the various sites. The new distribution of charge will lead to secondary fragmentations at sites other than those where the primary fragmentation took place.

This concept is important not only for a better understanding of the fragmentation of ions in the gas phase but also in the interpretation of mass spectra in terms of structural information.

Acknowledgment. This work was supported by a research grant from the National Institutes of Health (GM 05472).

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Received January 12, 1968

Extrinsic Field Acceleration of the Magnetic Parahydrogen Conversion

Sir:

This letter is to report an example of increased reaction velocity observed on application of an extrinsic magnetic field. The reaction was the heterogeneous catalytic parahydrogen conversion which, under the conditions and as shown by the absence of measurable hydrogen–deuterium equilibration, was entirely magnetic in mechanism. The intrinsic field was supplied by chromium ions.

Three catalyst samples were investigated. These were (1) synthetic ruby (a dilute solid solution of Cr_2O_3 in α-Al_2O_3) containing 1 atom % Cr and powdered to a specific surface of 2.0 m^2 as previously described,[1] (2) a supported chromia/alumina prepared by impregnating powdered synthetic sapphire (α-Al_2O_3) of specific surface 2.0 m^2 with the appropriate volume of dilute chromic nitrate solution, followed by drying and ignition in air at 500° for 2 hr, giving a sample containing 0.0028 wt % Cr_2O_3; and (3) a similar supported sample containing 0.045% Cr_2O_3.

The samples were placed in turn in a quartz reactor between the poles of an electromagnet and arranged for measurement of the orthohydrogen:parahydrogen concentration ratio, as described.[1] About 0.20 g of sample was used, and each sample was heated *in situ* in flowing hydrogen for 2 hr at 500° and then quenched to room temperature so as to prevent poisoning of the paramagnetic sites by chemisorbed hydrogen. (This procedure of quenching is equivalent to, and more convenient than, evacuation and cooling from 500°.) The hydrogen used was first passed through a palladium-silver purifier, then converted to 1:1 orthohydrogen:parahydrogen over a commercial chromia catalyst at −196°, and passed over the sample at 35 ml min^{-1}.

Figure 1 shows the parahydrogen conversion rate in μmoles of orthohydrogen formed per minute over each of the three samples, at zero field and at a field of 2000 Oe. The fractional rate increase on application of the field is stated. Figure 2 shows the percentage increase of conversion rate for the 0.0028% sample as a function of field strength.

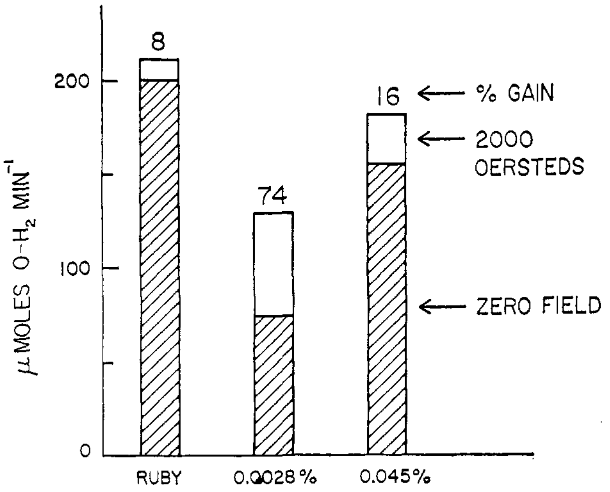

Figure 1. Increase in parahydrogen conversion rate at −100° on application of a 2000-Oe magnetic field for three chromia/alumina samples.

The fact that the zero-field conversion rates shown follow no particular pattern is of no consequence. The magnetic conversion rate is approximately proportional to $cp\mu^2/d^6$, where c is the number of paramagnetic species in the sample, p is the fraction accessible to molecular hydrogen, μ is the magnetic moment, and d the distance of nearest approach. In ruby the chromiums are isolated, but only a small and uncertain fraction is accessible. In the impregnated samples all the chromium is on the surface of the sapphire, but the fraction accessible depends on the cluster size; the effective magnetic moment of Cr^{3+} ions in antiferromagnetic clusters is considerably less than that in isolated Cr^{3+}.

