Decomposition of CH_2TCl^* Formed in Dichloromethane. The excitation energy of labeled molecules formed by recoil tritium substitution reactions comes primarily from the difference in kinetic energy between the reacting tritium atom and the displaced atom (H or Cl from dichloromethane). Since the substitution of T for Cl is approximately 1 ev exothermic, this energy should appear as excitation energy of the product molecule, together with any kinetic energy difference between the reacting T atom and the Cl atom replaced by it. Experiments with methyl fluoride have indicated that the energies of tritium atoms prior to substitution for H and for F are approximately equal;[48] no evidence exists concerning the kinetic energy of the displaced atoms in any recoil tritium system, although the assumption is often tacitly made that these atoms are in the thermal-to-1-ev region. The percentage decomposition of CH_2TCl^* after T-for-Cl and T-for-H reactions seems to indicate additional excitation energy in the former, for which about two-thirds of the molecules decompose as compared to only one-half of the latter at the same pressure (0.5 atm).

(48) E. K. C. Lee, G. Miller, and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 190 (1965).

Vibrationally Excited 1,2-Dichloroethane Produced by the Mercury Photosensitization of Dichloromethane[1]

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Abstract: The mercury photosensitization of dichloromethane has been examined as a prototype method for generating chemically activated alkyl halide molecules. It is shown that if the chlorine atoms are removed from the reaction system by a suitable scavenger, then the measured nonequilibrium unimolecular rate constant for HCl elimination from the chemically activated 1,2-dichloroethane formed by association of chloromethyl radicals agrees well with previously determined values. Some discussion of the reactions between the various chlorine-substituted alkyl radicals that may occur in the propene-inhibited system is presented. The chemically activated 1,3-dichloro-2-methylpropane formed by association of chloromethyl and 1-chloroisopropyl radicals does not undergo unimolecular reaction down to pressures of 2 mm. Calculated estimates for the HCl elimination rate constant from 1,3-dichloro-2-methylpropane support this observation; similar calculations were also done for *n*-chloropropane.

The gas-phase kinetics of chemically activated chloroethanes produced by the combination reactions of methyl- and chlorine-substituted methyl radicals have recently been reported[3,4] from this laboratory. Such chemically activated molecules possess $\sim$90 kcal mole^{-1} of vibrational energy and lose HCl by unimolecular reaction unless the excess energy is removed by collisions.[5] For reasonably efficient deactivating bath gases, such as CH_3Cl, one-half of the vibrationally excited molecules were stabilized at the following pressures: C_2H_5Cl, 35 cm; 1,2-$C_2H_4Cl_2$, 1.8 cm; 1,1-$C_2H_4Cl_2$, 110 cm; and 1,1,2-$C_2H_3Cl_3$, 2.2 cm. The H and Cl abstraction reactions by CH_2 from CH_3Cl and CH_2Cl_2 were used to produce the methyl and chloromethyl radicals.[3] On the basis of the work just mentioned, chemically activated chloroethanes would be expected in systems containing the appropriate radical precursors, *i.e.*, methyl and chlorine-substituted methyl radicals.[6] Systems that certainly should show evidence of these hot molecules and their subsequent reactions are the mercury photosensitization of various chloromethanes, especially CH_2Cl_2. In this paper data are presented which demonstrate that the chemically activated 1,2-$C_2H_4Cl_2$ generated *via* the mercury photosensitization of CH_2Cl_2 has the same kinetic behavior as the chemically activated 1,2-$C_2H_4Cl_2$ from the CH_2 + CH_3Cl or CH_2Cl_2 reaction systems.[3,4]

The primary processes in the mercury photosensitization of CH_3Cl have recently been measured.[7]

$$CH_3Cl + Hg(^3P_1) \longrightarrow CH_3 + Hg + Cl = 71\% \qquad (1a)$$

$$\longrightarrow CH_3 + HgCl = 29\% \qquad (1b)$$

The quenching cross section[8] is large (22 Å^2), and the over-all quantum yield is unity. These processes are followed by secondary radical reactions; fast hydrogen abstraction from CH_3Cl by chlorine atoms which gives CH_2Cl radicals is of particular importance. Gunning and co-workers[7-9] were mainly interested in the quenching reactions and apparently made no real ef-

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(1) Part of this work was presented at the Midwestern Regional American Chemical Society Meeting, Lawrence, Kan., Oct 1966.

(2) Alfred P. Sloan Foundation Fellow

(3) D. W. Setser, R. Littrell, and J. C. Hassler, *J. Am. Chem. Soc.*, **87**, 2062 (1965).

(4) (a) J. C. Hassler, D. W. Setser, and R. L. Johnson, *J. Chem. Phys.*, **45**, 3231 (1966); (b) J. C. Hassler and D. W. Setser, *ibid.*, **45**, 3237 (1966); (c) *ibid.*, **45**, 3246 (1966).

