Gas-Phase NMR Studies of Chemical Equilibria

1—Methodology

Robin K. Harris* and Renée C. Rao†

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Methods for obtaining ¹H NMR spectra of gases are discussed. Particular attention is paid to the nature of the tube and to the use of 'second sample' field/frequency locking. The question of the chemical shift reference is examined, and some results for tetramethylsilane gas are presented. Representative spectra are shown for three types of organic equilibria in the gas phase: keto-enol tautomerism, addition of methanol to acetaldehyde and *Z-E* isomerism of acetaldoxime.

INTRODUCTION

The observation of the ¹H nuclear magnetic resonance of hydrogen, reported by Purcell et al. in 1946,¹ was the first example of NMR spectroscopy applied to the investigation of a gaseous compound. Relatively few NMR studies on gases have followed, compared with the tremendously increasing number of papers dealing with NMR spectroscopy applied to liquids or solutions. This situation results mainly from the experimental difficulties in handling gases and from the low sensitivity inherent to NMR spectroscopy. Thus, although the signal of hydrogen at a pressure as low as 0.3 atm was reported as early as 1952,² it was usually necessary to work with pressures of at least 10 atm^{3,4} to obtain adequate signal-to-noise ratios. However, gas-phase measurements at low pressures would seem to be more amenable to interpretation than liquidstate results, since intermolecular interactions are then greatly reduced and since theoretical calculations usually refer to isolated molecules. Chemical shifts and coupling constants are influenced by medium effects both directly and indirectly (the latter case refers to changes arising from variations in conformational populations due to environment). Relaxation times are so heavily dependent on phase that completely different information may be obtained from studies of liquids and gases. Most gas-phase NMR studies to date have been direct investigations of the above parameters. However, there is considerable potential for more chemical studies by gas-phase NMR, particularly of equilibria or of exchange processes such as hindered internal rotation, and we have embarked on a programme of such studies.

The advent of time-averaging techniques and, more recently, of Fourier transform NMR, together with the common use of larger sample tubes, have offered the opportunity of studying fairly low pressures (<0.5 atm). Consequently a rapid increase of gas-

phase NMR studies can be foreseen. This paper describes in some detail the experimental requirements and difficulties encountered in ¹H gas-phase FT NMR measurements and how they are dealt with in our laboratory. It also gives some examples of spectra for organic equilibria.

THE SAMPLE

In general, variable-temperature operation is essential for gas-phase NMR, since appropriate pressures must be obtained for the full variety of compounds studied, and usually saturation vapour pressures provide the basic limitation of applicability of the technique. Therefore, considerable attention to this aspect of operation is necessary. In particular, in order to prevent the occurrence of excessive convection currents in the tube, possibly leading to condensation in the cooler upper regions, it is desirable⁵ that the sample is entirely situated in the temperature-controlled portion of the probe (ca 3-5 cm from the bottom of the insert in the case of the Varian XL-100 or HA-100 spectrometers). In effect, this implies the necessity of confining the gas to a small ampoule lying in the temperature-sensitive area. Such action minimizes temperature gradients and also improves the ability to achieve stable temperatures readily and reproducibly.

In addition, it is desirable to be able to spin the tubes without giving rise to interfering spinning side bands, both so as to make it possible to obtain spectra of gases and liquids under very similar conditions, and also because spinning improves⁶⁻¹¹ the resolution for gases as well as for liquids. Two other criteria for construction of suitable tubes for gas-phase NMR, in addition to the two mentioned above, may sometimes need to be invoked, viz. (i) the desirability, in some cases, for the emplacement of a capillary, centred inside the sample tube, to contain an external reference compound for chemical shift measurements, and (ii) the need for tubes equipped with vacuum-tight valves so that pressures can be readily varied (though for long-term work on important samples sealing will always be preferable).

* Author to whom correspondence should be addressed. † Present address: Laboratoire de Pharmacologie et de Toxicologie

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Fondamentales, 205 Route de Narbonne, 31078 Toulouse, France.

A number of devices have been proposed in the literature for minimizing convection or for limiting the sample to the thermostatted region of the insert; these have included use of loose glass-wool,¹² or of a constriction,^{6,13-15} or of some form of coaxial arrangement.^{7,8,16} Most have involved sealed systems, but some have incorporated valves.^{17,18} We have tested several devices (in conjunction with a Varian XL-100 spectrometer) and have found three to be of value in different circumstances.

