

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

## The Effect of Substitution on the Infra-red Absorption Spectrum of Acetic Acid

BY R. H. GILLETTE

In an earlier publication<sup>1</sup> from this Laboratory it was shown that the substitution of hydrogen atoms by chlorine in acetic acid giving progressively stronger acids is reflected also in a corresponding shift of the infra-red absorption band at 1721  $\text{cm}^{-1}$ . A more recent interpretation<sup>2</sup> of the infra-red absorption spectrum of the single and double molecules of acetic acid made it seem useful to investigate this substitution more thoroughly.

## Experimental

The apparatus and method were the same as used in the investigation reported in the preceding paper.<sup>2</sup> The absorption cells were made by cementing rock salt windows onto both sides of holes drilled in plate glass about 4 mm. thick. They were filled through narrow grooves sawed in the window and sealed with partially dried Glyptal cement. One cell was filled with the pure solvent and the others with solutions of the acids being investigated.

The absorption spectra of acetic acid and eight substituted acids are shown in Fig. 1 and Table I. In all cases the acids were dissolved in carbon tetrachloride to give 0.025  $M$  solutions and the measurements were taken at 25°. It had been found previously that the change in the position of absorption bands with concentration was very small. In the last column of Table I are recorded the dissociation constants of the acids at 25° when dissolved in water.

TABLE I

SHIFTS IN THE ABSORPTION BANDS OF THE SUBSTITUTED ACETIC ACIDS IN 0.025 MOLAR SOLUTIONS OF CARBON TETRACHLORIDE

No. in Fig. 1	Acid	$\nu_1$ , $\text{cm}^{-1}$	$\nu_2$ , $\text{cm}^{-1}$	$\nu_3$ , $\text{cm}^{-1}$	Dissociation constant
4	Acetic	2941	1721	1435	$1.86 \times 10^{-5}$
9	Monochloroacetic	2950	1736	1433	$155 \times 10^{-5}$
8	Dichloroacetic	3049	1751	1428	$5000 \times 10^{-5}$
7	Trichloroacetic	3030	1764	1416	$30,000 \times 10^{-5}$
6	Monobromoacetic	2976	1730	1447	$138 \times 10^{-5}$
5	Monoiodoacetic	2992	1721	1441	$74 \times 10^{-5}$
3	Dimethylacetic	2907	1715	1433	$1.4 \times 10^{-5}$
2	Trimethylacetic	2907	1704	1433	$0.98 \times 10^{-5}$
1	Diethylacetic	2910	1706	1433	$1.89 \times 10^{-5}$

(1) Bennett and Daniels, *THIS JOURNAL*, **49**, 50 (1927).(2) Gillette and Daniels, *ibid.*, **58**, 1139 (1936).

## Discussion

Before it is possible to make any interpretation of these results it is necessary to investigate the degree of association of the acids under the conditions of measurement. A search of cryoscopic measurements in the older literature<sup>3</sup> suggested that down to small concentrations (about 0.01  $M$ )

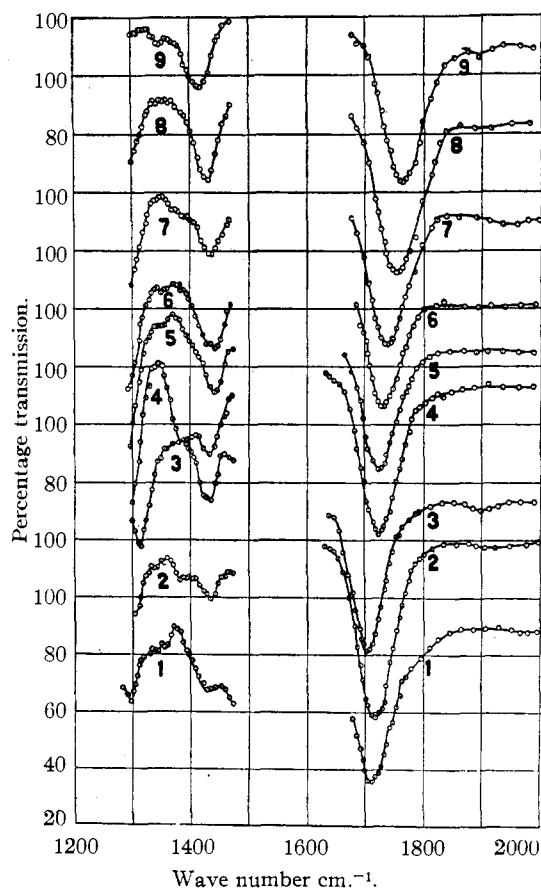


Fig. 1.—Displacements in the infra-red absorption spectrum produced by substituting various groups for hydrogen in acetic acid: 1, diethylacetic acid; 2, trimethylacetic acid; 3, isobutyric acid (dimethyl); 4, acetic acid; 5, iodoacetic acid; 6, bromoacetic acid; 7, chloroacetic acid; 8, dichloroacetic acid; 9, trichloroacetic acid.

