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Chlorination of Unsaturated Compounds in Nonpolar Media

Recognition of competition between polar and radical pathways clarifies the olefin-chlorine reaction.

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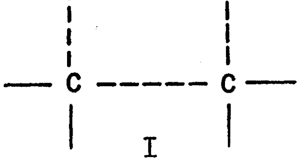
Reaction of olefinic organic compounds with halogens in solvents such as carbon tetrachloride is a standard method of preparing vicinal dihalides (*1*). Decoloration of a solution of bromine (or chlorine) is a traditional qualitative test for unsaturation (*2*). However, in spite of a long history of use of such halogenations for synthesis and analysis, their mechanism has remained unclear, largely because of reputed nonreproducibility, in a quantitative sense, owing to effects of surfaces, traces of moisture, light catalysis, and so on. Recent results in our laboratories have exposed the mechanistic pathways for chlorination of simple nonfunctionalized unsaturated molecules in nonpolar solvents. Application of this knowledge allows a much greater degree of product control than was previously possible.

Introduction to Mechanisms

Before we consider experimental data, it will be useful to describe possible mechanisms for the chlorination of olefins, certain of which have been elucidated historically under experimental conditions different from those described here. The conceptually simplest route would involve utilization of a four-center transition state (I)



I

in which the two chlorine atoms become attached to the *p*-orbitals of the double bond as the chlorine-chlorine bond breaks. This process, which for ethylene would be exothermic by about 38 kilocalories per mole (*3*), would lead one to expect *cis* addition. In fact, the generally observed products of addition are either the exclusively *trans* isomers or mixtures of *cis* and *trans* isomers (*4*); hence this one-step mechanism can be dismissed as a general phenomenon, and we must turn to multi-step pathways which involve shortlived intermediates.

A second possibility is a pathway involving free-radical reactions such as 1–4 (Fig. 1). Photochlorination of ethylene and chloroethylenes has been shown to follow this route in the vapor phase (*5*). The chief characteristics of this chain mechanism are (i) the requirement for chain initiation (radical formation, reaction 1) by cleavage of the chlorine-chlorine bond, a process which occurs readily on exposure to light or high temperature but which is not significant at ambient temperatures in the dark; (ii) the occurrence of long chains by successive repetitions of reactions 2 and 3, and hence susceptibility to inhibition by materials such as oxygen; and (iii) the probability that there will be substitution products from olefins more complicated than ethylene. The occurrence of such substitution (*6*) would involve replacement of reactions 2 and 3 by reactions 5 and 6 (Fig. 2). It has been shown that addition of chlorine atom to a double bond (reaction 2) and abstraction of saturated hydrogen atoms by chlorine atom (reaction 5) indeed occur with comparable rapidity (*7*). A classic example of the free-radical pathway is the vapor-phase chlorination of propylene, which shifts from production of 1,2-dichloropropane to allyl chloride as the temperature is increased, in the range 200° to 600°C (*8*). Apparently reaction 7 (Fig. 2) is somewhat faster than reaction 8 at moderate temperatures, but at high temperatures addition is reversible, whereas abstraction is not.

Radical chlorination under the specific conditions of the work discussed here (liquid phase at ambient temperature without irradiation) would be a reasonable possibility *if* (i) initiation of the reaction were supplied to overcome the high endothermicity of reaction 1, and (ii) no other process were more facile. In fact, in spite of several clues in the early literature, this pathway has generally been ignored by organic chemists.

A third and most widely studied mechanism is a polar pathway in which the chlorine-chlorine bond is broken heterolytically and carbonium ion intermediates occur. Findings such as (i) increases in rate as electron-donating substituents are placed on the double bond (*9*) and (ii) diversion of portions of product from dichloride formation by the addition of anions as well as the occurrence of products derived from incorporation of nucleophilic solvents (*10*) leave little doubt

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that reaction 9 (Fig. 2) is operative in *polar* solvents which support charge separation. More detailed stereochemical investigations (*4*) have shown that the positive ion may have the α-chlorocarbonium ion structure (reaction 9, II*a*) for certain olefins, but the bridged chloronium ion structure (II*b*) for others; cyclic intermediate II*b* is invoked to explain the exclusively *trans* addition which occurs for simple olefins such as *cis*- and *trans*-2-butene in, for example, acetic acid solvent.

Such a polar mechanism should be considered with caution when reaction is carried out in *nonpolar* solvents where charge separation is unfavorable. Nevertheless, this mechanism has been widely accepted even for the reaction conditions considered in this article.

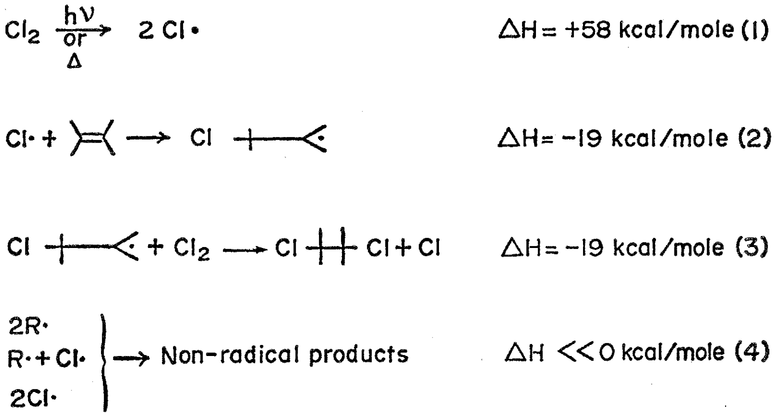

Fig. 1. Reactions 1–4 (see text).

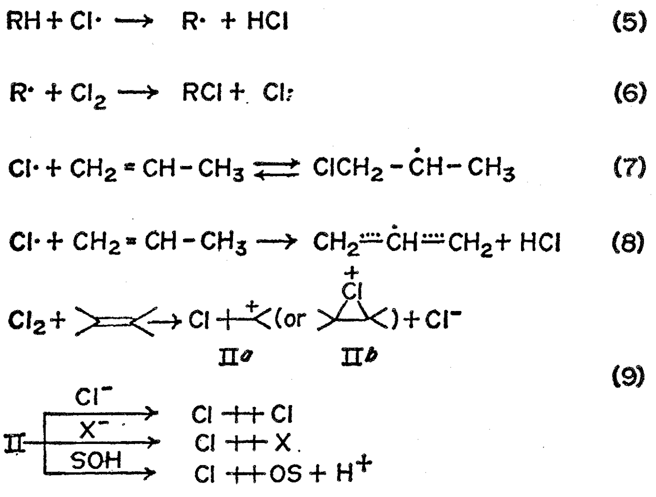

Fig. 2. Reactions 5–9.

