The Oxychlorination of Ethylene at High Temperatures

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The mechanism of ethylene oxychlorination to vinyl chloride (VCl) at 500-550° with an iron oxide containing catalyst has been established by deuterium labeling experiments. The data are consistent with a mechanism involving 1,2-dichloroethane (DCE) as the VCl precursor. The 2-chloroethyl radical or cation intermediate may directly contribute to VCl formation if certain kinetic requirements are satisfied, but neither direct substitution on ethylene *via* a vinyl radical nor any mechanism involving ethyl chloride contributes significantly.

The term "oxychlorination" describes a process whereby chlorination (usually of hydrocarbons) is achieved with hydrogen chloride and oxygen in the presence of a catalyst. These reactions are usually carried out in the vapor phase using a flow reactor. The catalysts are usually chlorides (and occasionally oxides) of metals with variable oxidation states.[1] Oxidation of the metal chloride is likely an important step in this catalytic process. The oxidized metal

$$2M^{+n}Cl_n + 2HCl + 0.5O_2 \longrightarrow 2M^{+(n+1)}Cl_{(n+1)} + H_2O$$

chloride can itself be the chlorinating agent for olefins at low temperatures (220–320°),[2] but, at higher temperatures, these metal chlorides catalyze the equilibrium among hydrogen chloride, oxygen, chlorine, and water. Under these conditions, elemental chlorine could be the important chlorinating agent.[3]

The use of iron oxide as a catalyst in the oxychlorination of saturated hydrocarbons has appeared in the patent literature.[1a,b] However, there are no reports regarding the mechanism of ethylene oxychlorination using this catalyst. Celite (trade name for diatomaceous earth) is a convenient source of low concentrations of iron oxide and was used in our experiments. When impregnated with manganese metaphosphate, it is an active catalyst for the oxychlorination of ethylene to vinyl chloride (VCl). A 50% conversion of ethylene with a 60% yield of vinyl chloride can be achieved at 550°.

The objective of this study was to establish the route followed by ethylene in its ultimate conversion into VCl. The three routes which we have considered are shown in Scheme I. In route 1 we consider the possibility that ethyl chloride is an intermediate. It is known that hydrogen chloride readily adds to ethylene at elevated temperatures. Although the equilibrium concentration of ethyl chloride is low at 550°,[4] it still must be considered, particularly if this equilibrium is established rapidly. Subsequent chlorination of ethyl chloride would likely occur in the 1 position as shown.[5] In route 2 we consider a vinyl radical as the intermediate in the so-called direct substitution route. The direct substitution route has been proposed in the chlorination of ethylene to VCl with elemental chlorine at elevated temperatures.[6] It has also been proposed in certain oxychlorination reactions.[7] Finally, in route 3 we consider 1,2-dichloroethane (DCE) and 2-chloroethyl radical or cation as the VCl precursors.

In this paper are reported two deuterium-labeling experiments which demonstrate that ethylene follows route 3 in its conversion into vinyl chloride.

Results and Discussion

If route 1 were operative, then the oxychlorination of ethylene with deuterium chloride should produce a large amount of VCl-*d*. No less than 66.6% of the VCl should be deuterated even if one ignores the expected deuterium isotope effect in the dehydrochlorination step,[8] but at 550° with a feed comprising DCl/C_2H_4/air = 2.5/1/2.5, we obtained only 13.9 ± 1.1% VCl-*d* (mass spectroscopy). Most of this can be accounted for in terms of hydrogen–deuterium exchange in ethylene. Analysis of the unreacted ethylene showed it to be 20 ± 0.9% deuterated. These data clearly rule out any significant contribution of route 1.

A choice between the remaining two routes was made on the basis of the deuterium isotope effects found in the oxychlorination of a nearly equal mixture of ethylene-d_0 and ethylene-d_4. In route 3, only a slight secondary isotope effect might be expected in the formation of DCE. Subsequent dehydrochlorination (k_9) by either the radical chain mechanism[9] or possibly a metal-catalyzed E2 mechanism[10] should provide a significant primary deuterium isotope effect. If VCl is derived from DCE, then the sum of the deuterated DCE and deuterated VCl should equal the sum of undeuterated DCE and undeuterated VCl, but this would not be sufficient evidence to exclude a contribution from step k_7. If this step was much faster than 2-chloroethyl radical or cation formation then the above equality would still hold.

A large primary deuterium isotope effect would be expected in k_4 of route 2. Therefore a significant contribution of route 2 to VCl production would cause a large difference in the sums of deuterated and undeuterated products.

