

Fig. 2.—Appearance potential curves of ions from B_2H_6 , BH_3 , and BH_2 .

did not affect BH_2 , BH_4 recombination. This is to be expected on the basis of the proposed steps if $BH_4 \rightarrow BH_2 + H_2$ is fast.

Appearance potential measurements provided good confirmation of the results, an estimate of the relative concentration of these species, and ionization potentials. Several points are to be noted with respect to these measurements. First, maximum borane and boryl radical concentrations were obtained when over 80% of the diborane was destroyed. Thus, even at ionizing voltages high enough to produce dissociative ionization of diborane, the ion current measured was due nearly exclusively to the unstable species. Second, the abundance of BH_3^+ from dissociative ionization of diborane is very small, being only 0.5% of the intensity of $B_2H_5^+$ at 70 v. Third, the stability of the flow system allowed the rather low signal-to-noise ratio to be overcome to a large extent by making relatively long measurements at each voltage. The results are presented in Fig. 2. From these data it may be inferred that the BH_2 concentration is about two to three times as large as the BH_3 concentration under these conditions. A preliminary analysis of the data by plotting log ion intensity *vs.* voltage curves and determining the voltage shift required to match the BH_3^+ ion curve from diborane gave the following ionization potentials: $I(BH_3) = 11.4 \pm 0.2$ and $I(BH_2) = 9.8 \pm 0.2$ e.v. using the appearance potential of BH_3^+ from diborane (13.1 ± 0.2 e.v.) for calibration. This value has been determined previously⁹ using argon as a standard and this and the appearance potential of

BH_2^+ (13.4 ± 0.1 e.v.) were checked in an independent measurement. The appearance potential of $B_2H_5^+$ from diborane with the furnace on was equal to the value obtained with the furnace off.

Previously estimated values for $I(BH_3)$ are in excellent agreement with this measured value.^{9,10} Estimated values for $I(BH_2)$ range between 0.5¹⁰ and 1.7⁹ e.v. lower than this measured value. Considering the assumptions made in estimates of this nature, the upper value agrees quite well with that measured.

In the usual manner,^{11,12} simple calculations using the measured ionization potentials and appearance potentials and the known value of $D(H-H)$ give values of $D(BH_3-BH_3) = 1.7$ and $D(H_2B-H) = 3.2$ e.v. Once more the agreement with previous deductions is very good.^{10,13} Although these values are subject to the limitations of electron impact studies^{11,12} they lend strong confirmation to the assignment of these species as BH_2 and BH_3 .

Two other systems have been briefly examined for BH_2 and BH_3 . The pyrolysis of borane carbonyl, BH_3CO , yielded BH_3 and CO upon heating as might be expected. Both BH_2 and BH_3 were detected in the pyrolysis of tetraborane.

More detailed work is in progress and a complete report will be presented later.

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(10) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discussions Faraday Soc.*, **35**, 201 (1963). See note added in proof.

(11) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths & Co. Ltd., London, 1958.

(12) C. A. McDowell, "Methods of Experimental Physics," D. Williams, Ed., Academic Press, New York, N. Y., 1962, p. 525.

(13) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

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Carbonyl-Stretching Absorptions in the Pentacarbonyl Hydrides of Manganese, Technetium, and Rhenium

Sir:

A recent structure determination for $HMn(CO)_5^2$ prompts us to report a new interpretation of its carbonyl absorptions which was originally suggested^{1b} by results of recent studies of the pentacarbonyl halides³ and structural developments on other metal hydride complexes.⁴ These ideas apply equally well to the pentacarbonyl hydrides of Tc and Re whose absorptions⁵

(1) (a) Work supported by Grant No. GP 1696 from the National Science Foundation; (b) the spectral interpretation presented here is taken in a large measure from pp. 48-68 of the dissertation presented by D. K. Huggins in partial fulfillment of the requirements toward a Ph.D. at the University of California, Los Angeles, Oct., 1963.

(2) Reported by J. A. Ibers at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964 (paper no. 50, Symposium on Metal Carbonyls and Related Complexes), cf. S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

(3) (a) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962); (b) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(4) S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).

