[Contribution from the Research Laboratory, General Electric Company]

# The Determination of Organic Peroxides

By Herman A. Liebhafsky and William H. Sharkey

Because of possible explosion hazards,[1] and for other reasons, a rapid, accurate method for determining organic peroxides was needed in connection with a synthesis involving the distillation of large amounts of *n*-butyl ether. A modification of iodometric methods already in the literature[2] seemed most likely to meet the following requirements: (1) a reaction system homogeneous even during the titration; (2) a negligible blank; (3) liberation of iodine complete in less than ten minutes; (4) accuracy to within two drops of 0.01 *N* solution.

Simple experiments showed that homogeneity and rapid iodine liberation both can be obtained in glacial acetic acid. Separation into two phases, which occurs more readily with *n*-butyl than with ethyl ether, is avoided at room temperature if less than 8 cc. of water is added to 5 cc. of *n*-butyl ether dissolved in 25 cc. of the acid. The blank, however, is a more serious problem, especially since there is no guarantee that the reaction between oxygen and iodide (the "oxygen error"), which gives rise to the blank, will proceed independently of the reaction between peroxide and iodide. Numerous trials, which cannot be described in detail, showed the blank to be unreproducible but always too high when oxygen was present, even though light was rigorously excluded between mixing and titration. It was found that the blank could be eliminated satisfactorily by adding about 1.5 g. of sodium bicarbonate to the reaction mixture; the carbon dioxide produced is effective not only because it is heavier than air, but also because it is liberated within the reaction mixture, which it thus frees of oxygen.

The logical order of mixing is acetic acid, sodium bicarbonate, potassium iodide solution. With this sequence no appreciable iodine need be formed provided the acetic acid contains enough water to ensure vigorous effervescence before the iodide solution is added. Unfortunately, this amount of water retards the reaction between peroxide and iodide more than is desirable and leads to a rapid exhaustion of the bicarbonate. The reaction mixture was accordingly prepared as follows. To 25 cc. of glacial acetic acid and approximately 1.5 g. of sodium bicarbonate in a glass-stoppered flask, 1 cc. of potassium iodide solution (0.4 g./cc.) is added. The mixture usually becomes faintly yellow. 0.01 *N* thiosulfate is now added, two drops at a time, with gentle swirling, until the color is that of the end-point. (It is safer to take the end-point as the faintest yellow perceptible to the eye; starch is an unsatisfactory indicator in this system.) Because the reaction between sodium thiosulfate and iodine does not seem to be instantaneous in this medium, there is danger of adding too much thiosulfate unless ten seconds or so intervene between successive additions. When no further deepening of the iodine color occurs, the sample for the peroxide determination (in our case usually 5 cc. of *n*-butyl ether) is added, the flask is stoppered and placed in a dark cabinet for five minutes, and the iodine titrated thereafter with standard 0.01 *N* sodium thiosulfate solution. The flask is subsequently replaced in the cabinet for a similar time; if no further iodine formation occurs, the titration is satisfactory. This analytical method, which already has proved useful for the determination of other peroxides, was tested specifically on hydrogen peroxide dissolved in glacial acetic acid, on benzoyl peroxide in the same solvent, and on the peroxides in *n*-butyl ether. In the two former cases, the volume of thiosulfate solution was within approximately 0.1 cc. of that known to be equivalent to the amounts of the

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(1) Rieche, *Z. angew. Chem.*, **44**, 896 (1931), gives the earlier literature. For recent correspondence on the subject, see *Chemistry and Industry*, **14**, 421, 580 and 964 (1936).

(2) (a) Rowe and Phelps, This Journal, **46**, 2078 (1924); (b) Marks and Morrell, *Analyst*, **54**, 503 (1929); (c) Van Winkle and Christiansen, *J. Am. Pharm. Assoc.*, **18**, 1247 (1929); (d) Wheeler, *Oil and Soap*, **9**, 89 (1932); (e) Green and Schoetzow, *J. Am. Pharm. Assoc.*, **22**, 412 (1933); (f) French, Olcott, and Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935). None of these methods meets all the requirements listed above.

