S 5. *Tetrahydrofurfuraldehyde. Part II. The Effect of Water and Ageing on its Physical and Chemical Properties.*

By J. G. M. Bremner and A. Robertson.

Tetrahydrofurfuraldehyde, unlike furfuraldehyde, turns viscous on addition of water and on ageing. The polymer formed on standing is a dimer, probably with an aldol structure; in its chemical reactions it behaves like the monomer.

Tetrahydrofurfuraldehyde differs from furfuraldehyde both in its reaction with water and in its behaviour on standing; furfuraldehyde is only partly miscible with water but tetrahydrofurfuraldehyde is completely so. The addition of water to the latter is, moreover, accompanied by a considerable evolution of heat and an increase in viscosity. On standing, furfuraldehyde slowly discolours through yellow to a very deep red and eventually sets to a black gel. The aldehyde can be recovered in very high yield from the coloured material by a simple distillation (Dunlop, Stout, and Swadesh, *Ind. Eng. Chem.*, 1946, **38**, 705). Discoloration is accompanied by oxygen absorption with the formation of high-molecular-weight substances responsible for the absorption in the visible region. The discoloration can be greatly accelerated by treatment with air in the presence of the usual oxidation catalysts and may also be retarded by the addition of antioxidants. On the other hand, tetrahydrofurfuraldehyde does not discolour on standing but becomes more and more viscous. The aldehyde may be recovered from this viscous material by distillation. It is the object of this paper to describe more fully the reactions of tetrahydrofurfuraldehyde both with itself, on standing, and also with water.

Addition of Water to Tetrahydrofurfuraldehyde.—A considerable heat evolution occurs on addition of water to the freshly distilled aldehyde. The viscosity increases markedly with the first addition of water but falls with further additions to give a clear homogeneous liquid. The refractive index increases with addition of water to a maximum, from $n_D^{18^\circ}$ 1·4463 to 1·4730, corresponding to 90% of tetrahydrofurfuraldehyde (Fig. 1). The aldehyde contents for the mono- and hemi-hydrates are 84·7 and 91·7%, respectively. Tetrahydrofurfuraldehyde is recovered from the aqueous solution by distillation at atmospheric pressure. A water azeotrope boiling just below 100° and containing 16% of aldehyde first distils and is followed by the dry aldehyde at 144°. Distillation at reduced pressure gave a viscous material, b. p. 40—43°/15 mm., which contained 83—88% of tetrahydrofurfuraldehyde. The glutaraldehyde–water system presents some similarity to the one under discussion (Harries and Tank, *Ber.*, 1908, **41**, 1701).

FIG. 1.

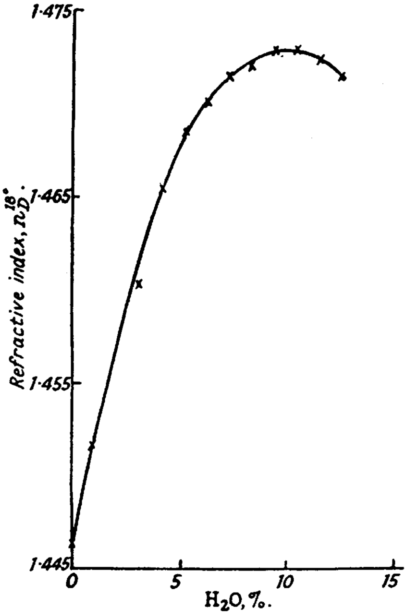
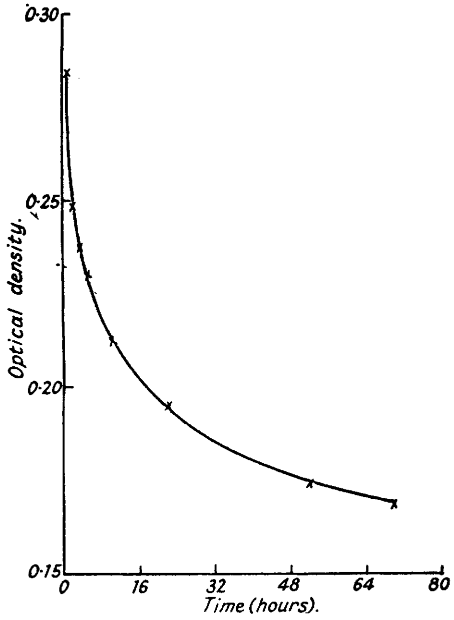


FIG. 2.



Behaviour of Tetrahydrofurfuraldehyde on Standing.—There is very poor agreement between the published values for the density and refractive index of tetrahydrofurfuraldehyde, as shown below :

Properties of tetrahydrofurfuraldehyde.

$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	Reference.
1·051	1·47036	Scheibler, Sotscheck, and Friese (*Ber.*, 1924, **57**, 1443)
1·0727	1·43658	*Idem* (*Ber.*, 1925, **58**, 1961)
1·10947 (25°)	1·4700—1·4708	Minne and Adkins (*J. Amer. Chem. Soc.*, 1933, **55**, 299)
1·0874	1·4473	This work

That these discrepancies are, in part, due to a slow change in properties on standing was shown by a periodic examination of tetrahydrofurfuraldehyde which was allowed to age in an atmosphere of nitrogen. Both the refractive index and the density increase as does the molecular weight, which was determined cryoscopically in benzene (see table). The viscosity also rises until the aldehyde has the consistency of a thick oil. Moreover, unlike the freshly distilled material, the aged product dissolves in water only slowly on warming.

