another straight line for the *p*-quinones.

3. The rates of photoöxidation for magnesium tetraphenylchlorin are lower than the corresponding zinc chlorin reactions by a factor of almost eight.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Photochemical Studies of the Porphyrins. III. The Photoöxidation of Chlorins by Oxygen

BY FRANK M. HUENNEKENS[1] AND M. CALVIN

In the previous paper of this series[1a] it was established that the zinc and magnesium complexes of tetraphenylchlorin may be photooxidized to the corresponding porphin utilizing various ortho- and para-quinones as the hydrogen acceptors. Traces of oxygen were found to interfere with the normal quinone–chlorin reaction and a method of de-oxygenating the solution with purified hydrogen was devised. From a biological point of view, molecular oxygen is of great importance for although it possesses a high oxidation potential and is the final electron acceptor in aerobic systems it is, nevertheless, unable to directly oxidize certain compounds; *e. g.*, reduced pyridinoproteins or cytochrome c. It was of interest to ascertain whether in this case oxygen might be competing with the quinone as an oxidant for the photoactivated zinc chlorin.

Experimental

Part 1. Apparatus and Materials.—The apparatus and materials used in these experiments were the same as described in the previous two papers of this series.[1,2]

The ultimate reaction product, called the zinc chlorin–oxygen complex, obtained when oxygen reacts with photo-activated zinc chlorin, was not isolated in pure form. For absorption spectra purposes a known solution of zinc chlorin, in a sealed Pyrex 1-cm. square cuvette, was exposed to bright sunlight for five minutes. The absorption spectrum of this "unbleached," straw-yellow solution was determined as rapidly as possible (within five minutes) using a Cary Recording Spectrophotometer. The molal extinction coefficients were calculated on the basis that conversion of the initial chlorin was quantitative. The "bleached" product was quite stable since the absorption spectrum of a solution, exposed to diffuse laboratory light for several days, did not change appreciably; furthermore, several different zinc chlorin solutions exposed to light under a variety of conditions yielded the identical product.

The absorption spectrum of the metal-free chlorin–oxygen product was obtained by removing the zinc from a known solution of the "bleached" complex by means of the hydrochloric acid–ammonium hydroxide treatment described in a previous paper.[1]

Rate runs in the presence of both oxygen and a quinone were made inadvertently during the early part of this investigation when imperfectly sealed reaction cells permitted small quantities of oxygen to enter. Since the reaction rate is independent of the concentration of the oxidant provided it exceeds a certain minimum (*ca.* 10^{-6} M for zinc chlorin), it is, therefore, unnecessary to know the exact amount of oxygen present.

When oxygen alone was the oxidant, 2 cc. of the chlorin solution and 1 cc. of benzene were delivered directly to the reaction vessel and since the solution was not de-oxygenated by freezing, evacuating and sweeping with hydrogen, no volume correction was required.

Part 2. Calculations.—As will be discussed more thoroughly in a later section, oxygen differs from the quinones in that after the primary oxidation of the chlorin to the porphin a secondary reaction takes place in which the hydrogen peroxide reacts further with the porphin to produce a "bleached" yellow product. This does not interfere with the normal measurement of the quantum yield, since of all the substances in solution only the chlorin absorbs the irradiating light (6225 Å.) and the method of following the reaction depends only upon the disappearance of the chlorin.

In the case of 1,4-benzoquinone and 9,10-phenanthraquinone several runs were made in the presence of oxygen. For these runs, the observed quantum yields (γ) has been multiplied by a correction factor (f) to give the hypothetical quantum yield (γ') which would have been obtained if the quinone alone had reacted with the porphin. This correction factor is derived as follows: consider an entire rate run and let

n = total number of chlorin molecules that have reacted (with quinone and oxygen)
n' = number of chlorin molecules that have reacted with oxygen alone
Q = total number of quanta absorbed
γ = measured quantum yield
γ' = quantum yield of the quinone–chlorin reaction only
$A_0 - A$ = change in the log $1/T$ (the usual log I_0/I from the Beckman Spectrophotometer) reading at 6225 Å. for the entire run

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[1a] Huennekens and Calvin, THIS JOURNAL, **71**, 4024 (1949).