(5) J. D. Hassler and D. W. Setser, *J. Phys. Chem.*, **71**, 1364 (1967).

(6) The importance of vibrationally excited molecules in the photolysis of CH_2Cl_2 (M. H. J. Wijnen, Sixth Informal Photochemistry Conference, University of California, Davis, Calif.; 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965) has been discussed; S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1967); see also ref 3.

(7) J. K. S. Wan, O. P. Strausz, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, 42, 2056 (1964).

(8) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 243 (1963).

(9) K. R. Osborn and H. E. Gunning, *Can. J. Chem.*, **37**, 1315 (1959).

Table I. Product Yields[a] from Mercury Photosensitization of CH_2Cl_2

Pressure, cm	1,2-$C_2H_4Cl_2$	C_2H_3Cl	1,1,2-$C_2H_3Cl_3$	*cis*-$C_2H_2Cl_2$[b]	1,1,2,2-$C_2H_2Cl_4$[c]
25	0.014	Trace	0.018	Trace	0.0072
11	0.018	Trace	0.023	Trace	0.0071
8.0	0.014	0.002	0.018	0.002	0.0067
2.5	0.023	0.003	No analysis	0.003	No analysis
1.0	0.015	0.011	No analysis	0.009	No analysis
12[d]	0.015	0.001	Trace	None	None
1.5[d]	0.023	0.026	0.001	None	None

[a] Product yields are tabulated in terms of cc (STP) of gas; the total product yield for each run can be obtained by summing the individual yields. [b] The main dichloroolefin that is formed from the decomposition of 1,1,2-$C_3H_3Cl_3$ is the *cis*-$C_2H_2Cl_2$.[4b] [c] No attempt was made to follow the trichloroolefin arising from the decomposition of $C_2H_4Cl_4$. [d] 15% Propene was added to the sample before photolysis.

fort to quantitatively measure the secondary reaction products;[10] ethane, C_2H_5Cl, and 1,2-$C_2H_4Cl_2$ were reported products, but vibrationally excited molecules were not discussed. In some earlier work Masson and Steacie[11] did find vinyl chloride to be a significant product, but they associated its production with complex radical reactions rather than from unimolecular reaction of vibrationally excited 1,2-$C_2H_4Cl_2$. From the nature of the products in the $Hg(^3P_1)$ reaction with CH_3Cl, it is apparent that CH_3 and CH_2Cl radicals were present; therefore, careful examination should show evidence of vibrationally excited chloroethanes.

The main purpose of this paper is to show that the formation and the subsequent unimolecular reactions of chemically activated chloroethanes are important secondary processes in the mercury photosensitization of CH_2Cl_2. In order to simplify the interpretation of the data, the Cl atoms were scavenged by propene in some of the experiments. Some of the various radical reactions which occur in the CH_2Cl_2 system and the CH_2Cl_2 plus propene system are discussed. The four-centered complex model previously used to calculate RRKM (Rice–Ramsberger–Kassel–Marcus) rate constants for the chloroethane[4c] was used to calculate expected values for HCl elimination rate constants from chemically activated (90 kcal mole^{-1}) *n*-chloropropane and 1,3-dichloro-2-methylpropane.

Experimental Section

The photolysis lamp was a General Electric germicidal lamp (G 15T8).[12] Propene and dichloromethane were purified by gas chromatography before being used. Reactants were saturated with Hg vapor at 25° and irradiated for 15–45 min in sealed quartz vessels placed adjacent to the lamp. The gas samples were measured in a standard vacuum line; constant quantities of reactants (2.0 cc of CH_2Cl_2 with various amounts of propene) were used with vessels of appropriate size to obtain the desired pressures.

After photolysis the samples were analyzed by gas chromatography using an Octoil-S column operated at various temperatures between 60 and 130°. The inlet system to the gas chromatography contained only metal valves; therefore, during photolysis and during the transfer to the gas chromatography inlet the sample was not in contact with stopcock grease. In the measurement and identification of some compounds it was necessary to trap various components and make several passes through the gas chromatograph. Each product was identified by matching retention times to known compounds and was quantitatively measured by comparison with empirical calibrations. In cases where identification based upon retention time from the Octoil-S column alone was doubtful, mass spectral cracking patterns and retention times for other columns were used to help in the identification. No attempt was made to measure hydrogen chloride.

