of the indicated solvent; then the combined organic layers were washed with several portions of water followed by saturated brine. The organic layer was dried over anhydrous sodium or magnesium sulfate, then filtered, and the solvent was evaporated from the filtrate under reduced pressure (water aspirator) using a rotary evaporator. The use of the terms "base wash" or "acid wash" indicate washing the organic solution with saturated aqueous sodium bicarbonate solution or with dilute aqueous hydrochloric acid, respectively, prior to the aforementioned wash with water.

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Ozonolysis of *trans*-2,3-Dichloro-2-butene. Isolation of α-Chloro Peroxides[1]

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Abstract: Ozonolysis of *trans*-2,3-dichloro-2-butene (**4**) in nonparticipating solvents or at the neat substrate yielded acetyl chloride (**5**), acetic acid (**7**), acetic anhydride (**11**), 2,2,3,3-tetrachlorobutane (**10**), diacetyl peroxide (**13**), *trans*-1,2-dichloro-1,2-dimethyloxirane (**14**), and the α-chloro peroxides 1,4-dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (**9**) and acetyl 1,1-dichloroethyl peroxide (**12**). Evidence was also obtained for the transient formation of a monomeric ozonide (**8**) of the substrate **4**. Structure proof is presented for the hitherto unknown α-chloro peroxides **9** and **12**, and a mechanism is suggested for the course of the ozonolysis reaction.

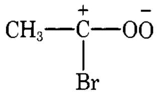
The reaction of ozone with purely hydrocarbon olefins has been and is still receiving broad attention, starting from the mode of initial attack of ozone via the nature and the fate of labile intermediates to the structure and the stereochemistry of the final ozonolysis products. By contrast, the interaction of ozone with olefins bearing halogen substituents at the double bond has not been the subject of systematic and detailed investigations thus far.

From scattered reports in the literature it became evident in a qualitative manner that halogen substituents in vinylic positions impart considerable ozone resistance to the corresponding double bonds. Thus, ozonolyses of compounds containing both nonhalogenated and mono-[2] or dihalogenated[3,4,5] double bonds in the same molecule were reported to lead to exclusive cleavage of the corresponding nonhalogenated double bonds.

The qualitative picture which emerged from such observations was substantially verified by the results of a quantitative study of the rates of reaction of ozone with ethylene and with the series of the mono-, di-, tri-, and tetrachloroethylenes: the relative rates decreased drastically in the above order, ethylene being approximately 25 000 times more reactive than tetrachloroethylene.[6]

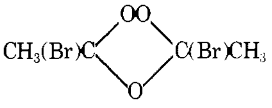
Very little information is available on the course and the nature of the products of the ozonolysis of halogenated double bonds. Substrates which have been studied under these aspects are 1,1-dichloroethylene,[7] tetrachloroethylene,[8] fluorinated C_2,[9,10] C_3, and C_4 olefins,[11] and 9,10-dibromo- as well as 9,10-dichloroanthracene.[12] However, these are probably not representative examples since they involve the ozonolysis of rather special types of haloolefins and in some cases also special (viz. gas phase) reaction conditions.

In an attempt at studying more representative substrate types, we have initiated work on the ozonolysis of 1,2-disubstituted dihaloethylenes and 1,2-disubstituted monohaloethylenes. The first substrate which we examined in this program was *trans*-2,3-dibromo-2-butene.[13] Its ozonolysis in nonparticipating solvents afforded the expected cleavage fragment acetyl bromide,[14] whereas products that would have been indicative of the formation of the corresponding zwitterion **1**, such as the monomeric ozonide **2** or the dimeric peroxide **3** could neither be isolated nor conclusively proven as intermediates.



$CH_3-\overset{+}{\underset{|\,Br}{C}}-\overset{-}{OO}$

1



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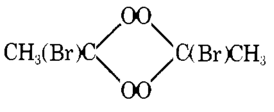


3

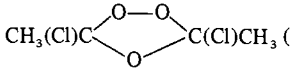
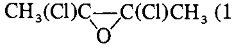
In the present paper we report about the ozonolysis of *trans*-2,3-dichloro-2-butene (**4**) which gave considerably more insight into the course of the ozonolysis of halogenated double bonds and which led to the isolation of well-defined α-chloro peroxides, a class of compounds that is largely unexplored.[15]

Results

Ozonolyses of *trans*-2,3-dichloro-2-butene (**4**) were carried out in pentane, in chlorinated hydrocarbons (dichloromethane, 1,1,2,2-tetrachloroethane), in esters, and at the neat substrate at −30 or −78 °C. NMR analyses of the crude reaction mixtures showed that in each case the same products were formed, albeit in different amounts (Table I).

