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CATALYTIC TRITIATION AND ^{3}H NMR SPECTROSCOPY OF COMPLEX ORGANIC MIXTURES - APPLICATION TO ENGINE OIL BASESTOCKS

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SUMMARY

Several catalytic hydrogen-tritium exchange procedures have been investigated in order to accomplish uniform and random incorporation of tritium into the diverse organic components present in two engine oil basestocks. The most successful procedure involved the use of Raney nickel and tritiated water at elevated temperatures. Comparative proton and tritium nuclear magnetic resonance spectroscopy shows that the incorporated tritium was representative of the organic components present in the basestocks. Comparative gas- and radio-gas chromatography studies provided supplementary information. These investigations demonstrate that engine oils can be satisfactorily labelled with tritium for studies of engine oil consumption.

Key Words: isotopic hydrogen exchange, catalytic tritiation, ^{3}H nmr spectroscopy, engine oil basestocks

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INTRODUCTION

During the operation of an internal combustion engine small amounts of lubricating oil pass into the engine's cylinders and are consumed with the engine's charge of fuel. Conventional methods for assessing the consumption of oil depend on either measuring a small mass difference, namely the amount introduced initially minus the remainder after a long period of engine operation (during which time consumption may not necessarily remain stable), or adding known amounts of oil over a similar period so as to maintain the oil level at a fixed value. Both constitute inherently unsatisfactory procedures for which an attractive alternative is required.

Analytical methods based on the use of radioactive isotopes offer high sensitivity and there have been several reports, for instance, (1-4) of their use in measuring oil consumption. Those involving, for example, ^{35}S, ^{65}Zn, ^{82}Br and ^{131}I all suffer from the potential disadvantage that not being truly representative of the oils they may not correctly reflect its rate of consumption. For this to be true one would need to be able to label the individual components of the lubricating oils (mainly hydrocarbons) in proportion to their concentration. To incorporate ^{14}C in this way would be very difficult, if not impossible, so ^{3}H is the preferred choice. An approximation to the above requirement has been achieved (5) by tritiating the oil and then fractionating it into several fractions before these were then recombined with appropriate amounts of corresponding unlabelled fractions to yield a uniformly labelled product. With the development of ^{3}H nmr spectroscopy (6) this is no longer necessary as the oil can be tritiated through the use of one or more catalytic procedures (7) and mere comparison of the ^{1}H and ^{3}H nmr spectra show how closely, or otherwise, the objectives have been achieved. A similar comparison between gas chromatographic and radio-gas chromatographic data provides complementary information. This approach, which has been previously illustrated in an oil shale research project (8,9) seems ideally suited for the complex organic mixtures encountered in engine oil basestocks.

The object of the present investigation was therefore to undertake the tritiation of two oil basestocks (10W/30 and 15W/40) to high specific activity in such a way that the incorporated label is both representative of the total organic material present and located in stable positions. Furthermore the preparations should be readily reproducible and the products free of any artifacts.

Initially both oil basestocks were tritiated by heating the inactive material in the presence of catalyst (pre-reduced PtO_2, Raney nickel, conc. HCl, or 10M NaOH) and tritiated water of 5 Ci ml^{-1} specific activity for a relatively short time (20 h.). Subsequently the experiments were repeated over a much longer time interval. Finally for the most successful catalytic procedures these were repeated using tritiated water of 50 Ci ml^{-1} specific activity. The products of these last reactions were then subjected to both ^1H and ^3H nmr and radio-gas chromatographic analysis.

EXPERIMENTAL

PtO_2 Isotope Exchange Procedure.

A known amount of the oil (50-100 mg) was placed in a narrow glass tube followed by a small quantity (~ 75 mg) of platinum dioxide that had been freshly reduced with sodium borohydride (10) and 5 µl of tritiated water before freezing the tube in liquid nitrogen, evacuating and sealing. After heating at the required temperature for the desired time the tube was cooled and the contents taken up in a few ml of ether. The catalyst was filtered off and the solution twice washed with 1 ml quantities of water in order to remove any labile tritium. After drying over anhydrous sodium sulphate the ether was removed by passing N_2 over the surface. The labelled oil was then normally dissolved in a small quantity of a deuteriated solvent e.g. $CDCl_3$ or C_6D_6, a trace of tetramethylsilane (TMS) added, the radioactivity measured and, if sufficient, the sample sent for ^3H nmr analysis. If the solution was too viscous further dilution with the deuteriated solvent was carried out and some 50 µl of this solution analysed.

