

Thermal and Hot Reactions of Chlorine Atoms with *cis*- and *trans*-1,2-Dichloroethylene¹

Chien M. Wai and F. S. Rowland

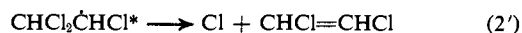
Contribution from the Department of Chemistry, University of California, Irvine, California 92664. Received October 2, 1968

Abstract: Energetic ³⁸Cl atoms react with *cis*- and *trans*-1,2-dichloroethylene in condensed phases to form both ³⁸Cl-labeled isomers of 1,2-DCE, with a preference (ranging between 56/44 and 70/30) for retention of the geometry of the original molecule. Hot substitution of ³⁸Cl for H to form CHCl=CCl³⁸Cl is also observed. The reactions observed in the gas phase are consistent with the decomposition of the excited CHCl³⁸ClCHCl* formed by addition of ³⁸Cl to either isomer of CHCl=CHCl. When used in scavenger (3%) concentrations in CH₂Cl₂, the CHCl³⁸ClCHCl* radicals are almost entirely formed by thermal ³⁸Cl atom addition. The *trans/cis* branching ratio for decomposition of excited CHCl³⁸ClCHCl* radicals is 0.50 ± 0.05, and τ < 10⁻¹⁰ sec for rotation about the C—C bond of this radical. The radical lifetime is about 5–7 × 10⁻¹⁰ sec when formed by thermal ³⁸Cl addition.

Chlorine atoms react with 1,2-dichloroethylene (DCE) by addition to the double bond, as in (1'), to form a trichloroethyl radical excited by the approximately 20 kcal/mole exothermicity of the reac-



tion, plus any kinetic energy of the reacting Cl atom. Decomposition of the trichloroethyl radical by loss of a chlorine atom, as in (2'), was first established by



observation of the geometric isomerization of *cis*- or *trans*-1,2-dichloroethylene at a rate considerably faster than that of the formation of the radicals, as determined by the production of tetrachloroethane.²⁻⁴ Recent measurement of the similar decomposition of monochloroethyl radicals formed by chlorine atom addition to ethylene indicates agreement now upon the general validity of the decomposition mechanism of reaction 2'.⁵⁻¹²

Our own experiments have sought information concerning the chemical reactions occurring when ³⁸Cl atoms with excess kinetic energy from nuclear recoil react with either of the CHCl=CHCl isomers. Thermalization of these ³⁸Cl atoms should provide opportunity for the isotopic analogs of (1') and (2'), as given in (1)–(3). Since the experimental techniques



involve the determination *only* of the chemical location of the ³⁸Cl atoms, the elimination of ³⁸Cl, as in (2b), will not result in a detectable product; the ³⁸Cl atom from such a decomposition must undergo some additional reaction characteristic of thermal chlorine atoms, including the possibility of recycling through (1).

In addition to the thermal chlorine atom reactions given above, hot chlorine atoms might also be expected, by analogy with other experiments involving energetic chlorine atoms, to undergo "direct" substitution of ³⁸Cl for Cl with retention of the same geometric structure, *cis* or *trans*, as the original reactant material; substitution of ³⁸Cl for H, as in (4); higher energy versions of (1)–(3); and perhaps other hot reactions.¹³⁻²⁰ Recent experiments have established that the characteristic reactions of recoil chlorine species are identical for the atoms formed in the very different nuclear reactions ⁴⁰Ar(γ,p)³⁹Cl and ³⁷Cl(n,γ)³⁸Cl,



and that they are the reactions of ground-state chlorine atoms with excess kinetic energy.^{15,16} In the present experiments, only the latter reaction has been utilized as the source of energetic chlorine atoms.

Experimental Section

Chemicals. Reagent grade *cis*- or *trans*-1,2-dichloroethylene normally contains a small amount of the opposite isomer; the isomers were obtained in >99.5% purity by gas chromatographic

(1) This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126, and constituted part of the thesis submitted by C. M. Wai in partial fulfillment of the requirements for the Ph.D. at the University of California, Irvine.

(2) P. B. Ayscough, A. J. Cocker, F. S. Dainton, S. Hirst, and M. Weston, *Proc. Chem. Soc.*, 244 (1961).

