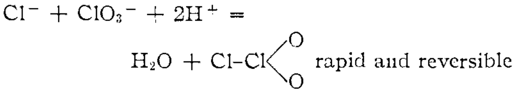
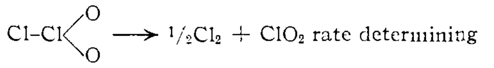
An isotopic tracer study of the oxidation of chloride ion by chlorate ion has been described by Taube and Dodgen.[12] They propose a mechanism to account for their results

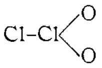


$$Cl^- + ClO_3^- + 2H^+ = H_2O + Cl\text{-}Cl(O)(O) \quad \text{rapid and reversible} \qquad (14)$$



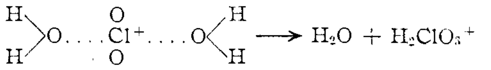
$$Cl\text{-}Cl(O)(O) \longrightarrow {}^1/_2Cl_2 + ClO_2 \quad \text{rate determining} \qquad (15)$$

The fact that the chlorate–water exchange is not induced during the oxidation of chloride by chlorate is in disagreement with reaction 14. However the existence of the unsymmetrical intermediate

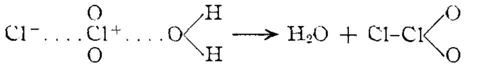


$$Cl\text{-}Cl(O)(O)$$

is suggested by the correlation of the rates of exchange and oxidation. The slow step of the exchange and of the oxidation of chloride may involve the displacement of water from doubly protonated chlorate ion as



$$H_2O\cdots Cl^+(O)_2\cdots OH_2 \longrightarrow H_2O + H_2ClO_3^+ \qquad (16)$$



$$Cl^-\cdots Cl^+(O)_2\cdots OH_2 \longrightarrow H_2O + Cl\text{-}Cl(O)(O) \qquad (17)$$

In the case of reaction 17, in the presence of arsenious acid, the intermediate Cl_2O_2 is removed rapidly. This produces the observed fourth-order rate law, equation 8.

It has been suggested[9] that the ion ClO_2^+ may be an intermediate in the exchange and the oxidations by chlorate ion, resulting from the dehydration of $H_2ClO_3^+$. Chlorine dioxide has been postulated to exist in an equilibrium

$$2ClO_2 = ClO_2^+ + ClO_2^- \qquad (18)$$

by electron transfer.[13] The fact that the chlorate–water exchange was not affected by the presence of added chlorine dioxide indicates that either chlorine dioxide does enter into such an equilibrium or that ClO_2^+ is not an intermediate in the exchange or both.

It has been reported that there is no appreciable exchange of chlorine atoms between chlorate ion and chlorine dioxide in acid or slightly alkaline solutions.[12] This suggests that no appreciable exchange takes place by the equilibrium

$$2ClO_2 + H_2O = 2H^+ + ClO_2^- + ClO_3^- \qquad (19)$$

The fact that ClO_2 did not change the rate of the chlorate–water exchange is in agreement with this suggestion.

A comparison of the rates of oxygen exchange between water and chlorate, bromate and iodate ions may be made. The iodate–water exchange is very fast, being complete in one minute under all conditions. The rate law for the bromate–water and chlorate–water at 25° may be expressed, assuming a first-order water dependence

$$R = (H^+)^2(H_2O)[1.2 \times 10^{-4}(BrO_3^-) + 1.6 \times 10^{-9}(ClO_3^-)] \qquad (20)$$

The activation energy for the BrO_3^-–H_2O exchange is 13,600 cal. per mole.

Although activation entropies for reaction 12 for the bromate–water and chlorate–water exchange cannot be calculated because of the unknown equilibrium constants in reaction 11 it appears qualitatively that the entropy of activation for the bromate–water exchange is more negative than for the chlorate–water exchange.

The inertness of the perchlorate ion to exchange is in line with its inertness to other reactions and its weak base strength. Exchange by way of reactions such as suggested by equations 11 and 12 would be very unfavorable.

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[12] H. Taube and H. Dodgen, THIS JOURNAL, **71**, 3330 (1949).