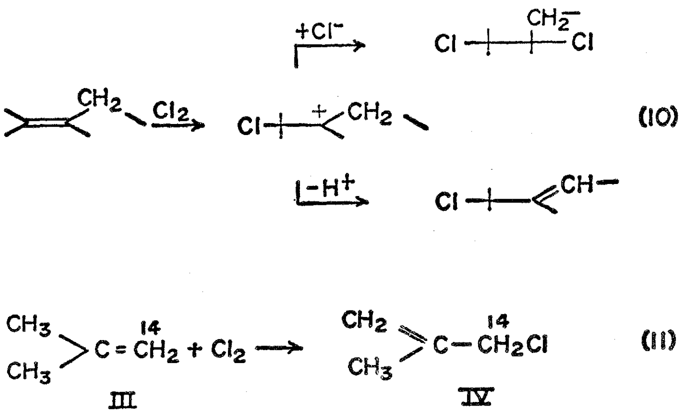

Fig. 3. Reactions 10 and 11.

Historical Background

Many data (*11*) suggest that, in the absence of light, simple olefins and chlorine react slowly, if at all, in the vapor phase at ambient temperatures; however, vigorous reaction ensues as soon as a liquid phase is present, even as a film on the wall of the reaction vessel. Olefins can be divided into two categories on the basis of the type of product produced in such chlorinations in nonpolar liquid phases; linear olefins (for example, 1-butene or 2-butene) give predominantly (60 to 80 percent) the expected addition products, whereas olefins with branching *at the double bond* (for example, isobutylene) give predominantly (> 80 percent) allylic chlorides with shifted double bonds. In 1948 Taft (*12*) proposed that the polar mechanism best correlated the existing data (on the usual assumption that only a single pathway was involved). The carbonium ion intermediate was thought either (i) to collapse with chloride ion to produce addition product or (ii) to eject a proton to produce substitution product (Fig. 3, reaction 10). The predominance of substitution product for branched olefins would be explained if tertiary carbonium ions showed a greater tendency toward proton loss than secondary ones did; the known larger elimination : replacement ratios in solvolysis of tertiary derivatives as compared to the ratios for secondary ones (*13*) supported this idea. This proposed polar mechanism received strong support from the observation (*14*) that liquid-phase chlorination of 1-C^{14} isobutylene (Fig. 3, reaction 11, structure III) at 0°C gave 3-chloro-2-methylpropene with label *only* in the 3-position (IV), as predicted by reaction 10; any symmetrical intermediate such as the 2-methylallyl radical is ruled out. Unfortunately, the (minor) substitution products from a linear olefin were not considered in any detail; if they had been, the polar mechanism would probably not have achieved its almost universal acceptance.

It must be pointed out that several early observations by Stewart and his coworkers (*15*) are not in accord with the polar mechanism. These workers discovered an apparently general phenomenon in which additive chlorination of an olefin induced substitution reactions of alkanes concurrently present in the reaction mixture. For example, into a solution of chlorine in pentane in the dark at room temperature (a stable

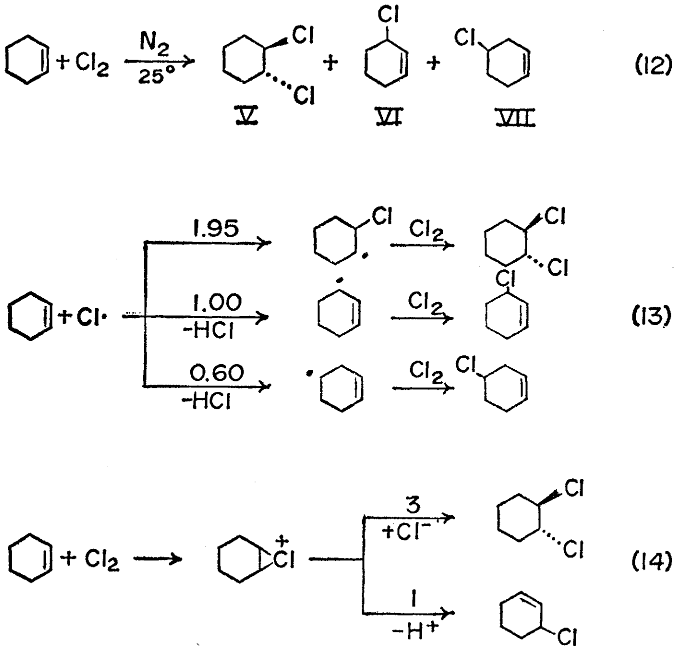

Fig. 4. Reactions 12–14.

system) gaseous ethylene was passed until the chlorine had disappeared. In addition to the expected 1,2-dichloroethane, substantial quantities of chloropentanes were formed. In terms of modern physical organic concepts, such facile attack on a completely saturated molecule strongly suggests free-radical reactions. However, at the time of the observations, the occurrence of radical chain reactions in liquid-phase organic reactions was just beginning to be recognized as an important phenomenon, and these observations seem to have been largely forgotten.

Competitive Reaction Pathways

A solution to the historical anomaly described above came recently with our discovery (*16, 17*) that both polar and radical reactions can occur during olefin chlorination and that any mechanistic interpretation must include both pathways. The balance between them was found to be a function of olefin structure, olefin concentration, and environmental factors such as light and oxygen (or air). I will briefly list the empirical principles concerning each of these factors before considering the experimental evidence from which they are derived.