(3) P. B. Ayscough, A. J. Cocker, and F. S. Dainton, *Trans. Faraday Soc.*, 58, 284 (1962).

(4) P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *ibid.*, 58, 295 (1962).

(5) G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens, and G. Verbeke, *Chem. Rev.*, 63, 355 (1963).

(6) M. L. Poutsma and R. L. Hinman, *J. Am. Chem. Soc.*, 86, 3807 (1964).

(7) P. B. Ayscough, F. S. Dainton, and B. Fleishfresser, *Trans. Faraday Soc.*, 62, 1838 (1966).

(8) J. H. Knox and J. Riddick, *ibid.*, 62, 1190 (1966).

(9) J. H. Knox, *ibid.*, 62, 1205 (1966).

(10) F. S. Dainton and P. B. Ayscough, "Photochemistry and Reaction Kinetics," Cambridge University Press, London, 1967, Chapter 4.

(11) D. C. Tardy and B. S. Rabinovitch, *Trans. Faraday Soc.*, 64, 1844 (1968).

(12) J. Franklin, P. Goldfinger, and G. Huybrechts, *Ber. Bunsenges. Physik. Chem.*, 72, 173 (1968).

(13) J. E. Willard, "Chemical Effects of Nuclear Transformations, Vol. 2, International Atomic Energy Agency, Vienna, 1965, p 221.

(14) F. S. Rowland, C. M. Wai, C. T. Ting, and G. E. Miller, ref 13, p 333.

(15) C. M. Wai and F. S. Rowland, *J. Phys. Chem.*, 71, 2752 (1967).

(16) C. M. Wai and F. S. Rowland, *J. Am. Chem. Soc.*, 90, 3638 (1968).

(17) C. M. Wai and F. S. Rowland, *J. Phys. Chem.*, 72, 3049 (1968).

(18) L. Spicer and R. Wolfgang, *J. Am. Chem. Soc.*, 90, 2426 (1968).

(19) C. M. Wai, Ph.D. Thesis, University of California at Irvine, 1967.

(20) L. Spicer, Ph.D. Thesis, Yale University, 1968.

separation, with repurification just prior to experiments to avoid the growth of the opposite isomer during storage. Analysis of samples after irradiation showed a negligible formation of the opposite isomer from radiation effects, and no correction was necessary for such impurities.

Experimental Techniques. The details of sample preparation, irradiation, and radio gas chromatographic analysis are adequately described elsewhere and are essentially unchanged from these previous descriptions.^{16,19,21} A typical radio gas chromatogram, taken on a 15-ft tritoyl phosphate column, is shown in Figure 1. Only reasonably volatile ³⁸Cl-labeled organic species have been identified and measured in these experiments. Molecules such as Cl³⁸Cl and H³⁸Cl have not been measured because of experimental difficulties with isotopic exchange. (A radio gas chromatogram of the radioactive products from a mixture of CH₃Cl, *cis*-1,2-DCE, O₂, and argon is shown in ref 16.) Absolute yield measurements, obtained for some gas-phase measurements, were monitored through comparison with the yield of the ⁴⁰Ar(n,γ)⁴¹Ar nuclear reaction.

