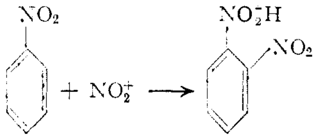
point charge. The actual charge distribution is doubtless intermediate between these extremes. We can consider that there is actually a fairly strong dipole with a component directed along the axis of the new bond. In the ortho transition state this dipole will interact in an attractive manner with the moment of one of the nitrogen–oxygen bonds of the adjacent nitro group.[27] The interaction cannot be other than repulsive for the meta and para transition states with the effect being the strongest with the latter. An interaction such as this would be sensitive to the extent to which the nitronium ion retains its shell of oriented solvent molecules in the transition state. Dispersal of the charge to the solvent would be expected to decrease the preferential stabilization of the ortho transition state. It is observed that the less polar solvents, *i.e.*, those containing the larger amounts of water or the nitric acid solutions, show the largest ortho/para ratios. We have shown earlier[12a] that the decrease in nitration rates with decreasing water content of sulfuric acid solutions can be most easily explained by assuming that the activity coefficient of the nitronium ion decreases appreciably. The assumption that the specific influence of solvent on the nitronium ion will persist in the transition state is reasonable.

An alternative to the above explanation of the ortho effect is one in which it is assumed that the ortho reaction proceeds by a new mechanism in which the proton is actually displaced in one concerted process and appears first on the oxygen of a neighboring group. The similarity in the rates



(2)

of nitration at all positions in our systems, suggests that if it is possible to carry out a concerted nitration at the ortho positions, there must be a very fine line of demarcation between the free energies of activation of the two step and concerted mechanisms. If this were the case, it might well be possible to induce the meta and para reactions to go by a concerted mechanism by the addition of gross amounts of bisulfate ion. This was done in the nitration of the chloro compound (run 8). A minor increase in the ortho/para ratio was observed indicating that no new mechanism for para nitration was brought into play. The addition of the same amount of potassium perchlorate gave a slightly larger increase in the ratio indicating that the influence of the anions does not depend upon their basicity. The exact significance of the generalized electrolyte effect is not obvious. It might have been anticipated that an increase in the ionic strength would decrease the ortho/para ratio. However, massive amounts of electrolytes may increase the activity of the nitronium ion, by decreasing its solvation energy.

The variation in the isomer ratios with temperature is interesting and indicates the intrusion of a second mechanism at high temperatures in the nitration of dichloronitrobenzene in fuming sulfuric acid. One would anticipate that meta substitution would involve the smallest activation energy since the classical explanation for meta orientation by the nitro function implies that the meta reaction derives its advantage from the relatively low potential energy of the transition state. The decrease, with increasing temperature, in the yields of meta isomers in 96% acid is consonant with this concept. However, in fuming acid the yield of meta product is virtually unchanged by an increase of the reaction temperature from 100 to 140° and the ortho–meta ratio is actually decreased. This can be accounted for if one assumes that at the higher temperature an appreciable amount of material is produced by the nitration of the conjugate acid of the mono nitro compound. The nitration of this species should involve a higher activation energy than the reaction of the neutral molecule and it would be expected that the presence of the positive charge on the first nitro group would increase the preference for the meta position and completely destroy the ortho direction through the interaction described above. The lower reactivity of the bromo compound as compared to the chloro analog may be attributed to the steric requirements of the bromine atoms.

As a general conclusion we can tentatively assume that all planar, non-linear substituents, in which the atom is at the negative end of a dipole, will exert an ortho orienting influence. The magnitude of this effect will be decreased by: (1) an increase in the dielectric constant of the medium, (2) a decrease in the ionic character of the new bond in the transition state or (3) an increase in the steric requirements of either the entering or the orienting group. The ortho influence should be virtually destroyed by addition of a proton to the orienting group. Since the dipolar attraction in attack at the ortho position cannot become positive for a linear group, the orientation influence of the cyano function is of great interest. As little reliable information can be gleaned from the literature we have undertaken a study of the dihalocyanobenzenes which are structurally analogous to the nitro compounds used in this investigation.

AMES, IOWA

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[27] An equivalent statement is that the positively charged entering group is closer to one of the oxygens of the nitro group than it is to the positively charged nitrogen of the latter function.