(A) Commercially available (Wilmad Glass Co. Inc., 514A-7-SJ, 12 mm o.d.) NMR tube assemblies for gas-phase work were tried. However, to meet the first requirement the glass stopper adapter was attached to a 4-5 cm length 10 mm o.d. ampoule. As these tubes are not intended for permanent sealing they are quickly evacuated and filled. They can thus be conveniently used for various substances. For accurate work it is very attractive to have the possibility of using the same tube for all the measurements.¹⁹ However, it is also highly desirable to be able to keep a sample unaltered for a given period. Three tubes were tested for a possible leak. They were carefully evacuated and then immediately weighed. For two of them the weight was found to increase continuously even during this first weighing, indicating that they are not airtight. Figure 1 shows the result obtained for the third one (the glass stopper had been carefully and evenly greased with high-vacuum grease, although the manufacturers state this is not necessary!). Permanently sealed tubes should therefore be used if any accuracy regarding the pressure or dilution is desired.

In addition to the easy handling already underlined, these tubes have two obvious advantages. Firstly, since they are not permanently sealed they offer the possibility of studying irreversible processes, as it is not necessary to test them for explosion resistance. Secondly, the volume is easier to measure than in the case of permanently sealed tubes.

In this work, the Wilmad tubes were used for preliminary experiments (e.g. to determine the amount of compound necessary to obtain satisfactory signal-tonoise ratios within a reasonable time) and when there was no need to keep a given sample for a long time (i.e. not for more than about 2 h).

(B) Figure 2 shows the type of permanently sealed tube which was used throughout this work for the accurate measurements (except for the study of TMS). The 10 mm o.d. ampoule is placed inside a standard 12 mm o.d. NMR tube using a single PTFE spacer. The system is able to spin (even fast, >25 Hz) without giving rise to spinning side bands, and the sample ampoule is easy to de-gas and seal. Similar coaxial arrangements have been reported by Drakenberg and co-workers.^{7,8} For type (B) tubes, when a reference capillary is needed it can be held by a microcell holder, provided that the upper part of the ampoule is a piece of a standard 5 mm o.d. NMR tube.

(C) The tube used for the study of the tetramethylsilane (TMS) gas-to-liquid shift (see below) was a standard 5 mm o.d. NMR tube containing a capillary held by a microcell holder. The tube was sealed and satisfactory results were obtained using either the 5 mm insert, the 12 mm insert and the corresponding 5 mm spinnerhead, or the 12 mm insert after the tube had been centred in an ordinary 12 mm NMR tube by means of two PTFE spacers. It must be emphasized that when a reference capillary was used the spectra obtained were always of much better quality with 5 mm than with 12 mm o.d. tubes.

For relatively non-volatile compounds (e.g. water or N,N-dimethylformamide), a known weight of substance can be put into a type (B) tube, and several freeze-pump-thaw cycles used for de-gassing. For more volatile compounds a known volume of already de-gassed substance can be condensed into the evacuated tube via a vacuum line. Care must be taken to have the sealing point within approximately 3 cm



Number of days _







Figure 2. Type (B) gas-phase NMR sample system. Parts a, b and c are from standard 10, 5 and 12 mm o.d. NMR tubes, respectively.

from the top of the 10 mm o.d. ampoule. After warming to room temperature, the tubes are always tested for explosion resistance by keeping them for several hours at ca 170-200 °C in an oil-bath.

For the tubes that were not to be permanently sealed [type (A)] the same procedure can be followed, except that rotating the glass stopper in the appropriate closed position replaces the operation of sealing, and explosion resistance tests are unnecessary.

It is desirable to estimate the volume and pressure of the sample tubes as closely as possible. Pressures can be known accurately only when the internal volume of the tube and the amount of gas enclosed in it have been measured with precision. These determinations are usually difficult.⁵ Nevertheless, for the relatively volatile compounds we tried to relate the manometer reading of the vacuum-line used to the amount of substance condensed in the tube attached to the vacuum-line. Four separate measurements were carried out with methanol. Assuming perfect gas behaviour it was found that a 1 mmHg depression of the manometer corresponded to ca 2.3×10^{-5} mol. It must be stressed that this value is only an estimate.