Results and Discussion

Thermal Addition of ³⁸Cl to CHCl=CHCl. Decomposition of CHCl³⁸ClCHCl* Radicals. The low activation energy for Cl atom addition to olefins makes both isomers of CHCl=CHCl efficient in reacting with thermalized ³⁸Cl atoms, and these molecules have been used as scavengers for the nuclear recoil studies of ³⁸Cl reactions with CH₃Cl.^{16,22} The competition between decomposition of CHCl³⁸ClCHCl* and its stabilization by collision shows a pressure dependence from which information about the decomposition rate can be obtained. A plot of the reciprocal yield of CHCl=CH³⁸Cl (sum of *cis* + *trans*) vs. pressure should give a straight line if the CHCl³⁸ClCHCl* radicals are essentially monoenergetic, as would be the approximate situation for the exothermic addition of thermal Cl to CHCl=CHCl. Deviation from such a straight line is expected if an appreciable contribution to the formation of CHCl=CH³⁸Cl is being made by decomposition of CHCl³⁸ClCHCl* radicals with substantially greater excitation energy as a consequence of initial formation by reaction of an energetic ³⁸Cl atom. The ratio of thermal-to-hot contributions to the formation of CHCl=CH³⁸Cl can be expected to be rather high in a system with CH₃Cl in 35-fold excess to *cis*-CHCl=CHCl. The data of Table I show a nearly straight line (dotted line of Figure 2) for such a graph, indicating that most of the radicals are indeed approximately monoenergetic in excitation energy. Correction for a small fraction of CHCl³⁸ClCHCl* radicals formed by hot ³⁸Cl atom addition, and thereby so excited as to undergo complete decomposition at pressures of 25–50 cm, produces the solid straight line of Figure 2. The correction factor used in Figure 2 is a fractional "hot" yield of CHCl=CH³⁸Cl of 0.015, as compared (see below) to the "thermal" yield of CHCl=CH³⁸Cl of 0.20.

The intercept of the straight line (~5) provides a direct reciprocal estimate of the total fraction (0.20) of ³⁸Cl atoms reacting with CHCl=CHCl to form CHCl=CH³⁸Cl at zero pressure. The slope of the straight line provides an approximate estimate of the

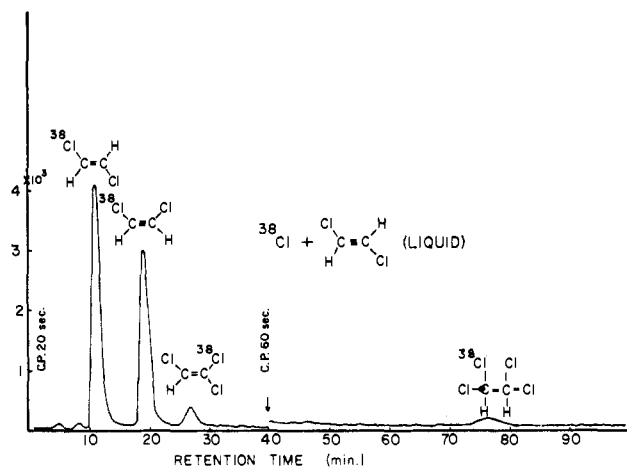


Figure 1. Volatile radioactive ³⁸Cl products from ³⁸Cl reactions with liquid *trans*-1,2-dichloroethylene: 15-ft tritoyl phosphate column operated at 80°, with He flow rate of 30 ml/min; irradiation time, 3 min at 20° and 10¹¹ n/(cm² sec).

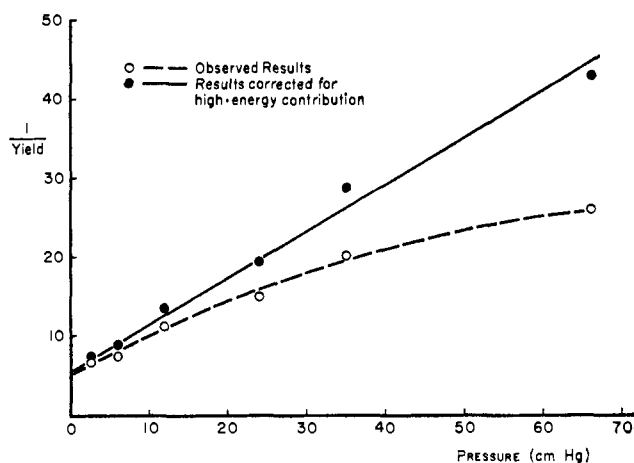


Figure 2. Reciprocal yield of *cis*- + *trans*-³⁸Cl-dichloroethylenes vs. pressure from *cis*-CHCl=CHCl scavenged CH₃Cl: O, observed data; ●, corrected data, assuming "hot" yield of 1.5%.