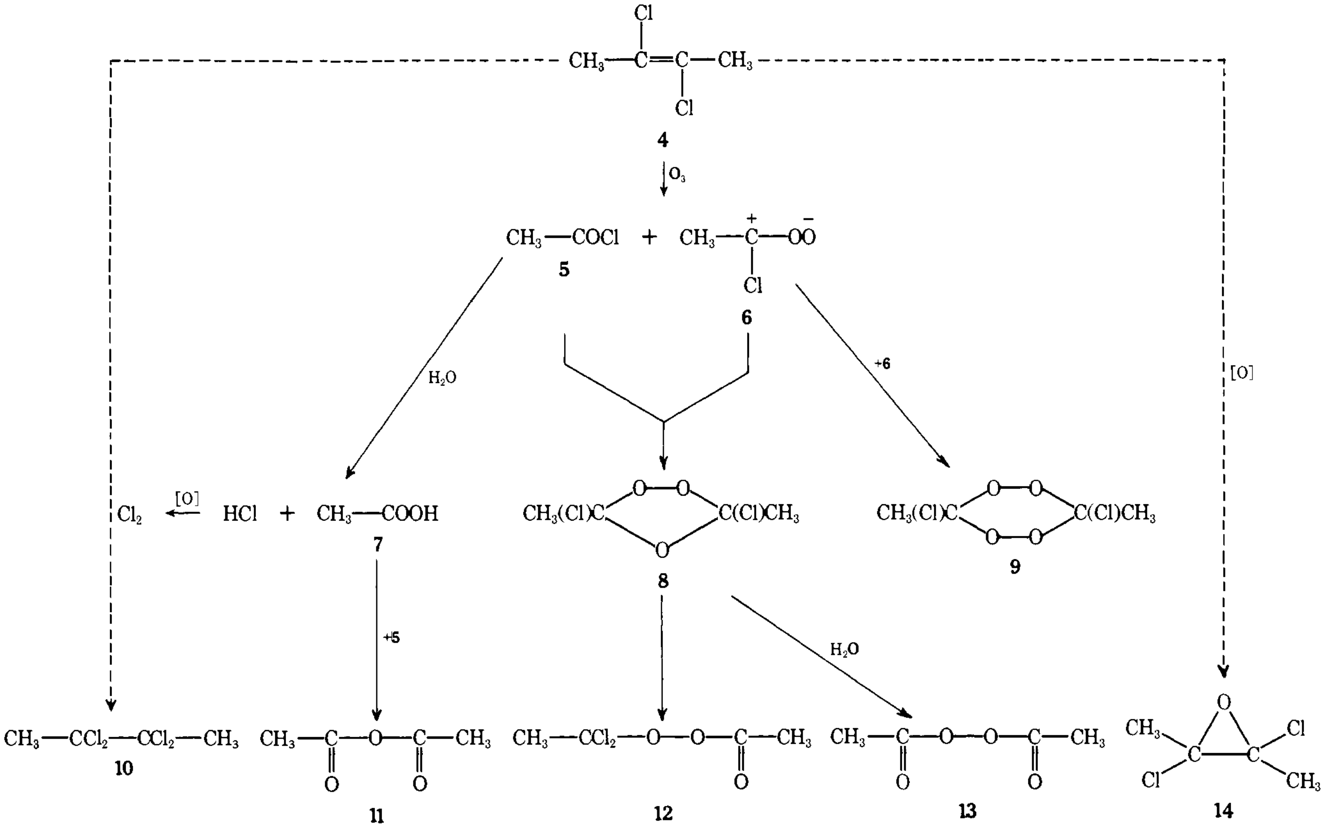
Workup of the reaction mixtures by various means (see Experimental Section) resulted in the isolation of acetyl chloride (**5**), 2,2,3,3-tetrachlorobutane (**10**), diacetyl peroxide (**13**), and the hitherto unknown α-chlorinated peroxides[15] **9** and **12** (Scheme I). In addition, acetic acid (**7**),