[13] W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1951, p. 178.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Dipole Moment of *p*-Benzoquinone[1]

BY LEONELLO PAOLONI[2]

RECEIVED NOVEMBER 1, 1957

The present status of the question of the apparent dipole moment of *p*-benzoquinone is summarized and some discrepancies in the published experimental results are pointed out. It is shown that contributions from the orbital moments of the lone pair electrons of the oxygen atoms under the action of the external field can explain the difference between the total polarization measured in the gas phase and that measured on the solid pelletted to maximum density, without requiring deformation of the planar arrangement of the nuclei. The experimental consequences of the proposed explanation are examined and the available evidence is discussed.

Introduction

The first report of dipole moment measurement on *p*-benzoquinone came from Hassel and Naeshagen[3] in 1929. Although the molecule was supposed to be planar the existence of a rather high apparent dipole, 0.67 D., did not raise much interest until Robertson[4] had shown that the molecule has a

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[1] Supported by a grant from the Alfred P. Sloan Foundation to Carnegie Institute of Technology.

[2] Laboratorio di Chimica Terapeutica, Istituto Superiore di Sanita, Roma, Italy.

[3] O. Hassel and E. Naeshagen, *Z. physik. Chem.*, **B6**, 445 (1929).

[4] J. M. Robertson, *Nature*, **134**, 138 (1934); *Proc. Roy. Soc. (London)*, **A150**, 106 (1935).

planar symmetrical structure. The Hassel and Naeshagen measurements were then repeated independently by LeFèvre and LeFèvre[5] and by Hammick, Hampson and Jenkins,[6] who confirmed the previous results. These last authors also measured the dipole moment of several 2,5-symmetrical-substituted benzoquinones and in all cases a dipole moment about 0.7 D. was found. In order to establish whether or not the measured moment was due to orientation polarization, ${}_{\mathrm{O}}P$, Coop and Sutton[7] carried out measurements in the vapor phase for a rather wide range of temperatures and pressures. Having found that total polarization is the same as in solution and independent of temperature, they concluded that the difference between total and electron polarization ${}_{\mathrm{T}}P - {}_{\mathrm{E}}P = 36.5 - 28.3 = 8.2$ cc., usually set equal to ${}_{\mathrm{O}}P + {}_{\mathrm{A}}P$, could not be attributed to orientation polarization. These experiments seemed to rule out the existence of a permanent dipole moment in *p*-benzoquinones, and they offered an explanation[7] in terms of an abnormally high atom polarization ${}_{\mathrm{A}}P$. A challenge to this interpretation came from Kofod[8] who determined the dipole moment of 2,5-di-*t*-butylbenzoquinone. The deformation of the molecule due to a bulky substituent always induces strains which reduce the possibility of movement of the nuclei relative to one another, under the influence of the applied electric field. According to the Coop and Sutton explanation a decrease of the dipole moment was expected; instead, a small increase was observed.

More recently Meredith, Westland and Wright[9] determined the polarization of solid benzoquinone pelletted to maximum density and found a substantial reduction in the difference ${}_{\mathrm{T}}P - {}_{\mathrm{E}}P$, the total polarization measured at 22 ± 2° being ${}_{\mathrm{T}}P = 30.1$ cc. Atom polarization is a property of the individual molecules and should be largely independent of the conditions under which it is measured; a consequence of this result therefore is that explanations based on atom polarization cannot be maintained. Thinking that orientation polarization might be responsible for the observed difference, Meredith,[9] *et al.*, studied the effect of temperature increase on the polarization of benzoquinone solutions in benzene and dioxane and found a decrease of polarization. Such a circumstance usually is regarded as an indication that solute molecules undergo orientation and therefore possess a permanent dipole moment. These measurements however are in marked disagreement with those previously made by LeFèvre and LeFèvre,[5] who determined the polarization of benzoquinone in carbon tetrachloride and in benzene at 25 and 45° and did not find any significant effect of either solvent or temperature, the ${}_{\mathrm{T}}P$ value being constant at about 41 cc. This circumstance seems to have been overlooked by Meredith,[9] *et al.;* the discrepancy in the experimental results can be settled only through other measurements.[10]

The situation summarized above seems to indicate altogether that the explanations based on a bending of the molecule[5,9] or on an abnormally high atom polarization[7] have little experimental support.[11] Although the experimental evidence at present available is in favor of a planar structure of benzoquinone, the published results cannot rule out the possibility of small deviations from planarity. The X-ray study of Robertson[4] does not take into account the thermal motion of the molecule in the crystal, and the electron diffraction measurements by Swingle[12] and by Kimura and Shibata[13] are consistent with the assumed D_{2h} symmetry without however proving such a symmetrical shape.