Table I. Pressure Dependence of Per Cent Yields of *cis*- and *trans*-1,2-Dichloroethylene from ³⁸Cl Reactions with CHCl=CHCl

Pressure, cm ²	Per cent yields		
	<i>trans</i> -1,2-DCE	<i>cis</i> -1,2-DCE	<i>trans/cis</i>
2.5	4.75 ± 0.05	10.20 ± 0.15	0.47
6	4.02 ± 0.04	8.90 ± 0.10	0.45
12	2.94 ± 0.03	5.90 ± 0.06	0.50
24	2.32 ± 0.02	4.34 ± 0.04	0.54
35	1.69 ± 0.01	3.28 ± 0.02	0.52
66	1.30 ± 0.01	2.54 ± 0.02	0.51
54 CH ₃ Cl + 4 <i>cis</i> ^b	1.75 ± 0.01	3.31 ± 0.02	0.53
50 CH ₃ Cl + 4 <i>trans</i> ^b	2.00 ± 0.01	3.68 ± 0.02	0.55

^a Each sample contained Ar:O₂:*cis*-1,2-DCE:CH₃Cl in the ratio 1:2:2:70. The Ar was present as a neutron monitor, utilizing the reaction ⁴⁰Ar(n,γ)⁴¹Ar. ^b Plus 2 cm of O₂ and 1 cm of Ar in each.

average lifetime of the CHCl³⁸ClCHCl* radicals formed by addition of thermal ³⁸Cl to CHCl=CHCl. This estimate is uncertain to about ± 50% (see Appendix I) since we have not directly measured the fractions of hot and/or thermal ³⁸Cl atoms reacting by other paths, such as (5) and (6). From the graph of Figure 2,

(21) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

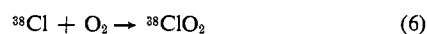
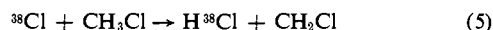
(22) The low activation energy for radical addition to CHCl=CHCl is an important factor in the success of CHCl=CHCl in preventing conflicting thermal radical-atom reactions in alkyl chloride systems.

Table II. ^{38}Cl -Labeled Products from Recoil ^{38}Cl Reactions with *cis*- and *trans*-1,2-Dichloroethylene

Phase Temp, °C Target Scavenger	Gas 20			Liquid 20				Solid -78	
	<i>cis</i> ^b O ₂	<i>trans</i> ^b O ₂	None	<i>cis</i> DPPH	None	<i>trans</i> DPPH	<i>cis</i> None	<i>trans</i> None	
Radioactive products (<i>cis</i> + <i>trans</i> = 100)									
Specific activity ^a (<i>cis</i> + <i>trans</i>)	18,000	17,000	14,000	11,000	15,000	14,500	22,000	20,000	
<i>trans</i> -CHCl=CH ³⁸ Cl	33 ± 1	36 ± 1	32 ± 1	30 ± 1	56 ± 1	58 ± 1	30 ± 1	66.7 ± 1.0	
<i>cis</i> -CHCl=CH ³⁸ Cl	67 ± 1	64 ± 1	68 ± 1	70 ± 1	44 ± 1	42 ± 1	70 ± 1	33.3 ± 1.0	
CHCl=CCl ³⁸ Cl	0.8 ± 0.2	0.9 ± 0.2	6.6 ± 0.3	8.5 ± 0.5	7.5 ± 0.4	8.9 ± 0.5	11.7 ± 0.5	10.7 ± 0.5	
<i>trans/cis</i>	0.49 ± 0.02	0.55 ± 0.02	0.46 ± 0.02	0.43 ± 0.02	1.26 ± 0.06	1.37 ± 0.06	0.43 ± 0.02	2.0 ± 0.1	

^a Specific activity: sum of yields of *trans*- and *cis*-1,2-DCE- ^{38}Cl divided by mass of target in sample and corrected for length of irradiation.

^b Approximately 15–18 cm of CHCl=CHCl, 2 cm of O₂, 50 cm of He.



the estimate can be made that decomposition and stabilization of CHCl³⁸ClCHCl* compete approximately equally at 10–15 cm pressure. Assuming that single collisions with CH₃Cl are sufficient to stabilize excited CHCl³⁸ClCHCl* radicals, the calculated decomposition rate thus corresponds to the mean time between collisions at these pressures, about $5\text{--}7 \times 10^{-10}$ sec. This lifetime is in quite respectable agreement with the decomposition rate estimated by Knox and Riddick⁸ of $k_2' = 2.5 \times 10^9 \text{ sec}^{-1}$.

