Gas-Phase Reactions of Atomic Chlorine with Vinyl Chloride

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The reactions of chlorine atoms with CH2=CHCl have been investigated over the pressure range from 70 to 4000 torr by using radioactive ³⁸Cl atoms formed by neutron irradiation of CClF₃. The only observed product when CH₂=CHCl is the sole substrate is CH2=CH38Cl in yields varying from 1.35% at 4000 torr to 44.2% at 71-torr total pressure. With HI present as a second substrate, CH₂ClCH₂³⁸Cl is observed as a major product with a yield as high as 78% at 4000-torr total pressure, and CH₃CHCl³⁸Cl is also found in yields of 2% or less. A 1,2-chlorine atom migration is required in the overall mechanism, and two quite different kinetic schemes fit the observed yields of CH2=CH38Cl and CH2ClCH238Cl very satisfactorily. The favored mechanism involves little initial preference for addition to the CH₂ or CHCl ends of CH₂=CHCl. The high yields of CH₂ClCH₂³⁸Cl at high pressures are preceded by a 1,2-chlorine atom migration from collisionally stabilized CH₂CHCl³⁸Cl radicals to form CH₂³⁸ClCHCl or CH₂ClCH³⁸Cl prior to abstraction of H from HI to form CH₂ClCH₂³⁸Cl. The absolute reaction rate for 38 Cl with CH₂=CHCl has been estimated from its relative rate vs. reaction with HI to be about 1.5 × 10^{-10} cm³ molecule⁻¹ s⁻¹. The energy barriers for chlorine atom addition to either end of CH₂=CHCl are no larger than a few hundred cal/mol, and the loss of chlorine atoms from excited CH2³⁸ClCHCl* or CH2CHCl³⁸Cl* radicals must also have barriers in the exit channels no larger than a few hundred cal/mol.

Introduction

Atomic chlorine reactions with olefins have long been described as "anti-Markownikoff" to signify preferential chlorine addition to the less substituted ethylenic carbon, consistent with the observation of a predominance of reaction products containing the corresponding radical entity.¹ In many instances, the experimentally observed addition products contain almost exclusively the anti-Markownikoff grouping, as with CH₂Cl in terminal olefins. This qualitative preference leads to the expectation that the yield from reaction 1 with vinyl chloride will be substantially

> $^{38}Cl + CH_2 = CHCl \rightarrow CH_2 ^{38}ClCHCl^*$ (1)

> $^{38}Cl + CH_2 = CHCl \rightarrow CH_2 CHCl^{38}Cl^*$ (2)

greater than for the alternate possibility of (2). Our radiotracer investigations of ³⁸Cl atom addition to propene,^{2,3} CH₂=CHBr,⁴ and $CH_2 = CHF^5$ have provided some quantitative information about the relative probabilities of formation of the products expected from either end of the substrate molecule. At the same time, they have raised critical questions about the actual mechanisms of product formation. In particular, they have supported attempts to isolate the initial addition process from possible subsequent reaction steps, such as 1,2-halogen migrations which could lead to observed products apparently belonging to a different initial path.²⁻¹⁰ The strong contrast in the mechanistic observations with CH2=CHBr and CH2=CHF makes CH2=CHCl an excellent substrate for additional investigation to clarify the overall mechanistic situation.

Extensive experiments carried out in the 1960s established many of the kinetic parameters for the addition of chlorine to vinyl

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chloride,¹¹⁻¹⁴ as well as for similar additions to other chloroolefins,¹⁴ but did not provide any direct evidence for the relative reaction rates in the initial choice between (1) and (2). In those experiments, the photolysis of Cl₂ served as the source of atomic chlorine and any collisionally stabilized C2H3Cl2 radicals analogous to those formed in (1) and (2) necessarily then reacted further with Cl₂, leading to CH₂ClCHCl₂ as the observed product for either reaction route. These experiments also provided evidence that the reversible loss of Cl from excited C₂H₃Cl₂* radicals was important for vinyl chloride, at least for pressures below 130 torr of olefin.¹¹⁻¹⁴ In our circumstances with radiotracer ³⁸Cl, the reversal of reaction 2 permits the loss of either Cl or ³⁸Cl and requires a different kinetic treatment than appropriate for the unlabeled experiments of ref 11-14. Our studies of ³⁸Cl reactions with several substrates have all indicated that loss of ³⁸Cl from excited radicals at low pressure can be an important contributory mechanism to the overall process.^{2-5,15,16}

No quantitative theoretical estimates appear to have been made for the relative rates of addition by routes 1 and 2, and few for similar systems. Bonacic-Koutecky et al. have estimated activation energy differences favoring addition at the CH₂ end of 4000 cal/mol for CH2=CHCH3 and 5400 cal/mol for CH2=CHF.17 However, laboratory experiments with ³⁸Cl and CH₂=CHF at room temperature and 232 K show a preference of only about a factor of 2 for addition to the CH₂ end of the molecule,⁵ although a 5400 cal/mol difference in activation energy should lead to a selectivity factor of 10⁴ at 298 K and 10⁵ at 232 K. Similarly, the 4000 cal/mol difference for propene would favor terminal over central addition by a factor of 10^3 , while the actually measured terminal/central ratios all fell in the range from 6 to 12.² Furthermore, these ratios with propene as the substrate systematically increased with the lowering of the concentrations of HI used to scavenge stabilized free radicals, consistent with the existence of a 1,2 central-to-terminal Cl shift in competition with reaction with scavenger HI.² The strong possibility therefore exists that the

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initial terminal/central addition ratio in propene was even less than the 6 observed with the highest HI concentrations. Competitive addition ratios at 25 °C from 2 to 6 correspond only to about 500–1000 cal/mol energy differences in the choice between addition to one or the other ends of the double bond. In both propene and CH₂—CHF, the observed preferences in the addition reaction occur qualitatively in the anti-Markownikoff direction but are quantitatively not strong. With both substrates, the summed rate constants for addition to both ends of the double bond exceed 10^{-10} cm³ molecule⁻¹ s⁻¹,^{2,5} indicating an activation barrier for addition of no more than a few hundred cal/mol at the CH₂ end of the molecule and not much more than 1000 cal/mol for the other end.

