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

The Oxygen Exchange Between Oxy-anions and Water. II. Chlorite, Chlorate and Perchlorate Ions[1]

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The kinetics of the isotopic exchange reaction between chlorate ion and water have been measured. In the region of 0.1 to 1.0 *f* chloric acid, the exchange follows the rate law $R = k(\mathrm{H}^+)^2(\mathrm{ClO_3}^-)$ where k equals 0.89×10^{-3} $1.^2$ moles^{-2} seconds^{-1} at 100° and ionic strength 1.34. The activation energy is 27,100 cal. per mole. The course of the reaction was not affected by added chlorine dioxide. The reaction proceeds faster in D_2O with R_d/R_h equal to 2.83. The exchange between chlorate ion and water is not induced during the oxidation of halide ions. The rate of this exchange is compared to the rates of other oxy-anion exchanges and the rates of oxidation of halide ions by chlorate. Perchlorate ion does not measurably exchange its oxygen with water over long periods of time at elevated temperatures and high acidities. Chlorite ion does not measurably exchange its oxygen with water under any condition where it is stable.

Introduction

The exchange of isotopic oxygen between water and chlorite, chlorate and perchlorate ions has been studied qualitatively by several workers.[2] No measurable exchange has been reported in neutral or slightly acidic solution. A measurable exchange has been reported for chlorate ion and water at an elevated temperature and a high acidity.[3] This paper is a report on the quantitative study of the rate of exchange between water and chlorate ions. Qualitative studies on the exchange of chlorite and perchlorate ions with water were performed.

Previous work[4] in this Laboratory on the bromate–water exchange has shown similarities between the kinetics of the bromate oxidation of halide ions and the exchange reaction. A mechanism involving the bimolecular displacement of water by the attacking species was postulated. These experiments were performed to see if this mechanism could be applied to reactions involving chlorate ion.

A study of the rates of exchange between water and the series of ions $\mathrm{ClO_2}^-$, $\mathrm{ClO_3}^-$, $\mathrm{ClO_4}^-$, was attempted in order to measure the effect of structure on the lability of the Cl–O bond. It is known qualitatively that reactivity increases in the series $\mathrm{ClO_3}^- < \mathrm{BrO_3}^- < \mathrm{IO_3}^-$ but there are few quantitative data to attempt any correlation of reaction mechanisms with the nature of the center atom of these oxy-anions. This work was done with the purpose of extending the knowledge of the reaction mechanisms of this type of molecule.

Experimental

Materials.—Oxygen-eighteen tagged water was obtained from the Stuart Oxygen Co. of San Francisco. Oxygen-eighteen tagged potassium chlorate was prepared by the disproportionation of Cl_2 in a hot solution of KOH in tagged water. Sodium chlorate was prepared by treating tagged potassium chlorate with Dowex-50 ion-exchange resin in the sodium form. The water used as a solvent was redistilled from an alkaline permanganate solution. Sodium chlorite, received from the Matheson Chemical Company, was purified by repeated recrystallizations. All other chemicals were reagent grade and used without further purification.

Experimental Procedures.—The chlorite–water exchange was studied by dissolving sodium chlorite of normal isotopic abundance in tagged water. Oxygen exchange reactions are, in general, more rapid in acidic solutions. This exchange was studied in solutions which were as acidic as possible, without causing complete decomposition of the chlorous acid. Solutions which were buffered with borate and acetate ions or were acidified with dilute perchloric acid were sealed into Pyrex ampules. The reactants were separated by precipitating $Pb(ClO_2)_2$. The dried precipitates were converted to O_2 for isotopic analysis by thermal decomposition in a vacuum system. The evolved oxygen was trapped carefully with liquid air before introducing it into the mass spectrometer.

The perchlorate–water exchange was expected to be very slow, and the exchange was studied in highly acidic solutions at elevated temperatures. Perchloric acid of normal isotopic composition was dissolved in tagged water. The concentration of the acid varied from 5.9 to 9.5 *f*. The solutions were sealed into Pyrex ampules and placed in a thermostat. For example, a solution of 9.54 *f* $HClO_4$ was held at 100° for as long as 63 days and at room temperature for 296 days. The reactants were separated by precipitating $KClO_4$. This precipitate was converted to O_2 for isotopic analysis by thermal decomposition.

