

[CONTRIBUTION FROM THE DOW CHEMICAL COMPANY]

The Low Temperature Autoxidation of Diethylene Glycol¹BY W. G. LLOYD²

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The autoxidation of diethylene glycol is studied in terms of products and rate-governing factors at 75°. The probable structure of the intermediate peroxide is developed, and the effects of oxygen pressure, glycol concentration, pH and temperature (35–95°) indicated. A long chain-length reaction with cross-termination and a competing heterolytic decay of the peroxide is proposed.

The growing industrial use of glycols has increased the interest in the degradative reactions which these compounds may undergo. An earlier study³ indicated some relationships between corrosion and free acids in glycol systems, as well as the ease of formation of acidic material upon contacting unstabilized diethylene glycol with air at elevated temperatures. The present work explores this autoxidation reaction at temperatures below 100°.

Results

Oxygen Consumption at 75°.—Samples of diethylene glycol (2,2'-oxydiethanol) were exposed to one atmosphere of oxygen with continuous stirring in a manometric apparatus. In the absence of initiator or inhibitor the glycol typically undergoes

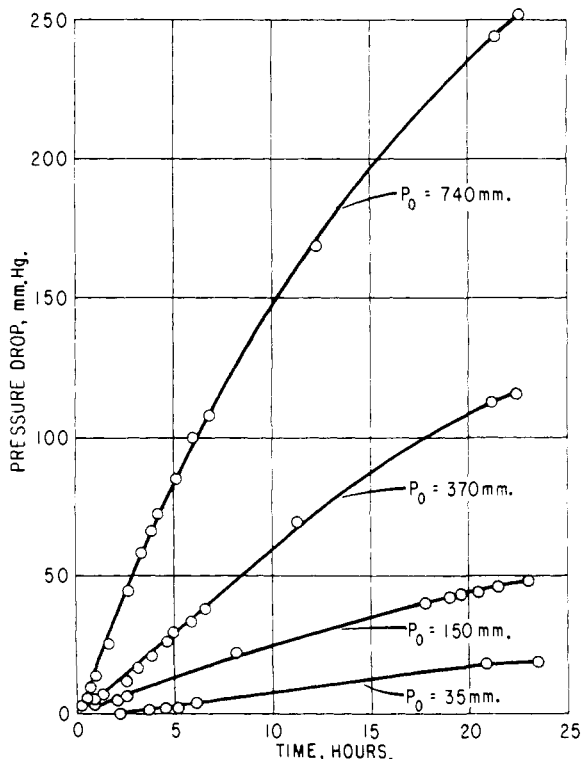


Fig. 1.—Effect of oxygen pressure upon diethylene glycol autoxidation at 75°; 1 mm. = 0.916 mmole per liter of glycol; P_0 = initial oxygen pressure.

(1) Presented in part before the Division of Organic Chemistry at the 128th meeting of the American Chemical Society, September, 1955.

(2) Technical Service and Development Laboratory, The Dow Chemical Co., Bay City, Michigan.

(3) W. G. Lloyd and F. C. Taylor, Jr., *Ind. Eng. Chem.*, **46**, 2407 (1954).

an induction period of 1–200 hours, depending upon its purity and history. Very little oxygen is consumed during induction periods, but at the end of these periods a rapid autoxidation ensues, with oxygen consumption rates of about 20 mmoles/liter/hour under the test conditions. The induction periods are reduced to essentially *nil*, and the autoxidation rates rendered more reproducible, by the introduction of a small amount of radical-source initiator. Triplicate runs with the same glycol at one-month intervals, with 0.10% azobisisobutyronitrile added, yielded oxygen consumption rates of 19.2, 19.7 and 21.3 mmoles/liter/hour. Several peroxides, *viz.*, *t*-butyl hydroperoxide, cumene hydroperoxide, acetyl peroxide, benzoyl peroxide and methyl amyl ketone peroxide, serve similarly as initiators. The autoxidation rate is substantially independent of the initiator used. Runs with 0.020–0.500% azobisisobutyronitrile show the rate to be independent of initiator concentration over this range. Subsequent runs, unless otherwise specified, are with 0.10% of the azo initiator.

