

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Kinetics of the Periodate Oxidation of 1,2-Glycols. II. Ethylene Glycol, Pinacol and *cis*- and *trans*-Cyclohexene Glycols

BY CHARLES C. PRICE AND MARTIN KNELL

The previous report<sup>1</sup> of the kinetics of the periodate oxidation of pinacol in solutions of varying *p*H showed a complex relation between the second-order rate constant for the reaction and the *p*H of the solution. There is a minimum in the *p*H range 4.5–5.5 and a maximum slightly on the basic side of neutrality. These observations have now been substantiated and extended; similar measurements have also been carried out with ethylene glycol and *cis*- and *trans*-cyclohexene glycols but no such complex variation in rate with *p*H was found with the latter substances.

The two cyclohexene glycols were prepared<sup>2</sup> from cyclohexene: the *cis*-isomer, m. p. 92°, by direct oxidation with dilute aqueous potassium permanganate and the *trans*-isomer, m. p. 100°, through hydration of cyclohexene oxide<sup>3</sup> with dilute hydrochloric acid.

Standard solutions of the various glycols were prepared from weighed samples. The concentrations were checked by oxidation with excess periodic acid. The reaction mixtures were prepared by mixing standard solutions of the glycol with standard periodate of given *p*H. The initial concentrations of periodate and glycol were approximately 0.01 molar in all the experiments reported herein.

Samples pipetted from reaction mixtures maintained at 25° were run into acidic potassium iodide and the liberated iodine titrated with standard sodium thiosulfate. Immediately after each reaction mixture was prepared, a sample was withdrawn and placed in the cell of a Hellige *p*H meter; the *p*H of the solution was thus observed throughout the course of the oxidation.

For a majority of initial values for the *p*H (approximately 1 to 7.5 and 10 to 11.5), the acidity remained essentially unchanged during the course of the reaction. In these cases, the second-order rate constant was determined readily as the slope of the straight line obtained by plotting

$$\frac{2.303}{A - B} \log \frac{A - x}{B - x}$$

(1) Price and Kroll, *THIS JOURNAL*, **60**, 2726 (1938).

(2) The authors are indebted to Harry Cohen for the preparation of these glycols.

(3) "Org. Syntheses," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1925, p. 35.

against the time in minutes (*A* and *B* are the initial concentrations of periodate and glycol, respectively, in moles per liter, and *x* is the amount which has reacted at time *t*).

Since periodic acid is dibasic whereas iodic acid is monobasic, in the range of *p*H from approximately 7.5 to 10 there should be, and is, a marked increase in basicity as the periodate is converted to iodate. Since the rate constant is dependent on the *p*H, in these instances the plot of

$$\frac{2.303}{A - B} \log \frac{A - x}{B - x}$$

against time is not a straight line but a smooth curve. The *slope* of these curves, however, should give the rate constant; tangents to the curves were therefore drawn at various points of known *p*H and the slope of the tangent was taken as the rate constant at that particular *p*H. That a fairly accurate estimate of the rate constant ( $\pm 10\%$ ) could be obtained in this manner is indicated by the fact that experiments at varying initial *p*H values gave rate constants in good agreement for points of corresponding *p*H.

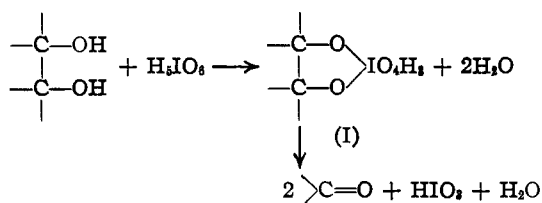
The results of all the kinetic measurements for all four glycols are summarized in Fig. 1, where the logarithms of the second-order rate constants for the oxidations are plotted against the *p*H of the reaction medium.

It will be noted that only pinacol shows a relatively complex variation in rate with the *p*H of the solution. For the other glycols on the basic side of neutrality the rate constants are roughly proportional to the hydrogen ion concentration (the dotted lines of unit slope in Fig. 1 represent such a dependence). On the acid side of neutrality, the rate constant for ethylene glycol is essentially independent of the *p*H. The same relationship *may* hold for the cyclohexene glycols. For the *cis*-isomer at *p*H values of 2, 3 and 6 and for the *trans*-isomer at 2 and 3 the reactions were complete in two minutes. For any value of the rate constant over about five hundred the reaction would reach completion (within the experimental error of about  $\pm 0.5\%$ ) in less than two minutes. We were thus unable to determine experimentally whether the rate of oxidation of the