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[1] (a) British Patent 1,303,369 (1966); (b) O. Reitlinger, U. S. Patent 2,674,633 (1954); (c) E. Gorin, U. S. Patent 2,451,821 (1948); (d) G. W. Hearne, U. S. Patent 2,399,488 (1946); (e) A. J. Johnson and A. J. Cherniavsky, U. S. Patent 2,746,844 (1956).

[2] (a) R. R. Arganbright and W. F. Yates, *J. Org. Chem.*, **27**, 1205 (1962); (b) P. P. Nicholas and R. T. Carroll, *ibid.*, **33**, 2345 (1968).

[3] W. F. Engel and M. J. Waale, *Chem. Ind.* (London), 76 (1962).

[4] G. Todos and L. F. Stutzman, *Ind. Eng. Chem.*, **50**, 413 (1958).

[5] P. H. Dirstine and E. L. Dance, U. S. Patent 2,628,259 (1953).

[6] (a) W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **5**, 449 (1940); (b) H. Groll, G. Berkeley, J. Burgin, and D. LaFrance, U. S. Patent 2,167,927 (1939).

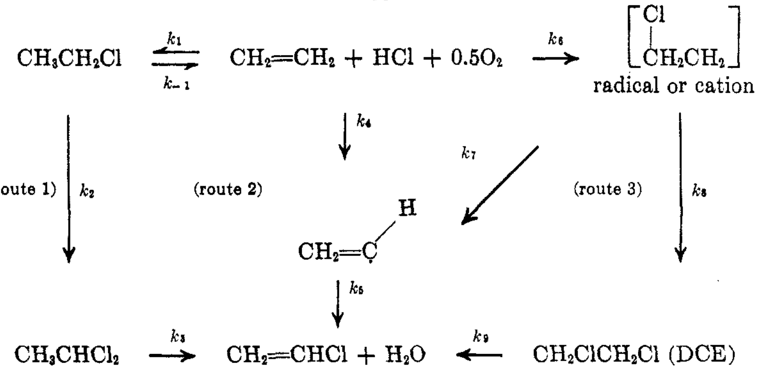
[7] K. Nawmbury, G. Schwedler, and G. Emig, *Chem.-Ing.-Tech.*, **39**, (9, 10), 505 (1967).

[8] D. H. Barton and K. E. Howlett, *J. Chem. Soc.*, 169 (1940).

[9] D. H. Barton and K. E. Howlett, *ibid.*, 115 (1949).

[10] H. Woller, *Angew. Chem. Intern. Ed. Eng.*, **7**, 232 (1968).

SCHEME I



The results shown in Table I were those obtained at 550° with a feed comprising $HCl/C_2H_4/C_2D_4/air = 2.5/0.47/0.53/2.5$. These data are entirely consistent with the results expected for route 3. The small differences between the expected and observed sums of products in Table I can be attributed to the hydrogen–deuterium exchange in our ethylene mixture (Table II). Route 3 is further supported by the absence of a deuterium isotope effect in ethylene consumption.

TABLE I

DEUTERIUM DISTRIBUTION IN PRODUCTS FROM THE OXYCHLORINATION OF A C_2D_4–C_2H_4 MIXTURE

	Observed				Expected route 3	
Run no.	[DCE-d_4/ DCE-d_0[a]	[VCl-d_3/ VCl-d_0][a]	[DCE-d_4 + VCl-d_3]	[DCE-d_0 + VCl-d_0]	[DCE-d_4 + VCl-d_3]	[DCE-d_0 + VCl-d_0]
1	2.9	0.75	47.9	52.1		
2	*b*	0.85				
3	3.2	0.85	50.2	49.8		
Av	3.1	0.81	49.1	50.9	52.6[c]	47.4[c]

[a] Traces of VCl-d_2 and -d_1, and DCE-d_3 and -d_2 were detected. [b] Mass spectroscopy showed DCE sample contaminated. [c] The 1.9% ethylene-d_2 present in our ethylene mixture was not considered in these values.

TABLE II

DEUTERIUM DISTRIBUTION IN UNREACTED ETHYLENE[a]

	Run no.		
	1	2	3
d_0	50.5	50.2	48.6
d_1	1.5	1.5	2.5
d_2	2.0	3.5	0.5
d_3	3.0	3.5	3.3
d_4	43.0	41.0	44.8

[a] Starting mixture d_0 = 46.4%; d_2 = 1.9%; d_4 = 51.6%.

The rate of oxychlorination is at least three times faster than the rate of ethylene-d_4 exchange to lesser deuterated ethylenes. Therefore, this exchange would not be expected to cause a large deviation from the expected results.

We can, therefore, conclude that route 3 is likely the exclusive route in the conversion of ethylene into vinyl chloride under our conditions. This mechanism is analogous to the addition–elimination mechanism proposed for the liquid phase chlorination of benzene.[11] Consistent with this conclusion is the fact that under these conditions, DCE is converted into VCl much more rapidly than ethylene.