The effect of oxygen pressure is illustrated by the curves in Fig. 1. A calculation of pressure dependency was made on the basis of six rate measurement sets in the range 296–707 mm. O₂. The dependency exponent, by the method of least squares,⁴ is 1.52, standard deviation 0.053. The effect of glycol concentration upon rate was investigated by a series of runs with chlorobenzene as an inert diluent. A log-log plot of concentration *vs.* autoxidation rate for samples containing 20.8, 32.7, 50.0, 80.6 and 99.9 mole % glycol yields an exponential dependency, by the method of least squares, of 1.44, standard deviation 0.011 (this precision is probably fortuitous). Dilutions with the more polar diluents, water or ethylene glycol, result in sharper declines in rate at diethylene glycol concentrations below about 90 mole %, and no simple kinetic dependency is obtained. The marked effect of pH upon autoxidation rate was investigated by a series of runs with 0.02–0.3% of various acidic, basic or buffering additives present; the results are shown in Fig. 2. As the pH's were determined at room temperature at 1:1 dilution with neutral deionized water, this relationship is only relative; however, the regularity of data indicates a general effect.

Autoxidation Products.—Formic acid is produced copiously in the autoxidations, occurring principally as the ester. Neither fractional crystallization of the *p*-toluidine derivative, strip chromatograms nor Duclaux numbers yield evidence of

(4) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 42–43.

any other acid from low temperature autoxidation; and no CO_2 has been detected in the gaseous products. Formaldehyde is also produced copiously, as indicated by abundant precipitation of its 2,4-dinitrophenylhydrazone and by its characteristic polarographic reduction wave. A small quantity of another dinitrophenylhydrazone displays characteristics consistent with those of the glyoxal bis-derivative. Water is also formed. Some less conspicuous products are indicated by mass spectrometer findings on a diethylene glycol sample⁵ which had been autoxidized for 21 hours at 75° : 0.9% monoethylene glycol, 0.5% dioxolanyl (mass 73), and traces of mass numbers 57-60 and 103-107. The formation of a dioxolane is consistent with the known ease of spontaneous condensation of aldehydes with *vic*-diols under acidic conditions. The sequence of masses 57-60 is suggestive of glycolic aldehyde, which would yield the glyoxal bis-derivative noted above.

In addition to these final products, an appreciable amount of organic peroxide is obtained in the course of the autoxidations, whether or not an initiator is employed. This peroxide reacts rapidly and completely at room temperature with arsenite or iodide ions, and is subject to a very fast ferric-catalyzed decay. This reactivity indicates a hydroperoxide structure. Direct infrared examination of the autoxidized glycol is prevented by the masking effect of the hydroxyl groups of the glycol; therefore the dimethyl ether (2,2'-dimethoxydiethyl ether) was studied. The fresh diether showed negligible O-H absorption, but an autoxidized sample, after drying, showed pronounced absorption at 3.0μ , with a weaker band at 11.9μ . Contact of the oxidized diether with ferric chloride at room temperature resulted in a markedly exothermal reaction and the simultaneous destruction of these absorption bands. Both the location of the absorption bands⁶ and the vulnerability of the peroxide to catalytic decay⁷ are strongly indicative of the hydroperoxide structure. In view of the observed inertness of monoethylene glycol to autoxidation under these conditions and of the well-known vulnerability of dialkyl ethers to low temperature autoxidation, the most reasonable structure seems to be the 1-hydroperoxide, *i.e.*, 1-hydroperoxy-2,2'-dihydroxydiethyl ether, $\text{HOCH}_2\text{CH}_2\text{OCH}(\text{OOH})\text{CH}_2\text{OH}$ (I).

Dynamic Autoxidations.—The dynamic apparatus was employed to permit periodic sampling of autoxidizing glycol. Instead of using the azo initiator, 5% of previously autoxidized glycol was added to provide a significant initial concentration of the glycol peroxide; this effectively eliminated lengthy induction periods. Runs at 75° showed

(5) The prepurified diethylene glycol used here was initially free of monoglycol and of the other impurities mentioned.

