 34	Run 35	Run 36	Run 37
Based on $\text{DCI}-\text{CH}_2\text{N}_2$ Exchange Mechanism				
CH_3Cl	4.6	8.2	4.9	22.1
CH_2DCl	29.8	32.0	30.0	38.8
CHD_2Cl	34.3	35.1	34.4	30.3
CD_3Cl	31.3	24.8	30.7	8.9
D/H	1.78	1.43	1.75	0.72
Based on $\text{DCI}-\text{CH}_2\text{N}_2$ and Hot Product Exchange Mechanism				
CH_3Cl	3.1	5.7	3.3	16.0
CH_2DCl	35.1	40.7	36.2	49.5
CHD_2Cl	23.4	28.7	24.7	26.0
CD_3Cl	38.5	24.9	35.8	8.5
D/H	1.92	1.36	1.80	0.73

($k_v + k_s$), assuming $R = 1$ and 3. The agreement between the predicted and experimental ratios could probably be made better by further raising the value of R . However, this comparison is deceptive. When the detailed distributions in each run were compared with those observed, it became evident that the cor-

respondence between this theory and experiment is far from satisfactory. This is graphically illustrated in Figure 3. The principal discrepancies are that while more trideuterated methyl chloride was formed than was predicted, the converse held for the dideuterated product.

$\text{DCI}-\text{CH}_2\text{N}_2$ and Hot Product Exchange Mechanism. The possibility for exchange between vibrationally excited methyl chloride and DCI was considered. By itself



does not account for the experimental fact that diazomethane becomes deuterated, unless exchange between hot methyl chloride and diazomethane is postulated as well (eq 5). However, this assumption led to pre-



dicted distributions which were less satisfactory than those derived from the above $\text{DCI}-\text{CH}_2\text{N}_2$ exchange mechanism. Furthermore, an exchange mechanism which relies exclusively on reactions with vibrationally hot methyl chloride would exhibit a much more pronounced dependence on inert gas pressure than was experimentally found.

It seems rather unlikely that any simple mechanism could predict the observed large deviations from the random distribution. Hence we conclude that probably