The volume of permanently sealed tubes is clearly difficult to measure as the sealing point cannot be predetermined with good precision. However, volume determinations of the type (B) tubes (carried out with distilled and de-gassed water, at room temperature) have indicated that the internal volume, V, is ca 2 ml. This is a lower limit, so that the actual pressures are usually inferior to those we quote, which were calculated assuming perfect gas behaviour and V = 2 ml over the whole temperature range (since Pyrex-glass expansion is negligible).²⁰

SPECTROMETER OPERATION

For solution-state NMR studies field-frequency locking may be achieved in a number of ways: the locking sample may be internal to the solution being studied, it may be in the annulus of a concentric-tube system, or it may be a 'second sample' (i.e. involving a separate detector coil). Both of the last two would be referred to as 'external' locking arrangements. The three possibilities exist for gas-phase work (see, for example, Ref. 16). However, the sensitivity difficulties inherent in NMR studies of gases make the use of internal or concentric-tube arrangements less favourable than for solutions. Moreover, the use of ²H resonance from deuteriated solvents, which is very convenient for solution work, is scarcely feasible for gases. Therefore, we have generally standardized on the use of a second-sample lock system, using the ¹⁹F resonance of hexafluorobenzene (b.p. 82 °C/760 mmHg) in a standard Varian accessory to the XL 100 spectrometer. Locking is achieved in the usual way, i.e. by locating the fluorine signal, centring it on the oscilloscope, then phasing to the absorption mode and finally locking on.

However, use of the second sample does introduce difficulties of homogeneity adjustment and of longterm stability. For instance, it is not possible to adjust the magnetic field homogeneity for optimum resolution via the lock signal. Tuning consequently has to be carried out on an internal lock and, therefore, on a sample other than the gas-phase one actually studied. Usually the homogeneity alters with time and from sample to sample, but mostly with changes of temperature. To ensure excellent homogeneity has proved to be very critical for ¹H gas-phase NMR spectroscopy, owing to the narrow proton chemical shift range and the small amount of compound when working at low pressures (resulting in a larger measuring time). In addition, it is expected that substituting the gas sample for the 'resolution' sample will reduce the homogeneity attained, at least slightly.

It has been found that the best way of meeting this homogeneity requirement is to adjust the homogeneity using a 'resolution' sample containing a deuterium internal lock and then to lock on the ¹⁹F external lock. As shimming must frequently be carried out at high temperatures, the 'resolution' sample chosen was a solution of dimethyl sulphoxide- d_6 (which provided the ²H signal for locking) in o-dichlorobenzene. To minimize the differences introduced by the tube substitution, shimming was always carried out on a sample contained in the same tube arrangement as the sample to be studied (i.e. either a 5 mm o.d. tube or a 10 mm o.d. ampoule). o-Dichlorobenzene was selected because of its high boiling point (179°C/760 mmHg) and because its NMR spectrum provides a good test of the resolution achieved. Dimethyl sulphoxide- d_6 , as a neat liquid, is known to start decomposing slowly at 100 °C. This decomposition is likely to be reduced in solutions and it was not found to be disturbing even up to 175 °C. It is advisable that the 'resolution' sample is degassed and sealed to prevent any paramagnetic linebroadening due to dissolved oxygen. Moreover, it proved difficult to lock on deuterium above ca 147°C when the sample was not permanently sealed. The 'resolution' sample used in our work was tested for explosion resistance at 180 °C.

After locking on deuterium (and when the temperature is stabilized) the shim coils are optimized in the usual way, the resolution is checked by recording the spectrum of o-dichlorobenzene, and then locking on the ¹⁹F external lock is carried out as already described. The resolution must then be checked by again recording the spectrum. It should be noted that when changing from deuterium to fluorine lock there is a considerable shift in resonance frequencies. The shift has been found to be +9 kHz, i.e. for the 'resolution' sample the sweep offset was 45166 Hz when locking on deuterium and 54166 Hz when locking on fluorine. Since the ¹⁹F lock does not control the field at the exact position of the sample, it must be emphasized that a field/frequency drift has to be expected over a period of time. The spectra shown in Fig. 3 were obtained without changing the setting of the shim coils. A spectrum similar to that in Fig. 3A was obtained when locking back on internal deuterium after recording spectrum D, indicating that the spectrometer was not detuned. The poor resolution observed is thus entirely due to the fluorine lock drift. Good resolution can usually be restored (at least temporarily) by recentering the fluorine signal on the oscilloscope and adjusting the drift controls.