The key reaction, previously unrecognized, is one between olefins and chlorine which produces unstable free radicals as primary products; these then serve as chain initiators for a radical pathway. This reaction and its resulting radical chain are in competition with a second reaction of olefins and chlorine which proceeds by way of a polar pathway. The observed dependence on olefin structure is as follows: linear olefins, free from other functionality (*18*), follow the radical pathway, whereas olefins with carbon-chain branching at the double bond follow the polar pathway. Second, the polar pathway is favored by dilution of the olefin—that is, there is a dependence on olefin concentration. Third, the dependence on environmental factors is seen to be straightforward as soon as one realizes that a radical component is present: oxygen is an efficient inhibitor of radical reaction, and light is a moderately efficient promoter. Unfortunately, the failure to carefully control these experimental variables in earlier work makes earlier data difficult to interpret in mechanistic terms. Also, many reactions described in the literature were run to high conversion of olefin to achieve maximum yields; under such conditions secondary reactions of primary products obscure the initial product distributions, which must be known to determine mechanisms.

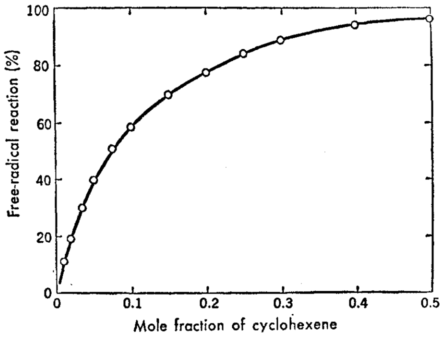

Fig. 5. Dependence of percentage of free-radical reaction on olefin concentration for chlorination of cyclohexene in $C_2F_3Cl_3$ at 25°C in the dark in the presence of nitrogen.

Chlorination of Cyclohexene

Before considering possible reasons for this previously unrecognized duality of mechanism, I present the example of cyclohexene (*16*) as typical of the data which led to the generalizations given above. Chlorination of pure cyclohexene (Fig. 4, reaction 12) at 25°C in the dark in the presence of nitrogen (hence the absence of oxygen) gave, under conditions of low conversion chosen to avoid secondary reactions, *trans*-1,2-dichlorocyclohexane (structure V), 3-chlorocyclohexene (VI), and 4-chlorocyclohexene (VII), in a ratio of 1.95 : 1.00 : 0.60. If cyclohexane was included in the reaction medium, chlorocyclohexane was produced as well. Repetition with external illumination (from sunlamps, through Pyrex glass) caused no changes in product ratios. However, if the system was kept saturated with oxygen, product VII (as well as chlorocyclohexane when cyclohexane was present) was eliminated and only products V and VI were formed (ratio, about 3:1) in a still rapid reaction. Our interpretation of these observations is that the *normal* reaction is entirely radical in character as evidenced by the production of VII and chlorocyclohexane, products not obtainable by the expected polar route, and the failure of deliberate efforts to enhance their production further by external initiation of the chain reaction. However, in the presence of oxygen as an inhibitor, the chain length of the radical component is severely decreased and a polar process takes over. The product-determining steps of the two pathways are summarized in reactions 13 and 14, in which the numbers over the arrows signify the relative rates of the competitive steps involved.

A number of control experiments (*16*) suggest that the radical pathway is initiated by a process indigenous to the reacting system and not by some adventitious factor such as glass surface, impurity, or moisture. Normally, initiators of radical reactions are mole-

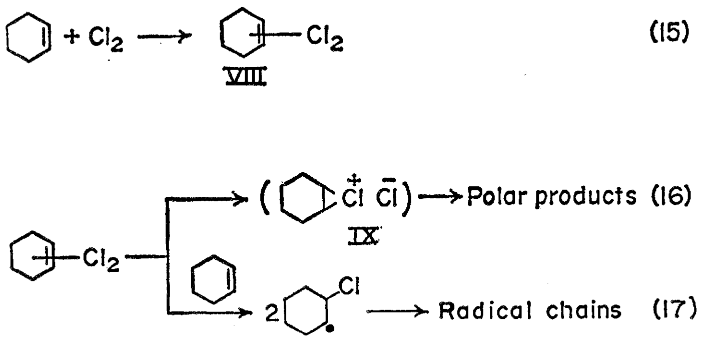

Fig. 6. Reactions 15–17.

cules with at least one relatively weak covalent bond which can be cleaved thermally or photolytically. However, the radical chlorination occurs in total darkness and at temperatures as low as −78°C. Hence we conclude that simple homolytic cleavage of the chlorine-chlorine bond (58 kcal/mole) will not explain the results and that there exists a specific *intermolecular* reaction between cyclohexene and chlorine that generates free radicals which serve as chain initiators. Actually, a surprising number of analogous radical-forming processes have been uncovered in recent years (*19*). This unexpected initiation reaction is, then, the key to interpretation of earlier results on olefin chlorination.

Let us now consider the concentration effect. When cyclohexene is diluted with an inert nonpolar solvent such as 1,1,2-trichlorotrifluoroethane, the ratio of VII to VI smoothly decreases from 0.60 and approaches 0 at infinite dilution; however, the effect can be counteracted with light. If one notes that VII is produced only by the radical pathway whereas VI is produced by both pathways, then it is apparent that, as dilution increases, the polar process begins to become competitive with the radical process, taking over completely at infinite dilution (Fig. 5). In kinetic terms, it appears (*16*) that the kinetic order of the overall radical process in olefin is greater than the kinetic order of the polar process.

The nature of the initiation step itself is still obscure, but it is evidently related to the observed greater kinetic dependence on olefin of the radical pathway. On the basis of a number of kinetic and thermodynamic considerations too detailed to elaborate here, I have proposed (*16*) that the radical-forming step utilizes at least two molecules of olefin and that the hypothetical scheme of Fig. 6 may apply. Olefin and chlorine may combine initially to form a complex (VIII) which either rearranges to ion pair IX, which is committed to polar-product formation (V and VI) (ion pair IX cannot be significantly dissociated to free ions in these nonpolar media), or reacts with more olefin to form a pair of radicals which initiate chain reactions. I emphasize that this sequence has not been put to experimental test, and that the difference in behavior between linear and branched olefins is not satisfactorily explained as yet (*17*). However, the fact that a transient species has been observed spectroscopically on mixing olefins and chlorine in nonpolar solvents and has been designated a charge transfer complex is suggestive (*20*). Finally, note that each encounter of chlorine and olefin which follows the polar route (proposed reactions 15 and 16) gives one molecule of "polar" product, whereas each encounter which follows the radical-forming route (proposed reactions 15 and 17) gives many thousands of molecules of "radical" product because of the chain character of the radical chlorination (reactions 2, 3, 5, and 6). Hence, when the observed result is a competitive mixture of polar and radical products, only a very small fraction of radical-forming reaction need be occurring.

