17. *The Oxidation of Glycols with Lead Tetra-acetate. A Kinetic Study.*

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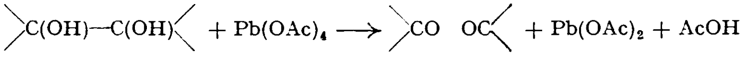
The rates of oxidation of a number of glycols by lead tetra-acetate have been measured in glacial acetic acid solution. The oxidation of ethylene glycol in aqueous acetic acid of varied composition has also been studied. A modification of the currently accepted mechanism of this reaction is proposed.

ALTHOUGH lead tetra-acetate is a very versatile oxidising agent (Criegee, "Newer Methods of Preparative Organic Chemistry," Interscience Publ., 1948, p. 1), perhaps its principal use is in the oxidation of glycols. Aldehydes or ketones are thus formed under very mild conditions (usually room temperature) :

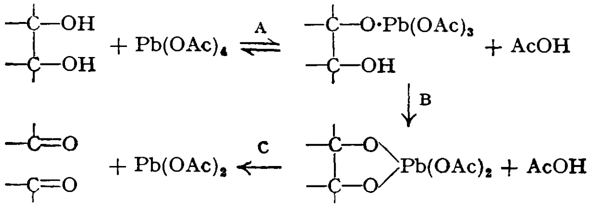


$$>C(OH)-C(OH)< + Pb(OAc)_4 \longrightarrow >CO \quad OC< + Pb(OAc)_2 + AcOH$$

Bell, Sturrock, and Whitehead (*J.*, 1940, 82) have found that this reaction is of first-order with respect to both glycol and lead tetra-acetate in acetic acid solution. Criegee (*Sitzungsber. Ges. Naturwiss. Marburg*, 1934, **69**, 26) has also found that the overall reaction is of second order in acetic acid but of a complex order when any other solvent is used. In addition, the rate of reaction is increased, by a factor of about 10^3, when acetic acid is replaced by benzene, nitrobenzene, 1 : 2-dichloroethane, or 1 : 1 : 2 : 2-tetrachloroethane.

Two other important points noted by Criegee are (*a*) that *cis*-glycols react more readily than the corresponding *trans*-compounds, the difference being more marked in 5-membered than in 6-membered rings, and (*b*) that lead tetra-acetate reacts with methyl alcohol, containing a small quantity of water, forming $Pb(OAc)_2(OH)(OMe)$.

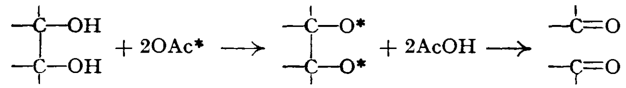
On the basis of these results, Criegee, Kraft, and Rank (*Annalen*, 1933, **507**, 159) proposed the following mechanism :



By assuming that stage (B) is rate-determining, they were able to satisfy both the second-order kinetics and the fact that a *cis*-glycol reacts more readily than its *trans*-isomer. Furthermore, the isolation of $Pb(OAc)_2(OH)(OMe)$ (see above) appears to support stage (A).

This mechanism was criticised by Waters (" Chemistry of Free Radicals," Oxford, 1946, p. 230) who proposed the following :

$$Pb(OAc)_4 \rightleftharpoons Pb(OAc)_2 + 2OAc^*$$



Although Waters satisfactorily explained the second-order kinetics, Kharasch, Friedlander, and Urry (*J. Org. Chem.*, 1949, **14**, 91) disproved this alternative suggestion by showing that acetyl peroxide (which definitely furnishes acetoxy-radicals) does not cause glycol fission.

Although Criegee and his co-workers have oxidised a large number of glycols, there has been no attempt to investigate the effect of substituents in simple aromatic glycols. The present work is concerned, *inter alia*, with the oxidation of tetra-substituted benzopinacols, which were chosen as they do not display optical isomerism.

EXPERIMENTAL

Reagents.—Lead tetra-acetate, prepared by Bailar's method (" Inorganic Syntheses," McGraw-Hill, 1939, Vol. 1, p. 47), was crystallised from acetic acid and stored in a desiccator under vacuum. The minimum purity (estimated by iodometric titration, see below) was 97·5%.

Acetic acid was purified by Eichelberger and LaMer's method (*J. Amer. Chem. Soc.*, 1933, **55**, 3633). The m. p. was always in the range 16·0—16·2°, corresponding to 0·2—0·3% of water (Rudorff, *Ber.*, 1870, **3**, 390). Water was twice distilled from potassium permanganate in an all-glass apparatus. All glycols were either distilled, or crystallised, twice : ethylene glycol, b. p. 177°, n_D^{19} 1·4289; propylene glycol, b. p. 186°, n_D^{20} 1·4310; glycerol α-monochlorohydrin, b. p. 129°, n_D^{21} 1·4778; (±)-*iso*butyl tartrate, m. p. 70°; pinacol hydrate, m. p. 46°; pinacol, m. p. 40°; benzpinacol, m. p. 185°; 4 : 4′ : 4″ : 4‴-tetramethoxybenzpinacol, m. p. 181°; 4 : 4′ : 4″ : 4‴-tetrachlorobenzpinacol, m. p. 173°; 4 : 4′ : 4″ : 4‴-tetramethylbenzpinacol, m. p. 183°.

