[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY]

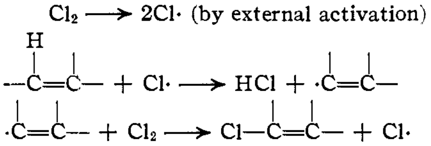
Substitution vs. Addition in the Low Temperature Non-activated Chlorination of Olefins, an Argument for an Ionic Substitution Mechanism

BY ROBERT W. TAFT, JR.

There are many facts that cannot be explained by making the generally prevailing assumption that low temperature substitution of chlorine in olefins and alkanes takes place by the same mechanism. For example by application of the method used to predict rather accurately the structures and relative amounts of substitution products for alkanes,[1] it might be expected that monosubstitution in isobutylene would give roughly $\frac{2(3.25)}{6.50 + 6(1)} \times 100$, or 52% 1-chloro-2-methyl-1-propene, and 48% 3-chloro-2-methyl-1-propene. In contrast to this prediction, actual results show 3% 1-chloro-2-methyl-1-propene and 97% 3-chloro-2-methyl-1-propene are produced.[2]

A more desirable mechanism results from a comparison of the mechanisms conceivable on the basis of our present knowledge of reaction mechanisms and existing experimental data. The mechanisms possible may be limited to

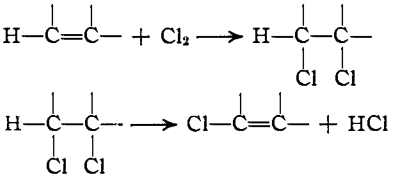
(a) Atomic displacement of hydrogen by chlorine by a chain mechanism. The mechanism for substitution in alkanes.[3]



$$Cl_2 \longrightarrow 2Cl\cdot \text{ (by external activation)}$$
$$\text{—}\overset{\overset{H}{|}}{C}=\overset{|}{C}\text{—} + Cl\cdot \longrightarrow HCl + \cdot\overset{|}{C}=\overset{|}{C}\text{—}$$
$$\cdot\overset{|}{C}=\overset{|}{C}\text{—} + Cl_2 \longrightarrow Cl\text{—}\overset{|}{C}=\overset{|}{C}\text{—} + Cl\cdot$$

This mechanism may be eliminated on the following basis. Isobutylene reacts with chlorine even at low temperatures predominantly by substitution, and this reaction takes place rapidly in the liquid or gaseous phase,[2] requires no external activation,[4] and is unaffected by the presence of oxygen.[5]

(b) Simultaneous elimination of the elements of hydrogen chloride from the chlorine addition product.

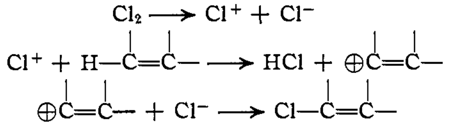


$$H\text{—}\overset{|}{C}=\overset{|}{C}\text{—} + Cl_2 \longrightarrow H\text{—}\underset{Cl}{\overset{|}{C}}\text{—}\underset{Cl}{\overset{|}{C}}\text{—}$$
$$H\text{—}\underset{Cl}{\overset{|}{C}}\text{—}\underset{Cl}{\overset{|}{C}}\text{—} \longrightarrow Cl\text{—}\overset{|}{C}=\overset{|}{C}\text{—} + HCl$$

(by either a free radical or ionic mechanism)

Mechanism (b) is unlikely because at room temperatures and pressures the equilibrium between aliphatic olefins, hydrogen chloride, and the hydrogen chloride addition products is greatly in favor of the latter as illustrated by the fact that a large quantity of tertiary butyl chloride is obtained in the chlorination of isobutylene.[4] The kinetic data of Price on the bromination of phenanthrene substantiate this conclusion.[6]

(c) Electrophilic displacement of a hydrogen of the olefin by Cl^+ ion.[7a]



$$Cl_2 \longrightarrow Cl^+ + Cl^-$$
$$Cl^+ + H\text{—}\overset{|}{C}=\overset{|}{C}\text{—} \longrightarrow HCl + \oplus\overset{|}{C}=\overset{|}{C}\text{—}$$
$$\oplus\overset{|}{C}=\overset{|}{C}\text{—} + Cl^- \longrightarrow Cl\text{—}\overset{|}{C}=\overset{|}{C}\text{—}$$

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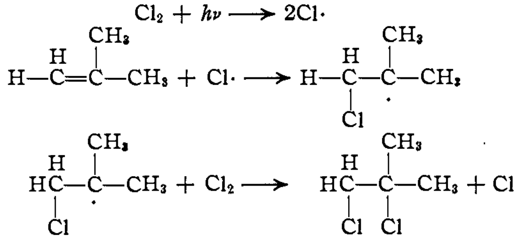
(1) Hass, McBee and Weber, *Ind. Eng. Chem.*, **28**, 333 (1936). In making this calculation it is assumed that the $H_2C=$ hydrogens behave as secondary hydrogen atoms.

