

PARAMAGNETICALLY REDUCED CARBON-13 RELAXATION TIMES
OF HYDROCARBON TYPES: AN AID TO THE QUANTITATIVE
ANALYSES OF SHALE OIL-DERIVED JET FUELS

D. M. Barnhart* and D. A. Netzel

U.S. Department of Energy
Laramie Energy Technology Center
P. O. Box 3395, University Station
Laramie, Wyo. 82071

ABSTRACT

The study includes determining the carbon-13 paramagnetically reduced spin-lattice relaxation times of representative hydrocarbon types, of a model mixture of hydrocarbon types and of an aromatic hydrocarbon added to syncrude JP-4 jet fuel. The paramagnetic relaxation reagent chromium acetylacetonate (CrAcAc) was used in all systems.

The limit of solubility of CrAcAc in 3 ml of jet fuel and 2 ml of CDCl_3 was found to be approximately 0.07 M. Using this concentration, the ^{13}C spin-lattice relaxation times (T_1) of aromatic compounds range from 0.5 to 0.9 seconds, and for n-alkanes the range was found to be 0.9 to 1.8 seconds. A concentration of 0.04 M CrAcAc was used for analytical analysis of average molecular structure parameters of syncrude JP-4 and four other jet fuels. This concentration was below the solubility limit and yet does not appreciably increase the T_1 values or the overall experimental time. The mole percent as determined by NMR of aromatics and alkanes found in syncrude JP-4 jet fuel was found to agree with mass spectral data.

INTRODUCTION

For several years the Department of Defense in cooperation with the Department of Energy has had research programs aimed at characterizing and evaluating liquid hydrocarbon fuels obtained from various fossil sources because the chemical composition of a jet fuel affects jet engine performance, power output, engine life, and operation cost. A number of techniques have been used with some degree of success to characterize hydrocarbon fuels. However, most techniques require a substantial amount of time and require the samples to be fractionated into various hydrocarbon types.

Carbon-13 and proton nuclear magnetic resonance spectroscopy (NMR) can be rapid and can be performed on either the total sample or its fractions. The technique has been used extensively to characterize various fossil fuels in terms of average molecular structure parameters¹⁻³, and thus NMR was chosen to characterize samples of jet fuels.

*Associated Western Universities faculty appointee from Eastern Montana College, Billings, Montana 59101

To use ^{13}C effectively as an analytical technique, the long spin-lattice relaxation times and variable nuclear Overhauser enhancement factor (NOE) for carbon atoms in molecules generally comprising jet fuels must be reduced or eliminated.

Spin-lattice relaxation times can be reduced, thereby reducing the experimental time, by using relaxation reagents⁴⁻⁹. Concurrent with the use of relaxation reagents is the near elimination of the NOE effect which, when present, prevents direct correlation of the area of the resonance peaks with the number of carbon atoms. The effects of relaxation reagents on quantitative analysis of complex mixtures such as petroleum crudes have been conducted^{10,11}. The results of these studies have shown that relaxation reagents are necessary for quantitative analyses if the analyses are to be performed in a reasonable time.

In this investigation, the effects of the relaxation reagent, chromium acetylacetonate (CrAcAc) on the carbon-13 relaxation times of carbon atoms in model compounds, a mixture of several model compounds, and a model compound in jet fuel were measured. Concentration levels of CrAcAc used in the relaxation study were limited to the solubility of CrAcAc in jet fuel. From the knowledge of relaxation times of model compounds in the presence of CrAcAc, optimal instrumental conditions were determined.

EXPERIMENTAL

Nuclear Magnetic Resonance

Carbon-13 spin-lattice relaxation times were determined on a Varian CFT-20 NMR spectrometer, using the standard inversion-recovery pulse sequence, $180^\circ\text{-}\tau\text{-}90^\circ\text{-T}$, where T is the delay time (in seconds) between the pulse sequence and τ is the time (in seconds) between the inversion pulse (180°) and the measuring pulse (90°). Relaxation times were calculated using a nonrectilinear, two-parameter exponential regression technique with the maximum signal amplitude fixed.