The existence of an apparent dipole moment requires however an asymmetrical charge distribution, and we decided therefore to investigate under what conditions this could be possibly compatible with the planar symmetrical arrangement of the nuclei in *p*-benzoquinone. The basic idea we have used is that the electron cloud around oxygen atoms can be deformed *under the influence of the applied external field* in such a way as to originate a dissymmetry in the charge distribution (actually a concentration of electrons on one side of the molecular plane through polarization of the oxygen lone pairs) which would justify the high value observed for the apparent dipole moment.

A main purpose of the present paper, to a certain extent admittedly a speculative one, is to suggest and stimulate some experiments which could clear up the entire question.

The Electron Distribution around Oxygen.—The electron configuration of oxygen, $1s)^2 2s)^2 2p)^4$, may give origin to a valence state for the bonded atom, expressed in a general form as $\mathrm{O}(sp^6,V_2)$ to show that two electrons are involved in two bonds, the other four being left out and forming two lone pairs; the orbitals involved in each case are some sp hybrids to be specified. The most general

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(5) R. W. J. LeFèvre and C. G. LeFèvre, *J. Chem. Soc.*, 1696 (1935).

(6) D. L. Hammick, G. C. Hampson and G. I. Jenkins, *Nature*, **136**, 990 (1935); *J. Chem. Soc.*, 1263 (1938).

(7) I. E. Coop and L. E. Sutton, *ibid.*, 1296 (1938)

(8) H. Kofod, *Acta Chem. Scand.*, **7**, 928 (1953).

(9) C. C. Meredith, L. Westland and G. F. Wright, This Journal, **79**, 2835 (1957).

(10) The measurements by Meredith, *et al.*,[9] in benzene solution at 20, 30, 35 and 40°, when interpolated give as approximated values for the total polarization ${}_{\mathrm{T}}P$ = 40 cc. at 25° and 31 cc. at 45°. Whereas the first value is fairly consistent with that found by LeFèvre and LeFèvre,[5] the second value is not. In order to ascertain whether a different processing of the experimental data could be responsible for the discrepancy, the measurements in benzene at 45° reported by LeFèvre and LeFèvre[5] have been treated according to the procedure indicated by Meredith, *et al.*[9] The result is ${}_{\mathrm{T}}P$ = 41.2 cc., essentially the same as the 40.8 cc. value given in the original[5] paper. Our suggestion is therefore that some impurity, present or developed in the used materials, is responsible for the different results. LeFèvre[5] purified *p*-benzoquinone through steam distillation and recrystallized it twice from boiling ligroin. Meredith, *et al.*,[9] used instead 95% ethanol. We have shown recently [L. Paoloni and G. B. Marini-Bettòlo, *Gazzetta chim. ital.*, **87**, 395 (1957)] that in both solvents *p*-benzoquinone easily undergoes photochemical reduction at room temperature, hydroquinone or quinhydrone being formed; small amounts of these impurities could have been present and affect the polarization measurements. For obtaining high purity quinones, it is necessary to handle them in a dark room, the most suitable procedure being a careful sublimation in the dark of the purest crystallized products.

(11) The discussions which follow are mainly concerned with the results obtained on the gas and on the compressed solid. The theories developed by G. I. Jenkins (*J. Chem. Soc.*, 864, 910 (1936)) and by J. Frank and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 1307 (1937), which try to justify the dipole moments observed in solution need not to be considered here.

