sophisticated experiments with doubly labeled precursors and dilution experiments to isolate the postulated intermediates, etc.

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Spectrum and Lifetime of the Acoustically and Chemically Induced Emission of Light from Luminol

Sir:

The emission of light from an acoustically cavitated alkaline solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione)[1,2] and the luminescence from the chemically induced oxidation of similar solutions[3-5] have been studied. We have investigated the mechanism of the light emission from an acoustically cavitated luminol solution by comparing its spectrum with that of its chemically induced luminescence and by measuring the lifetime of the excited species.

A scanning spectrophotometer as previously described[6] was used to obtain the spectra. A steady luminescence was produced by a solution of 300 mg of luminol and 20 g of sodium carbonate in 100 ml of 3% hydrogen peroxide contained in a quartz cell fitted at the entrance to the spectrometer. In the acoustic case a solution of 100 mg of luminol in 1 l. of 2 N sodium carbonate was circulated from a reservoir through a heat exchanger and either a 14-kHz tubular piezoelectric transducer or a 500-kHz cylindrical segment transducer attached to the entrance of the spectrometer. Each of these transducers produced a sound pressure of 2 atm rms at the focus, corresponding to an acoustic power in the cavitation region of about 3×10^4 W m^{-2}. Circulation of the sample solution without cavitation produced no light, and sonoluminescence from the cavitation of the sodium carbonate solution without luminol made a negligible contribution to the spectrum.

The spectra of the light emitted with the two sound frequencies and with the chemical oxidation were identical, and this spectrum is shown in Figure 1.

The excited species is clearly the same in each case, and it is probable that it is produced by the same chemical reactions, since it has been shown[2] that the acoustically induced light emission from neutral solutions is very feeble (evidently insufficient OH radicals are formed by the cavitation to produce the dinegative luminol ion), and the formation of hydrogen peroxide in cavitated water has often been observed. The spectrum has the same form as spectra previously reported for the chemical oxidation of luminol,[4,7,8] and its maximum energy occurs at a wavelength of 4330 ± 40 Å. The wavelength calibration has an accuracy of ±10 Å, and the resolution is better than 15 Å: by using different slit widths it was shown that the shape of the continuum was not limited by the resolution of the spectrophotometer. Furthermore, the spectra were found to be unaltered by substantial variations in the concentrations of the reactants.

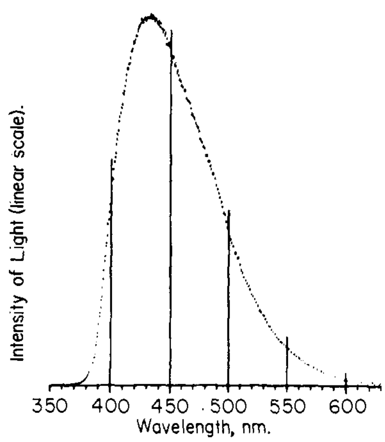

Figure 1. Spectrum of the acoustically or chemically induced light emission from luminol.

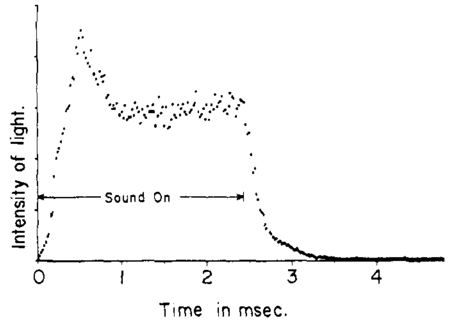

Figure 2. Intensity of light emission during and immediately after a sound pulse of 2.45-msec duration and of frequency 14 kHz.

A modification to the spectrometer arrangement made it possible to plot the light intensity as a function of time at any wavelength, and this was used to measure the lifetime of the light emission. The 14-kHz oscillator used to produce the cavitation was gated to produce pulses of sound of 2.45-msec duration. The intensity of luminescence during and immediately after the pulse is shown in Figure 2. The intensity increases steadily to its maximum over the first eight sound cycles and then declines to an equilibrium level. At the end of the pulse it takes only 140 μsec for the light intensity to fall to half its equilibrium value, and the shape of the curve during the decline is roughly exponential. The distribution was the same for all wavelengths.

This result contradicts Negishi's report[2] of a lifetime of the order 50 msec, and so we verified our result of 140 μsec by looking for a modulation in the light intensity of luminol cavitated at 14 kHz. Figure 3 shows that this intensity is modulated with peaks corresponding to excited species produced at those two phases of each sound cycle when the main and secondary flashes of sonoluminescence occur (these are attributed

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(1) E. N. Harvey, *J. Amer. Chem. Soc.*, **61**, 2392 (1939).

