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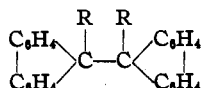
The Autoxidation of Some Substituted Difluoryls and Dixanthyls¹

BY HENRY W. SCHERP

Conant and Evans² have studied the rate of autoxidation of alkyl substituted dixanthyls in solution. They found that over a range of 0.0 to 0.6 mole of oxygen absorbed per mole of dixanthyl, the reaction resulted in the formation of the corresponding peroxide. The reaction followed a monomolecular course and the rate was independent of changes in the partial pressure of oxygen above the solution. The authors concluded that the reaction took place in two steps, (1) slow dissociation of the dixanthyl into free radicals (the monomolecular rate determining step) and (2) rapid combination of the latter with oxygen.

The autoxidation of hexaphenylethane has been studied by Mithoff and Branch³ and by Ziegler and co-workers.⁴ The former concluded that the reaction took place both by oxidation of the undissociated molecule and of the free radicals. Ziegler's findings were essentially the same, but he found that the reaction with iodine was more satisfactory for measuring the rate of dissociation.

The present work is an extension of the studies of Conant and Evans to include compounds in the fluorene series (diaryl difluoryls) of the type



where R may be a phenyl, biphenyl, *p*-tolyl, or *p*-anisyl group. Although closely related structurally to compounds of the hexaphenylethane type, these compounds in solution exhibit the color change which is characteristic of dissociation into free radicals, only at elevated temperatures. At room temperature they manifest their reactivity by undergoing autoxidation, with formation of the corresponding peroxides.^{5,6} In addition to the above, the rate of dissociation of dibenzyl dixanthyl has been determined and some of the work with dimethyl- and di-isoamyl dixanthyl has been reviewed.

(1) Abstracted from the doctoral thesis of the author, presented May 1, 1931. The author takes pleasure in acknowledging his indebtedness to Dr. James B. Conant, under whose direction this work was carried out.

(2) Conant and Evans, *THIS JOURNAL*, **51**, 1925 (1929).

(3) Mithoff and Branch, *ibid.*, **53**, 255 (1930).

(4) Ziegler, Ewald and Orth, *Ann.*, **479**, 277 (1930).

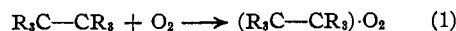
(5) Gomberg and Cone, *Ber.*, **39**, 2969 (1906).

(6) Schlenk and Herzenstein, *Ann.*, **372**, 30 (1910).

Except for some of the first experiments, which were conducted using an all-glass modification of the apparatus of Conant and Evans,² all measurements were made using the apparatus described by Hyde and the author,⁷ which measures changes in pressure at constant volume. The samples of material were introduced as a solution in capsules, ensuring rapid establishment of equilibrium conditions. Oxygen was present in such an excess that its partial pressure over the course of an experiment could be regarded as constant with an error of less than $\pm 2\%$. The solvent used in most cases was *sym*-tetrachloroethane, which also served as the manometric liquid. Otherwise, bromobenzene was used. The temperature was constant throughout an experiment, corrected, with an error of not more than $\pm 0.05^\circ$.

The results of some typical experiments in which 0.01 *M* solutions of di-*p*-tolyl difluoryl in tetrachloroethane were studied are shown graphically in Fig. 1. The values $-\log(1 - Z)$ (where *Z* is the fraction reacted, and equals moles of oxygen absorbed divided by moles of sample taken) were plotted against time in minutes. Each plot represents the points determined in duplicate runs at 25°. In A, the reaction was carried out in the presence of air; in B, of oxygen.

When the data were plotted as in Fig. 1, the points in each case fell on a straight line passing through the origin, showing that at a given partial pressure of oxygen in excess the reaction followed a monomolecular course. The slope of the line multiplied by 2.303 gave the value of the apparent first-order reaction velocity constant, *k*. The results have been interpreted on the assumption that the sole product of the reaction was the corresponding peroxide, according to the over-all equation



The validity of this assumption is indicated by the fact (1) that in all the cases studied the difluoryls combined with a total of one mole of oxygen per mole of substance, within the experimental error, and (2) that the values of *Z*, calculated from the graphically determined reaction velocity constants, agreed closely in all cases with the experi-

(7) Hyde and Scherp, *THIS JOURNAL*, **52**, 3359 (1930).