[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY]

The High Temperature Chlorination of Various Mono- and Dichloropropenes

BY G. W. HEARNE, T. W. EVANS, H. L. YALE AND M. C. HOFF

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The products from the high temperature substitutive chlorination of mono- and dichloropropenes have been characterized. The results are explained by a mechanism involving allylic radicals capable of reaction at two sites.

Introduction

The chlorination of propylene at elevated temperatures has been shown in an earlier publication[1] to lead predominantly to allyl chloride with a relatively small amount of dichloropropenes, dichloropropane and higher boiling chlorides. In recent years there has been an increasing interest in the polychlorides, known commercially as "D–D," because of their effectiveness as a nematocide. "The present work was undertaken to characterize some of the products which might be present in this mixture. The results were useful also in providing a better understanding of the nature of the high temperature substitutive chlorination of olefins.

Apparatus.—The reactor consisted of a quartz tube 2.0 cm. × 50 cm. surrounded by an electrically-heated steel block. The temperature throughout the reactor was measured by a thermocouple inserted in a quartz tube liner. The material to be chlorinated was fed from a 500-cc. graduate through a rotameter into a Pyrex evaporator heated with decalin. It was mixed with gaseous chlorine supplied from a weighed cylinder with the flow rate measured by an orifice meter. The reactants were mixed in a jet of quartz tubing 0.2 cm. in diameter attached directly to the reactor and arranged so that the chlorine entered as a side stream at right angles to the flow of the organic chloride. The re-

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(1) H. P. A. Groll and G. W. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).

TABLE I

CHLORINATION OF MONO- AND DICHLOROPROPENES

Quartz reactor 2.0 cm. × 50 cm.

Material chlorinated	Flow, mole/min. Organic chloride	Flow, mole/min. Chlorine	Temperatures, °C. Furnace block	Temperatures, °C. Tube maximum	Chlorine reacted, %	HCl, mole % of Cl_2	Unsatd. dichlorides yield based on Cl_2, %
1-Chloro-1-propene (mixed isomers)	0.240	0.061	570	560	97.5	102.0	79
2-Chloropropene	.299	.062	524	512	97.7	94.2	69
Allyl chloride	.304	.040	522	502	96.0	101.1	80
							Unsat. trichlorides
1,1-Dichloro-1-propene	0.10	0.05	560	550	100.0	100.0	51
2,3-Dichloro-1-propene	.24	.06	516	507	90.7	102.5	76
cis-1,3-Dichloropropene	.18	.06	523	517	95.0	108.5	73
trans-1,3-Dichloropropene	.18	.06	525	525	98.8	127.5	80
1,3-Dichloropropene (mixed isomers)	.25	.08	510	520	91.8	96.0	80

action products were passed through a tap water-cooled condenser into a 500-cc. flask maintained at room temperature where the bulk of the chlorinated product was collected. The effluent HCl containing some organic chlorides was passed through a water-scrubbing tower and the balance of the organic chlorides were collected as a water-insoluble layer at the bottom of the tower or in an alcohol–CO_2 cooled trap attached to the vent from the scrubbing tower. The percentage of chlorine consumed in the reactor could be determined by passing the entire chlorination product into a potassium iodide solution instead of the normal recovery system.

Materials Used for Chlorination and for Product Analysis.—2-Chloropropene (b.p. 22.0°) was obtained as a by-product from the high temperature chlorination of propylene. 1-Chloro-1-propene was prepared by treating 1,2-dichloropropane with 15% aqueous sodium hydroxide at 125° under pressure. This chloropropene was the major product from the dehydrochlorination and consisted of a mixture of 45% of the *cis* isomer (b.p. 32°) and 55% of the *trans* (b.p. 37°). 1,1-Dichloro-1-propene (b.p. 77°) was obtained from the Westvaco Chemical Division, Food Machinery and Chemical Corporation. 2,3-Dichloro-1-propene was obtained by alkaline dehydrochlorination of 1,2,3-trichloropropane. The isomers of 1,3-dichloropropene were isolated by careful fractionation of the dichlorides produced by the high temperature chlorination of propylene. The low boiling isomer is taken as the *cis* isomer as shown by Hatch and Perry.[2] 3,3-Dichloro-1-propene was prepared by reaction of acrolein with phosphorus pentachloride.

