Carbon-13 Spin-Lattice Relaxation: Carbon–Bromine Scalar and Dipole–Dipole Interactions

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Summary ^{13}C Nuclei bonded to bromine nuclei can undergo efficient scalar relaxation; the presence of nearly equal amounts of ^{79}Br and ^{81}Br isotopes can lead to observed "non-exponential" relaxation for the ^{13}C nuclei.

CARBON-13 spin–lattice relaxation mechanisms have recently received a great deal of attention.[1,2] Of four mechanisms that can result in spin–lattice relaxation of ^{13}C nuclei: dipole–dipole interaction, spin–rotation interaction, chemical shift anisotropy, and scalar interaction, only the first two are commonly encountered.[†] Spin–lattice relaxation of ^{13}C nuclei as a result of the scalar interaction[3] does not occur in most molecules because of stringent requirements needed to make this mechanism competitive with the other relaxation mechanisms. Efficient scalar relaxation[‡] of a ^{13}C nucleus requires that that nucleus be spin–spin (scalar) coupled to a nucleus, X, with nuclear spin $> \frac{1}{2}$ that is undergoing quadrupolar relaxation[3] at a rate comparable to the difference frequency between the ^{13}C and X nuclei (also, $T_1{}^X$ should not be too short, *e.g.*, $<10^{-5}$—10^{-6} s, for efficient scalar relaxation).

The Larmor frequencies of ^{79}Br and ^{81}Br nuclei are close to the Larmor frequency for ^{13}C (at 23·5 kG the difference between carbon and bromine Larmor frequencies for ^{79}Br is *ca.* 90 kHz; for ^{81}Br *ca.* 2 MHz); bromine quadrupolar relaxation rates are *ca.* 10^6 s^{-1}. Several groups have recently observed scalar relaxation of ^{13}C nuclei directly bonded to bromine in bromomethanes[4,5] and *p*-bromobenzonitrile.[6] It was noted that ^{79}Br and ^{81}Br, with different Larmor frequencies, and present in nearly equal abundances, should not be equally effective at relaxing ^{13}C nuclei. In the reported studies it was not possible, however, to detect separate relaxation for ^{13}C nuclei bonded to the two isotopes.

The spin–lattice relaxation behaviour of bromobenzene, determined by inversion–recovery pulse methods[7] on a Varian XL-100-15-FT n.m.r. system, indicates that scalar relaxation completely dominates the relaxation of ^{13}C nuclei bonded to ^{79}Br nuclei and that the scalar and/or dipole–dipole interaction between ^{13}C and ^{81}Br nuclei excludes ^{13}C–^{1}H dipole–dipole relaxation for ^{13}C nuclei bonded to the ^{81}Br isotope. The accuracy of these measurements coupled with determinations at three temperatures allows dissection of observed "non-exponential" relaxation into component exponential processes described by two T_1 constants. (Each T_1 describes relaxation in bromobenzene containing one bromine isotope). The experimental determinations of T_1 yielded data[§] which, when plotted as a logarithmic function of the waiting time, *t*, between the inverting pulse (180°) and the monitoring pulses ($90_\infty{}^\circ$ and $90_t{}^\circ$), described curves rather than the usual straight lines (see Figure). Using a linear combination of 2 exponential terms, it was possible to fit the observed curves and thus determine two T_1 constants (see Table). The high temperature experiments were required to confirm the relative efficiency of scalar relaxation with ^{79}Br.[8]

It is not possible from the experiments performed to differentiate quantitatively between ^{13}C–^{81}Br scalar relaxation and ^{13}C–^{81}Br dipole–dipole relaxation. However, the nuclear Overhauser effect (NOE) measurements indicate that ^{13}C–^{1}H dipole–dipole relaxation does not contribute significantly to the relaxation of ^{13}C nuclei bonded to either ^{79}Br or ^{81}Br in bromobenzene. It is likely that ^{13}C–^{81}Br dipole–dipole relaxation is dominant especially at intermediate to high temperatures[¶] where scalar relaxation to ^{81}Br should become less efficient,[8] and where T_1 approaches the expectation value for a substituted carbon in a typical mono-substituted benzene (*ca.* 100 s[2c]).

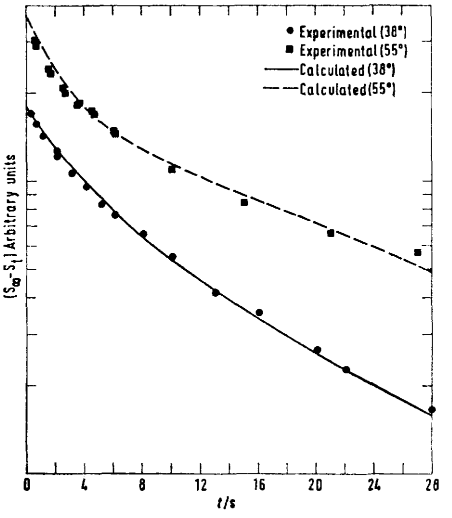

FIGURE. *Experimental and calculated determination of* T_1 *for the carbon atom bonded to bromine in bromobenzene.*

TABLE

^{13}C *Spin–lattice relaxation in bromobenzene*[a]

Temperature	T_1 ^{13}C–^{79}Br	T_1 ^{13}C–^{81}Br	NOE (η)
38°	3·6	16	0·0[b]
55°	2·2	22	—
125°	1·2	~26	0·0[b]

[a] Determined at 25·2 MHz; degassed (N_2 method). T_1 in sec; calculated from experimental curve (see Figure and text); estimated maximum error 15%. T_1 for the *ortho*- and *meta*-carbon atoms was 10·7 s and for the *para*-carbon, 6·8 s (38°). [b] Determined from total integrated peak intensity ratios; probable error $<0·1$. The NOE (η) for all protonated carbons was complete (2·0).

We have observed scalar relaxation between ^{13}C and bromine nuclei in several other compounds, including bromocyclohexane and 3- and 4-bromobiphenyl. In bromocyclohexane, NOE measurements indicated that one third of the relaxation of ^{13}C nuclei attached to bromine nuclei occurred by the scalar interaction.[8] Thus, scalar relaxation

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[†] Spin–rotation relaxation is normally found only in small, symmetrical molecules; the dipole–dipole mechanism usually dominates ^{13}C spin–lattice relaxation behaviour.

[‡] We treat here only scalar relaxation of the second kind according to the definition of Abragam (A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961, ch. 8).

[§] The pulse sequence used was $(T - 90_\infty{}^0\text{-}T - 180^0\text{-}t - 90_t{}^0)_x$ with the plotted quantity being $(S_\infty - S_t)$, the difference[7b] between the signals resulting from the $90_\infty{}^0$ and $90_t{}^0$ pulses (after Fourier transformation).

[¶] In bromobenzene, the non-protonated carbon–bromine internuclear distance is *ca.* 90% of the C–*ortho*-H distance, favouring C–Br dipole–dipole relaxation. At high temperatures, spin–rotation relaxation may become important for the ^{13}C–^{81}Br nuclei.

is able to compete with $^{13}C-^{1}H$ dipole–dipole relaxation even for protonated carbons, as previously indicated in the bromomethanes.

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[8] Detailed arguments will be presented elsewhere: G. C. Levy and F. A. L. Anet, unpublished results.