On the Interpretation of the High-Resolution ^{1}H, ^{13}C and ^{17}O NMR Data for Pivalic Acid at the Phase Transitions

DAGFINN W. AKSNES,[a] LIUDVIKAS L. KIMTYS,[b] VYTAUTAS J. BALEVICIUS[b] and MINDAUGAS Z. BALEVICIUS[b]

[a] Department of Chemistry, University of Bergen, N-5014 Bergen, Norway and [b] Department of General Physics and Spectroscopy, Vilnius V. Kapsukas State University, 232734 Vilnius, Lithuanian SSR, USSR

In this paper we report the results of ^{1}H, ^{13}C and ^{17}O NMR studies on pivalic acid giving special attention to changes occurring at the phase transitions. Furthermore, the temperature dependence of the hydroxyl and carbonyl IR stretching vibrations near the plastic-brittle crystalline phase transition has been observed. The two new IR bands which appear at 3550 and 1715 cm^{-1} have been assigned to the free OH and C=O stretching vibrations of terminal carboxyl groups in open dimers and/or polymers. In accordance with this assignment, the ^{1}H resonance line at 5.3 ppm which appears in the brittle phase, is attributed to the free OH protons in terminal carboxyl groups. An approximate treatment of the temperature dependence of the chemical shift of the carboxyl proton in the brittle crystalline phase is given. The electron charge distributions of the monomer and cyclic dimer of pivalic acid have been calculated by the CNDO/2 method. The measured ^{13}C chemical shifts have been found to correlate well with the calculated total electron charges. The downfield shift of the ^{1}H and ^{13}C resonances of the methyl group in the plastic phase is believed to arise from a small anisotropic contribution to the magnetic shielding due to a slight anisotropic tumbling of the molecules. Only one averaged ^{17}O resonance line, which appeared ca. 240 ppm downfield from external deuterium oxide, was observed for the carboxyl groups. The variation of the ^{17}O chemical shift with temperature is rationalized in terms of hydrogen-bonding effects.

The low and/or high temperature phases of pivalic acid, which is known as one of the "classic" crystals, have been studied by means of dielectric measurements,[1] nuclear spin relaxation,[2–5] high-resolution ^{1}H NMR[6–8] and ^{13}C NMR,[9–10] Raman spectroscopy,[11–13] and other methods.[14–17] Most of the experimental data have contributed to a better understanding of the mechanisms of self-diffusion and molecular re-orientations in the plastic phase. However, several peculiarities observed in the NMR spectra have so far not been satisfactorily accounted for.[6,10]

In the present work we report the results of ^{1}H, ^{13}C and ^{17}O NMR studies on pivalic acid giving special attention to changes occurring at or near the phase transitions. Our investigation also includes observing the temperature dependence of the OH and C=O IR stretching vibrations near the plastic-brittle phase transition point.

RESULTS AND DISCUSSION

The 90 MHz proton spectra have been measured in the solid and liquid phases of pivalic acid. The temperature dependence of the chemical shift of the carboxyl proton is shown in Fig. 1. The existence of hysteresis of the chemical shift near the plastic-brittle crystalline phase transition has not been observed previously.[6] A temperature study of the methyl proton region shows that a low-field satellite, which is absent in the plastic and liquid phases, appears at about 5.3 ppm in the brittle phase (Fig. 2).
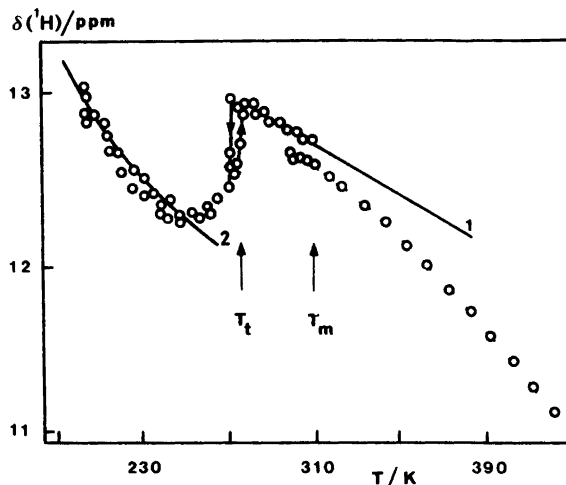
Fig. 1. Comparison of the experimentally measured temperature dependence of the chemical shift of the carboxyl proton (points) with (1) cyclic dimers[6] and (2) calculations based on eqn. (4).