Raney Nickel Isotope Exchange Procedure.

The catalyst which was prepared according to the method of Dominguez and Lopez (11), was transferred as a slurry in ethanol (0.05-0.5 ml) to a small tube. Excess ethanol was removed before adding the oil to be labelled (typically 15-100 mg) and tritiated water (5 µl). The contents were cooled with liquid nitrogen, the tube evacuated, and then sealed. After heating at a known temperature for a given time the tube was cooled, opened and the contents taken up in a few ml of ether. The subsequent workup was as for the PtO_2 procedure.

Acid (HCl) and Base (NaOH) Catalysed Isotope Exchange Procedure

To a known amount of the oil (usually 100 mg) in a narrow glass tube was added either 10 µl of concentrated hydrochloric acid or the same quantity of 10 molar sodium hydroxide solution followed by the tritiated water (5 µl). The tube was then sealed and the contents heated for the necessary length of time before working up as described above.

^1H and ^3H NMR Analysis

For ^1H nmr analysis of the inactive oils some 5-10 µl were dissolved in a deuteriated solvent (50 µl, usually $CDCl_3$ or C_6D_6) and a trace of internal standard (tetramethylsilane) added before transferring the solution to a 3 mm diameter tube (Wilmad SK 1374A).

For ^3H nmr analysis (and also ^1H nmr of the radioactive product) the procedure was the same except for the fact that the tube was now sealed. Experience showed that if more than 10 µl of the oil was used the solutions became unduly viscous and the nmr signals broadened considerably. The sealed tube was then mounted in spinner adapters for a 3 mm microprobe and the ^3H nmr spectrum obtained (mostly with ^1H noise decoupling at 25°C) with a Bruker WH90 pulse spectrometer operating at 96MHz for ^3H and with quadrature detection. The flip angle was usually 30°, the repetition interval 1.6 sec and, depending on the radioactivity present, between 10^4 and 10^5 transients were acquired.

The data was stored in 4K channels. Each FID was zero-filled to 8K and Fourier transformed to provide spectral display widths of up to 13 ppm. Referencing was to a ghost reference generated from the ^{1}H resonance frequency of the internal standard (measured at 90MHz) by multiplying by the Larmor ratio (1.06663974).

Gas and Radio-Gas Chromatographic Analysis

The gas chromatograph used was a Carlo Erba 4200 instrument that had been duly modified so that one of the two flame ionisation detectors could be used to detect radioactivity. Details of this modification have been published elsewhere (12). The column used was a 1m x 1/8" SS packed with 5% OV1 on Chromosorb W80-100 mesh.

Stability of the Label

The successful use of the products depends on the label being present in stable positions and ^{3}H nmr spectroscopy can provide this information in a most direct way—the spectra of solutions kept over a period of time are recorded.

RESULTS AND DISCUSSION

The ^{1}H nmr spectra of both oil basestocks were virtually identical, as also were the ^{13}C nmr spectra. The former were deceptively simple (see for example Fig. 1a), showing no sign of either an aromatic or unsaturated presence and characteristic of an aliphatic 'compound' with both CH_3 and CH_2 groups. The ^{13}C nmr spectra were a good deal more informative (see for example Fig. 1b) indicating the complex nature of the oil mixture with some thirteen discernible signals.

The catalytic tritiation studies provided very similar results for both oil basestocks, some of which are presented in Table 1. In the short-term low level tritiation studies Raney Nickel proved to be the most effective and sodium hydroxide the least effective catalyst and when the experiments were