(12) S. M. Swingle, This Journal, **76**, 1409 (1954)

(13) M. Kimura and S. Shibata, *Bull. Chem. Soc. Japan* **27**, 163 (1954).

sp orthonormalized hybrids which can be built up from the 2s and the 2p orbitals can be written as follows (reference system in Fig. 1)

$$\begin{aligned} t_1 &= (s)\cos\alpha\sin\beta\cos\gamma - (p_x)\cos\alpha\sin\beta\sin\gamma + (p_y)\sin\alpha - (p_z)\cos\alpha\cos\beta \\ t_2 &= (s)\sin\alpha\sin\beta\cos\gamma - (p_x)\sin\alpha\sin\beta\sin\gamma - (p_y)\cos\alpha - (p_z)\sin\alpha\cos\beta \\ t_3 &= (s)\cos\beta\cos\gamma - (p_x)\cos\beta\sin\gamma + (p_z)\sin\beta \qquad (1) \\ t_4 &= (s)\sin\gamma + (p_x)\cos\gamma \end{aligned}$$

Here (s) and (p_x) (p_y) (p_z) stand for the Slater nodeless orbitals defined as

$$(s) = \psi_{2s} = \left(\frac{\delta^5}{3\pi}\right)^{1/2} re^{-\delta r}$$

$$\left.\begin{aligned}(p_x) &= \psi_{2px}\\ (p_y) &= \psi_{2py}\\ (p_z) &= \psi_{2pz}\end{aligned}\right\} = \left(\frac{\delta^5}{\pi}\right)^{1/2} re^{-\delta r}\left\{\begin{aligned}&\sin\vartheta\cos\varphi\\ &\sin\vartheta\cos\varphi\\ &\cos\vartheta\end{aligned}\right. \qquad (2)$$

$$\text{with } \delta = \frac{Z}{n} - \frac{Z}{2}$$

Z being the effective charge of the atom.

The meaning of the hybridization parameters can be approximately illustrated by the statements that: α determines the angle between t_1 and t_2; they are symmetrical only when $\alpha = \pi/4$; β determines the angle of the plane of t_1 and t_2 with z-axis and the amount of deformation of the orbital t_3; γ determines the amount of sp hybridization of the orbital t_4 and the angle between z-axis and t_3. It has been pointed out by Coulson[14] that one of the consequences of hybridization is a displacement of the centroid of the electronic charge of the orbital from the nuclear center of the atom. This gives rise to an orbital dipole moment, whose resultant depends on the hybridization of the atom and on its bonding condition in the molecule. In order to evaluate the dipole moment it is necessary to determine the charge centroid of each orbital. The coördinates $\bar{\xi}_i = \bar{x}_i, \bar{y}_i, \bar{z}_i$ for the centroid C_i of the orbital t_i are obtained easily through the integrals

$$\bar{\xi}_i = \frac{\int \xi t_i^2\, d\tau}{\int t_i^2\, d\tau} \qquad (3)$$

ξ being any one of the coördinates x, y and z. Their expression is given in the Appendix. The components of the orbital dipole moments are then easily evaluated from the definition

$$\mu_\xi^{(i)} = q_i\bar{\xi}_i \qquad (4)$$

with q_i the charge of the orbital t_i. This relationship enables one to calculate the resultant of the orbital dipole moments as soon as the state of the oxygen atom in the molecule is specified.

In the present case, referring to Fig. 1, the orbital t_4 is constantly directed along the x-axis and is involved in the σ-bond of the carbonyl group; t_3 is used in the π-bond; t_1 and t_2 are occupied by the lone pair electrons.

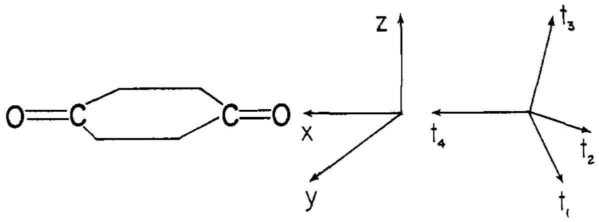

Fig. 1.—Reference system used in the calculation. Coördinate axes centered on the oxygen atoms. The molecule lies in the (x, y) plane.

Because the hybrids in the bonds must show the correct behavior with respect to all the symmetry operation of the molecule, the oxygen atom in the unperturbed *p*-benzoquinone molecule will have hybrids defined by eq. 1 with $\alpha = \pi/4$ and $\beta = \pi/2$; and it is easily found that in these conditions the resultant of the orbital dipole moments is always zero.