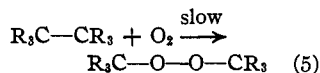
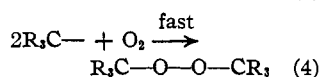
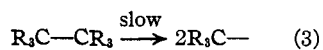
mental values, over as much as 85% of the course of the reaction. However, the reaction was usually followed only to the point, $Z = 0.6$ to 0.7 . Samples of material prepared at different times gave identical results.

range 0.2 to 1.43 atmosphere, and may be expressed by the equation

$$k = k_1 + k_2 \cdot P_{O_2} \quad (2)$$

where k is the observed constant, k_1 corresponds to a monomolecular reaction and k_2 corresponds

to a bimolecular reaction and represents the latter's rate constant at $P_{O_2} = 1$ atmosphere. Considering previous findings,^{2,3,4} three types of reaction probably occur simultaneously in solutions of the difluoryls exposed to oxygen.



The over-all rate observed would be determined by (3) and (5) with the latter predominant under the conditions used. From (2) and the data in Table I, values of k_1 (reaction (3)) and k_2 (reaction (5)) may be calculated. The values of k_2 are from 10 to 50 times those of

k_1 , and confirm the predominance of (5) at $P_{O_2} = 1$ atm. The calculated values of k_1 , the constant of the rate of dissociation, cannot be given much weight, since an error of, say, 2% in the determination of k would cause an error of as much as 100% in the value of k_1 .

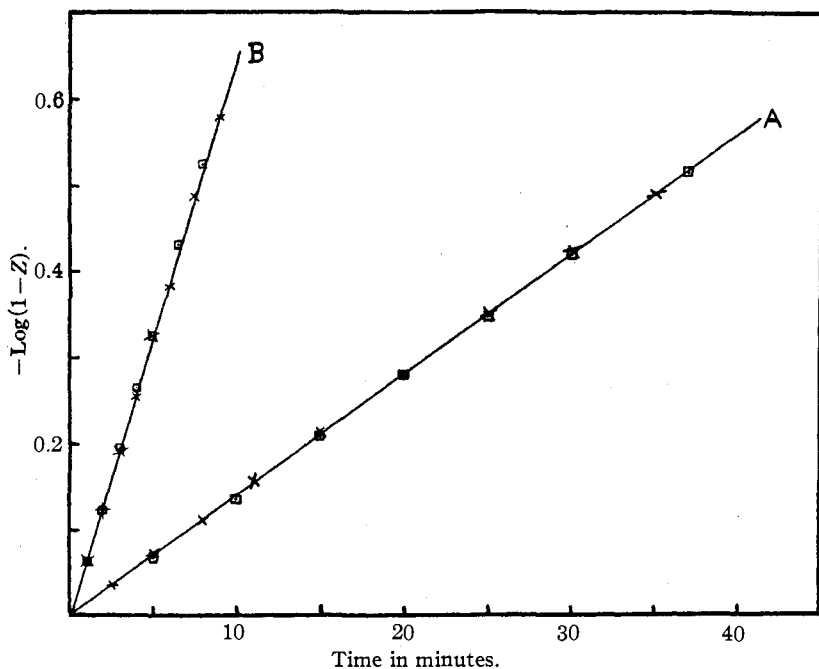


Fig. 1.—Rate of autooxidation of di-*p*-tolyl difluoryl at 25° in 0.01 *M* solution in tetrachloroethane. The points in A were determined in an atmosphere of air; those in B in an atmosphere of oxygen.

The results obtained with the difluoryls are summarized in Table I. It is evident that (1) the rate was dependent upon the partial pressure of oxygen above the solution, that (2) the rate constant was not affected (diphenyldifluoryl) by a 3.6-fold change in the initial concentration of substance, that (3) the rate was not affected by the presence of 1 or 0.1% hydroquinone, which is known to act as a negative catalyst in autoxidation reactions of the chain type. The ratios, k_{O_2}/k_{air} at 25°, are listed in the order in which the compounds appear in Table I, 4.4, 4.6, 3.7 and 4.4. At 0°, the ratios are 3.0, 4.3, 3.1 and 4.55. The ratio for a true bimolecular reaction, 4.76, is then so closely approximated in some of the cases as to be almost within the experimental error. The relationship between oxygen pressure (P_{O_2}) and velocity constant was studied in some detail in the case of diphenyl difluoryl. The results are shown graphically in Fig. 2, where the values of k have been plotted against P_{O_2} in atmospheres. It is evident that the relationship is linear over the