(5) (a) The maxima of the two principal bands in cyclohexane solution for the three pentacarbonyl hydrides have been reported: J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962); (b) spectra showing the principal absorptions of the pentacarbonyl hydrides in dilute solution have also been displayed previously [D. K. Huggins and H. D. Kaesz, *Can. J. Chem.*, **41**, 1250 (1963)], but the present spectra represent samples of even greater purity.

(9) W. S. Koski, J. J. Kaufman, C. F. Pachucki, and F. J. Shipko, *J. Am. Chem. Soc.*, **80**, 3202 (1958).

are entirely analogous (though not superimposable) with those of $\text{HMn}(\text{CO})_5$.

The absorptions for a carefully purified sample of $\text{HMn}(\text{CO})_5$ are shown in Fig. 1. The positions and relative intensities of the bands (calibrated against the 1847.8-cm^{-1} band in water vapor⁶) are: D, 2118 (vw); E, 2111 (vww); F, 2037 (vww); A, 2016 (vs); B, 2007 (s); C, 1981; (w); G, 1967 (vw) cm^{-1} . These are of a more desirable quality than those previously obtained in the gas phase,⁷ which, moreover, are difficult to compare especially in the minor peaks owing to band multiplicity arising from vibration-rotation interactions.

For a pentacarbonyl derivative of C_{4v} symmetry as is now known to be the case for $\text{HMn}(\text{CO})_5$,² we expect three principal bands.³ From the relative intensities we assign A as the principal band of e-species. In the upper trace, Fig. 1, we can see only one other principal band, B, which we take as one of the two expected modes of a_1 -species. However, from the pentacarbonyl halides and more specifically $\text{Re}(\text{CO})_5\text{Cl}$,^{3a} we may expect that the second a_1 -band will be at the highest frequency and possibly of vanishing intensity. Such a band has become visible at higher concentration, band D in the lower spectrum of Fig. 1, which we assign as the expected high energy a_1 -mode. This band has reached a minimum of relative intensity in the present derivative compared to spectra of other related derivatives such as the pentacarbonyl halides³ (which present an intermediate case) or the parent carbonyls⁸ (which present the opposite extreme in the intensity relationship of the corresponding absorptions of b_2 -species for $\text{M}_2(\text{CO})_{10}$). The high energy b_2 -band in $\text{Mn}_2(\text{CO})_{10}$ is of equal and possibly greater intensity than the lower energy band of the same species. In $\text{Mn}_2(\text{CO})_{10}$ the radial carbonyl groups are bent an average of about 4° out of the plane normal to the principal axis of the molecule in the crystal,⁹ a little less than what is found for $\text{HMn}(\text{CO})_5$.² If a geometrical factor is responsible for the intensity relationships in the a_1 (or b_2) bands,^{3a} then the extremes observed in the spectra for these two derivatives could mean that the similarity found in the crystal may not be preserved in solution (unless some other factor is responsible). The derivatives $\text{XMn}(\text{CO})_5$ may be arranged in the order $\text{X} = \text{H} < \text{Cl} < \text{Br} < \text{I} < \text{M}(\text{CO})_5$ in which the relative intensity of the high energy band is increasing; *i.e.*, the two bands are becoming more nearly equal. This trend is accompanied by a decreasing energy separation between the two bands with the exception of the pentacarbonyl hydride where this separation is less than for the halides though more than for the decacarbonyls.

Of the other minor bands observed here, we assign C and G as the ^{13}CO satellites of the principal bands A and B, respectively.^{10a,b} This leaves only the bands E and F unassigned; these could very likely belong to a minor constituent, isotopically substituted such that its

symmetry would be lower than that of the principal species and for which we may expect additional bands.^{10c} Alternatively, they might be combination modes or overtones.