A particular area of mechanistic interest in the addition of ³⁸Cl to CH2=CHCl is the question of halogen migration in the excited radicals as initially formed. The possibility of halogen migration as a later step separate from the addition itself complicates the mechanistic interpretations derived from the observed positions of individual halogen atoms in the products. Atomic chlorine reactions with CH2=CHBr lead at low pressures (<10 torr) to CH_2 =CHCl in high yield as the sole observed product.^{4,18-20} The general mechanism (I) usually invoked in explanation of this observation is based upon the postulate of strongly predominant anti-Markownikoff addition to form CH2ClCHBr*, followed by a 1,2-chlorine atom migration displacing Br.^{19,21} The time scale for such decomposition has been interpreted differently in various types of experiments and calculations, from as short as 10⁻¹³ s²⁰ to as long as 10⁻⁹ s.⁴ Our experiments on the reactions of thermal ³⁸Cl with vinyl bromide in the pressure range from 25 to 4000 torr showed yields of CH2=CH38Cl approaching 100% at pressures below 100 torr, in sharp contrast to yields of 75% for CH₂³⁸ClCH₂Br with no measurable CH₃CH³⁸ClBr in HI-scavenged CH_2 =CHBr at 4000 torr. These data can be consistent with the general mechanism (I) given above if either the 1,2-Cl migration or the loss of Br from CH₂CH³⁸ClBr* requires as long as 10^{-9} s. However, the same data are also satisfied by another mechanism (II) in which there is no more than a weak initial preference for addition on either end of the double bond. Addition to the CHBr end is then followed by Br loss in the decomposition of CH₂CH³⁸ClBr* on a time scale of 10⁻⁹ s, plus a postulate of rapid 1,2-bromine migration in the collisionally stabilized CH₂CH³⁸ClBr radical. Satisfactory sets of kinetic rate constants can be found to fit both mechanisms I and II, with no definitive experiments available to choose between them. Mechanism II gains support by analogy to our experiments with CH₂==CHF as substrate, for which halogen migration of Cl (or F) plays at most a minor role in mechanistic fits to the data.⁵ Experiments with CH_2 =CHCl as the substrate offer a situation potentially intermediate between the extremes furnished by CH2=CHBr and CH2=CHF.

Our experiments have utilized energetic ³⁸Cl atoms formed by the nuclear reaction ${}^{37}Cl(n,\gamma){}^{38}Cl$ in gaseous CClF₃ and then thermalized by multiple collisions of ³⁸Cl with the nearly inert CClF₃ prior to collision and reaction with vinyl chloride or other substrate present in low mole fraction. The technique relies upon different molecules as atom source ($CClF_3$) and as scavenger (HI), providing separate products for the alternate initial reaction routes 1 and 2. The atomic chlorine source CClF₃ has the great advantage that it is chemically inert toward reaction either with thermal CI atoms or with collisionally stabilized free radicals, leaving the role of scavenger molecule entirely to HI. Without some 1,2-halogen atom migration, the stabilized radical from (1) can be expected as $CH_2ClCH_2^{38}Cl$ and that from (2) as CH₃CHCl³⁸Cl. However, as described below, such 1,2-Cl atom migrations play an important role in the ³⁸Cl plus CH₂=CHCl system.

Experimental Section

The reactions of energetic ³⁸Cl atoms with CClF₃ lead to the formation of CCl³⁸ClF₂, C³⁸ClF₃, and some ³⁸Cl-labeled radical fragments which are the residues from decomposition of these compounds when formed with high vibrational energies.³ About 5% of all ³⁸Cl atoms formed in the system are found in these compounds derived from CClF₃, while the other 95% react thermally with minor substrates or with the container wall. In the presence of even small traces of CH₂=CHCl, the chemical behavior of most of this residual 95% is determined by thermal reactions of chlorine with vinyl chloride. When both CH₂=CHCl and some other substrate such as HI are simultaneously present in excess CClF₃, the distribution of ³⁸Cl reaction between the two substrates is determined by the relative reaction rates for thermal chlorine atoms with each.

The inert gas argon serves as a neutron flux monitor through the 40 Ar(n, γ) 41 Ar nuclear reaction. The thermal neutron irradiations were carried out in the Mark I TRIGA reactor of the University of California, Irvine. Thermal neutron fluxes and 38 Cl production were restricted by short irradiations (<2 min) and low power levels (10 kW) in order to minimize radiation alteration of the substrates. Sample mixtures containing CCIF₃, CH₂== CHCl, HI, and argon were prepared by the same vacuum line techniques described previously.²⁻⁵ All of the gases were obtained from Matheson gas products and were purified by the usual techniques.²⁻⁵ The total pressures in the samples were varied from 70 to 4100 torr, including from 20 to 40 torr of argon.

The separation and assay of the radioactive organic compounds were carried out by radio gas chromatography.³ The standard separation procedure applied for samples containing both CH2= CHCl and HI as substrates utilized three columns in series: a 15-ft silicone oil (siloil) column operated at 82 °C, followed by a 25-ft dimethylsulfolane (DMS) column and a 50-ft propylene carbonate on alumina column (PCA), both operated at room temperature. A potassium ferrocyanide stripper column was used to remove HI. In a typical separation, the eluant flow passed through all three columns for 27 min in the order listed above. The DMS column was then isolated, and eluant gas passed through it alone for another 49 min. Finally, the flow stream was directed through the siloil column alone. Under these conditions, the retention times were as follows (in minutes): ⁴¹Ar, 22; CH₂= CH38Cl, 66; CH3CHCl38Cl, 93; CH2ClCH238Cl, 123. Approximately 10% of the ³⁸Cl radioactivity ($t_{1/2} = 37.3$ min) remains after 123 min. Minor radioactivity peaks were also observed for the products from reactions of energetic ³⁸Cl with CClF₃. The elution time of CH₃CHCl₂ was checked on several individual experiments with the injection of a small macroscopic sample as a marker 1 min prior to injection of the radioactive sample aliquot.

A standard flow-through "sandwich" proportional counter was used for the detection of ${}^{38}Cl$ and ${}^{41}Ar$ radioactivities. The counter is made of stainless steel to permit operation at elevated temperatures and was routinely operated at 100 °C. At this temperature, the radioactivity peak of CH₂ClCH₂ ${}^{38}Cl$ spent somewhat more time in passage through the fixed gas volume of the counter than did the helium carrier gas. The delay is attributed to temporary adsorption on the internal walls of the counter, permitting the radioactivity of the molecule to be recorded over a longer period than expected from the transit time through the gas volume alone. A "sticking" correction factor of 1.3 was calculated from an intercomparison of the yields of C₂H₅ ${}^{38}Cl$ (no adsorption) and CH₂ClCH₂ ${}^{38}Cl$ in the gas proportional counter and, after trapping of each, in a NaI/Tl well scintillation counter.

Irradiated samples containing only CH_2 =CHCl as a substrate were analyzed with a two-column system containing the DMS and PCA columns in series. The ⁴¹Ar and C³⁸ClF₃ radioactivity peaks emerged at 15 and 24 min, respectively, and the flow was switched to pass through the DMS column alone after 37 min. The CH₂=CH³⁸Cl peak emerged at 59 min with this procedure. The molecular end products formed by further reactions of CH₂³⁸ClCHCl and CH₂CHCl³⁸Cl radicals are presumably at least C₄ compounds with prohibitively long gas chromatographic retention times for a 37-min half-life radioactivity. Such ³⁸Cl

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Figure 1. Percentage yields of CH₂—CH³⁸Cl from thermal ³⁸Cl reactions with CH₂—CHCl vs. total pressure in neutron-irradiated mixtures of CClF₃, CH₂—CHCl, and Ar. The right side of the rectangle indicates the sum of pressures for CClF₃ (\geq 94%) and CH₂—CHCl, and the left side indicates the sum of pressures including Ar, CClF₃, and CH₂— CHCl. The solid line represents the calculated kinetic fit with mechanism II (see Figure 2 and text) and $k_1/k_2 = 1.0$, $k_6/(k_1 + k_2) = 0.65$, $k_7 = k_8$ [M] at 65 torr, and $k_3 = k_4$ [M] at 220 torr. The dashed line represents $k_1/k_2 = 0.71$, $k_6/(k_1 + k_2) = 0.65$, $k_7 = k_8$ [M] at 100 torr, and $k_3 = k_4$ [M] at 260 torr.