Table I. Products from the Ozonolysis of *trans*-2,3-Dichloro-2-butene

	Solvent					
	None	CH_2Cl_2	$(CHCl_2)_2$	C_5H_{12}	$HCOOCH_3$	$HCOOCH_3$/TCNE[a]
Concn of **4**, mol/mol of solvent		0.33	0.66	0.4	0.1	0.05
Reaction temp, °C	−30	−30	−30	−78	−40	−40
% conversion	81	72	80	74	100	84
O_3 consumption, mol %[b]	61	60	70	62	105	
Products, mol %[c]						
CH_3COCl (**5**)	30	49	42	35	53 (31)[d]	64
CH_3CO_2H (**7**)	10	4	6	11	3 (20)	25[e]
$CH_3CO—O—COCH_3$ (**11**)	<1	1	<1	5	1 (<1)	
$(CH_3(Cl)COO)_2$ (**9**)	3	4	4	5	2 (2)	
 (**8**)	1	3	1	1	18 (2)	
$CH_3CCl_2OOCOCH_3$ (**12**)	8	4	7	4	4 (11)	
$CH_3CO—OO—COCH_3$ (**13**)	15	12	13	20	5 (9)	
$CH_3CCl_2CCl_2CH_3$ (**10**)	16	4	2	2	<1 (<1)	
 (**14**)	6	4	9	<1	2 (2)	
Other components	16[f]	15[f]	16[f]	17[f]	13[g] (23)[h]	11
Ratio of 5:6	2.9:1	3.6:1	3.2:1	2.8:1	4.0:1	

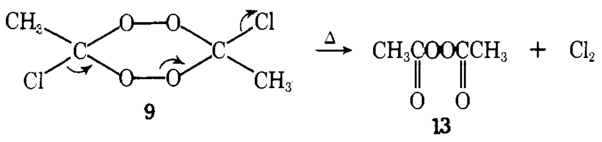
[a] TCNE ≡ tetracyanoethylene; applied in equimolar ratio with substrate **4**. [b] Based on olefin consumed as 100%. [c] Based on NMR analyses of crude reaction mixtures, using 1,1,2,2-tetrachloroethane as internal standard. [d] Numbers in brackets refer to the composition of the reaction mixture after 24 h standing at room temperature. The decrease of acetyl chloride is due to partial solvolysis and to reaction with methyl formate which led to the formation of methyl acetate. [e] Sum of acetic acid and of methyl acetate. [f] Based on a number of small, unassigned signals in the NMR spectrum of the crude reaction mixture. [g] 8% unidentified peaks and 5% methyl acetate. [h] 10% unidentified peaks and 13% methyl acetate.

Scheme I. Products from the Ozonolysis of *trans*-2,3-Dichloro-2-butene in Nonparticipating Solvents and Probable Course of the Ozonolysis Reaction



acetic anhydride (**11**), and *trans*-1,2-dichloro-1,2-dimethyloxirane (**14**)[16] could be shown to be minor reaction products by admixture of the respective authentic compounds to the reaction mixtures and subsequent NMR analysis.

The α-chlorinated peroxide 1,4-dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (**9**) was a colorless, crystalline material. Its NMR spectrum exhibited a singlet signal, the ir spectrum showed no absorption in the carbonyl region, and the field ionization mass spectrum showed the ions $(M - Cl)^+$, $(Cl_2)^+$, and $(CH_3CO)^+$. The compound had the typical smell of peroxides, it oxidized solutions of sodium iodide spontaneously, and it exploded violently when exposed to sudden temperature increases[17] or to shock. Upon gentle heating, however, it could be melted (mp ~50 °C) and in solution it could be thermally decomposed to form diacetyl peroxide and chlorine:



While the above data constitute compelling evidence for the structure of **9**, its stereochemistry could not be determined. NMR measurements between −60 and 42 °C showed no changes in the spectrum.

