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Quantitative Determination of Acetaldehyde in the Presence of Crotonaldehyde

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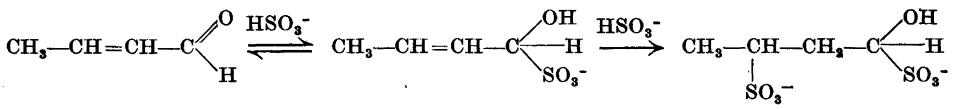
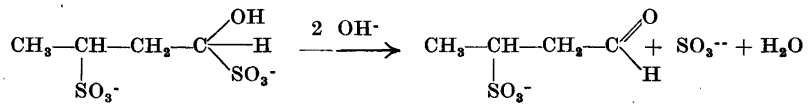
Numerous reagents, such as ammonia, hydrocyanic acid, and sodium bisulphite, which ordinarily do not react with the ethylenic linkage are known to add to the double bond in the α,β-unsaturated aldehydes and ketones [1]. The reaction of crotonaldehyde with bisulphite can be written as follows:



I II

The formation of the "normal" aldehyde bisulphite compound (I) takes place rather quickly. The addition of bisulphite to the ethylenic linkage proceeds comparatively slowly. When the "disulphonic" acid (II) is treated with weak alkali, the 1-sulphonic acid group is removed, whereas the 3-sulphonic acid group in the resulting sulphonic acid (III), remains unaffected:



II III

The bisulphite-addition compound of acetaldehyde is also decomposed in alkaline medium.

The method described in this paper is based on the facts given above. A mixture containing acetaldehyde and crotonaldehyde is treated with sodium bisulphite to form the bisulphite-addition compounds of these aldehydes. Subsequently, the mixture is made alkaline and the liberated acetaldehyde distilled off.

PROCEDURE

Ten to a hundred milliliters of an aqueous solution containing crotonaldehyde (<0.5 g) and acetaldehyde is transferred to a 200 ml Erlenmeyer flask and 25 ml approximately 10 % sodium bisulphite is added. The flask is tightly stoppered and allowed to stand overnight at 70—80° C. After cooling, 30 ml 1 *M* sodium bicarbonate is added and the liberated acetaldehyde distilled off to yield about 25 ml distillate (total distillation time approximately 15 min.). The end of the condenser tube dips below the surface of 10 ml 2 % sodium bisulphite contained in a volumetric flask which is cooled with ice-water. The amount of bisulphite in the collecting flask given above is sufficient provided that not more than 50 mg acetaldehyde is present. Otherwise the amount of bisulphite has to be increased. After standing for about ½ hour at room temperature acetaldehyde is determined according to the iodometric bisulphite method [2] or the colorimetric method with *p*-hydroxydiphenyl [3]. The bisulphite method is suitable for samples containing more than 10 mg of acetaldehyde. The colorimetric method is used at concentrations ranging from 0.0002 to 0.002 mg acetaldehyde per ml.

EXPERIMENTS AND RESULTS

In order to investigate whether crotonaldehyde reacts completely with sodium bisulphite and whether the sulphonic acid (III) remains unattacked during the distillation, experiments were performed with crotonaldehyde without the addition of acetaldehyde.

500 mg (7.13 mmoles) of crotonaldehyde (Eastman), redistilled *in vacuo* (b.p. 20°/30 mm), was treated according to the procedure described above. The iodometric determination indicated that "the bound bisulphite" in the distillate did not exceed 0.005 mmole. Fuchsine sulphurous acid gave no colour with a distillate to which no bisulphite had been added. On the other hand, if crotonaldehyde, redistilled at atm. pressure (b.p. 102.7°) was used, "the bound bisulphite" reached about 0.1 mmole and a bisulphite-free distillate gave a faint colour reaction with fuchsine sulphurous acid. The ultraviolet absorption spectrum of the bisulphite-free distillate, however, differed distinctly from that of crotonaldehyde. These observations indicate that distillation of commercial crotonaldehyde at atmospheric pressure may yield products containing carbonyl compounds as impurities.

Table 1.

Time of reaction (hours)	Added			Found	
	Sodium bisulphite 10 per cent (ml)	Crotonaldehyde (mg)	Acetaldehyde (mg)	Acetaldehyde (mg)	Relative error per cent
24	10	100	83.00	83.00 *	± 0.0
24	10	200	83.00	84.04 *	+ 1.3
24	10	250	83.00	81.84 *	− 1.4
24	10	250	41.50	42.24 *	+ 1.8
24	10	400	83.00	83.60 *	+ 0.7
17	25	50	10.00	9.75 *	− 2.5
17	25	500	10.00	10.38 *	+ 3.8
21	25	100	10.00	9.95 **	− 0.5
21	25	250	10.00	10.32 **	+ 3.2
7	25	500	10.00	9.95 **	− 0.5
21	25	250	1.000	1.001 **	+ 0.1

* According to the iodometric bisulphite method [2].
** According to the colorimetric method with *p*-hydroxydiphenyl [3].

In a further series of experiments, mixtures of crotonaldehyde (redistilled *in vacuo*) and acetaldehyde were treated according to the procedure described above and the acetaldehyde estimated in the distillates. As can be seen in Table 1 satisfactory values were obtained even in the presence of large amounts of crotonaldehyde.

SUMMARY

Acetaldehyde can be determined quantitatively in mixtures of acetaldehyde and crotonaldehyde by heating the mixture with bisulphite solution and subsequently distilling off the acetaldehyde in the presence of sodium bicarbonate.

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