Results

Photosensitization of CH_2Cl_2 and Chemically Activated 1,2-$C_2H_4Cl_2$. The products that were found in the photosensitization of CH_2Cl_2 are shown in Table I. At high pressures the main products are 1,2-$C_2H_4Cl_2$, 1,1,2-$C_2H_3Cl_3$, and 1,1,2,2-$C_2H_2Cl_4$. These products are consistent with the following set of primary reactions which would have been predicted by analogy with previous work with CH_3Cl[7] followed by fast hydrogen abstraction[13] by chlorine atoms.

$$Hg(^1S_0) + 2537\ \text{Å} \longrightarrow Hg(^3P_1) \tag{2a}$$

$$Hg(^3P_1) + CH_2Cl_2 \longrightarrow CH_2Cl + Cl + Hg(^1S_0) \tag{2b}$$

$$\longrightarrow CH_2Cl + HgCl \tag{2c}$$

$$Cl + CH_2Cl_2 \longrightarrow CHCl_2 + HCl \tag{2d}$$

At high pressures the combination reactions of these radicals produce three chloroethanes.

$$CH_2Cl + CH_2Cl \longrightarrow C_2H_4Cl_2^* \tag{3a}$$

$$CH_2Cl + CHCl_2 \longrightarrow C_2H_3Cl_3^* \tag{3b}$$

$$CHCl_2 + CHCl_2 \longrightarrow C_2H_2Cl_4^* \tag{3c}$$

Chlorine- and hydrogen-abstraction reactions by these radicals are slow processes at room temperature.[14] Nevertheless, small amounts of CH_3Cl and $CHCl_3$ were found in the photolyzed samples. Typical yields are shown in Table I. The quantity of 1,2-$C_2H_4Cl_2$ present is roughly twice that of $C_2H_2Cl_3$. Since self-combination rate constants of halogen-substituted radicals are nearly equal,[15] the different yields probably arise from a lower steady-state concentration of $CHCl_2$ relative to CH_2Cl. This is consistent with the two simultaneous primary processes with (2b) being of greater importance than (2c) as other investigators have found for CH_3Cl.[7] The quantity of $C_2H_3Cl_3$ is somewhat larger than $C_2H_4Cl_2$ because mixed combination rate constants are usually larger than self-combination rate constants [$k_{ab} \approx 2(k_{aa}k_{bb})^{1/2}$ see ref 14a and 10 for examples].

The data at high pressures certainly establish that the three chloroethanes were generated in the system. It

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[10] M. G. Bellas, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **43**, 1022 (1965). In this paper it was shown that the uninhibited mercury photosensitization of $CHClF_2$ gave CHF_2 and $CClF_2$ radicals and that these radicals yielded the expected combination products.

[11] C. R. Masson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 183 (1951).

[12] G. B. Kistiakowsky and C. S. Parmenter, *ibid.*, 42, 2942 (1965). These authors describe the characteristics of a lamp similar to the one employed in this work.

[13] (a) G. C. Fettis and J. H. Knox, *Progr. Reaction Kinetics*, **2**, 3 (1964) (this reference contains a summary of halogen atom reaction rates constants); (b) P. B. Ayscough, F. S. Dainton, and B. E. Fleischfresser, *Trans. Faraday Soc.*, **62**, 1838 (1966); (c) C. Cillien, P. Goldfinger, G. Haybrechts, and G. Martens, *ibid.*, **63**, 163 (1967).

[14] (a) W. G. Alcock and E. Whittle, *ibid.*, **62**, 134 (1966); (b) D. M. Tomkinson, J. P. Galvin, and H. P. Pritchard, *J. Phys. Chem.*, **68**, 541 (1964).

[15] H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37**, 700 (1962).

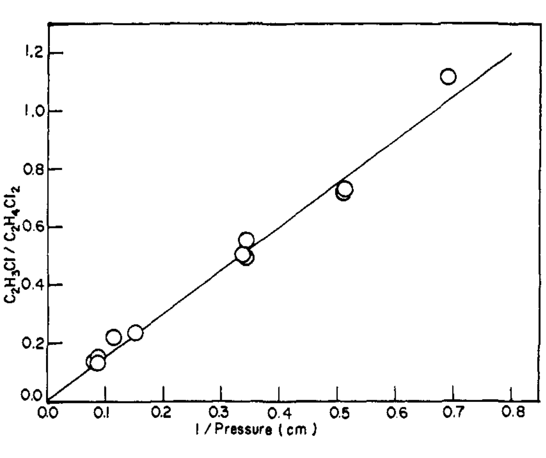

Figure 1. Plot of the ratio of the product yields, vinyl chloride/1,2-dichloroethane *vs.* 1/pressure for mercury photosensitization of 85% dichloromethane and 15% propene mixtures.