[2] Calvin and Dorough, *ibid.*, **70**, 699 (1948).

$C - C_0$ = change in the log $1/T$ reading at 4650 Å. (the expression is written as $C - C_0$ to keep it positive since $C > C_0$)

ϵ_a = extinction coefficient of zinc chlorin at 6225 Å.

ϵ_c = extinction coefficient of the zinc chlorin–oxygen product at 4650 Å.

K = $V \times N \times 10^3$, a conversion factor, which when multiplied by a concentration change, will give the change in number of molecules. (V is the volume of the solution in cc., N is Avogadro's number)

Now

$$\gamma = n/Q \text{ by definition} \quad (1)$$

$$n = [(A_0 - A) \times K]/\epsilon_a \quad (2)$$

Let us assume, as a first approximation, that the oxygen merely reacted with the chlorin to give the chlorin–oxygen product whose absorption spectrum has been measured and characterized by a band at 4650 Å. and, furthermore, that the rise in the 4650 Å. band is a measure of the oxygenation. Then

$$n' = (C - C_0) \times K/\epsilon_c \quad (3)$$

$$\gamma' = (n - n')/Q \quad (4)$$

Substituting Q from equation (1)

$$\gamma' = \frac{(n - n')}{n} \times \gamma \quad (5)$$

Replacing n and n' from equations (2) and (3) and cancelling K

$$\gamma = \gamma' = \left\{\frac{[(A - A_0)/\epsilon_a] - [(C - C_0)/\epsilon_c]}{(A_0 - A)/\epsilon_a}\right\} \times \gamma \quad (6)$$

This simple correction, applied to oxygenated runs, will give a corrected quantum yield approaching that of a run made in the absence of oxygen. A further improvement is possible. We have assumed that in the absence of oxygen, the 4650 Å. band should remain stationary. Since the extinction coefficient is greater for zinc chlorin than zinc porphin (*ca.* 2.0×10^3 compared to 1.8×10^3) a change from chlorin to porphin, without considering oxygenation, should result in a slight decrease of the 4650 Å. band. Thus, the term $(C - C_0)/\epsilon_c$ should be amended to read $[(C - C_0) + P]/\epsilon_c$ where P represents the number of log $1/T$ units that have been lost through the chlorin going to porphin. P is obviously some function of $(A - A_0)$ and we may let $P = f'(A_0 - A)$. f' is very difficult to evaluate since a rigorously derived expression must take into account not only the change in all three bands (6225, 5510 and 4650 Å.), but also the extinction coefficients of the chlorin, porphin and oxygenated product at these three wave lengths. Because of the complexity of this expression and the uncertainty of the numerical values for several of the nine extinction coefficients, it was decided to accept an empirical value of 0.037 for f'. Inserting this correction and knowing that $\epsilon_a = 54.9 \times 10^3$ and $\epsilon_c = 38.7 \times 10^3$, equation (6) becomes

$$\gamma' = \left\{\frac{\dfrac{(A_0 - A)}{54.9 \times 10^3} - \dfrac{(C - C_0) + 0.037\,(A_0 - A)}{38.7 \times 10^3}}{\dfrac{(A_0 - A)}{54.9 \times 10^3}}\right\} \times \gamma \quad (7)$$