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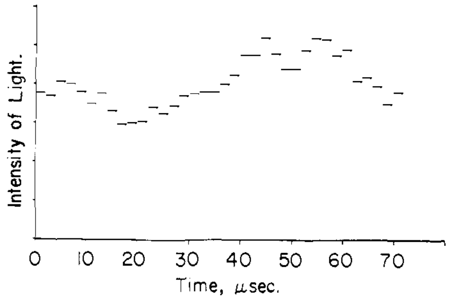

Figure 3. Light intensity distribution over one period of the 14-kHz sound, averaged over many cycles.

to bubble implosions; see ref 9). This modulation implies that the lifetime of the excited species must be comparable with the sound period of 70 μsec; if it were as long as 50 msec, no modulation in the light intensity would have been observed. However, this lifetime is much longer than the time taken for a cavitation bubble to implode and the duration of a sonoluminescence flash, which originates from within the bubble (see ref 10). Therefore, the acoustically induced emission of light from luminol must originate from the liquid surrounding the bubbles, and it can be described as a luminescence identical with that which can be induced chemically.

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The Direct Detection of the Axial Conformer of Methylcyclohexane by 63.1-MHz Carbon-13 Nuclear Magnetic Resonance at Low Temperatures

Sir:

A great deal of work has been done on the conformational equilibria of substituted cyclohexanes.[1] Perhaps the most unambiguous procedure for the determination of the relative amounts of equatorial and axial forms is to measure the nmr spectrum at such low temperatures (*e.g.*, −100°) that separate spectra are given by the two forms.[2] Integration then gives the desired result, provided that peaks do not overlap for all the nuclei under observation. With proton nmr, this method is easy to apply to many monosubstituted cyclohexanes, where (i) the methine proton on C-1 has quite different chemical shifts for the two forms and (ii) the equilibrium constant (K = [equatorial form]/[axial form] is not too large (the largest K which has been measured[2a] has a value of 29).

Methylcyclohexane meets neither of the above two requirements; furthermore, partial deuteration is not expected to solve the peak-overlap problem.[3] Thus there has been no report of the observation of the proton spectrum of the axial form of methylcyclohexane.

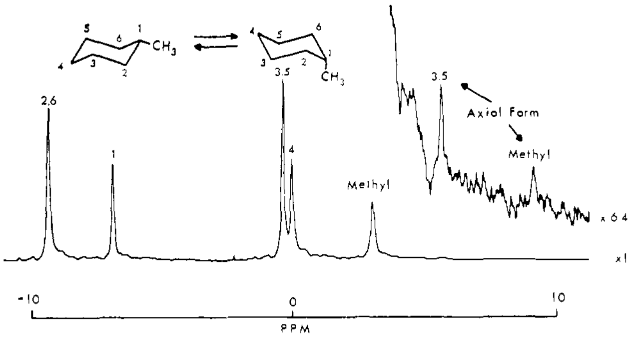

Figure 1. 63.1-MHz ^{13}C spectrum (protons noise decoupled at 251 MHz) of neat methylcyclohexane at −110°. C-4, which is expected to have the same chemical shift in both conformers,[4] was used as an internal reference; zero on this scale is about 102 ppm upfield from benzene and about 27 ppm downfield from TMS. Spinning 10-mm sample tubes were used and the sweep rate was 16 Hz/sec. The spectrum represents 96 scans summed on a Varian CAT.

The work of Dalling and Grant[4] indicates that the ^{13}C chemical shifts of the methyl and the 3- and 5-methylenes in the axial form of methylcyclohexane should be at several parts per million to higher field than the corresponding shifts in the equatorial form.

The 63-MHz ^{13}C nmr spectrum[5] of neat methylcyclohexane at −110° (Figure 1) shows not only the bands of the equatorial form, but also two weak bands of intensity ratio 2:1 at high field. These weak bands are assigned to the methylene (3 and 5) and methyl carbons of the axial form. The chemical shifts of C-3 and C-5 of the axial form are 6 ppm upfield from those of the equatorial form, essentially as predicted by Dalling and Grant.[4] The ^{13}C shift of the axial methyl group is 6 ppm to higher field than that of the equatorial methyl group, also in reasonable agreement with expectations from model compounds.[6]

The weak high-field bands of Figure 1 are not present at −75°, and thus are very unlikely to be due to chemical impurities.[7] Also, at −75°, the strong bands of

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[4] D. K. Dalling and D. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).

[5] Details of the spectrometer, which makes use of a 59-kG superconducting solenoid, will be described elsewhere; *cf.* F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, abstract of paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970. The room temperature ^{13}C spectrum of methylcyclohexane was in agreement with that given in ref 4.

[6] The ^{13}C chemical-shift difference between methyl group in methylcyclohexane at room temperature (weighted average (95:5) of equatorial and axial shifts) and the methyl groups in *cis*-1,4-dimethylcyclohexane (average of equatorial and axial shifts) is 2.66 ppm.[3] Thus the ^{13}C shift difference between an axial and equatorial methyl group should be 5.9 ppm, provided that the methyl groups in *cis*-1,4-dimethylcyclohexane do not influence each other's chemical shifts. On the other hand, if 1-*cis*-3-*trans*-5-trimethylcyclohexane[4] is used as a model a value of 4.1 ppm for this chemical-shift difference is obtained.

[7] The weak band in Figure 1 also cannot be due to spinning side bands since the spinning rate was only about 40 Hz, nor can they be due to $^{13}C-^{13}C$ coupling as such a coupling constant for a sp^3-sp^3 single bond is only about 35 Hz (R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962); K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963); F. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 5962 (1967)).