LABORATORY METHOD FOR THE PREPARA-TION OF ORGANIC ACID ANHYDRIDES

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In the various methods for the production of acetic anhydride, an alkali acetate is subjected to interaction with chlorine and sulphur. These elements are either introduced separately or part of the chlorine is beforehand combined with the sulphur to sulphur chloride, and the balance of the chlorine introduced into the reaction mixture in gaseous form.¹ These methods have, however, proved too cumbersome for laboratory purposes.

This paper describes a modification of the procedure, which is rapid, convenient for small-scale laboratory operation, and not limited to the preparation of acetic anhydride. An alkali or alkaline earth salt of an organic acid reacts with elementary sulphur and bromine according to the equation:—

$$8R\; COOM + S + 3Br_2 = 4(R.CO)_2O + 6MBr + M_2SO_4$$

(M = metal) and gives the corresponding anhydride.

The reaction may be initiated at room temperature. It is strongly exothermic, and cooling may be required in order to keep the reaction under control and to avoid losses of bromine by evaporation. Presence of water decreases the yield. In the case of sodium accetate, it is advisable though not necessary to carry out the reaction in presence of a small amount of acetic anhydride.

Experiments

(1) Acetic anhydride. To 50g. acetic anhydride in a round-bottomed flask of 1500 cc. capacity, placed in cold water, 450 g. of powdered sodium acetate (dried by fusion at 320° C.) and at the same time a solution of 22 g. sulphur in 320 g. bromine is added while stirring. The operation takes about 30 minutes.

The mixture is then stirred for a further 5 minutes, after which period the initially dark brownish-red colour has changed into pale yellow, and the anhydride is distilled off from a water-bath under reduced pressure. The crude anhydride (310 g.) is redistilled under normal pressure, and the fraction boiling between 134°—138° C. is collected. Yield, 295 g. of 98% purity = 87.5%. The so purified anhydride contains neither bromine nor sulphur compounds and leaves no residue on evaporation.

- (2) Propionic anhydride. To 40 g. fused and powdered sodium propionate in a flask of 250 cc. capacity a solution of 2 g. sulphur in 22 g. bromine was added while stirring. The temperature was kept at about 50° C. When the operation was completed, the anhydride was distilled off in vacuo. The crude product (25 g.) was fractionated under normal pressure, and the fraction 155°—156° C. was collected. Yield, 23 g. propionic anhydride of 90% purity = 85%.
- (3) Benzoic anhydride. To 57 g. dried and powdered sodium benzoate, in 100 cc. carbon tetrachloride, a solution of 1.8 g. sulphur in 24 g. bromine was added, while stirring. The reaction mixture was kept for 3 days, the solvent decanted and the residue extracted with ether. The two solutions were combined and the solvents evaporated. The residue obtained crystallized, m.p. 42° C. Yield, 60% of the theoretical.

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¹ Friedländer Vol. 10, pp. 66, 67; Vol. 11, p. 70. Chemisches Centralblatt, 1921, III, 1459; 1923, II, 961; 1928, II, 2548.

SOCIETY OF CHEMICAL INDUSTRY

LIVERPOOL SECTION

A meeting organized by the Liverpool Joint Chemistry Committee w. held under the auspices of the Royal Institute of Chemistry on October I at 6 p.m., in the Chemistry Lecture Theatre, University of Liverpool Dr. Brislee, the retiring Chairman of the Liverpool and North-Weste Section of the Royal Institute of Chemistry, passed on the office to Mr. Brearley, who is well known as an administrator and industrialist. Mr. Brearley, F.R.I.C., of Brothertons & Co., Ltd., then gave in a ve short time an extremely interesting Chairman's Address, under the time and extremely interesting Chairman's Address, under the time Sulphur Dioxide—Retrospect and Prospect." The address arranged around a number of slides, is not likely to be published in financial in the following paragraphs.

The sources of sulphur dioxide were outlined, including flue gases. estimate was made of the amount of sulphur available from coal and removal of SO₂ from super power station gases was mentioned; althou the SO2 might be recoverable, the large part of the cost must be debi to the prevention of a nuisance. The compulsory complete removal H₂S from coal-gas was discussed, old and new processes being include the H₂S is absorbed by iron oxide, α-aminopropionic acid, and ammoni thio-arsenate. Smelter gases are a valuable source of SO2 and recov processes can be made economical. The strongest source of SO₂ is burning of sulphur in air. To reduce SO₃ formation, a temperature hig than 800° C. is required, and to limit the amount of excess air the sulp and air must be in intimate contact. Swedish and British burners giv 14%—18% SO₂ were illustrated. In the preparation of pure SO₂, whet from weak or strong gases, the method is by solution in water and recov by boiling; very large amounts of water are necessary and econom production is controlled by the availability of waste heat and the contration of SO₂ in the gas. Processes have been used for very weak gin which SO₂ is absorbed in (1) a basic aluminium sulphate solution controlled $p_{\rm H}$, and (2) a mixture of xylidine and water. The gas a concentration is then dried and liquefied by compression and cool The bulk storage of liquid SO₂ was described, attention being paid to safety factors involved. An internal dip tube is fitted to cylinders arrangements were shown for using SO2 as gas and as liquid. Refer was made to corrosion with SO2; the dry liquid does not act on iron in the presence of moisture a protective film is formed. A severe corro of lead has been observed with aqueous solutions at 100° C. in the pres of chlorides and of free sulphuric acid; the end product is lead sulp and corrosion is avoided when chloride-free water is used. Indus uses of sulphur dioxide were discussed and included refrigeration, c bleaching, fractionation of hydrocarbons, polymerization of veget

There was a vigorous discussion in which Messrs. Wallace, Tillotson, Dally, and Emsley took part. Dr. L. J. Burrage proposed, Mr. L. V. Cocks seconded, a vote of thanks to Mr. Brearley for stimulating survey of the chemistry and technology of a simple mole

SOUTH WALES SECTION

A meeting of the Section was held jointly with the Royal Institu Chemistry at the University College, Cathay's Park, Cardiff, on Satu afternoon, October 28, when Mr. J. Colin Gullen (Aberthaw and B Channel Cement Company) lectured on "Modern Developmen the Control and Manufacture of Portland Cement." Starting the early history of the industry, the lecturer proceeded to describ preparation of the raw materials and how by differential screening i possible to eliminate undesirable fractions and thus ensure the corpoportions of lime and silica with little other impurities to product best type of cement. The flow diagram on slides was described sta stage, and future possible improvements pointed out, the lecturer of his interesting lecture with the methods of control and tests used.

Mr. Stanley Dixon occupied the chair and in his opening remarks a tribute to the work on behalfs of the Section done by his prede in office, Mr. Neil Lawson. A prolonged discussion followed, after a hearty vote of thanks was proposed to Mr. Gullen by Mr. Fred V and seconded by Mr. H. F. Adams.