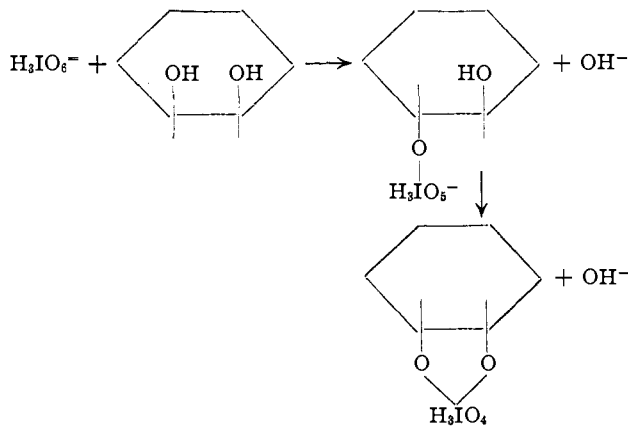
two cyclohexene glycols actually became independent of *pH* in acid solutions.

The previous observation that pinacol was oxidized more rapidly than ethylene glycol in basic solution but more slowly in acidic solution<sup>1</sup> is clearly indicated in Fig. 1.

Criegee<sup>4</sup> has already noted the fact that periodic acid, like lead tetraacetate, oxidized *cis*-glycols more rapidly than the *trans*-isomers, a fact which is also clearly indicated in Fig. 1 for *cis*- and *trans*-cyclohexene glycols. Criegee<sup>4</sup> has suggested that a logical interpretation of the more ready oxidation of *cis*-glycols might be the formation of a cyclic intermediate, an ester of periodic acid (I).



An interesting point in this connection is the mechanism of esterification to form such an ester of periodic acid. Since periodic acid could presumably contain only single or semipolar bonds uniting the oxygen and iodine atoms, the possibility of esterification through intermediate addition to a double bond is precluded and the most probable course for such a reaction would appear to be by a bimolecular inversion mechanism. Formation of a cyclic diester would thus involve two inversions and would proceed most readily when the two hydroxyl groups were *cis*.



For similar anionoid attack by undissociated periodic acid, an oxygen atom attached to iodine

(4) Criegee, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **69**, 25 (1934).

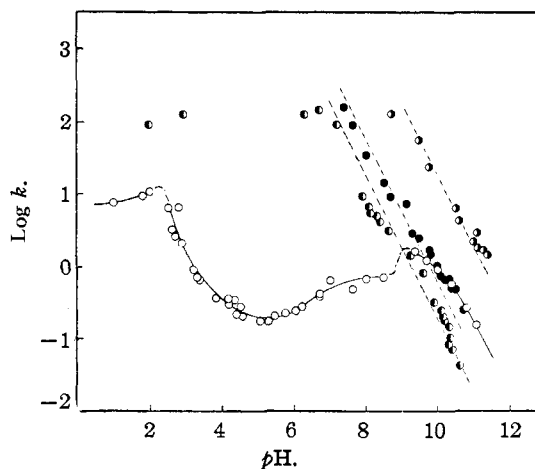
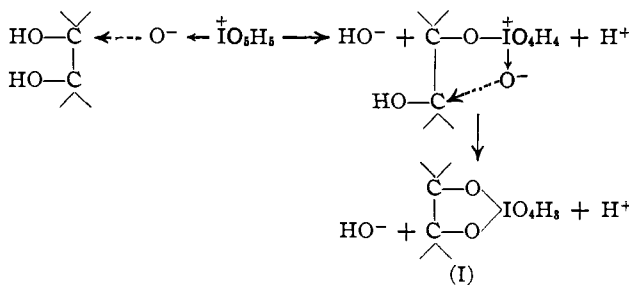


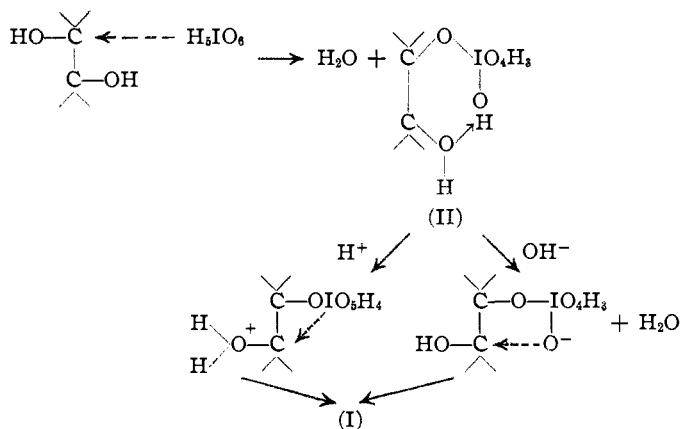
Fig. 1.—Logarithm of the rate constant plotted against the *pH* (dotted straight lines have unit slope): O, pinacol; ○, ethylene glycol; ●, *trans*-cyclohexene glycol; ◐, *cis*-cyclohexene glycol.

by a semipolar bond may serve as the anionoid center in the replacement of the hydroxyl group (with inversion).