was next attempted to lower the pressure and measure decreased yields of chloroethanes with concomitant increased yields of the appropriate olefinic decomposition products. Indeed, the C_2H_3Cl and $C_2H_2Cl_2$ (no attempt to follow C_2HCl_3 was made) yields do rise with a lowering of the pressure as shown by the data of Table I. This is consistent with a competition between collisional stabilization and unimolecular HCl elimination from the vibrationally excited chloroethanes (an asterisk signifies vibrational excitation).

$$C_2H_4Cl_2^* \xrightarrow{\omega} C_2H_4Cl_2 \quad (S_I) \qquad (4a)$$

$$\xrightarrow{k_{aI}} HCl + C_2H_3Cl \quad (D_I) \qquad (4b)$$

$$C_2H_3Cl_3^* \xrightarrow{\omega} C_2H_3Cl_3 \quad (S_{II}) \qquad (4c)$$

$$\xrightarrow{k_{aII}} HCl + C_2H_2Cl_2 \quad (D_{II}) \qquad (4d)$$

$$C_2H_2Cl_4^* \xrightarrow{\omega} C_2H_2Cl_4 \quad (S_{III}) \qquad (4e)$$

$$\xrightarrow{k_{aIII}} HCl + C_2HCl_3 \quad (D_{III}) \qquad (4f)$$

If these reactions describe the system, a plot[4] of $C_2H_3Cl/C_2H_4Cl_2$ *vs.* (pressure)$^{-1}$ should be a straight line with the slope of the line equal to the apparent nonequilibrium rate constant, $k_{aI} = \omega(D_I/S_I)$. Examination of the fourth and fifth entries of Table I shows that the values of k_{aI} are not constant. Since all the values for k_{aI} were consistently low relative to our earlier work,[3,4] it was immediately suspected that some process was removing C_2H_3Cl from the reaction system. The reactions of chlorine atoms with olefins are known to be faster than H-abstraction reactions,[13] and it seemed plausible that the chlorine atoms were preferentially reacting with the olefins (D_I, D_{II}, D_{III}) rather that with CH_2Cl_2. In order to check this possibility experiments were done with 15% added propene.[16] It is seen from Table I that the production of $C_2H_2Cl_4$ and $C_2H_3Cl_3$ is severely diminished; this can be explained by the propene scavenging the Cl atoms and thereby blocking reaction 2d and subsequent reactions involving $CHCl_2$ radicals. Of course, additional new products arise from the various combination and disproportionation reactions of CH_2Cl with the radicals resulting from the reaction of Cl with propene. These reactions and the reaction of Cl with propene are considered in the next section. At this point it is sufficient to note that the propene effectively removes the Cl atoms and, hence, protects all chlorinated olefin decomposition products arising by HCl elimination from the chemically activated chloroethanes.

Since the propene blocks the formation of $CHCl_2$ radicals, CH_2Cl is the only chlorine-substituted methyl radical present, and only one chemically activated chloroethane can be studied, namely, 1,2-$C_2H_4Cl_2$. A plot of D_I/S_I *vs.* (pressure)$^{-1}$ for runs with 15% propene at various total pressures is shown in Figure 1. A linear relation obviously exists, and a least-squares analysis of the line gave a rate constant of 1.5 ± 0.1 cm; collision cross sections of 4.7 Å for CH_2Cl_2 and C_3H_6 and 6.0 Å for 1,2-$C_2H_4Cl_2$ give $k_a = 1.7 \times 10^8$ sec^{-1}. This is in favorable agreement with our earlier results[4] which yielded a rate constant of 1.9×10^8 sec^{-1}.

Radical Reactions in the Photosensitization of CH_2Cl_2 with C_3H_6. Propene (15%) was used in most runs in order to ensure protection of vinyl chloride arising from reaction 4b. Since the quenching cross sections of propene and dichloromethane[17] are similar, the primary reactions in the mercury photosensitization of propene[18] must be included as a source of radicals. The main reactions are given below with (5a) contributing perhaps 85% to the primary step.

$$CH_3CH{=}CH_2 + Hg(^3P_1) \longrightarrow H + CH_2CH{=}CH_2 + Hg \qquad (5a)$$

$$\longrightarrow CH_3 + CH{=}CH_2 + Hg \qquad (5b)$$

Analogy with the results of $Hg(^3P_1)$ with butene-1[19] and C_2H_4[20] suggests that reactions 5 probably proceed through excited states; consequently, in certain pressure regions the reactions may be diminished by collisional stabilization. In addition to CH_2Cl and CH_2-$CH{=}CH_2$, the radicals that could be expected in high concentration are those resulting from the reaction of Cl with propene. The majority of the identified products are adequately explained by terminal addition.

