127. *A Study of the Mechanism of Oxidation with Chromic Acid. Part III. Glycol Fission with Chromic Acid and Chromyl Chloride.*

By R. Slack and William A. Waters.

Some carbon–carbon bond fission of 1 : 2-glycols can be effected by oxidation with chromic acid in aqueous sulphuric or glacial acetic acid solutions, and oxidation takes this course almost exclusively when chromyl chloride is used, both in carbon tetrachloride and in glacial acetic acid solutions. It has been found that chromyl chloride first reacts with 1 : 2-glycols to form a complex ($HO{\cdot}CR_2{\cdot}CR_2{\cdot}OH,2CrO_2Cl_2$) of Cr^{VI} which breaks down on addition of water, probably by hydrolysis to an oxygen di-radical (${\cdot}O{\cdot}CR_2{\cdot}CR_2{\cdot}O{\cdot}$) and a transient derivative of Cr^{V}.

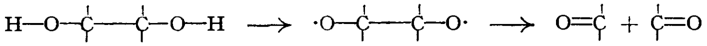
The oxidation of glycols by carbon–carbon bond fission, *e.g.*, $R{\cdot}CH(OH){-}CHR'(OH) \longrightarrow R{\cdot}CHO + R'{\cdot}CHO$, has customarily been thought to be a specific property of a few special oxidising agents such as lead tetra-acetate and periodic acid, but the postulation of a free-radical mechanism for this process (Waters, " The Chemistry of Free Radicals," Oxford, 1946) and its substantiation by the discovery that Fenton's reagent can lead to some glycol fission (Waters, *Nature*, 1946, **158**, 380) led us to examine whether any other common oxidising agents might also act, in part, in this way.

Preliminary experiments soon showed that both acid dichromate and acid permanganate solutions brought about the production of some formaldehyde from both ethylene glycol and glycerol, and of some acetaldehyde from 2 : 3-butylene glycol, whilst pinacol gave acetone in very good yield. This qualitative support for the view that homolytic bond fission may be concerned in oxidations brought about by chromic acid (compare Part I, Waters, *J.*, 1946,

1151; Part II, Slack and Waters, *J.*, 1948, 1666) has led us to study further the oxidation of 1 : 2-glycols by both chromic acid and chromyl chloride. As a result we have been able to gain much further insight into the mechanisms of the oxidations which can be effected by these two reagents.

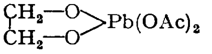
Previous evidence that chromic acid can break carbon–carbon bonds in glycols, though not unknown (see, *e.g.*, Zincke, *Annalen*, 1879, **198**, 123), is extremely rare, because in general investigators have not chosen suitable experimental conditions for isolating aldehydic products. A quantitative examination of the percentage yield of formaldehyde from ethylene glycol by chromic acid oxidation (see Table I) soon revealed the following facts : (*a*) Only a small percentage of the glycol undergoes carbon–carbon bond fission upon chromic acid oxidation in either dilute aqueous sulphuric acid or glacial acetic acid solutions. The major portion of the carbinol is oxidised in the normal way, *i.e.*, $\mathrm{CH(OH)} \longrightarrow \mathrm{C{=}O}$, to glyoxal and thence to oxalic acid. (*b*) Glycol fission can only be effected in the presence of added free acid; chromic acid (H_2CrO_4 or $H_2Cr_2O_7$) itself is not effective. (*c*) Under conditions in which pinacol is oxidised quite easily to acetone, *tert.*-butyl alcohol is completely resistant to oxidation. (*d*) In contrast, as in the oxidation effected by lead tetra-acetate (compare Leonard and Rebensdorf, *J. Amer. Chem. Soc.*, 1945, **67**, 49), chromic acid oxidises 2-hydroxytriethylamine, $\mathrm{NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$, by carbon–nitrogen bond fission to diethylamine and glyoxal, and not by carbon–carbon bond fission to formaldehyde. Triethylamine and dimethylaniline yield acetaldehyde and formaldehyde, respectively.

This broad survey showed that, whilst in the main the hypothesis of alcohol oxidation by hydrogen elimination from O—H bonds, *i.e.*,

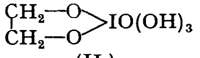


$$\mathrm{H{-}O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O{-}H} \longrightarrow \mathrm{\cdot O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O\cdot} \longrightarrow \mathrm{O{=}\overset{|}{\underset{|}{C}}} + \mathrm{\overset{|}{\underset{|}{C}}{=}O}$$

was untenable for chromic acid oxidation, it was clear that carbon–carbon bonds are more easily broken in 1 : 2-glycols than in simple paraffin chains. The analogies between chromic acid and both lead tetra-acetate and periodic acid were, however, too obvious to be overlooked.