(2) Groll, Hearne, Rust and Vaughan, *ibid.*, **31**, 1239 (1939). These investigations have shown that a liquid phase must be present in order to get a reaction at low temperatures, not only in the case of isobutylene, but with all other olefins investigated.

(3) Brown, Kharasch and Chao, THIS JOURNAL, **62**, 3435 (1940); also see reference 1 and Taft and Stratton, *Ind. Eng. Chem.*, **40**, 1485–1491 (1948).

(4) Unpublished experiments of the author from the Bailey Chemical Laboratories, University of Kansas. For example, a chlorination (of the type used by Taft and Stratton[3] to chlorinate isobutane) carried out in complete darkness at 30° with the passage of 10 moles of isobutylene and 11 moles of chlorine gave 1.8 moles of *t*-butyl chloride, 3.1 moles of β-methylallyl chloride, approximately 0.5 mole of 1,2-dichloro-2-methylpropane, and 3–4 moles of higher boiling chlorides. Lowering the temperature to 18° decreased the yield of β-methallyl chloride 20–30% and increased by about the same amount the yield of 1,2-dichloro-2-methylpropane.

(5) Burgin, Engs, Groll and Hearne, *Ind. Eng. Chem.*, **31**, 1413–1419 (1939). These authors established that in addition to this "unactivated" reaction, there is a reaction which is light catalyzed and inhibited by the presence of oxygen. 1,2-Dichloro-2-methylpropane is the principal product of this "activated" reaction. Although these authors did not propose a mechanism, their experimental evidence indicates that the "activated" reaction is probably a chain type free radical addition mechanism



$$Cl_2 + h\nu \longrightarrow 2Cl\cdot$$
$$H\text{—}\overset{H}{C}=\overset{CH_3}{\overset{|}{C}}\text{—}CH_3 + Cl\cdot \longrightarrow H\text{—}\underset{Cl}{\overset{H}{\underset{|}{C}}}\text{—}\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}\text{—}CH_3$$
$$H\underset{Cl}{\overset{H}{\underset{|}{C}}}\text{—}\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}\text{—}CH_3 + Cl_2 \longrightarrow H\underset{Cl}{\overset{H}{\underset{|}{C}}}\text{—}\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}\text{—}CH_3 + Cl\cdot$$

(6) Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 35.

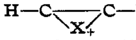
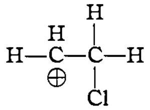
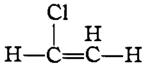
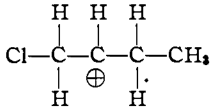
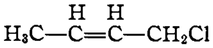
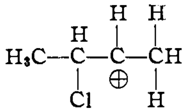
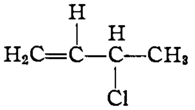
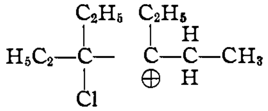
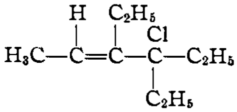
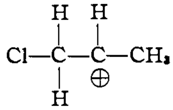
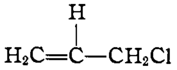
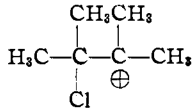
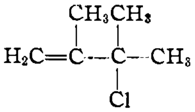
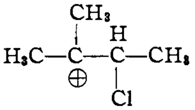
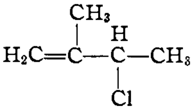
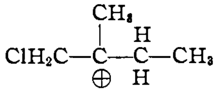
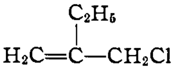
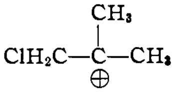
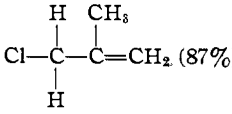
(7) (a) The Cl^+ ion need not be completely free. It may be combined with a negative Cl^- in a polarized chlorine molecule, Cl^+Cl^-, or it may be combined in some way with a catalyst molecule. The actual state of combination of this ion is not essential to the argument to be presented, and therefore will be represented as a free Cl^+ ion. (b) The formation of a relatively stable three membered ring of the type  as proposed by Roberts and Kimball (THIS JOURNAL, **59**, 947 (1937)) or an association complex of the type described by Price (*ibid.*, p. 39) in the case of bromination and iodination but not chlorination may be responsible for the fact that the former halogens have a much greater tendency to add than substitute. Interatomic distances, Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944) at least indicate that a less stable ring structure would result in the case of Cl than Br or I since the covalent radius of Br is only 0.40 Å. less than the C=C interatomic distance, that for I only 0.20 Å. less, whereas that for Cl is 0.55 Å. less.