A few experiments with cadmium iodide added to our reaction mixtures showed that its use detracted from our method. It appears to have been introduced (*cf.* (g) "U. S. Pharmacopoeia," 9th ed., 1916; and refs. 2a, 2c, and 2e) to minimize iodine liberation by oxygen in the qualitative test for peroxides in pharmaceutical ether, and then retained in the corresponding quantitative methods. It acts, through complex ion formation, to reduce the iodide concentration, but it is not very effective in dilute solution [Bates and Vosburgh, This Journal, **60**, 137 (1938)]. However useful it may be in qualitative tests, its value in quantitative determinations is doubtful since a lower iodide concentration means a longer time for complete reduction of the peroxide, other things being equal. Certainly it appears to have no place in a method where the blank is negligible.

peroxides used; in the latter case, the analysis was considered satisfactory because samples permitted to stand for different times gave concordant results.

With this analytical method available, the observations of Table I were made on peroxide formation in *n*-butyl ether.

TABLE I

| No. | Description of the ether | $10^3 \times$ peroxide normality |
|---|---|---|
| 1 | Stood in laboratory for several days | 2.1 |
| 2 | Exposed no. 1 to 2537 Å. (not monochromatic) for 30 min. | 7.1 |
| 3 | Exposed no. 1 to 3650 Å. (not monochromatic) for 30 min. | 7.1 |
| 4 | Left no. 3 near window for 1 day | 8.5 |
| 5 | No. 1 several days later | 3.3 |
| 6 | Refluxed no. 5 for 15 min. | 0.9 |
| 7 | Refluxed no. 6 for 15 min. longer | 0.5 |
| 8 | Fresh supply of ether | 4.6 |
| 9 | Bubbled oxygen for 15 min. through boiling no. 8 ether | 24.6 |
| 10[a] | Bubbled oxygen for 45 min. longer through boiling no. 9 ether | 66 |

[a] Intermediate values omitted. For an unknown reason, one of these was lower than the preceding value. This anomaly could not be reproduced.

The indications are that (1) exposure to ultraviolet radiation increases the peroxide concentration; (2) daylight is also effective; (3) refluxing destroys the peroxides; (4) bubbling oxygen through the boiling ether rapidly produces them. For the 5-cc. samples used, the average titration error (*ca.* 0.1 cc. of 0.01 *N* solution) corresponds to a peroxide concentration of $0.2(10^{-3})$ *N*.

**Rates of Reactions.**—During work on the analytical method, several observations on rates of reactions in glacial acetic acid containing water in varying amounts were made. These observations were confirmed in simple experiments, the results of which are given here in the hope that someone will find them sufficiently interesting to extend the investigations.

Owing to serious overstepping of the end-point, the titration of thiosulfate and iodine solutions in glacial acetic acid as a medium often gave erratic results when the amount of water in solution was small. The following experiment illustrates the difficulty involved: 100 cc. of glacial acetic acid and 1 cc. of 0.01 *N* sodium thiosulfate are thoroughly mixed, 0.6 cc. of 0.008 *N* tri-iodide solution is then added, and the solution shaken. Its color begins to disappear immediately, but the rate of disappearance decreases markedly with time. After several minutes, the solution is still colored; but it becomes colorless immediately upon being shaken with 10 cc. of water. If 10 cc. of water is added initially to the 100 cc. of acid, no appreciable persistence of color is observed. An experiment employing a photoelectric spectrophotometer confirmed these visual observations. The simplest, though by no means the only, explanation is that sodium thiosulfate and iodine do not react instantaneously in glacial acetic acid.

A crude measure of the rates at which various peroxides are reduced by iodide in glacial acetic acid was obtained in experiments carried out as follows. The peroxide solution was blown into the reaction mixture prepared as for the peroxide analysis, the initial time being observed on a suitable timer. A number of seconds later, when appreciable iodine formation had occurred, 0.01 *N* thiosulfate solution was added rapidly until the mixture was decolorized, at which point the final time was estimated. From the volume of thiosulfate solution required, the volume of thiosulfate, *a*, (determined on another sample) equivalent to the peroxide added to the reaction mixture, and the reaction time (in minutes), a first order rate constant, *k*, was calculated from the equation

$$kt = 2.3 \log \frac{a}{a - x}$$

The unproved assumption that the reaction is first order with respect to peroxides in this medium is based on reasonable analogy.[3] To measure the effect of added water on these reactions, a corresponding series of experiments with 3 cc. of water initially present in the reaction mixture was performed. The results are summarized in Table II. With the exception indicated, each value is the average of three rough determinations. In aqueous solution, with 0.1 *M* iodide and 1 *N* acid, *k* at 25° would be approximately[3b] 0.1(0.7 + 10.5) = 1. More precise work of this kind should shed some light on acetic acid as a reaction medium and on any kinetic relationships of the organic

TABLE II

| Peroxide | $H_2O_2$ in HOAc | $Bz_2O_2$ in HOAc | Peroxides in $n$-$Bu_2O$ |
|---|---|---|---|
| *k* (no added water) | 10[a] | 1.9 | 2.5 |
| *k* (3 cc. added water) | 1.6 | 0.9 | 0.9 |

[a] Order of magnitude based on a single observation. Iodide concentration for these experiments, roughly 0.1 *M*.