Branching Ratio for Formation of *cis* and *trans* Isomers. The data of Table I indicate that *trans*-CHCl=CH³⁸Cl and *cis*-CHCl=CH³⁸Cl are formed in the same ratio at all pressures, and from either isomer as the initial reactant. The general agreement between the pressure dependence of Figure 2 and other measurements of indisputably thermal chlorine reactions indicates that the initial energy of ^{38}Cl for the CHCl³⁸ClCHCl* radicals under observation in Table I is essentially thermal; the experiment thus provides a direct measurement of the *trans/cis* branching ratio of 0.50 ± 0.05 for such radicals formed by addition of thermal chlorine atoms.

This ratio is not in agreement with that given by Knox and Riddick, who found 22/78 or 0.28. However, the experimental technique in their nonisotopic experiment involved the measurement of the rate of formation of the *cis* isomer from the *trans* compound (or *vice versa*) vs. the rate of reaction of Cl with propane. In such experiments, the observed rate of product formation involves not only the *trans/cis* branching ratio, but also the rate of addition of Cl to the specific olefin, and the over-all rate of decomposition of the excited radical. The rate of addition of Cl to the *trans* and *cis* isomers need not be identical and is not calculated to be so by Knox and Riddick,⁸ the rate of decomposition of the excited radicals need not be identical when formed from the two isomers because of the difference in heat of formation (*cis*-CHCl=CHCl is 450 cal/mole more stable than the *trans* form)²³ of the initial reactant.¹¹ Since even the high-pressure ratio of *trans/cis* in Table I is indistinguishable from the average, and presumably contains a contribution of "hotter" radicals (estimated as 1.5% of the

3.8% total), our branching ratio measurement is quite insensitive to the average energy of the ^{38}Cl atoms and is certainly applicable to thermal chlorine atom systems. We believe that the branching ratio measurement of Knox and Riddick (and of Ayscough, *et al.*, who used a technique⁷ similar to theirs) still has errors in it from uncertainty in the rates of addition and decomposition of the radicals. Comparison of the last two lines of data in Table I indicates that the excited radicals formed by reaction with the *trans* compound decompose slightly more rapidly in our experiments than the radicals formed in otherwise identical experiments using the *cis* compound as scavenger, as would be expected for the more excited radicals formed from the less stable, higher energy *trans* isomer as parent.

Rate of Rotation of CHCl³⁸ClCHCl* Radicals. Knox and Riddick⁸ have reported that the radical intermediates appear to have free rotation in their experiments, and both Knox⁹ and Tardy and Rabinovitch¹¹ have used free rotation models in unimolecular reaction rate calculations. Our experiments confirm the rapidity of rotation in this system, since direct measurements of the branching ratio near 1 atm pressure indicate no significant difference for *cis* and *trans* initial reactants. Rotational averaging of the orientation about the C–C bond must be substantially faster than the rate of decomposition of the excited radical, which is in turn faster than the collision deexcitation rate near 1 atm pressure, *i.e.*, $\tau_{\text{rotation}} < 10^{-10}$ sec.

Isotopic Experiments on Thermal Halogen Atom Reactions. The formation of thermal ^{38}Cl atoms in CH₃Cl systems illustrates an important potential application of nuclear reaction sources for halogen atom studies. The source of the active ^{38}Cl can be a nearly inert molecule such as CCl₄, and the termination steps are of much less importance in a system in which the experimental technique follows only the initial step of the chain, leading to stable bonding for the radioactive atom, and essentially ignores the subsequent chain steps. Much more complete thermalization of the kinetic energy of the ^{38}Cl atom is readily feasible with high mole fractions of inert moderators,^{16,20} thereby permitting thermal atom studies in the almost complete absence of hot reactions of the atom involved.