TABLE I

EXISTING DATA ON LOW TEMPERATURE NON-ACTIVATED CHLORINATION OF UNSUBSTITUTED ALIPHATIC OLEFINS

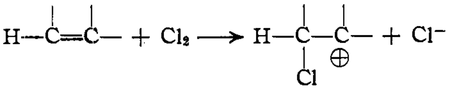
Substitution *vs.* Addition (all data for chlorination in presence of a liquid phase at a temperature no higher than 70°).

	Olefin	Proposed intermed. carbonium ions	No. of α-H's	% Substitution and subst. product.		% Addition	Ref.
1	Ethylene	 $H{-}\underset{\oplus}{\overset{H}{C}}{-}\underset{Cl}{\overset{H}{C}}{-}H$	2	33	 $H{-}\overset{Cl}{C}{=}\overset{H}{C}{-}H$	67	2
2	Butene-1	 $Cl{-}\underset{H}{\overset{H}{C}}{-}\underset{\oplus}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}CH_3$	4	43	 $H_3C{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_2Cl$	57	2
3	Butene-2	 $H_3C{-}\underset{Cl}{\overset{H}{C}}{-}\underset{\oplus}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}H$	4	23	 $H_2C{=}\overset{H}{C}{-}\underset{Cl}{\overset{H}{C}}{-}CH_3$	77	2
4	Tetraethylethylene	 $H_5C_2{-}\underset{Cl}{\overset{C_2H_5}{C}}{-}\quad\underset{\oplus}{\overset{C_2H_5}{C}}{-}\underset{H}{\overset{H}{C}}{-}CH_3$	4	60	 $H_3C{-}\overset{H}{C}{=}\overset{C_2H_5}{C}{-}\underset{C_2H_5}{\overset{Cl}{C}}{-}C_2H_5$	40	16
5	Propylene	 $Cl{-}\underset{H}{\overset{H}{C}}{-}\underset{\oplus}{\overset{H}{C}}{-}CH_3$	5	37	 $H_2C{=}\overset{H}{C}{-}CH_2Cl$	63	2
6	Tetramethylethylene	 $H_3C{-}\underset{Cl}{\overset{CH_3}{C}}{-}\underset{\oplus}{\overset{CH_3}{C}}{-}CH_3$	6	>90	 $H_2C{=}\overset{CH_3}{C}{-}\underset{Cl}{\overset{CH_3}{C}}{-}CH_3$		16
7	Trimethylethylene	 $H_3C{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\underset{Cl}{\overset{H}{C}}{-}CH_3$	7	70–80	 $H_2C{=}\overset{CH_3}{C}{-}\underset{Cl}{\overset{H}{C}}{-}CH_3$	10–15	16
8	2-Methylbutene-1	 $ClH_2C{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\underset{H}{\overset{H}{C}}{-}CH_3$	7	70–75	 $H_2C{=}\overset{C_2H_5}{C}{-}CH_2Cl$	10	16
9	Isobutylene	 $ClH_2C{-}\underset{\oplus}{\overset{CH_3}{C}}{-}CH_3$	8	93	 $Cl{-}\underset{H}{\overset{H}{C}}{-}\overset{CH_3}{C}{=}CH_2$ (87%)	7	2

The probability of mechanism (c) being the correct one is rendered very small by the theoretical consideration that a positive, electron seeking Cl^+ ion in reacting would attack the most electron-rich position in the olefin, which is at one of the carbons of the double bond, not at one of the adjacent hydrogen atoms; the mechanism for the addition of halogens to olefins supports this conclusion.

