[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

# *p*-Toluenesulfonyl and Iodo Derivatives of the Three Lower Polyethylene Glycol Monoethyl Ethers[1]

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As a prelude to a study of the hydroxyethyl ethers of cellulose,[3] it seemed advisable to check the physical properties of the *p*-toluenesulfonyl (tosyl) esters of simple monoethyl ethers in the polyethylene glycol series, and to examine the reactivities of the tosyloxy group during solvolysis and toward sodium iodide. The general formula of the compounds studied was $C_2H_5(OCH_2CH_2)_xR$, where $x$ was 1, 2 or 3, and R was OH, OTs or I. The marked tendency of some of the derivatives to undergo autoxidation during brief storage was noted, and the products formed in the thermal decomposition of the two higher tosylates were identified. A knowledge of these peculiarities made it possible to prepare the hitherto missing members of the above series.

Wurtz[4] noticed in 1859 that ethylene oxide slowly condensed with hydroxylic substances, and the employment of metallic catalysts by later investigators[5,6,7] to hasten such condensations resulted in a general method of preparing the monoalkyl ethers of polyethylene glycols. Another general method depended on the condensation of an appropriate sodium alcoholate with an appropriate alkyl halide.[8,9,10,11] The physical constants of lower members of the series, collected by Davidson,[12] revealed the interesting fact that the boiling points of the monoethyl ethers were very close to those of the next lower, unsubstituted polyethylene glycol. Unfortunately, this fact was overlooked until 1941, when Seikel[13] found that the monoethyl ether of diethylene glycol (x, 2; R, OH) could not be satisfactorily freed from ethylene glycol by fractional distillation. The observation that commercial samples of the monoether contained up to 28% of glycol explained in some degree the variable values quoted in the literature for the physical constants of this substance, and the many failures encountered in attempts to obtain crystalline derivatives.[14,15,16,17,18] The use of a sample adequately purified from glycol enabled Shupe[19] to crystallize the xanthate of diethylene glycol monoethyl ether, and recent workers[20] isolated crystalline tri-iodobenzoates of various monoethers of ethylene glycol and diethylene glycol without undue difficulty.

Cretcher and his collaborators[21,22] prepared the tosyl esters of a large number of the monoalkyl ethers of ethylene glycol, including that of the monoethyl ether (x, 1; R, OTs). The side reactions liable to occur during such tosylations were carefully investigated by Tipson,[23] who was able to improve the method of preparation. Although some of these esters were oils that decomposed on distillation,[22,24] the tosyl group was sufficiently resistant to hydrolysis to permit of their purification by thorough washing in cold water. The higher members of the series (x, 2 and 3; R, OTs) do not seem to have been accurately characterized, although presumably they were included in a patent by Adams,[24] which described the series in general terms as heavy, viscous oils, insoluble in water but soluble in organic liquids.

The action of sodium iodide in a ketone solvent would be expected to substitute an iodine atom for the tosyloxy group in the above esters, since all of the latter are derived from primary alcohol units.[25] β-Iodoethyl ether (x, 1; R, I), the product from the lowest member of the series, was first encountered in a preparation of ethylene di-iodide from ethylene and an alcoholic solution of iodine.[26] Later syntheses, which established the correct structure, involved the action of phosphorus tri-iodide on ethylene glycol monoethyl ether,[27,28] and of sodium iodide on β-chloroethyl ether.[29] Although decomposed by sodium ethylate at 150°[26,27] and by alcoholic silver nitrate,[30]

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(1) Abstracted from a Thesis presented to the Faculty of McGill University in June, 1947, by C. W. Tasker in partial fulfilment of the requirements for the Ph.D. degree.

(2) At above address.

(3) Tasker and Purves, THIS JOURNAL, **71**, 1023 (1949).

(4) Wurtz, *Compt. rend.*, **49**, 813 (1859); *Ann. chim.*, [3] **69**, 331 (1863).

(5) Altman and Kedrinskii, *Trans. Exptl. Research Lab. Kemgas.* Materials on Cracking and Chemical Treatment of Cracking Products, (U. S. S. R.), **3**, 341, 351; *C. A.*, **31**, 6196 (1936).

(6) Stanley and Youell, British Patent, 467,228 (June 3, 1937); *C. A.*, **31**, 7886 (1937); **33**, 2536 (1939).

(7) Zimakov and Churakov, *Org. Chem. Ind.* (*U. S. S. R.*), 1, 329 (1936); *C. A.*, **30**, 7540 (1936).

(8) Paloma, *Ber.*, **35**, 3299 (1902); **42**, 3873 (1909).

(9) Berggårdh, *Finska Kemistsam, fundet. Medd.*, **44**, 80 (1935); *C. A.*, **30**, 5559 (1936).

(10) Capinjola, THIS JOURNAL, **67**, 1615 (1945).

(11) Perry and Hibbert, *Can. J. Research*, **14B**, 77 (1936).

(12) Davidson, *Ind. Eng. Chem.*, **18**, 669 (1926).

(13) Seikel, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 388 (1941).

(14) Conn, Collett and Lazzell, THIS JOURNAL, **54**, 4370 (1932).

(15) Whitmore and Lieber, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 127 (1935).

(16) Veraguth and Diehl, THIS JOURNAL, **62**, 233 (1940).

(17) Mason and Manning, *ibid.*, **62**, 1635 (1940). This article reviews all attempts to prepare crystalline derivatives of ethylene and diethylene glycol monoethers.

(18) Manning and Mason, *ibid.*, **62**, 3136 (1940).

(19) Shupe, *J. Assoc. Official Agr. Chem.*, **24**, 936 (1941).

(20) O'Connell and Carey, THIS JOURNAL, **68**, 1865 (1946).

(21) Butler, Nelson, Renfrew and Cretcher, *ibid.*, **57**, 575 (1935).

(22) Butler, Renfrew, Cretcher and Souther, *ibid.*, **59**, 227 (1937).

(23) Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(24) Adams, U. S. Patent 2,266,141 (Dec. 16, 1942); *C. A.*, **36**, 2270 (1942).