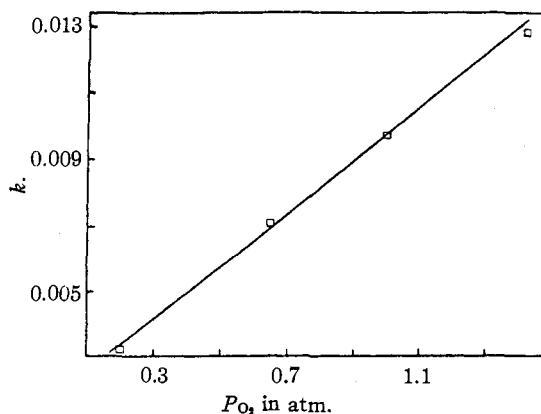


Fig. 2.—Variations in the rate constant (diphenyl difluoryl) with changes in the partial pressure of oxygen.

TABLE I
RATES OF AUTOXIDATION OF DIFLUORYLS

All measured in 0.01 molar solution in tetrachloroethane unless otherwise indicated. Those marked with an asterisk were measured in the modified Barcroft apparatus.

Substance	P_{O_2} , atm.	Expts.	Temp., °C.	Average value $k \times 10^2$	E , cal.
Diphenyldifluoryl	0.2	2	0	0.32	
	0.65	3	0	0.71	
	1.0	4	0	0.97	
	1.43	2	0	1.28	
	0.2	2	25	3.3	15,000
	1.0	2	25	14.6	17,500
	0.2	2	25	2.65*	
	1.0	2	25	14.2*	
0.0028 <i>M</i>	0.2	1	25	2.75*	
0.0028 <i>M</i>	1.0	2	25	13.8*	
Di- <i>p</i> -tolylidifluoryl	0.2	2	0	0.28	
	1.0	2	0	1.20	
	0.2	2	25	3.23	15,800
	1.0	2	25	14.9	16,300
Dibiphenyldifluoryl	0.2	2	0	0.173	
	1.0	2	0	0.54	
	0.2	2	25	2.1	16,200
	1.0	2	25	7.7	17,200
Di- <i>p</i> -anisylidifluoryl	0.2	2	0	0.224	
	1.0	2	0	1.02	
	0.2	2	25	2.8	16,400
	1.0	2	25	12.4	16,200
Diphenyldifluoryl with 1% hydro- quinone	0.2	1	25	3.2	
Diphenyldifluoryl with 0.1% hydro- quinone	0.2	2	25	2.61 3.3	

The mechanism postulated requires that the temperature coefficient of (5) shall be equal to or greater than that of (3) since the former tends to become less predominant at lower temperatures, as is indicated by the fact that the k_{O_2}/k_{air} ratios are lower, with one exception, at 0° than at 25°. This is inconsistent with the findings of Conant and Evans,² who reported that the dissociation reaction of the dixanthyls had an unusually high temperature coefficient, the values of E , the energy of activation, being of the order of 30,000 calories. On the other hand, the diaryldifluoryls are more closely related structurally to free radicals of the hexaphenylethane type. For the dissociation of the latter compound, Ziegler⁴ found the value of E to be 13,500. The values of E (calculated from the integrated form of the equation $d \ln k/dT = -E/RT^2$) for the difluoryls studied fell between 15,000 and 17,500. These values correspond, of course, most nearly to the bimo-

lecular reaction (5), since it is the latter with which the mechanism is principally concerned. Unfortunately, the rate constant of the monomolecular dissociation reaction cannot be determined from the data presented with sufficient accuracy to permit interpretation.