(d) An ionic type mechanism for which

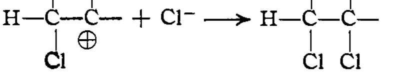
(1) the rate determining step is addition of a positive chlorine ion[7b] to form a carbonium ion and a negative chloride ion



$$H{-}\overset{|}{C}{=}\overset{|}{C}{-} + Cl_2 \longrightarrow H{-}\underset{Cl}{\overset{|}{C}}{-}\underset{\oplus}{\overset{|}{C}}{-} + Cl^-$$

(2) the intermediate carbonium ion follows two distinct reaction courses, rapidly and simultaneously, resulting in

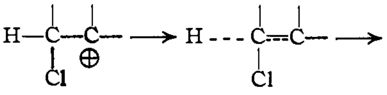
(a) Addition



$$H{-}\underset{Cl}{\overset{|}{C}}{-}\underset{\oplus}{\overset{|}{C}}{-} + Cl^- \longrightarrow H{-}\underset{Cl}{\overset{|}{C}}{-}\underset{Cl}{\overset{|}{C}}{-}$$

; to be designated as A.

and (b) Substitution



$$H{-}\underset{Cl}{\overset{|}{C}}{-}\underset{\oplus}{\overset{|}{C}}{-} \longrightarrow H\cdots\underset{Cl}{\overset{|}{C}}{=}\overset{|}{C}{-} \longrightarrow Cl\overset{|}{C}{=}\overset{|}{C}{-} + H^+$$

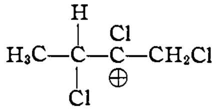
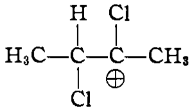
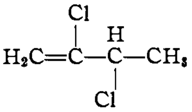
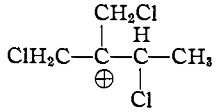
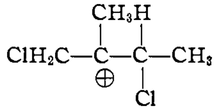
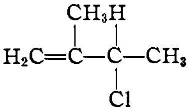
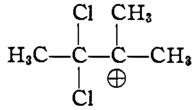
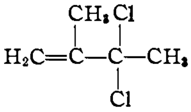
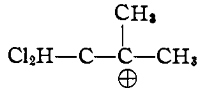
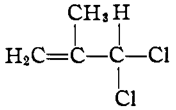
; to be designated as S.

By a process of elimination, (d) is the only likely mechanism. The ratio of addition products to those of substitution would accordingly be governed by the factors affecting the ratio of rates A/S.

A Corollary to Mechanism (d).—Since step 2(b) represents a very rapid disproportionation of a carbonium ion (a process which must be independent of the concentration of Cl^-), it is a corollary of mechanism (d) that *the double bond* resulting from the elimination of the proton *will be*

TABLE II

EXISTING DATA SIMILAR TO TABLE I FOR CHLORINE SUBSTITUTED ALIPHATIC OLEFINS

	Olefin	Proposed intermed. carbonium ions	No. of α-H's	% Substitution and subst. product.		% Addition	Ref.
1	1,2-Dichlorobutene-2	 $H_3C-CHCl-C^{\oplus}Cl-CH_2Cl$	3	0		100	16
2	2-Chlorobutene-2	 $H_3C-CHCl-C^{\oplus}Cl-CH_3$	4	55	 $H_2C=CCl-CHCl-CH_3$	45	16
3	3-Chloro-2-chloromethylbutene-1	 $ClH_2C-C^{\oplus}(CH_2Cl)-CHCl-CH_3$	5	<6		>90	16
4	3-Chloro-2-methylbutene-1	 $ClH_2C-C^{\oplus}(CH_3)-CHCl-CH_3$	6	65	 $H_2C=C(CH_3)-CHCl-CH_3$	30	16
5	2-Chloro-3-methylbutene-2	 $H_3C-CCl_2-C^{\oplus}(CH_3)-CH_3$	6	80	 $H_2C=C(CH_3)-CCl_2-CH_3$	10	16
6	β,β-Dimethylvinyl chloride	 $Cl_2H-C-C^{\oplus}(CH_3)-CH_3$	7	68	 $H_2C=C(CH_3)-CHCl-Cl$	32	16

formed preferentially between the carbon bearing the positive charge and *the most electron rich adjacent carbon atom*, the proton being emitted from the latter carbon atom. In other words the product formed by substitution is determined by the relative electron densities of the carbons adjacent to the positively charged carbon of the carbonium ion, and not the relative acidities of the various hydrogens. Thus the proton eliminated according to this corollary is not necessarily, and in most cases is not, the most acidic one.