The kinetics of the $\mathrm{ClO_3}^-$–H_2O exchange were studied in solutions acidified with sulfuric or perchloric acid. The ionic strength was maintained constant with added potassium sulfate or sodium perchlorate. The exchange of oxygen between sulfate ion and water is slow under the conditions used in this experiment.[5] The solutions were prepared by dissolving the proper amounts of tagged chlorate and inert salt in the solution of acid. Each sample was sealed in a Pyrex ampule and placed in a thermostatic bath held at 100.0°. The exchange was stopped by cooling the sample to room temperature and by neutralizing it. The hydrogen ion concentration of each sample was determined by titrating an aliquot with NaOH. In the experiments where perchloric acid was used to acidify the solution, a portion of the solvent water was distilled from the neutralized sample for isotopic analysis. The progress of the exchange reaction was followed by observing the increase of the oxygen-eighteen content of the solvent. The water was analyzed for oxygen-eighteen content by the method of Cohn and Urey.[6]

In the experiments where sulfuric acid was used to acidify the reaction mixture, the exchange was stopped by cooling the sample to room temperature and by neutralizing it with potassium hydroxide. Much of the K_2SO_4 was precipitated by adding alcohol and centrifuging. The remaining sulfate ion was removed by adding barium chloride. The solution was then evaporated to dryness and the potassium chloride and potassium chlorate collected. The chlorate in this mixture was converted to oxygen gas for isotopic analysis by thermal decomposition *in vacuo*.

Blank experiments showed this separation could be carried out without causing exchange.

Since the experiments using sulfuric acid were easier to perform and gave a higher precision, they were used to determine the orders of the reaction. There are some uncertainties in the corrections needed to calculate acidities in

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[1] This work was supported by funds supplied by the National Science Foundation.

[2] H. Taube, "Annual Reviews of Nuclear Science," Vol. 6, 1956, p. 282; M. Dole, *Chem. Revs.*, **50**, 275 (1952).

[3] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940).

[4] T. C. Hoering, R. C. Butler and H. O. McDonald, THIS JOURNAL, **78**, 4829 (1956).

[5] T. C. Hoering and J. W. Kennedy, *ibid.*, **78**, 4829 (1956).

[6] M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938).

sulfuric acid solutions due to the weakness of the second dissociation. Some of the experiments were repeated using perchloric acid to acidify the solution.

The isotopic analyses were made on a Consolidated Mass Spectrometer Model 21-401. The mass spectra due to the isotopic molecules were scanned enough times to reduce the errors in peak height measurement to less than 1%.

Calculations.—The chlorate–water exchange was followed by measuring the change in oxygen-eighteen content of either the water or the chlorate fraction as a function of time. The half-time for the exchange was determined by plotting the logarithm of one minus the fraction exchanged *vs.* time.[7] The fraction exchanged is defined by equation 1

$$F = \frac{O_t^{18} - O_0^{18}}{O_\infty^{18} - O_0^{18}} \qquad (1)$$

The symbol O^{18} indicates the atom fraction of oxygen-eighteen in the O_2 or CO_2 at the time indicated by the subscript. The rate of the reaction which leads to isotopic exchange was then calculated by

$$R = \frac{3(ClO_3^-)(H_2O)}{3(ClO_3^-) + (H_2O)} \times \frac{0.693}{t_{1/2}} \qquad (2)$$

The symbol R represents the rate of the reaction in gram-atom per liter per second, the quantities in parentheses are the formal concentrations in formula weights per liter and $t_{1/2}$ the half-time for exchange in seconds.

If a single path is available for the reaction which leads to exchange, the rate law at constant temperature may be given by

$$R = k(H^+)^m(ClO_3^-)^n(H_2O)^p\Gamma \qquad (3)$$

where Γ is some function of the activity coefficients of the reactants and the activated complex. The value of m was obtained by continuously varying the hydrogen ion concentration at several fixed chlorate ion concentrations while maintaining the ionic strength constant. In a similar manner, the value of n was obtained. There seems to be no suitable experimental method for the determination of p. The common solvents that could be used to vary the water concentration will not resist the attack of acid chlorate solutions at the temperature used. At the concentrations employed, the activity coefficients vary in an unpredictable way with the addition of inert solvents.