which reduces to

$$\gamma' = \{0.948 - [1.42\,(C - C_0)/(A_0 - A)]\} \times \gamma \quad (8)$$

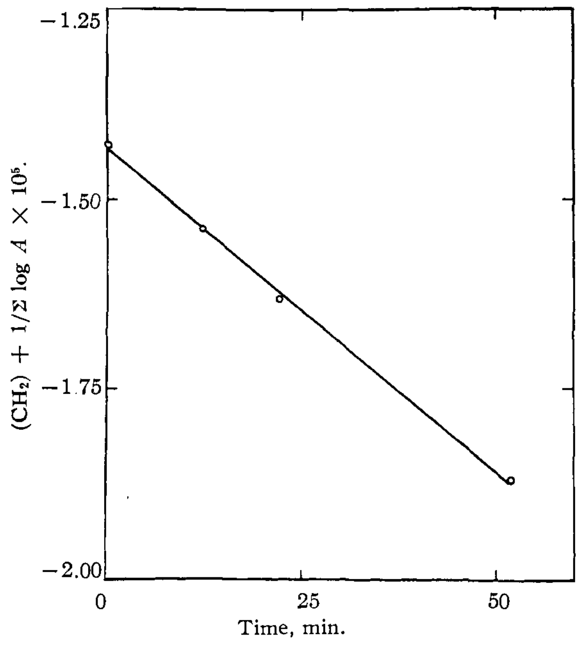

Fig. 1.—Run no. 48.

Part 3. Tabulation of Results.—Table I lists the data for a typical run, No. 48, in which both oxygen and 1,4-benzoquinone were present. The symbols are the same as those employed in the preceding paper.[1] The rate curve for this run, shown in Fig. 1, is essentially a straight line even though two competing reactions are being summed.

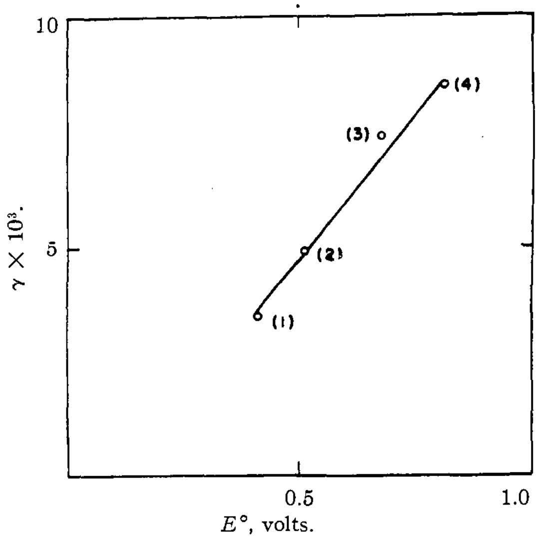

Fig. 2.—Comparison of oxygen with ortho-quinones: (1), 9,10-phenanthraquinone; (2), 1,2-naphthoquinone: (3) oxygen; (4) 1,2-benzoquinone.

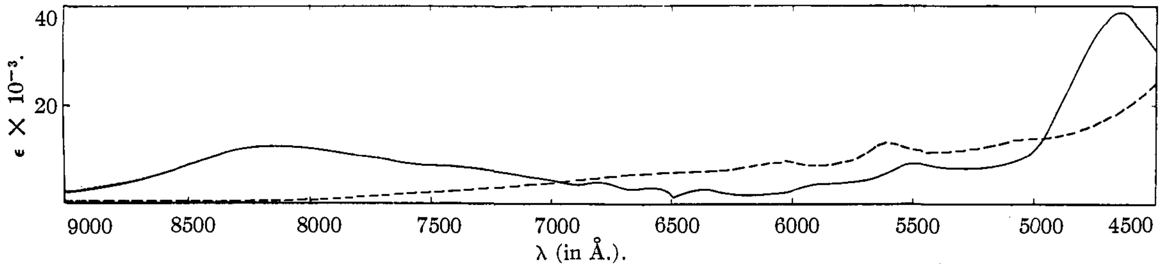

Fig. 3A.—- - - - - Magnesium tetraphenylchlorin-oxygen product in benzene; — zinc tetraphenylchlorin-oxygen product in benzene.