Experimental Section

General.—The chlorinated compounds were analyzed using an F & M 810 gas chromatograph on a 4 ft × 3/16 in. column containing 20% Ucon LB 550X, 60/80 mesh, on Chromosorb R. Ethylene and CO_2 were analyzed on a P.E. 154 gas chromatograph using a 2 ft × 3/16 in. column containing 30/60 mesh silica gel. The oxygen, nitrogen, and CO were analyzed on the same instrument with a 1 ft × 3/16 in. column containing 30/60 mesh Linde 5A Molecular Sieves. Mass spectra were obtained on a C.E.C. Model 21-103C.

Apparatus.—The oxychlorination reactions were carried out in a 4 in. × 0.25 in. Pyrex reactor wrapped with chromel heating wire. A thermocouple placed in a thermowell extending through the center of the reactor was connected to a temperature controller. Fisher-Porter and Matheson flowrators were calibrated and used for the various gaseous feeds. The lecture bottle containing the deuterium chloride was cooled to −78° to help to maintain a constant back-pressure as the gas was consumed.

Reagents.—Deuterium chloride (5 l., anhydrous, 99.0% minimum purity) and 2 l. of perdeuterioethylene 99.0% minimum purity were supplied by Merck Sharp and Dohme of Canada Ltd. The C_2D_4 was diluted with 2 l. of C_2H_4. The ethylene and hydrogen chloride both 99.0% minimum purity were supplied by Matheson Co. The gases were used without further purification.

The catalyst was a pelletized Celite impregnated with manganese metaphosphate. It was prepared by adding a solution of 15.4 g (0.07 mol) of $MnCl_2 \cdot 4H_2O$ and 26.6 g (0.23 mol) of H_3PO_4 (85%) to Celite, evaporating the water, and then heating for 24 hr at 550°. It has a surface area of 4.43 m^2/g and a total pore volume of 3.32×10^{-3} cc/g. Fresh catalyst (20 cc of 4/18 mesh) was used for each experiment.

Procedure.—With air passing through the catalyst bed, the reactor was heated to within 10° of the desired temperature. The hydrogen chloride and ethylene were then mixed at room temperature and immediately introduced into the catalyst zone. The reaction was run for 15 min to allow the system to equilibrate. Then the reactor effluent was directed through a scrub flask containing water, dried, and then passed through the gas chromatograph's sample loops. After the reaction had run for 15 more min, the feed gases were shut off and the gas chromatography lines were sealed. A gc sample was taken immediately for quantitative calculation of the product distribution. After this analysis was performed, the desired components were isolated by preparative gc and analyzed for deuterium content by mass spectrometry.

Oxychlorination of Ethylene with Deuterium Chloride.—The conditions for oxychlorination were as follows: $DCl/C_2H_4/air = 2.5/1/2.5$; temperature 540–550°; contact time = 7.0 sec. The products (per cent yield based on ethylene) were CO (34.4); CO_2 (2.2); VCl (58.9); 1,1-dichloroethylene (2.2); *trans*-1,2-dichloroethylene (1.1); *cis*-1,2-dichloroethylene (1.1); other samples ±3% these results; conversion C_2H_4 47.1%; carbon balance 101.6%.

Oxychlorination of Ethylene-d_0–Ethylene-d_4 Mixture.—The

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[11] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

conditions for oxychlorination were as follows: $HCl/C_2H_4/C_2D_4/$air = 2.5/1/2.5; temperature 490–505°; contact time = 7.0 sec at 500°. The products (per cent yield based on total ethylene) were CO (9.7); CO_2 (2.4); VCl (61.8); 1,1-dichloroethylene (3.2); CCl_4 (0.8); *trans*-1,2-dichloroethylene (4.8); *cis*-1,2-dichloroethylene (4.8); DCE (9.7); 1,1,2-trichloroethylene (0.8); 1,1,2-trichloroethane (2.4); other samples ±6% these results; conversion (C_2H_4 + C_2D_4) 50.7%; carbon balance 90.1%.

Registry No.—C_2D_4, 683-73-8; C_2H_4, 74-85-1.