Supporting Evidence for the Mechanism (d): (1) Relationship of Substitution to Addition.—Steps (1) and (2a) constitute the generally accepted mechanism for unactivated addition of halogens to olefins.[8] The reference gives the source of surveys covering experimental evidence supporting the addition mechanism. The extension of the addition mechanism to cover the simultaneous occurrence of substitution is expected from the kinetic results of Hughes and Ingold[9] on the hydrolysis of secondary and tertiary alkyl halides. Steps A and S correspond to the second steps in the S_N1 and E 1 mechanisms (respectively) of Hughes and Ingold.[10]

(2) Application to Environmental and Constitutional Influences.—A review of existing data on the low temperature chlorination of various olefins shows that (1) in several cases substitution exceeds addition; (2) for all olefins for which quantitative data could be found, the ratio of addition to substitution is a rough function of the number of hydrogen atoms[11] on the carbon atoms adjacent to the positively charged carbon of the proposed intermediate carbonium ion; and (3) in the case of isobutylene, the ratio of addition to substitution is reduced by raising the temperature.[4] Tables I, II, and III summarize the data for points (1) and (2).

In Table I, Markownikoff's rule has been used to give the manner of addition of the Cl^+ ion to the olefin. By assuming that the orientating influences of CH_3 and CH_2Cl groups are in the same direction,[12] the structures of the intermediate carbonium ions of the chloro-olefins 1, 2, 3 and 4 of

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[8] See for example, Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 241; Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 147; Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 55, 83, 222, 416.

[9] See for example, Hughes, *J. Chem. Soc.*, 978 (1946); Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941); Ingold, *ibid.*, **34**, 227 (1938); Hughes, *ibid.*, **37**, 604 (1941).

[10] The only difference is that in A and S the carbonium ions are chlorine substituted, whereas Hughes and Ingold have studied only the unsubstituted carbonium ions. Since the chlorine is not directly involved there seemingly should be little relative difference in the reaction processes by which these two types of carbonium ions tend to stabilize themselves. The author intends to make no claim to the originality of the proposed step resulting in substitution (2b).

[11] These hydrogen atoms will be referred to as α-hydrogens.

[12] For evidence supporting this assumption, see Mayo and Walling, *Chem. Rev.*, **27**, 355–356 (1940).

Table II were arrived at similarly. This procedure should not be open to serious objection since the use of Markownikoff's rule in all of these cases is in accord with modern theories of "normal" addition of both halogens and acids to C—C double bonds.[13,14]

TABLE III

SUMMARY OF DATA OF TABLES I AND II SHOWING DEPENDENCE OF SUBSTITUTION *vs.* ADDITION UPON THE NUMBER OF HYDROGEN ATOMS ON THE CARBON ATOMS ADJACENT TO THAT POSITIVELY CHARGED CARBON OF THE PROPOSED INTERMEDIATE CARBONIUM ION

No. of α-H's[17]	% Substitution	% Addition
2-3	0-35	60-100
4-5	10-60	40-90
6-7	70-85	10-30
8	93	7

If the analogy between the A and S and the S_N1 and E1 mechanisms is appropriate, the factors which Hughes and Ingold have found to affect the S_N1/E1 ratios should apply in a like manner to the A/S ratios. The available data,[18] existent only for solvents of the strongly ionizing type (ethyl alcohol and water) under neutral or acid conditions, show (1) the S_N1/E1 ratios are in the order: trimethylcarbonium ion $\ll$ dimethylcarbonium ion $\ll$ methylcarbonium ion, (2) the S_N1/E1 ratios decrease with increasing temperature,[19] and (3) these ratios are independent of the concentration or basicity of the reagent. The data indicate, further, that under these conditions the S_N1/E1 ratios are always greater than unity even for tertiary butyl carbonium ion (which gives 25% isobutylene)[20] but, however, as Hughes and Ingold point out,[21] as the reaction media become more and more non-ionizing these ratios should become smaller and smaller.

We conclude by applying these results to the A and S mechanisms that (1) since the reaction media in which the low temperature chlorination of olefins takes place (liquid olefin or liquid chlorination product[2]) are very non-ionizing, the ratio of addition to substitution might be sufficiently small in certain cases so that substitution would exceed addition; (2) the structural nature of the intermediate carbonium ion would affect the ratio of addition to substitution in the following relative orders trimethyl carbonium $\ll$ dimethyl carbonium $\ll$ methyl carbonium; (3) the ratio of addition to substitution would decrease with increasing temperature; and (4) the concentration of chlorine would not affect the ratio of addition to substitution. All but point 4, for which there is neither confirmable or confutable evidence, are verified by the data cited.