$$Cl + CH_3CH{=}CH_2 \longrightarrow CH_3CHCH_2Cl \qquad (6)$$

Other workers[21] have apparently reached a similar conclusion. It should, however, be noted that if allyl radicals were produced by H abstraction from propene, they would not have been distinguished from allyl radicals generated by (5a). The major products are explained by the reactions compiled in Table II which are typical radical reactions of CH_2Cl, C_3H_5, and C_3H_6Cl. Before discussing them in detail, it is worth noting that one small glpc peak, which, based upon its retention time, could be identified as 1,3-dichlorobutane, was present

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(16) The back dissociation of vibrationally excited radicals produced by the addition of Cl to $C_2H_2Cl_2$ has received considerable discussion: J. H. Knox and J. Riddick, *Trans. Faraday Soc.*, **62**, 1190 (1966); see also ref 13b. In order to reduce the possibility of back dissociation, propene was used as the scavenger for Cl. The larger number of degrees of freedom should ensure that C_3H_6Cl does not undergo appreciable back dissociation at pressures used in this work.

(17) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **41**, 1705 (1964); M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, *ibid.*, **41**, 768 (1964). The cross section of CH_2Cl_2 is not known, but adding the second Cl atom to CH_3Cl should increase the cross section from 22 to above 30 Å^2; the cross section for propene is about 30 Å^2.

(18) M. Avrahami and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963); C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, **42**, 1262 (1965).

(19) R. J. Cvetanovic and L. C. Doyle, *ibid.*, **37**, 543 (1962).

(20) D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Am. Chem. Soc.*, **85**, 862 (1963).

(21) J. A. Guercione and M. H. J. Wijnen, unpublished data quoted by R. J. Cvetanovic, *Advan. Photochem.*, **1**, 171 (1963).

Table II. Summary of Radical Reactions[a] for 85% CH_2Cl_2 and 15% C_3H_6 Mixture[b]

	Reactants	Combination products	Disproportionation products[c]
I	$\cdot CH_2Cl + \cdot CH_2Cl$	1,2-$C_2H_4Cl_2$	None
II	$\cdot CH_2Cl + CH_3\dot{C}HCH_2Cl$	$CH_2ClCHCH_3CH_2Cl$	a. $CH_3Cl + CH_2{=}CHCH_2Cl$
			b. $CH_3Cl + CH_3CH{=}CHCl$
			c. $CH_2Cl_2 + CH_3CH{=}CH_2$
III	$CH_3\dot{C}HCH_2Cl + CH_3\dot{C}HCH_2Cl$	$C_6H_{12}Cl_2$ (not measured)	a. $CH_2{=}CHCH_2Cl + CH_3CH_2CH_2Cl$
			b. $CH_3CH{=}CHCl + CH_3CHClCH_2Cl$
			c. $CH_3CH{=}CH_2 + CH_3CHClCH_2Cl$
IV	$\cdot CH_2Cl + \cdot CH_2CH{=}CH_2$	$CH_2ClCH_2CH{=}CH_2$	None
V	$\cdot CH_2CH{=}CH_2 + CH_3\dot{C}HCH_2Cl$	$C_6H_{11}Cl$ (not measured)	a. $CH_3CH{=}CH_2 + CH_3CH{=}CHCl$
			b. $CH_3CH{=}CH_2 + CH_2ClCH{=}CH_2$

[a] The reactions of the hydrogen atoms generated in reaction 5a have been ignored in the table and the text. They mainly abstract Cl from CH_2Cl_2 to give HCl and more CH_2Cl radicals. [b] Typical product yields at high pressure in units of cc at STP are: $C_4H_8Cl_2$, 0.03; C_4H_7Cl, 0.019; C_3H_7Cl, 0.003; $C_3H_6Cl_2$, 0.004; $CH_2{=}CHCH_2Cl$, 0.006; *cis*-$CH_3CH{=}CHCl$, 0.006; *trans*-$CH_3CH{=}CHCl$, 0.001; $C_2H_4Cl_2$, 0.049; CH_3Cl, 0.004. [c] The products of reaction Vb can arise by Cl or H transfer from different ends of the C_3H_6Cl radical.

to the extent of one-tenth of 1,3-dichloro-2-methylpropane. These two products arise from combination of CH_2Cl with $CH_3CHClCH_2$ and CH_3CHCH_2Cl radicals, respectively. This is tentative evidence that the ratio of terminal to nonterminal chlorine atom addition to propene is about 10:1.

Chlorine-substituted alkyl radicals disproportionate by both H and Cl transfer,[22] and both types of reactions are included in Table II. The disproportionation and combination reactions of CH_2Cl, CH_3CHCH_2Cl, and $CH_2CH{=}CH_2$ explain the main products. Since abstraction from CH_2Cl_2 by these radicals can be expected to be slow,[14] such reactions were not included in the table. Also, the relatively small yields of *n*-chloropropane and 1,2-dichloropropane support the validity of omitting such reactions. No attempt was made to identify the C_6 combination products; also biallyl would have been eluted from the Octoil-S column at the same time as CH_2Cl_2 ,and no effort was made to ascertain its presence. A typical product analysis is included in the table. It is obvious that the combination reactions are favored over the disproportionation reactions as would be expected.[22] A rather interesting general feature of the disproportionation reactions giving 1-chloropropene was the dominance of the *cis* over the *trans* isomer by a ratio of 5:1.