Figure 3. Instability of the fluorine lock. Spectra A, B, C and D were obtained under exactly the same conditions, at times t = 0, 5, 10 and 30 min, respectively, after optimizing the shim coils.

Achieving stable, good resolution therefore proved to be the cause of real difficulties, the more so since, as may be the case in any NMR experiment, factors other than those mentioned above can alter the magnetic field homogeneity, which then needs to be adjusted by reshimming. This means removing the sample from the probe, substituting the 'resolution' sample, waiting for temperature stabilization, shimming and again waiting for temperature stabilization of the sample under study. Although this process is obviously time consuming, it is often more rapid than trying to adjust the fluorine signal more than two or three times.

After very careful shimming adjustment the homogeneity is usually stable for at least 2–3 h. It is obviously necessary to repeat the shimming process whenever the probe temperature has been changed.

The fluorine-lock system is intended for use over the whole temperature range accessible for the XL-100 spectrometer. However, since hexafluorobenzene boils at 82 °C, we felt it to be important to monitor the temperature at the 'second-sample' capillary by means of a thermocouple when the probe temperature had to be raised above 100 °C. The thermocouple was first calibrated as usual, then one of its junctions was attached to the fluorine sample with a small piece of Sellotape and the thermocouple was used in the normal way. The temperature of the fluorine sample could thus be monitored as the probe temperature was raised step by step (usually not more than 5 °C at a time). The sample in the probe was that of ethylene glycol normally used for measuring the probe temperature. The temperature was always allowed to stabilize for 30–60 min before measurement. The results of two series of measurements are shown in Fig. 4, where the fluorine sample temperature has been plotted against the probe temperature. The temperature of the fluorine-lock sample increases only very slowly with the probe temperature and remains well below the boiling point of hexafluorobenzene.

Since this is an easy method of checking the fluorine sample temperature, we have used it during most of our gas-phase measurements. Probe temperatures as high as 175 °C can be retained for several hours without harming the fluorine sample.

In our experiments, the probe temperature is always measured by the temperature dependence of the chemical shift difference for ethylene glycol,²¹ using either 5 or 12 mm o.d. tubes, depending on the tube arrangement or insert used for the sample under study. The tube is always kept in the probe for at least 30 min before measuring the temperature; the ethylene glycol spectra are then recorded every 5 min or so until three consecutive measurements give identical results.

Spinning slightly increases the resolution for gasphase NMR at temperatures above the boiling point of the compound studied. Spinning rates between 12 and 20 Hz are typically used. However, at temperatures near or below the boiling point it is advisable not to spin the tubes, as very small liquid droplets along the walls of the tube may dramatically affect the spectrum.



Figure 4. mperature variation of the ¹⁹F 'second sample' with the probe temperature. The filled and open circles indicate the results of two independent series of measurements.

CHEMICAL SHIFT REFERENCE

For most of the earlier ¹H gas-phase NMR chemical shift measurements a gaseous reference was generally employed, the most widely used for that purpose being methane, either internally^{6.22} or externally.⁹ Other compounds such as ethane, ²³ ethylene²⁴ or $TMS^{8,10,25}$ have been employed as internal standards, and benzene¹⁸ as an external reference. However, when it is desired to compare the chemical shifts of liquid and gaseous compounds, all the measurements should be referred to the same reference signal (with suitable corrections for differences in bulk susceptibilities when necessary). In the liquid phase ¹H chemical shifts are now universally referred to TMS, and it therefore seems desirable that ¹H chemical shifts are also referred to TMS in the gas-phase. It should be emphasized that, in variable-temperature studies, the experimental chemical shifts are affected by the difference between two temperature dependences, that of the compound under investigation and that of the standard.

