

Reaction of Transition Metal Vapors with an Arene Matrix at Liquid Nitrogen Temperature [1a]

H. F. EFNER [1b], W. B. FOX, R. R. SMARDZEWSKI, and D. E. TEVAULT [1b]

Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

Received July 26, 1977

We wish to report preliminary results of our investigations of the mechanisms of metal atom reactions. Previously, Timms [2] had reported that bis(benzene)chromium is produced by the co-deposition of chromium atoms and benzene at -196°C followed by warmup to room temperature. Subsequently, Boyd *et al.* [3] reported that chromium atoms reacted with benzene in argon matrices to form bis(benzene)chromium. Timms [2] also found that the analogous co-condensation of iron vapors with benzene resulted in a highly reactive and thermally unstable complex. Recently, Klabunde *et al.* [4] have reported the formation of nickel(0) complexes from the reaction of nickel atoms with *F*-benzene or toluene. Chemical evidence indicates that the nickel-*F*-benzene co-condensate product exists as a 1:1 complex [4a].

In the present work, the reactions of metal atoms with arenes were studied by co-depositing either pure arenes (benzene, benzene- d_6 , fluorobenzene) or 1:1 mixtures of benzene/benzene- d_6 or benzene/fluorobenzene (200-400 micromol) with metal atoms (3-6 micromol) onto a liquid nitrogen-cooled cesium iodide window. The low temperature products were examined by infrared spectroscopy and several interesting results were observed. Co-deposition of these metals and arenes resulted in π complex formation as judged by characteristic shifts in the arene C=C stretching and out-of-plane C-H bending vibrations. Chromium atoms reacted upon co-deposition with benzene to form bis(benzene)chromium; the infrared spectrum of the product species isolated in a benzene matrix was in complete agreement with the reported spectrum for bis(benzene)chromium [3, 5]. Warming of the matrix to remove excess benzene caused no significant change in the bis(benzene)chromium spectrum.

Benzene complexes of iron, cobalt, and nickel did not exhibit the two strong absorptions in the far infrared characteristic of bis(arene) complexes [6], *i.e.*, the asymmetric metal-ring stretching and tilting vibrations observed at 490 and 458 cm^{-1} for bis(benzene)chromium [3, 5]. Instead, new bands of lesser intensities were observed in benzene matrices at 485 and 370 cm^{-1} for iron, 460 and 370 cm^{-1} for

cobalt, and 445 and 350 cm^{-1} for nickel. In addition, the 1485 cm^{-1} C=C stretching band of benzene [7] was shifted to lower wavenumbers by 43, 40 and 35 cm^{-1} for the iron, cobalt, and nickel co-condensates, respectively. In bis(benzene)chromium, the observed shift is 59 cm^{-1} [5d], while the same band is shifted by 37 cm^{-1} in benzene chromium tricarbonyl [8]. The 673 cm^{-1} out-of-plane bending mode of benzene [7] was displaced to higher wavenumbers by 112, 92, and 77 cm^{-1} for the iron, cobalt, and nickel complexes, respectively. In bis(benzene)chromium [5e] and benzene chromium tricarbonyl [8], the reported shifts are 121 and 111 cm^{-1} , respectively. The shifts of the 1485 cm^{-1} and 673 cm^{-1} benzene absorptions, indicative of π -complexes and the far-infrared bands, are consistent with relative metal-ring bond strengths of $\text{Cr} > \text{Fe} > \text{Co} > \text{Ni}$. The same trend has also been observed in the thermal stabilities of benzene complexes [4a].

The stoichiometries of the iron, cobalt and nickel adducts were determined to be 1:1 from the results of the mixed arene (benzene/benzene- $d_6 = 1$ or benzene/fluorobenzene ≈ 1) reactions. In each case only those absorptions corresponding to metal-benzene and metal-benzene- d_6 or metal-fluorobenzene complexes were observed [9]. For example, nickel complex bands were found at 350 and 445 cm^{-1} for $\text{Ni-C}_6\text{H}_6$ vs. 310 and 395 cm^{-1} for $\text{Ni-C}_6\text{H}_5\text{F}$, while bands at 310, 350, 395 and 445 cm^{-1} were observed in the mixed deposition case. The other observed bands in the mixed deposition experiment compared favorably with those observed in the individual metal-arene complexes. Warming of the iron, cobalt, and nickel containing benzene matrices did not produce noticeable changes until in the -100°C to -50°C range; the complex bands underwent uniform reductions in intensity due to complex decomposition.

Further reactions of metal atoms with arenes, in both pure substrate or argon matrices, are currently under investigation and will be reported in more detail at a later date.

References

- (a) Presented at 11th Middle Atlantic Regional Meeting, Newark, Del., April 1975, Abstr. IN-14; (b) National Research Council Resident Research Associate at the Naval Research Laboratory.
- P. L. Timms, *Chem. Commun.*, 1033 (1969).
- J. W. Boyd, J. M. Lavoie and D. M. Gruen, *J. Chem. Phys.*, **60**, 4088 (1974).
- (a) K. J. Klabunde and H. F. Efner, *J. Fluorine Chem.*, **4**, 114 (1974); (b) K. J. Klabunde, H. F. Efner, T. O. Murodock and R. Roppel, *J. Am. Chem. Soc.*, **98**, 1021 (1976).

- 5 (a) R. G. Snyder, *Spectrochim. Acta*, *10*, 807 (1959); (b) H. P. Fritz, W. Luttke, H. Stammreich and R. Forneris, *ibid.*, *17*, 1068 (1961); (c) H. P. Fritz and E. O. Fischer, *J. Organomet. Chem.*, *7*, 121 (1967); (d) L. Schafer, J. F. Southern and S. J. Cyvin, *Spectrochim. Acta*, *27A*, 1083 (1971); (e) S. J. Cyvin, J. Brunvoll and L. Schafer, *J. Chem. Phys.*, *54*, 1517 (1971).
- 6 (a) E. O. Fischer and H. P. Fritz, *Angew. Chem.*, *73*, 353 (1961); (b) H. P. Fritz, *Advan. Organomet. Chem.*, *1*, 240 (1964).
- 7 G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N.J. (1945), p. 365.
- 8 H. P. Fritz and J. Manchot, *Spectrochim. Acta*, *18*, 171 (1962).
- 9 Chromium atoms reacted with benzene/benzene-d₆ mixtures in argon matrices at 10 °K to give the expected pair of 1:2:1 triplets corresponding to bis(benzene)-, benzene(benzene-d₆)- and bis(benzene-d₆)chromium.