Communications to the Editor

Infrared Bands from Alkali Ion Motion in Solution

Sir:

Recently, this laboratory discussed the 5-μ infrared spectrum and the electrical conductance of THF solutions of Na$^+$Co(CO)$_4^-$ in terms of the presence of ion pairs.[1] We wish now to report the observation of infrared bands arising from the motion of the alkali ion in THF solutions of Li$^+$, Na$^+$, and K$^+$ salts of Co(CO)$_4^-$ and of Mn(CO)$_5^-$.

The assignment of a band at 190 cm^{-1} in solutions prepared by shaking Na amalgam with Co$_2$(CO)$_8$ in THF to a vibration of the Na$^+$ was first made last June.[2] Subsequently, however, we have found small amounts of Hg[Co(CO)$_4$]$_2$ present in solutions similarly prepared. Although precautions had been taken to eliminate impurities as a source of the observation in the original experiments (for example, a THF solution of Co$_2$(CO)$_8$ shaken with Hg did not show the 190-cm^{-1} band), this finding created a special difficulty because Hg[Co(CO)$_4$]$_2$ was found to have a band at 192 cm^{-1}. Consequently, we felt it necessary to eliminate Hg[Co(CO)$_4$]$_2$ as a possible source of this band in a more positive manner in order to place this interpretation on a firmer foundation.[3] To this end, Li$^+$Co(CO)$_4^-$, Na$^+$Co(CO)$_4^-$, and K$^+$Co(CO)$_4^-$ solutions in THF were prepared by methods which did not involve the presence of Hg at any stage. These solutions showed the same bands found in the original work. In addition, we also prepared Hg-free THF solutions of Li$^+$Mn(CO)$_5^-$, Na$^+$Mn(CO)$_5^-$, and K$^+$Mn(CO)$_5^-$ and found similar bands. These bands appear at 407, 190, and *ca.* 150 cm^{-1} in the Li$^+$, Na$^+$, and K$^+$ THF solutions of Co(CO)$_4^-$, respectively, with an uncertainty of perhaps 5 cm^{-1} due to the broadness of the bands. The corresponding bands in the Mn(CO)$_5^-$ solutions are seen 20–30 cm^{-1} higher in frequency. Solutions in the concentration range from 0.1 to 0.3 M were examined between 800 and 33 cm^{-1} with cell thicknesses between 0.1 and 0.5 mm.

These data indicate that these bands arise from vibration of the alkali ions in these solutions. Moreover, since the initial report,[2] Evans and Lo[4] have reported far-infrared bands in benzene solutions of tetrabutylammonium halides which they attribute to interionic vibrations. The primary significance of these data lies in their direct relation to the force field at the ion and to the structure of the aggregate of which it is a part. Our data suggest a force field dependence upon the cation. The fact that the frequency of a given alkali ion shifts with change in anion, coupled with the expected presence of ion pairs in these solutions,[1] suggest that the vibration takes place in an ion pair or higher aggregate involving the anion. The solvent is also expected to participate in the aggregate, but its role has not yet been established. The details of this work and other measurements now in progress will be reported separately.

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[1] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).

[2] W. F. Edgell and A. T. Watts, Abstracts, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1965, p 85.

[3] The band at 407 cm^{-1} assigned[2] to Li$^+$ motion in Li$^+$Co(CO)$_4^-$ appeared near an infrared-inactive mode of the Co(CO)$_4^-$ ion. Thus there was an outside possibility that its origin was in a breakdown of selection rules for the anion and, therefore, the cleanest proof of the correctness of the assignment required direct evidence on solutions of Na$^+$ salts.

[4] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

The Conformational Preference of the Cyclopropyl Substituent in Triarylmethyl Cations

Sir:

The ability of the cyclopropyl group to interact with an adjacent center of unsaturation is well documented.[1] Much recent work has been directed toward gaining an understanding of this interaction and its geometric requirements. A large number of nmr data[2] have been interpreted in terms of the postulate that maximum interaction between the cyclopropyl group and an adjacent p orbital occurs when the plane of the three-membered ring is parallel to the axis of the p orbital, *i.e.*, the bisected conformation A (Figure 1). Recent ultraviolet studies on a series of arylcyclopropanes, on the other hand, showed no evidence for a dependence of conjugation on geometry.[3]

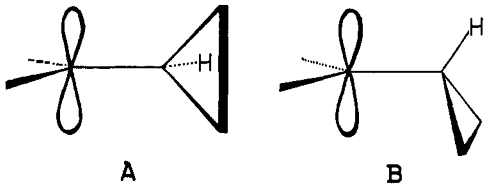

Figure 1.

Carbinol I, mp 99.5–100°, was prepared[4] in 57% yield by the reaction of the lithium reagent of *p*-bromophenylcyclopropane with diethyl carbonate. Carbinol I was converted to the corresponding carbonium ion II in trifluoroacetic acid solution and could be recovered in high yield upon basifying the solution. The results of the analysis of the nmr spectra of the cyclopropyl

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[1] M. Y. Lukina, *Russ. Chem. Rev.*, 419 (1962).

[2] (a) C. U. Pittman, Jr., and G. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); **87**, 5123 (1965); (b) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965); (c) N. C. Deno, H. G. Richey, J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

[3] A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

[4] Satisfactory elemental analyses were obtained for all new compounds.