Acetyl 1,1-dichloroethyl peroxide (**12**) was a colorless, viscous liquid. Its NMR spectrum exhibited two singlet signals of equal intensity, the ir spectrum showed a strong carbonyl absorption at 1800 cm^{-1}, and the field ionization mass spectrum showed the ions $(M - Cl)^+$, $(CH_3CCl_2)^+$, and $(CH_3CO)^+$. The compound had the typical smell of peroxides, oxidized sodium iodide, and was sensitive to sudden heating, but less explosive than **9**.[18]

Careful thermal decomposition of **12** in dichloromethane (Scheme II) afforded acetyl chloride (**5**) and acetic acid (**7**) as the major products, along with minor amounts of methane, chloromethane, chloroform, and 1,1,2,2-tetrachloroethane. These results can be readily explained by scission of the peroxide bond in **12** to form the radicals **15** and **16** and by subsequent radical decomposition (routes a), radical combination (routes b), and radical abstraction reactions (routes c, Scheme II).

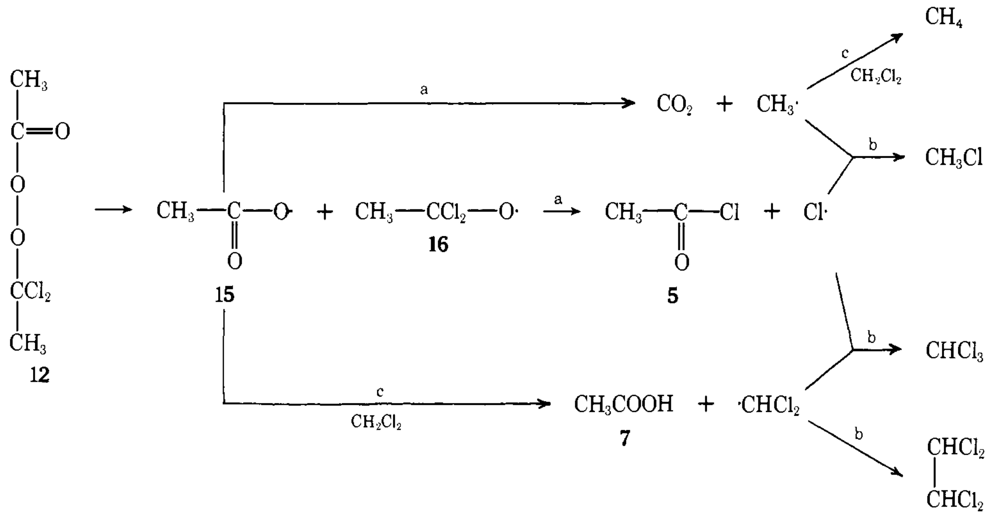
The formation of most of the ozonolysis products (viz. **5**, **7**, **9**, **10**, **11**, and **14**) can be readily explained if one assumes a Criegee-type cleavage of the double bond to form the fragments **5** and **6** (Scheme I). Partial hydrolysis of acetyl chloride (**5**) by traces of water produces acetic acid (**7**), acetic anhydride (**11**), and hydrogen chloride. Oxidation of the latter by ozone and/or peroxidic ozonolysis products yields water and chlorine, which in turn adds to the substrate **4** to form 2,2,3,3-tetrachlorobutane (**10**). Dimerization of the zwitterion **6** forms peroxide **9**, and oxidation of the substrate **4** by ozone and/or peroxidic products forms the epoxide **14**.

The mode of formation of the peroxides **12** and **13** was a priori less obvious (Scheme III). Peroxide **12** could have been formed by rearrangement of a monomeric ozonide of structure **8** or by reaction of acetyl chloride with the dimeric peroxide **9**, and diacetyl peroxide (**13**) could have been derived from **8**, **9**, or **12** by hydrolysis reactions or from **9** by dechlorination.