Conant and Evans² found that there was a parallelism between the tendency of solutions of the dixanthyls to develop color when heated, and the rate of autoxidation (dissociation). It was not possible to estimate satisfactorily the temperature at which solutions of the difluoryls first developed the color which is characteristic of dissociation into free radicals, since the phenomenon was not as sharply defined as in the case of the dixanthyls. However, at 70°, 0.05 molar solutions in ethyl benzoate in an atmosphere of nitrogen showed enough variation in color to be arranged as follows, in the order of increasing intensity: (1) di-*p*-tolylidifluoryl, (2) diphenyldifluoryl, (3) dibiphenyldifluoryl, (4) di-*p*-anisylidifluoryl. Arranged according to the rate of autoxidation at 0°, $P_{O_2} = 0.2$ atm., the order was (3), (4), (1) and (2). There was therefore no parallelism, a conclusion which might be predicted from the fact that the autoxidation was not much concerned with the dissociation. It should be noted in this connection that solutions of the difluoryls develop color at much lower temperatures (70 to 80°) than do solutions of compounds in the dixanthyl series having a comparable reactivity toward oxygen. Thus, Conant and Evans² reported 100° for dibenzylidixanthyl and 160° for di-isoamylidixanthyl.

The results of a review of the rates of autoxidation of dimethyl- and di-iso-amyl- and the measurement of that of dibenzylidixanthyl are given in Table II. There was a definite effect of changes in P_{O_2} upon the rate, except in the case of dimethylidixanthyl at 25°. However, the effect was far less than that observed with the difluoryls. If equation (2) is applied, it develops that the values of k_2 are less than those of k_1 , and at $P_{O_2} = 0.2$ atm., the measured value, k , may be regarded as the rate constant of the dissociation reaction, with an error of not more than $\pm 5\%$. It should be pointed out that the oxidation of the dixanthyl derivatives is complicated by the presence of side reactions of unknown nature, whose rate is probably proportional to oxygen concentration, that is, whose mechanism is probably straight bimolecular oxidation.

TABLE II
RATES OF AUTOXIDATION OF DIXANTHYLS

All measured in 0.01 molar solution, dimethyldixanthyl in bromobenzene, the others in tetrachloroethane.

Substance	PO ₂ , atm.	Temp., Expts. °C.	Average value k × 10 ²	E _a , cal.	k _{O₂} /k _{air}
Dimethyl- dixanthyl	0.2	1	25	0.176	31,000
	1.0	2	25	0.176	1.0
	0.2	2	45	3.0	
	1.0	2	45	4.5	1.5
	0.2	2	50	5.0	
	1.0	2	50	10.0	2.0
Di-isoamyl- dixanthyl	0.2	2	25	1.08	28,000
	1.0	2	25	1.38	1.3
	0.2	1	35	4.93	
	1.0	1	35	6.4	1.3
Dibenzyl- dixanthyl	0.2	2	0	18.6	27,100
	0.2	3	-11.2	2.2	
	1.0	3	-11.2	3.2	1.45

Experimental

Apparatus.—The apparatus and its manipulation have been fully described in an earlier publication.⁷

Preparation of Substances.—Diphenyl-, dibiphenyl-, and di-*p*-anisyl-difluoryl were prepared according to the directions of Schlenk^{8,9} from the corresponding 9-chloro-9-aryl fluorenes. The apparatus used for the preparation and recrystallization was similar to that described by Schmidlin,¹⁰ differing principally in that it was provided with sealed-in disks of alundum for filtration; m. p.'s, respectively, 241, 175, and 225°. All m. p.'s, were measured in an atmosphere of dry, oxygen-free nitrogen and were not corrected. The oxygen absorption was 97 to 100% of the theoretical. Di-*p*-tolylidifluoryl was prepared by the following series of reactions: fluorenone + *p*-tolylmagnesium bromide → *p*-tolylfluorene (not isolated), + anhydrous HCl → *p*-tolylfluorenyl chloride (m. p. 96.5°), + copper bronze (under nitrogen) → di-*p*-tolylidifluoryl; m. p. 216°; oxygen absorption, 99.2% of the theoretical. *Anal.* Calcd. for C₄₀H₃₀: C, 94.1; H, 5.9. Found: C, 94.1; H, 6.2. Molecular weight, cryoscopic in nitrobenzene, under nitrogen. Nitrobenzene, 24.13 g. Substance, 0.1255, 0.0702 g. Δ*T*, 0.070, 0.038°; mol. wt., 520, 536. Calcd. for C₄₀H₃₀, 510. Dimethyl- and dibenzylidixanthyl were prepared according to the methods given by Conant and co-workers.¹¹ M. p.'s, resp., 178 and 156°. Di-isoamylidixanthyl was provided by Dr. James B. Conant. After one crystallization from benzene and petroleum ether under nitrogen, the m. p. was 160°. Later preparations of the difluoryls were made by a method similar to that used for the dixanthyls: a 1-2% solution of the arylfluorenyl chloride in glacial acetic acid containing 5% of concd. hydrochloric acid was reduced by the addition of 3-5 times the theoretical amount of either vanadous or chromous chloride. The crude material was precipitated by

the addition of water, dried and recrystallized as many times as was necessary from benzene and petroleum ether in an atmosphere of dry, oxygen-free nitrogen.