(25) Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

(26) Baumstark, *Ber.*, **7**, 1172 (1874).

(27) Demole, *ibid.*, **9**, 746 (1876).

(28) Henry, *Bull. soc. chim.*, **44**, 459 (1885).

(29) Swallen and Boord, THIS JOURNAL, **52**, 651 (1930).

(30) Karvonen, *Ber.*, **42**, 687 (1909).

β-iodoethyl ether was stable to solid potassium hydroxide at 150°,[26,27] to tripropylamine at 100° for one hour,[30] and was affected neither by sodium amalgam,[26,27] nor by distillation (b.p. 155°) from pulverized silver[28] or metallic sodium.[30] The halogen atom in β-iodoethyl ether therefore has the low reactivity that is a general characteristic of β-, as opposed to α-halogen substituted ethers.[29] No reference has been found to the higher members of the iodinated ethers under consideration (x, 2 or 3; R, I).

## Experimental

**Materials and Reagents.**—Technical ethylene glycol monoethyl ether was thoroughly dried over anhydrous calcium sulfate and fractionally distilled through a Vigreux column. The fraction, free from aldehydes and peroxide, boiling correctly at 134.5° and with the correct refractive index of $n^{20}\mathrm{D}$ 1.4073, was collected.[31] A benzene solution of technical diethylene glycol monoethyl ether was selectively extracted with water, by Seikel's[13] procedure, to remove ethylene glycol. It was not found necessary to remove any residual traces of the glycol from the dried benzene solution by a subsequent selective oxidation with lead tetraacetate,[32] a reagent which, indeed, slowly oxidized the monoether. Care was taken to fractionate repeatedly until all traces of peroxide oxygen and aldehydes were absent from the product, which had the correct b. p. of 196° (760 mm.) and $n^{20}\mathrm{D}$ 1.4273.

Technical ethylene chlorohydrin was dried over anhydrous sodium sulfate and vacuum distilled. To avoid thermal decomposition,[33] a stream of dry carbon dioxide was passed through the still to prevent bumping. The fraction collected boiled constantly at 38.5–39.0° (10 mm.) and samples had the recorded constants b. p. 128.7° (760 mm.), and $n^{15}\mathrm{D}$ 1.4438.[34]

Ethyl *p*-toluenesulfonate, prepared by Tipson's[23] method in a crude yield of 73%, gave 49% of recrystallized material melting correctly at 33 to 34°. A similar preparation[23] gave an 83% yield of analytically pure ethylene glycol monoethyl ether *p*-toluenesulfonate, melting correctly at 18.5°. The tosyl chloride used in such preparations, together with all organic solvents, was carefully purified by standard procedures.

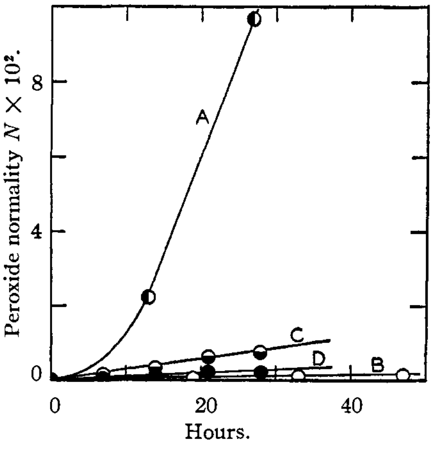

Fig. 1.—Peroxide formation: plot A, diethylene glycol monoethyl ether stored in light and air; plot B, the same in dark and nitrogen; plot C, ethylene glycol monoethyl ether in light and air; plot D, the same in dark and nitrogen.

**Analytical Methods.**—Combustion and other analyses were on the semimicro scale. Attempts were made to determine sulfur by a sodium peroxide fusion followed by a barium chloride titration with tetrahydroquinone as an internal indicator.[35] These attempts were discontinued because of difficulties with the end-point, and all sulfur analyses reported were by a standard Carius method employing barium chloride instead of silver nitrate.[36] Decomposition of the β-iodoethers by alcoholic caustic soda was quite inadequate to serve as a basis for rapid iodine estimations[37] and so the gravimetric Carius method[38] was used.

The fact that ethoxy estimations with hydriodic acid gave erratic and high results in the polyethylene oxide series[38,39,40,41] was thoroughly confirmed, but Morgan's[42] estimation for the ethylene as well as the ethyl iodide evolved from these substances was published too late for adoption in the present work.

**Peroxides and Autoxidation.**—Peroxides were detected by adding 1 cc. of the sample to 1 cc. of a 50% solution of aldehyde-free acetic acid. After shaking, a few mg. of potassium iodide was added and the mixture, together with a blank, was kept in the dark for five minutes. Even small traces of peroxide were sufficient to develop the deep color of free iodine. Quantitative estimations (Fig. 1) required a solution of potassium iodide in a glacial acetic acid–sodium bicarbonate mixture.[43] After discharging the slight yellow color of the mixture with 0.01 *N* sodium thiosulfate, better to a visual than to a starch end-point, the iodine liberated by the addition of the sample was titrated with the thiosulfate. This titration had to be carried out in stages at ten-second intervals, since the reaction was not instantaneous. With 5-cc. samples, the volume in cc. of peroxide oxygen per liter was 11.2 times the consumption of 0.01 *N* thiosulfate in cc.[44] The data were corrected for a blank which was usually 0.1 cc., and the limit of error of about 0.1 cc. corresponded to $2 \times 10^{-4}$ *N* peroxide.

Aldehydes were detected by Brady's 2,4-dinitrophenylhydrazine reagent[45] and were identified by Allen's[46] modification of the method. A red-orange 2,4-dinitrophenylhydrazone was obtained as small needles from samples of ethylene and diethylene glycol monoethyl ethers which contained peroxides. After recrystallization from glacial acetic acid or nitrobenzene, the hydrazone melted at 332° (cor.) and a mixed m. p., with authentic glyoxal-bis-2,4-dinitrophenylhydrazone (m. p. 330°[47]) was not depressed. Wieland and Wingler's work[48] was adapted for estimations of acidity caused by peroxide formation.