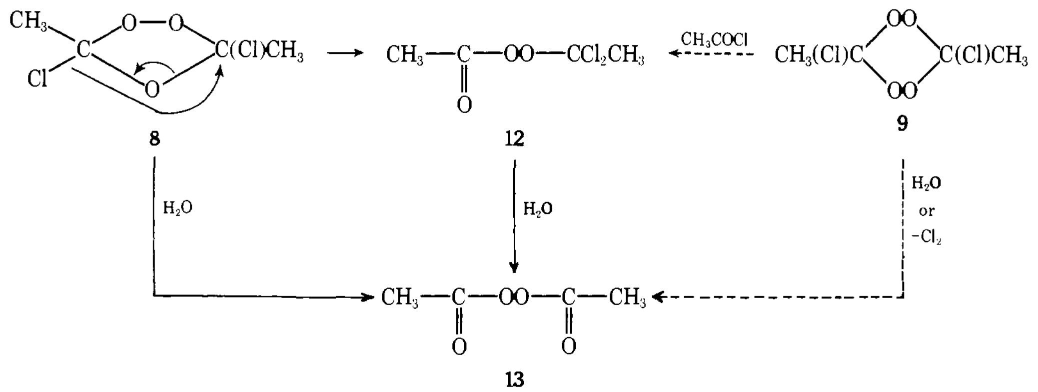
In model experiments we could show that reactions **9** → **12** and **9** → **13** (Scheme III) do not occur under the mild conditions of the ozonolysis reactions or of the NMR analyses. This pointed to a reaction course via the monomeric ozonide **8** as an intermediate for **12**[19] and for **13**. Although we were not able to isolate **8**, evidence for its transient existence as a precursor for **12** and **13** could be accrued from the following observations.

The NMR spectra of the crude reaction mixtures showed a singlet signal at δ 2.33 ppm which could not be assigned to any one of the identified ozonolysis products. This signal was very weak in most cases; if the ozonolyses were carried out in methyl formate at −40 °C, however, it amounted to 20% of the total signal intensity. Upon addition of sodium iodide to such NMR samples, the signal at 2.33 ppm disappeared immediately, while standing of the samples at room temperature resulted only in a gradual decrease of this signal and a concurrent increase of the signals corresponding to **12** and **13** (Table I, numbers in brackets). If the ozonol-

Scheme II. Thermal Decomposition of Acetyl 1,1-Dichloroethyl Peroxide (12)

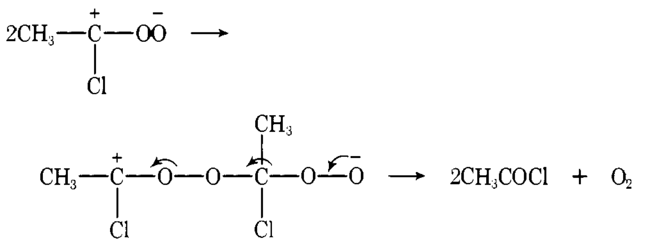


Scheme III. Possible Modes of Formation of Acetyl 1,1-Dichloroethyl Peroxide (12) and of Diacetyl Peroxide (13)



yses were carried out in methyl formate and in the presence of tetracyanoethylene, the NMR spectrum of the reaction mixture showed neither the signal at 2.33 ppm nor those corresponding to **12** and **13**, but an increase for the signal of acetyl chloride (**5**) (Table I).[20]

The quantitative results of the ozonolysis reactions (Table I) are seemingly incompatible with the reaction course outlined in Scheme I. Ozone consumption was in most cases below the usual 1:1 stoichiometry and the ratio of the initial cleavage fragments **5** and **6** (Table I, bottom line) was not balanced but reflected a preference for the formation of the acetyl chloride fragment **5**. These deviations from the 1:1 stoichiometries required by Scheme I may be due to side reactions which consume olefinic substrate **4** and zwitterion **6**. Such reactions could be (i) oxidation of hydrogen chloride by the ozonide **8** and subsequent addition of the chlorine formed to the substrate **4**,[21] and (ii) dimerization of the zwitterion **6** to form the linear intermediate **17**, followed by loss of oxygen and formation of acetyl chloride:[22]



$$2\mathrm{CH_3}-\underset{\mathrm{Cl}}{\overset{+}{\mathrm{C}}}-\mathrm{O}\overset{-}{\mathrm{O}} \longrightarrow$$

$$\mathrm{CH_3}-\underset{\mathrm{Cl}}{\overset{+}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\underset{\mathrm{Cl}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}-\overset{-}{\mathrm{O}} \longrightarrow 2\mathrm{CH_3COCl} + \mathrm{O_2}$$

If the latter reaction would produce singlet oxygen, cleavage of the substrate **4** into acetyl chloride (**5**) via a dioxetane intermediate would provide an additional route for olefin consumption without the use of ozone and without the concurrent formation of zwitterion **6**. Experiments are underway to examine this possibility.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were obtained on a Beckmann IR-8 spectrometer. Proton nuclear magnetic resonance spectra were obtained at 60 MHz on a Varian Associates A-60 spectrometer. Mass spectra were obtained on a Varian MAT-CH 4 spectrometer; field ionization spectra were obtained on a modified Varian MAT-CH 4 instrument. The ozonator was a Fischer-Labortechnik OZI-model.