Application of the field does not cause any change, temporary or permanent, of space velocity, and the reversible conversion rate change occurs abruptly when the field is applied or removed. The effect is observed as soon as the flowing hydrogen has had time (about 3 min) to reach the sensitive thermal conductivity cell used for analysis.

In view of these results it was thought that three possible explanations were worthy of consideration. The first is some field-induced relaxation of the normal exchange demagnetization in antiferromagnetics, but we have not been able to find any theoretical basis for this, except perhaps indirectly in the work of Néel on superantiferromagnetism.[2] The second is some form of dynamic polarization, or Overhauser effect,[3] but the much lower conversion acceleration over ruby argues against this explanation. The third possible explanation is related to the proposal of Nagaev[4] in which a large field-dependent increase of magnetic moment is predicted under certain conditions for two-dimensional layers of adsorbed paramagnetic atoms exhibiting exchange interaction. It is to be noted that our observation reported in Figure 2 confirms the field saturation effect predicted by Nagaev. Whether his predicted exponential decrease of moment with decrease of reciprocal temperature occurs can only be answered by more refined measurements, which are planned (the effect definitely is less at 25° than at −100°). It is also

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(1) P. W. Selwood, *J. Am. Chem. Soc.*, **88**, 2676 (1966).

(2) L. Néel, *Compt. Rend.*, **253**, 203, 1286, (1961).

(3) A. Abragam, "Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 392.

(4) E. L. Nagaev, *Kinetika i Kataliz*, **2**, 847 (1961).

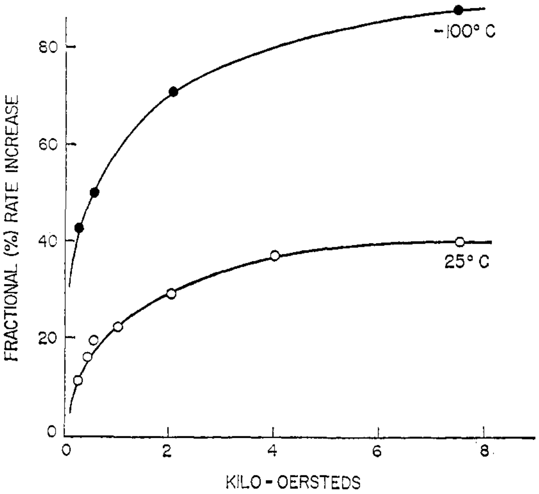

Figure 2. Fractional increase in parahydrogen conversion rate at 25 and −100° as a function of extrinsic field for 0.0028% chromia-alumina.

to be noted that a small fraction of the total chromium in the appropriate layer state would be sufficient to account for our observations. It is to be expected that, of the three samples investigated, that containing 0.0028% Cr_2O_3 would have the largest fraction of its chromia in this layer state.[5]

These observations of reaction acceleration caused by an extrinsic magnetic field, and the suggestion that the effect is due to some field-induced increase of effective magnetic moment in the catalyst, suggest that a reexamination of experimental data is called for in several areas. In particular, doubt is placed on the interpretation of previous magnetic susceptibility, epr, and nmr work on systems containing extremely thin layers of paramagnetic species in which exchange interaction may be present. This includes almost all transition metal oxides of interest in heterogeneous catalyst.

Acknowledgment. This work was supported in part under a grant from the Army Research Office (Durham).

(5) P. W. Selwood, forthcoming paper.

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Received March 30, 1968

A Hexacoordinated Low-Spin Cobalt(II) Complex

Sir:

The interesting question as to the existence of the truly hexacoordinated complex molecule, $Co^{II}L_6$, with spin $S = {}^1/_2$ has not yet been answered.[1] In this paper we present evidence to show that the unstable paramagnetic species derived by allowing phenyl isocyanide to react with pentakis(phenylisocyano)cobalt(II) perchlorate[2,3] (I) is a hexacoordinated low-spin Co(II) complex. The solvent used was $CHCl_3$ + CH_2Cl_2 (1:1), and all experiments were carried out at Dry Ice–acetone temperature (~−50°), unless otherwise specified.