The Action of the External Field.—Let us consider however the molecule under the action of an external electric field alternating with frequency lower than the frequency of the molecular vibrations. The influence of this field is isotropic on the two carbonyl groups, *acting on both in the same sense*, whatever the actual orientation of the molecule (unless this is aligned with its long axis parallel to the field, a very small percentage of the time in a random distribution). The non-bonding lone pair electrons, which are doubtless the most polarizable of the molecule, will have their average position displaced off to the same side of the molecular plane, and this effect may be described in a first approximation as a deformation of the atomic orbitals of the oxygen atom. The whole molecule may therefore be considered perturbed in such a way that the induced charge asymmetry gives origin to a dipole moment component along z-axis, μ_z, different from zero.

A general expression for the μ_z of each oxygen atom can be calculated from eq. 4 using the centroid coördinates given in the Appendix; the result is

$$\mu_z = A(q_\pi - 2e)\sin\beta\cos\beta\cos\gamma \qquad (5)$$

Here we have set $q_1 = q_2 = 2e$, the charge in each lone pair orbital; and $q_3 = q_\pi$, the charge in the oxygen orbital involved in the π-bond of the carbonyl group *in the actual condition of the molecule in the presence of the field.* Assuming now that the component μ_z has the same magnitude for the two oxygen atoms, the total contribution to the moment along z-axis is $2\mu_z$. Using eq. 4 it is also easily shown that no other contribution needs to be taken into account because one always has $\mu_y = 0$ and the μ_x components, although in general different from zero, cancel each other. The resultant induced moment of *p*-benzoquinone, under the conditions described above, is thus $\mu_R = 2\mu_z$ and can be written

$$\mu_R = A(q_\pi - 2e)\sin 2\beta\cos\gamma \qquad (6)$$

Because the orbital t_4 is intermediate between a pure p and a trigonal sp hybrid, $(^2/_3)^{1/2} \leqslant \cos\gamma \leqslant 1$; and in a direct approximate calculation of the π-electron distribution in *p*-benzoquinone,[15,16] it has

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[14] C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A207**, 63 (1951).

[15] L. Paoloni, *J. chim. phys.*, **51**, 385 (1954).

[16] S. Nagakura and A. Kuboyama, THIS JOURNAL, **76**, 1003 (1954).

been found that $q_\pi < 2e$. The resultant induced dipole moment is therefore different from zero only if $\sin 2\beta \neq 0$, which just expresses that t_1 and t_2 are projected out of the (x,y) plane and that the orbital t_3 is deformed due to its acquisition of some s character.

Of course eq. 6 accounts for the dipole moment only in terms of a perturbation of the normal orbital-following process in the presence of an external electric field, which can be accepted only as a first approximation. The reliability of the proposed criterion depends essentially on the circumstance that a small deformation will account for the observed dipole moment. Using for q_π the values[15,16] 1.30 and 1.50 and for $\cos \gamma$ the two extreme values 1 and $(^2/_3)^{1/2}$, it is found that the amount of s character to be acquired by t_3 ranges from 2.7 to 5.5%, that the net electron transfer for each lone pair on one side of the molecule is from 0.125e to 0.175e, and the deviation of t_1 and t_2 from the molecular plane is from 9 to 12°.

Thus the explanation suggested requires a very small modification, in the presence of the field, of the widely accepted symmetric picture, in the absence of a field, of 8 electrons in 8 p-orbitals.

It remains now to describe the mechanism by which the induced moment might operate. Under the action of the external field the electron distribution of the molecules is deformed in such a way that in spite of the persistent D_{2h} symmetric arrangement of the nuclei, the molecule has a dipole along the z-axis. This dipole moment confers to the molecule in the field an actual symmetrical top electronic configuration, its rotational selection rules are modified and a preferential orientation will take place in the direction of the field, before this direction changes as a consequence of alternation. When the field is inverted, if the frequency of the field is enough lower than the rotational frequencies of the molecule, the orientation will last also when the total dipole moment, following the field, reverses and changes its sign. This effect brings therefore in both cases an increase of the total polarization. It thus seems possible to understand in this way the origin of the measured dipole moment and why it can be observed in gas phase and in dilute solution but not in solid state when the free orientation of the molecules is not possible any more.

Moreover, by developing an argument previously used by Debye,[17] it can be shown[18] that orientation polarization in gas phase through an induced moment is approximately independent of temperature.

Conclusions

The explanation proposed above justifies the observed polarization on the basis of the high polarizability of the lone pair electrons of oxygen and the peculiar arrangement of the two carbonyl groups in *p*-benzoquinone, emphasizing what could be called an abnormal contribution from the term $_EP$ of the total polarization.