TABLE I

RUN NO. 48—ZINC CHLORIN WITH 1,4-BENZOQUINONE AND OXYGEN

Time	Log 1/T 6225 Å.	5510 Å.	4650 Å.	Chlorin concn.	$(CH_2) + 1/\Sigma$ log A
0	0.484	..	0.046	0.881×10^{-5}	−1.43
12	.465	..	.053	.845	−1.54
22	.448	..	.059	.817	−1.63
52	.408	..	.086	.744	−1.87

A summary of all the oxygenated runs, showing the correction factor (f) is presented in Table II. For comparison, a non-oxygenated run, indicated by a blank in the correction factor column, has been included for each quinone.

Summarized data and quantum yields for rate runs made with oxygen alone are listed in Table III.

Discussion

The experimental data suggest that as an oxidant for zinc and magnesium chlorins oxygen is similar in nature to the quinones. Oxygen is reduced to hydrogen peroxide, corresponding to the reduction of a quinone to the hydroquinone. Using 0.68 volt[3] as the standard oxidation potential of the latter couple and 0.0074 as the quantum yield for the oxidation of zinc chlorin by molecular oxygen a comparison is made, in Fig. 2, of oxygen with the ortho-quinones. The quinone values are taken from the preceding paper in this series.[1] While some doubt exists as to the accuracy of the value for the oxygen–peroxide couple, it would seem, nevertheless, that the agreement of oxygen with the ortho-quinone line is too good to be accidental.

In the case of oxygen, a secondary reaction takes place between the hydrogen peroxide and porphin in which the porphin is probably attacked at one of the methine bridges causing the great ring to open to a tetrapyrrole.

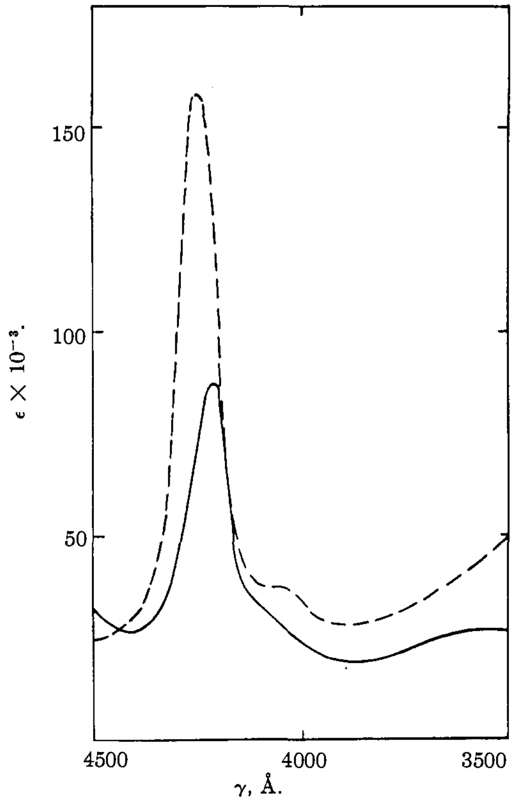

Fig. 3B.

In addition to being above to act as a hydrogen acceptor, oxygen, because of its paramagnetism, might conceivably exert another effect upon the reaction. The selection rule which prohibits transitions from the triplet to the ground singlet state is easily broken down in the presence of inhomogeneous magnetic fields or heavy atoms. The non-reactivity of copper chlorin toward quinones was attributed to the paramagnetism due to the one unpaired electron in the copper orbitals.[2] By similar reasoning, one might expect the paramagnetism of the oxygen molecule to shorten the lifetime of the triplet chlorin molecules causing any oxygenated run to have a slower rate than the corresponding quinone–chlorin reaction without oxygen. From the experimental evidence this is not the case for an ortho-quinone of lower potential than oxygen (*e. g.*, 9,10-phenanthraquinone). The presence of oxygen actually increases the over-all rate; furthermore, it has been demonstrated that oxygen does not inhibit, but competes with, a quinone–chlorin reaction. The oxygen is an external paramagnetic influence and apparently does not affect the chlorin transition probabilities to the same degree as the copper which is incorporated directly into the molecule.

