NMR Studies of Hydrogen Bonding.I.Chemical Shifts and Line Widths of Hydroxyl Proton Spectra in Salicylaldehyde

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: 小川, 莞爾, 松岡, 慎一, 千田, 勘太郎 メールアドレス: 所属:
URL	https://doi.org/10.24517/00011378

Sci. Rep. Kanazawa Univ.,
Vol. 11, No. 1, pp. 27–31
June 1966

NMR Studies of Hydrogen Bonding. I. Chemical Shifts and Line Widths of Hydroxyl Proton Spectra in Salicylaldehyde

Kanji OGAWA, Shin-ichi MATSUOKA and Kantaro SENDA

Department of Physics, Faculty of Science, Kanazawa University

(Received 27 April 1966)

Introduction

The possibility of applying proton magnetic resonance measurements to studies of hydrogen bonding became apparent following the observation of Arnold and Packard[1) that the chemical shift of the proton signal of ethanol OH group was temperature dependent. Thereafter, numerous investigators have reported that in the nuclear magnetic resonance spectra of solutions containing compounds capable of forming hydrogen bonds, the signal corresponding to the hydroxyl protons moves to higher field if the solutions are made more dilute or the temperature is raised. [2)–7)]

The existence of a temperature dependence of the resonance signal can be understood if there are alternative molecular states whose energy separation is of the order of kT. If the correlation time related to the lifetimes of the two or more states is sufficiently small, the proton resonance will be observed at the frequency corresponding to the average shielding for the states. Since changes of the temperature will alter the populations of the states, the resonance frequency will be temperature dependent.

Reeves[3)] studied the proton resonance spectra of decanoic acid between 25°C and 150°C and found that the temperature coefficient $\varDelta\delta/\varDelta T$, of the chemical shift of the carboxyl proton was 1.2×10^{-2} ppm/°C. And also, Davis and Pitzer[4)] reported $\varDelta\delta/\varDelta T=0.6\times10^{-2}$ ppm/°C for benzoic acid dimers and 1.3×10^{-2} ppm/°C for acetic acid dimers.

There seems no measurements on temperature dependent proton chemical shifts of salicylaldehyde, although some works[8)–9)] on the spin coupling of aldehyde proton in substituted benzaldehydes were published.

Salicylaldehyde forms intra- and inter-molecular hydrogen bonds in liquid phase, therefore from the temperature dependent chemical shifts of hydroxyl proton, the information of intra- and inter-molecular hydrogen bonds in salicylaldehyde is expected to be obtained.

Experimental

The proton resonance spectra were obtained with a JEOL's 3H-60 NMR instrument operating at 60 Mc and a VT-2 temperature control equipment.

With commercially available salicylaldehyde of special grade, pure liquid, 50 volume percent solution in carbon tetrachloride and 30 volume percent solution in carbon tetrachloride were prepared as samples, to which a small amount of tetramethylsilane was added as an internal reference. These samples were sealed off into 5 mm o.d. sample tubes and degassed by means of the freeze-pump and thaw method.

The chemical shift calibrations were performed with the modulation side-band technique and the modulation frequency was checked with an electronic counter.

The line widths were measured between half-maximum points in cps, which were directly obtained from recorder charts.

All measurements were carefully made under the condition of no saturation. Probable errors were estimated to be ±0.003 ppm for chemical shifts and ± 2 cps for line widths, while ± 2°C for temperature measurements.

Results and Discussion

Observed results of temperature dependent chemical shifts and line widths of hydroxyl proton in three salicylaldehyde samples are given in Fig. 1 and Fig. 2.