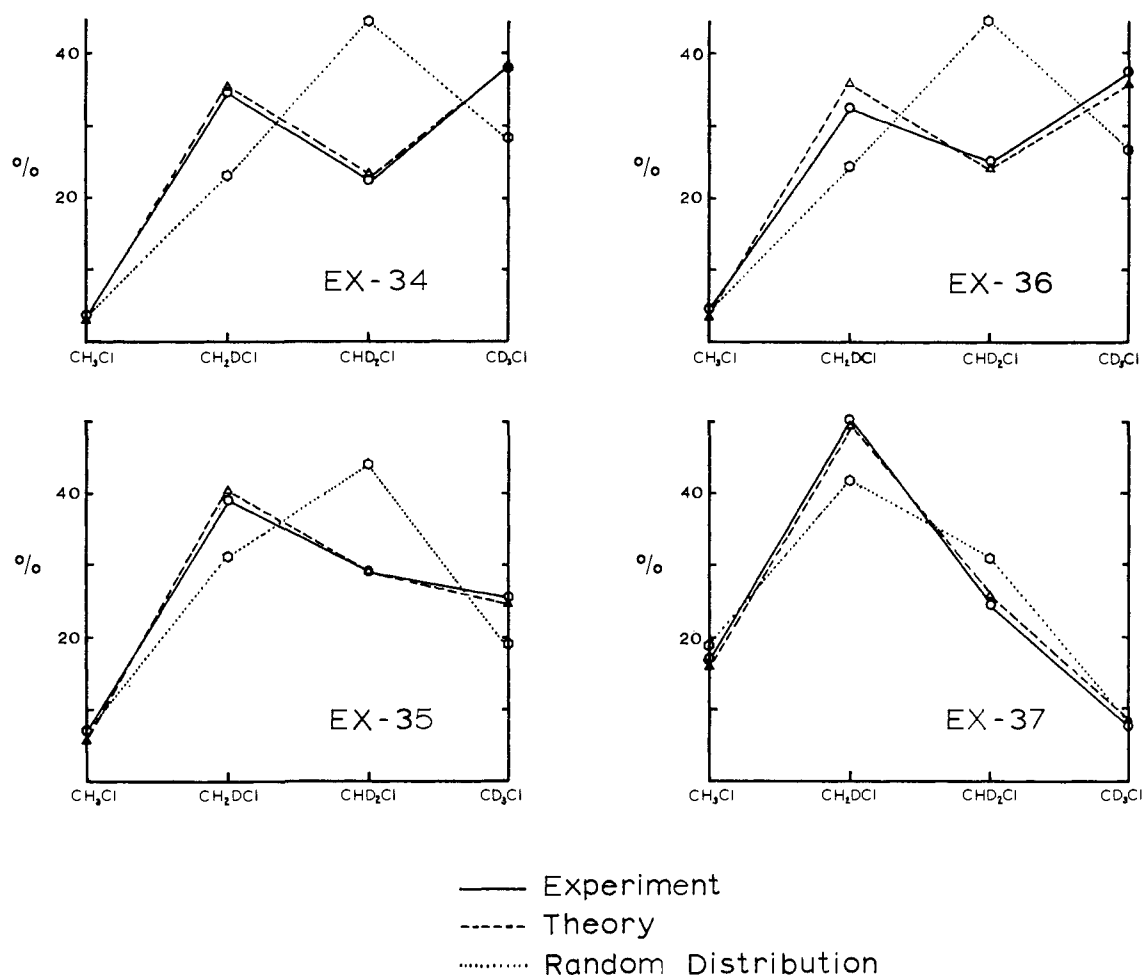


Figure 4. Comparison of the observed isotopic distributions in methyl chloride with those predicted by the $\text{DCI}-\text{CH}_2\text{N}_2$ and hot product exchange mechanism.

two processes, the direct $\text{DCI}-\text{CH}_2\text{N}_2$ exchange and the exchange between the vibrationally hot methyl chloride and DCI , operate concurrently. Please note that it is essential to include both steps in (1) and (2), reaction 4, and the deexcitation step



Reaction 5 is of no consequence under conditions of slow influx of diazomethane, since the latter reacts rapidly with the large excess of acid. The isotopic factor, R , applies only to the product formation steps 2a and 2b. The computational parameters are therefore k_e/k_s , k_v/k_s , k_x/k_d , and R . Upon varying these quantities, it became clear that the experimental results could not be accounted for when $k_v \gg k_s$. The condition that $k_v \ll k_s$ simply reduces the system of equations to that for $\text{DCI}-\text{CH}_2\text{N}_2$ exchange only, which was already shown to be insufficient. However, the alternative, $k_v \approx k_s$, does lead to a good fit with the data when the parameters assume the following values

$$\begin{aligned} k_e/k_s &= 1.40 \pm 0.10 & k_v/k_s &= 1.20 \pm 0.20 \\ k_x/k_d &= 150 \pm 30 & R &= 1.60 \pm 0.30 \end{aligned}$$

The uncertainties listed are the variations in the parameters which result in a significant deviation from the experimental distributions. Table IV gives predicted distributions in deuteration of methyl chloride, while

the theoretical predictions and the experimental distributions are compared in Figure 4.

There are two ways to interpret the production of unexcited methyl chloride (reaction 2b). (A) A surface reaction between DCI and CH_2N_2 , although unlikely, should not be entirely ruled out. One may propose that (2b) is a surface reaction which produces stable methyl chloride, while (2a) occurs homogeneously and produces vibrationally hot methyl chloride. A consequence of this assumption is that at higher ambient gas pressures the homogeneous reaction would be favored because of decreased diffusion to the walls, thus increasing the initial production of hot methyl chloride, which was not observed. However, the expected inert gas effect is partially compensated by reaction 6, which reduces the concentration of hot methyl chloride by collisional deactivation. (B) Another interpretation is that the critical energy for the exchange reaction between DCI and methyl chloride lies in the middle of the energy distribution of the nascent methyl chloride. Thus, about 55% of the newly formed product has sufficient vibrational energy to exchange with DCI , while 45% has less than the critical amount. This is illustrated in Figure 5. There is no way to distinguish between the two interpretations on the basis of the four runs 34–37.