A JEOL FX-270 superconducting NMR spectrometer was used to obtain proton and gated proton decoupled carbon-13 spectra used in quantitative analysis of mixtures and jet fuels. Pulse widths of 8 μsec (15 μsec 90°) and 5 μsec (14 μsec = 90°) were used for carbon-13 and proton spectra, respectively. Six seconds was used for the pulse delay for carbon-13 spectra and 2.5 seconds for proton spectra. Broadband proton decoupling gated ON during data acquisition was used for carbon-13 spectra to suppress the nuclear Overhauser effect.

Sample Source and Preparation

All hydrocarbon solutions were prepared using reagent-grade compounds dissolved in CDCl_3 . The relaxation measurements were made without vacuum degassing of the samples. The relaxation reagent, chromium acetylacetonate, was purchased from Alpha Products and used as received. Jet fuel samples were received from Wright-Patterson Air Force Base (WPAFB). All jet fuel samples were prepared using a standard

stock solution of 0.1 M CrAcAc in CDCl_3 . Two milliliters of this solution was syringe pipetted into a 5-ml volumetric flask, and fuel was added to the 5-ml level. All samples were then filtered via a syringe and 5- μ Teflon millipore filter into a 10-mm NMR tube.

RESULTS AND DISCUSSION

The carbon-13 spin-lattice relaxation times (T_1) for organic compounds range generally from 5 to 200 seconds. Relaxation times for ipso and bridged carbons of aromatic hydrocarbons are among the highest observed. Two methods are often used to overcome the problem of long relaxation times. One method is to reduce the pulse to a value between 45° and 75° , which in effect reduces the pulse delay time necessary to achieve spin equilibrium. A shorter delay time allows for faster pulsing. However, a pulse less than 90° reduces the signal intensity, and thus more pulses (additional time) will be necessary to achieve the desired S/N ratio. Optimum parameters of pulse Fourier transform NMR are discussed by Becker et al.¹². A second method is the addition of a paramagnetic relaxation reagent to the solution. Depending upon the concentration of the relaxation reagent, relaxation times of the order of 100 seconds can be reduced to a few seconds. Thus, short pulse delay times can be used, which in turn allows for shorter total time to achieve the desired S/N ratio. The disadvantages of using relaxation reagents are signal broadening, difficulties associated with the removal from the solution if recovery of the original solution is necessary, the relatively low solubility of the relaxation reagents in organic solutions, and the lower S/N ratio due to the absence of the NOE effect.

The solubility limit of the relaxation reagent in a given solution dictates the maximum amount of reduction in the observed relaxation time, and this in turn determines the overall experimental time necessary to obtain good S/N ratios for quantitative analysis.

The relaxation reagent, chromium acetylacetonate, is only partially soluble in a mixture of CHCl_3 and jet fuel. To determine the pulse delay time for a 90° pulse (maximum sensitivity) necessary to acquire quantitative results in the shortest possible time, two experiments were conducted: 1) the solubility of CrAcAc in a mixture of CHCl_3 and syncrude JP-4 jet fuel of various ratios was determined and 2) the maximum molar concentration of CrAcAc found for the mixture of CHCl_3 and jet fuel in the first experiment was used to study the reduction effect of CrAcAc on the carbon-13 relaxation times of model compounds of the types which could be found in jet fuels. With this information, a pulse delay time could be determined for a given ratio of CHCl_3 and jet fuel which would give good S/N ratio in the shortest possible time for quantitative determinations. The limit of solubility of CrAcAc in 3 ml of jet fuel and 2 ml of CDCl_3 was found to be approximately 0.07 M.

Relaxation Studies. - Table I lists the ^{13}C spin-lattice relaxation times for (1) the model compounds used in this study, (2) a mixture of several model compounds, and (3) 2,6-dimethylnaphthalene in syncrude JP-4 jet fuel. Also included in the table are the ^{13}C relaxation times of the carbon atoms in n-hexane and in 2,6-dimethylnaphthalene as a function of the molarity of CrAcAc. Carbon-13 chemical shifts for the

model compounds in CDCl_3 with and without the addition of CrAcAc are also listed in Table I.