***trans*-2,3-Dichloro-2-butene** (**4**) was prepared using a procedure of Scharf and Laux.[23] It was obtained in ≥95% purity by distillation over a 1-m spinning-band column; the remaining 5% was *cis*-2,3-dichloro-2-butene.

Ozonolysis Procedures. All ozonolyses were carried out in cylindrical reaction vessels which were dimensioned such that the ozone inlet tube was at least 5 cm submersed into the reaction solution. The ozonolysis vessels were equipped with a gas inlet tube, a dry ice cooled condenser, a pneumatic sampling device, and a cooled dropping funnel for the addition of reagents during or after the ozonolysis reactions. In order to avoid admission of moisture, cold traps (−78 °C) were put in the gas line before and after the reaction vessel.

Ozonolysis reactions in chlorinated hydrocarbons and in esters as solvents at −30 °C produced homogeneous solutions. Ozonolysis of the neat substrate at −30 °C or of **4** in pentane at −78 °C produced a colorless, solid precipitate, along with a homogeneous liquid phase.

Caution! Sudden explosions have occurred when the crude reaction mixtures were warmed up to room temperature, particularly when the ozonolysis was carried out at the neat substrate **4**. In most cases such explosions were preceded by bubbling of the mixture and by expulsion of gases.

Isolation of the Reaction Products 5, 9, 10, 12, and 13. Although the above products were formed in all ozonolysis reactions, certain reaction mixtures are better suited than others for the isolation of the individual components.

Acetyl Chloride (**5**). A solution of 1.24 g (0.01 mol) of *trans*-2,3-dichloro-2-butene (**4**) in 8.4 g of 1,1,2,2-tetrachloroethane was ozonized to completion at −30 °C and excess ozone was removed by a nitrogen stream. From the remaining crude reaction mixture acetyl chloride (**5**) was distilled off over a 10-cm packed column at room temperature and at reduced pressure (12 mm). Its ir spectrum was identical with that of authentic material.

1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (**9**). *trans*-2,3-Dichloro-2-butene (**4**) (5 g, 0.04 mol) was ozonized to completion at −30 °C. During the ozonolysis, peroxide **9** precipitated in part as a colorless, crystalline solid. The solution was cooled to approximately −50 °C and then decanted. The remaining solid was washed with cold pentane, filtered off by suction, and purified by sublimation (20 °C, 1 mm) to yield 50 mg of **9**: mp 50 °C dec., ir (KBr) 1380, 1190, 1175, 1115, 890, 750, 630 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.04 (s); field ionization mass spectrum, typical peaks at *m/e* 153, 155 $(M - Cl)^+$, 70, 72, 74 $(Cl_2)^+$, 60 $(CH_3COOH?)^+$, and 43 $(CH_3CO)^+$.

Anal. Calcd for $C_4H_6O_4Cl_2$: Cl,[17] 37.52. Found: Cl, 36.41.

Caution! This material is extremely sensitive to shock or to heat and may explode very violently. Explosions have also occurred when small samples of **9** were touched with a glass rod or with a spatula.

2,2,3,3-Tetrachlorobutane (**10**) was isolated from the mother liquors of the above decantation. To 17 g of combined mother liquors, approximately 5 ml of water was slowly added while the mixture was stirred and cooled with ice. Upon cooling of the hydrolyzed organic layer, 130 mg of **10** precipitated as a colorless solid, mp 176 °C (recrystallized from methanol). Ir and NMR spectra were identical with those of an authentic sample. The mass spectrum contained typical peaks at *m/e* 159, 161, 163, 165 $(M - Cl)^+$, 124, 126, 128 $(M\text{-}2Cl)^+$, 97, 99, and 101 $(M/2)^+$.