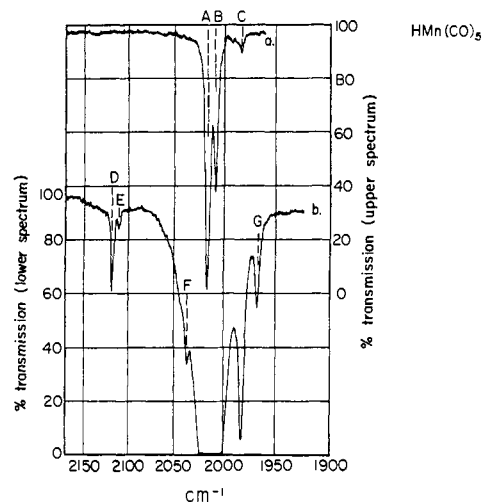


Fig. 1.—High-resolution infrared spectra in the carbonyl-stretching region for $\text{HMn}(\text{CO})_5$, LiF prism, Beckman IR 4, cyclohexane solution: (a) upper spectrum, approximately 3×10^{-6} mole/ml.; (b) lower spectrum, approximately 10^{-4} mole/ml.

One may calculate approximate force constants from the above proposed assignment of the principal bands, after the method of Cotton and Kraihanzel.¹¹ These give the values, $k_1 = 16.42$, $k_2 = 16.93$, and $k_i = 0.258$ mdyne/ \AA , which are in the proper magnitude and relative order $k_1 < k_2$ as required by simple valence-bond considerations,¹¹ and which serve as a check on the proposed assignment. One interesting consequence of this assignment is that the hydrogen atom as a ligand appears to have qualities more like a CO group than a halogen atom in its influence on the stretching frequency (or the force constant) of the CO group substituted *trans* to it.¹² This analogy is corroborated by other kinds of experimental evidence on other types of transition metal hydride complexes.¹³

The main difficulty which arose in previous attempts to propose a structure for the pentacarbonyl hydrides from the number of carbonyl absorptions is therefore a little clearer at present. It is difficult to know *a priori* which of the many weak bands (observed at increased spectral intensity in almost all carbonyl derivatives) must be counted as "principal" bands and which have arisen from other factors. An additional complication is found for the present derivatives; these were the most difficult of any of the carbonyl derivatives we have thus far encountered to free from trace impurities which gave rise to extraneous bands. The nature of the other bands and the question of the relative intensity of the highest lying a_1 -vibration in the

(6) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Natl. Bur. Std.*, **64A**, 1 (1960); band no. 50, Table 5.

(7) (a) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958); (b) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833, (1959).

(8) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, in press.

(9) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(10) See similar assignments following more extensive vibrational analyses: (a) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963); (b) R. S. McDowell, W. D. Horrocks, Jr., and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961); (c) L. H. Jones, *ibid.*, **36**, 2375 (1962).

(11) (a) The radial groups are designated as (2) and the axial group as (1), following the treatment in F. A. Cotton and C. A. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); *cf.* also, (b) C. A. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); (c) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(12) By comparison, the force constants for $\text{Mn}(\text{CO})_5\text{I}$ are $k_1 = 16.29$, $k_2 = 17.30$, and $k_i = 0.22$ mdyne/ \AA ; see ref. 8 and 11c; also see ref. 11b for a more extensive discussion of comparisons implied here.

(13) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

present derivatives are under further study in these laboratories.

(14) Publication No. 1675.

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Electron Spin Resonance Spectra of Different Solvates of *m*-Nitrophenol Negative Ion in a Mixed Solvent

Sir:

It is well known that e.s.r. spectra of many organic radicals and radical ions in solution are very sensitive to solvent composition.¹ Electron-nuclei spin-spin

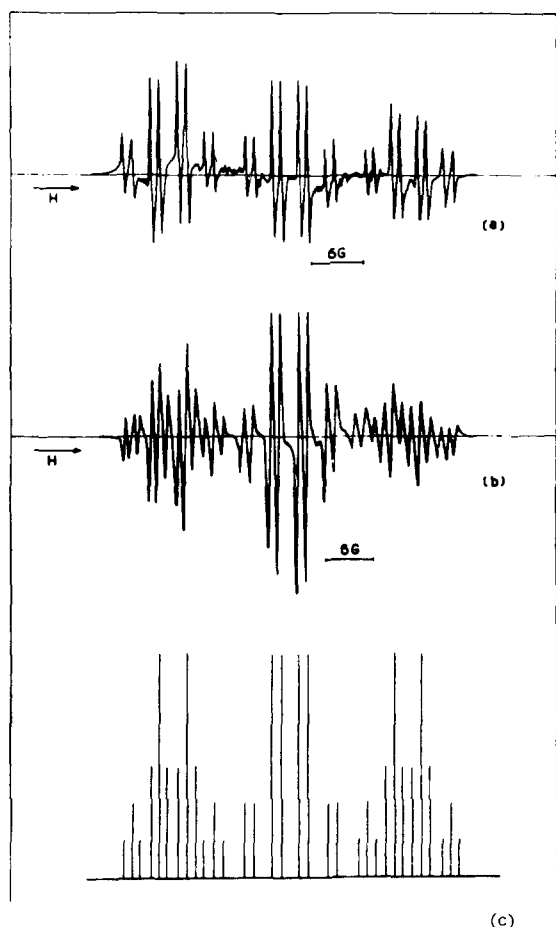
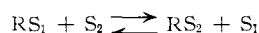