The ratio k_x/k_d was found to be 150. If we assume that the hot product exchange reaction 4 takes place

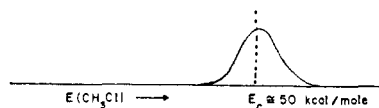


Figure 5. The relationship between the critical energy for the exchange reaction between DCl and methyl chloride and the internal energy distribution in the newly formed methyl chloride. E_c is the critical energy for the reaction $\text{DCl} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_2\text{DCl} + \text{HCl}$.

essentially at the collision frequency, then this ratio represents the number of collisions with argon necessary to deactivate the hot methyl chloride below the critical level required for exchange. In the analysis, all the deactivation was assumed to involve collisions with argon. If the deactivation probability for collisions with DCl were much greater than for collisions with Ar, it is possible that some of the relaxation would proceed *via* $\text{DCl}-\text{CH}_3\text{Cl}^*$ collisions. This possibility was tested by assuming that $k_d(\text{DCl})/k_d(\text{Ar}) = 10$. Although room-temperature relaxation data^{21,25,26} for methyl chloride suggest that this ratio may be as high as 100, at high vibrational excitation of the methyl chloride one expects it to be considerably smaller. The net result of this modification is that in order to fit the observed distributions, the value of k_e/k_s must be lowered, while k_v/k_s and R must be raised. However, the significance of these arguments is questionable, since the proposed model does not account in detail for the experimental observations, as shown below.

The Predicted Inert Gas Dependence. The predicted product distributions for experiments with high argon pressures offer a good test of the theory. As is indicated in Table III, the effect of increasing the inert gas pressure was (1) to decrease the deuterium content of the product species, and (2) to make the distribution of deuterated methyl chloride more nearly random. The predicted consequences of increasing the pressure by a factor of 4 (in run 37) are listed in Table V, along with

Table V. The Predicted Pressure Effect on Run 37 Using the $\text{DCl}-\text{CH}_2\text{N}_2$ and Hot Product Exchange Mechanism

	Ar = 200 Torr			Ar = 800 Torr		
	Pre-dicted	Ran-dom	Diff	Pre-dicted	Ran-dom	Diff
CH_3Cl	16.0	19.2	-3.1	15.9	23.5	-7.6
CH_2DCl	49.5	42.2	+7.2	57.6	43.7	+13.9
CHD_2Cl	26.0	31.0	-5.0	22.3	27.1	-4.8
CD_3Cl	8.5	7.6	+1.0	4.2	5.6	-1.4
D/H		0.73			0.62	

the corresponding random distributions. The model reproduces reasonably well the observed decrease in deuterium content; but instead of randomizing the distribution as the pressure is raised, *the model predicts a greater deviation from a random distribution*. A similar situation exists when reaction 2b is assumed to be a wall reaction (interpretation A). In that case, k_s is lowered to take into account the lower rate of diffusion to the walls. Thus, neither interpretation A nor B for reaction 2b is favored by the result of the high-pressure runs.

(25) J. C. McCoubrey, R. C. Milward, and A. R. Ubbelohde, *Proc. Roy. Soc., Ser. A*, **269**, 456 (1962).

(26) R. C. Milward and A. R. Ubbelohde, *ibid.*, *Ser. A*, **272**, 481 (1963).

Discussion of the Proposed Model. The major shortcoming of the proposed mechanism is its oversimplification of the reaction steps 4 and 6. Let us assume that the surface reaction plays only a minor role, and thus accept the second interpretation (B) of reaction 2b, as illustrated in Figure 5. If only *one* collision with argon were required to stabilize the methyl chloride, the assumed energy distribution would have no effect on the product distribution. However, when it is assumed that a significant number of collisions are necessary to stabilize the molecule, then the results should be sensitive not only to the energy distribution, but also to the detailed transition probabilities for collisional energy exchange. Unlike association reactions which initially produce a single molecule in a narrow energy range, the reaction between diazomethane and HCl must partition its energy between two products. While this energy need not be distributed randomly,²⁷ there may nevertheless be a broad energy distribution.²⁸ Unfortunately, no data concerning the transition probabilities at intermediate energies (relative to dissociation) are available. The derived value for k_x/k_d of 150 is certainly between the ground-state value²⁹ of about 2000 and the one above the dissociation limit³⁰ of 1-5. However, the lack of quantitative agreement between the predicted and the observed inert gas pressure dependence brings the significance of the ratio $k_x/k_d = 150$ into considerable question.

The question remains whether (a) the proposed model is qualitatively correct, but we lack at present the necessary energy transfer coefficients to predict the high pressure results quantitatively or, on the other hand, whether (b) no further refinements will reproduce these data. The fact that the low-pressure (200 Torr of Ar) runs are reproduced quantitatively reflects favorably on the model. The large deviations from statistical or random distributions observed, particularly with respect to the relative amounts of dideuterated and trideuterated products, strongly suggest the presence of two reactions responsible for exchange. Supporting evidence for the reaction between hot methyl chloride and DCl comes from experiments carried out in the presence of D_2O , as outlined below. Thus the weight of the evidence favors the conclusion that the proposed model is qualitatively correct, but that it has not yet been refined to the extent that one may quantitatively predict the inert gas pressure effect.