Acetyl 1,1-dichloroethyl peroxide (**12**) was isolated from crude reaction mixtures by chromatography on silica gel with dichloromethane. Best yields were obtained when the ozonolysis was carried out in the presence of pyridine. A solution of 5 g (0.04 mol) of **4** and 6.3 g (0.08 mole) of pyridine in 20 g of methyl acetate was ozonized to completion. The liquid part of the reaction mixture was decanted from the brown solid that had precipitated during the reaction. The solid was treated three times with 5 ml of dichloromethane. The extracts were combined with the liquid part of the reaction mixture. The solvents were largely removed by vacuum distillation at ambient temperatures and the residue was submitted to chromatography on silica gel (water cooled, jacketed column; 1.8 cm i.d.; 50 cm packing height).

Compound **12** (0.55 g) was obtained as a viscous liquid: NMR (CCl_4) δ 2.17 (s, CH_3CO) and 2.40 (s, CH_3CCl_2); ir (neat) 1800, 1440, 1380, 1365, 1185, 1132, 1080, 990, 853, and 705 cm^{-1}; mass spectrum by field ionization, major peaks at 137, 139 $(M - Cl)^+$, 97, 99, 101 $(CH_3CCl_2)^+$, and 43 $(CH_3CO)^+$; $n^{20}D$ 1.4457.

Anal. Calcd for $C_4H_6O_3Cl_2$: C, 27.74; H, 3.47; Cl, 41.04. Found: C, 27.96; H, 3.59; Cl, 40.95.

Caution! In its pure form this material may lead to violent explosions.[18]

Diacetyl peroxide (**13**) was isolated by chromatography on silica gel with dichloromethane from reaction mixtures that were obtained by ozonolysis of the neat substrate **4**. Its ir spectrum was identical with that of an authentic sample.

Thermal Decomposition of 1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (**9**). A solution of 20 mg of **9** in 1.5 ml of CCl_4 was sealed into a NMR sample tube and heated to 70 °C for 45 min. In the green yellow solution (chlorine!) diacetyl peroxide (**13**) was identified by NMR (admixture of authentic **13**) and ir analysis. Upon further heating to 70 °C, diacetyl peroxide was decomposed and increasing amounts of acetic acid (**7**) were formed.

In a separate experiment, a solution of 20 mg of **9** and two drops of **4** in 1.5 ml of CCl_4 was sealed into a NMR sample tube. After 2 days at room temperature, no change in the product composition was observed by NMR analysis. Subsequent heating of the sample to 64 °C for 5 h yielded diacetyl peroxide (**13**), acetic acid (**7**), and 2,2,3,3-tetrachlorobutane (**10**), as evidenced by admixture of authentic samples and NMR analysis.

Thermal Decomposition of Acetyl 1,1-Dichloroethyl Peroxide (**12**). A solution of **12** in dichloromethane was sealed into a NMR sample tube and heated to 60 °C for 10 h. NMR analysis showed singlet signals corresponding the acetyl chloride (**5**), acetic acid (**7**), methane, chloromethane, chloroform, and 1,1,2,2-tetrachloroethane, as evidenced by the admixture of the corresponding authentic samples. The major pyrolysis product acetyl chloride (**5**) was further identified by hydrolysis and concurrent formation of additional acetic acid (**7**); chloroform and 1,1,2,2-tetrachloroethane were also identified by GLC analysis.

Model Experiments Concerning the Mode of Formation of Acetyl 1,1-Dichloroethyl Peroxide (12) and Diacetyl Peroxide (13). (a) Attempted Reaction of 1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (9) with Acetyl Chloride. A solution of 40 mg (0.21 mmol) of **9** and 35 mg (0.45 mmol) of acetyl chloride in 1 g of dichloromethane was kept at ambient temperatures for 2 days and was then heated to 45 °C for 30 min. Neither **12** nor **13** could be detected by NMR analysis.

(b) Attempted Conversion of 1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (9) into Diacetyl Peroxide under Mild Conditions. To a solution of 40 mg of **9** in 2 ml of methyl acetate, 3 drops of water were added and the mixture was kept at room temperature for 1 day. NMR analysis showed that **9** was unchanged and no diacetyl peroxide (**13**) was formed.