TABLE I: Yields of CH₂=CH³⁸Cl from the Reactions of Thermal ³⁸Cl Atoms with Vinyl Chloride

	pressure, torr	percent yield CH ₂ =CH ³⁸ Cl	
CCIF ₃	CCIF ₃ CH ₂ =CHCl		
3960	40.1	38.6	1.35 ± 0.03
2030	19.7	40.5	3.11 ± 0.06
1020	11.0	39.0	6.4 ± 0.1
1000	10.7	39.4	6.8 ± 0.1
500	5.0	20.8	11.8 ± 0.1
250	3.4	20.2	20.3 ± 0.2
99	2.5	19.8	33.2 ± 0.4
48	2.9	20.1	44.2 ± 0.6

radioactivity bound in less volatile molecules is observed without specific chemical identification in a "back-flush" peak when the direction of flow of the eluant gas through the separation column is reversed for a time comparable to that allowed for forward flow. No separate analytical conditions were sought which might permit assay of specific C_4 or C_6 compounds in the absence of HI.

Results and Discussion

Reactions of Thermal ³⁸Cl with CH_2 =CHCl as the Sole Substrate. The observations from experiments with minor concentrations of CH2=CHCl in excess CClF3 are summarized in Table I for a range of pressures from 50 to 4000 torr. The only observed radioactive products were CH2==CH38Cl from thermal ³⁸Cl reactions with CH₂=CHCl, ⁴¹Ar used as the neutron flux monitor, and the molecules formed by energetic ³⁸Cl reactions with $CClF_3$. The mole fraction of CH_2 =CHCl was held at 0.01 for all total pressures >500 torr but was allowed to increase to 0.05 with 50 torr of $CClF_3$ for better control in sample preparation. By analogy to ³⁸Cl reactions with other substrates,²⁻⁵ the fraction reacting with CH₂=CHCl while the atoms are still energetic is not greater than about 2% at a mole fraction of 0.05 and is proportionately smaller for a mole fraction of 0.01. The contribution of argon to internal energy removal by molecular collision is quite minor for 40 torr in a total of 4000 torr but is probably not negligible for 20 torr in a total of 70 torr. Proportional diminution in argon and CClF3 pressures in the samples is not feasible because sufficient ⁴¹Ar is needed to provide precise monitoring of the neutron flux.

The data of Table I demonstrate that the yield of $CH_2 = CH^{38}CI$ increases rapidly with decreasing total pressure from 1.35% at 4000 torr to 44% at 50 torr of CClF₃. These data are graphed in Figure 1 in a form which displays the observed yields of CH₂=CH³⁸Cl over logarithmic ranges of pressure. The dashed and solid lines in Figure 1 are calculated from a mechanistic kinetic model described later. The first assumption in this mechanism is that the formation of CH_2 =CH³⁸Cl is initiated by the addition of ³⁸Cl to CH₂=CHCl by either reaction 1 or 2. The data in Figure 1 are graphed vs. the total sample pressures, which is equivalent to the assumption that CCIF₃, CH₂=CHCl, and argon are equally efficient in removing by collision the extra excitation energy of the free radical precursor(s) of CH_2 =CH³⁸Cl. At the higher pressures, of course, almost all of the deexciting collisions of radicals occur with CCIF₃, and the relative collision efficiencies of Ar and CH2=CHCl are of negligible importance in total energy removal. At the lower pressures, an appreciable fraction of such collisions occur with argon, which may not be as effective as CClF₃ in deexcitation of energetic radicals. The points in Figure 1 have been extended to the right to indicate the possible range of effective total pressures, varying for argon from collision efficiency equal to $CClF_3$ on the left to zero on the right.

The error estimates in Table I indicate the statistical precision available from the ratio of the observed number of radioactive decays for the two peaks of CH_2 — $CH^{38}Cl$ and ^{41}Ar . However, the error bars in Figure 1 are given as $\pm 10\%$, which is our estimate of the absolute reproducibility of the CH_2 — $CH^{38}Cl$ yields. The formation of CH_2 — $CH^{38}Cl$ presumably involves at least briefly a structure in a radical precursor for which both chlorine atoms are attached to the same carbon atom, as in $CH_2CHCl^{38}Cl^*$, permitting the subsequent loss of Cl by a reaction such as (3a).

$$CH_2 CHCl^{38}Cl^* \rightarrow CH_2 = CH^{38}Cl + Cl \qquad (3a)$$

 $CH_2CHCl^{38}Cl^* \rightarrow CH_2 = CHCl + {}^{38}Cl$ (3b)

$$CH_2 CHCl^{38} Cl^* + M \rightarrow CH_2 CHCl^{38} Cl + M$$
(4)

The observation that the yields of CH_2 = $CH^{38}Cl$ in Table I are pressure dependent in the 50-4000-torr range indicates that the decomposition in (3) of a radical such as $CH_2CHCl^{38}Cl^*$ (or of some predecessor configuration) occurs with a rate constant in the range of 10^9 s^{-1} , competitive with collisional deexcitation of the excited radicals, as in (4). Any molecule in the system can serve as the collision partner, M, for deexcitation, but most collisions occur with $CCIF_3$, and these encounters with polyatomic colliders are more likely to be important for energy removal than those with Ar or HI.

At least hypothetically, this excited $CH_2CHCl^{38}Cl^*$ entity could be an energetic radical intermediate or simply a configuration on the way to decomposition as, for example, might result from the collapse of a radical with the chlorine-bridged structure (A). It



seems likely, too, that the two chlorine atoms in CH₂CHCl³⁸Cl* would become chemically equivalent except for minor isotopic mass effects, and we have assigned $k_{3a} = k_{3b}$ in our kinetic modeling. While further reactions of the Cl atom from (3a) occur, our radioactive tracing of the sequence stops with CH₂=CH³⁸Cl. When ³⁸Cl is lost by (3b), no residual record exists that it was ever bonded to CH₂=CHCl, and the ³⁸Cl atom returns to the kinetic sequences again in the competition between (1) and (2).

Reactions of ${}^{38}Cl$ with CH_2 =CHCl in Competition with HI. Substantial additional information is gained by measurement of the radioactive products found from ${}^{38}Cl$ reactions with gas mixtures containing both CH_2 =CHCl and HI as substrates. In these systems, two additional labeled products are found, $CH_3CHCl^{38}Cl$ and $CH_2ClCH_2^{38}Cl$, each formed through hydrogen abstraction from HI by a stabilized $C_2H_3Cl^{38}Cl$ radical. The collisionally stabilized radical from (4) can be converted into