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(31) Tallman, THIS JOURNAL, **56**, 126 (1934).

(32) Hockett and McClenahan, *ibid.*, **60**, 2061 (1938); **61**, 1667 (1939).

(33) Bozza and Gallarati, *Giorn. chim. ind. applicata*, **13**, 163 (1931).

(34) Timmermans and Martin, *J. chim. phys.*, **25**, 411 (1928).

(35) Mahoney and Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 97 (1942).

(36) Niederl and Niederl, "Micromethods of Quantitative Organic Analyses," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942.

(37) Mahoney and Purves, THIS JOURNAL, **64**, 9 (1942).

(38) Meisenheimer, *Ber.*, **41**, 1015 (1908).

(39) Grün and Bockisch, *ibid.*, **41**, 3477 (1908).

(40) Davis, Ph.D. Thesis, New York State College of Forestry, Syracuse, N. Y., 1941.

(41) Lawrie, Reynolds and Ward, *J. Soc. Dyers Colourists*, **56**, 7 (1940). These authors did not report on the reproducibility of their ethoxy estimations.

(42) Morgan, *Ind. Eng. Chem., Anal. Ed.*, **18**, 500 (1946).

(43) Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).

(44) Lindgren and Vesterberg, *Svensk Farm. Tids.*, **47**, 17 (1943); *C. A.*, **38**, 2167 (1944).

(45) Brady, *J. Chem. Soc.*, 756 (1931). See also Brady and Elsmie, *Analyst*, **51**, 77 (1926).

(46) Allen, THIS JOURNAL, **52**, 2955 (1930).

(47) Glasstone and Hickling, *J. Chem. Soc.*, 824 (1936).

(48) Wieland and Wingler, *Ann.*, **431**, 301 (1923).

**Density and Molecular Refraction.**—Standard directions[49] were followed, densities being determined in 1.0 cc. and 0.1 cc. pycnometers and refractive indices with an Abbé refractometer kept to ±0.1° of the desired temperature and re-calibrated frequently. The Lorenz and Lorentz function was used to calculate molecular refractions from observed densities and refractive indices. Molecular refractions were also calculated from a table of atomic refractivities.[49] The results are collected in Table I.

**Triethylene Glycol Monoethyl Ether (x, 3; R, OH).**—A three-necked, round-bottomed, glass-jointed flask was equipped with a capillary bubbling tube, a mechanical stirrer with mercury seal and a reflux condenser closed by a calcium chloride drying tube. After adding 175 cc. of anhydrous methanol, the air in the system was thoroughly displaced by a stream of dry, oxygen-free nitrogen introduced through the capillary below the level of the methanol. Clean sodium (16.2 g., 0.704 mole) was then added piece by piece through the condenser and, when all had dissolved, 105 g. (0.784 mole) of pure diethylene glycol monoethyl ether was introduced. Keeping a large flow of nitrogen passing through the system, the stirrer was replaced by a plug, and the reflux condenser was turned downward for distillation. The methanol was then removed by gradually increasing the bath temperature to 100° and decreasing the pressure to 20 mm. The viscous, deep red-brown residue of the sodium alcoholate of the monoether was diluted with enough of the pure monoether to bring the molar excess over the sodium to 45%, and traces of methanol were eliminated by two to three days' heating at 100° (15 mm.).

A dropping funnel was attached while nitrogen perfused the system and 63 g. (0.774 mole or 10% excess) of pure ethylene chlorohydrin was slowly added, with vigorous stirring and heating under reflux at 70 to 80° for twelve hours. No volatile matter passed through the water-cooled condenser. The contents of the reaction flask were diluted with dry ether and filtered to recover 39.7 g. (95.6%) of sodium chloride. Evaporation of the ether and fractional distillation up to 95° at 15 mm. recovered some chlorohydrin and 33.3 g. of diethylene glycol monoethyl ether; refractionation of a higher-boiling fraction gave 48 g. of the same monoethyl ether and 38 g. of a fraction of b. p. 85–90° (0.5 mm.). Careful refractionation of the latter from a 50-cc. Widmer flask left 36 g. of pure triethylene glycol monoethyl ether having b. p. 86–91° (0.5 mm.).

*Anal.* Calcd. for $C_8H_{18}O_4$: C, 53.9; H, 10.2. Found: C, 53.7; H, 10.5.

The yield was 29% based on the sodium and 48% on the unrecovered monoethyl ether. An earlier run gave a 15% yield on the sodium, and another, using a larger excess of chlorohydrin, gave none of the desired product.

**Tosylate of Diethyleneglycol Monoethyl Ether (x, 2; R, OTs).**—A freshly purified, peroxide- and aldehyde-free sample of the monoethyl ether (30 g., 0.224 mole) was tosylated in anhydrous pyridine according to Tipson's procedure.[23] Four 100-cc. volumes of chloroform were used to extract the product from the final aqueous pyridine solution, and pyridine was removed from the extract by successive washing with ice-water, dilute sulfuric acid, ice-water and sodium bicarbonate solution. The chloroform was removed from the dried extract, using a capillary bubbler and pure dry nitrogen, by warming for ten hours at 42° (23 mm.), and finally for seven hours at 42–45° (0.1 mm.). The 51.1 g. (79.2%) of slightly yellow, viscous oil was analyzed without being fractionally distilled, since distillation caused decomposition.

*Anal.* Calcd. for $C_{13}H_{20}O_5S$: C, 54.2; H, 7.0; S, 11.1. Found: C, 53.8; H, 7.1; S, 11.1.

The substance was difficult to burn, for its sudden decomposition sent a rush of gas through the train. Other preparations resulted in yields of 84, 84 and 74%.