If one assumes that the second step, ring formation, is the rate-controlling step in the process, then the *cis*-isomers would indeed tend to react more readily than *trans*. For compounds in which the possibility of free rotation exists, any factor tending to hold the ester and adjacent hydroxyl groups on the same side of the molecule would exert an inhibitory effect on the rate-controlling step of ring formation. Such an effect might be caused by the association of an acidic hydrogen of the periodate in the mono ester with the adjacent hydroxyl group.

Tendency toward formation of such a chelated cyclic intermediate (II) would depend on the base strength of the hydroxyl group. The ring would be broken by acid since a proton from a strong acid would displace the acid hydrogen of the periodate, or by base since the acid hydrogen of the periodate would be neutralized. Disruption



of the chelate ring by either means would allow the molecule to assume a configuration more favorable for ring closure by inversion to form the cyclic diester. If pinacol is the only one of the four glycols sufficiently basic to chelate with the periodate group, the anomalous behavior of this glycol could be qualitatively accounted for since ring closure could occur more readily in strongly acidic or strongly basic solution than in the intermediate range. Actually one would predict that a tertiary hydroxyl group (as in pinacol) would be

more basic than a primary (as in ethylene glycol) or a secondary hydroxyl group (as in *cis*- and *trans*-cyclohexene glycols).

This mechanism, involving successive formation of a mono- and cyclic diester of periodic acid would satisfactorily account for the proportionality of the rate of oxidation to the hydrogen-ion concentration in basic media (or the equivalent inverse proportionality to hydroxyl ion concentration) since the more basic the solution, the greater would be the tendency toward saponification of the intermediate monoester before ring closure could occur.

### Summary

The second-order rate constants for the oxidation of ethylene glycol, pinacol, and *cis*- and *trans*-cyclohexene glycols by aqueous periodate have been determined over a considerable range in *pH*. The results have been interpreted on the basis of the suggestion by Criegee that the rate-controlling step of the oxidation is the formation of a cyclic diester of periodic acid.

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## The Action of Sodium on Hexamethylacetone

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In 1934 Favorsky and Nazarov<sup>3</sup> reported that the sodium ketyl of hexamethylacetone formed<sup>4</sup> tetra-*t*-butylethylene glycol, and that rearrangement of this glycol by means of sulfuric acid yielded tri-*t*-butylpinacolone. These highly branched chain compounds seemed worth while re-investigating, because this rearrangement of the glycol involves the only known case of a tertiary group migrating in an open chain compound from carbon to carbon,<sup>5</sup> the ketone formed is the

only known compound having three tertiary groups attached to a single carbon atom, and because it is not possible to prepare Fisher-Hirschfeld atomic models of either of these complex substances.

It was found that hexamethylacetone readily formed a ketyl with sodium, but the dimolecular ment of phenol ethers [Smith, *THIS JOURNAL*, **55**, 3718 (1933)], or substituted anilines [Hickinbottom, *J. Chem. Soc.*, 404 (1937)], where again the hindrance to the incoming group is reduced no doubt by the planar configuration of the benzene ring, and the presence of only one hydrogen atom at the place of entry. The only known migrations of a tertiary group from carbon to carbon are found in the Wagner rearrangements of bicyclic terpenes, or their derivatives, such as that of pinene hydrochloride to isobornyl chloride, in which it would appear any hindrance to acceptance of the migrating group is removed by having the place of entry held open by the rigid ring structure. In other cases, the tertiary group may start to shift, but due to its inability to enter a new position, it becomes lost en route as an olefin [Whitmore and Stahly, *THIS JOURNAL*, **55**, 4153 (1933); Nazarov, *C. A.*, **30**, 4147 (1936)], or, in the case of bicyclic terpenes, may appear in the 4 position as an isopropylidene group, as in the formation of dipentene from pinene. The ease of acceptance of a migrating group by another atom may therefore be as important, in determining the products of a rearrangement, as the actual migration tendencies of the groups themselves.

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(3) Favorsky and Nazarov, *Bull. soc. chim.*, [5] **1**, 46 (1934).

(4) After acidification.

(5) Migrations of tertiary groups from carbon to nitrogen are well-known, as in the Hoffman rearrangement of amides [Van Erp, *Rec. trav. chim.*, **14**, 1 (1895)], the Beckmann rearrangement of oximes [Wallach and Kempe, *Ann.*, **329**, 82 (1903)], and in similar rearrangements in which the nitrogen appears to be stripped here, at some moment, of all atoms save the adjoining carbon atom, and hence presents no hindrance to the incoming group. Similar migrations from oxygen or nitrogen to carbon are found only in the rearrange-