^{38}Cl Reactions with CHCl=CHCl as the Major Component. The observed ^{38}Cl -labeled products from the reactions with both *cis*- and *trans*-1,2-DCE are summarized in Table II for experiments carried out in the gaseous, liquid, and solid phases. The yields have been compared in each case to the sum of labeled *cis*- and

(23) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1954).

trans-1,2-DCE as 100. While no convenient internal neutron monitoring system has yet been routinely applied to the liquid and solid irradiations, rough comparisons of the magnitude of individual yields can be obtained from the specific activity measurements in each sample. Such data are included for each run in Table II and are estimated to be reproducible only to about $\pm 25\%$ because of uncertainty in positioning within the neutron flux of the reactor. The total yields represent 30–50% of the ^{38}Cl formed in the system.

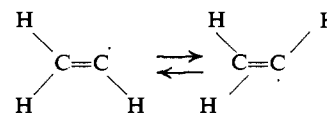
Hot Reactions, Gas Phase. The mechanisms found for $\text{CHCl}=\text{CHCl}$ as a minor component in CH_3Cl must also be present in the major component system, and the results of Table II are very consistent with those of Table I. The endothermic substitution of hot ^{38}Cl -for-H to form $\text{CHCl}=\text{CCl}^{38}\text{Cl}$ proceeds with a very minor yield, and the slight difference in *trans/cis* ratios for 1,2-DCE- ^{38}Cl may reflect a comparable amount of direct ^{38}Cl -for-Cl reaction. Other products were observed in even smaller yields (0.02 to 0.5 vs. 100) and could also be hot products; the yields of all of these are small enough, however, that no further studies were made of them.

The main gas-phase products are completely consistent with origin through reactions 1 and 2 and do not display any appreciable difference attributable to their energetic origin other than their occurrence in rather high yield at total pressures near 1 atm. Since the decomposition rate of excited $\text{CHCl}^{38}\text{Cl}^*\text{CHCl}$ radicals rises very rapidly with increasing energy,¹¹ this observation only implies extra excitation energy of about 0.5–1.0 eV; experiments at much higher pressures are required for further investigation, and can be conveniently carried out only through the addition of other gases because of the vapor pressure limitations of 1,2-DCE in the available nuclear reactor facilities.

Hot Reactions, Condensed Phases. The yields of the direct substitution product, $\text{CHCl}=\text{CCl}^{38}\text{Cl}$, are approximately 10–20 times higher in the condensed phases than in the gas phase. This observation probably represents the combination of two effects observed in other ^{38}Cl systems: (a) "cage" facilitation¹⁴ of the combination of ^{38}Cl atoms with $\text{CHCl}=\text{CCl}$ radicals; and (b) high collision density stabilization of excited $\text{CHCl}=\text{CCl}^{38}\text{Cl}^*$ molecules formed by direct replacement. No experiments directly analogous to the secondary decomposition of $\text{CHCl}=\text{CCl}^{38}\text{Cl}$ have been performed for ^{38}Cl -labeled olefins; such decompositions are quite common for ^{18}F and ^{38}Cl or ^{39}Cl substitutions in saturated molecules.^{24, 25}

The direct substitution of ^{38}Cl -for-Cl with preferential retention of the geometric configuration of the original reactant is observed for *cis*- and *trans*-DCE in both liquid and solid phases. In no case does the preferential retention favor the parent by more than 70/30, while the liquid systems show an asymmetry in yields that reflects the greater stability of the *cis* isomer.

Again, cage combination of ^{38}Cl with $\text{CHCl}=\dot{\text{C}}\text{H}$ radicals probably contributes to the $\text{CHCl}=\text{CH}^{38}\text{Cl}$ yields. ESR measurements indicate the existence of



vinyl radical isomers for time periods long enough to permit competition between isomerization and combination with ^{38}Cl in the cage.²⁶ Cage combination of ^{38}Cl with $\text{CH}_3\dot{\text{C}}\text{HCHClCH}_3$ radicals has already been shown to be competitive with the isomerization of these chlorobutyl radicals.¹⁴

Detailed comparisons of absolute yields will require chemical identification of all of the ^{38}Cl formed in these systems. The high yield in the gas phase, when compared to saturated alkyl halide systems, is attributable to the scavenging by the double bond of near-thermal and thermal ^{38}Cl atoms, followed by subsequent decomposition of the excited radicals. In the liquid phase, such radicals are immediately stabilized by collision and no longer contribute significantly to the $\text{CHCl}=\text{CH}^{38}\text{Cl}$ yields. Observation of the subsequent reaction products of these deexcited radicals is obscured with diphenylpicrylhydrazyl (DPPH) as scavenger, while the simpler Br_2 and I_2 scavenger systems have not been used because of the substantial yields of short-lived Br and I radioisotopes formed by (n, γ) reactions on the molecular halogens.