Experimental Results

A. The Chlorite–Water and the Perchlorate–Water Exchange.—Under all conditions studied, the remaining chlorite ion was less than 0.3% exchanged. No exchange was observed when most of the chlorous acid had decomposed. Therefore, it is concluded that under all conditions, the disproportionation and decomposition of $HClO_2$ is faster than the oxygen exchange with water.

Strongly acidic solutions of perchloric acid are stable at 100° but the observed exchange was less than 0.5% under all conditions used. In 9 *f* perchloric acid at room temperature, the half-time for exchange is estimated to be greater than one hundred years.

B. The Chlorate–Water Exchange.—The order of the rate law with respect to hydrogen and chlorate ion concentration was measured in solutions acidified with sulfuric acid. In Fig. 1, the hydrogen ion dependence is shown. The logarithm of the rate is plotted against the logarithm of the hydrogen ion concentration for several fixed chlorate ion concentrations. The points fall about lines of slope two. In solutions of sulfuric acid at the concentrations used in this experiment, a slight correction had to be made to the measured acidities of the solutions in order to obtain the hydrogen ion concentrations. This is due to the weakness of the second dissociation of sulfuric acid. Since there is some uncertainty in the activity coefficients in the solutions used, there will be some uncertainty in the values of the specific rate constants obtained. However, the procedure is adequate for determining the orders of the reaction.

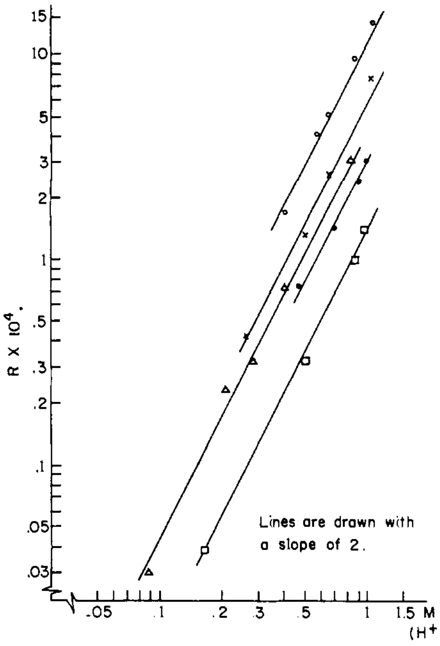

Fig. 1.—The hydrogen ion dependence in sulfuric acid: ○, 1.00 *f*; ×, 0.500 *f*; ●, 0.250 *f*; □, 0.100 *f*; △, 0.500 *f*, (perchloric acid).

In Fig. 2, the dependence on the chlorate ion concentration is shown. The logarithm of the rate

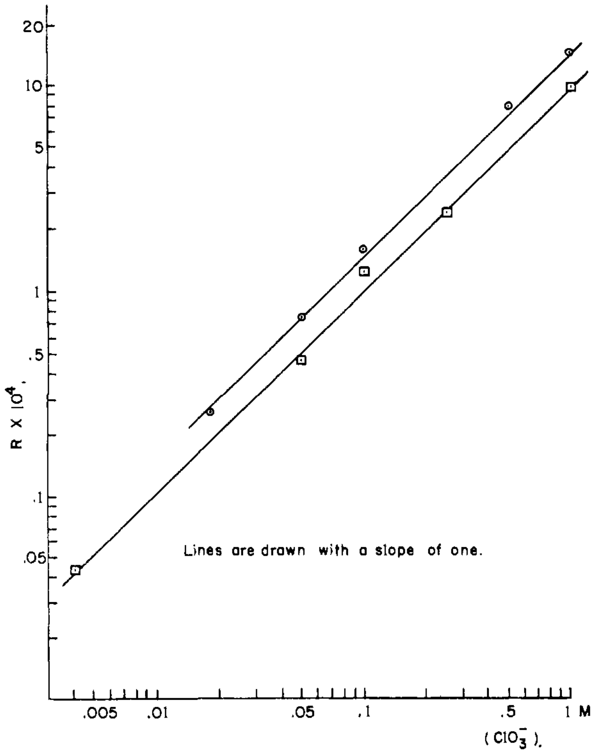

Fig. 2.—The chlorate ion dependence at two hydrogen ion concentrations: ○, 1.07 *f*; □, 0.866 *f*.