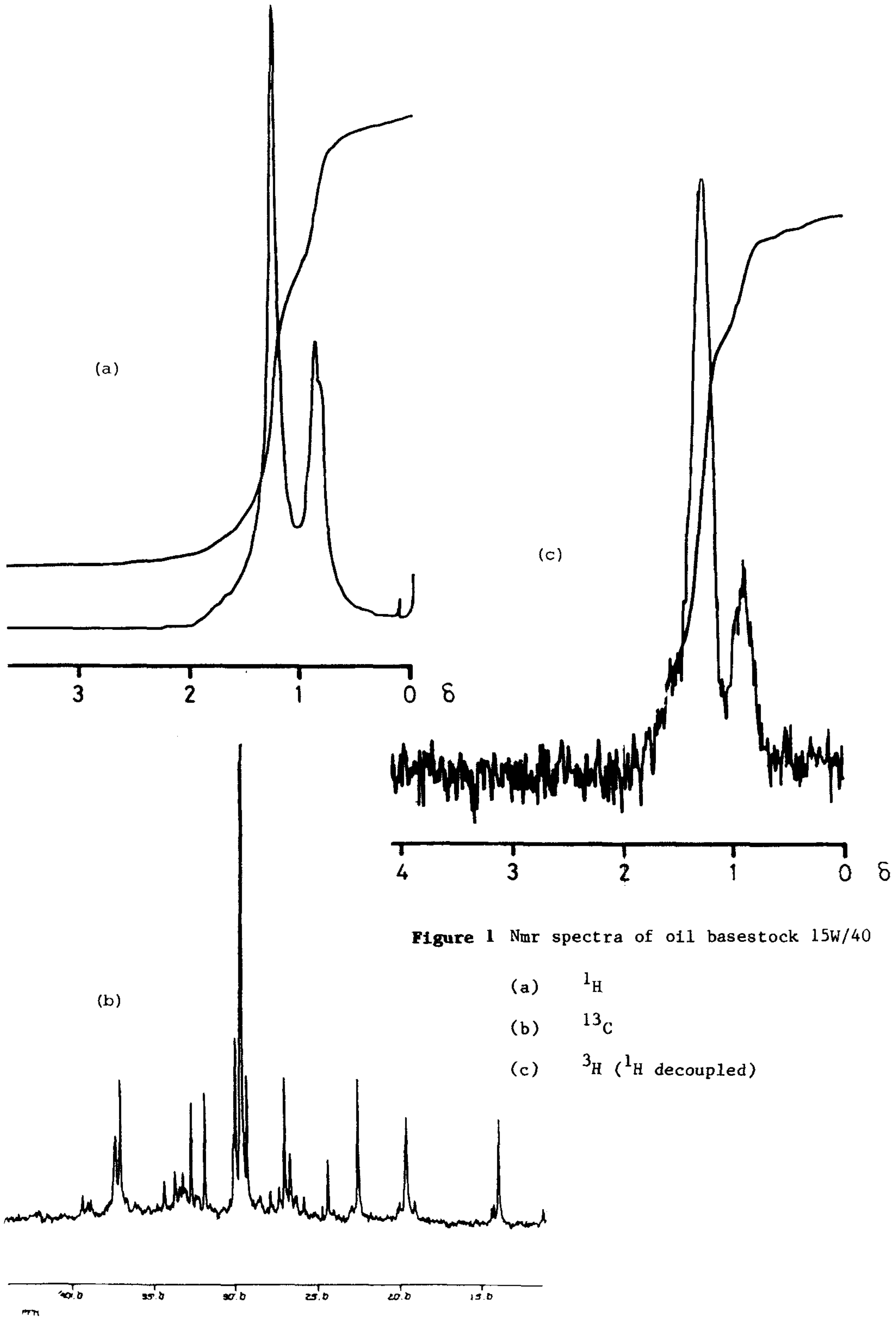

Figure 1 Nmr spectra of oil basestock 15W/40

(a) ^{1}H

(b) ^{13}C

(c) ^{3}H (^{1}H decoupled)

Table 1. Results of Various Catalytic Tritiations

Oil basestock (mg)	**Catalyst**	**Amount**	**HTO**	**Temp °C**	**Time**	**Radioactivit in product**
15W/40 (100)	PtO_2	75mg	5µl	120	20 hrs	5 µCi
"	Raney Nickel	~100mg	"	"	"	198 µCi
"	HCl	10µl.conc	"	"	"	54 µCi
"	NaOH	10µl of 10M	"	"	"	3 µCi
10W/30 (100)	Raney Nickel	~100mg	"	"	"	95 µCi
"	" "	"	"	150-180	4 weeks + 6 weeks at room temperature	6.0 mCi
" (50)	" "	~50mg	"*	"	8 weeks	26 mCi
15W/40 (50)	" "	"	"*	"	" "	30 mCi
" (25)	" "	"	"*	"	" "	12 mCi