(I.)



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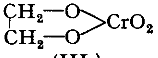


(III.)

In both these cases it has been suggested (Criegee, *Ber.*, 1931, **64**, 260; Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159; Price and Knell, *J. Amer. Chem. Soc.*, 1942, **64**, 552; Duke, *ibid.*, 1947, **69**, 3054) that glycol fission occurs by way of a cyclic compound such as (I) or (II) which then splits to an oxygen di-radical, and hence the possibility of the transient existence of a cyclic chromium intermediate (III) was envisaged.

Since Étard (*Ann. Chim. Phys.*, 1881, **22**, 218) has shown that intermediate organo-chromium complexes are regularly formed when hydrocarbons are oxidised by chromyl chloride in anhydrous solvents, it was thought that the oxidation of 1 : 2-glycols by chromyl chloride in non-polar solvents merited examination, though it was feared that the reaction might be extremely violent. Fortunately, it was then found that in dry carbon tetrachloride solution chromyl chloride reacted smoothly with a number of glycols, as for instance pinacol and hydrobenzoin, to give brownish insoluble *complexes* which could be separated and analysed. Both the *meso*- and the racemic form of hydrobenzoin reacted immediately with the chromyl chloride, and hence the complex formation is not dependent upon the presence of a *cis*-glycol structure. On addition of water these chromium complexes decomposed smoothly to give oxidised mixtures which made it evident that a high degree of glycol splitting had occurred. For instance, both hydrobenzoins regularly gave a yield of benzaldehyde of the order of 50%, although the resulting aqueous solution still contained sexavalent chromium. Under these conditions again *tert.*-butyl alcohol could not be oxidised.

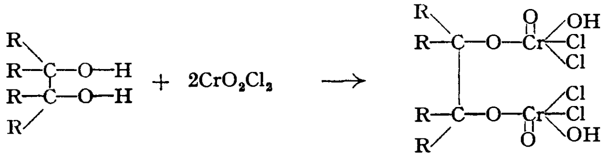
The analysis of these chromium complexes, detailed in Tables II and III, showed: (i) that the complex was formed without any loss of chlorine from the chromyl chloride; (ii) each glycol–chromium complex contains *two* chromium atoms, *i.e.*, one chromium atom must be attached to each carbinol group; (iii) the breakdown of the complex with water gives a mixture of Cr^{VI} and Cr^{III}, together with organic oxidation products in such proportions as to show conclusively that the initial complex is still a compound of sexavalent chromium, formed, without loss of any atoms, by the direct union of one molecule of glycol and two molecules of chromyl chloride, *i.e.*, $(\mathrm{HO{\cdot}CR_2{\cdot}CR_2{\cdot}OH,2CrO_2Cl_2})$.

Methods of study of the breakdown of these complexes were devised first for *meso*-hydrobenzoin, which was oxidised to a mixture of benzaldehyde and benzoic acid, but not at all to benzoin or benzil under these conditions. The benzaldehyde could be isolated as such by adding the solid complex to acid ferrous sulphate solution, and could be collected in about 40% yield. Still higher yields than this (*ca.* 50—60%) could be collected by decomposing the chromium complex with acid ferrous sulphate and immediately adding 2 : 4-dinitrophenylhydrazine, when the formation of the stable 2 : 4-dinitrophenylhydrazone protected the aldehydic group from further attack. From benzpinacol, $CHPh_2(OH){\cdot}CPh_2(OH)$, it was possible to establish that the initial yield of benzophenone was as much as 81% (Table IV). Though the titre of the quantity of iodine which is liberated when the complexes $(HO{\cdot}CR_2{\cdot}CR_2{\cdot}OH,2CrO_2Cl_2)$ are treated with potassium iodide solution corresponds very closely to the conversion of Cr^{VI} into Cr^{IV}, which is equivalent to the production of an equimolar mixture of benzaldehyde and benzoic acid from hydrobenzoin, the fact that a much higher percentage of benzaldehyde than this is first set free indicates that the *initial* breakdown of the complex must be the conversion of a Cr^{VI} compound into a derivative of Cr^{V}, which presumably disproportionates at once into Cr^{VI} (2 equivs.) and Cr^{III} (1 equiv.) or, alternatively, oxidises some of the free aldehyde.

