

Synthesis of a Silicone Derivative of Sucrose

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We wish to report the synthesis of a silicone derivative of sucrose. The compound, the octakis(trimethylsilyl) ether of sucrose, was prepared by treating sucrose in pyridine solution with trimethylchlorosilane (General Electric Silicone SC-01). Schwarz, Baronetsky, and Schoeller³ have reported the preparation of glucose derivatives.

The sucrose used was commercial grade material which was purified by recrystallization from aqueous ethanol and dried *in vacuo*; the silylating agent, assaying 85% minimum trimethylchlorosilane, was used without preliminary purification.

Trimethylchlorosilane (250 g., 2.3 mole) was added dropwise into a mechanically stirred solution of 85.6 g. (0.25 mole) sucrose in 1.5 l. of anhydrous pyridine, after which the reaction mixture was heated at 80°–85° for two hours. Upon completion of the reaction the excess pyridine was distilled off *in vacuo* and the residual slurry extracted thoroughly with petroleum ether. The ether extract was concentrated *in vacuo* and the viscous concentrate distilled in a Hickman alembic still at 0.02–0.05 mm. at 190°–200°.

The product was a clear, almost colorless oil with high viscosity, soluble in benzene, methanol, acetone, petroleum ether, diethyl ether, and chlorinated hydrocarbons, and insoluble in water. $[\alpha]_D^{20} + 3.47^\circ$ (50 wt. % in benzene); n_D^{20} 1.4434.

Anal.: Calcd. for $C_{36}H_{86}O_{11}Si_8$: mol. wt., 918. Found: Si, 23.3; mol. wt. (Rast), 933.

The data suggest that the compound may be a mixture containing some hepta or lower silicated derivatives. However, it is believed that these very possibly have higher boiling points or even would tend to polymerize without distillation.

The compound exhibited a marked tendency to hydrolyze in the presence of water. A sample, refluxed with water and chromatographed, showed a single spot which was identified as sucrose. Since the compound is volatile and can readily be hydrolyzed, yielding sucrose, it offers a good means for the analytical separation of sucrose by vapor phase chromatography and its identification.

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Reduction of Chlorobenzene at the Dropping Mercury Electrode

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Although there have been several attempts to reduce chlorobenzene and its derivatives at the dropping mercury electrode,^{1–3} they were not successful, ostensibly because of the extreme potentials involved. We wish to report the reduction of chlorobenzene and to suggest that other difficultly reducible organic substances will be accessible by the technique employed. Because our work lies primarily in the area of aliphatic halogen compounds, we do not intend to pursue further investigations of chlorobenzenes or unsaturated compounds which might now be reducible by others according to the procedure described herein.

Tetrabutylammonium iodide (TBI) has been shown to be the supporting electrolyte with the most negative decomposition potential of the substances tested in dioxane-water.⁴ Kolthoff and Coetzee⁵ found that several supporting electrolytes had the same decomposition potential in anhydrous acetonitrile. As might be expected, our work in anhydrous *N,N*-dimethylformamide (DMF) has shown that 0.05*M* TBI has an apparent decomposition potential of approximately –2.85 volts *vs.* the saturated calomel electrode (S.C.E.) and 0.05*M* tetraethylammonium bromide (TEB) “discharges” at –2.76 volts. Yet, contrary to obvious deduction, chlorobenzene in DMF solution with TBI as the supporting electrolyte yields only a marked rise in current just prior to the cathodic discharge, whereas with TEB as the supporting electrolyte chlorobenzene gives a clear wave with a flat plateau. The half-wave potential in 0.05*M* TEB is –2.58 volts *vs.* the S.C.E.

The reduction of chlorobenzene is influenced by the cation of the supporting electrolyte because no polarographic wave is observed when tetrabutylammonium bromide (or TBI) is used but waves are present with 0.05*M* tetraethylammonium iodide or perchlorate (or TEB) as supporting electrolytes. (The half-wave potentials are –2.58 for chlorobenzene in tetraethylammonium iodide and –2.60 in tetraethylammonium perchlorate.) With tetramethylammonium bromide a rise in current is discernible before cathodic discharge but the wave

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is not at all clear because of the high resistance of the solution.