The liquid-phase and solid-phase yields of the 1,2-DCE products are similar to the gas yields in magnitude, but the reaction mechanisms, as indicated by the isomer distributions, are quite different. Additional experiments involving ^{18}F , ^{38}Cl , and isotopes of Br and I with various olefins offer a promising approach to the study of both gaseous and condensed-phase halogen atom reactions.

Appendix I

Assume that a fraction F of the ^{38}Cl atoms becomes thermalized in the $\text{CHCl}=\text{CHCl}/\text{CH}_3\text{Cl}$ system, and then react by reactions 1 and 5 in proportion to k_1 ($\text{CHCl}=\text{CHCl}$) and k_5 (CH_3Cl). For experiments with varying total pressure but constant $\text{CHCl}=\text{CHCl}/\text{CH}_3\text{Cl}$ ratio, the proportion reacting by each path will be in proportion to $k_1:k_M$, in which $k_M = k_5(\text{CH}_3\text{Cl})/(\text{CHCl}=\text{CHCl})$. Thus the fraction $k_M/(k_1 + k_M)$ will be removed from the system, while $k_1/(k_1 + k_M)$ will be split between reactions 2 and 3. The fraction of $\text{CHCl}^{38}\text{Cl}^*\text{CHCl}$ radicals decomposing to $\text{CHCl}=\text{CH}^{38}\text{Cl}$ (*cis* or *trans*) will then be $(1/2)(k_2)/(k_2 + k_3P)$, in which P is the total pressure in the system; the fraction $k_3P/(k_2 + k_3P)$ will go into stabilized trichloroethyl products, and the remainder $(1/2)(k_2)/(k_2 + k_3P)$ will decompose into thermal ^{38}Cl atoms which can start through the cycle again. The final distribution of ^{38}Cl products among $\text{CHCl}=\text{CH}^{38}\text{Cl}$ and the end-products of (5) and (6) will have the same ratio as that found in each cycle. If the yield of ^{38}Cl as $\text{CHCl}=\text{CH}^{38}\text{Cl}$ from thermal ^{38}Cl reactions is designated as Y , then the dependence pressure of Y is given by (7).

(24) Y.-N. Tang and F. S. Rowland, *J. Phys. Chem.*, **71**, 4576 (1967).

(25) Y.-N. Tang, K. Lowrey, and F. S. Rowland, unpublished results.

(26) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

$$\frac{Y}{F} = \frac{\left(\frac{1/2}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right)}{\left(\frac{1/2}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right) + \left(\frac{k_3P}{k_2 + k_3P}\right)\left(\frac{k_1}{k_1 + k_M}\right) + \left(\frac{k_M}{k_1 + k_M}\right)} \quad (7)$$

This equation can be inverted and simplified to show a linear pressure dependence, as in (8), and is actually

$$\frac{F}{Y} = \left[\frac{k_1 + 2k_M}{k_1}\right] + \left(\frac{k_1 + k_M}{k_1}\right)\left(\frac{2k_3}{k_2}\right)P \quad (8)$$

plotted in the form given in (9).

$$\frac{1}{Y} = \frac{1}{F}\left[\frac{k_1 + 2k_M}{k_1}\right] + \frac{1}{F}\left(\frac{k_1 + k_M}{k_1}\right)\left(\frac{2k_3}{k_2}\right)P \quad (9)$$

The intercept of Figure 2 is simply the reciprocal of the yield of $\text{CHCl}=\text{CH}^{38}\text{Cl}$ at zero pressure and has a value of about 5, or a fractional yield of $\text{CHCl}=\text{CH}^{38}\text{Cl}$ at zero pressure of 0.20, regardless of the values of F and (k_M/k_1) .