Interestingly, Tischchenko[16] has reported that the presence of solid sodium bicarbonate reduces substitution and increases addition in the chlorination of olefins at low temperatures. While this reaction is most certainly a more complex three-phase surface phenomenon, it is evident that the presence of sodium bicarbonate (which increases the ionic character of the surface at which the chlorination takes place) produces results which are expected on the basis of the proposed mechanism.

The fact that the manner and degree to which environmental and constitutional influences affect substitution *vs.* addition is consequential to the mechanism (d) is strong argument in its favor.

The apparent dependence of the ratio of addition *vs.* substitution upon the number of α-hydrogen atoms is probably the result of hyperconjugative type resonance (Baker and Nathan effect).[22] For example, the proposed intermediate in the chlorination of ethylene has but two α-hydrogen atoms so that only three resonance structures[23] for this ion can be written, which are as follows

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[13] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 232, 241.

[14] In the case of olefins 5 and 6 of Table II, conflicts exist between resonance and inductive effects of CH_3 and Cl groups which make predictions impossible at present.[3] Therefore, the structure given for the carbonium ion of olefin 6, was based on Burgin, Hearne and Rust's[15] obtaining 1,1-dichloro-2-methyl-2-propanol by the chlorohydrination of β,β-dimethylvinyl chloride, bearing in mind that hypochlorous acid behaves effectively as Cl^+OH^- in adding to C—C double bonds. The carbonium ion structure given for olefin 5 must be regarded as questionable.

[15] Burgin, Hearne and Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

[16] Tischchenko, *J. Gen. Chem., U. S. S. R.*, **8**, 1232–1245 (1938); *C. A.*, **33**, 4190 (1939).

[17] Variations within these groups are probably due to differences in experimental conditions and to inductive affects which were not considered here.

[18] Hughes, Ingold, Masterman and McNulty, *J. Chem. Soc.*, 899 (1940).

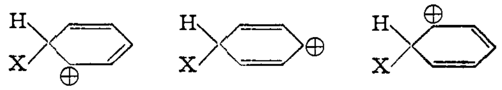
[19] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 669 (1941).

[20] Hughes, *J. Chem. Soc.*, 979 (1946).

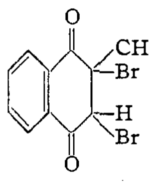
[21] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 665 (1941).

[22] Baker and Nathan, *J. Chem. Soc.*, 1844 (1935); Baker, *ibid.*, 1150 (1939).

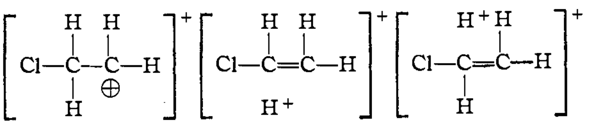
[23] If the argument presented here can be accepted as the explanation for the experimental results summarized in Table III, it points to an important role played by resonance in carbonium ion intermediates in determining their ultimate reaction course. For this concept is not restricted to hyperconjugative resonance, as it is apparently applicable to aromatic compounds in which the conventional type resonance occurs in the intermediates formed by the ionic attack of an electrophilic reagent. For example, the fact that substitution always occurs to the exclusion of addition in the case of benzene may be explained, according to this concept, on the importance of the contributions made by the resonance structures,



in the intermediate carbonium ion. In the case of the bromination of 2-methyl-1,4-naphthoquinone resonance of this type cannot occur in the intermediate carbonium ion and as expected the addition product, results.[24]



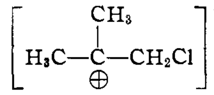
[24] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1944, p. 739.



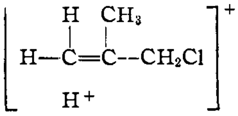
I IIa IIb

The proposed intermediate in the chlorination of isobutylene, however, has eight α-hydrogens, making it possible to write the nine resonance structures given below.