all carboxylic acids are nearly completely associated in non-polar solvents. This is confirmed by the recent accurate measurements of Bury and

(3) Auwers, *Z. physik. Chem.*, **12**, 689 (1893); Raoult, *Ann. chim.*, [4] **2**, 66 (1884); Rozsa, *Z. Elektrochem.*, **109**, 685 (1911); Peidle and Turner, *J. Chem. Soc.*, **109**, 685 (1911).

Jenkins<sup>4</sup> and Bell and Arnold.<sup>5</sup> The latter authors have shown in benzene solutions of concentrations from  $M = 0.01$  to  $M = 1.5$  trichloroacetic acid is completely associated. We assume, therefore, that under the conditions of our measurements all the acids were entirely present as dimers.

The three infra-red absorption bands which can be investigated in this solvent correspond to the frequencies  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  of the previous paper. The first of these ( $\nu_1$ ) (which has been omitted in Fig. 1 to conserve space) is mainly due to the C-H valence vibration, but is also in part made up of overtone and combination vibrations from other parts of the molecule. Thus it occurs even in trichloroacetic acid, but considerably displaced and much weaker. The remaining two bands are to be attributed to vibrations within the ring formed by the union of the two single molecules. Attempts to measure some of these bands in the single molecules at high temperatures were unsuccessful on account of decomposition.

It may be seen by reference to Table I that the band  $\nu_2$  is shifted toward higher frequencies by groups recognized by the organic chemist as electronegative, while it is shifted to lower frequencies by groups electropositive in the same sense. The uniform shift in the chloroacetic acids discovered by Bennett and Daniels is confirmed. The effect of the weight of the groups may be seen by considering the monohalogen acids.

(4) Bury and Jenkins, *J. Chem. Soc.*, 688 (1934).

(5) Bell and Arnold, *ibid.*, 1432 (1935).

Here the shift in the band decreases as the weight of the halogen increases until in iodoacetic acid it occurs in the same position as acetic. This suggests that there may be two opposing factors operative, one a weight factor and the other perhaps connected with the electron affinity or polarizability of the substituted group. It is noticeable that there is a correlation between the strength of the acid in aqueous solution and the position of this band. This is perhaps to be associated with changes in the contribution of ionic states to the energy of the molecule.

The remaining band,  $\nu_3$ , is shifted in each case in the opposite direction, but the displacement is smaller. This behavior was observed also in the investigation on the effect of association.<sup>2</sup> It does not seem possible in the light of our present knowledge to give an exact interpretation of these band shifts although they seem too uniform to be fortuitous.

The author is grateful to Dr. Farrington Daniels for helpful suggestions and for continued interest in this problem.

### Summary

1. The infra-red absorption spectra of acetic acid and eight substituted acetic acids have been measured in carbon tetrachloride solution. Certain uniform shifts in the absorption bands have been observed and correlated with other measurements.

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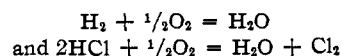
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K.

BY W. F. GIAUQUE AND J. W. STOUT

It has long been known to those interested in the accurate application of the third law of thermodynamics that measured entropy changes in reactions involving water did not agree with those calculated from low temperature heat capacity data. In early comparisons the inaccuracy of the available data seemed sufficient to explain the disagreement, but even after more accurate experiments were performed discrepancies still remained. The investigations of Wiebe, Johns-

ton, Overstreet, and one of us<sup>1</sup> on the entropies of hydrogen chloride, hydrogen, oxygen and chlorine, combined with very accurate determinations of the heats of reactions



(1) (a) Giauque and Wiebe, (HCl), *THIS JOURNAL*, **50**, 101 (1928); (b) Giauque and Johnston, (H<sub>2</sub>), *ibid.*, **50**, 3221 (1928); (c) Giauque and Johnston, (O<sub>2</sub>), *ibid.*, **51**, 2300 (1929); (d) Giauque, (H<sub>2</sub>), *ibid.*, **52**, 4816 (1930); (e) Giauque and Overstreet, (HCl), *ibid.*, **54**, 1731 (1932).