

206. *Metacetaldehyde : Its Preparation and its Influence on the Rotation of Ethyl Tartrate.*

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SINCE the respective influences of acetaldehyde and paracetaldehyde as solvents upon the rotation of ethyl tartrate were found to differ considerably (J., 1914, **105**, 348), we recently tried to examine metacetaldehyde in a similar manner.

Metacetaldehyde may be bought quite cheaply, but the best conditions for its preparation do not seem to have been published.

Kekulé and Zincke (*Annalen*, 1872, **162**, 145) claim to have prepared metacetaldehyde from acetaldehyde in the cold by the catalytic action of hydrogen chloride, sulphuric acid, zinc chloride, and calcium chloride; of these, we found hydrogen chloride to be much the most satisfactory. As the simplest method of adding easily a definite quantity of catalyst to acetaldehyde, we used a saturated solution of hydrogen chloride in paraldehyde, and added weighed quantities of this solution: 10 g. of paraldehyde at room temperature dissolved approximately 1.4 g. of the gas.

The best yield of metaldehyde was obtained as follows: To 50 g. of acetaldehyde was added 1 g. of paraldehyde containing 0.125 g. of hydrogen chloride, and kept between 0° and -3° for 2 hours; the metaldehyde, which had separated, was then filtered off. The filtrate, after another hour, between 0° and -3°, gave a further yield of metaldehyde. The total yield was approximately constant (1.41 g.) for these conditions.

We then attempted to determine the quantities of acetaldehyde and paraldehyde in the mixture from which the metaldehyde had separated, using the method of Richter (*Pharm. Z.*, 1912, **57**, 125). In three experiments the following results were obtained:

Metaldehyde.	Acetaldehyde.	Paraldehyde.
1.41	3.75	40.4
1.41	2.1	40.2
1.41	2.4	40.7

A certain amount of acetaldehyde is bound to be lost in filtration, but the ratio of metaldehyde to paraldehyde is fairly accurate.*

The influence of metacetaldehyde as a solvent upon the rotation of ethyl tartrate could not be satisfactorily examined, since metacetaldehyde is such a remarkably insoluble substance. All we succeeded in doing was to compare the rotation of a very dilute solution of metacetaldehyde in ethyl tartrate at about 50° with that of an approximately similar one containing paracetaldehyde, for different colours of light. The observed data were as follows:

Ethyl tartrate and paracetaldehyde. <i>p</i> = 2.21, relative to paraldehyde.			Ethyl tartrate and metacetaldehyde. <i>p</i> = 0.76, relative to metaldehyde.	
λ.	α.	[α].	α.	[α].
4359	14.26°	7.78°	16.31°	8.74°
4916	19.88	10.85	20.74	11.11
5461	20.20	11.03	21.34	11.44
5790	19.35	10.56	20.41	10.94
6234	18.12	9.89	18.99	10.18
6716	16.22	8.85	17.16	9.20
		$d_{40}^{50} = 1.171.$		$d_{40}^{50} = 1.175.$

These data yield dispersion graphs closely resembling each other, and, since that for metacetaldehyde lies wholly above that for paracetaldehyde, it appears that, under the conditions specified, the former enhances, slightly, the rotation of ethyl tartrate (which in the homogeneous condition for Hg_g at 50° is + 11.2°), whereas the latter slightly diminishes it. But naturally, the effects are small.

Little assistance could be obtained by the use of other inactive solvents, since of some twenty-five tried, only chloroform, ethyl benzoate, and toluene dissolved appreciable quantities—and then not more than 3%—of metacetaldehyde. We were therefore only

* Since in these experiments no metacetaldehyde had separated at room temperature, we thought it might be possible to follow the rate of change of acetaldehyde into paraldehyde by the use of ethyl tartrate as an active indicator, in the same way that the rate of transformation of *syn*- into *anti*-oximes, and other similar changes, have previously been examined (*J.*, 1907, **91**, 516; 1912, **101**, 26). Our experiments were vitiated by metacetaldehyde separating almost before any readings could be taken, owing to some catalyst apparently dissolved out of the soft glass of the polarimeter tube. We confirmed this by carrying out an experiment similar to that described above for the preparation of metacetaldehyde, but using acetaldehyde which had previously been kept for 3 hours in a soft glass tube. In this case metacetaldehyde separated under conditions in which it would not have been produced in hard glass flasks.

able to attempt one experiment using chloroform and one using toluene. The results are summarised below :

Observed rotations of various solutions in a 400 mm. tube.

	λ 5790.	λ 5461.	λ 4359.
1. Ethyl tartrate in chloroform ($c = 3.7876$)	-0.80°	-0.97°	-3.32°
2. 0.0896 G. of metacetaldehyde made up to 50 c.c. with solution (1)	-0.84	-1.02	-3.62
3. 0.0710 G. of paraldehyde made up to 50 c.c. with solution (1).....	-0.83	-1.01	-3.55
4. Ethyl tartrate in toluene ($c = 3.6021$)	—	$+0.368$	—
5. 0.0375 G. of metacetaldehyde made up to 50 c.c. with solution (4)	—	$+0.442$	—
6. 0.0405 G. of paracetaldehyde made up to 50 c.c. with solution (4)	—	$+0.384$	—

The effects, as was only to be expected, are small, but they are distinct and consistent. In all cases metacetaldehyde raises (in an absolute sense) the rotation of ethyl tartrate more than does paraldehyde.

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