by the decarboxylation of oleanolic acid. Oxidation of norechinocystenol-A gives the ketone norechinocystenone-A, which is different from oleanone prepared by the decarboxylation and dehydrogenation of oleanolic acid.

STANFORD UNIV., CALIFORNIA RECEIVED MARCH 28, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MONSANTO CHEMICAL CO., ST. LOUIS, MISSOURI]

Alkyl Sulfites—Cyclohexyl Sulfite

BY L. P. KYRIDES

In 1931 Voss and Blanke[1] reported the preparation of alkyl sulfites in high yields from primary and in fair yields from secondary alcohols. They also reported a yield of 54% of cyclohexyl sulfite—b. p. 182° (19 mm.), $n^{13.7}\text{D}$ 1.4865; S 13.16% (calcd. 13.02%). At about the same time Kitasato and Sone[2] reported that cyclohexyl sulfite made in the presence of pyridine boiled at 55° (12 mm.), which would appear to be too low for the boiling point of this ester.

Later, Carré and Libermann[3] cast doubt on the isolability of cyclohexyl sulfite, stating that cyclohexene was the only reaction product of cyclohexanol with thionyl chloride. The criticism of Carré and Libermann was countered by a subsequent report of Voss and Wachs[4] reasserting the isolation of cyclohexyl sulfite in a 42% yield, b. p. 173–173.5° at 14.5 mm.; $n^{17.3}\text{D}$ 1.48497; S, 12.85%. Finally, Carré and Libermann[5] made the categorical statement that "the new experiments have confirmed our previous results: the reaction of thionyl chloride with cyclohexanol gives mainly cyclohexene, with only a small quantity of cyclohexyl sulfite which we were unable to distil under vacuum without decomposition."

Having prepared cyclohexyl sulfite in these laboratories at three different times during the past twelve years and tested the products at intervals for stability, we concluded that, if properly prepared, the ester is stable over long periods of time. It distils within a very narrow range under a fairly good vacuum and always smells of sulfur dioxide and cyclohexene.

The procedure for the preparation of *n*-butyl sulfite given in "Organic Syntheses"[6] is not applicable to secondary alkyl sulfites. Following the reaction, distillation gives some olefin and the unchanged alcohol. Voss and Blanke obtained fair yields of secondary alkyl sulfites only by displacing the hydrogen chloride in the course of its liberation during the reaction with a stream of carbon dioxide. This elimination of hydrogen chloride appears to be of significance in driving the esterification to completion.

We have been able to improve the process, and consequently the yields, by carrying out the reaction under reduced pressure. Using the vacuum obtainable by an ordinary water pump, it was demonstrated that the halogen acid is removed quite successfully and excellent yields of both secondary and primary sulfites are obtained from the corresponding alcohols.

Since in the process for *n*-butyl sulfite referred to above 3–5% of butyl chloride is formed we chose a lower reaction temperature in order to minimize chloride formation. At the recommended temperatures (10–20°), the reaction proceeds quite rapidly, giving the high yields desired.

The following experimental work relating to improvements in the technique of preparing sulfites in general is submitted in order to clarify the situation regarding cyclohexyl sulfite.

Experimental

The apparatus consisted of a four-necked flask carrying an efficient reflux condenser, a thermometer for following the reaction temperature, a dropping funnel and an agitator revolving in a lubricated rubber sleeve[7] for operation under vacuum.

Cyclohexyl Sulfite.—Two hundred grams of anhydrous cyclohexanol was charged into the reaction flask and cooled with agitation to incipient crystallization (25°). Vacuum was applied (24″) and 121 g. of freshly distilled thionyl chloride was slowly dropped in. As the addition progressed and the cyclohexanol liquefied, the reaction temperature was lowered gradually. When about one-half of the thionyl chloride had been added (time fifteen minutes) the temperature had fallen to 15°. At this point, further addition of thionyl chloride induced the evolution of hydrogen chloride which further lowered the temperature. External cooling was discontinued when the temperature had fallen to 5° and addition of the rest of the chloride was regulated to maintain this temperature and the pressure given. Total addition time was forty-five minutes. The vacuum was now increased to 30″ in order to expedite the more complete elimination of hydrogen chloride which in turn lowered still further the temperature (0°). After a short time the flask was immersed in a water-bath and the temperature raised slowly to 55°, taking a half-hour for this operation. After an additional reaction time of a half-hour at 55°, vacuum was broken off and the liquid was transferred into a distillation flask with an attached Vigreux column. After separating a small amount of low boiling liquid under partial vacuum, the main fraction was distilled using a high vacuum pump. The distillate weighed 217 g. and boiled constantly at 134–136° at 3 mm. The low boiling fraction upon refractionation gave 11 g. of unreacted cyclohexanol. The yield of cyclohexyl sulfite was therefore 93.5% on cyclohexanol consumed and 86% on thionyl chloride used. There was evidence of evolution of

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(1) Voss and Blanke, *Ann.*, **485**, 272 (1931).

(2) Kitasato and Sone, *Ber.*, **64**, 1142 (1931).