Exchange with D_2O and D_2S . Several experiments were made by injecting diazomethane into DCl diluted in D_2O and argon. The results of two series of runs with varying D_2O pressures, from zero to its vapor pressure (P_0) of about 20 Torr at room temperature, are summarized in Table VI and Figure 6. Two striking features are revealed by these data. First,

(27) R. J. Campbell and E. W. Schlag, *J. Amer. Chem. Soc.*, **89**, 5103 (1967).

(28) (a) K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discuss. Faraday Soc.*, **44**, 183 (1967); (b) J. R. Airey, R. R. Getty, J. C. Polanyi, and D. R. Snelling, *J. Chem. Phys.*, **41**, 3255 (1964).

(29) (a) W. Griffith, *J. Appl. Phys.*, **21**, 1319 (1950); (b) J. C. McCoubrey, J. B. Parke, and A. R. Ubbelohde, *Proc. Roy. Soc., Ser. A*, **223**, 155 (1954); (c) R. Amme and S. Legvold, *J. Chem. Phys.*, **30**, 163 (1959); (d) T. D. Rossing and S. Legvold, *ibid.*, **23**, 1118 (1955).

(30) (a) D. C. Tardy and B. S. Rabinovitch, *ibid.*, **45**, 3720 (1966); **48**, 1283 (1968); (b) D. W. Setser and J. C. Hassler, *J. Phys. Chem.*, **71**, 1364 (1967).

Table VI. Distribution (%) of Deuterated $\text{CH}_n\text{D}_{3-n}\text{Cl}$ in the Presence of Varying Amounts of D_2O

	Runs with 0.45 Torr of CH_2N_2 ^a				
	D_2O , Torr				
	0.0	4.3	5.4	10.4	19.3
CH_3Cl	21.2	11.0	6.9	10.6	3.4
CH_2DCl	45.2	31.0	35.3	69.2	80.9
CHD_2Cl	26.5	35.0	34.0	16.0	12.4
CD_3Cl	7.1	23.0	23.7	4.2	3.3
D/H	0.66	1.31	1.39	0.61	0.63

	Runs with 0.07 Torr of CH_2N_2 ^a			
	D_2O , Torr			
	0.0	3.8	9.0	17.1
CH_3Cl	8.4	2.5	2.0	2.7
CH_2DCl	34.1	26.1	34.1	87.7
CHD_2Cl	35.2	31.8	31.1	7.4
CD_3Cl	22.2	39.0	32.7	2.1
D/H	1.33	2.24	1.85	0.57

^a The concentrations of DCl and Ar were 1.0 and 44 Torr, respectively.

the amount of deuteration increases sharply at low pressures of D_2O . Second, at the high relative pressures not only does the amount of deuterium in the methyl chloride decrease, but also the distribution of isotopes is drastically altered. As the pressure of D_2O is raised, one product, the singly deuterated methyl chloride, dominates. Again one must assume at least two types of reactions: one which accounts for an increase in deuteration at low pressures of D_2O , and another which not only suppresses this increased deuteration, but which also suppresses the deuteration of diazomethane by DCl as the concentration of D_2O approaches its saturation pressure.

The High- D_2O -Pressure Reaction. The presence of water inevitably raises the possibility of wall reactions because of the ease and tenacity with which it is adsorbed on glass surfaces. Indeed, it is reasonable to assume that at least one of the two reactions occurs on the walls, and consideration of many possibilities led to the conclusion that it is the high-pressure reaction which is heterogeneous. As is evident from Table VI, the product distribution at high D_2O pressures is different from any other encountered in this system. Furthermore, if one accepts the assumption of a wall reaction, it follows that it would dominate at a D_2O concentration near its vapor pressure, where adsorption is greatest, as is demonstrated by its adsorption isotherm.³¹ In fact, near the saturation limit, the adsorbed water is many layers deep and can be thought of as being essentially a film of liquid water.³² In that case, large amounts of DCl could dissolve in the water to make aqueous deuteriochloric acid. If the aqueous reaction between diazomethane and DCl were much faster than in the gas phase, it would dominate at high pressures of D_2O and produce the single product, CH_2DCl . Furthermore, inspection of the adsorption curve shows that an increase in D_2O pressure, from 10 to 20 Torr, results in a large proportional increase in the amount of adsorbed water and thus accounts for the striking change in the nature of the reaction. The rate of reaction between diazomethane and aqueous

(31) (a) J. J. Chessick, F. H. Healey, and A. C. Zettlemoyer, *J. Phys. Chem.*, **60**, 1345 (1956); (b) F. R. L. Schoening, *J. Appl. Phys.*, **31**, 1779 (1960).

