

BTFA(8), and PACA(10) between 2.65 and 2.78; FTFA(6) is slightly lower at 2.42.

The two Class C compounds show somewhat different behavior. DBM(2) is linear only to about 75 kbars and becomes independent of pressure above 120 kbars. On the other hand, DPM(3) is linear to 120 kbars. The conversion continues to increase thereafter, but at a much reduced rate. The high pressure behavior of FTFA(6), with the distinct leveling above 135 kbars, is intermediate between DPM(3) and DBM(2).

It appears from the $\log K$ - $\log P$ plots that there is a tendency for conversions to converge at high pressures. Thus derivatives with large initial conversions have small slopes and vice versa. This is demonstrated quite well in a plot of $\log A$ vs M in Fig. 15.

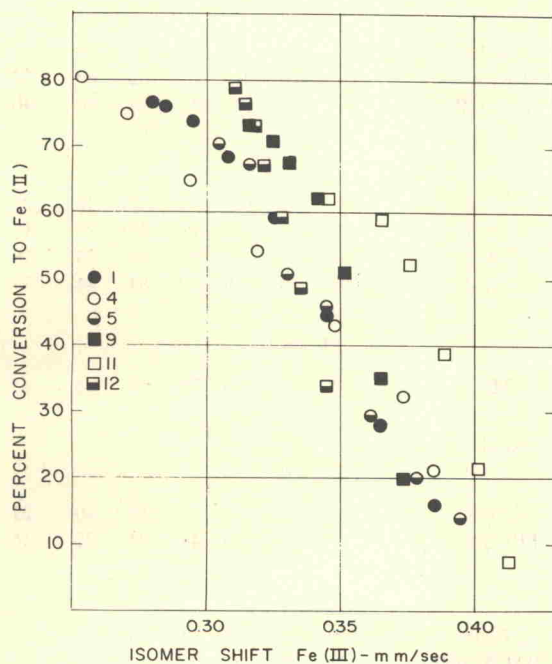


Fig. 16. Conversions vs isomer shift—Class A compounds.

All of the derivatives may be fit with a straight line. Such a correlation is noteworthy because the values of A and M cover large portions of the ranges found between ionic and covalent systems. As shown earlier, the electron donor ability decreases in the order $[DPM(3), MACA(9), PACA(10), EACA(12)] > [ACA(1), DBM(2), BA(4)] > [TFACA(5), FTFA(6), TTFA(7), BTFA(8), NACA(11)]$ where the members of each general group have been arbitrarily arranged in order of their reference codes. Good electron donating groups, with the exception of PACA(10), tend to have large A and small M values; electron donors of intermediate strength have intermediate A and M parameters; and poor electron donors have small A and large M values.

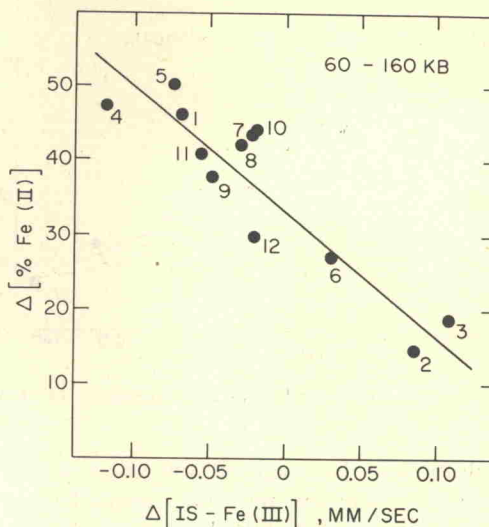


Fig. 17. Δ Conversion vs -isomer shift 60 to 160 kbars.

To the extent that the absolute value of the ferric isomer shift is a measure of the tendency of the ligand to enhance thermal electron transfer, it should be possible to correlate the Fe(III) isomer shifts and the extent of conversion to Fe(II). Class A derivatives, which are characterized as generally poor π acceptors with a range of σ donor properties, are plotted in this form of correlation in Fig. 16. There is some scatter but it is clear that, for this group of compounds, a high isomer shift (low electron density) may be associated with a small conversion and a low isomer shift (high electron density) with a high conversion. The derivative which deviates most from the rest of the compounds, NACA(11), typically shows dissimilar behavior in all of its Mössbauer parameters, perhaps due to resonance effects associated with the nitro group.

There is a reasonable correlation between isomer shift and conversion for the Class A compounds. However, as can be seen from Fig. 17, there is an excellent correlation for all twelve compounds for the *change* of

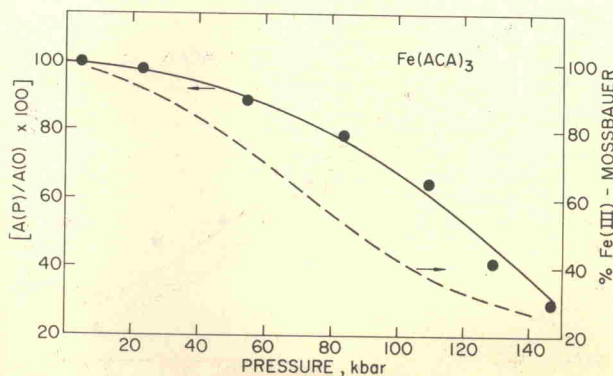


Fig. 18. Relative area under CT_1 peak vs pressure—ACA(1).