At temperatures just below the melting point a low-field satellite developed at the peak of the carboxyl proton and carboxyl and methyl carbon lines[6,10] whereas the quaternary carbon signal remained a singlet.[10]

The carboxyl proton is much more mobile than the methyl protons[4,8] due to proton exchange between the hydrogen-bonded carboxyl groups. Since the acid protons are moving through the lattice at a much faster rate than the methyl protons the carboxyl proton line of plastic pivalic acid is very narrow with a chemical shift comparable to that of the cyclic dimer obtained for the

pivalic acid-cyclohexane system.[18] The observed downfield shift of the carboxyl proton signal at the melting point, is largely attributed to environmental effects that change when the liquid to plastic phase transition occurs (*vide infra*).

At lower temperatures the plastic crystalline phase becomes metastable thus producing the observed hysteresis of the chemical shift of the carboxyl proton near the plastic-brittle crystalline phase transition (Fig. 1). A similar hysteresis, which usually appears in connection with first order phase transitions, has been observed for the dielectric constant[1] and ^{1}H relaxation
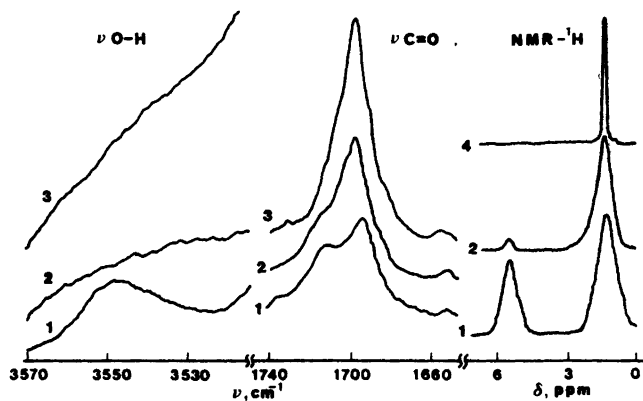

Fig. 2. Changes in the v_{OH} and $v_{C=O}$ stretching bands and ^{1}H NMR spectrum of pivalic acid at the plastic-brittle phase transition (T_t=279 K). (1) 243 K; (2) 258 K; (3) 293 K; (4) 310 K.

times[2,3] of pivalic acid.

The structure of pivalic acid is face-centred cubic and a combination of dielectric, NMR, light scattering and tracer diffusion studies have established that the molecules are randomly dimerized with one of the twelve nearest neighbours in the plastic phase.[17] However, the IR spectra in Fig. 2 show that two new bands appear at 3550 and 1715 cm^{-1} at the plastic-brittle crystalline phase transition. It is reasonable to assign these bands to the free OH and C=O stretching vibrations of terminal carboxyl groups in open chain dimers and/or polymers. The corresponding bands of the hydrogen-bonded groups appear at 3000 and 1700 cm^{-1}.

The chemical shift of the new line which appears at 5.3 ppm in the brittle phase is close to the reported chemical shift of the monomers (5.2±0.6 ppm) calculated from the concentration and temperature dependences of the carboxyl proton shift for pivalic acid in cyclohexane.[18] The line at 5.3 ppm can therefore probably be assigned to the terminal OH protons in open chain dimers and/or polymers. Increasing contributions of free OH protons could also explain the marked upfield shift of the averaged carboxyl proton signal at the transition point (T_t).

Since the interaction between the oxygen lone-pair lobes of neighbouring carboxyl groups of the cyclic dimer increases with decreasing interlattice dimension, a twisting of the carboxyl groups might arise. It has been found for the benzamide-succinic acid complex that the twist angle is about 20°.[19] By means of this distortion a separation of 3.6Å is achieved between the two oxygen atoms of neighbouring carboxyl groups. It is thus feasible that the cyclic dimers of pivalic acid are distorted to the extent that they form open dimers and/or polymers in the brittle phase.

The catemer motif, i.e. a chain of carboxyl groups linked to each other by single O−H⋯O bonds, has been observed for formic acid, acetic acid and β-tetrolic acid.[19] According to Leiserowitz,[19] however, the catemer motif is rarely encountered in the solid state of carboxylic acid R−CO$_2$H molecules. A definite conclusion concerning the possible formation of a catemer motif in the low temperature phase of pivalic acid will therefore have to await further evidence.

An approximate interpretation of the temperature dependence of the chemical shift of the carboxyl proton in the brittle crystalline phase

can be done by calculating the contribution of the electric field of the neighbour point-charges (q_i) to the chemical shift (δ).

$$\delta = -BE^2, \tag{1}$$

where

$$\vec{E} = \sum_i \vec{R}_i\, q_i/R_i^3, \tag{2}$$

and

$$\vec{R}_i = \vec{R}_{oi}[1 + \alpha(T - T_o)], \tag{3}$$

where B is a constant, R_i is the distance, and α is the linear expansivity. Finally, the following equation is obtained:

$$\delta = -B\left(\sum_i \vec{R}_{oi}\, q_i/R_{oi}^3\right)^2 \frac{1}{1 + 4/3\ \beta(T - T_o)}, \tag{4}$$

where β is the volume expansivity. The calculated values of $\delta = f(T)$ for $T_o = 200$ K and $\delta(T_o) = 13.03$ ppm is shown in Fig. 1. The good fit between the experimental and theoretical results supports the applied approximation.