Confirmation of these analytical figures for the breakdown of the initial glycol–chromyl chloride adducts was obtained by working in glacial acetic acid solution. In this solvent it was not possible to separate the primary products, but there were regularly obtained brown solutions which, when poured into acid ferrous sulphate containing dissolved 2 : 4-dinitrophenylhydrazine, gave aldehydic or ketonic products in yields of about 80—90%. There is, therefore, the strongest experimental evidence for supposing that a complex of sexavalent chromium is formed, and that this is decomposed by water to a transient derivative of quinquevalent chromium.

We would therefore suggest that the oxidation of 1 : 2-glycols by chromyl chloride proceeds by the following stages :

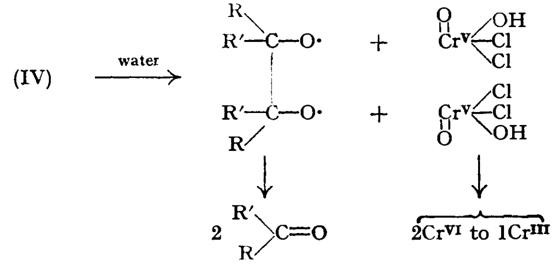
(*A*) Formation of an addition complex at each hydroxyl group :



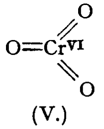
(IV.)

This must have the structure C—O—Cr because (*a*) neither chlorine nor hydrogen is lost in the complex formation, and (*b*) glycol fission with pinacol and benzpinacol shows that the original C—O link is preserved together with *all* the original CH groups.

(*B*) Breakdown of this complex to an organic di-radical and a derivative of Cr^{V}, followed immediately by (i) carbon–carbon bond fission of the organic di-radical, and (ii) disproportionation of the unstable inorganic Cr^{V} fragment :



This explanation of glycol fission by means of chromyl chloride is analogous to the explanation first offered by Criegee (*loc. cit.*) for glycol fission by lead tetra-acetate in so far as it requires the initial production of an organometallic complex, though the chromium analyses (Table III) show immediately that the formation of a *cyclic* complex is quite unnecessary. The lead, chromium, and presumably iodine complexes (I, IV, II) seem to be alike in that the heavy atom is attached to carbon through oxygen. The homolysis of the complex (stage *B* above) then, in all cases, occurs at the weak *oxygen–heavy atom* covalency, and evidently the driving force of this process is the tendency of the highly oxidised heavy atom (Pb^{IV}, Cr^{VI}, or I^{VII}) to achieve its more stable reduced form by withdrawing an electron into an inner orbital from the outermost valency shell. One of us (Waters, *Trans. Faraday Soc.*, 1946, **42**, 184) has already suggested tentatively that the oxidising power of chromium trioxide is to be associated with the double-bond character of its oxygen–chromium bonds. It may be significant that chromium trioxide (V) with three double bonds is more stable than chromyl chloride with but two (VI), and to suggest that the enhanced reactivity of chromyl chloride is due to electron withdrawal from the strongly electrophilic nucleus Cr^{VI} towards the chlorine nuclei. If this is so, then the withdrawal of further electrons from the chromium nucleus upon the formation of the unstable glycol–chromium chloride complex (IV) will give a still less stable structure in which the tendency of chromium to acquire complete control of one of the electrons of the O–Cr covalency, and to absorb it into an inner electronic shell, will be very strong indeed. The hydration of the last remaining Cr═O bond, upon the advent of water, would bring about a further electron withdrawl from chromium, and might well be the decisive factor in ensuring the homolysis of the Cr–O link.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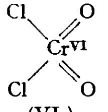
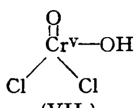

(VI.)


(VII.)

Finally, we would point out that, though we have obtained no evidence for the independent existence of the quinquevalent chromium fission product (VII), there is available a substantial amount of experimental proof of the real existence of compounds of quinquevalent chromium (*e.g.*, the pyridine and quinoline complexes; Weinland and Fridrich, *Ber.*, 1905, **38**, 3784).