If the ratio of propene to dichloromethane concentration is lowered so that the reaction of chlorine atoms with CH_2Cl_2 and C_3H_6 becomes competitive, then the products arising from the $CHCl_2$ radical must be added to the reaction scheme of Table II. Of particular interest are the combination products of $CHCl_2$ with CH_2Cl and CH_3CHCH_2Cl with CH_2Cl. If these combination rate constants are taken to be equal,[15] then the product yield ratio, $C_2H_3Cl_3/C_4H_8Cl_2$, gives the ratio of the radical concentrations, $[CHCl_2]/[C_3H_6Cl]$. This ratio is, in turn, equal to $k_{2d}[CH_2Cl_2]/k_6[C_3H_6]$ and a plot of $C_2H_3Cl_3/C_4H_8Cl_2$ *vs.* $[CH_2Cl_2]/[C_3H_6]$ should be linear with slope equal to the rate constant ratio. Such a plot is displayed in Figure 2, and the data, which are not of great accuracy, indicate chlorine atoms react about 200 times faster with propene than with CH_2Cl_2.

In earlier work[4b] we have suggested that $CHCl_2$ and CH_2Cl radicals participate, to a small extent, in a direct pressure-independent disproportionation reaction to give HCl and $C_2H_2Cl_2$ (the *cis* isomer was the major one), as well as combining to $C_2H_3Cl_3$. It was attempted to check this possibility by photosensitizing mixtures of CH_2Cl_2 with 2–4% propene or ethene. This small quantity of olefin should protect the *cis*-$C_2H_2Cl_2$ from attack by chlorine atoms but not prevent formation of the $CHCl_2$ radical. Unfortunately, the results were inconclusive, because, with propene as the addend, the $CH_2ClCH_2CH{=}CH_2$ product had the same retention time as *cis*-$C_2H_2Cl_2$; and with ethene, the combination product 1,3-$C_3H_6Cl_2$ had the same retention time as $C_2H_3Cl_3$. Further work is required using a different analytical scheme with careful attention given to protection of olefins and identification of products before this interesting question can be answered.

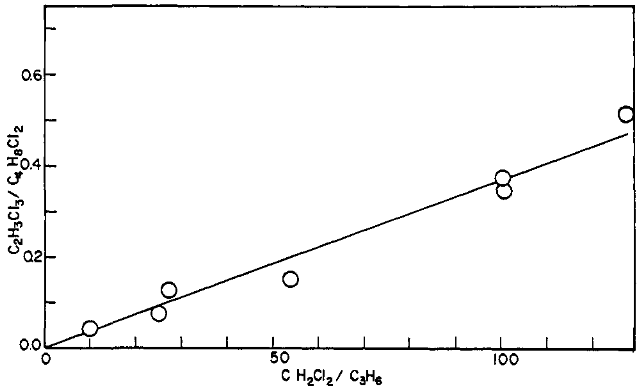

Figure 2. The ratio of the yields of 1,1,2-trichloroethane to 1,3-dichloro-2-methylpropane arising in the mercury photosensitization of samples containing various ratios of dichloromethane to propene.

Discussion

Unimolecular Reactions of the Chemically Activated Alkyl Chlorides. It is self-evident from this work that the mercury photosensitization of chlorinated methanes provides systems in which chemically activated molecules may exist. It is also evident that these reaction systems are somewhat complex and that care must be exercised in deducing the nonequilibrium rate constants from such studies. Further work is proceeding in our laboratory, and the measurement of the $C_2H_2Cl_4$ rate constant from the mercury photosensitization of $CHCl_3$ and C_3H_6 mixtures appears feasible. The early work of Gunning and co-workers is of considerable aid in helping to understand the systems. Other sensitiza-

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(22) (a) B. C. Roquitte and M. H. J. Wijnen, *J. Chem. Phys.*, 38, 4, (1963); (b) J. Heicklen, *J. Am. Chem. Soc.*, 87, 445 (1965).

tion methods, for example, hexafluorobenzene,[23] may also be effectively utilized to produce chemically activated chloroethanes from the chloromethanes.

This work has shown that the vibrationally excited 1,2-$C_2H_4Cl_2$ molecules generated by reaction 3a have the same nonequilibrium rate constant that was previously measured in the $CH_2 + CH_2Cl_2$ study.[4] Since the rate constant has now been independently measured in several systems, it must be considered well established.