**Tosylate of Triethylene Glycol Monoethyl Ether (x, 3; R, OTs).**—Tipson's procedure,[23] employing 0.056 mole (10g.) of the pure ether, 0.067 mole of tosyl chloride and 100 cc. of dry pyridine, gave 13.1 g. or 71% of a slightly yellow viscous oil. This oil was decolorized in hot benzene solution with adsorbent charcoal and, after recovery, was somewhat low in sulfur content but was halogen-free. Chilling caused the product to separate into two oily layers, but the fraction deposited from a hot, concentrated solution of petroleum ether (b. p. 30 to 60°) remained homogeneous when cooled, and was accepted as pure.

*Anal.* Calcd. for $C_{15}H_{24}O_6S$: C, 54.2; H, 7.3; S, 9.6. Found: C, 53.8; H, 7.4; S, 9.6.

Combustion difficulties were as encountered with the lower homolog. Other preparations gave 77% yields.

**β-Iodoethyl Ethyl Ether (x, 1; R, I).**—A solution of 0.0205 mole of pure ethylene glycol monoethyl ether tosylate and 0.05 mole of dry C. P. sodium iodide in 75 cc. of pure acetone was heated at 115° for two hours in a stainless steel bomb.[25] Filtration removed the crystalline deposit of sodium *p*-toluenesulfonate, and, after recovery, the residual slightly yellow oil was repeatedly distilled from solid sodium hydroxide.[30] The pure product, b. p. 154° (754 mm.), was isolated in 81% yield.

*Anal.* Calcd. for $C_4H_9OI$: I, 63.5. Found: I, 63.5.

**β-Iodo-β'-ethoxy Diethyl Ether (x, 2; R, I).**—A solution of 0.0626 mole of pure tosylated diethylene glycol monoethyl ether and 0.187 mole of sodium iodide in 625 cc. of dry acetone was kept for sixty hours at 22 to 23°. The filtrate from the precipitated sodium *p*-toluenesulfonate was concentrated *in vacuo* at 30° to a volume of 100 cc., and 200 cc. of dry ethyl ether was then added to precipitate residual sodium iodide. The ethereal solution and washings were extracted with 100 cc. of aqueous sodium thiosulfate to remove some free iodine, and after two extractions with ice-water were dried over anhydrous potassium carbonate. Removal of the ether, finally at 30° (0.06 mm.), and fractional distillation of the residue resulted in an 88% yield of a colorless oil, b. p. 42° (0.4 mm.).

*Anal.* Calcd. for $C_6H_{12}O_2I$: C, 29.5; H, 5.4; I, 52.0. Found: C, 29.8; H, 5.6; I, 51.5.

The pure substance was stable enough to undergo no change beyond slight discoloration when stored in a cool dark place for five months.

**β-Iodo-β'-ethoxyethoxy Diethyl Ether (x, 3; R, I).**—A solution of the corresponding pure tosylate, 0.042 mole, and sodium iodide, 0.141 mole, in 625 cc. of acetone was kept for five days at 20 to 25°. After recovering 96.7% of the theoretical amount of sodium *p*-toluenesulfonate, the product was isolated from the mother liquors as just described for the lower homolog. Distillation of the crude red oil gave a 73% yield of a clear, very slightly yellow oil, b.p. 97 to 98° (0.15 mm.).

*Anal.* Calcd. for $C_8H_{17}O_3I$: C, 33.3; H, 6.0; I, 44.1. Found: C, 33.4; H, 6.0; I, 44.0.

**Thermal Decomposition of Higher Tosylates.**—(a) Tosylated Diethylene Glycol Monoethyl Ether: The pure ester (22.6 g., 0.0786 mole) was slowly heated up to 160° in a 50-cc. distilling flask filled with glass wool and evacuated to 0.13 mm. pressure. The side arm of the flask was connected to another, which served as an air-cooled receiver, and then to a trap cooled in chloroform–Dry Ice. Slow, even distillation took place at 125° (0.13 mm.) with no increase in pressure, and some of the distillate kept solidifying at the entrance to the Dry Ice trap. The air-cooled receiver eventually contained 15.33 g. (97.4%) of a slightly yellow, slightly acid oil whose m. p. of 30 to 33° was increased to m. p. 34 to 35° by recrystallization from petroleum ether. The elementary composition, the refractive index of $n^{40}D$ 1.5050, and the m. p. were those of ethyl *p*-toluenesulfonate and a mixed m. p. with an authentic sample was not depressed.

A clear colorless solid, 6.65 g. (97%), b. p. 100°, m. p. 6 to 9°, $n^{25}D$, 1.4190, collected in the Dry Ice trap, was

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(49) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940.

slightly impure 1,4-dioxane, which when pure has the constants $n^{25}D$ 1.4198 and m. p. 11.8°.[50a] This conclusion was confirmed by the preparation of the crystalline bromine addition compound with the proper m. p. 65 to 66°, undepressed by admixture with an authentic specimen.

(b) Tosylated Triethylene Glycol Monoethyl Ether: The pure ester (3.6 g., 0.011 mole) was heated at 0.03 mm. pressure in equipment as described in (a), but made from 10-cc. flasks. Even, smooth distillation occurred at 133 to 135° with no increase in pressure. The air-cooled receiver contained 2.03 g. (76.6%) of a slightly yellow, slightly acidic oil, $n^{25}D$ 1.5010, which after recrystallization melted at 18 to 19° and had $n^{25}D$ 1.5030. These were the constants of pure tosylated ethylene glycol monoethyl ether and a mixed m. p. was not depressed.

The Dry Ice trap contained 0.94 g. of a slightly unsaturated liquid that on distillation yielded 0.6 g. (62.8%) of nearly pure 1,4-dioxane with the constants b. p. 100°, $n^{25}D$ 1.4190, m. p. 8 to 10°. The identity was confirmed by preparing the orange-yellow bromine addition compound, m. p. 65 to 66°.

