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Removal of Oxygen from Samples used in Nuclear Magnetic Resonance Studies of Spin–Lattice Relaxation Times

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Summary It is demonstrated that conventional degassing procedures for the removal of oxygen from samples used in n.m.r. studies are unsatisfactory, and a versatile chemical alternative is described.

THE measurement of spin–lattice relaxation times, T_1, and particularly the dependent Nuclear Overhauser Effect, N.O.E., are being used increasingly as aids in the solution of chemical problems. It has long been recognized that molecular oxygen significantly reduces the values of T_1 and the N.O.E., and attempts to remove it are normally made by the familiar freeze–thaw degassing procedure or by passing oxygen-free gas through the sample. In common with others[1,2] we have found that it is difficult to employ these procedures efficiently and we now describe a simpler and more effective chemical method.

Air-saturated benzene has a T_1 value of 4·6 s, as measured by the a.f.p.[3] procedure. Repeated freeze–thaw degassing of the same sample in a vacuum line operating at a typical pressure of 10^{-3} torr increases the value to 5·5 s; similarly small increases of less than 1 s in the T_1 values of other compounds are achieved. We have employed the same method at *ca.* 10^{-5} torr to increase the value of T_1 to the order of the widely quoted (e.g. ref. 4), but probably incorrect, value of *ca.* 19 s. Despite taking all reasonable precautions to ensure the success of the degassing technique the values of T_1 obtained are quite irreproducible. Similarly, bubbling oxygen-free nitrogen through the sample, and sealing it under this gas also provides low and irreproducible values for T_1.

Because of the difficulties and unreliability of these procedures we have investigated chemical means of deoxygenating samples. Although some such methods have been reported[1,5] they are extremely tedious to implement. We have, therefore, sought an alternative procedure employing readily obtainable materials that obey the three criteria, (i) they should be soluble in a wide variety of solvents and be capable of use with liquids immiscible with the primary solvent, (ii) have low vapour pressures to

TABLE. A comparison between the ^1H T_1 values of physically and chemically degassed compounds.

Compound	T_1/s Literature	 This work (309 K)
Benzene	19·3[4]	23·6[a]
Toluene Ring	16·0[4]	22·2[b]
CH_3	9·0[4]	11·9[b]
p-Xylene Ring	14·0[4]	16·7[b]
CH_3	7·5[4]	7·3[b]
Acetone	15·8[8]	17·6[c,d]
Methylene chloride ..	28·5[9]	36·1[d]

[a] Four samples were prepared, two by distillation under reduced pressure (10^{-3} torr) from a previously stirred heterogeneous mixture with water containing $[Co^{II}(bipy)_3](ClO_4)_2$ and sodium borohydride and two from a homogeneous solution containing dimethyl sulphoxide. [b] Distilled under reduced pressure from a previously stirred homogeneous mixture with dimethyl sulphoxide containing the deoxygenating compounds. [c] The estimated experimental error for 13 determinations is ±0·2 s. [d] Distilled under reduced pressure directly from a homogeneous solution containing the deoxygenating compounds.

facilitate their easy removal from the subject material by its distillation, and (iii) remove oxygen in a reversible colour indicating reaction. The compound we have found to fulfil these requirements is $[Co^{II}(bipy)_3](ClO_4)_2$[6] with sodium borohydride. In an oxygenated homogeneous mixture these give a pale yellow-brown solution which changes on the removal of oxygen to an extremely oxygen sensitive intense blue solution. If solutions are subsequently oxidised by dioxygen they may be reduced again in the presence of excess sodium borohydride, but the oxidation–reduction cycle may not be reversed indefinitely.

We have used the two compounds mentioned above at extremely low concentrations (to minimize potential reduction of the sample) in hetero-and homo-geneous mixtures to deoxygenate several materials the T_1 values of which are well documented.[7] The values we have obtained by the a.f.p. method, using a Varian HA100D spectrometer, are compared in the Table with possibly the longest literature times available. It is apparent that our values are significantly longer than those of other workers, by up to 7 s, and that our method of degassing samples is, in addition to being simple, reproducible and much more efficient than those reported previously.

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