Apparatus.—A bath was used whose temperature was controlled within ±0·05°. The slow reactions were performed in a calibrated standard 50-ml. flask (slow method) and the fast reactions in a " Dreischenkelrohr " (Criegee, *Annalen*, 1932, **495**, 219) (fast method).

Methods of Estimation.—*Slow method.* The glycol (*ca.* 10^{-3} mole) was weighed into the reaction vessel, which was brought to the temperature of the bath. A solution of lead tetra-acetate (*ca.* 2·5—3·0 × 10^{-2}M) in acetic acid, also heated in the bath, was added to make up to the mark. When the glycol dissolved slowly, it was first dissolved in acetic acid in the flask and then a known volume of a solution of lead tetra-acetate was added, along with acetic acid to make up to the mark, so that the resulting molarities were the same as quoted above. 5-Ml.

aliquots were withdrawn at determined times and added to 4—5 ml. of " stopping solution," *i.e.*, potassium iodide (100 g.) and sodium acetate (500 g.) dissolved in water (1 l.). The iodine liberated was titrated with 0·02N-sodium thiosulphate (starch). It was unnecessary to filter off the precipitated lead iodide as recommended by Bell, Sturrock, and Whitehead (*loc. cit.*). The lead tetra-acetate solution was also estimated.

Fast method. Previously determined solutions (3 ml. of each) of lead tetra-acetate (*ca.* 2·5—3·0 $\times 10^{-2}$M) and glycol (*ca.* 2 $\times 10^{-2}$M) in acetic acid were placed in each of the lower bulbs of the " Dreischenkelrohr." " Stopping solution " (4 ml.) was placed in the side bulb. After attaining temperature equilibrium in the bath (10 minutes), the reacting solutions were mixed and, at a definite time, the " stopping solution " was added. The liberated iodine was estimated as above.

The lead tetra-acetate solutions were found to be stable under the various conditions used.

All experiments were performed in duplicate (agreement within 5%), and the accuracy obtained by the two methods is approximately the same.

Results.—The reaction of ethylene glycol with lead tetra-acetate, in acetic acid containing 10 moles % of water, at 25° is given below as a typical example; the slow method was used.

Initial glycol concn. = 0·01966M ($\equiv$ 7·845 ml. $Na_2S_2O_3$).
Initial lead tetra-acetate concn. = 0·02629M ($\equiv$ 10·495 ml. $Na_2S_2O_3$).
First lead tetra-acetate estimation = 9·730 ml. (*b*).
Equivalent glycol concn. = 7·080 ml. (*a*).

Time (min.)	70	110	150	210	270	330	420
Titre obs.	8·55	8·04	7·60	7·03	6·58	6·20	5·72
Titre calc.	8·56	8·06	7·61	7·04	6·58	6·18	5·71

By plotting $\log_{10} a(b - x)/b(a - x)$ against t and calculating the slope by the method of least squares, k was calculated from the equation $k = 2{\cdot}303 \times \text{slope}/(b - a)$ and found to be $1{\cdot}84 \times 10^{-3}$ mole^{-1} l. sec.$^{-1}$. The results obtained at different temperatures are summarised below (averages in parentheses):

Temp.	35·15°	25·00°	17·90°
10^3k	6·55, 6·13 (6·34)	1·93, 1·83 (1·88)	0·695, 0·714 (0·704)

The bimolecular constants obey the Arrhenius equation as shown by the following data, where the calculated values are given by $k = 7{\cdot}75 \times 10^{13}\ e^{-22{,}610/RT}$:

Temp.	35·15°	25·00°	17·90°
10^3k obs.	6·34	1·88	0·705
10^3k calc.	6·37	1·80	0·708

The results obtained with different glycols in acetic acid (0·2—0·4% of water) are summarised in Table 1, duplicates being shown:

TABLE 1.