TABLE II: Observed Yields of ³⁸Cl-Labeled Products from Reactions of ³⁸Cl with CH₂=CHCl Mixtures with HI

pressure, torr			percent yield ³⁸ Cl			
CClF ₃	CH ₂ =CHCl	HI	Ar	CH ₂ ClCH ₂ ³⁸ Cl	CH ₃ CHCl ³⁸ Cl	CH2=CH38Cl
3940	40.4	10.0	40.3	78	0.76 ± 0.04	1.04 ± 0.03
3950	40.0	20.2	39.3	74	1.26 ± 0.04	0.81 ± 0.02
3920	40.5	40.0	40.8	57	1.32 ± 0.05	0.71 ± 0.03
3930	41.2	41.2	38.8	53	1.34 ± 0.05	0.64 ± 0.02
4090	10.1	11.0	40.1	56	0.85 ± 0.04	0.58 ± 0.02
3880	40.3	80.8	39.8	39	1.05 ± 0.05	0.50 ± 0.02
3980	42.2	126	40.0	29	0.71 ± 0.04	0.37 ± 0.02
3940	10.2	39.3	39.2	23	0.51 ± 0.03	0.29 ± 0.02
1970	20.4	20.8	39.1	55	1.18 ± 0.05	1.31 ± 0.03
1010	10.6	11.6	39.3	51	0.93 ± 0.07	2.53 ± 0.06
480	4.9	4.9	38.5	45	0.55 ± 0.12	4.7 ± 0.1
450	24.8	24.8	20.2	44	1.66 ± 0.07	4.7 ± 0.1
480	5.2	10.2	21.1	33	0.58 ± 0.06	3.4 ± 0.1
480	5.7	16.9	20.4	24	0.40 ± 0.04	2.5 ± 0.1
91	7.8	4.1	19.9	44	0.78 ± 0.11	16.1 ± 0.7
90	5.4	5.9	21.3	33	1.1 ± 0.3	13.0 ± 0.3
85	6.8	11.5	19.6	26	1.97 ± 0.13	10.4 ± 0.7
87	5.2	10.2	20.0	25	1.31 ± 0.11	8.8 ± 0.7
85	5.9	14.7	21.1	17	1.55 ± 0.12	7.2 ± 0.6
82	5.2	15.7	21.4	15	2.04 ± 0.14	7.5 ± 0.6
80	4.6	14.7	18.1	14	1.34 ± 0.11	5.8 ± 0.5
76	5.1	20.0	19.9	12	1.44 ± 0.33	5.9 ± 0.3
79	5.0	20.6	20.0	10	1.91 ± 0.12	4.4 ± 0.5
71	5.4	24.4	20.1	11	1.15 ± 0.32	4.8 ± 0.3

a stable molecule measurable by gas chromatography through the formation in (5) of 1,1-dichloroethane. At the same time, the

$$CH_2CHCl^{38}Cl + HI \rightarrow CH_3CHCl^{38}Cl + I$$
 (5)

$$^{38}\text{Cl} + \text{HI} \rightarrow \text{H}^{38}\text{Cl} + \text{I}$$
 (6)

inclusion of HI as an additional substrate provides competition through reaction 6 with the initial reactions 1 and 2 of the thermalized ³⁸Cl atoms. The radical formed in (1) can undergo the corresponding ³⁸Cl atom loss of (7), or collisional stabilization in (8), with conversion of the radical from the latter to CH_2ClCH_2 ³⁸Cl by reaction with HI in (9). We assume here that no more complicated intermediate exists which might intermix or scramble the isotopic labeling of chlorine—only the ³⁸Cl atom is lost in reaction 7.

$$CH_2^{38}ClCHCl^* \rightarrow CH_2 = CHCl + {}^{38}Cl \qquad (7)$$

$$CH_2^{38}ClCHCl^* + M \rightarrow CH_2^{38}ClCHCl + M$$
(8)

$$CH_2^{38}ClCHCl + HI \rightarrow CH_2^{38}ClCH_2Cl + I$$
 (9)

The yields of CH_2 — $CH^{38}Cl$ and the two dichloroethanes are given in Table II for a series of experiments with varying [HI]/[CH₂—CHCl] ratios in the pressure range from 100 to 4200 torr. The maximum organic yield for ³⁸Cl, found at high total pressure and low [HI]/[CH₂—CHCl] ratio, has 80% of the ³⁸Cl radioactivity bonded to carbon, almost all as CH₂ClCH₂³⁸Cl. The observed total organic ³⁸Cl yield is less at higher [HI]/[CH₂— CHCl] ratios because more ³⁸Cl is diverted to H³⁸Cl by reaction 6 in those systems.

If the mechanism of reaction leading to CH_2 = $CH^{38}Cl$ were simply addition to the CHCl end of CH_2 =CHCl, followed by either loss of Cl or stabilization, then experiments with HI present should show yields of CH_2 = $CH^{38}Cl$ and $CH_3CHCl^{38}Cl$ varying with pressure in a complementary manner. However, as shown in Table II, the measured yields of $CH_3CHCl^{38}Cl$ in HI-scavenged systems are never higher than 2% and clearly do not mirror the changes in CH_2 = $CH^{38}Cl$ yield with pressure at any given $[HI]/[CH_2$ =CHCl] ratio. Loss of ^{38}Cl by (3b), followed by recycling through the competitive routes 1, 2, and 6, would transfer some of the ^{38}Cl atoms into $H^{38}Cl$ at low pressures and reduce the fraction of ^{38}Cl distributed between CH_2 = $CH^{38}Cl$ and $CH_3CHCl^{38}Cl$. Nevertheless, a strong complementary relationship, even if not summing to a constant total yield, should still exist at all pressures with this mechanism and is quite inconsistent



Figure 2. Schematic diagram illustrating kinetic mechanisms I and II for thermal ³⁸Cl reactions with vinyl chloride and hydrogen iodide. In mechanism I, $k_2 << k_1$ and k_{10} (heavy black line) is the major source of CH₂CHCl³⁸Cl* radicals under most conditions; k_{11} is assumed equal to 0. In mechanism II, $k_1 \simeq k_2$ and $k_{10} = 0$; the k_2 , k_{11} route (heavy white lines) is a major source of CH₂ClCl₂³⁸Cl at high total pressures.

with the observations in Table II. Comparable but even more extreme behavior has been observed for the addition of ³⁸Cl to CH₂==CHBr, for which the observed high-pressure products are predominantly CH₂BrCH₂³⁸Cl, a smaller yield of CH₂==CH³⁸Cl, and <0.2% CH₃CHBr³⁸Cl, while at low pressures 90 ± 10% of thermal ³⁸Cl is found in the form of CH₂==CH³⁸Cl.⁴

Mechanisms Involving 1,2-Halogen Migrations. Product yields of 78% for $CH_2ClCH_2{}^{38}Cl$ at high pressures and 44% for $CH_2==CH{}^{38}Cl$ at low pressures demonstrate that an appreciable fraction of the reacting ${}^{38}Cl$ atoms are being registered in both categories. Chlorine atoms are therefore mechanistically observable in a 1,2-dichloro configuration at 4000 torr and yet in a 1,1 configuration at low pressure on the reaction path to chlorine atom loss. Similar observations with $CH_2=CHBr$ substrate have been rationalized by 1,2-halogen migration in either of two quite different reaction mechanisms, one involving a 1,2-chlorine migration in an excited radical and the other a 1,2-bromine shift in a thermalized radical.⁴ Two analogous mechanisms can be applied to the $CH_2=CHCl$ data, each including reactions 1–9, as illustrated in Figure 2. The differences between the two mechanisms for ${}^{38}Cl$ plus $CH_2=CHCl$ lie in the choice of 1,2chlorine atom shifts to accommodate both the high- and lowpressure data. In mechanism I, the 1,2-chlorine shift occurs by reaction 10 in the excited $CH_2^{38}CICHCl^*$ radical from (1), while

$$CH_2{}^{38}ClCHCl^* \rightarrow CH_2CHCl{}^{38}Cl^*$$
(10)

$$CH_2CHCl^{38}Cl \rightarrow CH_2ClCH^{38}Cl$$
 (11a)

$$CH_2CHCl^{38}Cl \rightarrow CH_2^{38}ClCHCl \qquad (11b)$$

in mechanism II the shift takes place in reaction 11 with the stabilized $CH_2CHCl^{38}Cl$ radicals from the sequence of (2) followed by (4). In mechanism II, an important fraction of the initial addition reactions must occur by (2) to form $CH_2CHCl^{38}Cl^*$ directly, in contrast to the anti-Markownikoff prediction of mechanism I in which (2) is a minor pathway relative to (1).