From similar studies with a variety of olefins have arisen the principles stated in the preceding section. It now seems clear that the data which Taft (*12*) attempted to correlate by hypothesizing a polar mechanism were derived partly from radical reactions (most of the linear olefins) and partly from polar reactions (the branched olefins). Thus, while the conclusions drawn from the labeling experiment with isobutylene (*14*) were indeed valid, they applied only to that olefin; a different result would have been obtained for a nonbranched olefin. Having recognized this duality of mechanism, we can now consider the dependence of each pathway on olefin structure.

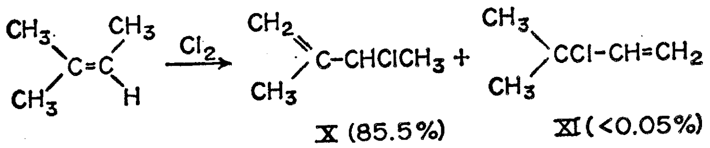

Fig. 7. Structures X and XI.

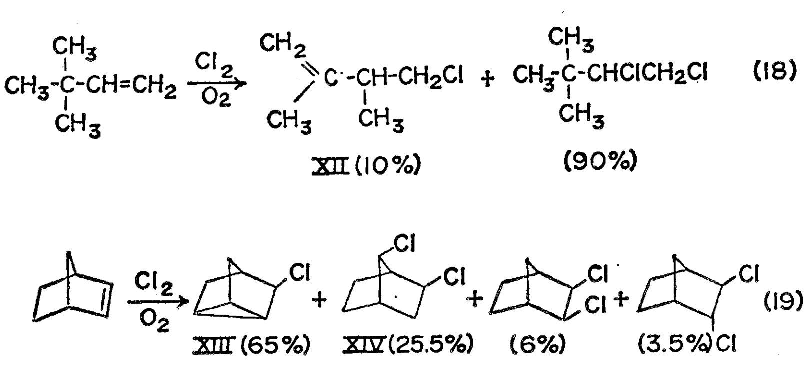

Fig. 8. Reactions 18 and 19.

The Polar Pathway

In this and the succeeding section I focus on the comparative behavior of a series of simple alkylated ethylenes: 1-butene, *cis*-2-butene, *trans*-2-butene, isobutylene, 2-methyl-1-butene, trimethylethylene, and tetramethylethylene. Although the first three of these would normally react by way of the radical pathway, use of oxygen to isolate the polar pathway in all cases gave the products shown in Table 1.

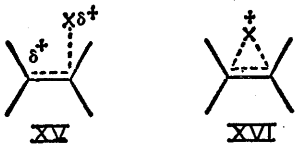

Fig. 9. Structures XV and XVI.

Most of these compounds have been chlorinated previously under less rigorous conditions, and many of the products have been observed qualitatively (*11*, *21*); our use of modern analytical techniques, particularly gas-liquid partition chromatography, has permitted quantitative analysis even of very minor products (*22*). The following generalizations can be drawn. (i) Linear olefins give a preponderance (>95 percent) of addition products formed in a *trans* addition in all cases where stereospecificity has been determinable. The minor amounts of substitution products are formed by elimination in the direction away from the added chlorine atom; that is, allylic rather than vinyl chlorides are formed. Both results are consistent with the intermediacy of a cyclic chloronium ion (*4*, *23*). The relatively large amounts (20 to 30 percent) of substitution products reported in earlier studies (*11*) almost surely involved radical reactions. (ii) Branched olefins give >85 percent of allylic substitution products along with minor amounts of addition products. If there is more than one type of allylic proton that may be lost, as in 2-methyl-1-butene, no great selectivity is observed. The absence of significant amounts of vinylic chlorides again suggests a bridged ion; however, if bridged, the ion must be unsymmetrical enough to explain attachment of chlorine to the primary or the secondary, rather than the tertiary, carbon atom in the substitution product. For example, trimethylethylene gives at least 1000 times as much 3-chloro-2-methyl-1-butene (Fig. 7, structure X) as 3-chloro-3-methyl-1-butene (XI).

Reactions proceeding by way of polar mechanisms are often characterized by Wagner-Meerwein rearrangements of initially formed carbonium ions to more stable ones by alkyl migrations. Skeletal rearrangements have been observed during polar chlorination of rather special molecules as evidenced, for example, by products XII, XIII, and XIV (Fig. 8) (*22*, *24*).

By experiments involving competitive reactions, the relative rates of electrophilic attack of chlorine on various alkylated olefins were determined. In Table 2, selected values are listed and compared with other addition reactions. Knowing the greater stability of tertiary than of secondary carbonium ions, one would predict a rate order

$$\text{trimethylethylene} \simeq \text{isobutylene} > \text{2-butene} \simeq \text{1-butene}$$

for the addition of an electrophile to a double bond with formation of a carbonium ion (transition state XV) (Fig. 9). This order is observed for the addition of a proton during hydration of olefins (*25*). However, for polar chlorination in nonpolar solvents (*22*) and bromination in methanol (*26*), the order is

$$\text{trimethylethylene} > \text{isobutylene} \simeq \text{2-butene} > \text{1-butene}$$

and the rates seem to depend only on the total number of alkyl groups on the double bond, regardless of their placement. In fact, the relative chlorination rates correlate well with $\Sigma\sigma^*$ for all substituents on the double bond, regardless of position, where σ^* is a measure of the inductive electron-releasing power of the alkyl substituents (*27*) (Fig. 10). Such behavior suggests a transition-state structure XVI (Fig. 9), in which the addend is symmetrically placed between the termini of the double bond and little positive charge is generated on the carbon (*22*, *28*).

In summary, then, the rate of polar chlorination of a given olefin is related to the inductive electron-releasing properties of the groups attached to the double bonds, while the nature of the products (addition or substitution) is determined by the structure of the olefin—linear or branched.