The chemical shift of the carbonyl carbon of pivalic acid[10] shows the same characteristic temperature dependence, with a marked downfield shift at the liquid plastic crystalline phase transition, as that of the carboxyl proton. The chemical shift of the methyl carbon is practically independent of temperature with the exception of a discontinuous downfield shift of 0.33 ppm at the transition point T_m.[10] A similar downfield shift (ca. 0.4 ppm) has been observed for the corresponding methyl proton line although the proton measurements are more limited due to extensive line broadening in the plastic phase. On the basis of the well-known mechanism of association of carboxylic acids it can be concluded that the methyl groups of pivalic acid are not involved in association. It is therefore reasonable that the discontinuous change of the chemical shift at the liquid-plastic crystalline phase transition is the result of intramolecular effects, influenced by reorientations of the functional groups.

This idea can be pursued by calculating the electron charge distribution of the monomer and cyclic dimer of pivalic acid by using the CNDO/2 method. Fig. 3 presents the correlation between measured $\delta(^{13}C)$ values and calculated $s(q_s)$,
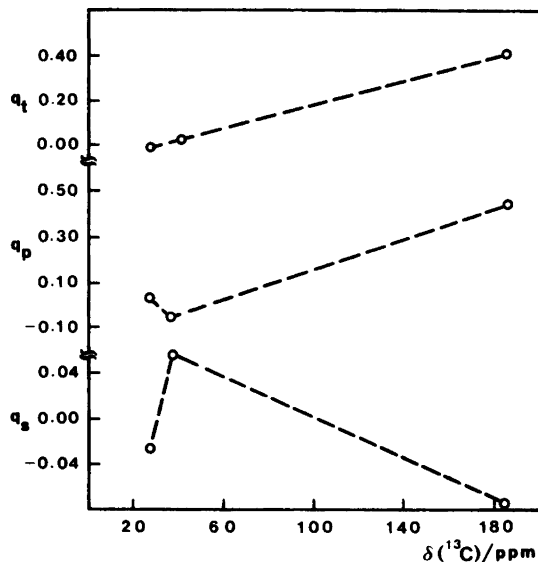
Fig. 3. Correlation between measured $\delta(^{13}C)$ values and calculated q_s, q_p and q_t electron charges of methyl, quarternary and carbonyl carbons of pivalic acid.

$p(q_p)$ and total (q_t) electron charges on the corresponding carbons of pivalic acid. The correlation only between the $\delta(^{13}C)$ values and the total electron charge seen i Fig. 3 is consistent with previous results of related correlation studies.[20,21] Fig. 4 shows the total electron charge on methyl (C_m), quaternary (C_q) and carbonyl (C_c) carbons as well as carboxyl hydrogen (H_c), as function of the dihedral angle, ψ, between the C—CH_3 and C—OH bonds. The electron charge on the methyl carbon displays much larger orientational dependence than the carbonyl carbon whereas this effect is negligible for the quaternary carbon. However, each of the three methyl carbons are taking part in rapid conformational changes (*cis⇌trans*). Thus the averaged q_t value of the three methyl carbons is not sensitive to the relative orientation of the carboxyl and *tert*-butyl groups; q_t changes from −0.0019 for a *cis* conformation to −0.0018 for a *trans* conformation. This result leaves little doubt that other factors must be responsible for the discontinuous downfield shift of the methyl carbon signal.

It is worth noting that another parameter, namely the one-bond $^{13}C-{}^1H$ coupling constant of the methyl groups of orientationally disordered crystals, is also affected by the liquid to plastic crystalline phase transition.[9,22] The significant reduction of the one-bond $^{13}C-{}^1H$ coupling constant in the plastic as compared to the liquid phase, was thus largely attributed to motionally averaged dipole—dipole interactions due to a slightly anisotropic tumbling of the molecules in the plastic phase.[22]

In CH_3F and CF_4 marked downfield shifts of the ^1H and ^{19}F resonances were observed when the solvent changed from isotropic to nematic.[23-25] Even the highly symmetrical molecules tetramethyl silane and neopentane exhibit small direct dipolar splittings in a nematic solvent, indicating that they probably suffer small shift anisotropies as well.[25,26] It is therefore reasonable to believe that the observed downfield shifts of the methyl proton and carbon resonances in the plastic phase of pivalic acid may arise from the anisotropic nature of the magnetic shielding.