(32) K. Kawasaki, K. Kanau, and Y. Sekita, *J. Phys. Soc. Jap.*, **13**, 222 (1958).

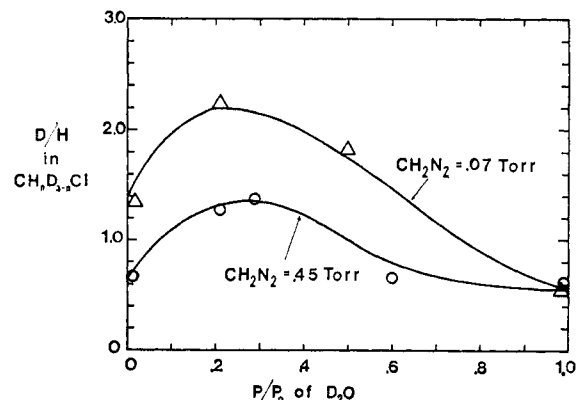


Figure 6. The effect of D_2O concentration (plotted as a reduced pressure, where P_0 is the equilibrium vapor pressure) on the amount of deuterium incorporated in the methyl chloride. The detailed distributions of deuterated methyl chlorides are shown in Table VI.

hydrogen chloride has not been measured. However, it is reasonable to assume that it is much faster than the gas-phase reaction, since water is known to catalyze acid-base reactions.³³

An attempt was made to increase the surface area in the reaction vessel in order to observe the effect on the product distribution. Unfortunately, experimental difficulties prevented an unambiguous interpretation of these data. The proof for the existence of a surface reaction was then approached from a different direction. Because the vapor pressure is a strong function of the temperature, increasing the temperature from 20 to 50° would place 20 Torr of D_2O at about $P/P_0 = 0.20$. If the high- D_2O -pressure reaction takes place on the glass surface in a layer of liquid water, then heating the vessel should increase deuteration. Furthermore, if the vessel is saturated with D_2O at high temperatures (50°), then the product methyl chloride should again be mostly the singly deuterated product. Table VIIA shows that the experimental data agree with the above predictions.

Table VII. Products from Various DCL- CH_2N_2 Reactions Carried Out in the Presence of D_2O

D_2O , Torr	A. P/P_0 Dependence		
	18 ^a	18 ^b	90 ^c
CH_3Cl	3.4%	3.2%	10.1%
CH_2DCl	80.9	48.7	74.5
CHD_2Cl	12.4	31.8	12.6
CD_3Cl	3.3	16.3	2.7
D/H	0.63	1.1	0.56

	B. Inert Gas Dependence ^d	
	Run 123 Ar, 500 Torr	Run 124 Ar, 40 Torr
CH_3Cl	20.4%	3.6%
CH_2DCl	40.0	28.6
CHD_2Cl	29.4	33.6
CD_3Cl	10.2	34.2
D/H	0.76	1.96

^a $P/P_0 = 1.0$, 20°. ^b $P/P_0 = 0.2$, 50°. ^c $P/P_0 = 1.0$, 50°. ^d The effect of inert gas pressure on the reaction $\text{D}_2\text{O} + \text{CH}_2\text{DCl}^* \rightarrow \text{CHD}_2\text{Cl}^* + \text{HDO}$. The concentrations for runs 123 and 124 are DCl = 1.07 Torr, $\text{CH}_2\text{N}_2 = 0.16$ Torr, and $\text{D}_2\text{O} = 3.5$ Torr.

(33) H. Tram, *Z. Phys. Chem. (Leipzig)*, **105**, 397 (1923).

The Low-D₂O-Pressure Reaction. The product distribution at low pressures of D₂O is characterized by a marked increase in deuteration. Since D₂O is known to exchange with diazomethane,²³ the effect of reaction 7 on the amount of deuteration was carefully con-



sidered. On the basis of a number of experiments at both high and low pressures of D₂O, it was concluded that the rate of reaction 7 is less than 1/200th of the rate of methyl chloride formation. This rules out the possibility that the above reaction was responsible for the increased methyl chloride deuteration at low pressures of D₂O.