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(3) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., New York, N. Y., 1938, p. 38.

TABLE II

QUANTUM YIELDS—ZINC TETRAPHENYLCHLORIN

Run	Chlorin concn. $\times 10^5$	Quinone	Quinone concn.	Slope (M) $\times 10^9$	V	k_1 $\times 10^{22}$	D	I_0 $\times 10^{14}$	γ	f	γ'
57	1.25	1,4-Benzo-	4.38×10^{-4}	2.38	2.31	7.14	1.06	6.95	0.0048	0.422	0.0020
48	1.25	1,4-Benzo-	5.55×10^{-5}	1.48	2.42	6.82	0.70	4.58	.0047	.447	.0021
51	1.25	1,4-Benzo-	5.55×10^{-3}	1.75	2.39	6.90	1.47	9.64	.0026	.745	.0020
40	1.25	1,4-Benzo-	5.55×10^{-4}	1.64	2.32	7.11	0.82	5.38	.0043	.526	.0023
70	1.25	1,4-Benzo-	2.57×10^{-2}	1.20	2.28	7.23	1.25	8.20	.0020	...	.0020
32	1.68	9,10-Phenanthra-	5.38×10^{-4}	2.32	2.42	6.82	1.04	6.82	.0059	.549	.0033
58	1.25	9,10-Phenanthra-	5.96×10^{-5}	1.98	2.34	7.05	1.08	7.08	.0040	.788	.0032
46	1.25	9,10-Phenanthra-	2.98×10^{-3}	1.24	2.49	6.62	0.84	5.52	.0034	...	.0034

TABLE III

QUANTUM YIELDS—OXYGEN UPON ZINC AND MAGNESIUM TETRAPHENYLCHLORINS

Run	Chlorin	Chlorin concn. $\times 10^5$	Oxygen concn.[4]	Slope (M) $\times 10^9$	V	$k_1 \times 10^{22}$	D	$I_0 \times 10^{-14}$	γ
73	Zinc	1.25	7.28×10^{-3}	3.90	3.00	5.50	1.47	9.64	0.0074
67	Magnesium	0.551	7.28×10^{-3}	0.467	3.00	5.50	1.38	9.05	.00094

The spectra of the "bleached" products of zinc and magnesium chlorins, shown in Fig. 3, are markedly different. Even more surprising are the spectra of the metal-free products (Fig. 4) since, at this point, the compounds would have been identical provided that the hydrogen peroxide had attacked each of the original metallochlorins in the same manner. The obvious differences between the behavior of zinc and magnesium chlorins with oxygen suggests that the reaction may not be clean-cut but rather a compromise between several possibilities. Calvin and Dorough[2] have found that the "bleached" zinc chlorin product, when chromatographed on talc, yielded traces of metal-free chlorin and porphin as well as two unknown substances characterized by blue zones on the column.

Consistent with this is the observation that reaction rates and quantum yields toward a given oxidant change from one metallochlorin to another as illustrated in Table III of this paper and Table VI of the preceding paper.[1] Calvin and Dorough[2] showed that toward 1,2-naphthoquinone copper chlorin is only about one-hundredth as reactive as zinc chlorin. As would be expected, zinc chlorin solutions, in the presence of oxygen, are "bleached" within a few minutes by diffuse indoor light, whereas copper chlorin solutions under