**Rate of Solvolysis of the Tosylates.**—In all cases 0.0015 mole of the tosylate was washed with anhydrous methanol into a 250-cc. volumetric flask to which 25 cc. of water was added. After being made up to the mark with anhydrous methanol at 25°, the solution was transferred to a 500-cc. flask equipped with a water-cooled reflux condenser and drying tube. Samples removed after various periods of heating at 65 ± 1° were rapidly cooled to 25° and 10-cc. aliquots were titrated with 0.1 *N* sodium hydroxide, using a microburet. Since the molar ratio of water to tosylate was 1.557 to 0.0015, the amount of water remained practically constant and the solvolysis was assumed to follow a first order rate course given by $kt = 2.303 \log a/(a - x)$, where $a$ was the initial concentration of tosyl ester and $(a - x)$ the concentration remaining after any time $t$. The quantity $(a - x)$ was readily calculated from the titrations. Table II and Fig. 2 summarize the results.

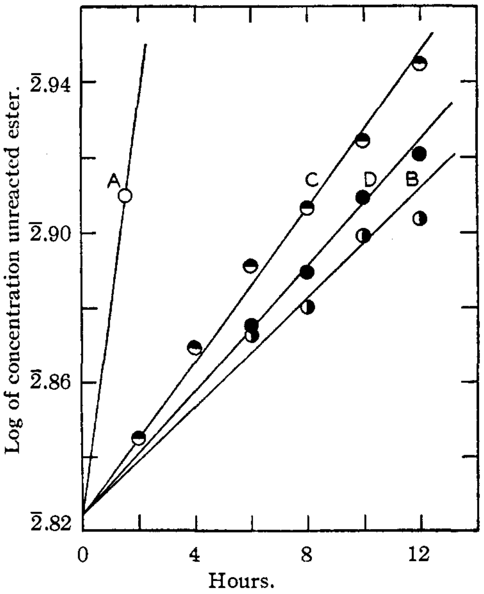

Fig. 2.—First order solvolyses of various *p*-toluenesulfonates in excess 90% aqueous methanol at 65°: plot A, ethyl; plot B, β-ethoxy ethyl; plot C, 2-(β-ethoxyethoxy)-ethyl; plot D, 2-(β-ethoxyethoxyethoxy)-ethyl *p*-toluenesulfonate.

**Rate of Iodination of the Tosylates.**—The tosyl ester, 0.0025 mole, and 0.0075 mole of dry, C. P. sodium iodide were completely dissolved in exactly 25 cc. of pure acetonylacetone by shaking the mixture for about five minutes in a 50-cc. glass-stoppered flask. The refractive index of the solution was promptly noted on an Abbe refractometer. The solution was then kept in the dark at 22 ± 0.5° and at intervals of two hours samples were removed by a capillary pipet and transferred directly into the refractometer for measurement. This technique was possible because the sodium *p*-toluenesulfonate separated as large crystals that settled readily. When the change in refractive index became slow, the solution was kept at 100° under a reflux condenser for two hours in order to complete the iodination. After making the final measurement at 22°, the sodium salt was recovered, washed, dried and weighed as a check on the completeness of the reaction. The recovery was 95.4 to 99.4%.

In order to calculate rate of iodination constants, the assumption was made that the refractive index varied linearly with the replacement of tosyloxy groups by iodine atoms. The moles of tosylate, $x$, converted at any time $t$ was then given by the change in refractive index at that time divided by the over-all change observed after the iodination was complete. This over-all decrease varied from $n^{22}D$ 0.0033 to $n^{22}D$ 0.0040 with different tosylates. If $a$ was the initial concentration of tosyl ester, 0.1 mole per liter, and $b$ that of sodium iodide, 0.3 mole per liter, the rate of iodination was given by the second order relation

$$k_2t = \frac{2.303}{(a - b)} \log \frac{b}{a}\frac{(a - x)}{(b - x)}$$

The results are summarized in Table II and Fig. 3, the former of which includes runs with tosylated ethanol and ethylene glycol monoethyl ether in which $a = b = 0.15$ mole per liter. In these cases the rate equation reduced to $k_2t = x/a(a - x)$.

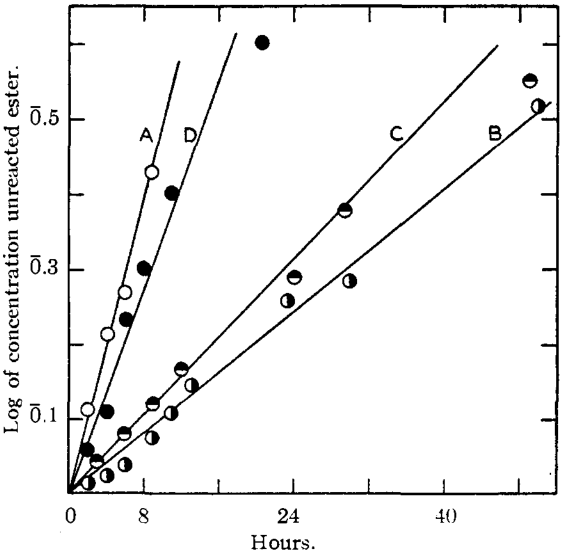

Fig. 3.—Second order iodination of various *p*-toluenesulfonates with sodium iodide in acetonylacetone at 22°: plot A, ethyl; plot B, β-ethoxy ethyl; plot C, 2-(β-ethoxyethoxy)-ethyl; plot D, 2-(β-ethoxyethoxyethoxy)-ethyl *p*-toluenesulfonate.

## Results and Discussion

The monoethyl ethers of both ethylene glycol and diethylene glycol readily formed peroxides and acidic products, the peroxide oxygen or acidic normalities sometimes exceeding 0.2 *N*

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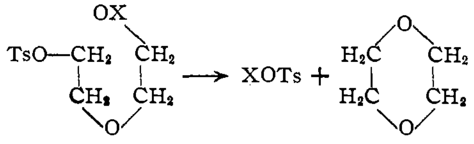
(50) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1st ed., 1941 (a) p. 457; (b) p. 428.

after storage in diffuse daylight and over a drying agent for prolonged periods. Storage even for one or two weeks was quite capable of producing peroxide oxygen normalities of the order of 0.04 *N* without causing a significant change in refractive index, a correct value of which was in consequence no decisive test of purity. Since both monoethyl ethers were practically odorless when quite pure,[12] the "fruity" odor they usually possess was tentatively attributed to aldehydes and other contaminants resulting from autoxidation.