The ^{17}O measurements were performed on the slightly enriched $(CH_3)_3$ $CCO^{17}OD$ sample. The chemical shifts were referenced to external $D_2{}^{17}O$. Only one ^{17}O resonance line was observed with a chemical shift equal to the weighted average value between the carbonyl and hydroxyl oxygen atoms. Satisfactory ^{17}O resonance signals with a linewidth at half-height
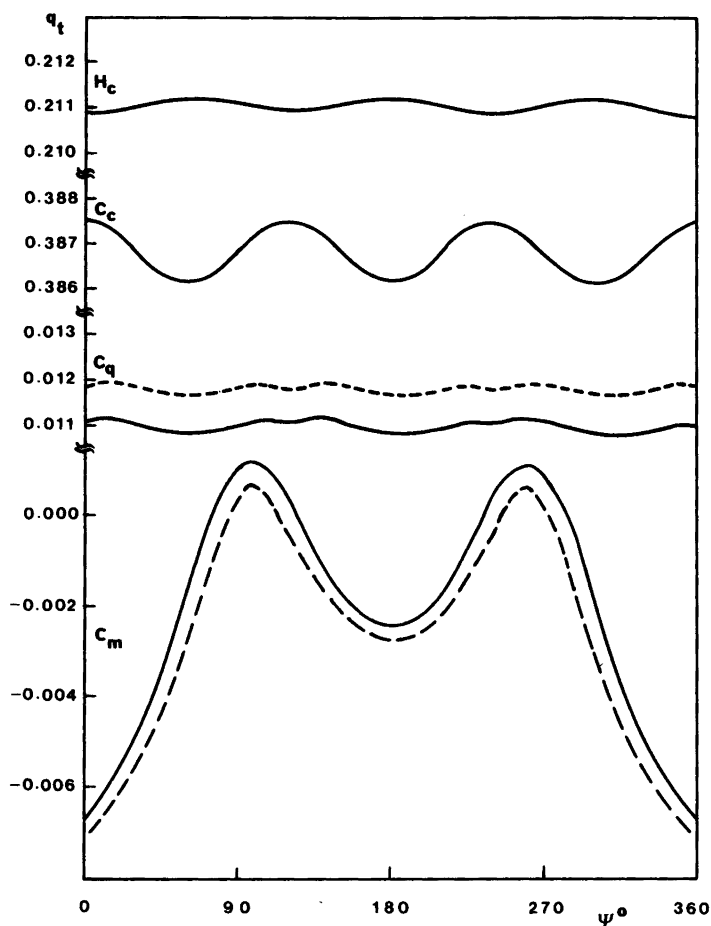
Fig. 4. Total electron charges of methyl, quarternary and carbonyl carbons as well as carboxyl hydrogen of the cyclic dimer (solid lines) and monomer (dashed lines) of pivalic acid. The following values of q_t for C_c and H_c of the monomer have been calculated: $q_{mon} \approx q_{dim} - 0.01$ and $q_{mon} \approx q_{dim} - 0.04$, respectively.

of 300−400 Hz, were obtained in the temperature range 296−319 K. The ^{17}O signal measured at 296, 301, and 319 K appeared at 235, 238, and 243 ppm, respectively. The ^{17}O chemical shift for liquid pivalic acid is thus quite close to that reported for the acetic acid dimers (254 ppm).[27] The temperature variation of the ^{17}O signal in pivalic acid is the opposite of that observed for the ^1H and ^{13}C resonances of the carboxyl group. This observation can, however, be rationalized in terms of hydrogen-bonding effects.[27,28] Breaking of hydrogen-bonds involving the carbonyl and hydroxyl oxygen atoms has thus been reported[27] to produce a net downfield ^{17}O shift (*ca.* 6 ppm in

acetic acid) in contrast to the effect on the ^1H and ^{13}C resonance signals.

EXPERIMENTAL

Commercial pivalic acid, $(CH_3)_3CCOOH$, was purified as explained in a previous paper.[10] The deuterated pivalic acid, $(CH_3)_3CCOOD$, which was used for the ^{17}O measurements, was prepared from the corresponding chloride $(CH_3)_3CCOCl$ and D_2O slightly enriched in oxygen-17. The NMR spectra were measured at 2.1 T on a Bruker CXP 100 spectrometer equipped with external deuterium lock. For the ^{17}O measurements the number of transients

accumulated with a 90° pulse and an acquisition time of 0.2 s was in the range 10^4–10^5 to get spectra of reasonable signal to noise ratios. The sample temperature was stabilized to within ±0.5 K by means of a Bruker B-ST 100/700 c temperature control unit.

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