The low and high boiling isomers of 1,2,3-trichloropropene were prepared by dehydrochlorinating 1,2,2,3-tetrachloropropane with an equimolar quantity of alcoholic alkali. This tetrachloride, b.p. 165.3–166.0°, n^{20}_D 1.4925, d^{20}_4 1.4970 was prepared by passing chlorine into liquid 2,3-dichloro-1-propene at room temperature. The low boiling trichloride has been assigned the *trans* configuration as shown by Hatch, *et al.*[3] These unsaturated trichloride isomers were shown to be identical with those prepared by high temperature chlorination of 2,3-dichloro-1-propene except that two absorption bands (8.28 and 12.75μ) were found in the low boiling isomer from the high temperature chlorination which were not present in the product from dehydrochlorination of the 1,2,2,3-tetrachloropropane. These were believed to be caused by the presence of a minor amount of an isomeric trichloride.

The reaction products were identified by distillation, chlorine analysis and in most cases by comparison of their infrared spectra with those of authentic materials prepared from other sources. Chlorination conditions are outlined in Table I, the nature of the chlorides produced in Table II and their physical properties in Table III.

TABLE II

COMPOSITION OF THE UNSATURATED DICHLORIDES FROM MONOCHLOROPROPENE CHLORINATION

Material chlorinated	Products 3,3-Dichloro-1-propene	Products 2,3-Dichloro-1-propene	Products *cis*-1,3-Dichloropropene	Products *trans*-1,3-Dichloropropene
1-Chloro-1-propene (45% *cis* and 55% *trans*)	9	1	44	46
2-Chloropropene	None	100	None	None
Allyl chloride	9	3	43	45

COMPOSITION OF THE TRICHLORIDE FRACTION FROM DICHLOROPROPENE CHLORINATION

	1,3,3-Trichloro-1-propene low boiling isomer	1,3,3-Trichloro-1-propene high boiling isomer	*trans*-1,2,3-Trichloropropene	*cis*-1,2,3-Trichloropropene	1,1,3-Trichloro-1-propene
1,1-Dichloro-1-propene					100
2,3-Dichloro-1-propene			50[a]	50	
cis-1,3-Dichloropropene	55	45			
trans-1,3-Dichloropropene	35	65			
1,3-Dichloropropene (58% *cis* and 42% *trans* isomers)	50	50			

[a] A small amount of an impurity believed to be an isomeric trichloride was indicated to be present in this fraction.

TABLE III

PHYSICAL PROPERTIES OF DI- AND TRICHLOROPROPENES

Chloride	B.p., °C.	d^{20}_4	n^{20}_D
3,3-Dichloro-1-propene	83.2–83.8	1.1580	1.4485
2,3-Dichloro-1-propene	93.5–93.6	1.2150	1.4609
cis-1,3-Dichloropropene	103–104	1.225	1.4699
trans-1,3-Dichloropropene	112.0–112.2	1.226	1.4750
1,1,3-Trichloro-1-propene	132–133	1.3983	1.4962
1,3,3-Trichloro-1-propene (low boiling)	128	1.3758	1.4869
1,3,3-Trichloro-1-propene (high boiling)	136.2–136.8	1.3898	1.4965
trans-1,2,3-Trichloropropene	136.2–137.2	1.4019	1.4984
cis-1,2,3-Trichloropropene	148.6–149.2	1.4286	1.5050

Discussion

When the process for chlorinating propylene to allyl chloride was first developed, several questions were asked about the nature of the reaction. Does it involve the direct replacement of an allylic hydrogen atom by chlorine; does chlorine add to the double bond followed by dehydrochlorination; or does some other mechanism apply? The products from the high temperature chlorination of 2-butene are crotyl chloride and 3-chloro-1-butene. Is one of these the primary and the other a rearranged product? Allyl chloride forms 10% 3,3-dichloro-1-

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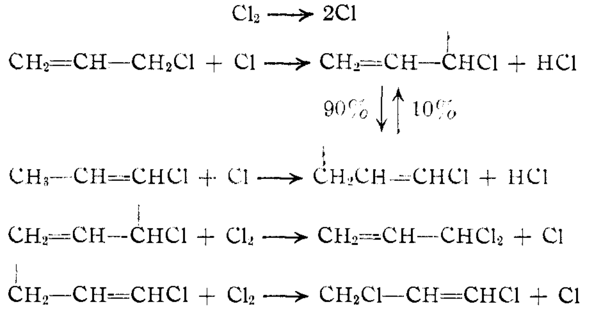
[2] L. F. Hatch and R. H. Perry, THIS JOURNAL, **71**, 3262 (1949).

