Tetrahedron Letters No.47, pp. 4747-4749, 1967. Pergamon Press Ltd. Printed in Great Britain.

## MÖSSBAUER EFFECT IN FERROCENYLCARBONIUM ION

Joseph J. Dannenberg and John H. Richards

Gates and Crellin Laboratories of Chemistry,<sup>\*</sup> California Institute of Technology, Pasadena, California 91109

(Received in USA 10 August 1967)

We should like to report the  $Fe^{57}$  Mössbauer effects in ferrocenylcarbonium ion and ferrocenylcarbinol in frozen solution.

The measurements were made at 137 °K utilizing a Co<sup>57</sup> source diffused into metallic chromium. The carbonium ion was prepared by dissolving ferrocenylcarbinol in concentrated sulfuric acid. Freezing point depression measurements confirm the existence of the carbonium ion under these conditions (1). The carbinol was in benzene solution. An absorber thickness of 1 mm. of 40 mg./ml. solutions was used in both cases. More complete experimental data will be reported subsequently. The isomer shifts and quadrupole splittings obtained are listed in Table I.

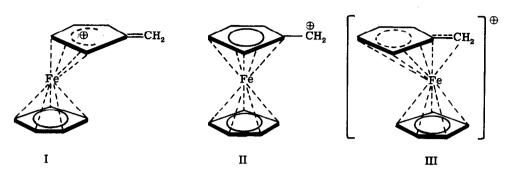
## TABLE I

## Mössbauer Effect Data

	Isomer Shift (mm./sec.)	Quadrupole Splitting (mm./sec.)
Ferrocenylcarbinol	0. 56	1.99
Ferrocenylcarbonium Ion	0. 57	2. 29

The virtual identity of the isomer shifts of the carbonium ion and the carbinol indicate that there is probably a relatively small difference in the electron density at the iron nucleus between these two species. Iron coordinates only sixteen electrons (rather than eighteen as in ferrocene and ferrocenylcarbinol) in the model, I, for the carbonium recently suggested by

<sup>\*</sup>Contribution No. 3553.



Pettit (2) and this model should have a different electron density at the iron nucleus than the carbinol.

Lesikar (3) has reported that the effect of substituents on the quadrupole splitting of ferrocene derivatives is small, and that electrophilic substituents tend to decrease the quadrupole splitting. The data of Table I indicate that the quadrupole splitting of the carbonium ion is 15% <u>larger</u> than that of the carbinol. Since the quadrupole splitting of the carbinol is the same as that of ferrocene (3), the quadrupole splitting of the carbonium ion must also be greater than that of ferrocene. In the resonance model for the carbonium ion, II, the methylene group should approximate a strongly electrophilic substituent and this model would predict a smaller quadrupole splitting for the carbonium ion than for the carbinol.

The iron participation model, III (4), in which one of the cyclopentadienyl moieties of ferrocene is replaced by a fulvene moiety which is bonded at all six carbons to the same iron orbitals used to bond the cyclopentadienyl ring (5), appears to be in agreement with the Mössbauer effect results, although these results alone do not unambiguously establish this model. Wertheim and Herber (6, 7) explain the small range of quadrupole splittings observed for ferrocene derivatives by suggesting that the electric field gradient at the iron nucleus is affected much more by changes in  $\pi$ -bonding ligands than by  $\sigma$ -bonding substituents attached to these ligands. Thus, in structure III, the nature of the  $\pi$ -bonding ligand is somewhat different from the analogous ligands in the ferrocene derivatives studied by Lesikar (3) and could account for the anomalous quadrupole splitting.

Finally, we wish to suggest the technique of measuring Mössbauer effects of cations in frozen solution has significant advantages, as use of a crystalline salt as an absorber gives Mössbauer effects which are dependent upon the anion present (6), presumably because of interactions within the crystal. <u>Acknowledgements</u>: We should like to thank Dr. E. Kankeleit for allowing us to use his equipment and for many useful discussions, and the National Science Foundation (NSF-GP-5190) for support.

## REFERENCES

- M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, <u>Tetrahedron Letters</u>, 1695 (1966).
- (2) J. D. Fitzpatrick, L. Wattson, and R. Pettit, <u>Tetrahedron Letters</u>, 1, 1299 (1966).
- (3) A. V. Lesikar, J. Chem. Phys., 40, 2746 (1964).
- (4) E. A. Hill and J. H. Richards, J. Am. Chem. Soc., 83, 3840 (1961).
- (5) J. J. Dannenberg, Ph. D. Thesis, California Institute of Technology, 1966; J. J. Dannenberg, M. I. Levenberg, and J. H. Richards, to be published.
- (6) G. K. Wertheim and R. H. Herber, J. Chem. Phys., 38, 2106 (1963).
- (7) G. K. Wertheim and R. H. Herber, J. Am. Chem. Soc., 84, 2274 (1962).