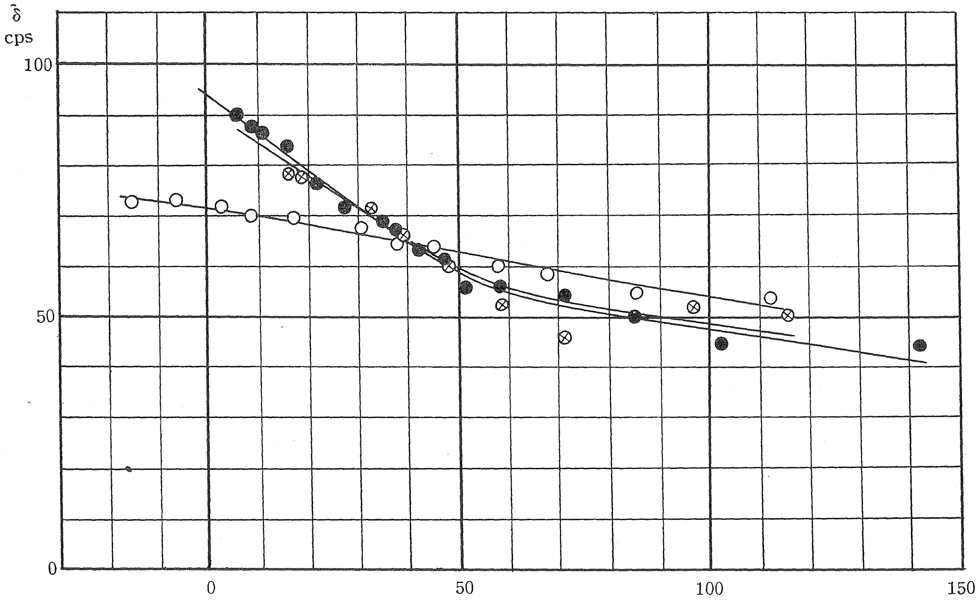

Fig. 1. Chemical shifts of hydroxyl proton refered to aldehydic proton vs. temperature for various solutions of salicylaldehyde in CCl_4.
● pure. ⊗ 50% dilution. ○ 30% dilution.

In Fig. 1, it is clearly shown that the temperature dependence of chemical shifts δ of hydroxyl proton in pure sample is the same as that of 50% solution, within experimental errors, and that two different temperature coefficients of δ are obtained for both samples. These values of coefficients are

$$\Delta\delta/\Delta T = 1.1 \times 10^{-2}\ \mathrm{ppm/°K} \qquad \text{for } T \leq 330°\mathrm{K},$$

$$\Delta\delta/\Delta T = 0.20 \times 10^{-2}\ \mathrm{ppm/°K} \qquad \text{for } T > 330°\mathrm{K}.$$

For 30% solution, however, a simple linear dependence of δ on T was found over all temperature range studied, and the temperature coefficient for this case was estimated as

$$\Delta\delta/\Delta T = 0.20 \times 10^{-2}\ \mathrm{ppm/°K}.$$

It is generally said that in salicylaldehyde there are intramolecular and intermolecular hydrogen bonds, and that the shifts of hydroxyl proton spectra to higher fields following dilution or heating are caused by rupture of hydrogen bonds.

It thus seems probable that the hydrogen bonded species with larger temperature coefficient in Fig. 1, are clearly reduced by dilution and heating, therefore these species are inter-molecular dimers. Then, at the temperature higher than 330°K or in the solution below about 30% dilution, most species are monomers and the smaller temperature coefficient comes from strong intramolecular hydrogen bondings.

The temperature dependence of chemical shifts of protons involved in hydrogen bonds has hitherto been attributed to shifts in association equilibria favoring a large fraction of brocken hydrogen bonds with increasing temperature. But another mechanism which based on the dependence of the shift for the associated species on the degree of excitation of the hydrogen-bond-stretching vibrational mode was presented by Muller and Reiter[6]. In this paper, we will try to interpret the several experimental results following the treatment of Muller and Reiter.

Formation of a hydrogen bond of the type O_1——H······O_2, is accompanied by the down field shifts resulting from the electrostatic field originating at O_2. Because the H······O_2 bond is very weak, the complex has a low frequency (typically 150 cps) vibrational mode and so several excited states of this vibrational mode are significantly populated even at temperatures as low as 250°K. Moreover, because the expectation value $\bar{R}$ of H······O_2 distance depends upon the degree of excitation, the observed chemical shift δ has to be given by Eq. (1),[6] and is obviously temperature dependent.

$$\delta = \sum_i \delta_i \exp(-E_i/kT) / \sum_i \exp(-E_i/kT). \tag{1}$$

In Eq. (1), E_i and δ_i are energy and chemical shift corresponding to the i-th excited vibrational mode.

Now, it was assumed that the chemical shift δ_i follows the equation,[10]

$$\delta_i = -3.0 \times 10^{-12}.\ E_{zi} - \frac{881}{216}\frac{a_0^3\ E_{zi}^2}{mc^2}\ , \qquad (2)$$

where, E_{zi} is the component of the electrostatic field in a direction from O_2 to O_1.

In order to calculate E_i and $\bar{R}$, further, a potential function V of hydrogen bonding was assumed as[11])

$$V = \begin{cases} -A/(R-\frac{R'}{2})^2, & \text{for } R \geqq R_0 \\ \infty & \text{for } R < R_0, \end{cases} \qquad (3)$$

where R is the H······O_2 distance and R' is the distance between O_2 and the center of charge distribution of the lone pair of O_2. And we put R_0 to be 1.8Å.

By assuming that E_{zi} arises from a point charge q associated with the lone pair of electrons of O_2, and placing this charge on the H······O_2 line, the next relation was used to calculate E_{zi},

$$E_{zi} = -q/(\bar{R}-R')^2\ . \qquad (4)$$

Since the extreme shift of the proton signal between the nonassociated and completely associated states was estimated[11]) to be −7.0 ppm, δ_0 in Eq. (1) or Eq. (2) was put as this value. Adopting the values $\bar{R} = 1.8$ Å and $R' = 0.8$ Å, $q = -1.7 \times 10^{-10}$ esu was obtained by Eq. (4).