(6) N. A. Milas, R. L. Peeler, Jr., and O. L. Mageli, *THIS JOURNAL*, **76**, 2322 (1954); G. K. Minkoff, *Proc. Roy. Soc. (London)*, **A224**, 176 (1954); A. R. Philpotts and W. Thain, *Anal. Chem.*, **24**, 638 (1952); O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *ibid.*, **23**, 282 (1951).

(7) Some recent reviews of hydroperoxide chemistry include L. Bateman, *Quart. Rev.*, **8**, 147 (1954); C. E. Frank, *Chem. Rev.*, **46**, 155 (1950); J. E. Leffler, *ibid.*, **45**, 385 (1949); A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 96ff; J. P. Wibaut and A. Strang, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **55B**, 207 (1952).

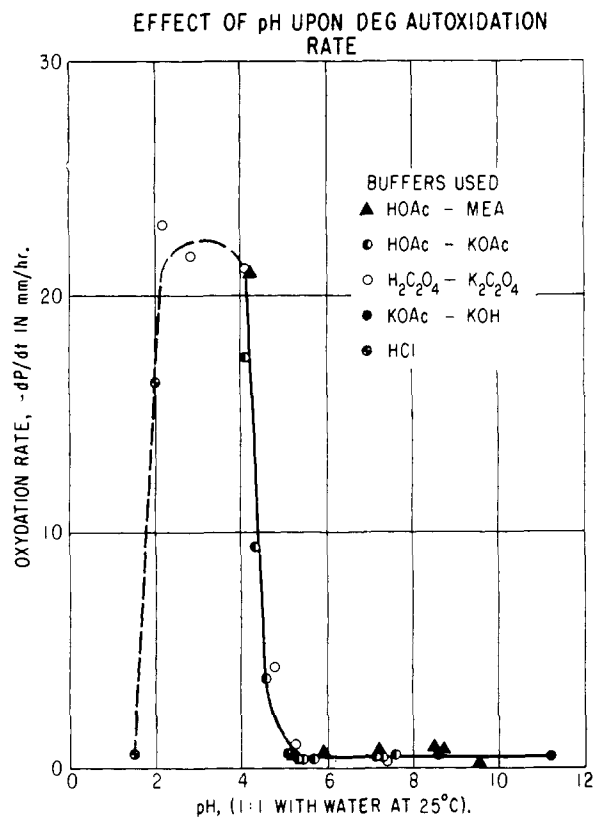


Fig. 2.—Effect of pH upon diethylene glycol autoxidation rate at 75° .

total aldehyde and total acid concentrations to increase essentially linearly with time. Assays for total acid and total aldehyde were close to identical in magnitude throughout the run; for example, six acid determinations taken between 46 and 54 hours averaged 418 meq./liter, while the six concurrently sampled aldehyde assays averaged 415 meq./liter. In no instance was a large variation noted from this 1:1 ratio. However free aldehydes (measured polarographically) levelled off at concentrations of 40-60 meq./liter.

The effect of temperature upon autoxidation rate was investigated by a series of runs at 35 – 95° , the oxidation being tracked by peroxide and total acid assays (Figs. 3 and 4). The decrease in equilibrium peroxide level at higher temperatures is typical of many autoxidations. However the near-independence of rate of final product formation upon temperature above 75° is more unexpected. Oxygen solubility in diethylene glycol is not limiting in this range; it decreases only about 15% from 50 to 94° .

The Glycol Peroxide.—The peroxide content of autoxidized glycol samples decreases with time, due to a spontaneous decay reaction. This first-order decay has been examined at three temperatures in the absence of accelerators or inhibitors; the values obtained for the rate constant are $9.0 \times 10^{-5} \text{ sec.}^{-1}$ at 75° , $1.6 \times 10^{-5} \text{ sec.}^{-1}$ at 55° , and $1.1 \times 10^{-6} \text{ sec.}^{-1}$ at 26° . The Arrhenius E is 18.7 kcal. (estimated precision $\pm 4\%$); the frequency factor is $4.8 \times 10^7 \text{ sec.}^{-1}$. This estimate of activation energy is 8-10 kcal. lower than those