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Selective Autoxidation of Some Phenols Using Bis(salicylaldehyde)ethylenediiminecobalt Catalysts

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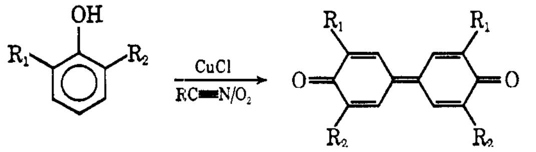
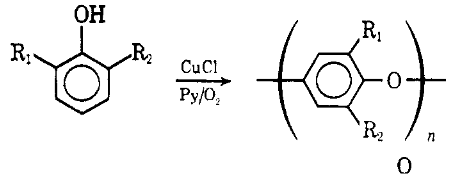
Catalyzed oxidation of phenols can result in hydroxylations, Diels–Alder coupling, aminations, benzoquinones, diphenoquinones, or polymers, depending on the particular catalyst system employed. We have found that two catalysts belonging to the salcomine [bis(salicylaldehyde)ethylenediiminecobalt (II)] family of complexes can be used to produce selectively 2,6-substituted benzoquinones, 3,3′,5,5′-tetrasubstituted diphenoquinones, or 2,6-substituted phenylene oxide polymers from several 2,6-substituted phenols. Conditions favoring the benzoquinone formation employ the salcomine monopyridine catalyst in high concentration and low temperature whereas the diphenoquinone is favored using the O_2-bridged salcomine dimer in low concentration and at high temperature. 2,6-Phenylene oxide polymers form when an amine is added to the system catalyzed by the O_2-bridged salcomine dimer. Evidence is presented for an equilibrium between a mononuclear salcomine and its O_2-bridged dimer. Selectivity of the catalysts may be associated with this equilibrium.

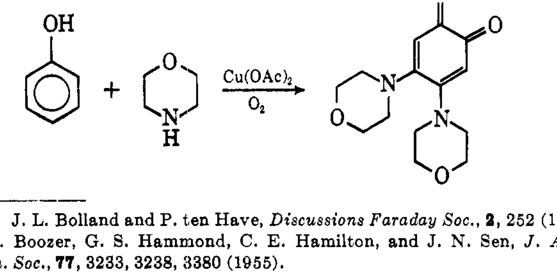
The catalyzed autoxidation of phenols is interesting both in mechanistic studies and in various syntheses.[1,2] Tetraalkyldiphenoquinones (eq 1), polyphenylene ethers (eq 2), and *o*-benzoquinones (eq 3) can be selectively prepared by proper choice of catalyst, solvent, and phenol.[3-6]



(1)



(2)



(3)

It is probable that the only function of oxygen in any of these reactions is to reoxidize copper from the 1+ to the 2+ state.[7,8] The suggestion that phenoxyl radicals are intermediates fails to account for the dramatic effects that result when the ligands on the copper catalyst are changed.

Recent work by van Dort and Geursen[9] and workers at Dynamit Nobel[10] has shown that copper is not the only metal that can be used in these reactions. Cobalt, as a salcomine,[11] produces all three classes of products (eq 4).

A similar reaction in chloroform gave a 26% yield of benzoquinone, an 11% yield of polymer, and no detectable diphenoquinone. It is curious that in contrast to the copper catalyst,[6] the cobalt catalyst produced little or no *o*-benzoquinone even with phenols having open 2 positions.

Although 13 other examples are given, only 2,6-diphenylphenol gave all three products. In the other cases, the benzoquinones were often the only identified product in yields ranging from 80% for 2,6-di-*t*-butylphenol to 36% with 2,3-dimethylphenol.

Until recently, nearly all of the interest in salcomines has been in the area of physical chemistry with surprisingly little emphasis on their chemical reactions, even though it has been known for about 25 years that certain salcomines can combine reversibly with molec-

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(1) J. L. Bolland and P. ten Have, *Discussions Faraday Soc.*, **2**, 252 (1948); C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233, 3238, 3380 (1955).

(2) C. D. Cook, *J. Org. Chem.*, **18**, 260 (1953); E. Muller, A. Schick, R. Mayer, and K. Scheffler, *Ber.*, **93**, 2649 (1960); D. A. Bolon, *J. Amer. Chem. Soc.*, **88**, 3148 (1966); H. S. Blanchard, *J. Org. Chem.*, **25**, 264 (1960).

(3) A. S. Hay, U. S. Patent 3,210,384 (1965); *Chem. Abstr.*, **64**, 17494*b* (1966).

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(6) W. Brackman and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **74**, 937 (1955).

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(8) H. S. Blanchard, H. Finkbeiner, and G. F. Endres, *Soc. Plastics Eng. Trans.*, **2**, 110 (1962).

(9) H. M. van Dort, and H. J. Geursen, *Rec. Trav. Chim. Pays-Bas*, **86**, 520 (1967).

(10) Dynamit Nobel Aktiengesellschaft, Dutch Patent 6,609,843 (1967).

(11) The generic term salcomine has been applied to Schiff base coordination compounds consisting of salicylaldehyde, cobalt, and an amine. Salcomine (salco) is bis(salicylaldehyde)ethylenediiminecobalt(II). The bissalicylaldehyde Schiff base ligand is abbreviated as salen.