The relaxation times measured in this study were determined without degassing of the samples. The literature values of the relaxation times for the carbon atoms in the model compounds were, for the most part, determined under more exacting conditions and represent the longest possible relaxation times.

A survey of the data in Table I indicates that CrAcAc at a concentration of about 0.073 M reduces all ^{13}C relaxation times of aromatic compounds to values ranging from 0.5 to 0.9 seconds. For n-alkanes using 0.073 M CrAcAc , the ^{13}C relaxation times range from .9 to 1.8 seconds. CrAcAc has less effect on alkanes than aromatics, which is to be expected because of the type of bonding orbitals associated with the two classes of compounds.

The concentration effects of CrAcAc on the relaxation times of n-hexane and 2,6-dimethylnaphthalene were determined and are shown in Figure 1. For comparison, the ^{13}C relaxation time for benzene¹³ as a function of the molar concentration of CrAcAc is also given in Figure 1. It is seen from both Table I and Figure 1 that all relaxation times for aromatic carbons as well as the substituted alkyl carbons have, in general, the same dependency on the molar concentration of CrAcAc . Thus, it is possible to establish the pulse delay time ($5T_1$) for any given concentration of CrAcAc necessary to give quantitative useful ^{13}C NMR spectra.

Two additional experiments were conducted to determine whether or not the paramagnetically reduced relaxation times are significantly different for 1) a mixture of model compounds and 2) a model compound in syncrude JP-4 jet fuel. Table I lists the ^{13}C relaxation times observed for the model mixture containing n-hexane, 1-ethyl-2-methylbenzene, and 2,6-dimethylnaphthalene in CDCl_3 and containing 0.072 molar CrAcAc . As expected, the relaxation times for the carbon atoms of n-hexane and 2,6-dimethylnaphthalene in the mixture varied little from the values obtained for the individual compounds. However, the T_1 values for 1-ethyl-2-methylbenzene appear to be slightly higher than expected. The differences in T_1 observed (10 to 30 percent) are most likely due to differences in CrAcAc concentration and sample preparation.

The paramagnetically reduced relaxation times for carbon atoms of 2,6-dimethylnaphthalene in syncrude JP-4 jet fuel produced from shale oil differ only slightly (~15 to 20 percent) from values obtained for the pure compound. Crude shale oils contain appreciable amounts of free radicals, and any contribution of the paramagnetic effects of free radicals which may or may not exist in refined jet fuel on the ^{13}C relaxation time of 2,6-dimethylnaphthalene is minimal.

Quantitative Analysis. - Since shale oil-derived jet fuels are complex mixtures of aromatic and aliphatic compounds, conditions established for quantitative NMR were performed on the previously mentioned model mixture of approximate mole fraction ratios of 0.1:0.25:0.65 for 2,6-dimethylnaphthalene, 1-ethyl-2-methylbenzene and n-hexane, respectively.

With accurate weighing, the ^1H and ^{13}C NMR spectral areas could be predicted by direct counting of the various hydrogens and carbons in different site positions for the three types of molecules comprising the mixture. This mixture was also subjected to direct analysis by both ^1H and ^{13}C NMR spectroscopy.

Syncrude JP-4 jet fuel has been extensively studied previously in this laboratory by both NMR and mass-spectral techniques¹⁴ and elsewhere by NMR¹⁵. The structural parameters¹⁴ for this fuel are considered to be fairly well known, and therefore quantitative NMR analysis with and without CrAcAc under the same instrumental conditions was used to confirm the applicability of the method to jet fuel analysis. Table II lists the NMR structural parameters for syncrude JP-4 jet fuel with and without CrAcAc. Also listed are the mass spectral data for comparison. The mass spectral data were obtained using a modified version of the ASTM procedure D2781-71 and are in volume percent; whereas the NMR data are reported in mole percent. For aromatic and alkane hydrocarbons, a nearly 1:1 correspondence exists between mole percent and volume percent¹⁴. The data in Table II show that the jet fuel sample containing CrAcAc gives results that agree closely with mass spectral data. Table III lists the NMR structural parameters for four additional jet fuel samples.