Lothe and Rogers⁶ have thoroughly investigated the effect of supporting electrolytes on the reduction of carbon tetrachloride in methanol (and aqueous methanol) solutions. They detected a shift of 0.06 volt in the half-wave potential toward more positive values in changing from TBI to TEB as the supporting electrolyte. The average $E_{1/2}$ for carbon tetrachloride with these electrolytes in methanol is -0.85 volt. This would be in proportion to a shift from the hypothetical $E_{1/2}$ for the chlorobenzene with TBI in DMF of -2.8 volts (*i.e.* near the discharge potential) and the $E_{1/2}$ for chlorobenzene with TEB in DMF of -2.6 volts, a difference of 0.2 volt in 2.7 volts.

A possible explanation for such a shift at very negative potentials is given by the work of Laitinen and Nyman⁷ wherein it was shown that the cathodic discharge in liquid ammonia with TBI as the supporting electrolyte involved direct dissolution of electrons. With TEB in liquid ammonia, they found that a combination of both direct electron dissolution and amalgamation of the tetraethylammonium cation probably occurred at the discharge potential. In the present work the tetraethylammonium ions may be acting as intermediaries in the transfer of electrons from the cathode to the difficultly reducible chlorobenzene. When TBI is the supporting electrolyte, the tetrabutylammonium ions do not readily accept and then transfer electrons to the chlorobenzene; thus no reduction occurs until the electron dissolution process begins. This hypothesis is supported by our finding that mere addition of TEB to a solution of chlorobenzene in DMF already containing TBI allows the characteristic reduction wave for chlorobenzene to appear.

The chlorobenzene wave is diffusion controlled and has a slope of 0.09 volt. In a useful range of concentrations for analytical purposes, from 0.2 to $1 \times 10^{-3}M$ chlorobenzene with 0.05M TEB in DMF, the best value of the diffusion current is 4.5 microamperes per millimole. The diffusion current constant is subject to some error because of the rapid drop rate at extremely negative potentials but is of the order of 2.6 if a correction factor of 0.87⁸ is applied to the fraction $i_d/m^2t^{1/2}$.

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Attempts were made to reduce vinyl chloride and acetylene, both previously reported as unattacked at the dropping mercury electrode,¹ and a distinct rise in current just prior to the cathodic discharge was detected. However, no half-wave potential could be measured. Ethylene does not produce an increase in current before the discharge potential of TEB.

EXPERIMENTAL

A Pecsok-Juvet⁹ cell thermostated at $25^\circ \pm 0.1^\circ$ was used in conjunction with a Leeds and Northrup Type E Electrochemograph for the initial work. The cell resistance (with 0.05M TEB) was 6000 ohms. Later experiments employed a cylindrical cell with a fine sintered-glass disk sealed in a side arm located near the bottom of the cell similar to that of Kolthoff and Coetzee.⁵ A saturated calomel cell fitted with a side tube closed by an agar plug could be inserted in the side arm of the polarographic cell. The capillary and nitrogen inlet tube were introduced through a standard taper joint in the top of the polarographic cell. The resistance of this cell was of the order of 3000 ohms with 0.05M TEB. All half-wave potentials reported have been corrected for IR drop. Matheson, Coleman, and Bell reagent chlorobenzene (n_D^{20} 1.5242), redistilled Eastman White Label DMF, Eastman White Label TEB and tetramethylammonium bromide, and Southwestern Analytical Chemicals TBI, tetrabutylammonium bromide, and tetraethylammonium iodide were employed. The tetraethylammonium perchlorate was synthesized according to Kolthoff and Coetzee.⁵ The electrode characteristics were: $m = 1.20$ mg./sec. and $t = 4.9$ sec. for $h = 66.1$ cm., open circuit in 0.05M TEB in DMF. The diffusion currents were measured and the half-wave potentials determined by the "third method" described by Müller.¹⁰

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