The measurement of the rate constant for 1,3-dichloro-2-methylpropane was attempted; however, even at a pressure of 2 mm, no decomposition product was detected. The quantity of 1,3-dichloro-2-methylpropane relative to other products did decline at the lower pressures, but this was attributed to a changed steady-state radical concentration rather than to unimolecular decomposition. Because of the difficulty of protecting the decomposition product, C_2H_2Cl, from Cl atoms and simultaneously having an appreciable concentration of $CHCl_2$ radicals present, no attempt was made to measure the constant for 1,1,2-$C_2H_3Cl_3$. In previous work of a somewhat limited nature, the one-half stabilization pressure for these molecules was found to be 2.2 cm. An interesting question concerning α,α and α,β HF elimination from vibrationally excited 1,1-$C_2H_4F_2$ and 1,1,2-$C_2H_3F_3$ has recently been raised.[24] In our previous work with 1,1,2-trichloroethane, α,β elimination would have been indistinguishable from α,α elimination. Apparently, α,α elimination is not important for C_2H_5F or 1,2-$C_2H_4F_2$.[24]

The interpretation of the unimolecular HCl and HBr elimination reactions from vibrationally excited chloro-[4c] and bromoethanes[25] has been thoroughly treated in other places, and there is no need for repetition. It is of interest, however, to consider 1,3-dichloro-2-methylpropane and examine the predictions of the RRKM theory of unimolecular reactions for the elimination rate constant based upon the four-centered activated complex model.[4c] In a series of papers,[26-28] Rabinovitch and co-workers have shown that the microscopic unimolecular rate constants for a homologous series of compounds at approximately the same energy can be experimentally observed in chemical activation systems and that the rate constants are adequately explained by the RRKM theory of unimolecular reactions if all internal degrees of freedom are considered to be active. We have done calculations for *n*-C_3H_7Cl as well as for dichloro-2-methylpropane in order to have a connecting link between C_2H_5Cl and $C_4H_8Cl_2$. The procedures for doing the calculations were identical with those used in previous work,[4c,25] and descriptions of the models and equations will not be given. The critical energy for HCl elimination from C_3H_7Cl and $C_4H_8Cl_2$ was taken to be the same as for C_2H_5Cl, *i.e.*, 55 kcal mole^{-1}. Vibrational frequencies and moments of inertia for C_3H_7Cl were obtained from the literature; for $C_4H_8Cl_2$ these quantities were estimated by analogy with similar molecules. The frequencies and moments of inertia for the activated complexes were obtained by using the four-centered complex developed for C_2H_5Cl and C_2H_5Br as a framework and then removing frequencies associated with a hydrogen atom and adding frequencies characteristic of a CH_3 or CH_2Cl group. In each case the frequencies were finally adjusted so that the preexponential factors of the thermal activation unimolecular rate constants were about 2×10^{13} sec^{-1}, which are typical values for the alkyl chlorides and bromides. These models give rate constants at 90 kcal mole^{-1} of 5×10^7 and 1×10^6 sec^{-1} for C_3H_7Cl and $C_4H_8Cl_2$, respectively. For C_2H_5Cl at this level of energy the rate constant[25] was 2.0×10^9 sec^{-1} which agreed closely with the experimental value. On the basis of this calculation, appreciable decomposition of the $C_4H_8Cl_2$ would not be expected at pressures above 1 mm; the calculations thus support the experimental evidence. In view of the uncertainties in thermochemistry and the models, it may be anticipated that the present calculations are reliable to within a factor of 3–5. The calculated variation of the microscopic rate constants for the alkyl halide homologous series is similar to that found for the cyclopropane series;[28] this would be expected on the basis of similarities of the critical energies and levels of activation.

Radical Reactions. These experiments were not designed to study the radical reactions, and, consequently, little quantitative data were obtained. Very little work has been done on the reactions of Cl atoms with propene[21,29] in contrast to quite extensive studies with ethene and chlorine-substituted ethenes.[16,30] The rate constant for reaction of Cl atoms with CH_2Cl_2 has been reported[13] as $1.3 \times 10^{13} \exp(-2960/RT)$ cc mole^{-1} sec^{-1} which at 25° is 8.6×10^{10} cc mole^{-1} sec^{-1}. Since our results show that the Cl reacts some 200 times faster with C_3H_6 than with CH_2Cl_2 at 25°, the rate constant with C_3H_6 must be $\sim 10^{13}$ cc mole^{-1}. This estimate of the rate constant is close to that obtained[29] in competitive photochlorination experiments with propane–propene mixtures. Within our experimental error, the rate constant for propene is the same as that for ethene which apparently has zero activation energy.[30]