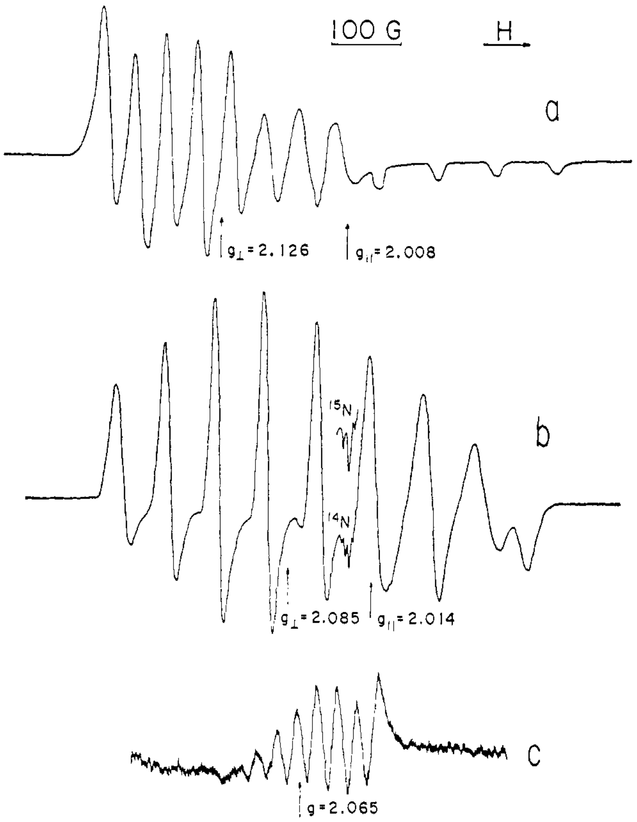

Figure 1. Esr spectra of cobalt(II) phenyl isocyanide (L) complexes, in solution: (a) $Co^{II}L_5$ at 77°K; (b) $Co^{II}L_6$ at 77°K; (c) $Co^{II}L_6$ at 248°K. The esr parameters of the frozen systems were determined by computer simulation.

On adding slightly more than 1 equiv of isocyanide to the solution of blue hydrated form of I, a reversible color change from blue-green to orange was seen on freezing at 77°K. With a large excess of isocyanide, the orange color remained on thawing, but at room temperature the color quickly turned brownish. Thus there appears to be an equilibrium between I and some unstable orange species II.

The conversion from I to II can be followed better by observing esr absorption at 77°K. Progressive addition of isocyanide to the solution of I causes a monotonic decrease in the spectrum (Figure 1a) of I, with a concomitant rise of the new peaks shown in Figure 1b, presumably of the orange species II. The spectrum of I was completely replaced by that of II when 1.3 ± 0.1 mole equiv of isocyanide was added to a 10^{-2} *M* solution of I. The latter spectrum can be interpreted as the superimposed parallel and perpendicular absorptions, each split into eight lines by ^{59}Co nuclear interaction with coupling constants 64.0 and 75.0 G, respectively. The liquid solution shows an eight-line spectrum (28-G splitting) with unsymmetrical intensity distributions (Figure 1c). The *g* values and the hyperfine (hf) constant in frozen and liquid solution, respectively, are consistent with each other, indicating that the two spectra do represent the same species.

The same spectrum of II, but less intense, was obtained when varying amounts of H_2O, NH_3, or $NH_2CH_2CH_2NH_2$ were added to the solution of I. These reagents, which decompose I in solution at room tem-

(1) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 10.

(2) A. Sacco, *Gazz. Chim. Ital.*, 84, 370 (1954); J. M. Pratt and P. R. Silverman, *Chem. Commun.*, 117 (1967).

(3) J. M. Pratt and P. R. Silverman, *J. Chem. Soc., A*, 1286 (1967).