Compound	Temp.	$k \times 10^3$	$10^{-14}A$	*E* (kcal.)
Ethylene glycol *	18°	0·408, 0·379	17·1	22·1
	25	1·02, 1·04		
	35	3·23, 3·35		
Propylene glycol *	18	4·06, 3·66	1·82	22·1
	25	9·39, 9·67		
	35	33·8, 31·0		
Glycerol α-monochlorohydrin *	18	1·70, 1·61	6·55	23·4
	25	4·32, 4·54		
	35	16·1, 14·7		
*iso*Butyl tartrate *	18	2·12, 2·38	38·2	20·2
	25	5·29, 4·85		
	35	15·7, 15·5		
Pinacol *	18	6·44, 5·78	7·34	22·7
	25	14·8, 14·7		
	35	53·0, 53·0		
Pinacol hydrate *	18	5·34, 5·18	1·59	23·2
	25	13·9, 14·6		
	35	48·6, 48·4		

Compound	Temp.	$k \times 10^3$	$10^{-10}A$	*E* (kcal.)
Benzpinacol †	18°	95·4, 89·5	16·6	13·6
	25	160, 161		
	35	328, 354		
4 : 4′ : 4′′ : 4′′′-Tetramethoxybenzpinacol †	18	383, 367	43·2	13·4
	25	618, 581		
	35	1290, 1390		
4 : 4′ : 4′′ : 4′′′-Tetramethylbenzpinacol †	18	160, 174	9·09	15·3
	25	329, 337		
	35	715, 773		
4 : 4′ : 4′′ : 4′′′-Tetrachlorobenzpinacol †	18	49·1, 47·1	3·30	15·7
	25	93·4, 88·8		
	35	216, 226		

* By slow method. † By fast method.

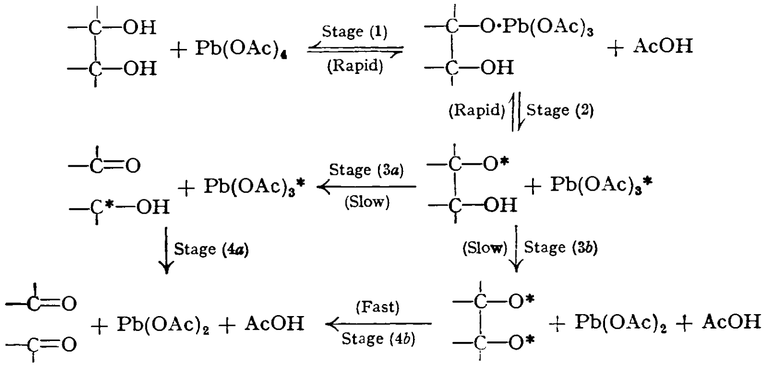
The results obtained with ethylene glycol in aqueous acetic acid are summarised below, duplicate values of *k* being shown:

TABLE 2.

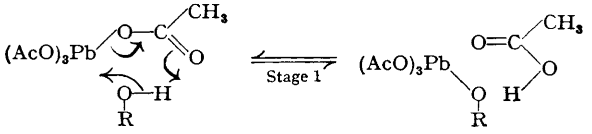
H_2O, moles %	*T*	$k \times 10^3$	*A*	*E* (kcal.)	H_2O, moles %	*T*	$k \times 10^3$	*A*	*E* (kcal.)
1	18°	0·408, 0·379	$1·73 \times 10^{13}$	22·1	20	18°	1·08, 1·08	$4·71 \times 10^{13}$	23·4
	25	1·02, 1·04				25	3·04, 2·70		
	35	3·23, 3·35				35	10·60, 10·66		
5	18	0·550, 0·522	$1·42 \times 10^{13}$	21·5	30	18	1·73, 1·96	$3·24 \times 10^{14}$	23·0
	25	1·26, 1·37				25	4·13, 4·50		
	35	4·47, 4·39				35	15·6, 14·9		
10	18	0·695, 0·714	$7·75 \times 10^{13}$	22·6	40	18	3·76, 3·75	$9·20 \times 10^{10}$	17·8
	25	1·93, 1·83				25	7·91, 8·34		
	35	6·70, 6·25, 6·08				35	21·4, 20·0		

DISCUSSION

Although Criegee has shown that his mechanism is concordant with the observed second-order kinetics, it is naturally possible to formulate many mechanisms which satisfy this requirement. The following mechanisms are satisfactory in this regard and it is desired to compare them with Criegee's formulation.



It is thus seen that stage (1) is the esterification proposed by Criegee and the following scheme is proposed :

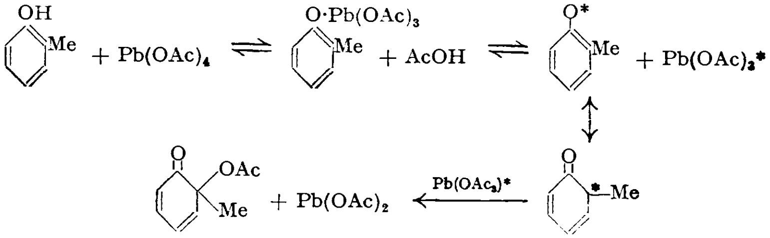


The present work supports Criegee's arguments for the validity of this stage because it is seen that, with the substituted benzpinacols, electron-releasing groups (Me, OMe), accelerate the reaction whereas an electron-attracting group (Cl) retards it. This is in accord with the fact that the Pb–OR bond formation would be favoured by increased availability of electrons on the oxygen atom, thus displacing the equilibrium to the right. Furthermore, work on aryl iodosoacetates strongly supports this view (see following paper) as it has been found that the rate is increased when an electron-attracting group is on the aryl nucleus and decreased when an electron-donating group is present.