Although complicated somewhat by heterogeneous effects, the authors[29] of the photochlorination study of propene did not interpret their data in terms of redissociation of vibrationally excited chloropropyl radicals. Since propene is such an efficient scavenger relative to CH_2Cl_2 and since the ratio of C_2H_3Cl plus $C_2H_4Cl_2$ to $C_4H_8Cl_2$ is constant down to pressures of about 1 cm, the present data also corroborate such conclusions. Below 1 cm pressure the chloropropyl radical may be redissociating, but, on the other hand, other pressure-dependent radical concentrations may also be changing the (C_2H_3Cl plus $C_2H_4Cl_2$)/$C_4H_8Cl_2$ ratio. The longer lifetime of the chloropropyl radicals relative to chlorethyl radicals[16] would be expected since the former has more internal degrees of freedom.[26]

The 1- and 3-chloropropenes arise from several disproportionation reactions, and it is impossible from the present data to deduce the various disproportionation–

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combination ratios. It is apparent from comparison of the quantity of the combination product from reaction II of Table II to the sum of the chloropropene yields that combination dominates over disproportionation. The quite significant yield of 1,2-$C_3H_6Cl_2$ is also evidence that Cl atom transfer is important in these disproportionation reactions. Such results have been previously observed for chloroethyl radicals.[22] A novel feature is the 5:1 dominance of *cis*- over *trans*-1-chloropropene. This chloropropene isomer arises from the removal of a hydrogen from the chlorinated end of CH_3CHCH_2Cl during disproportionation. In view of the widely accepted loose nature of the activated complex for disproportionation reactions, it is surprising that small stereochemical effects are important. It should be noted that the *cis*-halopropenes are perhaps slightly more stable than the *trans* isomers.[31]

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cis–trans Isomerization and Pulsed Laser Studies of Substituted Indigo Dyes[1]

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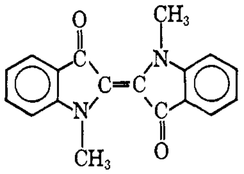
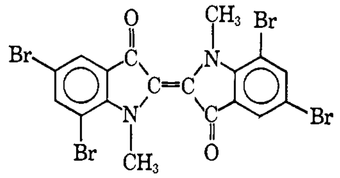
Abstract: The photochromic behavior of N,N′-dimethylindigo and N,N′-dimethyl-5,5′,7,7′-tetrabromoindigo was investigated in the visible region with photostationary and flash photolysis techniques and at 6328 and 6943 Å with laser systems. Calculated spectra of the *cis* isomers, quantum yields (~0.01 in benzene) for the *trans* → *cis* photoconversions, lifetime estimates of intermediates, and kinetic data for the *cis* → *trans* thermal isomerization are presented. The latter process was found to be acid catalyzed and was studied in detail for dimethylindigo in alcohol–water solutions. Laser experiments at high intensities (~10^{26} quanta/(sec cm^2)) give rise to the observation of a short-lived transient state believed to be the triplet intermediate in the photoisomerization process.

Geometrical isomerization of highly substituted ethylenic structures is a basic photochromic mechanism[2] and has been studied for several classes of compounds including polyenes and carotenoids,[3] stilbenes,[4,5] azo compounds,[6,7] conjugated anils[8] and nitriles,[9] and cyanine,[10] thioindigo, and indigo dyes.[11] Although *cis–trans* isomerization of indigo itself has not been observed,[11] alkyl substitution at the nitrogen atom allows photoconversion to occur between the *cis* and *trans* structural isomers.[12,13] We have obtained quantitative spectroscopic evidence for the photoisomerization of N,N′-dimethylindigo (I) and N,N′-dimethyl-5,5′,-7,7′-tetrabromoindigo (II) by conventional flash photolysis and photostationary methods and by unique measurements carried out with a pulsed ruby laser. Additionally, the thermal *cis* → *trans* conversion of I was found to be acid catalyzed, and rate constants for this process in a variety of solvents also are reported.



I



II

The previous qualitative observations on compound I by Weinstein and Wyman[12] differ significantly from the work reported by Pummerer and Marondel.[13] Both groups reported a decrease in optical absorption at 650 mμ when I was irradiated with yellow light (λ >520 mμ), but the former emphasizes that the thermal back reaction (*cis* → *trans*) proceeds rapidly (seconds) in benzene, whereas Pummerer and Marondel report a long-lived (18 hr) photoinduced absorption band at 410 mμ in carbon tetrachloride. Their assignment of this band to the *cis* isomer does not correspond with Weinstein and Wyman's data, nor does it follow the photoisomerization expected by comparison with analogous structures such as N,N′-diacetylindigo[11] and thioindigo.[14] Pummerer and Marondel also reported photo-

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