In view of the fact that under ordinary conditions methyl chloride does not exchange with D₂O, the possibility remains that vibrationally hot methyl chloride does exchange. If this is the case, then one should observe an inert gas pressure dependence. This was indeed found, as is shown in Table VIIB. A quantitative analysis of these runs is difficult to make, because the change in pressure affected the exchange reaction between hot methyl chloride with D₂O as well as the exchange with DCl. However, it should be noted that the product distribution in run 124 (Table VIIB) is considerably closer to random than it is (for instance) in run 34. The average deviation from randomness in run 34 is 11.2%, whereas in run 124 it is only 2.0%. Within the framework of the model, closer approach to randomness implies that a greater fraction of the nascent methyl chloride leaves with an internal energy above the critical energy for exchange with D₂O. It is for this reason that a quantitative interpretation is impractical, for to do so another four species CH₂D_{3-n}Cl[±] would have to be introduced into the kinetic scheme. (The dagger indicates an energy content sufficient for reactivity with D₂O, but insufficient for reactivity with DCl; that they should differ is not unreasonable).

Semiquantitative analyses of runs 123 and 124 support the value of $k_x/k_d = 150$, found for the reaction in the absence of D₂O. If we assume that exchange between hot methyl chloride and D₂O occurs essentially at every collision, then runs 123 and 124 imply that to within a factor of 3, about 100 collisions with argon are necessary to deactivate hot methyl chloride relative to exchange with D₂O.

Exchange with D₂S. Several preliminary runs with HCl (or HBr) and CH₂N₂ were carried out in the presence of D₂S.²⁴ The results of this study were not consistent. One group of experiments indicated considerable deuteration, while another suggested no deuteration attributable to a reaction between hot methyl chloride and D₂S. There was no basis for questioning the reliability of either group of experiments, and thus a decision concerning the reactivity of the hot methyl chloride with D₂S must be postponed until the source of irreproducibility has been uncovered.

Discussion

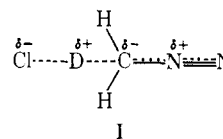
Thus far the data on the rates of the overall reaction (part I) and the hydrogen/deuterium exchange ratios (part II) have been treated separately. However, these two types of experiments establish requirements concerning the nature of the intermediate complex.

Further, in order to convert the ratios of rate constants which were obtained in the exchange study into absolute values, the absolute rate of one of the reactions must be known. The directly measured rate is the overall rate of methyl chloride formation (disappearance of diazomethane).

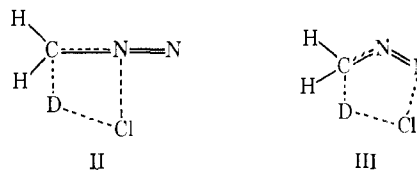
Structure of the Intermediate Complex. We previously concluded that the zero or slightly negative activation energy for the reaction between HCl and CH₂N₂ indicates the formation of a complex, possibly in equilibrium with the reactants. A similar interpretation is useful for explaining the H-D exchange between DCl and diazomethane. However, these experiments suggest that the complex does not attain equilibrium with respect to H-D exchange, since product formation competes with the exchange reaction. In fact, the probabilities for exchange and for product formation were found to be comparable, indicating that $\kappa \approx k_u \ll k_{-a}$ (eq 3). From these considerations it can be concluded that, whereas interconversion between complex and reactants is rapid and occurs many times before the formation of methyl chloride, the probability for H-D exchange in CH₂N₂ is comparatively infrequent. This can be accounted for by either a very short-lived complex, or by a complex which is geometrically not well suited for such an atom-switching reaction.

A rough estimate of the concentration of the complex (and thus a measure of its lifetime) can be obtained by assuming a ΔH° of -5 kcal mol^{-1} and a ΔS° of -30 eu for the reaction $\text{HCl} + \text{CH}_2\text{N}_2 \rightleftharpoons \text{complex}$. At equilibrium this leads to a 2% concentration level for the complex, and argues that it is a rather long-lived species. To account for the small amount of deuteration, one is forced to conclude that the complex is not well suited for exchange.

Hassler and Setser² proposed a structure for the transition state based on linear approach of the two molecules, illustrated by I. Such a linear approach



seems unlikely, because exchange of a D for an H would be impossible. Also it is difficult to imagine a relatively stable complex with this structure. Two more likely structures for the complex are II and III.



Much interest has recently been generated³⁴ by the possible existence of diazine intermediates, similar to II, which decompose in solution by releasing nitrogen. Complex III derives its plausibility from its similarity to the noncyclic diimide, which is known³⁵ to react in

(34) (a) D. M. Lemal and T. W. Rave, *J. Amer. Chem. Soc.*, **87**, 393 (1965); (b) D. M. Lemal and S. D. McGregor, *ibid.*, **88**, 1335 (1966); (c) L. A. Carpino, *Chem. Commun.*, 494 (1966); (d) J. P. Freeman and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 1761 (1967).