The differences between the two mechanisms are illustrated in Figure 2 with the heavy black line for k_{10} in (I) and the heavy white lines for k_2 and k_{11} in (II). The migrating Cl atom in CH₂CHCl³⁸Cl could be either the unlabeled atom in (11a) or the radioactive atom in (11b). None of our experiments are sensitive to the mechanistic difference between (11a) and (11b), and reaction of either radical with HI would lead to a product indistinguishable from that found in (9) because we have no tracer (e.g. ¹³C) which records the initial C-Cl bonding.

Mechanism I is comparable to that usually applied to the CH2=CHBr system and adopts as the major reaction route initial anti-Markownikoff addition of ^{38}Cl to the CH₂ end of CH₂= CHCl to form CH₂³⁸ClCHCl*, as in (1). The formation of CH₂=CH³⁸Cl from this radical is then dependent upon the 1,2-chlorine shift in the excited radical in (10), in competition with loss of ${}^{38}Cl$ by (7) or collisional stabilization in (8). With direct addition of ${}^{38}Cl$ to CH_2 in (1) as the only route to the $CH_2^{38}Cl$ group (i.e. $k_{11} = 0$), yields as high as 78% for $CH_2ClCH_2^{38}Cl$ at 4000 torr in Table II require that k_1/k_2 be at least a factor of 5, while quantitative inclusion of reaction 6 raises the minimum value for k_1/k_2 to about 10 for mechanism I. The observed pressure dependence of the CH_2 == $CH^{38}Cl$ yield can then be qualitatively simulated through the assumption that the 1,2 migration in (10) is the needed reaction occurring on a time scale competitive with collisional stabilization of the excited radical. An alternative formulation of mechanism I can include the Clatom-bridged intermediate (A) as a long-lived intermediate rather than simply the transition state for (10).

Mechanism II is analogous to that proposed⁴ for addition to CH_2 — CHBr and permits addition to each of the CH_2 and CHClends of vinyl chloride as significant reaction routes. No isomerization of $CH_2^{38}ClCHCl^*$ is postulated (i.e. $k_{10} = 0$), and the only pathways open to excited CH238ClCHCl* radicals are those involved in the pressure-dependent competition between decomposition by (7) and stabilization in (8). Competitive pathways are also open for the CH₂CHCl³⁸Cl^{*} radicals from (2), including loss of Cl (or ³⁸Cl) in (3) or collisional stabilization in (4). In mechanism II, the necessary path to furnish high yields in the 1,2-dichloro configuration at high pressures is accomplished by the 1,2-chlorine migration of (11). The only route to ${}^{38}Cl/Cl$ substitution with the formation of CH_2 =CH³⁸Cl in this mechanism is initiated by (2) and must include sufficient ³⁸Cl to provide a yield of 44% at low pressure. The implication then is that k_2 must be roughly comparable to k_1 , although the low-pressure yield of CH2=CH38Cl can be enhanced by multiple passes of 38Cl through the reaction cycles after loss from excited radicals by either reaction 3b or 7.

Competition between HI and CH_2 =CHCl for Thermal ³⁸Cl. The kinetic data of Table II can be used not only to furnish information about the reaction rates of (1) and (2) relative to one another but also to provide data on the sum of their relative rates vs. the competing reaction with HI by (6). In mechanism I as outlined above, initial reaction of ³⁸Cl with CH₂=CHCl leads eventually to the formation of either CH₂=CH³⁸Cl by (3a), CH₂ClCH₂³⁸Cl by (9), or CH₃CHCl³⁸Cl by (5). While (3a), (5), and (8) all convert ³⁸Cl atoms into stable products containing C-³⁸Cl bonds measurable by radio gas chromatography, the loss of ³⁸Cl by (3b) leaves no labeled product to mark the occurrence

of the initial addition reaction with CH₂=CHCl. Consequently, at low pressures a smaller fraction of ³⁸Cl should be measurable in these stable organic compounds, and the relative reaction rate for ³⁸Cl with CH₂=CHCl vs. HI should appear to decrease. Such a decrease in observed product formation from CH₂=CHCl is actually found at lower pressures as described below. However, the pressure dependence of the summed reaction yields for carbon-bonded ³⁸Cl cannot be satisfied with (3b) as the only ³⁸Cl loss process because only a very small fraction of the initial ³⁸Cl atoms react in mechanism I through the route of (2) and (3b). Good agreement to the kinetic mechanism can only be obtained with the inclusion of loss of ³⁸Cl from CH₂³⁸ClCHCl* by (7) in competition with its isomerization (10) and stabilization (8). At low pressures the losses of ³⁸Cl by (7) plus minor amounts from (3b) can become more and more important, and the observed sum of organic ³⁸Cl yields will diminish with decreasing pressure for a fixed [HI]/[CH₂=CHCl] ratio.

Mechanism I with 1,2-Chlorine Shift Away from CH238Cl. The experimental data in Tables I and II provide information only about relative rates of reaction because all of the thermalized ³⁸Cl atoms eventually react by some route to form $H^{38}Cl$, CH_2 = CH³⁸Cl, CH₃CHCl³⁸Cl, or CH₂ClCH₂³⁸Cl. The important kinetic parameters for mechanism I are then (a) the ratio k_1/k_2 for addition to either end of CH₂=CHCl, (b) the ratio $k_6/(k_1 + k_2)$ for reaction with HI vs. CH₂=CHCl, (c) the relative rates of reaction k_{10}/k_7 through isomerization and by loss of ³⁸Cl, and (d) the ratio $k_7/k_8[M]$ of ³⁸Cl loss and collisional stabilization by (8). Two kinetic parameters of lesser importance are the average energy losses in collisions with $CClF_3$ by $CH_2^{38}ClCHCl^*$ radicals in (8) and by CH₂CHCl³⁸Cl* radicals in (4). While "weak" collisions with energy losses of only a few kcal/mol per collision are often found for such radicals, the competitive decomposition reactions of (3) and (7) are both thermoneutral, requiring all of their initial excitation energy to reverse the chlorine atom addition by chlorine atom loss. Consequently, even 1 or 2 kcal/mol of energy loss in a collision will effectively close these decomposition channels, and we have assumed that the basic collisions of (4) and (8) are "strong" enough that single encounters are sufficient to prevent (3) and (7), respectively.