The experiment summarized in Fig. 1, plots A and C, showed that very carefully purified diethylene glycol monoethyl ether greatly exceeded its lower homolog in ability to accumulate peroxide when kept in Erlenmeyer flasks exposed to diffuse daylight. Plots D and B record the great decrease in peroxide formation observed when aliquots of the same pure samples were stored under nitrogen in dark, glass-stoppered bottles. This result was to be expected, but for unknown reasons the monoethyl ether of triethylene glycol in all conditions tried gave negative tests for peroxide. Peroxide-containing ethylene glycol monoethyl ether yielded the crystalline bis-2,4-dinitrophenylhydrazone of glyoxal, which no doubt arose from glycolic aldehyde. Aldehydes are known to be primary decomposition products of peroxides[48,51] and, indeed, Milas[52] clearly showed that glycolic aldehyde was formed in the autoxidation of 1,4-dioxane. The same dinitrophenylhydrazone was isolated from peroxide-containing diethylene glycol monoethyl ether but failure to detect ethoxyacetaldehyde or hydroxyethoxyacetaldehyde, $HO-CH_2-CH_2-O-CH_2-CHO$, either as such or as dinitrophenylhydrazones, suggested that in this monoether both ether oxygen atoms acted as centers for peroxide formation. Ethoxy groups presumably produced acetic acid, since no acetaldehyde could be detected.

It was observed that tosylated diethylene glycol monoethyl ether appeared to distil smoothly at 125° (0.13 mm.), but the distillate consisted of 1,4-dioxane and ethyl *p*-toluenesulfonate, each recovered in 97% yield. The tosyl ester of triethylene glycol monoethyl ether decomposed similarly at 134° (0.03 mm.) to 1,4-dioxane (63%) and the crystalline tosylated monoether of ethylene glycol (76%), together with a somewhat unsaturated, acidic mixture that was not further examined. In both cases, therefore, the dominant reaction was a thermal cleavage represented by the equation



Structure I

in which X is $C_2H_5$ or $C_2H_5O-CH_2-CH_2-$. Ethyl *p*-toluenesulfonate and tosylated ethylene glycol monoethyl ether were stable to the cracking temperature, in accord with Tipson's observation that both could be purified by distillation under diminished pressure.[23] The thermal breakdown of the higher tosylates to 1,4-dioxane was not inconsistent with the fact that $\beta,\beta'$-dichloroethyl ether, when heated with aqueous caustic soda at 200°, yielded principally 1,4-dioxane and $\beta$-chloroethyl vinyl ether, rather than the divinyl derivative expected.[53] Cretcher and his coworkers[22] found that decomposition occurred during the high vacuum distillation of the tosylated monochlorohydrin of diethylene glycol; corresponding diethers yielded low-boiling fractions on distillation,[54] and only 30 to 40% of the original diether. Gallaugher and Hibbert[55c] noted that polyethylene glycols and their derivatives gave volatile, sweet-smelling distillates, sometimes at very low temperatures, and that the monochlorohydrin of tetraethylene glycol decomposed at 140°.

Such observations suggested that the OTs and X groups in Structure I might be replaceable in certain cases by hydroxyl, alkoxyl, halogen or similar units without abolishing the tendency of the polyethylene oxide chain to yield dioxane when heated. Anomalous physical properties, indeed, led to the inference[55b] that an intramolecular attraction existing between the hydroxyl groups of diethylene glycol maintained the molecule in a conformation approximating that of 1,4-dioxane. A more usual mode of decomposition was revealed in a recent careful study,[56] which showed that monoethers of ethylene and diethylene glycols were partially interconvertible when heated at 105 to 130° in presence of 1.5% sulfuric acid.

Although diethylene glycol readily yielded a white, crystalline monosodium salt when treated with metallic sodium or sodium methylate,[11] the monoethyl ether of the same glycol decomposed in part to very dark red-brown viscous materials under similar circumstances. Condensation of the resulting crude mixture with ethylene chlorohydrin gave the monoethyl ether of triethylene glycol in a yield whose small amount might possibly be attributed in part to thermal decomposition during the fractional distillation. The preparation of the corresponding tosylate was uneventful, but the thermal instability of this compound, and also of tosylated diethylene glycol monoethyl ether, made it prudent to conduct the double decompositions with sodium iodide near 23°,[57] instead of at the more usual temperature of

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(51) Clover, THIS JOURNAL, **44**, 1107 (1922).

(52) Milas, *ibid.*, **53**, 221 (1931).

(53) Cretcher, Koch and Pittenger, *ibid.*, **47**, 1173 (1925).

(54) Liston and Dehn, *ibid.*, **60**, 1264 (1938).

(55) Gallaugher and Hibbert, *ibid.*, (a) **58**, 813 (1936); (b) **59**, 2514; (c) **59**, 2521 (1937).

(56) Dolgopolev, Melnikow and Nametkin, *J. Applied Chem.* (*U.S.S.R.*), **20**, 486 (1947).

(57) Tipson, Clapp and Cretcher, *J. Org. Chem.*, **12**, 133 (1947), also used room temperature when iodinating the *p*-toluenesulfonates of ethanol, glycol and other alcohols with sodium iodide in acetone.

100 to 110°. The resulting β-iodoethers, like other members of the class,[28,29,58] were quite stable when distilled.

