It is convenient to group the derivatives studied into smaller classes (A, B, and C) so that the pressure behavior may be discussed. These classifications are based on the isomer shift behavior of both oxidation states as a function of pressure above 40–50 kbars. They are not rigid, e.g., at low pressures PACA(10) is more like a Class A compound and at high pressures FTFA(6) approaches Class C behavior.

Similarities in behavior of the Fe(II) isomer shifts which lead to classifications will be considered first, followed by an examination of the consistencies in the Fe(III) isomer shifts.

Some interesting observations may be made if smoothed data for all the derivatives are plotted on a single figure as shown in Fig. 7. The six derivatives drawn with solid curves, ACA(1), BA(4), TFACA(5), MACA(9), NACA(11), and EACA(12) will be referred to as Class A. These are closely grouped at low pressures with Fe(II) isomer shifts in the range 1.26–1.32 mm/sec, typical of systems with little or no metal-to-ligand backdonation.
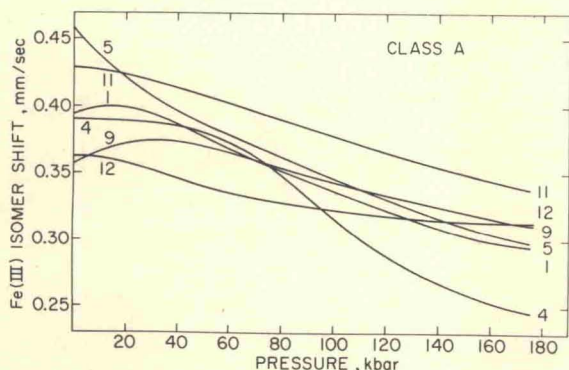

Fig. 8. Fe(III) isomer shifts vs pressure—Class A.

On the basis of Fe(II) isomer shift data, the members of the second class are FTFA(6), TTFA(7), BTFA(8), and PACA(10). The Class B derivatives have distinctly smaller low pressure Fe(II) isomer shifts (1.06–1.14 mm/sec) than the members of Class A. Such values indicate a considerably larger backdonation. However, the decrease of Fe(II) isomer shifts with pressure is not nearly as large as Class A; the final values lie between 0.99–1.06 mm/sec. This is due to a reduction in backdonation as explained in the following section on Fe(III) isomer shifts. Fe(III) isomer shift data for FTFA(6) and PACA(10) are somewhat atypical for this group. The former exhibits properties similar to Class C at high pressure and the latter to Class A at low pressure. Nevertheless, this grouping will be retained for purpose of discussion.

The final grouping of DBM(2) and DPM(3) in Class C appears somewhat arbitrary on the basis of Fe(II) isomer shift data. However, the classification may be rationalized on the basis of Fe(III) isomer
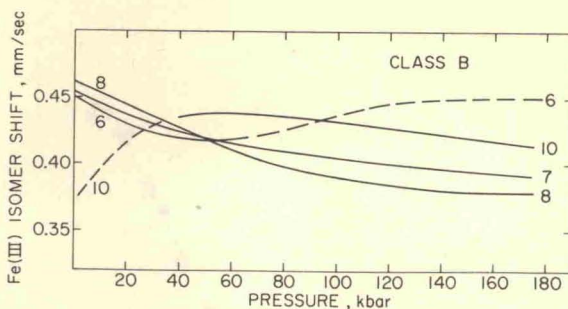

Fig. 9. Fe(III) isomer shifts vs pressure—Class B.

shifts. Although both DBM(2) and DPM(3) show lower Fe(II) isomer shifts than members of Class A, their smoothed values completely bracket those of Class B. The very low Fe(II) isomer shift of DBM(2) indicates rather extensive backdonation to the aromatic terminal substituents. Certainly the tertiary butyl groups in DPM(3) would not allow for as much delocalization.