The experimental technique is much easier and faster with an internal than with an external reference.¹⁹ The latter requires corrections for bulk susceptibilities to be made. The corresponding bulk susceptibilities must therefore be known, and the liquids used should be chemically pure. In addition to these difficulties, capillaries need to be carefully centred in the sample tube and, for accurate results, it seems preferable that the same capillary is used for all the measurements. If the chemical shift variation of TMS gas with respect to TMS liquid is known as a function of temperature, it would be possible to use TMS gas as an internal reference for gas samples, provided this variation is not altered by mixing TMS with foreign gases. In this section the results of preliminary experiments on the possibility of using TMS gas as an internal reference for ¹H gas-phase measurements are reported.

The type (C) tube arrangement (10 mg of TMS) was used, with the capillary containing neat TMS. The pressure in the tube was below 5 atm. Figure 5 shows a spectrum obtained with this arrangement. In Fig. 6 the gas-to-liquid shift in resonance frequency, Δ_1 , observed for TMS is plotted against temperature. The is approximately linear, relationship obeving $\Delta_1/\text{Hz} = 145-0.34t/^{\circ}\text{C}$. In the case of a symmetrical non-polar molecule such as TMS, $\sigma_{\rm w}$ (the contribution to shielding due to intermolecular dispersion forces) can be calculated from the observed gas-to-liquid shift. The value of σ_w , determined by extrapolation to zero pressure of gas, has been reported²³ to be -0.205or -0.228 ppm (two independent determinations) at 30 °C. In order to compare the results obtained here with this earlier determination, σ_w has been calculated at 30 °C using $\sigma_{\rm w} = \sigma_{\rm m} - \sigma_{\rm b}$, where $\sigma_{\rm b}$ is the bulk susceptibility correlation and $\sigma_{\rm m}/\rm{ppm} = -\Delta_1/100 \text{ Hz}$ (ignoring effects of gas pressure). The value of $\sigma_{\rm b}$ was obtained using the following expression²⁶ for the temperature dependence of the density, d, of liquid TMS:

$d/g \,\mathrm{cm}^{-3} = 0.6634 - 0.001042 \times t/^{\circ}\mathrm{C}$

The expression for $\sigma_{\rm b}$ in the case of a cylindrical



Figure 5. ¹H NMR spectrum of TMS at 60 °C using tube arrangement (C). The strong peak at high frequency is due to the liquid phase; the weaker peak at low frequency is due to the gas. The spectrometer conditions were as follows: SW 1000 Hz; AT 4 s; PW 1 μ s (a 90° pulse has PW 50 μ s); NT 50; SE 2; spinning rate 32 Hz.

sample is^{19,27} (in e.m.u.)

$$\sigma_{\rm b} = \frac{2}{3}\pi \frac{d}{M} \chi_{\rm M}$$

where *M* is the molar mass and $\chi_{\rm M}$ is the molar susceptibility. (In the SI system this equation should read $\sigma_{\rm b} = d\chi_{\rm M}/6M$, since volume susceptibilities in SI are 4π times those in any unrationalized system such as e.m.u.) For TMS $\chi_{\rm M}$ (e.m.u.) = 74.8×10^{-6} mol cm⁻³ (ref. 28). Thence, we find the value of the 'excess shift', $\sigma_{\rm w}$, when going from the gas to the liquid phase at 30 °C is -0.226 ppm, which is in good agreement with those previously reported.²³

As chemical shifts should actually be referred to TMS (5% v/v) in solution in chloroform, the gassample tube was broken so that the same capillary could be used to measure the shift between neat TMS and the solution as a function of temperature. These measurements were performed using an HA-100



Figure 6. Chemical shift difference between liquid and gaseous TMS, $\Delta_1/Hz = 100 \ (\delta_{TMS}^{liq} - \delta_{TMS}^{aas})/ppm$, as a function of temperature, *t*.

spectrometer in the frequency-sweep CW mode at 99.896 MHz, the chloroform providing the signal necessary for the field/frequency lock. The data are plotted in Fig. 7, yielding $\Delta_2/\text{Hz} = 43.7 \pm 0.06t/^{\circ}\text{C}$.