The Radical Pathway

Radical reaction is readily achieved for terminal and linear internal olefins since it is the "normal" behavior; it can be largely isolated for 1,1-dialkylethylenes such as isobutylene by external illumination. However, for tri- and tetraalkyl olefins, the polar reaction is so rapid that the radical reaction has not been observed. Therefore this part of the discussion covers a narrower range of structure than the discussion of the polar reaction. The radical products from the isomeric butenes are shown in Table 3, which is analogous to Table 1 for the polar reaction. Certain generalizations can be drawn and compared with those for the polar reaction. (i) Addition product predominates but now addition is nonstereospecific. (ii) Both possible allylic isomers (shifted and unshifted double bonds) form, but the geometri-

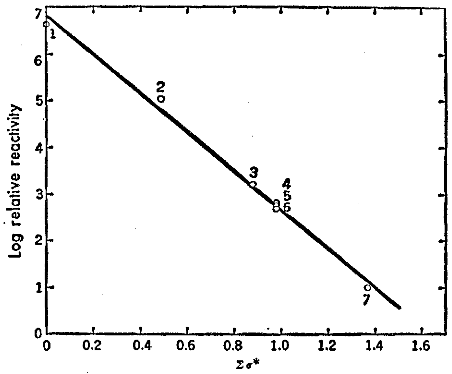

Fig. 10. Dependence of relative reactivities of olefins with respect to polar chlorination on the inductive constants (σ^*) of the groups attached to the double bond: 1, tetramethylethylene; 2, trimethylethylene; 3, 2-methyl-1-butene; 4, *cis*-2-butene; 5, isobutylene; 6, *trans*-2-butene; 7, 1-butene.

Table 1. Major products from chlorination of pure olefins by way of the polar mechanism.

Olefin	Temperature (°C)	Substitution product*	Addition product*
1-Butene	−9	1-chloro-*trans*-2-butene 1-chloro-*cis*-2-butene } (3)	1,2-dichlorobutane (97)
trans-2-Butene	−9	3-chloro-1-butene (2)	*meso*-2,3-dichlorobutane (98)
cis-2-Butene	−9	3-chloro-1-butene (3)	*dl*-2,3-dichlorobutane (97)
Isobutylene	−9	3-chloro-2-methylpropene (87)	1,2-dichloro-2-methylpropane (13)
2-Methyl-1-butene	25	2-(chloromethyl)-1-butene (58) 1-chloro-2-methyl-*cis*-2-butene (29) 1-chloro-2-methyl-*trans*-2-butene (8)	1,2-dichloro-2-methylbutane (5)
Trimethylethylene	25	3-chloro-2-methyl-1-butene (85.5)	2,3-dichloro-2-methylbutane (14.5)
Tetramethylethylene	25	3-chloro-2,3-dimethyl-1-butene (99.7)	2,3-dichloro-2,3-dimethylbutane (0.3)

* Percentage yield of each product in parentheses.

$$CH_3\cdot + CH_3CH_3 \longrightarrow CH_4 + \cdot CH_2CH_3$$
$$\Delta H = -4 \text{ kcal/mole} \quad E_a = 11.8 \text{ kcal/mole} \quad \log A = 12.0 \qquad (20)$$

$$Cl\cdot + CH_3CH_3 \longrightarrow HCl + \cdot CH_2CH_3$$
$$\Delta H = -5 \text{ kcal/mole} \quad E_a = 1 \text{ kcal/mole} \quad \log A = 13.2 \qquad (21)$$

Fig. 11. Reactions 20 and 21.

Table 2. Relative reactivities of olefins in electrophilic addition reactions.

Olefin	Chlorination*	Bromination†	Hydration‡
1-Butene	1.0§	1.0§	
cis-2-Butene	6.3 × 10	4.3 × 10‖	< 0.001
trans-2-Butene	5.0 × 10		
Isobutylene	5.8 × 10		1.0§
Trimethylethylene	1.1 × 10^4	1.2 × 10^3¶	0.58
Tetramethylethylene	4.3 × 10^5	9.6 × 10^3	

* Competitive chlorination in nonpolar media in the presence of oxygen at −9° to 25°C (*22*). † Direct rate measurements in methanol-0.2*N* NaBr at 25°C (*26*). ‡ Direct rate measurements in 1.0*N* HNO_3 at 25°C (*25*). § Assigned as unity for this column. ‖ *cis*-2-Pentene. ¶ 3-Methyl-2-pentene.

cal isomerism of the original double bond is retained. (iii) Products derived from abstraction of all possible hydrogens, not just allylic ones, are formed.

Radical chlorination can be separated into two phases: (i) the attack of chlorine atom by way of addition or hydrogen abstraction (reactions 2 and 5), which determines the overall ratio for addition and substitution products, and (ii) the reaction of the resulting radicals with molecular chlorine (reactions 3 and 6), which determines the ultimate structure of the individual addition and abstraction products. Through competitive reactions between various olefins [as well as other unsaturated materials considered below (*29–31*)] and cyclohexane, as a common standard, the relative rates of addition of chlorine atom to various types of unsaturation (k_a, defined for the molecule as a whole) and relative rates of abstraction of various types of hydrogen (k_t, defined per reactive hydrogen) have been determined relative to $k_t \equiv 1.00$ for abstraction of a single cyclohexane hydrogen atom. Typical values are given in Tables 4 and 5; since the temperature effects are small, results for chlorine atom at −9° and 25°C have been combined in a single list. In Tables 4 and 5 these values are contrasted with analogous reported values (*32–34*) for methyl radical, a well-characterized carbon radical.