And it is probably worth remarking that such a contribution would be expected to be present also in the event of small deviation of *p*-benzoquinone from the planar D_{2h} symmetry, as well as in the asymmetrical substituted *p*-benzoquinones.

If this explanation is correct there are several experimental consequences which can be used to verify it.

(1) The direction of the dipole moment is normal to the molecular plane. The orientation of the molecules should allow one to observe an electrical birefringence in the vapor phase and perhaps also in solution. The relaxation time can also be determined. No report on such measurements is available in the literature.

(2) The out-of-plane bending vibrations of the C=O groups are expected to have rather high intensity because they involve a large variation of the dipole moment. An intense absorption band near 120 cm.$^{-1}$ has been observed by Cartwright and Errera[19] who consider the band due to a fundamental vibration of the entire molecule and suggest a bending mode. Moreover a modification of the intensity pattern of the rotational spectrum is to be expected as a consequence of applying an external electric field, both in the rotational structure of vibrational bands and in the microwave region. Investigations of this kind have not yet been carried out.

(3) The same kind of dipole moment is to be expected for other planar molecules having two carbonyl groups pointing in opposite directions. In addition to the substituted quinones referred to above, it has been found that 1,1,3,3-tetramethylcyclobutane-2,4-dione (dimethylketene dimer), whose planar structure has been proved recently by Friedlander and Robertson,[20] has a dipole moment 0.72 D.[6] A dipole moment 0.71 has been reported[3] for anthraquinone and 0.6 for chloranil.[21]

(4) The existence and the properties of quinhydrones can be considered as chemical evidence of the easy polarizability of the lone pair electrons and their migration on one side of the molecule. A sandwich structure with the two molecules 3.2 A. apart has been reported[22] for the quinhydrone of *p*-benzoquinone.

Acknowledgments.—The author is greatly indebted to Dr. R. G. Parr for his encouragement, for many helpful suggestions and a substantial improvement of the manuscript; and to Dr. A. G. Jeffrey for a discussion of the literature on crystal structure determinations.

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[17] P. Debye, "Polar Molecules," Dover Publications, Inc., New York, N. Y., p. 30.

[18] The induced dipole moment, which brings orientation of the molecule in the field $F = (X, Y, Z)$, is proportional to the field strength, and the internal deformation energy is[17]

$$u = \mu_x X + \mu_y Y + \mu_z Z = \alpha(X^2 + Y^2 + Z^2) = \alpha F^2$$

α being dependent on the orientation of the molecule in the field. The average moment with respect to all the possible orientations is

$$\bar{\mu} = \left\{\left(\bar{\alpha} + \frac{\overline{\alpha^2}}{kT} F^2 + \cdots\right)\Big/\left(1 + \frac{\bar{\alpha}}{kT} F^2 + \cdots\right)\right\} F \simeq \bar{\alpha} F$$

provided $(\bar{\alpha})^2 \simeq \overline{\alpha^2}$, and then $\bar{\mu}/F$ is approximately independent of T.

[19] Private communication to Hammick, *et al.*,[6] quoted in *J. Chem. Soc.*, 1265 (1938).

[20] P. H. Friedlander and J. M. Robertson, *ibid.*, 3083 (1956).

[21] R. W. J. LeFèvre, "Dipole Moments," Methuen and Co., London, 1948, p. 100.

[22] K. Nakamoto, THIS JOURNAL, **74**, 1739 (1952); K. Suzuki and S. Seki, *Bull. Chem. Soc. Japan*, **26**, 372 (1953).

Appendix

The only integrals different from zero which arise when developing eq. 3 are those of the form

$$\int \xi \, \mathrm{sp}_\xi \, d\tau = \frac{5}{2\sqrt{3}} \frac{1}{\delta}, \text{ atomic units, } \xi = x, y, z$$