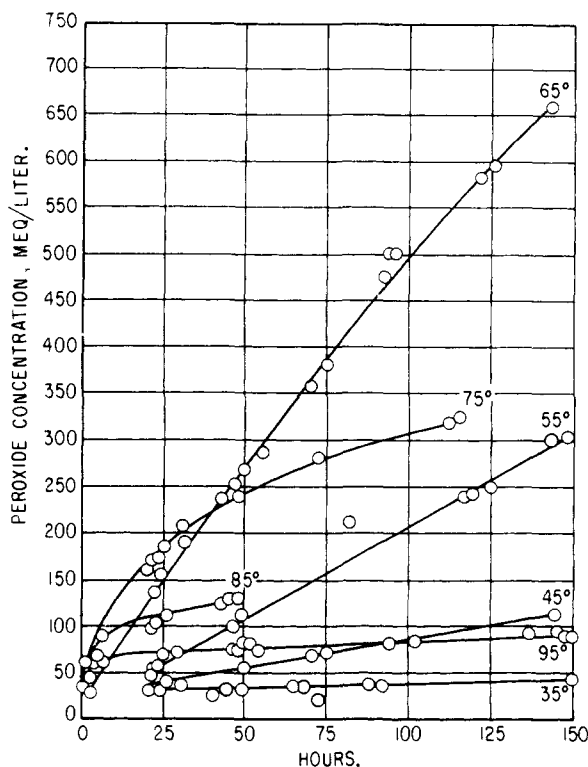


Fig. 3.—Development of peroxide in diethylene glycol at 35–95°; initial peroxide concn. was 30–40 meq./l.

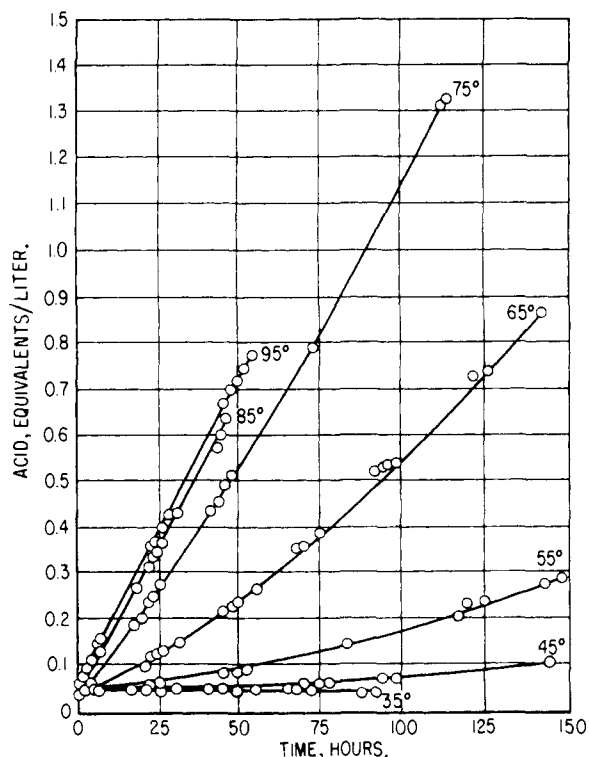


Fig. 4.—Development of acid in diethylene glycol at 35–95°; initial acid concn. was 35–45 meq./l.

recently reported for several hydrocarbon hydroperoxides⁸; possibly this is due to O–O bond la-

(8) J. R. Thomas, *THIS JOURNAL*, **77**, 246 (1955).

bilization, since if structure I is correct, this is a per-hemiacetal. If the spontaneous decay of the peroxide is both homolytic and auto-induced,^{8,9} the decay rate should be decreased by the addition of a radical-trap to the system. The rate at 75° with 0.0094% hydroquinone present was still first order with respect to peroxide concentration but was greatly retarded, $k = 5.1 \times 10^{-6}$ sec.⁻¹. An explanation for the apparent paradox of first-order kinetics in an auto-induced reaction has been developed for the case of diaryl peroxides.⁹

The glycol peroxide is itself an effective autoxidation initiator. Treatment of a pure sample of diethylene glycol with a small amount of autoxidized glycol, to make up a peroxide concentration of 3.0 meq./liter, rendered the glycol readily oxidizable, with an induction period of less than half an hour. Concurrent control runs with the pure glycol showed the induction period to be greater than 170 hours. Other oxidation products identified above have no effect upon the induction periods of pure glycol samples. However, even in the presence of peroxides or other initiating agents, radical-trap additives effectively inhibit the autoxidation. Thus a typical glycol charged with 0.10% azobisisobutyronitrile showed no induction period in the manometric apparatus at 75°, and commenced an immediate rapid autoxidation; but in the presence of 0.049% hydroquinone no autoxidation occurred during a 120-hour test.