Procedure.—Since the difluoryls dissolved but slowly in the solvent chosen, tetrachloroethane (and for that matter in all the customary organic solvents), it was decided to have the sample in solution at the start of an experiment. The sample (0.05 millimole) was weighed into a capsule made by blowing a thin-walled bulb of 1.5 to 2-cc. capacity on the end of a 10-cm. length of glass tubing, 4.5 mm. in diameter. Any material adhering to the wall of the tube was removed by means of a pipe-stem cleaner. Then, while the sample was protected from heat by slipping a disk of asbestos paper onto the neck of the capsule, the latter was drawn out to a capillary of 0.1 to 0.2 mm. diameter at a point 2 to 3 cm. above the bulb. The capsule was then attached, glass to glass, to a Y-shaped adapter, to one of whose arms was sealed a small buret (glass stop-cock). The remaining arm of the adapter was connected to a vacuum and purified nitrogen system. The capsule was swept out several times with nitrogen, the required amount of freshly boiled and cooled solvent was drawn in from the buret and the sample was dissolved by gentle warming. The solution was cooled below the temperature of the thermostat, the capillary was broken at its midpoint and the capsule was placed quickly in the absorption apparatus, which had been charged with the proper amount of solvent. The apparatus was mounted in the thermostat and slowly shaken until the manometer reading was constant within 0.5 mm. Diffusion of oxygen into the capsule is minimized by the presence of the capillary and of nitrogen in the capsule under a pressure equal to or greater than that of the environment. The rest of the determination is carried out in the manner described previously.⁷ In those cases where the apparatus was to be swept out with a given gas mixture, the contents of the capsule were equilibrated in the thermostat and the capillary was sealed with a little paraffin. This procedure sometimes did not give perfect equilibration as was shown by a shift in the apparent zero reading. Correction was made by extrapolation or, when the reaction was slow enough, the zero reading was made one minute after the capsule was broken. It was found that the total absorption of oxygen as measured by the technique outlined was the same as that observed when the sample was introduced in the solid state. The error in the partial pressure of oxygen caused by the presence of the nitrogen in the capsule, was small enough to be ignored.

In the experiments where the oxygen pressure was other than 0.2 atm. (air) or 1 atm. (pure oxygen), the absorption apparatus was connected to a large reservoir containing pure oxygen and provided with a suitable manometer. The experiment was then conducted as usual, except that the apparatus was left open to the reservoir throughout.

Summary

The autoxidation of some diaryldifluoryls has been studied. The reaction takes place principally by oxidation of the undissociated molecule, and to a small extent by oxidation of the free radicals formed by dissociation of the difluoryl.

(8) Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1753 (1910).

(9) Schlenk and Mair, *Ann.*, **394**, 196 (1912).

(10) Schmidlin, *Ber.*, **41**, 423 (1908).

(11) Conant and co-workers, *THIS JOURNAL*, **47**, 572, 3068 (1925); **48**, 1743 (1926).

It has been confirmed that the autoxidation of dialkyl dixanthyls, at least in the early stages of the reaction, is dependent almost solely upon slow

dissociation into free radicals, which are themselves very rapidly oxidized.

THE CHILDREN'S HOSPITAL RECEIVED JANUARY 17, 1936
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[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Concentration of Deuterium in Organic Compounds. II. A General Discussion with Particular Reference to Benzene

BY MALCOLM DOLE

The abundance of deuterium in naturally occurring hydrogen compounds has been investigated by a number of workers. These researches may be divided into two classes: the first type of research consists in the investigation of naturally occurring water, while the second type consists in the investigation of water obtained in the combustion of hydrogen-containing organic substances. It is the latter type with which this paper is concerned; hence researches in which water only was investigated will not be discussed further. Table I summarizes data obtained by previous workers in the second type of investigation; that is, organic compounds were burned, and the density of the water obtained was measured after a careful purification of the water. These data, however, are subject to all or some of the following uncertainties which make the calculation of the deuterium concentration entirely unreliable.