(35) (a) P. C. Huang and E. M. Kosower, *ibid.*, **90**, 2354, 2362, 2367 (1968); (b) D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

solution by releasing nitrogen. Since no example of a diimide bonded to chloride is known, its effect on the complex's stability cannot be evaluated. Unfortunately, all the analogies available pertain to substances in solution. This investigation has shown that the reaction of DCl with diazomethane in water solution is different from the gas-phase reaction (the former is much faster and does not result in deuteration of the diazomethane), and thus indicates that in solution no reversible complex is formed but rather that once the two molecules come together they react to form stable products.

The Absolute Rate for Exchange. An absolute value for the rate of HCl-CH₂N₂ exchange now can be obtained. The rate of production of methyl chloride as reported in part I is identified with the sum of the rates for product formation ($k_s + k_v$), which was found to be $7 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. By fitting the proposed exchange mechanism to the experimental data, the ratios k_e/k_s and k_v/k_s were calculated to be 1.4 and 1.2, respectively. From these, the ratio $k_e/(k_s + k_v)$ is 0.64. This yields $k_e = 4 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$. Unfortunately, no absolute values can be obtained for the exchange rate between vibrationally hot methyl chloride and DCl.

The Role of Vibrational Excitation in Bimolecular Reactions. The search for homogeneous reactions involving "hot" methyl chloride has uncovered two examples: hydrogen-deuterium exchange occurs between "hot" methyl chloride and DCl and D₂O. No homogeneous exchange between hot methyl chloride and the reactants D₂, CD₄, CD₃Br, and C₂D₄ was found; the results with D₂S are ambiguous. On this basis we conclude that the critical energies for the reactions which were found not to take place are higher than the internal energies available in the nascent methyl chloride. There are obvious differences between DCl and D₂O on the one hand, and the unreactive molecules on the other; the former are highly polar, have acidic deuteriums, and are generally reactive.

Conventional activation energies for exchange between methyl chloride and any deuterated molecules have not been measured. However, exchange reactions between a number of small molecules have been studied in shock tubes, where the heterogeneous contributions are completely avoided. These results, which have been recently summarized,³⁶ have in common the fact that all the activation energies are lower than half the bond dissociation energies. Since the number of examples is small, only a vague prediction can be made of the critical energies for the CH₃Cl + DX exchanges. The reaction most analogous to it is CH₄-D₂, which has an activation energy of 52 kcal mol⁻¹. Thus the failure of the hot methyl chloride ($\approx 50 \text{ kcal mol}^{-1}$) to exchange with D₂ is not unreasonable. Clearly the direct determination of the activation energies for H-D exchange between methyl chloride and DCl, D₂O, D₂, etc. would be a critical test for the proposed model.

The two major conclusions drawn by Bauer and coworkers on the basis of their shock tube results are (i) that vibrational energy in one of the reactants is necessary for exchange to occur and (ii) that the

relative translational energy of the reactants is of little significance. The experiments described in this work have now confirmed the first prediction, that reaction takes place at room temperature provided sufficient vibrational energy resides in one of the reactants. Support for the second point, that relative translational energy is unimportant, has recently been provided by Jaffe and Anderson.³⁷ They were able to produce a beam of HI molecules with low internal energy but with high translational energies of relative motion with respect to target DI, varying from 20 to 109 kcal mol⁻¹ in the center of mass coordinates. Within the limits of their detector noise (1 molecule out of 2000) they found no product HD. Since the relative translational energy was clearly above the activation energy, the only conclusion to be drawn is that a high translational energy is not sufficient to induce an exchange.

Other authors have also observed an increase in reactivity as a result of vibrational excitation of one of the reactants. Kapralova³⁸ proposed a reaction step involving vibrationally hot HF to account for the inert gas dependence of the upper ignition limit in the HF-H₂ reaction. However, this interpretation has been called in question.³⁹ More recently, Schmeltekopf⁴⁰ found vibrationally excited nitrogen reacts faster than thermal nitrogen by a factor of 40. In a more detailed manner, Chupka⁴¹ studied the reaction of H₂⁺(*v*) with He to give HHe⁺ and H. From this he was able to derive reaction cross sections as a function of the vibrational level ($v = 0-5$) in H₂⁺ and the relative kinetic energy of translational motion (from 0 to 7 eV). The results indicate that energy in the vibrational modes of H₂⁺ is much more effective in promoting reaction than is an equivalent amount of energy in relative translation. In fact, when $v = 0$ the reaction probability is nearly zero regardless of the translational energy. That is, all equal energy cells in phase space are not equivalent with respect to the reaction probability.