Abstraction of hydrogen by methyl radical correlates reasonably well with the strength of the C–H bond broken. The successive 4-kilocalorie-per-mole decreases in bond energy with change from primary to secondary to tertiary C—H bonds are reflected in an approximately 50-fold increase in rate of abstraction of a tertiary compared to a primary hydrogen. Also, the resonance energy (~ 12 kcal/mole) of the allyl radical (*35*) leads to substantial rate enhancements for abstraction of allylic hydrogens. In contrast, chlorine atom exhibits only 1/10 the difference in rate of abstraction between primary and tertiary hydrogens and exhibits essentially no rate enhancement for abstraction of allylic hydrogens. A similar lack of acceleration in chlorination of benzylic positions has been known for some time (*36*). A comparison of the thermodynamic and kinetic parameters for reaction of methyl radical and chlorine atom with a common substrate, ethane, is shown in reactions 20 and 21 (Fig. 11) (*37*). The two reactions are almost equally exothermic, and yet there is a difference of ~ 10 kcal/mole in activation energy. The reason generally accepted (*38*) is that, whereas the transition state for the methyl case is adequately represented by structure XVII (Fig. 12), in the chlorine case charge-separated structures (XVIII) serve to lower the barrier for reaction, owing to the difference in electronegativity of the atoms between which hydrogen is being transferred. Application of the Hammond principle (*39*) suggests that the transition state for hydrogen abstraction by chlorine atom will then resemble starting materials much more closely than products. The major factor controlling reactivity then becomes the availability of electrons in the C—H bond being attacked by the highly electrophilic chlorine atom, which would be expected to seek out positions of high electron density. The lack of rate enhancement by an adjacent double bond then becomes understandable since, in the ground state, the double bond withdraws electrons *inductively* and, in the transition state, little stabilization caused by allylic resonance has developed. The importance of polar factors in chlorine atom reactions is shown dramatically by the very low rate of attack on the electron-poor C—H bond

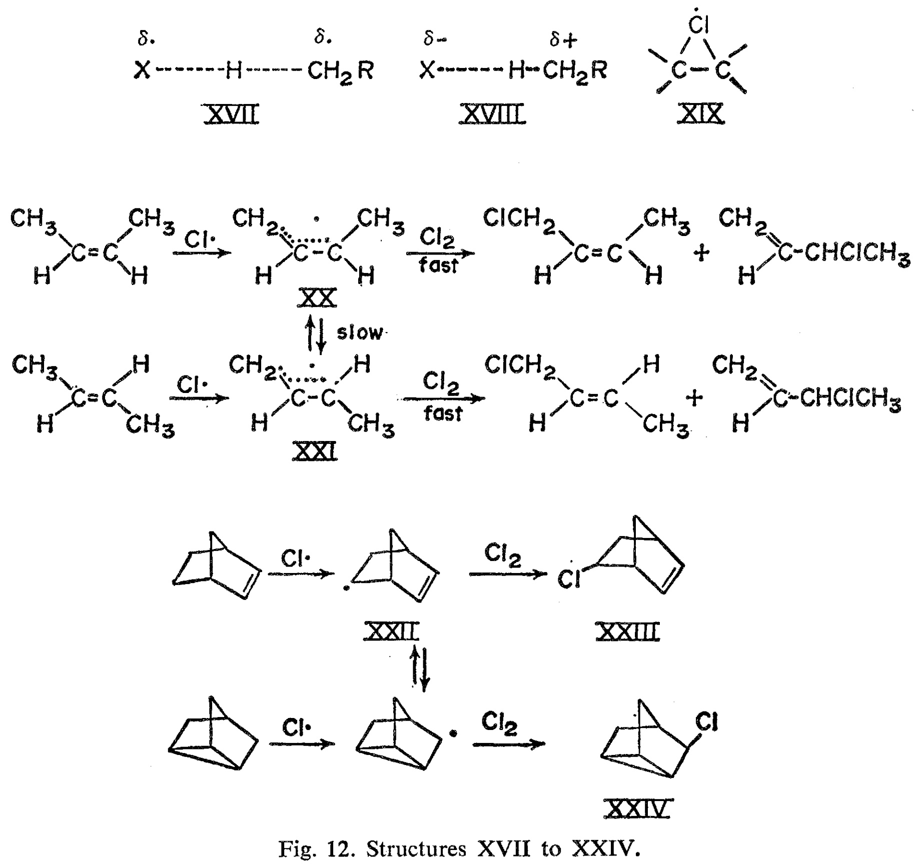

Fig. 12. Structures XVII to XXIV.

in chloroform even though a stable trichloromethyl radical is ultimately formed (as shown by the high rate of attack by methyl radical). Finally, there is a factor which has not been emphasized in most discussions of chlorine atom selectivity: if the activation energy, E_a, for a primary hydrogen is already as low as 1 kcal/mole owing to the inherent characteristics of the reaction, little more rate enhancement is possible no matter how the substrate is modified, since one is already close to the diffusion-controlled limit.

With respect to the rates of addition of chlorine atom to unsaturated linkages, not enough values are known to provide a complete picture. However, the extreme lack of selectivity is again apparent, particularly in the failure of butadiene to react significantly faster than a terminal olefin. (Note the 100-fold rate enhancement for methyl radical which reflects formation of an allylic radical.)

The dominant feature of the second step of the chain, reactions 3 or 6 (Figs. 1 and 2), is the rapidity of reaction of alkyl radicals with chlorine molecules (*40*). Addition produces a *β*-chloroalkyl radical which reacts with chlorine in a nonstereospecific fashion. Hence, if any bridged radical XIX (Fig. 12) is involved at all (*41*), it does not have sufficient lifetime to effect stereospecific addition, as the cyclic chloronium ion does. Abstraction of allylic hydrogens produces resonance-stabilized allylic radicals which react with chlorine at both termini to produce mixtures of allylic chlorides. Such allylic radicals can exist in geometrically distinct forms such as XX and XXI derived from *cis*- and *trans*-2-butene, respectively (*42*); reaction with chlorine is rapid enough to prevent any interconversion of the radicals by rotation. Abstraction of saturated hydrogens normally results in replacement of hydrogen by chlorine without skeletal rearrangement except for very special radicals likely to rearrange; an example is the 5-norbornenyl radical (XXII) (Fig. 12), which gives both 5-chloronorbornene (XXIII) and chloronortricyclene (XXIV).

Conjugated Dienes: Butadiene

Discovery of the duality of the mechanism for chlorination of olefins leaves earlier results concerning chlorination of other unsaturated materials, such as dienes and acetylenes, open for reinvestigation. Our studies of these materials have not been as extensive as our studies of olefins, but they do suggest guidelines for further research. Here I consider specifically chlorination of butadiene and 1-butyne as simple models for dienes and acetylenes.

