J. Phys. Chem. A **1997,** *101,* 2817−2818 **2817**

EPR Spectrum of NaCO

H. A. Joly* and J. A. Howard

Department of Chemistry and Biochemistry, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

Received: December 10, 1996⊗

Reaction of ground state Na atoms with ^{13}CO in an adamantane matrix in a rotating cryostat at 77 K gives a mononuclear monoligand complex whose EPR spectrum consists of an isotropic quartet of doublets with $a(\mathrm{Na}) = 889$ MHz, $a(^{13}\mathrm{C}) = 21.8$ MHz, and $g = 2.0015$. This suggests that a Na atom can interact with one CO to generate NaCO with a singly occupied molecular orbital that is made up of Na 3s and C 2s orbitals with *ca*. 96% unpaired spin population in the Na 3s orbital.

A matrix isolation infrared spectroscopic study of solid argon containing vapor-deposited ground state Na atoms and CO has shown that there are no IR bands that can be assigned to the bound mononuclear monoligand complex NaCO,[1] although liquid ammonia solutions of Na are known to react with CO to give sodium acetylenediolate, $Na_2C_2O_2$.[2] This is in contrast to the results obtained for Li atoms where a plethora of mononuclear and polynuclear carbonyls, *e.g.*, LiCO, $Li(CO)_2$, $Li(CO)_3$, Li_2CO, Li_3CO, and $Li_2C_2O_2$ are produced.[2−5]

Ab initio calculations at the CI level have suggested that the lowest $^2\Sigma$ electronic state of linear NaCO is either repulsive[6] or weakly bonding with a Na−C distance of 0.45 nm.[7] Density functional theory calculations[8] give two minima. The lowest one is bent with a $^2A'$ electronic state and a NaCO angle of 132.8° and is a weakly bound van der Waals complex with a dissociation energy of 5.4 kJ mol^{-1}. The second minimum is a metastable linear structure, similar to that described by Pacchioni,[7] with a dissociation energy of 0.84 kJ mol^{-1}.

We have investigated the reaction of Na atoms with CO in an adamantane matrix at 77 K in a rotating cryostat.[9,10] The reaction products have been examined by electron paramagnetic resonance spectroscopy (see Figure 1) and the results are reported here.

Na atoms and CO in adamantane at 77 K give a dark purple, almost black, deposit with an overall EPR spectrum that has all the features given by Na atoms in adamantane, *i.e.*, matrix-isolated Na atoms in two magnetically distinct trapping sites and pseudorotating Na_3,[11] plus an additional quartet with a large Na hyperfine interaction. The lowest and highest field lines of this new spectrum occur at 2833.9 and 3788.5 G at a microwave frequency of 9339.3 MHz. An exact solution of the Breit-Rabi equation gives the magnetic parameters $a_{\mathrm{Na}} = 889$ MHz and $g = 2.0015$. This Na coupling constant is 50 MHz larger than the coupling constant for Na atoms trapped in the major trapping site (site I) of adamantane (839 MHz) and is almost identical to the hyperfine interaction of gas-phase Na atoms (885.8 MHz).[12]

When ^{13}CO is used instead of natural CO, the quartet spectrum is replaced by a quartet of doublets with a doublet spacing of 8 G. This spectrum at a high microwave power (20 mW) is shown in the figure. An exact analysis of this spectrum gives $a_{\mathrm{Na}} = 889$ MHz, $a_{\mathrm{C}} = 21.8$ MHz, and $g = 2.00155$. Clearly the carrier of this spectrum has the stoichiometry NaCO. Dividing a_{Na} by $A = 927.1$ MHz and a_{C} by $A = 3777$ MHz, where A is the appropriate one-electron parameter,[13] gives unpaired 3s and 2s spin populations, ρ_{3s} and $\rho_{2s'} = 0.96$ and 0.006.

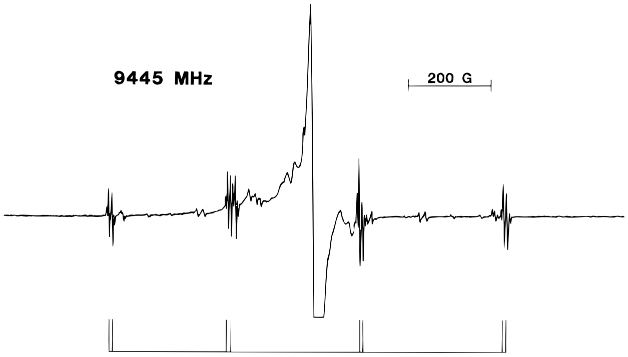

Figure 1. The EPR spectrum given by vapor deposited Na atoms and ^{13}CO in adamantane at 77 K and high microwave power (20 mW). The stick diagram gives the predicted quartet of doublets from $Na^{13}CO$ computed by using the parameters given in the text.

The four transitions from NaCO are accompanied by satellite lines that are more pronounced than they are for Na atoms in site I. The separation between the main and satellite lines is 4.5 G which is close to the resonance frequency of the proton, $g_N\beta_N H$, where g_N and β_N are the proton g factor and nuclear magnetron, respectively, and H is the applied magnetic field. The intensity of the spectrum of NaCO is proportional to the square root of the microwave power from 5 to 250 μW, whereas the intensity of the Na atom spectrum begins to level off at *ca*. 5 μW. The relaxation time for NaCO is, therefore, much shorter than it is for matrix-isolated Na atoms. Efficient relaxation occurs because of a magnetic interaction between NaCO and the adamantane protons. This property enables intense EPR spectra of NaCO to be obtained at high microwave power.