TABLE I

DENSITIES, SPECIFIC AND MOLECULAR REFRACTIONS OF SERIES $C_2H_5(OCH_2CH_2)_xR$

| Series | Refractive index $n_D$ | °C. | $d^a$ | Molecular refraction Obs. | Calcd.[b] | Diff. |
|---|---|---|---|---|---|---|
| Alcohols, R = OH | | | | | | |
| x = 0[c] | 1.3610 | 20 | 0.7894[d] | 12.92 | 12.96 | −0.04 |
| 1[e] | 1.4074 | 20 | .9297[d] | 23.88 | 23.84 | +0.04 |
| 2[f] | 1.4273 | 20 | | | | |
| | 1.4254 | 25 | .9855 | 34.88 | 34.72 | +0.16 |
| 3[g] | 1.4380 | 20 | 1.0211[d] | 45.78 | 45.60 | +0.18 |
| Tosylates, R = OTs | | | | | | |
| x = 0 | 1.5067 | 35 | | | | |
| | 1.5050 | 40 | 1.1637[h] | 51.04 | 40.16[j] | 10.88[k] |
| 1 | 1.5032[l] | 25 | 1.1677 | 61.79 | 51.04[j] | 10.75[k] |
| | 1.5000 | 35 | | | | |
| | 1.4981 | 40 | | | | |
| 2 | 1.4976 | 25 | 1.1599 | 72.80 | 61.92[j] | 10.88[k] |
| 3 | 1.4959 | 25 | 1.1698 | 82.99 | 72.80[j] | 10.17[k] |
| Iodides, R = I | | | | | | |
| x = 0 | 1.5133 | 18.5 | 1.930[m] | 24.30 | 24.24 | +0.06 |
| 1[n] | 1.4996 | 15 | 1.6698[o] | 35.21 | 35.12 | +0.09 |
| | 1.4965 | 20 | | | | |
| 2 | 1.4908 | 20 | | | | |
| | 1.4881 | 25 | 1.5210 | 46.24 | 45.99 | +0.25 |
| 3 | 1.4889 | 20 | | | | |
| | 1.4870 | 25 | 1.4557 | 56.93 | 56.87 | +0.06 |

[a] Densities at 25–25° unless otherwise mentioned. [b] From tables of atomic refractivity, ref. 49. [c] Ref. 50 b. [d] At 20°/20°. [e] Ref. 31. [f] Ref. 13. [g] Davidson's value of $n^{26}D$ 1.4389 (ref. 12) was high, probably because of contamination with diethylene glycol, $n^{20}D$ 1.4475. [h] At 40°/40°. [j] Contribution of –O–$SO_2$ group omitted. [k] Contribution of –O–$SO_2$ group. [l] Tipson (ref. 23) found $n^{25}D$ 1.5026. [m] At 18.5°/4°. Quoted from Beilstein. [n] Ref. 30. [o] At 15°/4°.

Table I, column 5, records the molar refractions of compounds rigorously purified for the first time during this research, together with relevant data from the literature. The fact that values in the ethylene glycol monoethyl ether and in the β-iodoether series agreed closely with those calculated from a table of atomic refractivities (column 6) argued for the purity of the samples examined. In the first and second of these series the average increments occasioned by addition of an ethylene oxide unit were 10.95 and 10.88, respectively, in good agreement with the theoretical value of 10.88.[59] Since the observed increments in the tosylates, 10.98 ± 0.21, were also in good agreement, it followed that the tosylates were probably pure and that the presence of the sulfonic group occasioned no marked change in the molecular refraction of the remaining atoms. Column 7, giving the difference between the calculated molecular refraction of these atoms and that observed for the tosylate, therefore represents the molecular refraction of the O–$SO_2$ group. The result, 10.53 ± 0.35, was somewhat higher than the molecular refraction of 9.7 ± 0.2 found for the O–$SO_2$ group in several esters of ethylene sulfonic acid,[60] perhaps because of different amounts of optical exaltation.

Inspection of column 2, Table I, reveals that specific refractive indices in the series R–OH increased with $x$ but that the increment decreased. This tendency was true of the polyethylene glycol series[55a] and was included in a generalization about specific refraction by Smiles.[61] The values for tosylated and iodinated derivatives in Table I, however, decreased as each series was ascended and were in opposition to the generalization. Conn and his co-workers,[14] on the other hand, found no regular trend in refractive index in passing from the benzoates and $p$-nitrobenzoates of a number of ethylene glycol monoethers to the corresponding diethylene glycol derivatives. It is probable that in this and in much other work in the polyoxyethylene series,[14,18,62] the accuracy of the recorded physical constants was often impaired by the presence of impurities originating in autoxidation, incomplete fractional distillation or in thermal cracking.

Figures 2 and 3 record the relative rates of solvolysis of the tosylates in a large excess of aqueous methanol (1:9) at 65°, and their relative reactivities toward sodium iodide. The solvolyses followed a first order course and all the observations fell, within the experimental error, on the lines shown in Fig. 2. This error reflected the uncertainty of ± 0.05 cc. in the titrations of acidity, and corresponded to 14 to 8% in the log $(a-x)$ values for solvolysis up to 10% completion. Between 10 and 20% completion the errors in log $(a-x)$ were 8 to 4%, being least for the fastest reaction. Iodinations (Fig. 3) were carried out with sodium iodide in acetonylacetone and the progress of the reaction was followed by the change in refractive index of the solution. Since the error in the refractometer readings was about $\pm 10^{-4}$, the extent of iodination was in serious doubt in the initial stages, and by 5 to 7.5% in the later stages of the reactions. Within these limits all observations fell upon straight lines passing through the origin, when second order kinetics were assumed,[63] but did not define the slope of the lines within 15%. Second order kinetics also applied to the reaction of ethyl $p$-toluenesulfonate, and other substituted benzene sulfonates, with sodium ethylate in absolute ethanol.[64]

The rate constants (Table II) refer only to the over-all kinetics of solvolysis and iodination since actual reaction mechanisms and possible side-reactions were not determined. Ethyl $p$-

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(58) Cretcher and Pittenger, THIS JOURNAL, **47**, 163 (1925).

(59) Zimakov, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 913 (1947), decided that the possession of the same molecular refraction by ethylene oxide itself could be attributed to a chance cancellation of theoretical errors.

(60) Whitmore and Landau, THIS JOURNAL, **68**, 1797 (1946).

(61) Smiles, "Relations between Physical Properties and Chemical Constitution," Longmans, Green and Co., London, 1910, p. 267.