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(7) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951.

is plotted against the logarithm of the chlorate ion concentration for several fixed hydrogen ion concentrations. The points fall about a straight line of slope one.

In order to eliminate any uncertainty due to the calculation of hydrogen ion concentration, the values for the specific rate constant were determined in solutions acidified with perchloric acid. The results are shown in Table I. The third-order specific rate constants were calculated from the rate law

$$R = k(H^+)^2(ClO_3^-) \qquad (4)$$

TABLE I

RATE OF THE CHLORATE–WATER EXCHANGE IN SOLUTIONS ACIDIFIED WITH PERCHLORIC ACID

$T = 100.0°$, ionic strength = 1.34

(H^+), moles/l.	(ClO_3^-), moles/l.	Rate $\times 10^4$, g. atom/l.	$k \times 10^3$ sec.
0.836	0.500	3.13	0.897
.404	.500	0.740	.907
.285	.500	.322	.793
.210	.500	.237	1.07
.0892	.500	.0308	0.775

Activation Energy.—The rate of the exchange was determined at several different temperatures between 85 and 100° in solutions 1.07 *f* in hydrogen ion and 0.100 *f* in chlorate ion. A plot of the logarithm of the rate *vs.* the reciprocal of the absolute temperature gave a straight line with a slope corresponding to an activation energy of 27,100 cal. per mole.

Rate of the Exchange in Deuterium Oxide Solvent.—The rate of the exchange was studied in a solution of water of normal hydrogen isotope content at a hydrogen ion concentration of 0.96 *f* and chlorate ion concentration of 0.25 *f*. Then the same amounts of potassium chlorate and sulfuric acid were added to mixtures of deuterium oxide and protium oxide. The mole fraction deuterium was varied from natural abundance up to 89.3 atom %. The measured rates of the exchange could be expressed as the quadratic function

$$R \times 10^4 = 4.8N^2 + 0.7N + 3.0 \qquad (5)$$

where R is the rate in gram-atom/l. sec. and N is the atom fraction deuterium. The ratio of the rates in pure deuterium oxide to that in normal water is calculated from (5) to be 2.83.

Catalysis of the Exchange.—Experiments were performed to check for catalytic effect on the rate by glass surfaces, light and added chlorine dioxide. No effect was observed. A study was made of the possible induced exchange between chlorate ion and water during the reduction of chlorate ion by iodide and chloride ion. No change in the oxygen-eighteen content was observed after ten per cent. of the chlorate had been reduced.

Discussion

The exchange of oxygen between chlorate ion and water followed the rate law

$$R = k(H^+)^2(ClO_3^-) \qquad (6)$$

where k has the value 0.89×10^{-3} l.^{2} mole^{-2} seconds^{-1} at 100° and with the ionic strength maintained at 1.34 with perchloric acid and sodium perchlorate. The activation energy was 27.1 kcal. per mole in the region of 85 to 100°. If a first-order dependence on the water concentration is assumed, the fourth order specific rate constant is 1.6×10^{-9} at 25°. The rate of reduction of chlorate ion by halide ion in the presence of arsenious acid has been studied by Skrabal and Schreiner.[8] The rates of the reductions and of the oxygen exchange can be expressed

$$R = 1.6 \times 10^{-9}(H^+)^2(ClO_3^-)(H_2O) \qquad (7)$$

$$R = 4.5 \times 10^{-5}(H^+)^2(ClO_3^-)(Cl^-) \qquad (8)$$

$$R = 9.3 \times 10^{-5}(H^+)^2(ClO_3^-)(Br^-) \qquad (9)$$

$$R = 2.0 \times 10^{-3}(H^+)^2(ClO_3^-)(I^-) \qquad (10)$$

where the value of k is in l.^{3} mole^{-3} seconds^{-1} at 25°.