The results of the two series of measurements (Figs 6 and 7) were then combined to give Δ , the chemical shift of TMS in solution (in chloroform) with respect to TMS_{gas}:

$$\Delta/\text{Hz} = 101.3 - 0.40 \times t/^{\circ}\text{C} = 100(\delta_{\text{TMS}}^{\text{solution}} - \delta_{\text{TMS}}^{\text{gas}})/\text{ppm}$$

The data given above should enable chemical shift results obtained using TMS gas as an internal reference for gas-phase work to be related to standard solution-phase references. However, additional studies of different TMS gaseous dilutions in a variety of foreign gases are probably desirable before TMS gas can be considered as an entirely suitable internal reference for ¹H gas-phase NMR.

CHEMICAL EQUILIBRIA IN THE GAS PHASE

Our interest has centred on gas-phase studies of chemical equilibria using NMR, rather than the more common investigations of shielding effects for small molecules. This section gives some instances where we have shown investigation to be feasible. These relate to three separate chemical situations: (a) keto-enol tautomerism; (b) reversible additions to the carbonyl double bond of aldehydes; and (c) Z-E isomerism in acetaldoxime.

Under the first heading we have examined acetylacetone (b.p. $139 \,^{\circ}C/746 \,\text{mmHg}$) in the range $113-174 \,^{\circ}C$ and ethyl acetoacetate (b.p. $180.8 \,^{\circ}C/760 \,\text{mmHg}$) in the range $143-174 \,^{\circ}C$. Figure 8 shows the spectrum of gaseous acetylacetone at *ca* 0.2 atm in a type (A) tube (i.e. not permanently sealed) at $146 \,^{\circ}C$. This was obtained using only 100 transients and the signal-to-noise ratio is ample to establish the enol-keto ratio as 72% enol (a significantly lower value than found for solutions in 'inert' solvents at ambient room temperature).

In the second category we have examined the equilibria



 $H_3CCHO + H_3COH \rightleftharpoons H_3CCH(OH)OCH_3$

Figure 7. Chemical shift difference between TMS (neat liquid) and TMS (5% v/v in chloroform), $\Delta_2/Hz = 100 (\delta_{TMS}^{lig} - \delta_{Solution}^{solution})/ppm$, as a function of temperature, t.



Figure 8. 100 MHz ¹H NMR spectrum of gaseous acetylacetone at 146 °C. The signals are marked E for the enol form and K for the keto form. The OH (enol)signal is not visible. From high to low frequency the observed peaks are due to =CH-, -CH₂-, -CH₃ and -CH₃, in order.

and

$$H_3CCH(OH)OCH_3 + H_3COH \rightleftharpoons$$

 $H_3CCH(OCH_3)_2 + H_2O$

Figure 9 shows the spectrum of a mixture containing originally 69×10^{-5} mol of acetaldehyde and 46×10^{-5} mol of methanol in a type (B) (sealed) tube at 114 °C using 50 transients. At this temperature all the compounds should be in the gase phase. It is evident that acetaldehyde, methanol, 1,1-dimethoxyethane and water are all present, but no signals are seen which could be assigned to 1-methoxyethanol.

The Z-E thermal uncatalysed isomerism of acetaldoxime (b.p. 114 °C) has been examined in the gas phase. Figure 10 shows the proton spectrum of a type (A) tube containing 32×10^{-5} mol of acetaldoxime and 4.6×10^{-5} mol of tetramethylsilane (total pressure *ca* 6 atm) at 136 °C. Signals due to the Z and E forms are readily distinguished. The shift difference between the CH signals (0.77 ppm) appears to be significantly larger than that for the neat liquid (0.60–0.65 ppm, depending on temperature). At 136 °C the spectrum







Figure 10. 100 MHz ¹H NMR spectrum of acetaldoxime in the gas phase at 136 °C. The resonances due to the *Z* and *E* forms are indicated. Band H is assigned to the hydroxyl groups of both forms and T is due to tetramethylsilane.

shows the equilibrium results in 40% of the E form, probably within experimental error of the value (38%) found for the E form in the neat liquid at the same temperature.

Full details of work with all three systems will be published in separate papers in due course. At this point it may be noted that the question of whether a proper equilibrium has been established in the gas phase under given conditions is a difficult one.

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