CONCLUSIONS

The limit of solubility of CrAcAc in 3 ml of jet fuel and 2 ml of CDCl_3 was found to be approximately 0.07 M. Using this concentration, the ^{13}C spin-lattice relaxation times (T_1) of aromatic compounds range from 0.5 to 0.9 seconds, and for n-alkanes the range was found to be 0.9 to 1.8 seconds. A concentration of 0.04 M CrAcAc was used for analytical analysis of average molecular structure parameters of syncrude JP-4 and four other jet fuels. This concentration was below the solubility limit and yet does not appreciably increase the T_1 values on the overall experimental time. The mole percent as determined by NMR of aromatics and alkanes found in syncrude JP-4 jet fuel was found to agree with mass spectral data.

REFERENCES

1. Clutter, D. R., Petrakis, L., Stenger, R. L., Jr., and Jenson, R. K., Anal. Chem., 1972, 44, 1395.
2. Cantor, D. M., Anal. Chem., 1978, 50, 1185.
3. Gillet, S., Rubini, P., Delpuech, J., Escalier, J., and Valentin, P., Fuel, 1981, 60, 221.
4. Levy, G. C., and Edlund, U., J. Am. Chem. Soc., 1975, 97, 4482.
5. Gansow, O. A., and Burke, A. R., J. C. S. Chem. Comm. 1972, 456.

6. LaMar, G. N., J. Am. Chem. Soc., 1971, 93, 1040.
7. Barcza, S., and Engstrom, N., J. Am. Chem. Soc., 1972, 94, 1762.
8. Levy, G. C., Edlund, U., and Hexem, J. G., J. Magn. Reson. 1975, 19, 259.
9. Freeman, R., Pachler, K. G. R., and LaMar, G. N., J. Chem. Phys., 1971, 55, 4586.
10. Shoolery, J. H., and Budde, W. L., Anal. Chem., 1976, 48, 1458.
11. Thiault, B., and Mersseman, M., Org. Magn. Resonance, 1976, 8, 28.
12. Becker, E. D., Ferretti, J. A., and Gambhir, P. N., Anal. Chem., 1979, 51, 1413.
13. JEOL Technical Bulletin NBS-11, 1977, 10.
14. Netzel, D. A., and Hunter, P. M., Report of Investigation, DOE/LETC/RI-81-1.
15. Dorn, H. C., Final Progress Report for the Period March 23, 1978 to August 30, 1979, Under Naval Research Laboratory Contract No. N0012-78-0424. Available from National Technical Information Service, U.S. Dept. of Commerce, 5285 Port Royal Circle, Springfield, VA 22161

ACKNOWLEDGMENT

This work was partially supported by contract (MIPR FY1455-81-NO619) with the Air Force Aero Propulsion Laboratory, Wright-Patterson AFB.

DISCLAIMER

Mention of specific brand names or models of equipment is made for information only and does not imply endorsement by the Department of Energy.

TABLE I. - Carbon-13 chemical shifts and spin-lattice relaxation times for model compounds