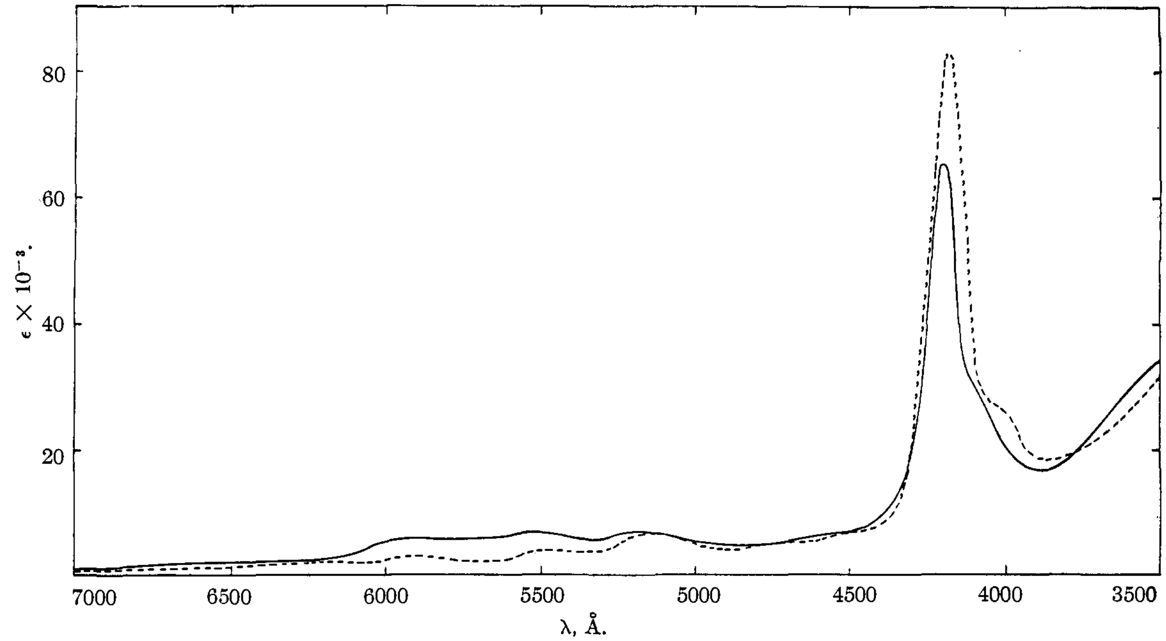

Fig. 4.— - - - -Magnesium tetraphenylchlorin-oxygen product (metal-free); — zinc tetraphenylchlorin in benzene.

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(4) Solubility of oxygen in benzene at 19°: "International Critical Tables," 1st ed., 1928, Vol. III, pp. 261–283.

similar conditions are stable for many hours.

The absorption curves of the metallochlorin "bleached" products are qualitatively similar to the curves for irreversible "bleaching" of chlorophyll by oxygen in acetone, as reported by Aronoff and MacKinney.[5] Furthermore, in the same paper, these authors report a value of 5×10^{-4} for the quantum yield of irreversible "bleaching" of chlorophyll solutions in benzene. This is in order of magnitude agreement with our value of 9.4×10^{-4} for the quantum yield of the photooxidation of magnesium chlorin by oxygen.

Summary

1. Zinc and magnesium tetraphenylchlorins may be photo-oxidized by molecular oxygen in a manner similar to ortho- and para-quinones.

2. Oxygen does not inhibit a chlorin–quinone reaction but merely reacts competitively with the quinone for the chlorin (at least for quinones of lower oxidation potential than oxygen).

3. A secondary reaction occurs between hydrogen peroxide and the porphin yielding a product similar to that obtained by "bleaching" chlorophyll in the presence of oxygen.

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(5) Aronoff and MacKinney, THIS JOURNAL, **65**, 956 (1943).

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

The Extraction of Gallium Chloride by Isopropyl Ether

BY NORMAN H. NACHTRIEB AND ROBERT E. FRYXELL

The distribution of gallium chloride between aqueous hydrochloric acid and diethyl ether has received the attention of several workers. Grahame and Seaborg[1] report that the distribution is independent of gallium concentration in the range 10^{-12} to 10^{-3} molar, but Swift[2] reports a relatively greater extraction for higher concentrations.