The information desired from the slope ($=0.6 \text{ cm}^{-1}$)

of the straight line in Figure 2 is actually the ratio k_3/k_2 , and is somewhat uncertain to the extent that the value of $(1/F)[(k_1 + 2k_M)/k_1]$ is known to be 5 from the slope, but what is needed is $(1/F)[(k_1 + k_M)/k_1]$. In one limit, $k_M \ll k_1$, the ratio $(2k_3/k_2)(5) = 0.6 \text{ cm}^{-1}$, while in the other, $k_M \gg k_1$, $(2k_3/k_2)(5/2) = 0.6 \text{ cm}^{-1}$. Therefore, $0.06 \text{ cm}^{-1} \leq k_3/k_2 \leq 0.12 \text{ cm}^{-1}$. Actually, since F by definition cannot exceed unity, the intercept of 5 requires a finite upper limit of 2 for the ratio k_M/k_1 , and an upper limit for k_3/k_2 of $\leq 0.10 \text{ cm}^{-1}$. From the intermediate value of $k_3/k_2 = 0.08 \text{ cm}^{-1}$, and the assumption of deexcitation in a single collision, decomposition and stabilization of the trichloroethyl radical complete equally at 12 cm pressure, *i.e.*, $k_2 \cong 2 \times 10^9 \text{ sec}^{-1}$.

A more exact calculation would require that the products from (1) + (3) be distinguished from those of (5), or from (6), in order to measure k_M and F .

The reaction rates of thermal Cl atoms with CH_3Cl and with $\text{CHCl}=\text{CHCl}$ in 35-fold excess of the former are estimated to be comparable, with a large uncertainty,^{5,10} and $k_M/k_1 \sim$ unity is not an unreasonable value. Experimentally, isotopic ^{38}Cl exchange should be expected for H^{38}Cl and any products of $^{38}\text{ClO}_2$ reactions.

A Nuclear Magnetic Resonance Study of Structure and Bonding in Methyllithium

L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker

Contribution from the Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640. Received September 5, 1968

Abstract: Structure and bonding in methyllithium have been examined using carbon, lithium, and proton nuclear magnetic resonance measurements. The observation of ^{13}C - ^7Li spin-spin coupling in tetrahydrofuran, ether, and triethylamine defines the structure of the methyllithium tetramer in these solutions. The small upfield displacement of the ^{13}C chemical shift of methyllithium (relative to methane) is interpreted as evidence for predominant sp^3 hybridization of carbon in this species. The use of existing linear relationships between ^{13}C chemical shifts and substituent electronegativity indicates that lithium in the tetramer is substantially more electronegative than atomic lithium. Similar relationships between charge density on carbon and ^{13}C chemical shifts for substituted methanes infer that charge separation in the carbon-lithium bond of methyllithium is ~ 0.1 electron. Calculation of the ionicity of the carbon-lithium bond from Pauling's equation infers that bonding is predominantly covalent.

Abundant experimental evidence supports the use of nuclear magnetic resonance measurements as a probe for studying molecular structure and bonding. For example, the recently reported observation of ^{13}C - ^7Li spin-spin coupling in methyllithium¹ provided novel evidence supporting the tetrameric structure suggested^{2,3} for methyllithium in donor solvents.

Carbon-13 chemical shifts and ^{13}C - ^1H coupling constants have been shown to be sensitive measures

of the hybridization of the examined carbon. Such measurements have been used, for example, to study hybridization in arylmethyllithium reagents.⁴ ^{13}C chemical shifts have further been shown to relate to charge density at carbon or electronegativity differences between carbon and a substituent X.⁵

We report measurements of ^{13}C , ^7Li , and ^1H chemical shifts for methyllithium in tetrahydrofuran, diethyl ether, and triethylamine solutions. These results are discussed in terms of the structure of methyllithium

(1) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Am. Chem. Soc.*, **90**, 3244 (1968).

(2) R. Waack and P. West, *J. Organometal. Chem.* (Amsterdam), **5**, 188 (1966); *J. Am. Chem. Soc.*, **89**, 4395 (1967).

(3) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 2174 (1966).

(4) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *ibid.*, **88**, 1272 (1966).

(5) See, *e.g.*, P. Bucci, *ibid.*, **90**, 252 (1968).