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(15) α-Chloro peroxide structures have been assigned to the oligomeric autoxidation products of monomers containing vinyl chloride moieties, but to our knowledge no pure individual compounds have been isolated: (a) K. Mayumi, O. Shibuya, and S. Ichimese, *Nippon Kagaku Zassi*, **78**, 280 (1957); (b) G. A. Razuvaev and K. S. Minsker, *Zh. Org. Khim.*, **28**, 983 (1958); (c) M. Lederer, *Angew. Chem.*, **71**, 162 (1959); (d) H. A. Barabashina and L. S. Boguslavskaya, *Sov. Chem. Ind. (Engl. Transl.)*, **3**, 151 (1973).

(16) For an independent synthesis of this compound by peracid oxidation of **4**, see K. Griesbaum, R. Kibar, and B. Pfeffer, *Justus Liebigs Ann. Chem.*, 214 (1975).

(17) Attempted elemental analysis of **9** resulted in the complete shattering of the combustion equipment and insertion of a sample of **9** into the heated port (approximately 250 °C) of a mass spectrometer resulted in a violent explosion.

(18) Attempted injection of **12** into the inlet port of a gas chromatograph resulted in an explosion and the concomitant destruction of the syringe. Elemental analysis of **12** could be carried out without explosion.

(19) There is experimental evidence that the conversion of **8** into **12** may, at least in part, be brought about by reaction of acetyl chloride with the ozonide **8**. Addition of excess CD_3COCl to solutions containing **8** resulted in the formation of a mixture of **12** and of $CH_3CCl_2{-}OO{-}COCD_3$. The latter was isolated by chromatography; its structure was proven by the fact that the field ionization mass spectrum shows the fragments CH_3CCl_2 and CD_3CO, but no CD_3CCl_2 fragment. Treatment of **12** with excess of CD_3COCl did not lead to the formation of $CH_3CCl_2{-}OO{-}C({=}O)CD_3$.

(20) Prevention of ozonide formation in the presence of tetracyano ethylene has been amply demonstrated. The reactions lead to the formation of carbonyl fragments of the corresponding olefinic substrates and to tetracyanoethylene oxide: R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).

(21) Indeed, addition of concentrated aqueous hydrochloric acid to a mixture containing **8** and unconverted substrate **4** resulted in the rapid disappearance of **8** and the concomitant formation of 2,2,3,3-tetrachlorobutane (**10**).

(22) Reactions of this type have been formulated previously in order to explain the overbalance of carbonyl fragments in some ozonolysis reactions. See e.g., S. Fliszár and M. Granger, *J. Am. Chem. Soc.*, **91**, 3330 (1969), and literature cited therein.

(23) H. D. Scharf and F. Laux, *Synthesis*, **11**, 582 (1970).

Electron Bridges in the Mechanisms of Chromic Acid Oxidation of Alcohols

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Abstract: The temperature dependence of the kinetic isotope effect criterion (TIC) has been applied in studies of the Cr(VI) oxidation of a variety of alcohols. Cyclohexanol, 1-phenylethanol, and benzhydrol, regarded as normal in their behavior, display TIC parameters which are fully consistent with a pericyclic transition state of H transfer. The highly hindered alcohol di-*tert*-butylcarbinol shows evidence of a large tunneling correction which is also variable and dependent on $[H^+]$. Electron-withdrawing substitution, as in trifluoromethylphenylcarbinol, appears to exert very similar effects. These have been rationalized as an alteration in transition-state structure which allows for H transfer through the associated structure of the solvent and the ligands of the octahedral chromium (chromate ester) complex, whose decomposition is occurring in the rate-determining step of the oxidation process. While pericyclic electron transfer (where hydrogen is performing the role of the electron bridge) has not been previously identified in familiar redox systems, the transfer of electrons through a bridging structure of water molecules is not unprecedented[12-14] as an inner sphere "coordination mechanism".

The Cr(VI) oxidation of alcohols is regarded as a two-step reaction; the initial, ordinarily rapid, equilibrium formation of chromate ester is followed by a rate-determining decomposition to product. Three possible modes of hydrogen transfer have been proposed in discussions[1] of the ester decomposition mechanism (see Scheme I). Considerations bearing on possible