(62) McKinley and Nibarger, THIS JOURNAL, **61**, 373 (1939).

(63) McCleary and Hammett, *ibid.*, **63**, 2254 (1941).

(64) Morgan and Cretcher, *ibid.*, **70**, 375 (1948).

TABLE II

APPROXIMATE RATE CONSTANTS FOR SOLVOLYSIS AND IODINATION OF THE TOSYLATES

| Tolsylate $C_2H_5(OCH_2CH_2)_xOTs$ | Solvolysis $k_1$[a] | Iodination $k_2$[b] | $k_2$[c] |
|---|---|---|---|
| x = 0 | 0.124 | 0.56 | 0.66 |
| 1 | .017 | .12 | .06 |
| 2 | .023 | .15 | |
| 3 | .019 | .36 | |

[a] In aqueous methanol (1:9) at 65 ± 1°; first order; unit, hours$^{-1}$. [b] With 0.1 mole of tosylate and 0.3 mole of iodide per liter at 22 ± 0.5°; second order; units, liters, moles$^{-1}$, hours$^{-1}$. [c] With 0.15 mole per liter both of tosylate and of iodide.

toluenesulfonate ($x = 0$) obviously was most reactive, as might have been expected from the known depressing effect of a β-ether group on the reactivity of organic halides, and from the similarity between halides and sulfonates.[57] Tosylated ethylene glycol, for example, hydrolyzed twelve times more slowly than tosylated ethanol.[65] The differences between the solvolysis rate constants for the higher tosylates ($x$ = 1, 2 and 3, Table II) probably fell within the experimental error, and the same remark was true of the iodination rate constants for the tosylates with $x$ = 1 and 2. The results in general suggest that the tosylation–iodination reaction as applied to cellulose acetates and ethers is valid for research on hydroxyethylcelluloses.

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## Summary

1. The following compounds were obtained pure: triethylene glycol monoethyl ether, its *p*-toluenesulfonate, the *p*-toluenesulfonate of diethylene glycol monoethyl ether, β-ethoxyethoxy-β'-iododiethyl ether and β-ethoxy-β'-iododiethyl ether. A new preparation of β-iodoethyl ether was described.

2. Diethylene glycol monoethyl ether was particularly liable to peroxide formation, was partly decomposed by sodium methylate, and yielded a tosylate decomposing at 125° (0.13 mm.) to equimolar amounts of 1,4-dioxane and ethyl *p*-toluenesulfonate. The latter product was replaced by tosylated ethylene glycol monoethyl ether when tosylated triethylene glycol monoethyl ether was thermally decomposed at 134° (0.03 mm.). Ethyl *p*-toluenesulfonate was more reactive toward solvolysis in 90% methanol, and toward iodination with sodium iodide in acetonylacetone, than the higher tosylates.

3. Data for the molar refractivities of the above series of compounds were completed, and the molar refraction of the O–SO$_2$ group in *p*-toluenesulfonates was found to be 10.5 ± 0.35.

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(65) Foster and Hammett, THIS JOURNAL, **68**, 1736 (1946).

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

# *p*-Toluenesulfonyl Chloro and Iodo Derivatives of an Alkali-Soluble Hydroxyethylcellulose[1]

BY CLINTON W. TASKER AND C. B. PURVES[2]

Hydroxyethyl ethers of cellulose were first described by Hubert[3] in 1920, but excited no general interest until 1933, when the publications of Shorygin and Rymaschewskaja[4] commenced. These articles, together with those of Sönnerskog,[5] and Schorger and Shoemaker,[6] and also the relevant patents[7-19] showed that hydroxyethyl-

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(1) Presented at the Chicago meeting of the American Chemical Society, April, 1948. Abstracted from a Thesis presented to the Faculty of McGill University in June 1947, by C. W. Tasker in partial fulfilment of the requirements for the Ph.D. degree.

(2) At above address.

(3) Hubert, *J. Soc. Chem. Ind.*, **42**, 348A (1923); German Patent 363,192 (1920).

(4) Shorygin and Rymaschewskaja, (a) *Ber.*, **66**, 1014 (1933); (b) *J. Gen. Chem.* (*U. S. S. R.*), **7**, 2428 (1937); (c) *ibid.*, **8**, 1903 (1938).

(5) Sönnerskog, *Svensk. Papperstidn.*, (a) **48**, 413 (1945); (b) **49**, 409 (1946).

(6) Schorger and Shoemaker, *Ind. Eng. Chem.*, **29**, 114 (1937).

(7) Schorger, U. S. Patent (a) 1,863,208 (June 14, 1932); (b) 1,914,172 (June 13, 1933); (c) 1,941,277; (d) 1,941,278 (Dec. 26, 1933).

(8) Powers, Bock and Houk, U. S. Patent 2,087,549 (July 20, 1937).

(9) Berger and Bidaud, U. S. Patent 2,047,189 (July 14, 1936).

(10) Ellis, British Patent 408,730 (April 19, 1934).

(11) Seymour and Salvin, U. S. Patent 2,134,895 (Nov. 1, 1938).

(12) I. G. Farbenindustrie Aktiengesellschaft, British Patent (a) 383,612 (Feb. 12); (b) 383,617 (Feb. 13, 1931).

(13) Lilienfeld, U. S. Patent (a) 1,589,606 (June 22, 1926); (b) 1,722,927 (July 30, 1929); (c) 2,265,919 (Dec. 9, 1941).

(14) Richter, U. S. Patent 2,054,299 (Sept. 15, 1936).

(15) Broderick, U. S. Patent (a) 2,173,470; (b) 2,173,471 (Sept. 19, 1939).

(16) Thomas and Oxley, British Patent 463,317 (March 23, 1937).

(17) Levesley and Craik, U. S. Patent 2,046,174 (June 30, 1936).

(18) Oxley, Thomas and Downing, U. S. Patent 2,184,564 (Dec. 26, 1939).

(19) Dreyfus, (a) U. S. Patent 1,502,379 (July 22, 1924); (b) British Patent 478,259 (Jan. 17, 1938).