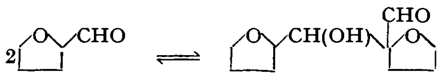
Change in properties of tetrahydrofurfuraldehyde on standing.

Ageing period.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	M.	$M[R_L]_D$.	$M[R_L]_D$ ($M = 100$).
(Freshly distilled)	1·0874	1·4473	120	29·5	24·6
6 hrs.	1·0990	1·4509	133	—	—
24 ,,	1·1130	1·4581	140	35·1	24·5
48 ,,	1·1206	1·4629	166	40·7	24·5
72 ,,	1·1270	1·4660	174	42·8	24·3
96 ,,	1·1297	1·4676	183	45·1	24·6
Weeks	1·1610	1·4762	200	48·6	24·3

On long standing the molecular weight rises to a value corresponding to a dimer. The calculated molar refractivity from Eisenlohr's values (Gilman, " Organic Chemistry," Vol. II, 2nd Edn., 1943, 1751) is 24·7, similar to the experimental value for the freshly distilled aldehyde. The aged material has, however, a molar refractivity almost twice this figure. If, however, refractivities are calculated from the molecular weight of the monomer (100), an almost constant value close to the theoretical one is obtained regardless of the ageing period. This implies that the refractivities of the bonds broken on standing are similar to those formed. Distillation of the viscous polymer took place without decomposition to give the mobile monomer.

The aged polymer was aldehydic, giving a strong reaction with Schiff's reagent. It reacted quantitatively as the monomer with hydroxylamine hydrochloride and also gave the same 2 : 4-dinitrophenylhydrazone as the freshly distilled material. This indicates the change brought about by standing to be reversible.

The change in physical properties on standing may be simply interpreted as due to a process of aldolisation :



The aldol-type *dimer* has a calculated refractivity of 48·8 compared with 48·6 for the aged material. An attempt to prepare the aldol by treatment of the aldehyde with 10% potassium hydroxide in the presence of dibutylamine (cf. Batalin and Slavina, *J. Gen. Chem. Russia*, 1937, **7**, 202) was unsuccessful, as hydration occurred when the aqueous reagent was added. The effect of dry sodium hydrogen carbonate on the freshly distilled aldehyde was shown, however, to accelerate the increase in refractive index. After 17 hours' contact with 6% bicarbonate the refractive index rose from 1·4470 to 1·4670 as compared with 1·4570 in its absence.

An examination of the infra-red spectrum of the aldehyde during ageing showed an appreciable weakening of the band at 1730 cm.$^{-1}$ due to the carbonyl group and of that at 2710 cm.$^{-1}$ due to the C–H bond in CHO. The variation in the optical density at 2710 cm.$^{-1}$ with time (Fig. 2) resembles the change occurring in refractive index as given numerically in the table above. The absence of bands at 1640 cm.$^{-1}$ and 3200 cm.$^{-1}$ indicates the absence of a carbon–carbon double bond. A band at 3390 cm.$^{-1}$ which developed during ageing indicated the formation of a hydroxyl group. No evidence for intermolecular hydrogen bonding was obtained. The weakening of the carbonyl and the development of a hydroxyl group are consistent with aldol formation.

The hydrogenation of the aged product to a β-glycol would represent unequivocal evidence for the aldol structure. The absorption both at room temperature and at 50° in the nickel-catalysed hydrogenation was, however, twice that expected and indicated that the material was behaving as the monomer in this, as in other, reactions.

EXPERIMENTAL.

Physical Measurements.—*Molecular weight.* This was determined by the depression of freezing point of benzene solutions. With *cyclo*hexanol, depolymerisation tended to occur and lower values were obtained.

Density. A dilatometric method was used, the flask being designed to allow accurate reading to 0·01 ml.

Refractive index. This was measured on an Abbé refractometer.

Characterisation of Aged Product.—The aged *product* (Found : C, 59·9; H, 8·0. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%) gave a positive reaction with Schiff's reagent, and with a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid it gave a 2 : 4-dinitrophenylhydrazone, m. p. 134°, identical (mixed m. p.) with that from the freshly prepared material; the aldehyde content, as determined by titration of the acid liberated on reaction with a solution of hydroxylamine hydrochloride in aqueous methanol (Found : CHO, 28·8. $C_9H_{15}O\cdot CHO$ requires CHO, 14·5%), indicated that it has reacted as the monomer.

Hydrogenation of Aged Product.—15 G. of aged tetrahydrofurfuraldehyde were hydrogenated at atmospheric pressure in the presence of 1 g. of Raney nickel catalyst at 20°. The reaction was slow and finally ceased after the absorption of 3·5 l. of hydrogen. The product, b. p. 178°, gave a 3 : 5-dinitrobenzoate, m. p. 83°, identical (mixed m. p.) with a specimen prepared from tetrahydrofurfuryl alcohol. Tetrahydrofurfuryl alcohol was also obtained as the only product when 90 g. of the aged tetrahydrofurfuraldehyde were hydrogenated at 50° and 150 atm. pressure with 10 g. of Raney nickel catalyst.

The authors wish to thank Dr. R. R. Coats, Miss M. L. Allan, and Mr. A. E. Bell for their part in the experimental work. The infra-red examination was carried out by Mr. Kletz, and the pressure hydrogenation by Mr. R. B. Wright. Many helpful discussions were held with Mr. R. P. Bell, F.R.S.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, BILLINGHAM DIVISION,
BILLINGHAM-ON-TEES, CO. DURHAM.

[*Received, June 22nd,* 1948.]