and it is easily found that the coordinates for the charge centroids are

$$\begin{aligned}
C_1 = \bar{x}_1 &= -A \cos^2 \alpha \sin^2 \beta \sin \gamma \cos \gamma \\
\bar{y}_1 &= A \sin \alpha \cos \alpha \sin \beta \cos \gamma \\
\bar{z}_1 &= -A \cos^2 \alpha \sin \beta \cos \beta \cos \gamma \\
C_2 = \bar{x}_2 &= -A \sin^2 \alpha \sin^2 \beta \sin \gamma \cos \gamma \\
\bar{y}_2 &= -A \sin \alpha \cos \alpha \sin \beta \cos \gamma \\
\bar{z}_2 &= -A \sin^2 \alpha \sin \beta \cos \beta \cos \gamma \\
C_3 = \bar{x}_3 &= -A \cos^2 \beta \sin \gamma \cos \gamma \\
\bar{y}_3 &= 0 \\
\bar{z}_3 &= A \sin \beta \cos \beta \cos \gamma \\
C_4 = \bar{x}_4 &= A \sin \gamma \cos \gamma \\
\bar{y}_4 &= 0 \\
\bar{z}_4 &= 0
\end{aligned}$$

where

$$A = 5a_0/\sqrt{3}\delta \qquad a_0 = 0.5292 \times 10^{-8} \text{ cm.}$$

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WYOMING]

The Effect of Methyl Substitution on the Periodate Oxidation of *cis*- and *trans*-Cyclopentanediol-1,2[1]

BY VERNON C. BULGRIN AND GEORGE DAHLGREN, JR.

RECEIVED MARCH 3, 1958

The mechanism of the periodate oxidation of *cis*- and *trans*-cyclopentane-diol-1,2 and methylated derivatives is shown to be similar to that for pinacol. The reaction proceeds through apparently bimolecular non-catalyzed and acid-catalyzed paths. The effect of methyl substitution on the rate of the reaction, and the inertness of the *trans*-1,2-dimethyl compound toward oxidation by periodate support the postulate of a cyclic intermediate, the formation of which is rate determining.

Introduction

The periodic acid cleavage of vicinal glycols has been shown to proceed through either of two mechanisms. The first of these involves the formation of an intermediate complex between the oxidant and the reductant, the rate-determining step being the disproportionation of the intermediate. Such a mechanism results in pseudo first-order kinetics if glycol is present in sufficient excess. The second of the two involves no kinetically detectable amount of intermediate, is second order and involves, contrary to the first, a hydrogen ion catalyzed path as well as the non-catalyzed path. Duke and Bulgrin[2,3] were able to assign the former reaction scheme to the periodate oxidation of ethylene and methylated ethylene glycols, with the exception of pinacol. The reactive periodate species was shown to be a monovalent periodate ion, presumably IO_4^-; equilibrium and rate constants were determined for the formation and disproportionation, respectively, of the intermediate. Pinacol was found to follow the second scheme, both uncatalyzed and hydrogen ion catalyzed second-order paths being available. It was suggested that in the case of pinacol, the reaction is second order because the complex-forming step has become rate determining.

Bulgrin[4] studied the rates of cleavage of *cis*- and *trans*-cyclopentane-diol-1,2 by periodate and found the reaction to be second order but was unable to demonstrate hydrogen ion catalysis at 0°.

The question of the nature of the intermediate has not been answered fully. Criegee[5] and Price[6,7] have suggested a cyclic complex between glycol and a periodate species. Such an intermediate would be consistent with the specificity of periodate for cleavage of vicinal glycols. In forming the complex, a tetrahedral IO_4^- ion may coördinate a glycol molecule in the same way it coördinates two water molecules to form the octahedral $H_4IO_6^-$ ion.

Levesley[8] and Cordner and Pausacker[9] have concluded that the oxidation of vicinal glycols by lead tetraacetate probably does not involve a cyclic intermediate; Cordner suggests a monoesterification type mechanism. Criegee,[10] in his study of the lead tetraacetate oxidation of glycols, was unable to assign a single mechanism to cover all cases.

Wiberg and Saegebarth[11] state that a monoesterification type mechanism in the periodate oxidation of glycols does not agree with the experimentally observed rule that *cis*-compounds react faster than *trans*- and conclude that the intermediate is cyclic.

Buist and Bunton[12] have presented data, including some spectroscopic data, from which they conclude that the intermediate is not only cyclic but is necessary for the reaction to take place.

A kinetic study of the periodate oxidation of methylated *cis*- and *trans*-cyclopentanediol-1,2 was undertaken in order to help clarify the nature of the intermediate and to determine the extent of steric effects on the reaction.

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