The mechanism of the exchange and of the oxidation by chlorate and bromate ion has been postulated to proceed by reactions of the type

$$2H^+ + ClO_3^- = H_2ClO_3^+ \text{ rapid and reversible} \qquad (11)$$

$$X + H_2ClO_3^+ \longrightarrow XClO_2 + H_2O \text{ rate determining} \qquad (12)$$

where X is a halide ion or water.[9]

The deuterium isotope effect on the rate of the exchange is of similar magnitude to that observed during the oxidation of halide ions by halate ions.[10] If the course of the reaction is that as shown by equations 11 and 12 with an acid–base pre-equilibrium, the inverse isotope effect on the rate requires that the equilibrium in (11) lies farther to the right in the case of deuterium substitution. It has been shown that weak acids are less dissociated in D_2O than in H_2O.[10] The fact that the rate of the exchange is a quadratic function of the mole fraction of deuterium in the solvent is a consequence of the addition of two protons.

Edwards has proposed an empirical equation relating the rates of bimolecular nucleophilic displacements and the parameters of the system.[11] This equation is

$$\log \frac{k}{k_0} = \alpha E_n + \beta H \qquad (13)$$

where k and k_0 are the respective specific rate constants when halide or water is the donor particle, α and β are constants for a particular substrate. E_n and H are nucleophilicity and basicity constants for the donor particle. Equation 13 was applied to the rate laws (7) to (10) based on reaction 12 as the rate-determining step. The values of E_n and H given by Edwards are used. The results are shown in Table II. In view of the long extrapolation from 100 to 25° and of the uncertainties in the ionic strengths involved, the correlation between the rates is good.

TABLE II

CORRELATION OF THE FOURTH-ORDER SPECIFIC RATE CONSTANTS[a] IN EQUATIONS 7 TO 10 BY THE EMPIRICAL EQUATION OF EDWARDS[11]

Donor	E_n	H	k (calcd.)	k (obsd.) 25°
H_2O	0	0	....	1.6×10^{-9}
Cl^-	1.24	−3.00	4.7×10^{-5}	4.5×10^{-5}
Br^-	1.51	−6.00	7.1×10^{-5}	9.3×10^{-5}
I^-	2.06	−9.00	1.8×10^{-3}	2.0×10^{-3}

[a] The values of α and β are 4.42 and 0.34, respectively.

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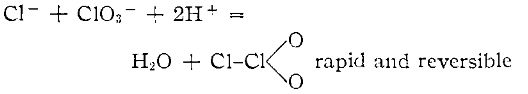
(8) A. Skrabal and H. Schreiner, *Monatsh.*, **65**, 213 (1935).

(9) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).

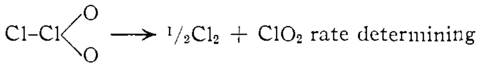
(10) K. Wiberg, *ibid.*, **55**, 721 (1955).

(11) J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954).

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

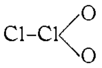


$$\mathrm{Cl^- + ClO_3^- + 2H^+ = H_2O + Cl{-}ClO_2} \quad \text{rapid and reversible} \quad (14)$$



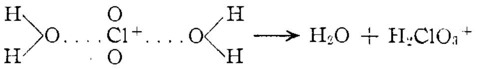
$$\mathrm{Cl{-}ClO_2 \longrightarrow {}^1/_2Cl_2 + ClO_2} \quad \text{rate determining} \quad (15)$$

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

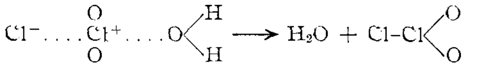


$$\mathrm{Cl{-}ClO_2}$$

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



$$\mathrm{H_2O\cdots ClO_2^+\cdots OH_2 \longrightarrow H_2O + H_2ClO_3^+} \quad (16)$$



$$\mathrm{Cl^-\cdots ClO_2^+\cdots OH_2 \longrightarrow H_2O + Cl{-}ClO_2} \quad (17)$$

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

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

$$\mathrm{2ClO_2 = ClO_2^+ + ClO_2^-} \quad (18)$$

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 $\mathrm{ClO_2^+}$ 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

$$\mathrm{2ClO_2 + H_2O = 2H^+ + ClO_2^- + ClO_3^-} \quad (19)$$

The fact that $\mathrm{ClO_2}$ 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

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

The activation energy for the $\mathrm{BrO_3^-}$–$\mathrm{H_2O}$ 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.

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

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

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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).