

Concerning the Chemical Shift Data (^{17}O , ^{13}C , ^1H) of Formaldehyde[†]

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The ^{17}O NMR signal of formaldehyde was measured and the literature values of the ^{13}C and ^1H signals are discussed. They are compared with values obtained by other spectroscopic methods and by *ab initio* calculation.

KEY WORDS ^{17}O NMR; ^{13}C NMR; ^1H NMR; formaldehyde; methanal

The NMR shift values of formaldehyde (methanal; $\text{CH}_2=\text{O}$), the simplest carbonyl compound, have frequently been the subject of theoretical calculations. The experimental values, however, are still unknown (^{17}O) or at least problematic (^{13}C), because in most aprotic solvents formaldehyde is rapidly polymerized, whereas in protic solvents it undergoes rapid nucleophilic addition reactions; this makes CH_2O solutions difficult to manipulate. Only a few years ago, adequate publications on reliable preparative procedures have made formaldehyde solutions easily accessible, particularly in ethereal solvents, e.g. THF and dimethyl ether.^{2,3}

We have measured CH_2O in THF solution and found $\delta(\text{O}) = 656.5$ ppm with $\nu_{1/2} = 300$ Hz (23 °C; for technical details of measurement, see Ref. 1) (Table 1).

Shift values can also be evaluated by combining the paramagnetic part of the shielding tensor, σ^p , which can be obtained experimentally by molecular beam or microwave measurements,⁴ with the diamagnetic part, σ^d , accessible by calculations.⁵ By this method, a formaldehyde shift value of $\delta(^{17}\text{O}) = 683$ ppm has been

evaluated⁴ [gas phase, using $\delta(^{17}\text{O}) = 307.9 - \sigma(^{17}\text{O})^6$]. In comparing this gas-phase value with the result of the above NMR measurement in THF solution, one has to keep in mind that the carbonyl oxygen shifts are subject to particularly important solvent effects; for instance, the oxygen in acetone resonates in acetonitrile at 568 ppm and in hexane at 580 ppm.⁷ Under these circumstances, the agreement between the ^{17}O shift values obtained by two different spectroscopic techniques can be considered to be good.

On the other hand, by simple extrapolation from the measured shift values of Me_2CO (572 ppm) and MeHCO (596 ppm), $\delta(^{17}\text{O})(\text{CH}_2\text{O}) = 620$ ppm had been estimated.⁸

Ab initio IGLO calculations yielded $\delta(^{17}\text{O})(\text{CH}_2\text{O}) = 767$ ppm;⁹ in a recent application of the IGLO program, using a calculated (6–31G**) geometry, $\delta(^{17}\text{O})(\text{CH}_2\text{O}) = 737$ ppm was found.¹⁰ Earlier calculation had yielded still higher shift values.¹¹

In view of the practical difficulties mentioned above, one wonders about the provenance of the ^{13}C and ^1H shift values found in textbooks and tables and used as references for comparison with theoretical calculations. One often sees $\delta(^{13}\text{C})(\text{CH}_2\text{O}) = 197$ ppm,¹² (or 186 ppm,¹³ depending on the conversion basis), citing Ref. 5. The authors,⁵ however, quote 'P. C. Lauterbur (private communication)'; on closer inspection of the text it becomes clear that this value results from an extrapolation of the (measured) shift values of Me_2CO and MeHCO to H_2CO , i.e. it is only an estimate. It therefore appears that the first NMR measurements of the ^{13}C chemical shift values of formaldehyde are those in the preparative notes cited above: $\delta(^{13}\text{C})(\text{CH}_2\text{O}) = 194$ ppm (THF)³ and 196.7 ppm (dimethyl ether);^{2a} published as simple structure confirmations, they might have escaped spectroscopists' attention.

Whereas efforts to determine the ^{13}C shift value of CH_2O by microwave measurements combined with calculations (see above) were not satisfactory,^{4,5} recent *ab initio* calculations by both the IGLO and the LORG programs gave good agreement with the experiment: $\delta(^{13}\text{C})(\text{CH}_2\text{O}) = 195.8^{13}$ and 190,¹⁴ respectively. These values refer to the gas phase; it has been shown that

Table 1. ^{17}O , ^{13}C and ^1H chemical shift values δ of formaldehyde (ppm), H_2O resp. TMS = 0; downfield positive)

| Method | ^{17}O | ^{13}C | ^1H |
|--------------------------------|--------------------|---------------------------------------|---------------------------------------|
| NMR measurement | 656.5 ^a | 194 ^b ; 196.7 ^c | 9.58 ^d ; 9.53 ^a |
| Other spectroscopic techniques | 683 ^a | | 10.6 ^a ; 12.3 ^f |
| Calculations | 767 ^a | 195.8 ^g ; 190 ^h | 9.5 ⁱ |

^a This work.

^b Ref. 3.

^c Ref. 2a.

^d Ref. 16.

^e Microwave; Ref. 4.

^f Beam maser; Ref. 17.

^g Ref. 9.

^h Ref. 14.

ⁱ Ref. 16.

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† NMR of Terminal Oxygen, Part 18. For Part 17, see Ref. 1.

^{13}C shift values of carbonyl carbon are much less subject than ^{17}O to solvent effects.¹⁵

For ^1H shift values, early NMR measurements on solutions prepared by techniques similar to those cited above are available (although rarely quoted):¹⁶ $\delta(^1\text{H})(\text{CH}_2\text{O}) = 9.58$ ppm (THF) and 9.61 ppm (MeCN); we found 9.53 ppm (THF).

Other spectroscopic techniques (combined with calculations) yield $\delta(^1\text{H})(\text{CH}_2\text{O}) = 10.6$ ppm (microwave gas)⁴ and 12.3 ppm (beam maser, gas);¹⁷ IGLO calculations gave 9.5 ppm (gas).¹⁸

Note added in proof

We have also measured samples of CH_2O in acetonitrile. CH_2O was prepared from paraformaldehyde which

had been dried and stored over P_2O_5 at room temperature, depolymerized following Refs 2b and 3 and distilled together with acetonitrile. The 2.5 M solution was kept for <1 h at -20°C . We found (at about room temperature): $\delta(^{17}\text{O})(\text{CH}_2\text{O}) = 648.2$ ppm ($\nu_{1/2} = 50$ Hz; <19 K scans in <10 min), $\delta(^{13}\text{C})(\text{CH}_2\text{O}) = 198.2$ ppm (460 scans) and $\delta(^1\text{H})(\text{CH}_2\text{O}) = 9.93$ ppm.

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