[3] L. F. Hatch, J. J. D'Amico and E. V. Ruhnke, *ibid.*, **74**, 126 (1952).

propene and 90% 1,3-dichloropropene. Is the former an intermediate in the preparation of the major component?

Chlorine addition followed by dehydrochlorination of 1,2-dichloropropane is untenable as shown by the previous publication.[1] The high temperature chlorination is very specific in that the monochloride fraction contains 96% allyl chloride whereas the pyrolysis of dichloropropane forms a mixture of about 60% allyl chloride and 40% 1-chloro-1-propene.

An insight into the nature of the high temperature chlorination was gained by the experiment on the chlorination of 1-chloro-1-propene. The dichloride fraction is identical with that derived from allyl chloride, *i.e.*, 10% 3,3-dichloro-1-propene and 90% 1,3-dichloropropene. The formation of some 1,3-dichloropropene from 3,3-dichloro-1-propene by allylic rearrangement could conceivably occur to a certain extent particularly in the presence of metals. However, the reverse of this rearrangement is very unlikely. It is believed that the formation of an identical mixture of the two unsaturated dichlorides from both unsaturated monochlorides can best be explained by a mechanism involving free radicals.



$$Cl_2 \longrightarrow 2Cl$$

$$CH_2{=}CH{-}CH_2Cl + Cl \longrightarrow CH_2{=}CH{-}\overset{|}{C}HCl + HCl$$

$$90\% \downarrow\uparrow 10\%$$

$$CH_3{-}CH{=}CHCl + Cl \longrightarrow \overset{|}{C}H_2CH{=}CHCl + HCl$$

$$CH_2{=}CH{-}\overset{|}{C}HCl + Cl_2 \longrightarrow CH_2{=}CH{-}CHCl_2 + Cl$$

$$\overset{|}{C}H_2{-}CH{=}CHCl + Cl_2 \longrightarrow CH_2Cl{-}CH{=}CHCl + Cl$$

The reaction of a chlorine atom with both allyl chloride and 1-chloro-1-propene is written as forming an equilibrium mixture of two chloroallyl radicals. These may be considered to be the two tautomeric forms of the same radical stabilized by resonance or it may be more nearly correct to state that the chloroallyl radical has the structure $\overset{|}{C}HCl{-}\overset{|}{C}H{-}\overset{|}{C}H_2$ which can be attacked from either end. The ratio between 3,3-dichloro-1-propene and 1,3-dichloropropene will depend upon the relative reactivity of the radical at these positions.

Thus the high temperature chlorination of the straight chain olefins does not strictly speaking involve the replacement of an allylic hydrogen atom by a chlorine atom. An allylic hydrogen atom is removed, but because of the mobility of the resultant radical, chlorine may enter at a different position from that occupied by the original hydrogen atom. This could not be detected when the allylic radical is symmetrical as in the case of propylene, 2-chloropropene and 1,3-dichloropropene which form allyl chloride, 2,3-dichloro-1-propene and 1,3,3-trichloro-1-propene, respectively. However, the chlorination of 2,3-dichloro-1-propene leads to the formation of a small amount of what is believed to be 2,3,3-trichloro-1-propene together with the principal product 1,2,3-trichloropropene as would be expected. The formation of both crotyl chloride and 3-chloro-1-butene from 2-butene is probably the result of the two possible reaction centers of the intermediate radical rather than allylic rearrangement between the chlorides. No isomerization of 2-butene to 1-butene takes place during the chlorination.

By analogy with the chlorination of 1-chloropropene, the chlorination of 1,1-dichloro-1-propene might be expected to form a small amount of 3,3,3-trichloro-1-propene together with the major product 1,1,3-trichloro-1-propene. However, the former could not be detected. This would indicate that this dichloroallyl radical is predominantly of the structure $CCl_2{=}CH{-}CH_2{-}$.

The chlorination of either *cis*- or *trans*-1,3-dichloropropene leads to a mixture of both the *cis* and *trans* forms of 1,3,3-trichloro-1-propene. This is not surprising in view of the mechanism outlined above.

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