

Effect of Deuterium Substitution on the Heat of Solution of t-Butyl Chloride

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Summary The difference between the heat of solution of t-butyl chloride and that of its [$^2\text{H}_6$]-derivative in absolute ethanol is 22 cal./mole.

We report what appears to be the first example of the effect of deuterium substitution on the heats of solution of an organic compound. We have measured the heat of solution of 2-chloro-2-methylpropane and 2-chloro-1,1,1,3,3,3-hexadeuterio-2-methylpropane in absolute ethanol. The hexadeuterio-compound was used because of the ease of preparation from $(\text{CD}_3)_2\text{CO}$.

The absolute ethanol was prepared by the method of Murr and Shiner¹ with the slight modification that molecular sieves were used for drying the nitrogen. The [$^2\text{H}_6$]-t-butyl alcohol was prepared according to the method of Shiner² from $(\text{CD}_3)_2\text{CO}$ and was then treated with concentrated hydrochloric acid. The heats of solution

were obtained using a calorimeter described in the literature.³ The calorimeter has a sensitivity of about 0.02 cal. and an optimum heat range of 2–10 cal.

The heat of solution for t-butyl chloride in absolute ethanol was 332 ± 8 cal./mole and that for [$^2\text{H}_6$]-t-butyl chloride was 310 ± 5 cal./mole. These values are for five different runs for each of the chlorides and from three different preparations of the chlorides. The difference between the heat of solution of t-butyl chloride and of its [$^2\text{H}_6$]-derivative is 22 cal./mole. This difference is larger than the experimental error in the measurements. This is the first example of a difference in the heat of solution of an organic compound resulting from an introduction of deuterium directly on to carbon.

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¹ B. L. Murr and V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 4672.

² V. J. Shiner, jun., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, 1963, **84**, 2413.

³ G. L. Bertrand, R. D. Beaty, and H. A. Burns, *J. Chem. and Eng. Data*, 1968, **13**, 436.