The activation energy requirements for isomerization reactions as postulated in (10) or (11) are very uncertain, and the possible dependence of either k_{10} or k_{11} on the excitation energy of the radical is completely unknown. Because the thermodynamic requirement from the difference in energy between thermal CH₂ClCHCl and CH₂CHCl₂ radicals is much less than the excitation energy following atomic chlorine addition to CH₂—CHCl, isomerization in either direction is at least possible while the radicals are still excited. We have made no attempt to model quantitatively the possible excitation energy dependence of either k_{10} or k_{11} in our kinetic mechanisms because the data can be rather satisfactorily rationalized with only semiquantitative considerations such as the assumption of a fixed value for k_{10} in competition with k_7 and k_8 [M].

A satisfactory fit to the yields of CH₂==CH³⁸Cl and CH₂ClCH₂³⁸Cl in Tables I and II can be found with mechanism I and the following five parameters: $k_1/k_2 = 20$, $k_6/(k_1 + k_2)$ = 0.58, $k_7 = k_8$ [M] at 210-torr pressure, $k_3 = k_4$ [M] at 2000 torr, and $k_{10}/k_7 = 1.0$. An alternate set of parameters which fits the data not quite as well but which is probably close enough to be acceptable is found with $k_1/k_2 = 10$, $k_6/(k_1 + k_2) = 0.56$, $k_7 = k_8[M]$ at 190 torr, $k_3 = k_4[M]$ at 1100 torr, and $k_{10}/k_7 = 1.0$. (The rate constants for k_7 and k_{10} were not constrained to be equal in these parameter fits, but variations in the value of k_{10}/k_7 showed best fits near 1.00 ± 0.05 in both sets.) Attempted fits with progressively smaller ratios of k_1/k_2 below 10 all resulted in more and more severe difficulties with the pressure dependence of the $CH_2 = CH^{38}Cl$ yields. The generalization then follows that the observed yields of CH2==CH38Cl and CH2ClCH238Cl can be explained quantitatively, but only if the anti-Markownikoff preference in initial addition is very strong, with $k_1/k_2 > 10$. A mechanistic problem immediately raised by this conclusion is the necessity for an explanation of nearly exclusive addition by (1)



Figure 3. Relative yields of $CH_2CICH_2^{38}CI$ and $CH_2=CH^{38}CI$ from reactions of thermal ³⁸Cl with $CH_2=CHCl$ vs. [HI]/[$CH_2=CHCl$] molar ratio. Approximate total pressures (in torr): 4000, O; 2000, \blacktriangle ; 1000, \blacksquare ; 500, \square ; 120, \blacksquare . Solid and dashed lines represent calculated ratios from mechanism II with parameters as given below Figure 1 and in text.

with CH₂=CHCl in contrast to a corresponding observation of about 2 for k_1/k_2 in ³⁸Cl reactions with CH₂=CHF.⁵

None of our attempted parameter adjustments with mechanism I have been able to account for the dependence of yields vs. pressure found for $CH_3CHCl^{38}Cl$. This difficulty is illustrated with the first parameter set given above, which predicts yields of 4.1% for $CH_3CHCl^{38}Cl$ at 4035 torr and $[HI]/[CH_2=CHCl]$ = 0.25 and 0.83% at 124 torr and $[HI]/[CH_2=CHCl]$ of 3.05. The corresponding measured yields are almost reversed in Table II, with 0.76% at 4035 torr and 2.04% at 124 torr.

Mechanism II with 1,2-Chlorine Shift Away from the CHCl³⁸Cl Group. The alternative mechanism (II) is dependent upon radical isomerization through the 1,2-chlorine shifts of reaction 11 to account for the pressure dependence of the yields of CH₂—CH³⁸Cl and CH₂ClCH₂³⁸Cl. The variable parameters with this mechanism include the first four of the set used for mechanism I, plus a fifth parameter involving the rate of 1,2-chlorine shift in reaction 11 vs. abstraction of hydrogen from HI in (5). We have again assumed that single collisions are strong enough to stabilize excited free radicals against loss of Cl by reactions 3 or 7. With this mechanism, the observed data can be satisfactorily fitted with a range of parameter combinations.

A first test of such combinations can be made through examination of the required preference in the initial addition reaction. The magnitudes of k_1 and k_2 were therefore set equal to one another, and the remaining parameters were then optimized until a good fit was obtained to the data. The calculated yields of CH_2 =-CH³⁸Cl are graphed in Figure 1 as a solid line for k_1/k_2 = 1.00, $k_6/(k_1 + k_2) = 0.65$, $k_7 = k_8$ [M] at 65 torr, and $k_3 = k_4$ [M] at 220 torr. Further tests of the ability of this set of parameters and this kinetic mechanism to match the experimental observations are shown in Figures 3 and 4. Mechanism II with these values clearly simulates the yield data for CH_2 =-CH³⁸Cl and CH_2CICH_2 ³⁸Cl well enough to be accepted as a consistent rationalization of our experimental data.

We have explored the acceptable ranges of these parameters and have found that the ratio k_1/k_2 can be varied substantially, while still fitting the experimental data. One of the best-fitting set of such parameters is shown in Figure 1 as the dashed line and corresponds to $k_1/k_2 = 0.71$, $k_6/(k_1 + k_2) = 0.65$, $k_7 = k_8$ [M] at 100 torr, and $k_3 = k_4$ [M] at 260 torr. This set of parameters is actually contrary to the "anti-Markownikoff" rule, with k_1 less favored than k_2 , and indicates that our data are incapable of distinguishing quantitatively among several hypothetical ratios of k_1/k_2 in the range near 1.0.



Figure 4. Reciprocal summed yields of $CH_2ClCH_2^{18}Cl$, $CH_3CHCl^{38}Cl$, and $CH_2=CH^{38}Cl$ from thermal ³⁸Cl reactions with $CH_2=CHCl$ vs. [HI]/[$CH_2=CHCl$] molar ratio. Approximate total pressures (in torr): 4000, Δ ; 500, \odot ; 120, O. Solid lines represent calculated ratios from mechanism II with either set of parameters for Figure 1; cross-hatched area represents range of pressures with and without argon included in total.

An important characteristic of the data in Table II is the nearly constant value at any given pressure for the ratio of the yields of $CH_2ClCH_2{}^{38}Cl$ and $CH_2=CH{}^{38}Cl$ as the ratio $[HI]/[CH_2=CHCI]$ is varied. The implication of such a constant ratio is that all ${}^{38}Cl$ atoms are introduced into the competition among (1), (2), and (6) in such a way that fixed fractions at each pressure proceed to the various end products. As diagramed in Figure 2, both mechanisms I and II meet this requirement with rate constant ratios fixed for each competitive situation as soon as the pressure is specified. The predictions from mechanism II for the two sets of parameters given above are shown in Figure 3, together with the experimental data from Table II on the $(CH_2ClCH_2{}^{38}Cl)/(CH_2=CH{}^{38}Cl)$ ratios.