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[3] (a) Mohammad and Liebhafsky, THIS JOURNAL, **56**, 1680 (1934); (b) Liebhafsky and Mohammad, *ibid.*, **55**, 3977 (1933).

peroxides to hydrogen peroxide; that some simple relationships may exist is obvious from the above data.

### Summary

A modified iodometric method for the determination of organic peroxides is described.

Certain observations have been made on the formation and decomposition of peroxides in *n*-butyl ether.

When tri-iodide solution is added to excess sodium thiosulfate in glacial acetic acid, the color fades at a measurable rate. The addition of water of course causes the fading to become practically instantaneous.

Crude rate measurements show that benzoyl peroxide and the peroxides in *n*-butyl ether are about equally reactive toward iodide in glacial acetic acid, and not much less reactive than hydrogen peroxide in the same medium. The addition of water retards all three reactions about equally.

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# The Dipole Moments and Structures of Chlorine Compounds of Germanium, Chromium, Selenium and Tellurium

BY C. P. SMYTH, A. J. GROSSMAN AND S. R. GINSBURG

The dipole moments of monochloro and dichlorogermane, chromyl chloride, diphenylselenium dichloride and tellurium tetrachloride have been measured with the object of studying the structures of the molecules and obtaining information as to the magnitudes of the bond moments in the molecules. The moments were obtained with the apparatus and methods previously described,[1,2] with the exception of that of monochlorogermane, which was measured in the vapor state by Mr. R. H. Wiswall, Jr., the dielectric constants being determined at three temperatures so close together that the moment was calculated by subtracting a calculated molar refraction from the polarization. The experimental measurements on solutions of dichlorogermane in carbon tetrachloride carried out by Dr. George L. Lewis already have been published and discussed elsewhere. The value of the moment is included in Table II for comparison with that of monochlorogermane.

## Preparation of Materials

**Benzene**[1] **and carbon tetrachloride**[2] were purified as in the work previously described.

**Monochloro- and Dichlorogermane.**—A kilogram of germanite containing 6% of germanium dioxide was obtained from the Foote Mineral Company and treated according to a procedure described by Professor J. H. Müller of the University of Pennsylvania in a communication to Professor N. H. Furman of Princeton University, to both of whom the authors wish to express their gratitude. By this procedure germanium was extracted from its ore as the tetrachloride, which was then hydrolyzed to form the dioxide. After the reduction of the latter in an atmosphere of hydrogen, it was combined with magnesium. The resulting germanide, treated with hydrochloric acid in an atmosphere of hydrogen, gave monogermane, which was purified by fractionation and mixed with an equal volume of hydrogen chloride over aluminum chloride as a catalyst according to the method of Dennis and Judy.[3] The resulting monochlorogermane and dichlorogermane were separated by fractionation at low temperatures, between 2 and 3 cc. of monochlorogermane and 1 cc. of dichlorogermane being obtained in the liquid form. In spite of careful fractionation, the samples could not be regarded as very pure. The stability of the monochlorogermane was sufficient to permit of its measurement in the vapor state over a limited temperature range, while decomposition of the dichlorogermane was rendered negligible by measurement in dilute solution.

**Chromyl Chloride.**—The compound was prepared by the method given by Henderson and Fernelius[4] and distilled at reduced pressure in an apparatus which had been dried by thorough baking.

**Diphenylselenium Dichloride.**—Material from the Eastman Kodak Company was recrystallized from dry benzene and dried in a vacuum desiccator.

**Tellurium Tetrachloride.**—Twenty-eight grams of C. P. tellurium in the form of sticks was placed in a distilling apparatus, which was then evacuated and baked. The gently heated tellurium was treated with a slow stream of dry chlorine, which converted it first into a black amorphous mass of tellurium dichloride and then into the white, crystalline tetrachloride. The latter was distilled into a side-arm where it gave an amber liquid, which solidified to white crystals.

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[1] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[2] Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

[3] Dennis and Judy, *ibid.*, **51**, 2321 (1929).

[4] Henderson and Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., Inc., New York N. Y., 1935, p. 143.