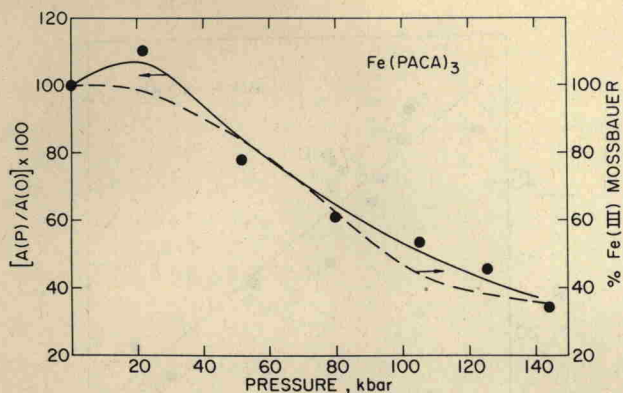


FIG. 19. Relative area under CT_1 peak vs pressure—TFACA(5).

isomer shift over the range 60–160 kbars vs the *increase* in conversion over the same range. The isomer shift depends, as discussed earlier, on a complex mixture of σ and π overlap. The conversion depends only on the location of the ligand π orbitals vis a vis the metal d_π orbitals. While the change in isomer shift with pressure contains both σ and π elements, it is apparent that the *relative* values of the change measure quite accurately the *relative* increase in availability (among the compounds) of the ligand π electrons, as the pressure increases.

Optical Spectra

Much consideration has been given to the assignment of the peaks (or band centers) of the ligand anions^{34–36} and of their iron chelates.^{37–48} The situation can best be explained by reference to the observed peaks in ferric acetylacetonate. There is general agreement that the high energy peaks at 235 and 272 $m\mu$ are intraligand ($\pi \rightarrow \pi^*$) transitions. There are two bands of slightly lower, but still high, intensity ($\log \epsilon \sim 3.5$) at 351 $m\mu$ and 431 $m\mu$. These are almost certainly associated with charge transfer as they do not appear in the ligand spectrum. A number of authors^{41,42,44–46,48} have assigned the higher energy peak to metal to

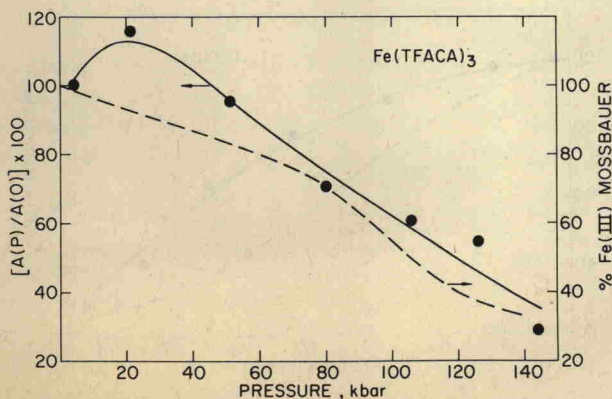


FIG. 20. Relative area under CT_1 peak vs pressure—PACA(10).

ligand ($t_{2g} \rightarrow \pi_4^*$) electron transfer possibly with some admixture of $\pi \rightarrow \pi^*$ character.

The second charge transfer peak at 431 $m\mu$ is the only one which has aroused appreciable controversy. Barnum^{39,40} noted that $n \rightarrow t_{2g}$ and $n \rightarrow e_g$ as well as four $\pi_3 \rightarrow t_{2g}$ transitions were possible but did not make any assignment; in fact, he assumed the $\pi_3 \rightarrow t_{2g}$ transitions were forbidden. Murakami and Nakamura⁴¹ assigned the 431 $m\mu$ peak to an $n \rightarrow e_g$ transition from the oxygen

TABLE V. Relative area of optical charge transfer bands.

Derivative	Pressure (kbar)						
	20	40	60	80	100	120	140
A- CT_1 band							
Class A							
ACA(1) ^a	98	94	88	79	68	53	37
TFACA(5) ^a	113	104	89	75	62	49	37
MACA(9) ^a	111	108	101	91	78	60	40
Class B							
FTFA(6) ^a	111	112	100	78	57	38	20
TTFA(7) ^a	99	86	65	48	35	25	17
BTFA(8) ^a	107	93	78	63	48	33	18
PACA(10) ^b	107	94	78	65	53	44	37
Class C							
DPM(3) ^a	108	102	90	79	68	56	45
B- CT_2 band							
Class A							
ACA(1) ^c	100	98	92	77	58	40	21
TFACA(5) ^c	99	84	63	44	31	22	(16)
Class B							
BTFA(8) ^a	109	105	86	64	(41)		
PACA(10) ^c	101	92	82	72	(62)		
Class C							
DPM(3) ^a	111	82	48	14			

^a Normalized at 4 kbar.

^b Normalized at 1 atm.

^c Normalized at 22 kbar.

nonbonding electrons. This was concurred with by Singh and Sahai⁴² but Lintvedt and Kernitsky,⁴⁸ while agreeing that it was a reasonable assignment, concluded that the ground state should contain both oxygen nonbonding and π components. Hanazaki, *et al.*^{45,46} on the other hand, assigned the 431 $m\mu$ peak predominantly to $t_{2g} \rightarrow \pi_4^*$ character with a small amount of admixed locally excited triplet configuration. Grobely *et al.*⁴⁴ also attribute $t_{2g} \rightarrow \pi_4^*$ character to the 431 $m\mu$ peak. Still one more interpretation was given by Mathews,⁴³ who treated two other iron chelates,