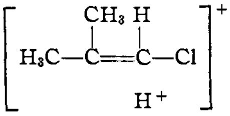
The greater number of possible resonance structures in the latter case than the former means that the positive charge of the carbonium ion will be more effectively transferred from the positively charged carbon atom to the surrounding α-hydrogen atoms in the latter case than in the former, because of the greater contribution to the normal state of these two systems made by structures IV and V than by structures II. This greater distribution of the positive charge away from the carbon atom (at which addition occurs) would according to Hughes and Ingold[21] lower the ratio $S_N1/E1$ and by our analogy lower the ratio of rates A/S. This relationship, then, is in accord with the fact that at low temperatures isobutylene chlorinates largely by substitution, while ethylene chlorinates largely by addition.[23]



III



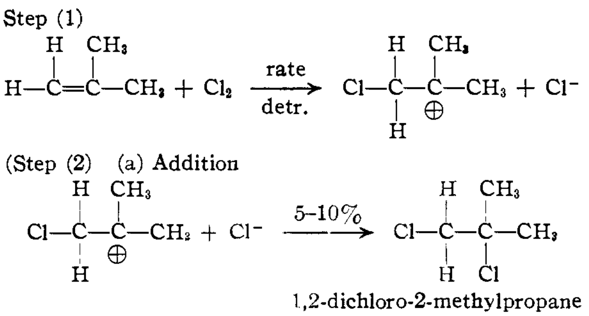
IV 6 equivalent structures of this type are possible

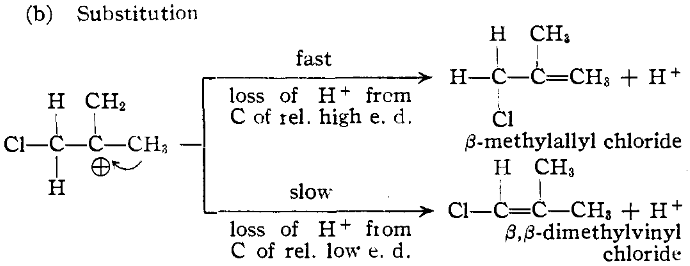


V 2 equivalent structures of this type are possible

(3) **Application to Structure of Substitution Product. Use of Mechanism (d) to Predict Olefin Chlorination Results.**—As noted in the introductory remarks, modern theories of organic reactions have failed to explain why allylic chlorides always predominate overwhelmingly over vinylic chlorides (except, of course, for ethylene). The mechanism (d) together with its corollary, however, provide a theoretical basis for this behavior.

For example, consider the chlorination of isobutylene. On the basis of mechanism (d) we could expect (1) 85–90% substitution, and 10–15% addition because of the large number (8) of α-hydrogen atoms,[25] and (2) a great predominance of β-methylallyl chloride over β,β-dimethylvinyl chloride in view of the much greater electron density of the carbon of a methyl group than that of a chloromethyl group. This scheme may be represented by equations in the following manner



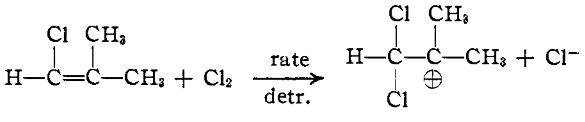


The expectations are in good agreement with the report of Burgin, Engs, Groll and Hearne[5] that the low temperature chlorination of isobutylene gives the following products: β-methylallyl chloride—87%; β,β-dimethylvinyl chloride—3%; 1,2-dichloro-2-methylpropane—6%; and others—4%.

The formation of β-methylallyl chloride cannot be explained by assuming that the most acid hydrogen (that of the CH_2Cl group) is eliminated giving β,β-dimethylvinyl chloride, which then rearranges to β-methylallyl chloride, since at low temperatures β-methylallyl chloride instead rearranges to β,β-dimethylvinyl chloride.[15]

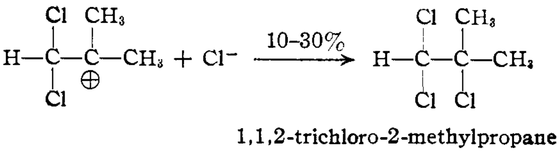
Particularly striking is the result of application of mechanism (d) to the chlorination of β,β-di-methylvinyl chloride. Representing this reaction according to the above scheme, we have:

Step (1) Formation of a carbonium ion by addition of Cl^+ ion.[11a]



The intermediate carbonium ion has 7 α-H atoms, therefore the expected relative amounts of addition and substitution are as indicated.[25]