Discussion.—The concerted β -cleavage mechanism proposed by George and Walsh¹⁰ has been found to apply to a large number of tertiary and secondary hydroperoxides and, in this case, given peroxide structure I, it fits the major products very well, and is consistent with the HCHO/HCOOH product ratio of unity. The effects of pH and polar diluents upon rate strongly suggest competing heterolytic decay of the peroxide. Heterolytic decay is well known for hydrocarbon hydroperoxides,⁷ and a similar homolytic-heterolytic competition has recently been proposed to account for phenomena associated with the autoxidation of *d*-limonene.¹¹ The development of a peroxide intermediate which (at lower temperatures) does not rapidly attain a steady-state level suggests a fairly long kinetic chain length. The substantially equal dependence of rate upon oxygen pressure and glycol concentration is rather unusual. A reasonable explanation of this "anomalous" dependency has been developed by Bateman and Morris¹² in terms of the dominance of cross-termination over homoradical terminations.

One further kinetic relationship is indicated by the above data. If the peroxide concentration curves (Fig. 3) are fitted to quadratic equations to permit integration of the equation

$$d(\text{acids})/dt = k(\text{peroxide})^n$$

the corresponding acid formation curves (Fig. 4) fit very well for $n = 0.5$. The 65° data show this

(9) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(10) P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

(11) E. E. Royals and S. E. Horne, Jr., *THIS JOURNAL*, **77**, 187 (1955).

(12) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **49**, 1026 (1953).

relationship best, due to the wide range of peroxide concentrations obtained.

However, the rapid attainment of steady-state rate in oxygen consumption runs, and the indicated third-order dependency, $d(O_2)/dt = -k(O_2)^{1.5}$. (DEG)^{1,5}, implies a more complex reaction sequence than can be explained on the basis of present information. Thus a rigorous kinetic treatment of this reaction will have to await further work.

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Experimental

Materials.—Ethylene glycol and diethylene glycol are current production from the Dow Chemical Co., used without further purification for most determinations. The diglycol employed for product identification is a doubly redistilled center-cut, b.p. 130° (10 mm.), and spectroscopically free of monoglycol and other contaminants. Diethylene glycol dimethyl ether is from the Ansul Chemical Co., Marinette, Wisconsin. Azobisisobutyronitrile, benzoyl peroxide and hydroquinone are from the Eastman Kodak Co.; *t*-butyl hydroperoxide and methyl amyl ketone peroxide are from the Lucidol Division, Novadel-Agene Corp.; cumene hydroperoxide is from the Hercules Powder Co.; and acetyl peroxide (25% in dimethyl phthalate) is from the Buffalo Electro-Chemical Co. Other chemicals are regular reagent grade.

Oxygen Consumption Tests.—One hundred ml. of the glycol (with initiator) is placed in a 2-liter erlenmeyer flask fitted with a 18/9 male spherical joint and containing a $\frac{5}{8}$ " \times $\frac{5}{16}$ " d. Teflon-clad Alnico stirring bar. The flask is flushed vigorously for five minutes with oxygen or the desired gas mixture. A capillary extension, fitted with spherical joints, is then connected and the flask immersed in a thermostated water-bath. After standing five minutes to permit rough thermal equilibration the extension is secured to a manometer, and a magnetic stirrer motor, located beneath the bath and centered under the flask, is put into operation at 400 ± 10 r.p.m. Periodic readings of bath temperature, differential pressure and absolute barometric pressure are made. The bath temperature, maintained with an inverse Fenwal thermostat through a Lumenite relay, holds within 0.5° and usually 0.2°. Large variations in the magnetic stirrer r.p.m. cause some variation in oxidation rate; this is controlled by operating the stirrer through a Sola voltage-regulating transformer, and is checked periodically with a Strobotac stroboscopic tachometer.