When the temperature is increased from 77 K, in 10° intervals, NaCO disappears faster than Na atoms in site I. The spectrum of NaCO is, however, still visible at 190 K but disappears at *ca*. 200 K.

It is apparent that a species with the stoichiometry NaCO is produced by reaction of Na atoms with CO in an adamantane matrix at 77 K that is persistent in this environment up to 200 K. It has almost all the unpaired spin located in the Na 3s orbital and a small unpaired spin population in the C 2s orbital. This suggests that the Na atom interacts with the C rather than the O of CO. Repulsion between the singly occupied 3s sodium orbital and the highest occupied 5σ molecular orbital of CO (a localized lone pair on the carbon atom) might be expected to render linear NaCO unbound. Bending would reduce the Na−

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S1089-5639(96)04033-9 CCC: $14.00 Published 1997 by the American Chemical Society

CO repulsion and allow 3s to $2\pi^*$ donation. On the other hand, linear NaCO could be bound by a three-electron system which would be consistent with the small value of the ^{13}C hyperfine interaction. Furthermore, bent NaCO would be expected to have an anisotropic EPR spectrum unless it is freely rotating in an adamantane matrix. The question does remain whether NaCO is a *bona fide* complex or matrix assisted system. A referee has suggested that the presence of spin flip satellite lines in the spectrum and the shorter relaxation time relative to isolated Na atoms support a matrix assisted system. If this is the case, the line widths are remarkably small.

It is of interest to compare the magnetic properties of NaCO with those of other monocarbonyls given by reaction of ^{2}S ground state atoms with CO, *i.e.*, HCO, LiCO, CuCO, and AgCO. HCO has unpaired s spin populations of 26.7 and 9.9% on the H and C nuclei,[14] quite different to those of NaCO. LiCO has almost all the unpaired spin population on the CO moiety and is a tight ion pair Li^+CO^-.[4] CuCO has unpaired s spin populations of 66 and 5% on the Cu and C nuclei.[15,16] High-level theoretical calculations[17−20] have shown that this complex is bent with a CuCO angle of *ca*. 139° and a binding energy of *ca*. 21 kJ mol^{-1} AgCO has unpaired spin populations of 1.003 and 0.8% on the Ag and C nuclei,[21−22] values that are closer to those of NaCO than those of either HCO or CuCO.

Acknowledgment. We thank the referees for some pertinent comments. This work was supported by an operating grant (H.A.J.) from the National Sciences and Engineering Research Council of Canada.

References and Notes

(1) Ayed, O.; Manceron, L.; Silvi, B. *J. Phys. Chem.* **1988**, *92*, 37.

(2) Ozin, G. A.; Moskovits, M. In *Cryochemistry*; Wiley: New York, 1976; Chapter 8.

(3) Ayed, O.; Loutellier, A.; Manceron, L.; Perchard, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 8138.

(4) Silvi, B.; Ayed, O.; Person, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 8148.

(5) Krishnan, C. N.; Hauge, R. H.; Margrave, J. L. *J. Mol. Struct.* **1987**, *157*, 187.

(6) Reiland, W.; Tittes, H. U.; Hertel, I. V.; Bonacic-Koutecky, V.; Persico, M. *J. Chem. Phys.* **1982**, *77*, 1908.

(7) Pacchioni, G. *Theor. Chim. Acta* **1983**, *62*, 461.

(8) Pullumbi, P.; Bouteiller, Y.; Perchard, J. P. *J. Chem. Phys.* **1995**, *102*, 5719.

(9) Bennett, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1.

(10) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381.

(11) Howard, J. A.; Hampson, C. A.; Histed, M.; Morris, H.; Mile, B. *NATO ASI Ser., Ser B* **1987**, *158*, 421.

(12) Kusch, P.; Hughes, V. W. In Handbuch der Physik; Flügge, S. Ed.; Spinger-Verlag: Berlin, 1959; Vol. 37, Part 1.

(13) Morton, J. R.; Preston, K. F. *J. Magn. Reson., Ser. A* **1978**, *30*, 577.

(14) Adrian, F. J.; Kim, B. F.; Bohandy, J. *J. Chem. Phys.* **1985**, *82*, 1804.

(15) Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 813.

(16) Chenier, J. H. B.; Hampson, C. A.; Howard, J. A.; Mile, B. *J. Phys. Chem.* **1989**, *93*, 114.

(17) Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **1994**, *229*, 577.

(18) Fournier, R. *J. Chem. Phys.* **1993**, *98*, 8041.

(19) Barone, V. *Chem. Phys. Lett.* **1995**, *233*, 129.

(20) Fournier, R. *J. Chem. Phys.* **1995**, *102*, 5396.

(21) Kasai, P. H.; Jones, P. M. *J. Phys. Chem.* **1985**, *89*, 1147.

(22) Chenier, J. H. B.; Hampson, C. A.; Howard, J. A.; Mile, B. *J. Phys. Chem.* **1988**, *92*, 2745.