

**109. The Preparation of Organic Compounds containing Deuterium.  
Dideuteromalonic Deuteracid and Trideuteracetic Deuteracid.**

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THE preparation of organic compounds containing deuterium in place of protium is most practicable when hydrogen-free substances are allowed to react with reagents containing only deuterium. In this manner the reaction of certain carbides with 'heavy' water has already been used in the preparation of tetradeuteromethane and dideuteracetylene (Urey and Price, *J. Chem. Physics*, 1934, 2, 300; Murray, Squire, and Andrews, *ibid.*, p. 714).

Two reactions involving oxides of carbon offer much better possibilities from a preparative point of view, *viz.*, (1)  $\text{CO} + \text{NaOD} \longrightarrow \text{D}\cdot\text{CO}_2\text{Na}$ ; (2)  $\text{C}_3\text{O}_2 + 2\text{D}_2\text{O} \longrightarrow \text{CD}_2(\text{CO}_2\text{D})_2$ . The second of these has been studied because a simple subsequent stage (elimination of carbon dioxide) leads to the formation of the corresponding acetic acid (*trideuteracetic deuteracid*), which can be readily converted into the acid chloride.

Carbon suboxide in benzene solution reacted slowly but completely with an equivalent amount of water having a deuterium content of more than 99.5%. The resulting *dideuteromalonic deuteracid* had an m. p. (128—130°, decomp.) definitely lower than that of ordinary malonic acid (134—135°, decomp.).

Ultimate analysis for carbon and hydrogen established clearly the effect of increased molecular weight. The following table shows the results of such analyses, together with the molecular weight, determined by titration with standard alkali.

Malonic acid.	C, %.	H, %.	D, %.	M.	
From 20% 'heavy' water .....	34.3	3.8	—	—	} Found
" 99.5% " .....	33.4	—	7.1 *	—	
" " " .....	33.3	—	7.1 *	—	
" " " (resublimed) .....	33.5	—	7.0 *	107.9	
$\text{CH}_2(\text{CO}_2\text{H})_2$ .....	34.6	3.9	—	104.0	} Calc.
$\text{CD}_2(\text{CO}_2\text{D})_2$ .....	33.3	—	7.4	108.1	
$\text{CH}_2(\text{CO}_2\text{H})_2 : \text{CD}_2(\text{CO}_2\text{D})_2 = 4 : 1$ .....	34.3	—	—	—	

\* These figures were calculated on the assumption that the water weighed in the combustion was pure  $\text{D}_2\text{O}$ , which, in view of the methods of microanalysis, is probably not true.

The conversion of the malonic acid into the acetic acid by simple heating to 150° was quantitative, making the production of trideuteracetic deuteracid from deuterium oxide substantially quantitative. The product was very pure, judged by the properties of 'light' acetic acid made by the same method. The m. p. (15.8°) was lower than that of 'light' acetic acid (16.6°), but the depression was not as pronounced as in the case of acetic deuteracid (CH<sub>3</sub>·CO<sub>2</sub>D), for which Lewis and Schutz (*J. Amer. Chem. Soc.*, 1934, **56**, 493) found 13.3°.

A direct comparison of the vapour pressures of 'light' and 'heavy' acetic acid offers another clear example of a deuterium compound having a higher vapour pressure than its protium analogue. The data (pressures in mm. Hg) are recorded below :