Chlorination of butadiene is known to give two major products (Fig. 13): 3,4-dichloro-1-butene (XXV) and *trans*-1,4-dichloro-2-butene (XXVI). Their relative amounts seem to depend on the reaction conditions (*43*). The view that this reaction proceeds by electrophilic attack of chlorine, formation of an allylic carbonium ion, and collapse of this ion with chloride ion at both termini has been widely accepted (*44*). In fact, chlorination of pure butadiene in the dark under nitrogen has now been shown to be almost entirely radical in nature (*31*) and hence proceeds through the addition of chlorine atom to form an allylic radical (radical XXI with CH_3 replaced by CH_2Cl) which reacts with chlorine to produce XXV and XXVI in a ratio of 22 to 78. As discussed above, addition of chlorine atom is no faster for butadiene than for a terminal olefin, 1-butene (if one considers the statistical factor). In exact parallel to linear olefins, use of radical inhibitors allows isolation of a polar pathway which also produces XXV and XXVI, but in a ratio of about 55 to 45. Also, even without inhibitors the polar pathway begins to be evident at low diene concentration. The polar-reaction rate is significantly slower for butadiene than for 1-butene. Hence, even though an (at least potentially) allylic carbonium ion is formed, the transition state does not receive resonance stabilization from the second double bond. This conclusion, although surprising at first, is consistent with our generalization for olefins that in the polar transition state there is very little development of positive charge on the carbon.

Table 4. Relative rates of hydrogen abstraction by various radicals.

Hydrogen type	Radical Cl· (−9° to 25°C)*	 CH$_3$· (182°C)†	 CH$_3$· (65°C)‡
Primary	0.37	0.14	
Secondary	1.00§	1.00§	
Tertiary	1.45	7.6	
Primary allylic	0.65	2.2	2.2§
Secondary allylic	.76	8.3	22.9
Tertiary allylic		24.9	97.
Secondary propargylic	.27	8.0	36.5
Chloroform	.002	25–50	

* Data from *17, 29, 30,* and *31.* † Data from *32.* ‡ Data from *33.* § Relative value for each column.

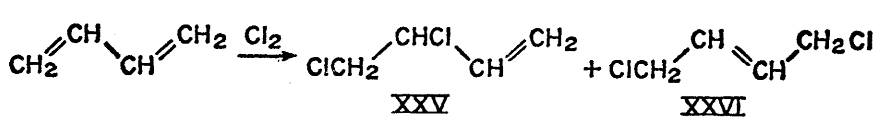

Fig. 13. Structures XXV and XXVI.

Table 3. Major products from chlorination of pure olefins by way of the radical mechanism at −9°C.

Olefin	Substitution product*	Addition product*
1-Butene	3-chloro-1-butene (2.5) 4-chloro-1-butene (4.5) 1-chloro-*cis*-2-butene } (7.5) 1-chloro-*trans*-2-butene } (7.5)	1,2-dichlorobutane (85.5)
trans-2-Butene	3-chloro-1-butene (4) 1-chloro-*trans*-2-butene (14)	*meso*-2,3-dichlorobutane } (82) *dl*-2,3-dichlorobutane } (82)
cis-2-Butene	3-chloro-1-butene (6) 1-chloro-*cis*-2-butene (10)	*meso*-2,3-dichlorobutane } (84) *dl*-2,3-dichlorobutane } (84)
Isobutylene	3-chloro-2-methylpropene (< 50)	1,2-dichloro-2-methylpropane (> 50)

* Percentage yield of each product in parentheses.

Successively methylated butadienes have not been studied in detail, but very cursory studies (*45*) suggest that, as with olefins, a crossover point is reached at which the rate of polar reaction will become more rapid than the rate of free-radical reaction. More examples are needed to complete the picture, but diene behavior seems to parallel olefin behavior rather closely.

Acetylenes: 1-Butyne

At temperature of −9°C, both pure 1-butene and pure butadiene consume chlorine essentially as fast as it is fed into the reaction vessel; this is true even for the slower oxygen-inhibited reactions. By contrast, 1-butyne, a terminal acetylene, can coexist with chlorine in the dark for measurable periods (*30*). In an oxygen atmosphere, an hour can pass with little reaction taking place; thus the rate of polar reaction is obviously much slower for an acetylene than for a correspondingly substituted olefin and, because of possible intrusion of other reactions over this long time span, the products of the polar reaction for 1-butyne have not been quantitatively determined, but addition products seem to predominate. Replacement of the oxygen inhibitor by nitrogen gives little rate enhancement, hence any radical-forming reaction must also be much slower for 1-butyne than for either 1-butene or butadiene. By comparison with these rather sluggish reactions, photochlorination is very rapid; in this way one can clearly study the radical chlorination.

Table 5. Relative rates of addition of various radicals to unsaturated molecules.

Unsaturate	Radical	
	Cl · (−9° to 25°C)*	CH_3 · (65°C)†
1-Butene	11.7	11.7‡
trans-2-Butene	11.7	3.0
Isobutylene	< 11.	15.7
1-Butyne	9.7	6.0§
Butadiene	~18.	1100.

* Data from *17, 29, 30,* and *31.* Data relative to $k_t \equiv 1.00$ for secondary hydrogen; see Table 4. † Data from *33* and *34.* ‡ Assigned for this column. § Propyne.

By comparison with radical olefin chlorination, one would expect chlorine atom to undergo three elementary reactions with 1-butyne. (i) Abstraction of the saturated hydrogen should give radical XXVII (Fig. 14); in fact, the expected product, 4-chloro-1-butyne (XXVIII), is produced in a yield of 2 to 3 percent. (ii) Abstraction of the hydrogen adjacent to the triple bond should give radical XXIX, which can be considered a resonance hybrid of propargyl and allenyl structures. A few quantitative data have recently been published concerning the product-forming behavior of propargyl radicals. When generated in the presence of *t*-butyl hypochlorite, propargyl chlorides are the major product (*46*), although in the specific case of XXIX small amounts of allenyl chloride have also been detected (*30*). Reaction of unsubstituted propargyl radical with tributyltin hydride gives methylacetylene and allene in a ratio of 5.2 to 1.0 (*47*).