The importance of vibrational excitation in bimolecular reactions, particularly for reactions with activation energies above about 25 kcal, seems now to have been established for a limited number of cases. However, there are many unanswered questions, answers to which may be provided by experiments which approach these problems from the direction of energy distribution in the products of exothermic reactions. Then, on the basis of microscopic reversibility, one can calculate the cross section for the reverse reaction.⁴² The results of such studies have suggested that the role of vibrational excitation in bimolecular reactions may not be equally important for all classes of reactions, *i.e.*, that the redistribution of energy in the transition state is very sensitive to the shape of the potential function at the saddle point as well as the location of the saddle point along the reaction coordinate.⁶ For

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example, the series of $H + X_2 \rightarrow HX + X$ ($X = \text{halogen}$) reactions serves as an example in which the vibrational energy of the newly formed HX molecule varies from 50 to 80% of the total energy released.²⁸ The cross sections for the reverse, endothermic reactions ($\Delta H_r^\circ = 30\text{--}50 \text{ kcal mol}^{-1}$) have been predicted to be highly peaked when most of the reactant energy is in the form of vibration.^{42a} Even more dramatic are the results from molecular beam studies⁴³ as well as Monte Carlo calculations,^{6, 44-46} which show that for the reactions

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$A + BC \rightarrow AB + C$ ($A = \text{Cs, K, Rb}$; $BC = \text{Br}_2, \text{I}_2, \text{ICl, IBr}$), more than 90% of the available energy is released in the vibrational mode of the product AB .

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Dynamic Polarization of Phosphorus Nuclei by Nitroxide Radicals

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Abstract: Dynamic nuclear polarization in six phosphorus compounds by four nitroxide radicals in liquid solution reveals several examples of stereospecific intermolecular hyperfine couplings. Trimethyl phosphate shows the expected weak scalar coupling with all four radicals. Di-*t*-butyl nitroxide and triacetone amine nitroxide fail to couple effectively with sterically unshielded phosphines and phosphites. These same two radicals show extremely strong coupling with dimethyl phosphite, suggesting a transient hydrogen bond $\text{P-H} \cdots \text{O-N}$.

Recent experiments² in dynamic nuclear polarization (dnp) have shown that free radicals can be used to probe the physical and chemical phenomena associated with molecular encounters in liquid solutions. Intermolecular hyperfine coupling in liquids depends on stereospecific interactions between certain atomic sites on radical and receptor molecules. The scalar coupling appears to reflect not only the static disposition of electronic orbitals on both molecules, but also the distortions of the orbitals as the two molecules come into contact. The investigation of molecular atomic sites and transient intermolecular bonding by dnp is conceptually complementary to the "spin-labeling" techniques,^{3,4} which use either epr or nmr exclusively and depend on a more or less permanent attachment of molecules. Dnp is, of course, a combined epr-nmr technique, and functions diagnostically not only during firm attachment, but also during short-lived complexations and elastic collisions.

Phosphorus is especially well suited for dnp investigations; it has a nuclear spin $1/2$, a reasonably strong nmr signal, and is readily available in a great diversity of compounds. It is, moreover, an element of prime interest in the life sciences. Since nitroxides are highly

adaptable radicals for spin-labeling studies, we have examined dnp with an array of variegated phosphorus compounds in solution with nitroxides having different free-electron orbital disposition. The combinations were expected to show a variety of collisional interactions between the radical electron and the receptor P nuclei and to reveal varying propensities for complexation and transient bond formation.

Theory

The usefulness of dnp in study of molecular collisions arises from the scalar hyperfine interaction between the radical electron and the receptor nucleus. Intermolecular scalar coupling depends on the intimacy and duration of an encounter, the effective availability of the radical electron, and the responsiveness of the various spin-polarization pathways near the receptor nucleus. Strong spin coupling is found between atomic sites on radical and receptor molecules which share a tendency to form a bond. A strong interaction is also felt by receptor nuclei adjacent to such a site, or more distant, but connected to it by electron resonating structures. The latter can act as long-range carriers of spin information through their delocalized orbitals.

Both quantum mechanical and phenomenological theories for dnp have been presented in detail^{5,6} and need no repetition here.

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