$(p_D - p_P)$ .				$(p_D - p_P)$ .				$(p_D - p_P)$ .			
<i>T.</i>	<i>p<sub>P</sub></i> .*	Obs.	Calc.†	<i>T.</i>	<i>p<sub>P</sub></i> .*	Obs.	Calc.†	<i>T.</i>	<i>p<sub>P</sub></i> .*	Obs.	Calc.†
20.0°	11.7	0.7	0.7	50.0°	56.6	3.0	3.05	80.0°	202.3	10.3	10.4
25.0	15.5	0.9	0.9	55.0	70.9	3.8	3.8	85.0	243.7	12.4	12.4
30.0	20.6	1.2	1.15	60.0	88.9	4.7	4.7	90.0	293.7	14.7	14.8
35.0	26.8	1.5	1.5	65.0	110.0	5.8	5.8	95.0	349.9	17.4	17.5
40.0	34.8	1.9	1.9	70.0	136.0	7.1	7.1	100.0	417.1	20.8	20.8
45.0	44.4	2.4	2.4	75.0	165.9	8.5	8.6				

\*  $p_P$  and  $p_D$  are the vapour pressures of 'light' and 'heavy' acetic acid respectively,  $p_P$  being taken from data of Ramsay and Young (*J.*, 1886, **49**, 790); the intermediate values have been interpolated mathematically.

† The figures in this column are calculated from the equation  $\log_{10} p_D/p_P = 3.94/T_{\text{abs.}} + 0.0106$ .

Lewis and Macdonald (*J. Amer. Chem. Soc.*, 1933, **55**, 3057; cf. Taylor and Jungers, *ibid.*, p. 5057) have attributed the difference of volatility of 'light' and 'heavy' forms of associated substances to the existence of co-ordinated hydrogen bonds; and from the lower volatility of the 'heavy' modifications of such compounds as water and ammonia, which yield associated liquids but unassociated vapours, they inferred that the 'deuterium bond' (—D—) must be stronger than the 'protium bond' (—H—). It can be seen theoretically that, if the co-ordinated bond exists, the difference must be in the direction which Lewis and Macdonald deduced from observation; for this bond must give rise to its own increment in the zero-point energy of the molecule, and since the restoring forces on electrically identical isotopes must be the same, the zero-point energy increment for the co-ordinate bond must be smaller for the heavier hydrogen isotope, the dissociation energy of which will be correspondingly larger.

In contrast to such substances as water and ammonia, the 'light' and 'heavy' forms of compounds which do not associate either as liquid or as vapour have almost identical vapour pressures. Lewis and Schutz (*loc. cit.*) recognised a third class of substance in those which yield definitely associated vapours: these present the interesting possibility that the 'heavy' forms could be more volatile than the 'light.' Hydrogen fluoride and acetic acid, which both yield associated vapours, are now known as illustrations of this effect (Lewis and Schutz, *loc. cit.*; Claussen and Hildebrand, *J. Amer. Chem. Soc.*, 1934, **56**, 1820), and it seems particularly noteworthy that trideuteracetic deuteracid is appreciably more volatile than acetic acid, despite the considerable difference of rotational inertia arising from the terminal distribution of the variable masses, protium and deuterium.

#### EXPERIMENTAL.

*Preparation of Carbon Suboxide.*—Diacetyltartaric anhydride (50 g.) (Wohl and Österlin, *Ber.*, 1901, **34**, 1144) was converted into carbon suboxide exactly as described by Hurd and Pilgrim (*J. Amer. Chem. Soc.*, 1933, **55**, 757). The oxide was distilled into a graduated tube cooled to -78°, the yield being just over 6.3 c.c. (0°) ( $d_4^{20}$  1.114). Dissolved carbon dioxide was removed by warming to 0° for a few moments. The oxide was stable at -78° over periods of several days, and in benzene solution it could be preserved at the ordinary temperature for several weeks without polymerisation.