Compound	Carbon position	¹³ C chemical shift (ppm) ^{a, b}		¹³ C Spin-lattice relaxation time (sec.)						
		with CrAcAc	without CrAcAc							
n-Hexane	1	14.15	14.22	0.000 M ^c	0.210 M	0.041 M	0.073 M	0.121 M	0.072 M	
	2	22.88	23.02	14.75 ± .69 ^d	4.54 ± .11	2.37 ± .02	1.55 ± .04	1.04 ± .06	1.25 ± .05	
	3	31.86	32.00	14.78 ± .99	4.44 ± .08	2.27 ± .04	1.68 ± .01	0.94 ± .02	1.85 ± .16	
n-Dodecane	1	14.14						0.072 M		
	2	22.83						1.20 ± .03		
	3	32.09						1.19 ± .02		
	4	29.52						1.29 ± .02		
	5,6	29.83						0.88 ± .02		1.03 ± .02
Tetralin	1,2	136.91						0.073 M		
	3,6	129.09						0.94 ± .05		
	4,5	125.44						0.81 ± .07		
	o-CH ₂	29.45						0.75 ± .06		
	p-CH ₂	23.39						0.74 ± .02		
1-Ethyl-2-methylbenzene	1	135.59	135.64					0.075 M		0.072 M
	2	142.21	142.33					0.89 ± .02		1.23 ± .08
	3	130.08	130.29					0.97 ± .07		1.25 ± .08
	4	126.09	126.33					0.93 ± .06		0.07 ± .08
	5	125.70	126.02					0.78 ± .05		1.03 ± .03
	6	127.93	128.10					0.77 ± .06		1.16 ± .06
	o-CH ₂	19.06	19.16					0.87 ± .03		1.10 ± .06
2,6-Dimethylnaphthalene	o-CH ₂	26.24	26.49					0.87 ± .03		0.87 ± .03
	p-CH ₂	14.42	14.54					0.78 ± .03		1.14 ± .05
	1,5	127.05	127.40	0.024 M	0.045 M	0.078 M		0.072 M	0.042 M	
	2,6	134.34	134.41	1.59 ± .03	1.10 ± .04	0.71 ± .03		0.84 ± .02	1.12 ± .03	
	3,7	126.58	126.52	2.47 ± .06	1.43 ± .03	0.92 ± .03		0.96 ± .08	1.31 ± .03	
Acenaphthene	4,8	128.08	128.25	1.79 ± .05	1.10 ± .04	0.76 ± .03		0.97 ± .04	1.29 ± .04	
	9,10	131.96	132.45	1.69 ± .02	1.07 ± .02	0.73 ± .04		0.80 ± .06	0.98 ± .04	
	o-CH ₂	21.52	21.66	2.70 ± .06	1.45 ± .05	0.84 ± .05		0.99 ± .07	1.17 ± .05	
	1,8	145.91		1.81 ± .04	1.26 ± .02	0.81 ± .02		0.88 ± .06	1.01 ± .03	
	2,7	119.10								
Acenaphthalene	3,6	127.72						0.072 M		
	4,5	122.19		0.000 M				0.55 ± .07		
	9	139.28		0.70 ^e				0.54 ± .06		
	10	131.62		5.6				0.58 ± .05		
	o-CH ₂	30.27		5.6				0.54 ± .05		
Acenaphthalene	1,0	139.55						0.075 M		
	2,7	124.02						0.75 ± .02		
	3,6	127.57						0.59 ± .03		
	4,5	126.08						0.63 ± .01		
	9	128.17						0.65 ± .01		
	10	127.99						0.83 ± .05		
	11,12	129.25						0.74 ± .01		
							0.70 ± .02			

^aRelative to tetramethylsilane (TMS)

^bIn COCl₂

^cMolarity of CrAcAc

^dH. J. M. Dirksal et al., J. C. S. Chem. Comm., 1973, 757.

^eT. D. Alger et al., J. Phys. Chem., 1980, 84, 632.

TABLE II. - Average molecular structure parameters and mole percent aromatics and alkanes for syncrude JP-4 jet fuel with and without CrAcAc

	Without CrAcAc	With 0.04 M CrAcAc	Mass spectral ^a data
Hydrogen aromaticity	.037	.045	
Carbon aromaticity	.108	.113	
Mole percent aromatics	12.4	11.1	11.4
Percent mono-	12.4	8.8	11.4
Percent di-	.0	2.3	0.0
Fraction of substituted and bridged carbons	.03	.02	
Fraction of unsubstituted carbons	.07	.09	
Mole percent alkanes	87.6	88.9	88.6
Fraction of n-alkanes	.54	.56	
Fraction of branched alkanes	.46	.44	
CH ₂ /CH ₃ ratio	1.9	2.1	
Carbon chain length	9.0	8.3	
Total atomic H/C ratio	2.02	2.02	
Aromatic H/C ratio	.69	.80	
Alkane H/C ratio	2.18	2.17	

^aVolume percent

TABLE III. - Average molecular structure parameters and mole percent aromatics and alkanes for NASA jet fuels^a