Fig. 1.—E.s.r. first derivative spectrum of *m*-nitrophenol ion in 50% water-DMF with electrolyte 0.1 *M* NEt_4ClO_4 : a, at room temperature; b, same at 0°; c, reconstruction of spectrum b based on superposition of the two spectra arising from two species in 1:1 ratio and differing only in a_N .

coupling constants undergo conspicuous variations with solvent and the behavior has been explained² through the formation of "solvates" or "complexes" in which the radical is linked to one or more solvent molecules as for example in the model reaction



where R is the radical and S_1 and S_2 are the two solvents.

The e.s.r. spectra obtained up to now in these cases always presented hyperfine patterns indicating coupling

constants corresponding to weighted averages of the values existing in the pure solvents.

During the course of an investigation of the e.s.r. spectra of *m*-nitrophenol negative ion produced by electrolysis in water-dimethylformamide (DMF) mixtures we have obtained spectra which are very clearly due to the superposition of two radical species which we logically identify with two different solvates.

Figure 1a shows the spectrum of *m*-nitrophenol anion in an approximately 50% mixture of water and DMF. The hyperfine pattern is due to a major triplet arising from the nitrogen coupling of 14.6 gauss; this splits into quartets (intensity 1:3:3:1) due to three almost equivalent protons and furthermore into doublets, the last splitting arising from the remaining proton with the smallest coupling constant.

The pattern remains practically the same in going from pure water to pure DMF, the only feature influenced being the main nitrogen splitting which decreases smoothly from 14.6 gauss in pure water to 12.3 gauss in pure DMF. The proton coupling constants are not influenced much by solvent composition at least up to almost unit DMF mole fraction where differences are noted among the three almost equivalent protons.

Figure 1b shows the spectrum obtained from the same solution of Fig. 1a at a lower temperature. The pattern of the central group is not affected but the two side groups now have a larger number of lines. The reconstruction of Fig. 1c shows how the pattern is easily explained on the basis of the superposition of two spectra of the type of Fig. 1a differing only in the major nitrogen splitting. Some of the lines of the side groups have a greater width because the overlapping is not so perfect as postulated in the reconstruction. We note also that in both spectra the high field group lines are wider than the corresponding low field ones as is currently observed in many cases.³

It is clear from this experiment that, in the case of sufficiently large differences among some coupling constants of the two alleged "solvates" RS_1 and RS_2 , it is possible to obtain conditions of sufficiently low rate of exchange among the two species such that the two spectra can be detected at the same time. Further details on this phenomenon and a comprehensive quantitative discussion will be published shortly.

(3) P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

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Novel C-4 Modified Tetracycline Derivatives

Sir:

The reaction of amphoteric tetracycline 1 with *N*-chlorosuccinimide to yield 11a-chlorotetracycline-6,12-hemiketal 2 has been reported.¹ A less than drastic change in chlorination conditions—treatment of tetracycline hydrochloride with *N*-chlorosuccinimide in water—leads to the isolation of a drastically different product, 4-oxo-4-dedimethylaminotetracycline 4,6-hem-

(1) R. K. Blackwood, J. J. Beereboom, H. H. Rennard, M. Schach von Wittenau, and C. R. Stephens, *J. Am. Chem. Soc.*, **83**, 2773 (1961); **85**, 3943 (1963).

(1) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

(2) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).