* 50 Ci ml^{-1}, in all other cases 5 Ci ml^{-1}

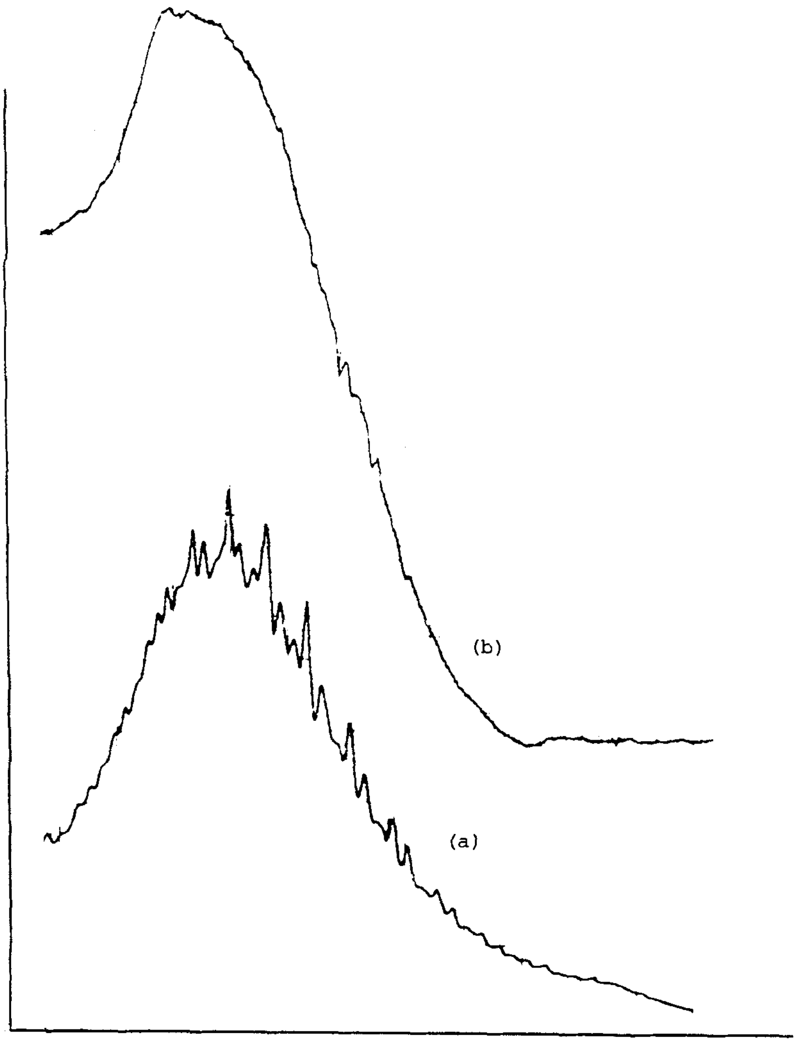

Figure 2 Gas chromatogram (a) and radio-gas chromatograph (b) of oil basestock 15W/40

extended over a longer period the results for Raney Nickel were again best. Using the high level tritiated water it was possible to produce some 10-30 mCi of product, more than sufficient for a ^{3}H nmr spectrum even allowing for the fact that the high viscosity permitted the use of only 10-20% of the product. The result in Figure 1c shows that the two large signals effectively reproduce those in the corresponding ^{1}H nmr spectrum with the same relative intensities. The Raney Nickel method is therefore able to achieve the objectives as set out, very much in the same way as it did for the diverse organic solutes present in an oil shale process water (8,9).

Despite its unique application for elucidating the radiochemical character of a sample, nmr spectroscopy is relatively insensitive to the analysis of multicomponent mixtures and radiochromatographic methods must be used to substantiate the relationship of incorporated radioactivity and concentration of constituents. The gas chromatogram of oil basestock 15W/40 (Fig. 2a) illustrates the difficulty associated with the separation of a large number of similar hydrocarbons. Although the broad peak contains some sign of fine structure the corresponding radio-gas chromatogram (Fig. 2b) shows even less. The radioactivity is clearly associated with the main components of the oil basestock but only when a better separation can be achieved will it be possible to comment in detail on the relationship between radioactivity and the concentration of individual components. In this respect the present oil basestock study is more demanding than the previously reported oil shale project (9).

Finally, monitoring of the ^{3}H nmr spectra of samples of both oil basestocks over a period of approximately 6 months failed to reveal any release of tritium (as tritiated water) or the formation of other products. Clearly both products satisfy the specified requirements and provide another example of the possible use of complex labelled mixtures.

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