*Conversion into Malonic Acid.*—'Heavy' water (containing 20% or 99.5% deuterium; about 1 g.) was weighed accurately into a Pyrex tube, 1.5 × 25 cm., sealed at one end and frozen at -78°. Carbon suboxide (equivalent amount measured by volume) was distilled into the

tube from its graduated container, benzene (10 c.c. per g. of water; dried first by phosphoric oxide and then by standing with carbon suboxide for many days with subsequent distillation, only the middle third being collected) was added, the tube sealed, and shaken at the ordinary temperature. After several days, the tube was opened, and the crystals which had separated were washed with dry benzene and dried over phosphoric oxide at 0.01 mm. The rate of reaction was greatest in the experiment with 20% 'heavy' water, in which case crystals had appeared after 2 hours. The m. p.'s of the malonic acid from 20% and from 99.5% 'heavy' water were 131—132.5° and 128—130° (both decomp.), respectively, the latter being unchanged by sublimation at 100°/0.01 mm. The molecular weight of the *dideuteromalonic deuteracid* (10.4 mg.) was determined by titration with *N*/100-sodium hydroxide. The results and other analyses are recorded in the table on p. 492.

Three separate portions of 1 g. of 'heavy' water were so treated, and each gave an almost quantitative yield of the malonic acid. In one case the product was red, owing to polymerisation of a slight excess of carbon suboxide employed. This impure sample, however, on decomposition as below, gave pure acetic acid.

The benzene used as solvent for the carbon suboxide was thoroughly washed with distilled tap water (no exchange occurs by such treatment; Ingold, Raison, and Wilson, *Nature*, 1934, 134, 734), dried over anhydrous sodium sulphate, distilled, and burnt over red-hot copper oxide in a stream of nitrogen. Isotopic analysis, by density determination, of the water so obtained failed to show evidence of the occurrence of interchange between the deuterium and the hydrogen atoms of the benzene, within the limit afforded by the accuracy of the pyknometical measurements ( $\pm 1$  in  $10^6$ ; cf. Day, Hughes, Ingold, and Wilson, *J.*, 1934, 1593). This implies that, allowance being made for the proportions in which benzene and deuterium oxide were used, any loss by exchange of deuterium from the deuterium oxide could not have exceeded 0.01 atom %.

*Conversion of the Malonic Acid into the Acetic Acid.*—The malonic acid was thoroughly dried by heating to 100°/0.01 mm. in the first bulb (A) of an apparatus consisting of three small Pyrex bulbs (each 10 c.c.) connected in series and followed by a phosphoric oxide tube. Rubber connexions were avoided. On immersion of A in a bath at 140—150°, decomposition ensued, and the acetic acid was carried over into the second bulb (B, bubbler type) cooled to 0°. After the tube connecting A and B had been sealed, the acetic acid was purified from a small amount of malonic acid by distillation, without ebullition, at 0.02 mm. into the third bulb C, cooled to 0°, B being maintained at 30°.

'Light' acetic acid made by this method had m. p. 16.65° (lit. 16.6°). Two different samples of *trideuteracetic deuteracid* had m. p. 15.75° and 15.76° (Found: C, 37.4; D, 12.0.  $\text{CD}_3\cdot\text{CO}_2\text{D}$  requires C, 37.5; D, 12.6%.  $\text{CH}_3\cdot\text{CO}_2\text{H}$  requires C, 40.0; H, 6.7%). The m. p.'s had a range of about 0.2°.

*Vapour-pressure Measurements.*—A simple differential tensimeter, in which two bulbs similar to C were connected to a U-tube containing pure mercury, was used. By means of an arrangement of taps, both bulbs could be exhausted simultaneously. 'Light' and 'heavy' acetic acid (each from the corresponding malonic acid), having been distilled each into one of the bulbs, were alternately frozen with evacuation to 0.01 mm. and liquefied, until all appreciable occluded and dissolved gases had been removed. The bulbs were then sealed off.

The difference in the height of the mercury menisci was measured by the use of a cathetometer. Direct readings were obtained from the scale of the latter, and the differences were checked by direct visual estimation by focusing the cathetometer cross-wires on a vertical calibrated glass scale attached to the U-tube. The results of the measurements are summarised in the table on p. 493, the values in col. 3 (accurate to  $\pm 0.1$  mm.) having been interpolated graphically from many readings taken at temperatures slightly above and below the figures quoted.

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