Step (2) (a) Addition



1,1,2-trichloro-2-methylpropane

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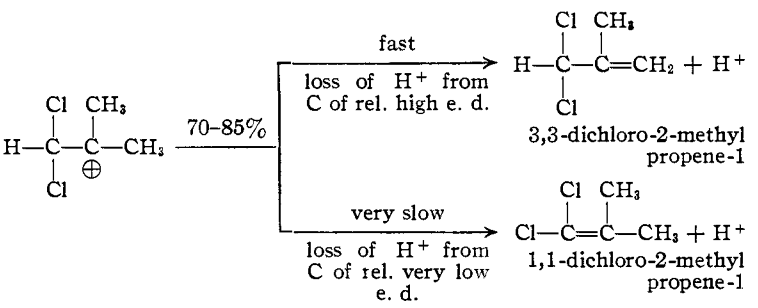
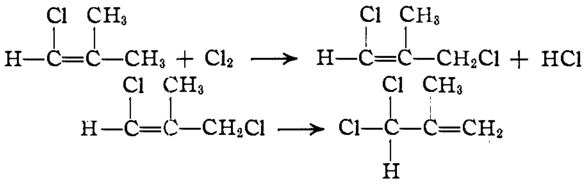
(25) See Table III.

(b) Substitution



These predictions are in good agreement with the 68% yield of 3,3-dichloro-2-methylpropene-1 and 32% yield of 1,1,2-trichloro-2-methylpropane reported by Tischchenko[16] in the chlorination of β,β-dimethylvinyl chloride at 0°.

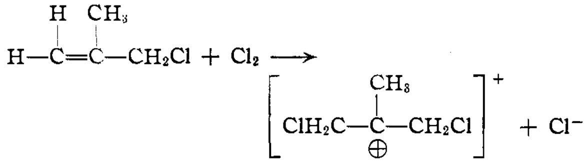
Again, this reaction cannot be explained in terms of the following course involving a rearrangement



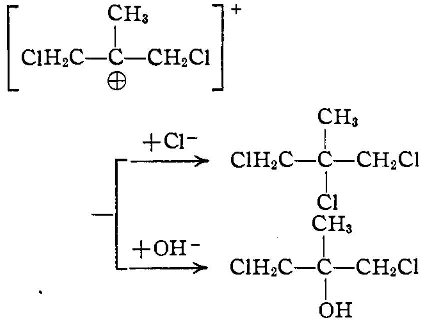
For Whaley[26] has reported that under these chlorination conditions 3,3-dichloro-2-methylpropene-1 instead rearranges to 1,3-dichloro-2-methylpropene-1.

(4) **Application to Chlorohydrination of Olefinic Chlorides.**—Burgin, Hearne and Rust[15] have used the concepts involved in mechanism (d) to explain successfully the products of the chlorohydrination of β,β-dimethylvinyl chloride and β-methylallyl chloride. For example

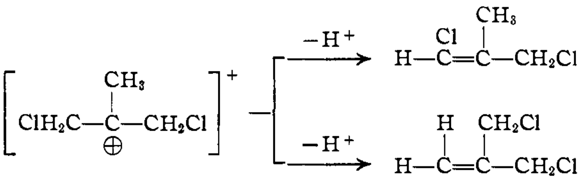
Step (1)



Step (2) (a) Addition



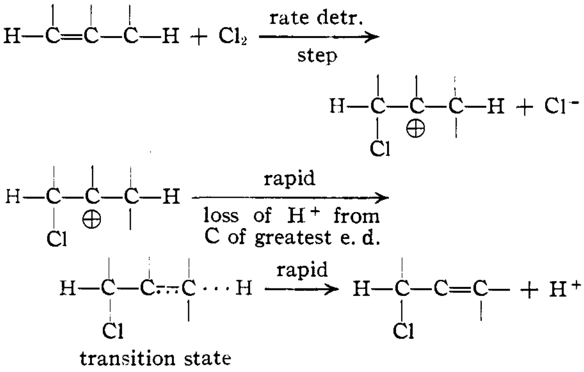
(b) Substitution



Acknowledgments.—I wish to express my appreciation to Drs. R. Q. Brewster, C. A. VanderWerf and M. S. Newman for their suggestions. I am especially indebted to Dr. A. L. Henne for his helpful criticisms and suggestions.

Summary

The following ionic mechanism for the substitution in the low temperature non-activated chlorination of olefins has been shown to be consistent with existing experimental data



$H^+ + Cl^- \longrightarrow HCl$

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[26] Private communication from Whaley, Research Laboratories, Halogen Chemicals.