Dynamic Autoxidations.—A cylindrical Pyrex vessel is charged with 200 ml. of the glycol, immersed in a thermostated bath, and dried prewarmed oxygen is introduced at the bottom at a rate of 0.57 ± 0.01 l./min. A glass percolator assembly causes the rising oxygen to function as a gas-lift, expelling the glycol at the top of the percolator through nine 0.5-mm. holes. The lifted glycol then cascades down the cylinder wall, returning to the main charge. The exit

gas passes upward through a packed water-cooled condenser, then out through a conventional gas-absorption train. An external sampling assembly permits the periodic withdrawal of small portions of glycol by hypodermic syringe for assaying.

Qualitative Procedures.—The acid was first checked by strip chromatograms; with 96 parts of 95% EtOH and 4 parts concentrated NH₄OH on Whatman No. 1 paper, *R*'s of 0.40–0.44 were obtained, eliminating difunctional acids. Dilute Duclaux numbers yielded: unknown—3.4, 4.1, 4.5; formic acid—3.5, 4.2, 4.6; acetic acid—6.6, 7.1, 7.6; other reference acids much more remote. The unknown acid reduced alkaline permanganate, reduced mercuric acetate, and did not form a precipitate with aqueous CaCl₂; the *p*-toluicide derivative, m.p. 51° uncor.; listed m.p. for formic acid derivative 53°.¹⁸ The aldehyde was first investigated by determining the reduction half wave potential, using a Sargent M-III Polarograph with a mercury-saturated calomel electrode system and an alkaline electrolyte derived from Kolthoff and Lingane,¹⁴ consisting of KOH 0.100 *N*, KCl 0.0100 *N*, methyl red $2.0 \times 10^{-4}\%$ and brom cresol green $4 \times 10^{-5}\%$. Autoxidized glycol yielded sharp half waves slightly dependent upon concentration and in the range -1.68 to -1.70 v. (*vs.* S.C.E.). Authentic HCHO yielded half waves at -1.68 to -1.69 v. No other aldehyde tested or listed in reference 14 affords a half wave within 50 mv. of this value. The predominant 2,4-dinitrophenylhydrazone, m.p. 161–162°; authentic HCHO derivative m.p. 166–167°; mixed m.p. 163–164°; AcH derivative m.p. 168°; mixed m.p. (AcH and unknown) about 130–155°. In addition to this MeOH-soluble derivative identified as formaldehyde dinitrophenylhydrazone, another dinitrophenylhydrazone was obtained in small quantities, very slightly soluble in MeOH, m.p. about 305°, and displaying a marked color shift from orange to blue upon addition of methanolic NaOH to its methanolic solution. A qualitative comparison of its absorption profile (400–800 $m\mu$ range) with that of an authentic sample of glyoxal bis-dinitrophenylhydrazone indicated an identical color shift. However the instability of the alkaline color and the very small quantities obtained prevent a firm identification.

Quantitative Procedures.—Total acids were determined by a modification of the serum bottle technique¹⁵; 1–2 ml. samples are placed in 10-ml. serum bottles containing 2–4 ml. of 0.5 *N* NaOH in MeOH (quantities varied according to estimated total acids) and the stoppered bottles heated for 30 minutes in a 60° bath, then cooled and back-titrated with standard 0.1 *N* HCl, using a semimicro buret and phenolphthalein. Total aldehydes were determined by adding 1.00-ml. samples to 50 ml. of freshly filtered deaerated 2,4-dinitrophenylhydrazine reagent (saturated in aqueous 2 *N* HCl). The solutions, kept under N₂ in iodine flasks, were allowed to stand 24 hours, then heated for four hours on a steam-bath, cooled and filtered and the precipitates dried under vacuum and weighed. Free HCHO was determined polarographically as described above. Peroxides were determined by the arsenite method¹⁶; direct iodometric methods are not suitable for this system due to significant iodine reduction by the product mixture.

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(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., 1948, p. 222.

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, pp. 653ff.

(15) D. M. Smith, J. Mitchell, Jr., and A. M. Billmeyer, *Anal. Chem.*, **24**, 1847 (1952).

(16) S. Siggia, *Ind. Eng. Chem., Anal. Ed.*, **19**, 827 (1947); S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 100–103.