A third test of any proposed kinetic mechanism is its ability to emulate the competition between HI and CH₂=CHCl for thermal ³⁸Cl atoms. At high pressures, essentially all ³⁸Cl atoms remain bonded to carbon once addition has occurred, because neither (7) nor (3) competes appreciably with collisional stabilization at 4000 torr. However, the loss of ³⁸Cl by (7) or (3b) leaves no stable ³⁸Cl-labeled product and the apparent summed rate constant for k_1 plus k_2 vs. k_6 is diminished at low pressures. The experimental data from Table II are graphed in Figure 4 in the form of reciprocal total yields vs. [HI]/[CH2=CHCl] ratio and demonstrate the expected increase in reciprocal total yield as the pressure is lowered at fixed [HI]/[CH₂=CHCl] ratio. Mechanism II leads to predictions of linear behavior with increasing [HI]/[CH2=CHCl] ratio, as graphed in Figure 4. The slopes of these lines at each pressure are quite dependent upon the assumed value of $k_6/(k_1 + k_2)$, and the same sets of parameters used in Figures 1 and 3 have also been applied in Figure 4. In this case, the predictions for the two sets of parameters are essentially indistinguishable from each other, and the linear plots of Figure 4 correspond to both the dashed and solid lines used in Figures 1 and 3. The cross-hatched lines at low pressure indicate the uncertainty caused by the variable choice between zero and unity for the collision efficiency of argon vs. $CClF_3$ in stabilization of excited radicals. The actual data at high [HI]/[CH₂=CHCl] ratio tend to drift above the linearity expected from the mechanism, probably as the consequence of complications introduced into experiments in which HI is actually the major reacting substrate.

The general agreement between the predictions from mechanism II and the experimental data is quite satisfactory for either of the two sets of parameters used for illustration, although the fit is marginally better with the dashed lines from the parameter set with $k_1/k_2 = 0.71$. The mechanistic significance of a value of k_1/k_2 less than 1.0, if established to be correct, would be that the preference in the initial reaction is for addition to CHCl rather than to CH₂ by a factor as large as 1.4. However, additional parameter sets have also been found which fit the data nearly as well as those illustrated in Figures 1, 3, and 4, including sets with different k_1/k_2 values ranging from about 0.35 to 1.7. In each case, the best value of $k_6/(k_1 + k_2)$ is about 0.65, and the ratios of reaction rates with HI and CH₂=CHCl at various pressures are roughly the same as those found for the parameter sets illustrated in Figures 1, 3, and 4.

The best data fits for all values of the ratio k_1/k_2 have been found with different rates of Cl atom loss for reactions 7 and 3, e.g. 65- and 220-torr equivalent pressures in one set and 100 and 260 torr in the other. These parameters can readily be varied to agree within the statistical factor of 2 (i.e. two chlorine atoms on one carbon atom in CH₂CHCl³⁸Cl^{*}) and even to equal equivalent pressures while still maintaining fairly good fits to all of the experimental data. The potential significance of a factor of 3 in reaction rate for two different C₂H₃Cl³⁸Cl^{*} radicals is lessened by this uncertainty in the fitting of parameters.

The ultimate conclusion from this data treatment is that the experimental observations can be consistently explained with mechanism II for a range of parameters in which k_1 and k_2 are approximately comparable in magnitude. If mechanism II is correct, then the initial addition of chlorine atoms to CH₂—CHCl does not show a strong preference for either end of the molecule. Its "anti-Markownikoff" character is at most quite weak and is in some doubt because of the existence of satisfactory parameter fits to the observation data with k_1/k_2 less than 1.0.

The fifth parameter for data fits with mechanism II represents the competition for the stabilized $CH_2CHCl^{38}Cl$ radical between isomerization by (11) and reaction with HI in (5). A strong possibility exists that no single-valued parameter can satisfactorily represent this competition because the probabilities of (5) and especially of (11) may be dependent upon the internal energy of the "stabilized" radical. A similar possibility exists for k_{10} in mechanism I. While a single collision with CClF₃ may be sufficient to prevent reaction 3 for CH₂CHCl³⁸Cl*, the radical itself is probably still rather highly excited after its first collision, i.e. stabilized against loss of chlorine by (3) but still far above thermal energies. The appropriate choice for k_{11} may continue to decrease for many more collisions before the CH₂CHCl³⁸Cl radical is really thermalized.

We have not found a single value for the parameter expressing this competition which succeeds in matching the experimental yields for CH₃CHCl³⁸Cl. We do note, however, that the yields of CH₃CHCl³⁸Cl in Table II are uniformly greater at higher absolute HI concentrations in the several instances in which experiments have been carried out with the same [HI]/[CH₂= CHCl] ratios but with different absolute concentrations of both. The only parameter in mechanism II which is affected by the absolute concentrations of HI is the competition between isomerization in (11) and reaction with HI in (5). The increased yields of CH₃CHCl³⁸Cl for higher absolute concentrations of HI are qualitatively consistent with the expectation that more radicals would be trapped by (5) before isomerization by (11) could occur.

Choice between the Two 1,2-Chlorine Shift Mechanisms? Two alternate mechanisms have been devised, each of which is reasonably satisfactory in accounting for the yields of CH_2 — $CH^{38}Cl$ and $CH_2ClCH_2^{38}Cl$ shown in Tables I and II. The yields of the third product $CH_3CHCl^{38}Cl$ have not been quantitatively accounted for with a single-valued parameter for either mechanism I or II, although (II) is qualitatively superior in this respect. In these circumstances, additional corroboratory evidence can be sought from related or analogous experiments.

The addition of thermal ³⁸Cl atoms to CH_2 —CHF has been shown to occur with a preference toward the CH_2 end by a factor of 2.⁵ The corresponding quantitative choices in the CH_2 —CHCl system are either a factor of 10 or larger with mechanism I or roughly comparable (i.e. 0.35–1.7) with mechanism II. In the absence of any special factor which would cause Cl atoms to be much more effective than F in directing incoming ³⁸Cl atoms away from the halogenated end of the olefin, the smaller preferences found in fitting the data with mechanism II appear to be more consistent with the CH₂=CHF results.

Numerous studies have been carried out in condensed phases on the occurrence of 1,2-chlorine atom isomerizations in various systems.⁷⁻¹⁰ The consistent observation in these cases has been isomerization from the carbon atom with multiple halogen substituents toward the carbon atom with one or zero halogen atoms attached, e.g. $CCl_3CHCl \rightarrow CCl_2CHCl_2$.¹⁰ The direction of isomerization by (11) in mechanism II is in agreement with these other experiments, while that of (10) in mechanism I operates in the opposite direction. Again, the assumptions of mechanism II are more consistent with the overall body of experimental data.

While our overall conclusion is that mechanism II is strongly preferred as the correct explanation for the observations in the 38 Cl plus CH₂==CHCl system, one additional caveat needs to be entered. If isomerization by 1,2-chlorine shift can take place at all, then it likely will proceed more rapidly with higher excitation energies. The possibility then exists that the initially highly excited radicals formed in (1) and (2) can both undergo rapid 1,2-chlorine shifts to form the other, effectively erasing the information about the site of the original reaction. Certainly, if reasonably satisfactory parameters can be found for mechanisms I and II separately, then they can also be found for a more complex mechanism including both (I) and (II), and this possibility cannot be eliminated as an explanation for our CH2=CHCl yield data. The occurrence of 1,2-chlorine shift reactions in both directions is most likely with the highest excitation energies, and therefore during the time period immediately following the addition reaction and prior to the first collision with another molecule. Most other experimental investigations of 1,2-chlorine atom shifts have been carried out in condensed phases,⁷⁻¹⁰ with minimal elapsed time between addition and first collision. Gas-phase experiments permit longer survival of the radical with all of its initial excitation energy and are the most likely to be subject to 1,2-chlorine atom migration in both directions. Nevertheless, we have no evidence requiring isomerization in the direction of reaction 10 and prefer the simpler mechanism II to a combination of (I) and (II). The apparent lack of need for 1,2-chlorine atom shifts in explanation of the experiments with CH2=CHF5 tends also to make the need for a combination of (I) plus (II) in the CH2=CHCl system less likely.