(3) Carré and Libermann, *Bull. soc. chim.*, [5] **2**, 160 (1935).

(4) Voss and Wachs, *Ber.*, **68**, 1939 (1935).

(5) Carré and Libermann, *Bull. soc. chim.*, [5] **3**, 144 (1936).

(6) "Organic Syntheses," Coll. Vol. II, 1943, p. 112.

(7) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Vol. 21, p. 40.

traces of cyclohexene and sulfur dioxide in the exit gases during the reaction and distillation. The finished product also gave positive evidence of traces of these two products. The cyclohexyl sulfite was redistilled a year later and its boiling range and refractive index (n^{25}D 1.4848) were found unchanged. After another two years the material boiled constantly at 165° under 14 mm. with no change in the refractive index. Upon analysis the product contained 13.10% sulfur against 13.02% expected. These results substantiate Voss and Blanke's statements regarding cyclohexyl sulfite.

It was observed that unless the reaction is carried out to completion, as indicated, cyclohexyl sulfite cannot be distilled successfully under vacuum because of the continuous decomposition of the product to sulfur dioxide and cyclohexene. This fact would explain the inability of the French workers to isolate the product. Repeated distillation after long standing has not given evidence of deterioration, excepting for the smell of sulfur dioxide and cyclohexene. It was also observed that cyclohexyl sulfite containing very small amounts of sulfuric acid can be distilled under vacuum without decomposition.

Following the procedure given, no difficulty was experienced in the preparation of other esters such as:

Sulfite	Yield, %	Boiling range, °C.
Dimethyl	84	124–127
Diethyl	Quantitative using slight excess of anhydrous ethanol	154–157
Isopropyl	(Refractionated) 84% on isopropanol	73–74° at 25 mm.
n-Butyl	Yield (refractionated) 92.5% on butanol	124–126° at 29 mm.
Methylhexylcarbinyl	85 (reaction temp. 20–25°)	147–149° at 5–6 mm.

It should be noted that with methanol, ethanol and isopropanol, the reaction should be carried under a lower vacuum because of their low boiling points. It is advantageous to regulate the vacuum so that the alcohol barely refluxes during the addition and later to increase the vacuum.

Summary

Sulfites are obtained in excellent yields from the reaction of primary and secondary alcohols with thionyl chloride using low pressures during the operation.

Cyclohexyl sulfite made by the above procedure is a relatively stable product and can be redistilled repeatedly without change in composition.

ST. LOUIS, MO. RECEIVED JANUARY 31, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON, AND THE DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY]

On the Thermodynamics of Azeotropic Solutions. I. Shift of Equilibrium in Binary Systems[1]

BY O. REDLICH AND P. W. SCHUTZ

Among the numerous authors who have contributed to the vast amount of experimental data on azeotropic solutions in early and recent times, several have felt the advantages which are to be expected from a thermodynamic discussion.[1a] Obviously thermodynamic predictions are apt to enhance the value of available data and the efficiency of new experimental research, especially in the field of industrial applications.

Apart from the well-known fundamental properties of azeotropic solutions, theoretical discussions either referred to the properties of solutions in general and arrived only at qualitative conclusions regarding the azeotropic properties,[2] or started from special relationships[3] between vapor pressure and composition which are necessarily of restricted validity.

Actually the problem of the shift of azeotropic equilibrium can be easily formulated in a general way and solved by straightforward thermodynamic methods.

The azeotropic equilibrium of a solution of two miscible liquids is characterized by three intensive variables: the composition, which is equal for the liquid and the vapor, the temperature and the pressure. Under the condition, that the azeotropic equilibrium should be maintained, only one of these variables is independent. The shift of equilibrium is therefore exhaustively described by two relations between the variables.

In the development it is assumed only that the vapor is a perfect gas mixture. This restriction can be removed without any essential difficulty but the practical gain would be small and by no means sufficient to justify the complication of the formulas.

In the following, the standard notation of Lewis and Randall is used, the pure components being chosen as reference states. The heats of vaporization of the two components from the solution are denoted by $\Delta H_1 = \Delta H_1^0 - \bar{L}_1$ and $\Delta H_2 = \Delta H_2^0 - \bar{L}_2$, where ΔH_1^0 and ΔH_2^0 are the heats of vaporization of the pure components, and $\bar{L}_1$ and $\bar{L}_2$ the relative partial molal heat contents.

The relationship between azeotropic pressure and temperature is represented by

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{az} = \left(\frac{\partial P}{\partial T}\right)_{N_2} + \left(\frac{\partial P}{\partial N_2}\right)_T \left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{az} \qquad (1)$$

The last term is equal to zero since $(\partial P/\partial N_2)_T = 0$ constitutes one of the fundamental properties of the azeotropic equilibrium.

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(1) Original manuscript received December 23, 1942.

(1a) See for instance R. W. Merriman, *J. Chem. Soc.*, **103**, 628 (1913).

(2) *Cf.* M. S. Wrewsky (Vrevskii), *Z. physik. Chem.*, **83**, 551 (1913), and previous papers.

(3) See H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942); J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1900): and refs. 7 and 8.