The fact that a significant amount of glycol fission can be achieved with aqueous solutions of chromic acid would appear to indicate that this reagent has some slight action on H–O bonds. Chromyl chloride can undoubtedly attack C–H bonds in Étard oxidations of hydrocarbons such as toluene, and it is difficult to see why a similar attack on C–H does not occur easily in glycols such as hydrobenzoin, or again why this reagent does not attack *tert*-butyl alcohol.

EXPERIMENTAL.

Fission of 1 : 2-*Glycols with Chromium Trioxide.*—The aliphatic glycols were carefully purified by fractional distillation, *n*-octane-4 : 5-diol being prepared from butyroin (Snell and McElvain, *Org. Synth.*, Coll. Vol. II, p. 114) by the method of Bouveault and Locquin (*Bull. Soc. chim.*, 1906, **3**, **35**, 644). *meso*-Hydrobenzoin (Buck and Jenkins, *J. Amer. Chem. Soc.*, 1929, **51**, 2163) was crystallised to constant m. p. Oxidations were carried out either in aqueous or in aqueous acetic acid solution at 90° by adding a standard solution of chromium trioxide dropwise to a known amount of glycol which was always taken in excess. In order to minimise secondary oxidation of aldehydes, a current of carbon dioxide was used to sweep out the volatile product through an efficient fractionating column into ice-cold saturated solutions of either (i) 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, or (ii) aqueous dimedone. When (ii) was used the effluent gases were finally passed through (i) so as to provide a rapid visual check of quantitative absorption of carbonyl compounds. Following Yoe and Reed (*Ind. Eng. Chem. Anal.*, 1941, **13**, 238), the dimedone reagent was buffered to pH 4·0 for the determination of acetaldehyde, and to pH 4·6 for that of formaldehyde. In the former case the reagent was used in very large excess, and then gave a recovery of 85—90%. Yields in Table I are calculated on the basis $HO{\cdot}CHR{\cdot}CHR{\cdot}OH \longrightarrow 2R{\cdot}CHO$.

TABLE I.

Glycol fission with chromium trioxide.

Expt. no.	Glycol (large excess).	Solvent (ml.).	H_2SO_4, conc. (ml.).	CrO_3 (ml. of 2%).*	Yield, %.	Collector.*
1	Ethylene	40	5	10	1·8 CH_2O	D
2	,,	40	5	10	1·7 ,,	DNP
3	,,	40 (A)	0	10 (A)	0·0 ,,	DNP
4	,,	40 (A)	5	10 (A)	trace ,,	DNP
5	2-Butylene	40	5	10	[Me·CHO + $(MeCO)_2$]	
6	,,,	40	5	10	20·2 Me·CHO	D
7	,,	40 (A)	5	10	28·2 ,,	D
8	,,	40	5	(10 of 0·5%)	30·4 ,,	D
9	,,	40 (A)	0	10 (A)	18·2 ,,	D
12	Octane-4 : 5-diol	40 (A′)	5	10 (A′)	15·0 Pr·CHO	D
13	,,	49 (A′)	5	10 (A′)	24·2 ,,	D
14	,,	40 (A′)	5	10 (A′)	27·9 ,,	D
15	,,	40 (A)	0	10 (A) (of 0·5%)	16·0 ,,	D

* A = glacial acetic acid; A′ = 50% acetic acid; D = saturated dimedone; DNP = 2 : 4-dinitrophenylhydrazine.

Reaction of 1 : 2-*Glycols with Chromyl Chloride.—Materials.* The previously mentioned glycols were used, together with racemic hydrobenzoin, prepared by Breuer and Zincke's method (*Annalen*, 1879, **198**, 154), and benzpinacol, which was made by reduction of benzophenone with *iso*propyl alcohol (Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 391) or with zinc and acetic acid (Sagumenny, *Bull. Soc. chim.*, 1880, **34**, 329).

Chromyl chloride was prepared by the method of " Inorganic Syntheses " (1946, II, 205); a very pure product (*ca.* 99%) is obtainable without distillation if a number of washings with concentrated sulphuric acid are carried out. The carbon tetrachloride was purified with Fehling's solution to remove chloroform. This was found to be an essential precaution.

Methods of analysis. The glycol–chromyl chloride *complexes* were precipitated when the reactants were mixed in dry cold carbon tetrachloride solution. They were filtered off in sintered-glass crucibles. washed with carbon tetrachloride, and dried in a vacuum. Chlorine was determined as silver salt after decomposition of the complex with dilute nitric acid and extraction of organic material with ether; total chromium was determined by reduction of Cr^{VI} with alcohol, precipitation as $Cr(OH)_3$, and ignition to Cr_2O_3; sexavalent chromium was determined by adding the complex to acidified potassium iodide and subsequently titrating with thiosulphate.