	VN-80-71 ERBS-35	VN-80-72 ERBS-3B	VN-80-73 3B-11.8	VN-80-74 3B-12.1
Hydrogen aromaticity	.252	.050	.144	.111
Carbon aromaticity	.550	.190	.385	.288
Mole percent aromatics	82.3	19.7	45.2	33.4
Percent mono-	69.8	15.0	34.8	25.5
Percent di-	12.4	4.7	10.4	7.9
Fraction of substituted and bridged carbons	.0	.0	.0	.0
Fraction of unsubstituted carbons	.23	.10	.15	.10
Mole percent alkanes	17.7	80.4	54.8	66.6
Fraction of n-alkanes	.30	.46	.40	.37
Fraction of branched alkanes	.70	.54	.60	.63
CH ₂ /CH ₃ ratio	.72	1.9	1.8	1.9
Carbon chain length	11.3	10.0	10.4	7.6
Total atomic H/C ratio	1.38	1.77	1.60	1.68
Aromatic H/C ratio	.58	.47	.60	.65
Alkane H/C ratio	2.35	2.08	2.23	2.10

^aContains .04 M CrAcAc

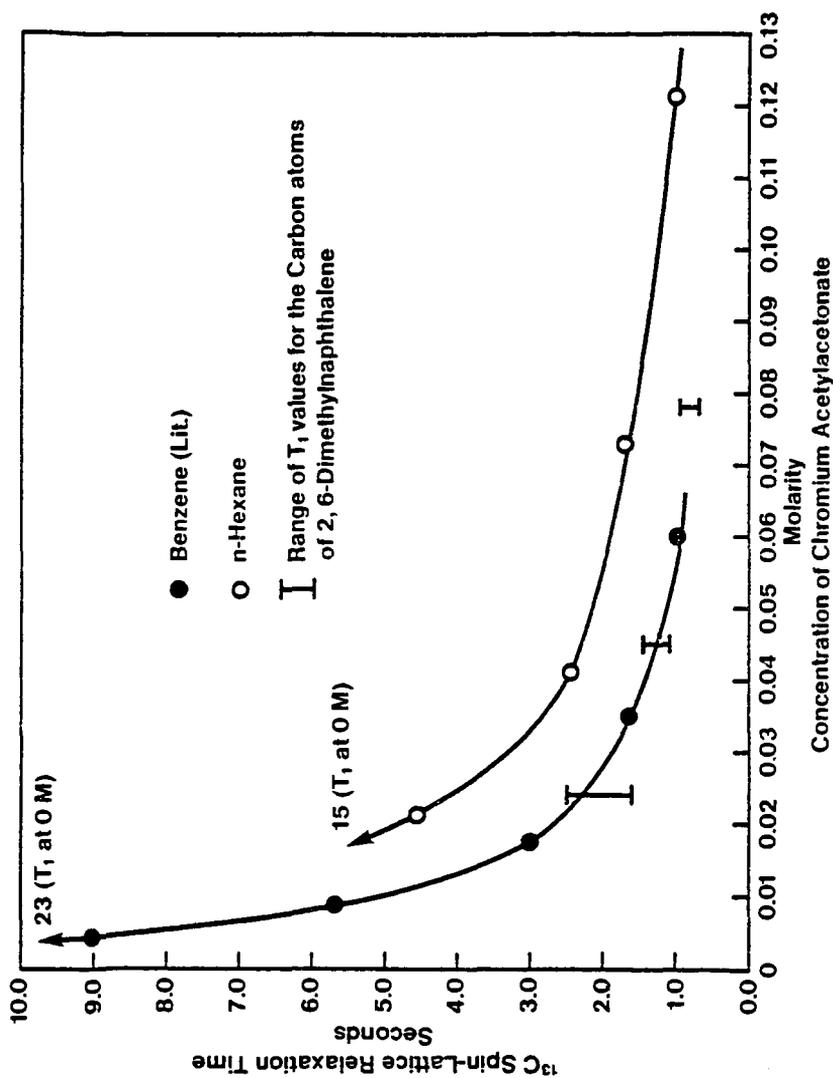


FIGURE 1. - Spin-Lattice Relaxation Times for Hydrocarbons as a Function of the Concentration of Chromium Acetylacetonate