It is well known that the distribution of gold chloride[3,4] and ferric chloride[5,6,7,8] between aqueous hydrochloric acid and ethers is dependent on the concentration of the metal chloride. In a recent paper the present authors reported data for ferric chloride showing that this distribution (using isopropyl ether) follows the simple Nernst distribution law for sufficiently low ferric chloride concentrations.[7] It was suggested that the existence of polymers in the ether phase need not be postulated to explain the dependence of the distribution on iron at higher concentrations, but alternatively, the anomaly may be due to a self-promoted activity of ferric chloride in the aqueous phase.

This paper reports a similar study which has been made of the distribution of gallium chloride between aqueous hydrochloric acid and isopropyl ether.

Experimental

Preparation of Solutions.—For the majority of the experiments, radioactive Ga^{72} was used to facilitate analysis. The gallium was received as a mixture of oxide and nitrate.[9] A solution was prepared by dissolving 0.0559 g. of this material in 20.0 ml. of 7.30 molar hydrochloric acid, purified by extraction with two 20-ml. portions of isopropyl ether, and won back from the ether with water to provide a gallium tracer solution. This solution was diluted to 50.0 ml. It was assigned a concentration of 0.00594 *M*, based upon a gravimetric determination of the gallium in the oxide–nitrate mixture after its activity had decayed.

A stock solution of inactive gallium chloride was prepared as follows: 5.1457 g. of gallium metal (99.9%) was dissolved in hot aqua regia, evaporated to a sirupy consistency twice with 10-ml. portions of concentrated nitric acid, and finally taken to dryness. The residue was heated at *ca.* 260° until the nitrate was completely converted to oxide. An excess of concentrated hydrochloric acid (20.0 ml.) was added; warming effected complete solution. It was discovered that by warming and blowing air over the surface of this solution, a gel formed which would not redissolve on dilution. Apparently, this was a basic salt, since addition of a few ml. of hydrochloric acid caused solution. Aeration of the solution at room temperature was successful in removing the small excess of hydrochloric acid. Analysis of this solution after dilution to 75.0 ml. gave: $(Ga) = 0.8957\ M$, $(Cl^-) = 2.677\ M$.

The isopropyl ether was purified by shaking with alkaline potassium permanganate solution, drying over calcium chloride, and distilling. The fraction boiling in the range 66.5 to 67.5° at 747.1 mm. was collected.

Analytical Methods.—Measurement of the radioactivity of the samples served as a determination of relative concentrations of gallium. Aliquots of solutions were evaporated just to the point of dryness under an infrared lamp on 1″ copper disks having spun-up edges. Counting rates were determined with a thin-wall mica window Geiger–Müller tube in conjunction with a Higginbotham type scaler. Whenever possible, a total count of at least 5,000 was registered. The background of the counter was 28 counts/minute. The statistical error was probably lower than the errors due to self-absorption and to handling an isotope with a half life of only fourteen and one-tenth hours. The latter error was minimized by counting consecutively the copper disks corresponding to the ether and aqueous phases of a single extraction.

Gallium analyses listed in Table I and those noted in Table II were performed by the 8-hydroxyquinoline–potassium bromate titration method as described by Kolt-

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(1) D. C. Grahame and G. T. Seaborg, THIS JOURNAL, **60**, 2524 (1938).

(2) E. H. Swift, *ibid.*, **46**, 2375 (1924).

(3) W. A. E. McBryde and J. H. Yoe, *Anal. Chem.*, **20**, 1094 (1948).

(4) F. Mylius and C. Hüttner, *Ber.*, **44**, 1315 (1911).

(5) R. W. Dodson, G. J. Forney and E. H. Swift, THIS JOURNAL, **58**, 2573 (1936).

(6) J. Axelrod and E. H. Swift, *ibid.*, **62**, 33 (1940).

(7) N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948).

(8) C. H. Craft and G. R. Makepeace, *Ind. Eng. Chem., Anal. Ed.*, **17**, 206 (1945).

(9) Supplied by Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tennessee.