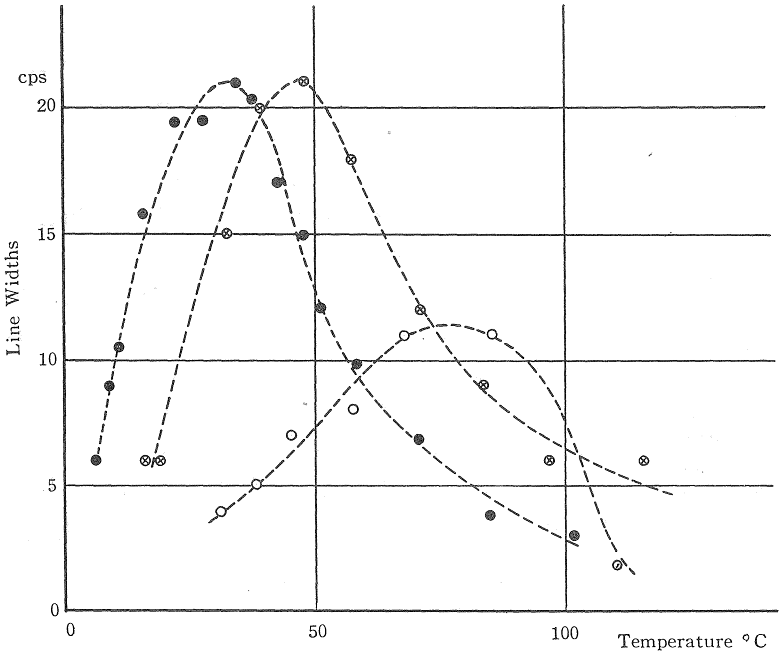

Fig. 2. Line widths of hydroxyl proton vs. temperature for various solutions of salicylaldehyde in CCl_4.
● pure. ⊗ 50% dilution. ○ 30% dilution.

Using Eqs. (1) ~ (4) and experimental values of $\Delta\delta/\Delta T$ which are the function of A, the following values of hydrogen bonding energy were estimated after tedious numerical calculations. That is, for $\Delta\delta/\Delta T = 1.1 \times 10^{-2}$ ppm/°K, $A = 1.2 \times 10^{-29}$ erg cm^2/molecule which corresponds to hydrogen bond energy of 1.7 Kcal/mol, and for $\Delta\delta/\Delta T = 0.20 \times 10^{-2}$ ppm/°K, $A = 10 \times 10^{-29}$ erg cm^2/molecule or hydrogen bond energy is 14 Kcal/mol. These values of bond energy seem to be the rather likely values.

On the other hand, when the temperature is raised, the changes of line widths of hydroxyl proton spectra were observed shown in Fig. 2. Since the hydrogen bond energy was estimated to be 1.7 Kcal/mol for inter-molecular hydrogen bonds as mentioned above, which corresponds to the temperature of 100°C, it was inferred that the complete rupture of the inter-molecular hydrogen bond may occur at that temperature. While the difference of the chemical shifts between intra-molecular and inter-molecular bonded states was estimated to be about 30 cps from Fig. 1. It therefore seems reasonable to say that when both intra-molecular and inter-molecular bonded species are present, or at the temperature range lower than 100°C, the spectral line shows broadening of which maximum value is smaller than 30 cps.

More precise analysis is now in progress.

Acknowledgement

The authors wish to thank Mr.Y. Hiwatari for his helpful discussions.

References

1) J. T. Arnold and M. E. Packard, J. Chem. Phys. 19, 1608(1951).
2) W. G. Schneider, H. J. Bernstein and J. A. Pople, J. Chem. Phys. 28, 601(1958).
3) L. W. Reeves, Trans. Faraday Soc. 55, 1684(1959).
4) J. C. Davis, Jr. and K. S. Pitzer, J. Chem. Phys. 64, 886(1960).
5) J. C. Davis, Jr., K. S. Pitzer and C. N. R. Rao, J. Chem. Phys. 64, 1774(1960).
6) N. Muller and R. C. Reiter, J. Chem. Phys. 42, 3265(1965).
7) T. Yonezawa, H. Saito. S. Matsuoka and K. Fukui, Bull. Chem. Soc. Japan 38, 1431 (1965).
8) D. G. Kowalewski and V. J. Kowalewski, J. Chem. Phys. 37, 1009(1962).
9) S. Forsen and T. Alm, J. Mol. Spectroscopy 17, 13(1965).
10) T. W. Marshall and J. A. Pople, Mol. Phys. 1, 199(1958).
11) A. L. Porte, H. S. Gutowsky and I. M. Hunsberger, J. Am. Chem. Soc. 82, 5057(1960).