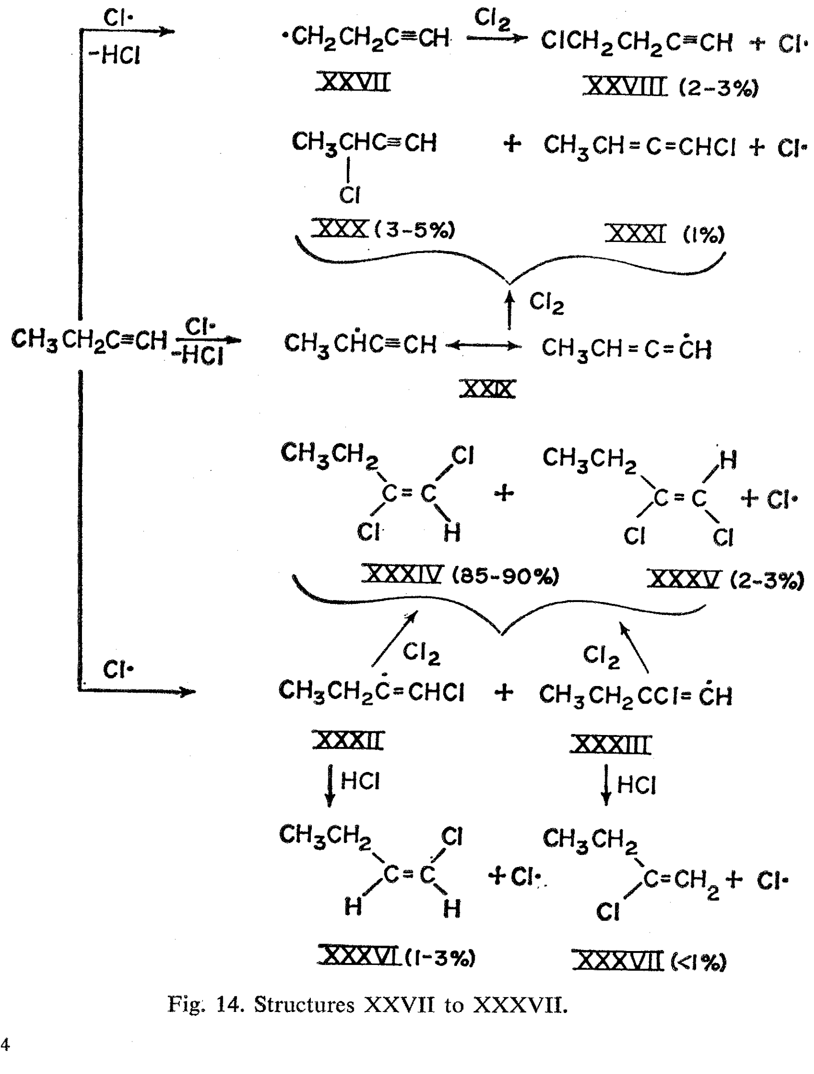

Fig. 14. Structures XXVII to XXXVII.

In the present case, radical XXIX was found to react with molecular chlorine to produce 3-chloro-1-butyne (XXX) and 1-chloro-1,2-butadiene (XXXI) in a ratio of about 4 to 1 (overall yield, 4 to 6 percent). (iii) Chlorine-atom addition to the triple bond would be expected to produce vinyl radical XXXII; the observed addition products are *trans*-dichloride XXXIV and *cis*-dichloride XXXV in yields of 85 to 90 percent and 2 to 3 percent, respectively. However, two unexpected products remain to be accounted for, *cis*-1-chloro-1-butene (XXXVI) and 2-chloro-1-butene (XXXVII), in yields of 1 to 3 percent and 0.5 to 1 percent, respectively. Several control experiments (*30*) show that the source of these vinylic chlorides is diversion of vinyl radicals from dichloride formation through reaction with the hydrogen chloride produced by the abstraction reactions. A typical secondary alkyl radical reacts very much more efficiently with chlorine than with hydrogen chloride because the former reaction has $E_a < 1$ kcal/mole (*40*), whereas the latter has $E_a \geqq 9$ kcal/mole because of the endothermicity of the reaction [$D_{\mathrm{H-Cl}} = 103$ kcal/mole and $D_{\mathrm{R_2CH-H}} = 94$ kcal/mole (*3*), where D is the dissociation energy of the bond indicated]. However, $D_{\mathrm{CH_2=H-H}} = 105 \pm 3$ kcal/mole (*48*), and thus reaction of a vinyl radical with hydrogen chloride is thermoneural and could reasonably compete with reaction with chlorine. Since not only XXXVI but also XXXVII is formed, chlorine-atom addition must occur to a significant extent at the substituted, as well as at the favored, terminal carbon atom. Although specific terminal addition is an almost universal characteristic of radical additions, the unselective nature of chlorine atom certainly qualifies it as a reasonable exception to the rule. Any explanation of the mechanism for the observed dichloride stereochemistry (*trans*/*cis* ~ 35) is now complicated by recognition that both radicals XXXII and XXXIII are formed and are thus precursors of dichloride. The stereochemistry of vinyl radicals is a subject of active research (*49*) and is too complex to summarize here.

In addition to chlorination of acetylene itself (see *50*), a number of alkylacetylenes have been chlorinated at 65° to 70°C in a vapor-liquid phase reaction in the presence of an infrared lamp and have produced mainly *trans*-dichlorides, tetrachlorides, and additional, unidentified materials (*51*). Unfortunately, it is difficult to relate the conditions of these studies directly to ours. As with dienes, more work is needed to elucidate the potential polar pathway and its relationship to the radical pathway. However, our work (*30*) with 1-butyne should serve as a starting point and mechanistic model for the radical pathway.

Summary

Our work has shown that the apparently simple chlorination of unsaturated materials in nonpolar media is actually rather complex because of the occurrence of competitive reaction pathways, one polar and one radical. Means of recognizing, predicting, and separating the pathways have been developed, and general characteristics of each with respect to relative rates and product distributions have been elucidated. A most intriguing discovery is that of the spontaneous generation of radicals by interaction of certain unsaturates and chlorine; much more work is needed for clarifying the nature of this unexpected reaction.

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