The pressure behavior of Fe(III) isomer shifts can now be considered in terms of consistencies with and deviations from the classification which has been presented. The smoothed values for all of the derivatives are arranged by classes in Figs. 8, 9, and 10. The ability of the Fe(III) isomer shift to reflect the electron donor tendencies of the surrounding ligands, at least in the low pressure region, has already been noted. Thus it is reasonable that for Class A the electron donating methyl [MACA(9)] and ethyl [EACA(12)] derivatives should have low isomer shifts and that the electron withdrawing trifluoromethyl [TFACA(5)] and nitro [NACA(11)] derivatives have high isomer shifts, with ACA(1) and BA(4) intermediate. Because of the fairly broad range of properties, the atmospheric isomer shifts cover a rather large range, from 0.36–0.46 mm/sec. The typical behavior of the ferric isomer shift, as observed in many other compounds, is to decrease with pressure because of an expansion of the d orbitals and subsequent reduction of shielding of the $3s$ orbital. Evidence for such metal orbital expansion
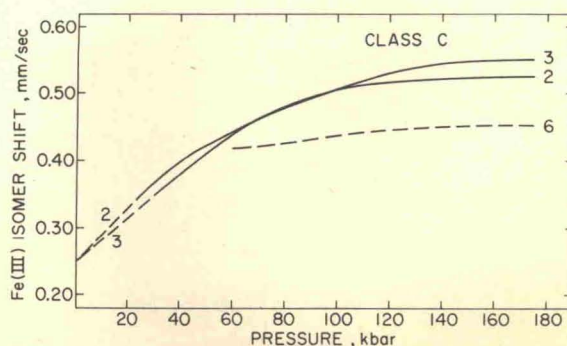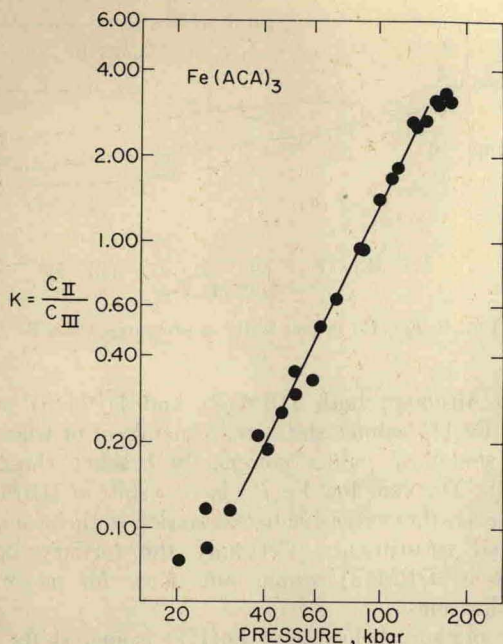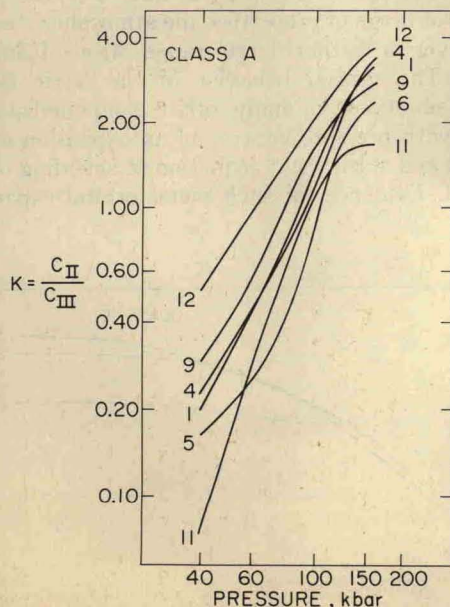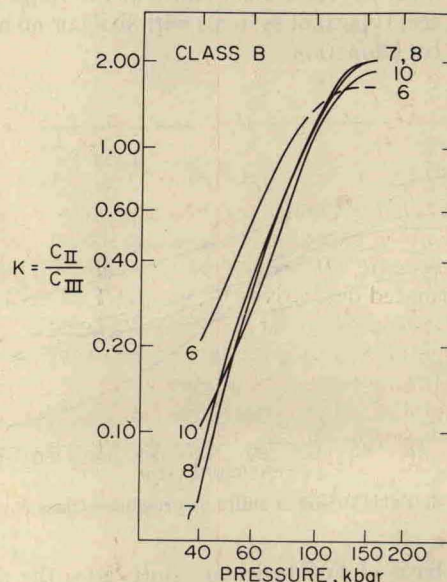

Fig. 10. Fe(III) isomer shifts vs pressure—Class C.

FIG. 11. Log K vs log P—ACA(1).

FIG. 12. Log K vs log P—Class A.

in terms of competition among the various contributions to the isomer shift. It is presumed that all of the derivatives have some $4s$ occupation in the ferric state, the extent varying from compound to compound. The inductive effects exhibited by the various substituents through the σ bonding system should be important in this respect, with good σ donors such as the alkyl groups increasing the $4s$ augmentation and poor σ donors such as the trifluoromethyl group decreasing it. With pressure the $4s$ orbital, which is σ antibonding, will increase in energy with respect to the metal $3d$ and ligand π and π^* orbitals due to increased overlap with ligand σ orbitals. This will cause a decrease of $4s$ occupation and an increase in isomer shift which of course is counter to the result expected from a delocalization of the metal d electrons. Thus a competitive balance will be maintained for each compound and

is provided by measurements of the Racah parameter B in other transition metal chelates in which decreases of 5%–10% in 100 kbars were obtained.[31,32] The isomer shifts for the Class A compounds do show net decreases over the pressure range but in the low pressure region, except for TFACA(5), they exhibit very small decreases or even increases and subsequent maxima at moderate pressures. This behavior may be explained

FIG. 13. Log K vs log P—Class B.

the possibility of maxima in the isomer shift curves is apparent.

In contrast to the other derivatives of Class A, TFACA(5), a strong σ acceptor with the highest initial isomer shift, shows a very large initial decrease in IS. This may be attributed to a very low initial $4s$ occupation so that the spreading of the d orbitals is the predominant pressure effect. The initial differences in behavior among the members of Class A are reduced above 100 kbars as the smoothed curves for four of the derivatives [ACA(1), TFACA(5), MACA(9), and EACA(12)] form a narrow band of about 0.02 mm/sec width with NACA(11) lying about 0.03 mm/sec above and BA(4) from 0.03–0.05 mm/sec below. In its shift behavior, BA(4) shows quite a large decrease with pressure and is again lower than the other members