Stage (2) represents a normal dissociation of quadrivalent lead compounds which has already been postulated by many authors (cf. Kharasch, Friedlander, and Urry, *J. Org. Chem.*, 1951, **16**, 533).

Stage (3*a*) is analogous to the decomposition of the *tert.*-butyloxy-radical into methyl radical and acetone (Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88). However, it is incorrect to assume this stage, for it was found that lead tetra-acetate remained unchanged in the presence of *tert.*-butyl alcohol and triphenylmethanol. As Merz and Waters (*J.*, 1949, S 21) have found that Fenton's reagent readily oxidises *tert.*-butyl alcohol, stage (3*a*) must be abandoned, as it is similar to the established intermediates involved in oxidation by Fenton's reagent. Consequently, stage (3*b*) is preferred and this may be regarded as being simultaneous with stage (2). It is thus seen that the products resulting from stage (3*b*), and their subsequent decomposition, are the same as those that have already been postulated by Waters (*op. cit.*) for this reaction.

A homolytic fission is to be preferred in place of Criegee's cyclisation mechanism for the following reasons. (*a*) Lead tetra-acetate displays radical reactions in glycol fission which are consistent with nearly all other reactions of this compound. (*b*) The oxidation of phenols by lead tetra-acetate in acetic acid (Wessely, Lautebach-Kiel, and Sinwel, *Monatsh.*, 1950, **81**, 811; Wessely and Sinwel, *ibid.*, p. 1055) can be explained by the same type of mechanism. These authors found that phenols are oxidised to derivatives of *cyclo*hexadienone at room temperature; *e.g.*, *o*-cresol yields 2-acetoxy-2-methyl*cyclo*hexa-3 : 5-dien-1-one. This reaction is now assumed to occur as follows:



(*c*) The oxidation of *trans*-decalin-9 : 10-diol, which, as Criegee, Büchner, and Walther (*Ber.*, 1940, **73**, 571) have stated, cannot form a cyclic intermediate, can now be accommodated by this theory. It is no longer necessary to assume, as these authors do, that the oxidation of this particular compound proceeds by a different mechanism. (*d*) Criegee and Büchner (*ibid.*, p. 563) have found that the pinacols formed by the reduction of *cyclo*pentanone, *cyclo*hexanone, and *cyclo*heptanone are oxidised more rapidly the larger the ring system. It may be possible to explain this fact by assuming that the initial homolytic fission will occur more readily if the attached rings are large enough to strain the bonds involved. Similarly, the observed increase in rate (and decrease in A and E) of aromatic glycols, compared with aliphatic compounds, may be explained (see Table 1).

However, the crucial point that has not yet been explained on the basis of this mechanism is the fact that *cis*-glycols react more readily than *trans*-compounds. It has been shown (Martinet and Martinet, *Bull. Soc. chim.*, 1949, **57**, 71; Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 415) that glycols with free rotation display intramolecular hydrogen bonding. It would also be expected that *cis*-glycols would display this type of bonding whereas *trans*-glycols would be bonded intermolecularly. Thus, whereas only one hydrogen participates in hydrogen bonding in *cis*-glycols, both may participate in *trans*-glycols with a consequent diminution in rate (for further discussion of this point, see following paper).

It is seen (Table 2) that the variations of A and E with solvent composition were markedly similar. It is possible that the initial increase in A and E is due to a change in the dielectric constant of the medium but, after a critical value of *ca.* 25 moles% of water, the water molecules tend to replace acetic acid in the solvating atmosphere, with a subsequent decrease in A and E. This is in contrast to the explanation given by Criegee and Büchner (*loc. cit.*) that "nascent" lead dioxide is the oxidising agent.

Finally, we think some of Criegee's results should be regarded with caution. For example (*Sitzungsber. Ges. Naturwiss. Marburg*, 1934, **69**, 26), he has investigated no fewer than 18 reactions whose half-time is less than 10 seconds solely by means of a "Dreischenkelrohr." The rate constants given for these reactions are meaningless. In addition, nearly all his A and E values have been determined from measurements made at only two temperatures, and the water content of his acetic acid has never been rigidly specified except in the one paper by Criegee and Büchner (*loc. cit.*)

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