TABLE I

RELATIVE DENSITIES OF WATER OBTAINED IN THE COMBUSTION OF HYDROGEN-CONTAINING ORGANIC SUBSTANCES

Author	Substance burned	O ₂ Source ^a	γ^b
Dole ^c	Benzene	Air	7.9
	Oklahoma kerosene	Air	6.2
	Honey	Air	4.1
Dole ^d	Benzene	Electrolysis	0
	Cholesterol	Air	0
Emeléus, James, King, Pearson,	Alcohol	Air	3
	Beet molasses	Air	2.9
Purcell and Briscoe ^e	Yeast from the above	Air	2.1
	Mixed molasses	Air	5.3
	Fusel oil	Air	4.0
	Sucrose	Linde?	8.6
	Cane sugar (Trinidad)	Air	7.56
	Salix caprea, wood	Linde?	3.2
	Motor petroleum	Linde?	11 ^g
Filippova, ^f Greene and Voskuyl ^h	Corn oil	Air	4.9
	Natural gas	Air	5.7
Moser ⁱ	Illuminating gas	?	0
	Anthracite coal	?	0
Okabe and Titani ^j	Filter paper	Air	6.3
	Cotton	Air	5.7
	Cedar wood	Air	4.5
	Bamboo	Air	4.4
Snow and Johnston ^k	Natural Oklahoma butane	Linde	6.1 (corr.?)
	Molasses	Air	2.8

Titani and Harada ^m	Crude cane sugar	Air	7.8
	Cane sugar, purified	Air	7.4
	Beet sugar, purified	Air	6.5
	Grape sugar (dextrose)	Air	6.4
	Milk sugar (lactose)	Air	5.9
	Soluble starch	Air	3.9
	Rice flour (starch)	Air	6.0
	Wheat flour (starch)	Air	6.0
	Potato starch	Air	5.9
	Dextrin	Air	5.4
	Galactan	Air	4.8
	Mannan	Air	5.8
Washburn and Smith ⁿ	Dry willow wood	Linde	3.2
			(corr.?)
Washburn and Smith ^o	Anthracite coal	?	0
	Natural propane	?	0

^a In this column "Linde" means oxygen obtained from liquid air, "Linde?" means commercial oxygen of unknown origin, "electrolysis" means electrolytic oxygen, "corr.?" means a correction has been applied to the density data for the oxygen used but that this correction is uncertain. ^b γ means the density difference between the water under investigation and normal water expressed in p. p. m. ^c M. Dole, *J. Chem. Phys.*, **2**, 337 (1934). ^d M. Dole, *ibid.*, **2**, 548 (1934). ^e H. J. Emeléus, F. N. James, A. King, T. G. Pearson, R. H. Purcell, H. Y. A. Briscoe, *J. Chem. Soc.*, (London), 1207, 1948 (1934). ^f N. S. Filippova, *J. Chem. Phys.*, **3**, 316 (1935). ^g Calculated from Filippova's estimated concentration of deuterium and not corrected for the type of oxygen used. ^h C. H. Greene and R. J. Voskuyl, *THIS JOURNAL*, **56**, 1649 (1934). ⁱ H. Moser, *Physik. Z.*, **35**, 682 (1934). ^j K. Okabe and T. Titani, *Bull. Chem. Soc. Japan*, **10**, 465 (1935). ^k R. D. Snow and H. L. Johnston, *Science*, **80**, 210 (1934). ^l T. Titani and M. Harada, *Bull. Chem. Soc. Japan*, **10**, 41 (1935). ^m T. Titani and M. Harada, *ibid.*, **10**, 205, 261 (1935). ⁿ E. W. Washburn and E. R. Smith, *Science*, **79**, 188 (1934). ^o E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12**, 305 (1934).

1. The atomic weight of the oxygen used in the combustion may not be the same as normal atmospheric oxygen. Both Smith¹ and Klar and Krauss² have found that commercial oxygen obtained in the fractional distillation of liquid air has a slightly higher atomic weight than atmospheric oxygen, the increase given by Smith for

(1) E. R. Smith, *J. Chem. Phys.*, **2**, 298 (1934); *Science*, **79**, 454 (1934).

(2) R. Klar and A. Krauss, *Naturwiss.*, **22**, 119 (1934).