TABLE II.

Analyses of chromyl chloride complexes ($HO{\cdot}CR_2{\cdot}CR_2{\cdot}OH,2CrO_2Cl_2$).

Chloride analyses.			Total chromium analyses.		
Wt. of complex, g.	Wt. of AgCl, g.	Cl, %, found.	Wt. of complex, g.	Wt. of Cr_2O_3, g.	Cr, %, found.
meso-Hydrobenzoin complex.*					
0·4002	0·4211	26·1	0·2853	0·0833	19·1
0·4886	0·5300	26·9	0·1858	0·0573	20·3
Racemic hydrobenzoin complex.*					
0·5179	0·5671	27·1	0·5112	0·1551	20·7
Pinacol complex.†					
0·4061	0·5380	32·8	0·4112	0·1510	25·1

* $C_{14}H_{14}O_6Cl_4Cr_2$ requires Cl, 27·1; Cr, 19·9%.
† $C_6H_{14}O_6Cl_4Cr_2$ requires Cl, 33·2; Cr, 24·3%.

TABLE III.

Yields and proportion of Cr^{VI} *on hydrolysis of complexes.*

Glycol taken :		CrO_2Cl_2 taken :				
g.	moles.	g.	moles.	Complex collected, g.	Yield, %.	Cr^{VI}, %, found.
meso-Hydrobenzoin complex.						
0·224	0·001	0·1704	0·0011	0·2870	54·8	13·7
0·224	0·001	0·2324	0·0015	0·3991	76·2	13·3
0·224	0·001	0·2324	0·0015	0·3889	74·2	13·0
0·224	0·001	0·4647	0·003	0·5176	98·8	12·1
0·224	0·001	0·4647	0·003	0·5197	99·2	13·8
Racemic hydrobenzoin complex.						
0·224	0·001	0·4645	0·003	0·5112	97·6	12·9
Pinacol complex.						
0·118	0·001	0·351	0·0023	0·4112	96·2	20·3

The benzpinacol complex was too hygroscopic, and too soluble in carbon tetrachloride, for convenient collection or accurate analysis.

Determination of Organic Fission Products.—The following methods were used : (*a*) Solid products prepared by precipitation from carbon tetrachloride were decomposed by the aqueous 2 : 4-dinitrophenylhydrazine reagent (above) in the presence of an excess of ferrous sulphate and sulphuric acid. The 2 : 4-dinitrophenylhydrazone was collected, dried at 110°, and weighed.

(*b*) A known amount of glycol was dissolved in purified glacial acetic acid, and a *freshly-prepared* solution of chromyl chloride in the same solvent was added in amount very slightly more than two molar proportions. The solution was adjusted to a known volume with either acetic acid or ferrous sulphate in sulphuric acid, and aliquots were then added to the 2 : 4-dinitrophenylhydrazine reagent containing ferrous sulphate in large excess. The results in Table IV show that, provided conditions are such that an *immediate* removal of aldehyde can be obtained, an almost quantitative fission of the glycol–chromyl chloride complex to $2R{\cdot}CHO$ and $2Cr^V$ must occur. If, on the other hand, reaction mixtures are first decomposed by ferrous sulphate solution and then treated with 2 : 4-dinitrophenylhydrazine, the yields of aldehyde are much lower. Evidently free aldehyde is oxidised in preference

TABLE IV.

Yields of organic products from glycol fission.

Glycol.	Procedure.	Yield, %.*	
meso-Hydrobenzoin	(a)	52	Ph·CHO
do.	(a)	48·2	
do.	(a)	60	
do.	(b)	84·2	
do.	(b)	88	
do.	(b)	89	
Racemic hydrobenzoin	(b)	89·6	
do.	(b)	91	
Benzpinacol	(b)	81	$COPh_2$
Pinacol	(b)	68	$COMe_2$
do.	(b)	71	

* Calculated from weight of 2 : 4-dinitrophenylhydrazone collected.

to Fe^{++}. In each experiment the 2 : 4-dinitrophenylhydrazone was collected, recrystallised, and shown to be a chemically pure product.

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