Absolute Reaction Rate for Thermal Chlorine Atom Addition to $CH_2 = CHCl$. The data displayed in Figure 4 demonstrate its validity as measures of the relative rates of reaction 6 with HI vs. $(k_1 + k_2)$ with CH₂=CHCl at various pressures. When extrapolated to infinite pressure, the ratio of $k_6/(k_1 + k_2)$ has the value 0.65 and can be used directly to estimate the absolute rate for reaction of thermal chlorine atoms with CH2=CHCl if the absolute value for k_6 is known. Similar ratios in competition with HI have been used to estimate the absolute reaction rate constants for addition to CH2=CH2,²² CH2=CHF,⁵ and other olefins.^{15,16} In all of these CH₂=CHX experiments, the ratio of k_6/k_{olefin} has been about 0.6-0.7, indicating that the addition reactions for ³⁸Cl atoms with CH2=CH2, CH2=CHF, and CH2=CHCl all proceed with reaction rates in the range of $(1.5 \pm 0.4) \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹. Such rapid rates correspond approximately to addition on nearly every collision with each of these substrates. The further implication of such very high collision efficiencies for reaction is that the energy barrier for addition by atomic chlorine to CH₂=CHX systems is quite low, in the range of several hundred cal/mol. With the choice of mechanism II and its roughly comparable values for k_1 and k_2 , the energy barrier toward addition of Cl to the CHCl end of CH₂=CHCl is also no larger than a few hundred cal/mol. The loss of Cl from either of the excited C₂H₃Cl³⁸Cl* radicals must then by microscopic reversibility also have barriers no larger than a few hundred cal/mol in the exit channels. These conclusions can be important in

⁽²²⁾ Iyer, R. S.; Rogers, P. J.; Rowland, F. S. J. Phys. Chem. 1983, 87, 3799.

estimation of the rates of decomposition of excited radicals by chlorine atom loss.

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Registry No. CH₂=CHCl, 75-01-4; ³⁸Cl, 14158-34-0; CClF₃, 75-72-9; HI, 10034-85-2; H, 1333-74-0; CH₂³⁹ClCHCl, 96915-22-9; CH₂CHCl³⁹Cl, 96915-23-0; chlorine, 22537-15-1.

Temperature and Concentration Range of the Blaxial Nematic Lyomesophase in the Mixture Potassium Laurate/1-Decanol/D₂O

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Two different planes of the three-dimensional phase diagram of the lyotropic mixture potassium laurate/1-decanol/D₂O are investigated by optical microscopy, conoscopy, and X-ray diffraction techniques. For appropriate concentrations, the temperature range of the biaxial nematic phase goes up to 15 °C.

Introduction

Mixtures of amphiphilic molecules and water may give nematic lyomesophases under proper temperature-concentration conditions.¹ From symmetry considerations,² two uniaxial and one biaxial $(N_{BX})^3$ nematic phases are expected. Depending on whether the director (\vec{n}) orients parallel or perpendicular to the magnetic field (\tilde{H}) , these uniaxial phases have been classified⁴ as calamitic (N_c) and discotic (N_D) , respectively. The three nematic phases N_D , N_{BX} , and N_c present a recent interest from both theoretical² and experimental⁵⁻⁷ points of view.

In 1980 Yu and Saupe published³ a phase diagram of the lyotropic mixture potassium laurate/1-decanol (at 6.24 wt %)/D₂O where the different phases are identified by conoscopic and NMR measurements. Their phase diagram presents reentrant N_c and N_{BX} phases.

On the other hand, Hendrikx and co-workers⁵ studied the phase diagram of the same mixture at a slightly different 6.27 wt % of 1-decanol (texture analysis, neutron, and X-ray measurements). They observed some differences by comparing to the diagram of ref 3: the N_{BX} phase and the reentrant character of the N_c phase were not observed. The discrepancies between these phase diagrams are important and seem not to be explained simply by the difference in the alcohol concentration. Moreover, the reentrant behavior of the N_c and N_{BX} phases was not observed in recent laser conoscopic measurements⁷ performed on a mixture which had to present this feature according to the ref 3 phase diagram.

In this paper we present a detailed study of the potassium laurate 1-decanol D_2O phase diagram in two different planes of the concentration-temperature space at a constant 1-decanol concentration (6.24 wt %) and at a fixed ratio between the potassium laurate (KL) and 1-decanol (DeOH) concentrations, R = [KL]/[DeOH] = 4, in which larger temperature ranges of the N_{BX} phase are found. The nematic phases are determined by crossing the results from three experimental techniques: optical microscopy (by observing the textures), conoscopy (by measuring the order parameter in the uniaxial and biaxial phases), and X-ray diffraction (by identifying the microscopic structure of the phases).

Experimental Section

Mixtures. The 1-decanol is from Fluka (p.p.a. >99%), the D_2O is from CEA Saclay, and the potassium laurate is synthesized and recrystallized in the laboratory from commercial lauric acid (Fluka p.p.a >99%). Its clarification point is 395 °C as described in ref 8. Special care is taken to avoid the contact of the KL with humid atmosphere. If not, the hydration of the amphiphilic molecules could increase the water concentration in the mixture and shift the transition temperatures in an uncontrolled manner. Mixtures are reported in previously well-cleaned glass tubes by carefully weighing each compound at a 0.005% accuracy. The sealed tube is then shaken in an electric vibrator and centrifuged for some minutes. This procedure is repeated several times until the mixture is homogeneous. It is then stored in a temperature-controlled stage at about 25 °C.

Optical Microscopy. Samples are sealed in flat microslides from Vitro Dynamics Inc. with inside dimensions $100-\mu m$ thickness, 1-mm width, and 3-cm length, and placed in a temperaturecontrolled stage (of 1 °C accuracy). A polarized light microscope is used to observe the sample textures (orthoplan, Pol Leitz). Such an observation is an easy way to determine the temperature of the phase transitions, except in the case of the N_c-N_{BX} transition which can just be denoted by the occurrence of a faint veil.

Conoscopy.⁷ Samples are sealed in a glass cell of 1-mm thickness (from Hellma). The cell is placed in a servocontrolled thermostat (of 0.02 °C accuracy) which is itself held in a horizontal magnetic field of about 5 kG. The orientation of the sample (in the N_D phase at the beginning of each experiment) is achieved by repeated rotations of the cell around the vertical direction in the magnetic field. The conoscopy is made with a He-Ne laser beam converging in the sample with a half-angle aperture of 50°. It allows one to determine unambiguously the macroscopic symmetry of each phase and to find their phase transition with a good temperature resolution (0.02 °C). This method always gave transition temperatures consistent with those found by the direct optical observation.

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